Journal of Environmental Management 146 (2014) 189–197

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Characteristics of biochars from crop residues: Potential for carbon sequestration and soil amendment

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ARTICLE INFO

Article history:
Received 17 June 2014
Received in revised form
1 August 2014
Accepted 7 August 2014
Available online

Keywords:
Biochar
Crop residue
Pyrolysis
Carbon
Sequestration
Recalcitrance

ABSTRACT

Biochar has potential to sequester carbon in soils and simultaneously improve soil quality and plant growth. More understanding of biochar variation is needed to optimise these potential benefits. Slow pyrolysis at 600 °C was undertaken to determine how yields and characteristics of biochars differ when produced from eight different agricultural residues. Biochar properties such as carbon content, surface area, pH, ultimate and proximate analysis, nutrient and metal content and the R_{50} recalcitrance index were determined. Significant variations seen in biochar characteristics were attributed to feedstock variation since pyrolysis conditions were constant. Biochar yields varied from 28% to 39%. Average carbon content was 51%. Ash content of both feedstocks and biochars were correlated with biochar carbon content. Macronutrients were concentrated during pyrolysis, but biochar macronutrient content was low in comparison to biochars produced from more nutrient rich feedstocks. Most biochars were slightly alkaline, ranging from pH 6.1 to pH 11.6. pH was correlated with biochar K content. Aromaticity was increased with pyrolysis, shown by a reduction in biochar H/C and O/C ratios relative to feedstock values. The R_{50} recalcitrance index showed biochars to be either class 2 or class 3. Biochar carbon sequestration potential was 21.3%–32.5%. The R_{50} recalcitrance index is influenced by the presence of alkali metals in the biochar which may lead to an under-estimation of biochar stability. The residues assessed here, at current global availability, could produce 373 Mt of biochar. This quantity of biochar has the potential to sequester 0.55 Pg CO_2 yr^{-1} in soils over long time periods.

1. Introduction

This study characterises biochars produced from eight agricultural residues and assesses the global potential of these residues to sequester carbon in soils. Biochar, a recalcitrant form of carbon made by the thermo-chemical conversion of biomass (Manya, 2012), is increasingly discussed as a potential tool in research fields such as negative emissions technologies, climate change mitigation, soil quality and food security. The production and use of biochar, including its addition to soils, animal feed and building products, may offer an opportunity to tackle a number of these issues simultaneously (Xu et al., 2012; Zhao et al., 2013). Production of biochar can also yield oil and gas products which could be used as a renewable energy source (Manya, 2012). The thermal decomposition of biomass into biochar, oil and gaseous products can be achieved using a number of processes including (slow, intermediate or fast) pyrolysis, gasification, hydrothermal carbonisation (HTC), torrefaction and traditional carbonisation methods (Bridgwater, 2003; van der Stelt et al., 2011). Slow pyrolysis produces higher biochar yields relative to the other processes, and is considered further here. During pyrolysis the biomass is heated in the absence of oxygen so that full combustion does not occur. Volatiles and semi-volatiles are released from the biomass as oil and gas products and chemical and physical changes leave a biochar product. Depending on vapour residence time, a secondary char forming process may occur with vapours re-condensing onto the char material, further increasing biochar yields (Antal, 2003).

It is reported within the literature that the characteristics of the biochar product are influenced by many variables such as the biomass feedstock, the temperature of pyrolysis, the maximum temperature of pyrolysis, the hold time at the maximum temperature, and the pyrolysis atmosphere. For example, biochar characteristics such as fixed carbon, surface area, ash content, nutrient content, pH and cation exchange capacity may vary between

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http://dx.doi.org/10.1016/j.jenvman.2014.08.003
0301-4797/

biochars due to both feedstock properties and process conditions (Manya, 2012). The source(s) of variation in biochar characteristics require further research including the effects of initial feedstock characteristics on those of the biochar. Studies which include detailed characterisation of the biochar feedstock are limited in number. Studies which explore the effects of feedstock on biochar characteristics, detailing the characteristics of biochars produced from different feedstocks under uniform process conditions, are also limited. The variety of process conditions used in studies throughout the literature often makes it difficult to compare results regarding the effect of feedstock properties on biochar characteristics. Various potential biomass feedstocks exist for biochar production including agricultural and forestry residues, municipal wastes, animal manures and purpose grown biomass. A number of factors should be considered, however, when determining feedstock suitability, such as the desired biochar characteristics, sustainability requirements, possible toxicity of the biochar and end-use. A prominent research focus for the application of the biochar is its use in soil amendments. This may enable removal of carbon from the atmosphere resulting in long term storage of carbon, with potential co-benefits such as soil improvement and increased plant growth (Biederman and Harpole, 2013). Upon addition of biochar to soil, the variation seen in biochar characteristics can lead to variation in the effects on soil processes and plant growth. The important agronomical properties of biochars when used in soil amendment include porosity, pH, water holding capacity, nutrient content and cation exchange capacity. It is also essential that the biochars contain low levels of contaminants. Improving knowledge of the properties of biochars produced from different crop residues using a uniform pyrolysis process will enable further understanding of how feedstocks affect biochar characteristics. It will also enable discussion of their potential effects on soils, and of the potential of biochars to sequester carbon. This study documents eight crop residues and their resulting biochars, exploring the effects of feedstock on biochar yield and characteristics. This primary data is combined with a modelling study, providing projections of the carbon sequestration potential of the residues assessed. This brings together a number of methodologies and different areas of biochar research.

2. Materials and methods

2.1. Feedstock selection

Agricultural crop residues are an often under-utilised resource which, if large scale conversion to biochar and co-products was achieved, could offer both agronomic and carbon sequestration benefits. Eight agricultural crop residues were selected here for analysis. Crop production data for the years 2004–2006, from the Food and Agriculture Organisation's (FAO) statistical database; FAOSTAT, was used to determine regionally predominant crop types (FAO, 2014). Residue to product ratios (RPRs) from the literature were applied to the production quantities of the predominant crop types, determining those crop types that would yield the highest residue quantities. The RPR values were calculated as averages from the literature (Supplementary Material, Table S1). Crops with high productivity and high RPR were chosen for analysis due to their potential availability, in large quantities, for biochar production. The feedstocks used for biochar production were: coconut husk, coconut shell, cotton stalk, olive pomace, palm shell, rice husk, sugarcane bagasse, and wheat straw.

Wheat straw and rice husk samples were sourced from fields in the Faisalabad District, Punjab province, Pakistan (31 21 N, 72 59 E), Sugarcane bagasse was sourced from Samundri, Pakistan (30 48 N, 71 52 E). Samples were transported in plastic bags and, on receipt, ground and sieved to 1.4–2.8 mm particle size. Coconut husk and shell, and palm kernel shells were sourced from the waste stream of coconut and palm kernel oil processing in the western region of Ghana. The coconut and palm kernel shells, as received, ranged from 3.35 to 10 mm particles. Cotton stalks were sourced from Northern Syria. Olive pomace, sourced from the waste stream of an olive processing plant in the Southern Mediterranean region, was received in powdered form with particle size <2 mm. All samples were stored in air tight containers after grinding, prior to pyrolysis.

2.2. Pyrolysis reactor

A laboratory scale fixed-bed slow pyrolysis reactor was developed to pyrolyse the biomass feedstock. The reactor was 250 mm in length by 30 mm internal diameter and was externally heated by a 1.2 kW tube furnace (Supplementary Material, Figure S2). A stainless steel sample crucible was used to hold 6 g of each crop residue sample. The eight biomass types were pyrolysed separately with a heating rate of 5 °C min^{-1} and peak temperature of 600 °C which was held for one hour. The intermediate peak temperature of 600 °C was used here as lower pyrolysis temperatures may result in incomplete charring of the feedstock material and higher pyrolysis temperatures may reduce the yield of biochar. Williams and Besler (1996) produced biochar at yields of between 16.2% and 60.8% from the pyrolysis of wood with temperatures ranging from 300 °C to 720 °C and heating rates of between 5 °C min^{-1} and 80 °C min^{-1}. Biochar yields were higher at lower temperatures and lower heating rates and, whilst the highest biochar yields were achieved at 300 °C, the higher yields may indicate incomplete conversion of biomass to biochar. Although it is well documented that increased temperature corresponds to a decreased yield of char, it has also been documented that the quality of char may increase with increasing temperature. Other studies have found an increase in carbon content and calorific value of the biochars with increasing temperature (Peters, 2011). Biochar recalcitrance is also seen to increase with increasing temperature (Harvey et al., 2012). Pyrolysis at 600 °C was used to balance these factors. Pyrolysis was undertaken in a nitrogen (N_2) atmosphere with a flow rate of 200 ml min^{-1} at 20 °C and 1 bar. The N_2 carrier gas was introduced 10 min before heating commenced to purge oxygen from the system. Biochar was collected and weighed after cooling. The oil product was collected using a three condenser system, with glass wool used to remove uncondensed semi-volatiles from the gas stream. Product gases were collected in a gas tedlar bag and analysed off-line by gas chromatography.

2.3. Analytical methodology

Proximate analysis of the raw feedstocks and biochars was conducted using a standardised method. Samples, in a ceramic crucible with lid, were oven dried at 105 °C for 2 h then heated to 550 °C and held for 4 h. The lids were removed and the samples held at 550 °C for 1 h to combust the fixed carbon, leaving the residual ash. Moisture, volatiles and ash were calculated by direct weight loss and fixed carbon content calculated by difference. Carbon, hydrogen, nitrogen, sulphur and oxygen content of the feedstocks and biochars was determined by ultimate analysis using a Flash 2000 organic element analyser with thermal conductivity detector. 3 μg of each sample was analysed, in duplicate, with vanadium pentoxide (V_2O_5) added to aid combustion. Oxygen was calculated by difference. Carbon yield, defined here as % carbon retained from the original biomass carbon, was calculated from the ultimate analysis results. Macronutrient content of feedstocks and biochars was analysed using inductively coupled plasma mass spectrometry (ICP-MS). 0.2 g of sample was digested in 8 ml of