

B19: Changes in chemical composition of wood chars as a result of varying charring conditions

C.E. Rostad, D.W. Rutherford, R.L. Wershaw

US Geological Survey, Lakewood, CO

The US Geological Survey has a long-term interest in pyrogenic constituents in soil, sediments, and water. Interest in using charcoal as an agricultural soil amendment to increase soil fertility and enhance carbon sequestration is increasing.

Difficulties in analyzing for pyrogenic carbon in soils and sediments, and the inability to separating pyrogenic materials from other forms of soil organic matter, led us to produce chars from wood and wood components under controlled conditions in the laboratory, varying charring time and temperature. Changes in char composition were examined by Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (NMR), mass loss, and elemental composition (carbon, hydrogen, and oxygen). The Boehm titration method was used to measure the content of the acidic functional groups and lactones. This method measures the amount of NaOH, NaHCO₃, and Na₂CO₃ neutralized by the char and enables the determination of total acidity and the fraction of acidity associated with the strong acid fraction, the moderate acid and lactone fraction, and weak acid fraction.

Carbon, hydrogen, and oxygen analysis of uncharred and charred materials showed an increase in percentage carbon, and decreases in hydrogen and oxygen percentages, with charring for all tested materials. Analysis of the hydrogen/carbon and oxygen/carbon atomic ratios for the residual char and for the material lost from the char showed that hydrogen and oxygen were lost more rapidly than carbon from the char during the initial periods of charring. This is consistent with either the loss of aliphatic carbon to volatile degradation products or with the conversion of aliphatic carbon into fused aromatic ring compounds.

Charring conditions have substantial impact on the acid functional group content of chars. Low temperatures (250°C) and long charring times (greater than 72 hours) produce chars from cellulose and cellulose-containing materials (wood and bark) with the highest acid functional group content (comparable to humic materials as high as 8.8 milliequivalents per gram). Acid functional group and lactone content decreases as charring temperature increases for cellulose and cellulose-containing materials. Total acidity in lignin did not change substantially with low temperature charring (250 to 400°C).

This study shows that more acid functional groups are produced at low temperatures than are produced at the higher temperatures used to produce high surface area and porosity in chars. These acid functional groups may be more important than high surface area for sorbing cations and possibly other nutrients. This points out the need for further study into the charring characteristics and charring parameters needed to produce the optimum soil amendment.

B20: The sorption of water by wood char

D.W. Rutherford, C.E. Rostad, R.L. Wershaw

US Geological Survey, Lakewood, CO

Previous studies suggest that the presence of pyrogenic materials in soils might increase the soil water holding capacity. Using chars as amendments to enhance soil productivity and to sequester carbon is of increasing scientific interest. Chars are of interest to the agricultural community because of their effects on soil physical properties such as water retention and aggregation.

Several studies have reported mixing chars in soil and measuring the change in soil water holding capacity. Typically, the chars used in these studies have been byproducts from the pyrolysis of biomass for hydrogen fuel and bio-oil production. This study has evaluated the range of water holding capacities possible from low temperature chars more typical of chars produced on-site from agricultural waste products.

In previous work, we reported the changes in chemical and physical composition of chars that were produced from wood and wood components (cellulose, lignin, wood, and bark) at various charring times (1 hour to 168 hours) and charring temperatures (200°C to 500°C). One product of this work is a set of well-characterized chars, which may be representative of chars produced by natural fires and may be more applicable to chars produced as soil amendments from agricultural waste products.

Water uptake isotherms have been measured on individual chars so that the sorption capacity of each char is not confounded by the state of soil aggregation or mineral contributions. These isotherms show that water uptake by char involves a complex combination of absorption and adsorption. In most cases, the water uptake equals or exceeds the water uptake of the uncharred parent material.

B21: Composition of the Humin Fraction and Coarse Char of Terra Preta de Índios Soils by NMR, Multivariate Curve Resolution and Scanning Electron Microscopy

G. Song¹, E.H. Novotny^{1, 2}, E.R. deAzevedo³, T.J. Bonagamba³, M.H.B. Hayes¹

¹Chemical and Environmental Sciences, University of Limerick, Ireland;

²Embrapa Solos, Rio de Janeiro-RJ, Brazil;

³Instituto de Física de São Carlos - USP São Carlos-SP, Brazil

The high and specific soil organic matter (SOM) contents of the Amazonian Dark Earths (Terra Preta de Índios), and their high contents of P and Ca provide high natural fertility to the soils. Biochar or pyrogenic carbon plays a major role for the SOM stability in these soils and it also provides a significant potential for carbon sequestration and sustainable ecosystems. There are several studies of the humic acids of Terra Preta de Índios soils, however, because of the difficulties in isolation, there is less awareness of humin, the most abundant SOM component. In this study, humic materials were extracted using the IHSS procedure and by exhaustive sequential extraction procedures (0.1 M NaOH + 6 M urea and DMSO + 6% H₂SO₄). Solid-state ¹³C NMR spectroscopy and Multivariate Curve Resolution (MCR) were used for characterisations; additional Scanning Electron Microscopy images were taken from the coarse char fraction. MCR resolved the spectral matrix in three components, and these components can be attributed to wood-like material (vegetal debris), humin, and oxidised biochar material. The wood component spectrum agrees very well with the spectrum of pure eucalyptus wood. On the other hand, the humin spectrum shows an intense signal in the alkyl region (0

40 ppm) with a prominent signal of crystalline polymethylene at 33 ppm. These signals, in association with the carboxyl signal (173 ppm), indicate the fatty acid origin of these compounds. Additionally some altered aromatic compounds (broad and featureless signal at 130 ppm) and cellulosic material (110 and 70 ppm) also are present in this component spectrum. And finally, the oxidised biochar component is characterised by the broad and featureless signal at 128 ppm and the carboxyl at 172 ppm. The shoulder at 167 ppm is evidence for carboxyl directly attached to the aromatic backbone. With regard to the estimated concentrations of each of these components, DMSO/H₂SO₄ solvent is very efficient for solubilising the humin fraction. Moreover, the disruption of the clay aggregates, by ultrasonication, to allow additional oxidised char to be solubilised, and the alkaline urea system is still more efficient in extracting this oxidised char.

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B22: Pyrolytic char characterization for its use as soil amendment

C. Steiner, K. Harris, J. Gaskin, K.C. Das

Department of Biological and Agricultural Engineering, University of Georgia, Faculty of Engineering, Athens GA 30602, USA

The removal of crop residues for bio-energy production reduces the formation of soil organic carbon (SOC) and therefore has negative impacts on soil fertility. Pyrolysis generates liquid or gaseous fuels and a char (biochar) recalcitrant against decomposition. If biochar is used to cycle carbon (C) and nutrients back into agricultural fields, then the use of crop residues as potential energy source or to sequester carbon and improve soil quality can be complementary, not competing uses.

To gain more information about the agronomic potential of biochar, we analyzed CEC, pH, and total and Mehlich-I extractable nutrient content of biochar produced from poultry litter (PL), peanut hull (PH) and pine chips (PC) produced at 400 and 500° C with or without steam activation. The Mehlich I extraction was used as an indicator of plant available nutrients from the biochar. We also leached biochar samples and analyzed the leachate for water soluble organic and inorganic C.

The total and Mehlich-I extractable nutrient concentrations in biochar were strongly influenced by the feedstock. Most nutrients (P, K, Ca and Mg) were concentrated in the biochar and increased further with increasing volatilization losses of C, hydrogen (H), oxygen (O), and nitrogen (N) (decreased conversion efficiency) at higher temperature. Even large proportion of the nitrogen (N) in feedstock was retained in biochar, but the alterations in chemical structure are likely to have long-term consequences for N availability. Other parameters like CEC were influenced by the feedstock and significantly higher in biochar produced at lower temperature. Water soluble C was influenced by the production temperature. The higher temperature reduced the concentration of organic carbon but increased inorganic carbon significantly.

B23: Development of porosity and surface area in chars due to thermal degradation of wood and wood components

R.L. Wershaw, D.W. Rutherford, C.E. Rostad,

US Geological Survey, Lakewood, CO

Chars produced as high surface area sorbents generally are produced at high temperatures and usually employ activation methods. Optimizing chars with particular properties such as resistance to degradation or ability to improve soil fertility may require different charring conditions.

Wood, bark, cellulose and lignin samples were charred at temperatures ranging from 250°C to 500°C for times ranging from 1 hour to 168 hours in experiments aimed at understanding the development of porosity in low temperature chars. Structural changes were examined by changes in porosity as measured by nitrogen gas adsorption. ¹³C NMR spectrometry, mass loss, and elemental composition were combined to estimate the mass of aromatic and aliphatic carbon remaining in the char. Mass loss and elemental composition were combined to estimate the chemical composition of material lost for various time intervals of heating.

None of the materials tested developed porosity at or below the charring temperature of 250°C. Porosity appeared for cellulose, wood, and bark samples when charred at 300°C between 1 and 8 hours. Porosity appeared in lignin when charred at 300°C between 24 and 48 hours. For a fixed charring time, porosity generally increased with charring temperature. For a fixed charring temperature, porosity generally increased to a maximum and then decreased with time. Decomposition, as measured by mass loss and decrease in H/C and O/C ratios and changes in IR and NMR spectra varied continuously with time, while the increase in porosity appeared suddenly and showed a maximum, after which porosity decreased with time. Aromatic carbon mass determined by NMR spectra, elemental composition, and mass loss, were the best indicators of porosity changes. The charring process appeared to initially create aromatic carbon from aliphatic carbon, forming fused ring structures, which provide a matrix in which microporosity can develop. The porosity did not develop until the loss of aliphatic carbon was complete and aromatic carbon began to be lost.

Technical Session 3:

Biochar Amendments to Soils

Oral Presentations

Biochar in rice-based systems: characteristics and agronomic effects

S.M. Haefele¹, C. Knoblauch², Y. Konboon³

¹International Rice Research Institute, Los Baños, Philippines;

²University of Hamburg, Hamburg, Germany;

³Ubon Ratchathani Rice Research Center, Ubon Ratchathani, Thailand;

Although rice residues constitute an enormous resource, farmers often struggle with the huge amounts and actual management practices can have negative side effects including problems during soil preparation, burning of rice residues and related air pollution, and considerable methane emissions from the anaerobic mineralization in flooded rice fields. Use of rice residues for energy production and recycling of the by-product biochar could help to address these issues, reduce the negative effect of rice-based systems on the global climate,