Characterization of Biochars Produced from Cornstovers for Soil Amendment

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Abstract
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Disciplines
Biochemical and Biomolecular Engineering | Biomechanical Engineering | Bioresource and Agricultural Engineering | Other Mechanical Engineering

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Characterization of Biochars Produced from Cornstovers for Soil Amendment

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Through cation exchange capacity assay, nitrogen adsorption—desorption surface area measurements, scanning electron microscopic imaging, infrared spectra and elemental analyses, we characterized biochar materials produced from cornstover under two different pyrolysis conditions, fast pyrolysis at 450 °C and gasification at 700 °C. Our experimental results showed that the cation exchange capacity (CEC) of the fast-pyrolytic char is about twice as high as that of the gasification char as well as that of a standard soil sample. The CEC correlates well with the increase in the ratios of the oxygen atoms to the carbon atoms (O:C ratios) in the biochar materials. The higher O:C ratio was consistent with the presence of more hydroxyl, carboxylate, and carbonyl groups in the fast pyrolysis char. These results show how control of biomass pyrolysis conditions can improve biochar properties for soil amendment and carbon sequestration. Since the CEC of the fast-pyrolytic cornstover char can be about double that of a standard soil sample, this type of biochar products would be suitable for improvement of soil properties such as CEC, and at the same time, can serve as a carbon sequestration agent.

Introduction

The world currently faces a systematic problem of increased CO2 emissions, decreased soil-carbon content, and global-climate change (global warming). In certain areas, agriculture and intensive tillage have also caused a 30–50% decrease in soil organic carbon (SOC) since many soils were brought into cultivation more than 100 years ago (1). To solve this massive global energy and environmental sustainability problem, it likely requires a comprehensive portfolio of R&D efforts with multiple energy technologies. Application of a modern biomass pyrolysis for producing biofuels and biochar is possibly a significant approach for global carbon capture and sequestration at GtC scales (2). This “carbon-negative” biomass-pyrolysis energy-production concept of applying biochar as a soil amendment and carbon sequestration agent was initiated in 2002 by Danny Day of Epirida Power and Life Sciences Inc. and one of us (Lee) with a provisional U.S. patent application followed by a PCT application (3). Certain related studies including biochar-related soil research have also indicated the possibility of using biochar as a soil amendment for carbon sequestration (4–7). This paper explores the effect of pyrolysis conditions on biochar properties. Biochars were produced by two distinct processes: fast pyrolyzer at 450 °C and air-blown gasification at 700 °C. Biochar characterization included cation exchange capacity assays, nitrogen adsorption—desorption surface area measurements, scanning electron microscopic imaging, infrared spectra analysis, and elemental analysis. This paper reports these characterization studies for the cornstover-derived biochar materials in relation to their potential application as a soil amendment and carbon sequestration agent.

Experimental Materials and Methods

Biochar Materials. Biochars (sample IDs 1 and 2) for these studies were produced by Iowa State University using two distinctive processes: gasification and pyrolysis. Round bales of cornstover were purchased from a local farmer for the production of biochar. No effort was made to control for the dirt content of the stover, which was observed to be variable and could add significantly to the ash content of the feedstock. Biochars from gasification (sample ID 1) were obtained from a pilot-scale, air-blown gasifier located at the Iowa Energy Center’s BECON facility in Nevada, IA. The gasifier employs a bubbling fluidized bed reactor operated at 700 °C and an equivalence ratio between 0.25 and 0.30. The gasification system is rated at 800 kW thermal input, which corresponds to an average throughput of 180 kg/h of solid biomass fuel. Although the primary product from the reactor is syngas (a mixture of carbon monoxide, hydrogen, and light alkanes), between 5 and 10 wt-% of the biomass is converted to fine charcoal, which is elutriated from the fluidized bed with the produced gas flow and recovered by two gas cyclones in series immediately downstream of the gasification vessel. The bed media consists of sand mixed with a small quantity of limestone, making up about 5% of the total bed weight, to prevent agglomeration of the bed material arising from alkali in the biomass feed. The sand originates from near Eau Claire, Wisconsin (Red Flint Sand and Gravel) and is approximately 95% silica, 2% iron oxide, 0.9% aluminum oxide, with the balance being trace amounts of other oxides. Attrited bed media can also elutriate from the reactor and be collected by the cyclones along with the charcoal. Gasification biochars are a mixture of charcoal and minerals from the inorganic ash content of the biomass, dirt incorporated into stover during corn harvesting and stover baling, and bed media that elutriate from the gasifier. Further details on the operation of the gasifier are found in reference (8). Biochars from fast pyrolysis (sample ID 2) were obtained from a process development unit (PDU) located at the Iowa Energy Center’s BECON facility. Like the gasifier, the fast pyrolyzer is a bubbling fluidized bed but it is only rated at 25 kW thermal input, which corresponds to 5–6 kg/h biomass throughput, and uses nitrogen instead of air as fluidization gas. The bed media is similar to that used for the gasifier except that no limestone is added since agglomeration is less of a problem at the lower operating temperature of the pyrolyzer (450 °C). Biochar yields are around 15 wt-%. Like the larger gasifier, the pyrolyzer uses two gas cyclones in series to capture biochar, which consists of both charcoal and inorganic compounds of similar origin to the mineral matter in the gasification biochar. Additional details can be found in ref 9.
Reference Soil Sample. The control soil sample (sample ID 15) was obtained from a surface soil of 0–15 cm deep at the University of Tennessee’s Research and Education Center, Milan, TN (358560N latitude, 888430W longitude). The soil at the site is a moderately well-drained Alfisol (soil series: Grenada silt loam) that is classified as a thermic Oxyaquic Fraglossudalf (10). The soil texture (over the surface 15 cm of mineral soil) is 13% sand, 62% silt, and 25% clay. This soil sample was used as a control material in the cation exchange capacity measurement assays.

Cation Exchange Capacity and Its Assay Protocol. The cation exchange capacity (CEC) is defined as the amount of exchangeable cations such as Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$, and NH$_4^+$ bound to a sample of soil and is usually reported as molar equivalents of monovalent cations bound per weight of soil. It is complemented by the exchangeable cation status, which is the amount of specific ions bound to a given amount of soil or sediment. Since the carbohydrate portion composed of cellulose, hemicellulose, starch, and pectin is degraded more easily than the lignin, humus is largely composed of residues derived from lignin. Composition of soil humus resembles its lignin precursor, possessing phenolic and alcoholic hydroxyls, but has more carboxylic acid groups. Depending on pH, these hydroxyl, carboxylate, and carbonyl groups are able to chelate metals, binding Fe$^{3+}$ and Al$^{3+}$ strongly, but Mg$^{2+}$ only weakly, while binding of Ni$^{2+}$, Pb$^{2+}$, Ca$^{2+}$ and Zn$^{2+}$ is intermediate in strength. Clays are largely composed of hydrated aluminum and silicon oxides, which have different ion exchange properties (11). The CECs of the archeological biochars of Brazil have been shown to resemble those of humus (12). The CEC is therefore an important indicator for potential application of biochar as a soil amendment and carbon sequestration agent.

A modified barium chloride compulsive exchange method (13) was used in this study to determine the CEC for the biochar samples and a soil control from a standard test site as described above in West Tennessee (University of Tennessee Research and Education Center, Milan, TN). The detailed CEC protocol and data tables are given in the Supporting Information (SI). The test materials were ground for 4 min in a SPEX CertiPrep 8000-D Mixer mill with 1 cm steel balls. All samples were assayed in duplicate (i.e., $n = 2$) 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$_2$SO$_4$ and the CEC determined again. Milieu equivalents of acid required for pH adjustment were determined by weighing the titration containers. A further-modified CEC procedure using 10-fold concentrated (0.100 M) MgSO$_4$ for barium displacement and 0.015 M instead of 0.0015 M MgSO$_4$ for the conductivity titration was also carried for the biochar and soil samples.

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 ohm-cm) and dried to fix the biochar samples onto the wafer. A more detailed description of the biochar SEM imaging method is presented in the SI.

Biochar Surface Area Analysis. 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. BET surface areas, are taken from a multipoint plot over a P/Po range 0.05–0.35.

### FIGURE 1. Comparison of Cation Exchange Capacities. The CEC values were determined at pH 8.5 in duplicate ($n = 2$) for cornstover chars 1 (gasification at 700 °C) and 2 (fast pyrolysis at 450 °C), and for a soil control (15).

![Graph showing CEC values for different samples](https://example.com/graph1.png)

### FIGURE 2. Cation exchange capacities (CEC) of biochars 1 (gasification char) and 2 (fast pyrolytic char) and soil control that had been ground 4 min were determined for pH values from 8.5 to 5.0.

![Graph showing CEC vs pH for different samples](https://example.com/graph2.png)

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 using WinPro IR software. Samples were prepared in KBr, 10 wt % and pressed into a pellet. Spectra shown are normalized at ca. 850 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. The observed cation exchange capacity of the biochars varied dependent on the type of pyrolytic treatment (Figure 1). Under a standard assay condition of pH 8.5, the fast pyrolytic char had higher CEC (26.36 ± 0.1676 cmol kg$^{-1}$) than the gasification char (10.28 ± 2.909 cmol kg$^{-1}$). The control soil (sample 15) has a CEC value of 12.51 ± 0.3032 cmol kg$^{-1}$.

Negative values were observed for the CEC determination at pH values less than 7 (Figures 2, 3, 4) although the CEC value of the fast pyrolytic char (sample 2) is relatively higher than that of the gasification char (sample 1) at the tested pH range from 5 to 8.5. The CEC vs pH curves show that the biochars have ion exchange characteristics similar to those observed for humic substances (13), consistent with their composition of residual lignin containing its substituted aromatic rings intact, which have also been shown to survive pyrolysis (14, 15). The CEC curves of the two biochar samples...
The soil sample following wet sieving that retained particles effects of the acid on the biochar materials. Chemical moieties such as hydroxyl or carboxylate groups would be consistent with displacement of cations from acid to adjust the pH than did the soil control (Figure 5). This required the addition of much larger amounts of sulfuric magnesium sulfate displacement. The biochar samples influence the CEC determination by barium chloride-associated ash contents during the loading at pH 8.5. The of the bound cations of the biochar material including its replacement of the bound cations by the added acid is pH dependent. Acidification appears to result in release of bound cations, at pH values lower than 7, resulting in negative CEC values. Negative CEC values observed for soil organic matter have been reported to be due to the presence of bound Ca$^{2+}$ (13). The negative values are probably due to the replacement of the bound cations by the added acid (protons) and/or the inability of the barium to displace all of the loaded Ba$^{2+}$ from the char materials. However, the results from the standard CEC assay using 0.01 M MgSO$_4$ (Figures 1 and 2) are probably more relevant to the physiological soil nutrition conditions.

Overall, the CEC assay showed that the CEC of biochar 2 produced from cornstover with the 450 °C fast pyrolysis process is twice higher than that of biochar 1 produced from cornstover through the 700 °C gasification process. This result indicated that it is important to control the biomass pyrolysis conditions to produce desirable biochar properties in relation to soil amendment and carbon sequestration. Since the CEC of the fast-pyrolytic char 2 can be twice higher than that of the standard soil sample 15, use of biochar products like biochar 2 could improve soil properties such as by increasing the CEC and at the same time serve as a carbon sequestration agent.

Biochar FTIR Results. As shown in Figure 6, samples 1 and 2 of the gasification char (700 °C) and fast pyrolytic char sized 106 µm (0.0041 in.) and larger (Figure 3). The effect of the wet sieve treatment on the CEC varied dependent on the sample. The CEC values obtained were similar to those before sieving for char 2, but decreased 2-fold or greater for chars 1, 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 (see SI Table S1-1). 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. Following the wet sieve procedure, it was noted that the aqueous extract from the char 2 had a dark brown color, while the extracts from char 1 and the soil control had little or no color (see SI Figure S4-1). The aqueous extracts from chars 1 and 2 were scanned in a UV visible spectrophotometer (Unicam) from 200 to 800 nm (SI Figure S4-2). The extract from char 2 had strong absorbance in the UV region characteristic of phenolic and carbonyl groups, which is consistent with the survival of parts of the lignin in the biomass following the pyrolysis.

The assays that used 0.1 M MgSO$_4$ to displace the barium gave CEC values approximately twice those obtained with the concentration (0.01 M) described in the literature (Figure 4). Under the enhanced assay condition using 0.1 M MgSO$_4$ to displace the barium, the fast pyrolytic char still showed higher CEC (50.967 ± 1.890 cmol kg$^{-1}$) than the gasification char (19.251 ± 0.1488 cmol kg$^{-1}$). The control soil (sample 15) showed a CEC value of 29.853 ± 3.098 cmol kg$^{-1}$ in this case. This observation appears to indicate that the lower concentration of Mg$^{2+}$ seems not sufficient to force exchange of the all of the loaded Ba$^{2+}$ from the char materials. However, the results from the standard CEC assay using 0.01 M MgSO$_4$ (Figures 1 and 2) are probably more relevant to the physiological soil nutrition conditions.
(450 °C) showed characteristic bands similar to that of cellulose (15, 17). It is clear from the baseline corrected FTIR spectra of 1 and 2, that with increased temperature, there is a remarkable decrease in features associated with O–H stretch (3600–3100 cm⁻¹), C=C and C=O stretching (1740–1600 cm⁻¹), and aromatic C=C and C–H deformation modes of alkenes (1500–1100 cm⁻¹), and the C–O–C symmetric stretching (1097 cm⁻¹) characteristic of cellulose and hemicellulose (pyranose rings and guaiacyl monomers). There are also absorption bands arising from aromatic C–H out of plane vibrations (three peaks 890, 797, and 723 cm⁻¹) however, these remain intact and the ratio of intensity of these compared relative to intensities at 1650–1500 cm⁻¹ for sample 1 is greater despite the increase in char temperature. This feature can be described as a larger degree in condensation of 1 relative to 2. In summary the FTIR show there is a loss of oxygen content in char 1 comparing to 2, implied by the loss of O–H (3600–3100 cm⁻¹) and the ratio of intensities for the C=O and C=C bands (1700–1500 cm⁻¹) to the shoulder (1200–1100 cm⁻¹) arising from aromatic (substituted) C–H deformations as well as the decrease in ratio of the C–O–C (1097 cm⁻¹) to the shoulder at 1200–1100 cm⁻¹. These features are thought to be due to both the dehydration of the cellulosic and ligneous components as well as an increase in degree of condensation above 400 °C.

Biochar Elemental and Proximate Analysis Results. The volatile matter (VM) content is a useful qualitative measurement of the labile components, Table 1. The VM of sample 1 is 60% less than 2, as a result of increased charring temperature. Both cornstover char samples have a high ash content (58%) but relatively low %C (ca. 33%) and %O (5–8.6%), in comparison to wood and grass chars at similar temperatures (16). The fixed carbon is slightly larger for sample 1, which is typical for this temperature range (>600 °C) and is a reflection of more, highly condensed, thermally stable components formed at higher temperatures (16–18). The lower %O content and lower O:C ratio of sample 1 suggest condensation and dehydration reactions respectively. This also correlates to the FTIR spectra in Figure 6, where the O–H stretching band (3200–3600 cm⁻¹) and C=O and C=C (1600–1740 cm⁻¹) intensities are more intense for 2. Interestingly, the CEC values are also consistently higher up to a factor of 2 (biochar 2 = 26.4 cmol kg⁻¹, biochar 1 = 10.28 cmol kg⁻¹) for biochar 2 (Figure 1). It appears that the CEC values correlate with the O:C ratios of the samples. The higher the O:C the higher the CEC value.

Biochar Surface Analysis Results. BET analysis, Figure 7 and Table 2, of both samples were outgassed a minimum of 8 h at 200 °C. In general the isotherms are of Type I, which indicates microporous solids having relatively small external surfaces. Here, the surface areas were 29 and 12 m²/g for ground samples 1 and 2 respectively, and after wet sieving, the surface areas increased to 154 and 26 m²/g for sample 1 and 2 (see SI). 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 bottleneck or slit-shaped pores. There is no distinct curvature at low relative pressure (P/Po), 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 do not close before reaching a relative pressure of <0.3 in the desorption process indicating that microporosity is present. BET surface areas of sample 1 are consistently higher than that of sample 2. This correlates with the SEM images where the pore wall structure, or “tubules” are seen to remain intact for sample 2, whereas sample 1 shows irregular, undefined structure with large open areas, allowing for more porosity and surface area. Antal and Gronli (18) discuss the effects of temperature on pore structure, surface area and adsorption properties of charcoal. In general, it is found that surface area increased with increasing char temperature, one possibility in surface area increase may be due to increased micropore volume from the removal of the volatilized residual material upon heating at higher temperatures that blocked micropores. Also, due to corn stover’s high content of inorganic materials that partially fill or block access to micropores, wet sieving may remove those inorganic materials which led to higher surface areas of 1 and 2.

SEM imaging (SI Figure S2-1) of char 1 shows that most of the cell walls are obliterated, and no appreciable pore structure is left. In sample 2, SI Figure S2-2, tubules are shown to remain intact, which correlates well that a large pore size distribution is seen in the gas sorption method above. McGinnies and Beall described similar SEM images which showed the disappearance of cell wall layers based on temperature and time (19, 20).

TABLE 1. Biochar Elemental and Proximate Analysis Results from Galbraith Laboratories, Knoxville, TN

<table>
<thead>
<tr>
<th>sample</th>
<th>% loss on drying</th>
<th>% volatile matter @950 °C</th>
<th>% ash</th>
<th>% fixed carbon (by difference)</th>
<th>C% (mol %)</th>
<th>H% (mol %)</th>
<th>N% (mol %)</th>
<th>O% (mol %)</th>
<th>S% (mol %)</th>
<th>O:C (mol ratio)</th>
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</thead>
<tbody>
<tr>
<td>1 (grind)</td>
<td>2.2</td>
<td>7.6</td>
<td>58.8</td>
<td>32.6</td>
<td>33.5 (0.028)</td>
<td>1.04 (0.010)</td>
<td>1.02 (0.0007)</td>
<td>5.1 (0.003)</td>
<td>&lt;0.3</td>
<td>0.11</td>
</tr>
<tr>
<td>2 (grind)</td>
<td>2.3</td>
<td>12.7</td>
<td>58.0</td>
<td>28.7</td>
<td>33.2 (0.028)</td>
<td>1.4 (0.014)</td>
<td>0.81 (0.0006)</td>
<td>8.6 (0.005)</td>
<td>&lt;0.3</td>
<td>0.20</td>
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</table>

*Average percentages of two analyses, with the exception of % loss on drying, which is from a one-time analysis. SD < 10%. SD = standard deviation.
In summary, the CEC of the fast pyrolytic char 2 is about twice as high as that of the gasification char 1. The CEC values correlate well with the O:C ratios of the biochar samples. That is, the higher the O:C, the higher the CEC value. A 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. The CEC values of both gasification char 1 and fast pyrolytic char 2 were not diminished by wet sieving, implying that the cation binding sites will not leach out following soil application. The reduction in the O:C ratio as well as the loss of cellulose and other carbohydrates detected by NMR (see SI) and FTIR of the gasification char, as compared to the fast pyrolytic char, correlates well with a recent study on temperature effects on composition of fescue and pine chars (16). SEM spectra also correlate well with the surface areas for both samples, showing pore size distribution in 2. The greater surface area of the gasification char is consistent with the increase in surface area reported for fescue for temperatures above 500 °C (16). These results indicated that it is important to control the biomass pyrolysis conditions including selecting the appropriate pyrolysis methods to produce desirable biochar properties in relation to soil amendment and carbon sequestration. Since the CEC of the fast pyrolytic cornstover char 2 is substantially higher than that of the standard soil sample 15, it is possible to use biochar products like biochar 2 to improve soil properties such as CEC and, at the same time, to serve as a carbon sequestration agent in soil.

Acknowledgments

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Supporting Information Available

(1) The detailed protocol for biochar sample grinding, sieving, and cation exchange capacity (CEC) determination and includes CEC data tables and calculation equations; (2) the detailed description of scanning electron microscopic (SEM) sample preparation and imaging procedures; (3) solid state NMR 13C spectrum of gasification cornstover char; and (4) filtrate examinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Beall, F. C.; Blankenhorn, P. R.; Moore, G. R. Carbonized wood—Physical properties and use as an SEM preparation. Wood Sci. 1974, 6, 212.

TABLE 2. BET Measurements

<table>
<thead>
<tr>
<th>sample cornstover biochar</th>
<th>surface area (multipoint BET) m²/g</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>29</td>
</tr>
<tr>
<td>1 sieved with 160 µm sieve</td>
<td>154</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>2 sieved with 160 µm sieve</td>
<td>26</td>
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