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Chemical characterization of chars developed from thermochemical treatment of Kentucky bluegrass seed screenings

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HIGHLIGHTS

- ▶ This is the first characterization of char from gasified grass seed screenings.
- ▶ The char did not contain toxic levels of metals or PAHs.
- ▶ Char: a bioenergy production byproduct derived from non-food crop residues.
- ▶ The char has numerous soil amendment and industrial applications.

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ABSTRACT

Seed mill screenings would be a considerable biofeedstock source for bioenergy and char production. Char produced from the gasification of residues resulting from cleaning of grass seed and small grains could be recycled to a cropping system as a soil amendment if chemical characterization determined that the gasification process had not produced or concentrated deleterious chemical or physical factors that might harm the environment, crop growth or yield. Previous reports have shown that char derived from the pyrolysis of a variety of biomass feedstocks has potential to enhance soil quality by pH adjustment, mineral amendment, and improved soil porosity. The objective of this research was to characterize char produced from Kentucky bluegrass seed mill screenings (KBss) by a small-scale gasification unit, operated at temperatures between 600 and 650 °C, with respect to polycyclic aromatic hydrocarbons, selected heavy metals, as well as other physical and chemical characteristics, and determine its suitability for agricultural application as a soil amendment. We utilized KBss as a model for seed and grain-cleaning residues with the understanding that chemical and physical characteristics of char produced by gasification or other cleaning residues may differ based on soil and environmental conditions under which the crops were produced. Our results support the hypothesis that KBss char could be applied in a cropping system without toxic environmental consequences and serve multiple purposes, such as; recycling critical plant macro- and micro-nutrients back to existing cropland, enhancing soil carbon sequestration, managing soil pH, and improving water holding capacity. Crop field trails need to be implemented to further test these hypotheses.

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1. Introduction

Char, the charcoal-like material remaining after biomass has been subjected to incomplete combustion, has potential as a soil amendment to sequester carbon (Lehmann et al., 2006; Vacari et al., 2011) and improve soil quality factors such as pH, water holding capacity, and mineral enrichment (Major et al., 2010). Used as a soil amendment, char, frequently referred to as biochar when it is produced under pyrolysis conditions (i.e., approximately 500 °C in the absence of oxygen) can affect the availability of certain trace elements for plant uptake, and in some cases, mitigate negative effects of these elements on plant growth (Namgay et al., 2010). Sorptive characteristics along with the capacity of alkaline char to raise the pH of acidic soils play a major role in the observed impact of char on soil (van Zwieten et al., 2010).

Char properties including pH, mineral and elemental composition, cation exchange capacity (CEC), and potentially the presence of chemicals that could prove detrimental to soil properties are related to the biomass source and method of preparation (Garcia-Perez, 2008; Verheijen et al., 2010). Elemental analyses of chars show considerable variability in the composition of C, Si, Ca, Mg, N, P, and other elements between different biomass feedstocks

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(Chan and Xu, 2009; Liesch et al., 2010). For instance, depending on the feedstock, char pH ranged from 6.2 to 9.6, C content ranged from 172 to 905 g kg^{-1}, N content ranged from 1.7 to 78.2 g kg^{-1}, and P ranged from 0.2 to 73 g kg^{-1} (Chan and Xu, 2009). In addition to this broad range noted in chars produced from different feedstocks, significant differences in elemental composition occur among varieties and cultivars of potential biomass feedstock species (El-Nashaar et al., 2009, 2010a,b).

Successful application of char as a soil amendment will almost certainly require a chemical characterization as part of the permitting process required by most localities. In general, chemical characterization for permitting processes addresses the potential for negative impacts of land application due to the presence of possible heavy metals or organic contaminants in the char. Relatively few published studies have quantified the heavy metals along with the secondary organic contaminants in gasification char produced at temperatures less than 700 °C, particularly in units like those designed for small-scale implementation (Boateng et al., 2007).

The objective of this research was to characterize char produced from Kentucky bluegrass (*Poa pratensis* L.) seed mill screenings (KBss) by a small-scale gasification unit operated at temperatures between 600 and 650 °C with respect to polycyclic aromatic hydrocarbons (PAHs) and selected heavy metals as well as other physical and chemical characteristics and determine its suitability for agricultural application as a soil amendment. Residues from grass seed and wheat production fields and screening mills would be a considerable biofeedstock source for on-farm bioenergy production by gasification systems. Further, the gasification byproduct char, if found non-toxic, could be recycled as a soil amendment to improve soil quality and enhance crop production. Therefore, in this study char produced from gasification of KBss was used as a model for char produced during gasification of other seed or small grain seed cleanings, an abundant and inexpensive feedstock available throughout the world wherever seed crops or small grains are produced.

2. Materials and methods

2.1. Char production

Char from KBss was generated in a farm-scale gasification unit located on a farm near Rockford, WA, courtesy of Farm Power (Banowetz et al., 2010). The stainless steel reactor was air-blown and operated at temperatures ranging from 600 to 650 °C at a feed rate of 60 to 80 kg h^{-1}. The KBss were produced during the seed cleaning operation and consisted largely of small straw components, immature seeds, and remnants of seed coats. The mixture had moisture content of 14% and the predominant particles in the feedstock were less than 5 cm in length.

2.2. Chemical analyses

Char solids analysis (total solids is defined as the sum of the homogenous suspended and dissolved materials in a sample) was determined using EPA method 160.3 M. The elements Ag, Al, As, Ba, B, Cd, Ca, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, and Zn were quantified using EPA methods 3010A and 6010B and Hg using EPA method 7471A (Columbia Analytical Services, Kelso, WA and USDA-ARS, Corvallis, OR) using inductively coupled plasma optical emission spectrometry (ICP-OES). Total C and N were determined using a LECO TruSpec combustion analyzer (LECO, St. Joseph, MI). The toxicity characteristic leaching procedure (TCLP) for metals was conducted using EPA method 1311 for metals. The TCLP for semi-volatile organic compounds including PAHs was determined by High Resolution Gas Chromatography/High Resolution Mass Spectroscopy (HRGC/HRMS) using the following methods; EPA preparation method 1311, EPA extraction method 3501C, and GC/MS EPA method 8270C (Columbia Analytical Services, Kelso, WA). Plant available nutrient determination of NO_3, NH_4, P, incubation-N, and mineralizable N and CEC were determined by Central Analytical Laboratory, Oregon State University, Corvallis, OR. For Cl analysis, char and soil samples were extracted with deionized water and shaken on a New Brunswick Scientific shaker (NBS, Edison, NJ, USA) for 30 min at 350 rpm. After shaking, samples were filtered through Whatman Qualitative No. 42 filters (particle retention 2.5 μm) (Florham Park, NJ) that had been washed three times with 1% H_2SO_4 (v/v) and deionized water. The filtrate was analyzed colorimetrically for Cl (QuickChem method 10-117-07-1-C) on a Lachat flow injection autoanalyzer (Hach, Loveland, CO). Char conductivity and pH was determined using a reference electrode and pH or conductivity meter. The soil used for reference was sampled from a field where the Kentucky bluegrass was grown for seed (Rockford, WA) and was identified as a Freeman series consisting of a very deep, moderately well drained soil formed in loess with a minor amount of volcanic ash mixed in the surface.

2.3. Column elution

A 2.3 cm glass column containing 5 g KBss char was first eluted with 250 mL double deionized water followed by 250 mL of 0.5 M K_2SO_4. Aliquots of 25 mL each were collected during the elution process. Each aliquot was analyzed for NH_4, NO_3, TOC, total nitrogen (TN), Al, As, B, Ca, Cd, Cu, Fe, Hg, Mg, Mn, Mo, Na, Ni, P, Pb, S, and Zn, as described above, with the exception that TOC was quantified using a Shimadzu Total Organic Carbon analyzer.

2.4. Char particle size distribution

The particle size distribution of dry KBss char particles was determined using an array of metal sieving trays sized from 63 to 2000 μm. The results were expressed on a mass basis. A crude char bulk density (volume of the sample and of the pore space) was determined by oven drying the sample at 105 °C until a constant weight was achieved and then final weighed recorded. The weighed sample's volume was determined in a graduated volumetric cylinder after it had reached a final "settled" volume.

2.5. Proximate and ultimate analyses

Proximate and ultimate analyses were performed on crude (non-screened) Kentucky bluegrass seed, KBss, and KBss char. Laboratory analyses were conducted by Wyoming Analytical Laboratories (Laramie, WY) in accordance the American Society for Testing Materials D1762-84.

3. Results and discussion

3.1. Proximate and ultimate analysis

There are no formal classification system for charcoals but the proximate and ultimate analyses that quantify volatile matter, fixed C, and ash content is useful for comparing char (Antal and Grønli, 2003). These analyses provide measure of the stable (fixed C) and labile component of char materials at high temperature and thus maybe useful in evaluating general stability in soils. The amount of fixed C in char, as well as other factors, is a function of temperature during combustion and the feedstock source and is characterized from low to high (Lehmann et al., 2006; Lehmann, 2007). Classification of chars with respect to fixed C have been