A feasibility study of agricultural and sewage biomass as biochar, bioenergy and biocomposite feedstock: Production, characterization and potential applications

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HIGHLIGHTS

- PSD biochar was found to have the highest surface, carbon content and lowest ash content.
- PSD biochar is suitable for carbon sequestration, remediation and biocomposite construction.
- Syngas from PSD and PG pyrolysis yielded syngas having highest calorific values (15-16 MJ/dsm).
- BL, PG and SS derived biochars have potential as liming agents due to their high ash content.

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ABSTRACT

In this study, we pyrolysed six waste derived biomass: pine sawdust (PSD), paunch grass (PG), broiler litter (BL), sewage sludge (SS), dewatered pond sludge (DWP), and dissolved air-floatation sludge (DAF) into biochar. Biochars were characterized using scanning electron microscopy, energy dispersive X-ray spectrometry, X-ray diffraction, Fourier transform infrared spectroscopy, inductively-coupled plasma mass spectrometry, ^{13}C-solid-state nuclear magnetic resonance spectroscopy, and X-ray photoelectron spectroscopy to evaluate their feasibility for potential agronomic and environmental applications. Syngas produced during the pyrolysis process was also analyzed to determine the energy values. Results show that PSD biochar has the utmost potential for carbon sequestration and contaminant remediation due to its high surface area, aromaticity and carbon content. Additionally given its low ash content, PSD biochar could also potentially be used as filler in wood plastic biocomposites. Low levels of heavy metals (Cr, Cu, Zn, As, Cd, Hg, and Pb) in all biochars suggest that biochars are also applicable for land application according to the United States Environmental Protection Agency regulation 40 CFR part 503. The composition of syngas evolved during the pyrolysis of feedstocks showed little difference in the calorific values, ranging from 12–16 MJ/dsm with PSD having the maximum calorific value of 16 MJ/dsm.

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1. Introduction

Biochar is a carbon-rich byproduct that is produced when biomass (e.g. agricultural crop residues, wood, waste) is pyrolysed, i.e. heated to temperatures of 400–700 °C in an oxygen-depleted environment (Kookana et al., 2011). Several agronomical benefits can result from using biochar as a soil amendment: it can be added to degraded soils to improve soil structure and fertility (Chan et al., 2007; Lehmann et al., 2006); it can improve cation exchange capacity and reduce aluminium toxicity to plants (Chan et al., 2007); it can also improve water retention leading to higher crop productivity (Glaser et al., 2009). Additionally, biochar production and soil amendment can sequester carbon and reduce greenhouse gas emissions (van Zwieten et al., 2010; Wang et al., 2013), mitigate nutrient leaching and increase biological activity (Lehmann, 2007). From an environmental aspect, biochar can have a significant influence on the mobility and retention of chemicals in soils. Its addition to soil amendment applying biochar might be an effective way to remediate land contaminated with various organic and inorganic contaminants associated with agriculture and livestock wastes (Kookana et al., 2011). Biochars produced from a range of biomass have been shown to remove contaminants such as metals (Uchimiya et al., 2011), PAHs (James et al., 2005), pesticides (Zheng et al., 2010), herbicides (Cao et al., 2009), steroid hormones (Sarmah et al., 2010) and veterinary antibiotics (Teixido et al., 2011;

Zheng et al., 2013). It is for this reason that some authors have described biochar as a 'supersorbent' (Koelmans et al., 2006; Lohmann, 2003).

In the past several authors have evaluated properties of biochars produced from a variety of biomass such as: wood (Kloss et al., 2012); apricot stone, hazelnut shell, grape seed and chestnut shell (Ozcimen and Ersoy-Mericboyu, 2010); orange peel (Chen and Chen, 2009); green waste (Zheng et al., 2010) and paper mill sludge and poultry litter (Singh et al., 2010; van Zwieten et al., 2010). However, to date there is a dearth of information on the pyrolysis of waste biomass; such as paunch grass, saw dust, broiler litter, sewage sludge and chicken sludge. In New Zealand (NZ) these materials have no or negative value and would normally be discarded as waste in landfills. However, stringent regulations and legislative issues with the existing treatments (which includes waste residue run-off, odors and land availability) are stimulating the waste management sector and the regional councils to identify alternative and long-term viable options for their safe disposal in a sustainable way while gaining environmental and agronomic benefits.

While converting wastes into biochar through pyrolysis is potentially an effective waste management solution, economic feasibility of producing biochar for agronomic use is governed by the value of the biomass feedstock used. In the NZ business environment, where stationary energy is among the cheapest in the developed world, it is essential in projecting economics to obtain a secure, long-term supply of biomass at a low cost. This presents the need for new technologies which could accommodate lower grade feedstocks to produce energy in usable forms to complement biochar production. Low grade biomass feedstocks bring both challenges and opportunities. The range of biochars produced in this study is chemically and physically diverse and therefore the scope for benefits and potential risks is very broad.

Feedstock and pyrolysis conditions are the most important factors controlling the physical and chemical properties of the resulting biochar (Downie et al., 2009) and ultimately deciding its end application. The overarching objective of this study was therefore to evaluate the physical and chemical properties of six biochars produced from a variety of agricultural and sewage biomasses using an array of spectroscopic techniques, and to provide a balanced perspective on their potential agronomic and environmental applications pertinent to the properties of each biochar.

2. Methods

2.1. Feedstock selection

Six feedstocks were used in this study. Pine sawdust (PSD) was sourced from a saw mill. Sewage sludge (SS), the product of the post activated sludge wastewater system was obtained from a wastewater treatment plant near Hamilton, NZ. Paunch grass (PG), the residual undigested grass from cow stomachs was collected from an abattoir near Hamilton, NZ.

Broiler litter (BL), dewatered pond sludge (DWPS), and dissolved air floatation (DAF) sludge were supplied by a chicken factory (Inghams Enterprises Pty Ltd). BL was a mixture of chicken feces and bedding material such as untreated pine shavings. DWPS was the excess biomass from an activated sludge wastewater system (sequential batch reactor and aeration pond). DWPS was thickened in two stages, first using a disc thickener with addition of coagulation polymers and then using a screw press (with addition of more coagulation polymers) to a final total solid content of approximately 13%. DAF sludge was poultry wastewater treated by the addition of coagulant, flocculent and dissolved air.

2.2. Biochar production

All the feedstocks were pyrolysed using a full-scale continuous steam gasification slow pyrolysis process. The process involves delivery of up to 2 tonne/h of feedstock from a hopper into a spiral heat exchanger which is heated counter currently with hot boiler gasses. The feedstock residence time in the heat exchanger is 8–10 min with a highest heat treatment temperature (HTT) of 680 °C, which was monitored with a thermocouple placed on the body of the pyrolysis unit. The pyrolysed char was separated gravitationally from the hot gasses which were condensed in an air condenser. Hot air recovered from the condenser was recycled back into the feed system. Syngases flared during the process were also captured in tedlar bags for further gas composition analysis.

2.3. Biochar characterisation

The biochars were homogenized and grounded to <2 mm prior to analysis and characterisation using various techniques. The pH and EC of the biochars were measured on 1:10 water extracts shaken for 24 h in a rotary drum shaker and then centrifuged, using a PHM62 standard pH meter calibrated with pH 4 and 7 buffer solutions and an in-house conductance meter with a cell constant $K = 0.69$ cm^{-1}. The C, H, N, S, and O (by difference) contents were determined using an EA 1108 CHNS-O analyzer at the Campbell micro analytical laboratory in Dunedin, NZ. The ash content of the biochars was determined according to Active Standard (ASTM D5630), which involved heating in furnace at 590 °C for 12 h and measuring the weight loss gravimetrically. Exchangeable cations were determined using Inductively Coupled Plasma Mass Spectroscopy (ICP–MS). The specific surface area (SSA) of biochars was measured using the BET nitrogen adsorption isotherm method. Biochars were further characterized using a range of techniques: scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), inductively coupled plasma mass spectrometry (ICPMS) following acid digestion, energy dispersive X-ray analysis (EDS), ^{13}C-solid-state nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopy (XPS). Full descriptions of the experimental protocols, sample preparation and analysis for these techniques are presented in supplementary information.

2.4. Gas analysis

The composition, energy value and estimates of the volume of syngases produced from each feedstock were also determined. This provides information on the energy potential the syngas contribution to the economic case of the operation. Syngases flared during the production of biochars from each of the feedstocks were periodically collected using tedlar bags and later analyzed for compositions and calorific value. Gas analyses were carried out at CRL Energy Ltd. (Wellington, NZ) using an Agilent 3000A microgas chromatograph. In order to obtain a coarse estimate of relative volumes of gas produced by each feedstock, the time taken to fill a 5 L tedlar bag mid-way through the pyrolysis process was determined in several replications.

3. Results and discussion

3.1. Basic proximate and ultimate analysis

Proximate and ultimate analyses were performed to obtain C, H, N, S, and O contents, ash content, pH and EC as well as calorific values for biochars (Table 1). The fixed C content for PSD biochar was the highest at ~91% followed by BL biochar (87%) and was lowest for PG biochar at (~65%). Carbon content of biochars is a function of a multitude of factors such as pyrolysis temperature, residence time, moisture content of the biomass, and the composition of the biomass, including whether they are primarily cellulosic (e.g. grassy) lignocellulosic (i.e. woody), or contain little cellulose or lignin (e.g. algal biomass or well-processed biomass that is substantially of microbial origin). Since HTT and residence time were kept constant for all the biochars in this study, C contents of biochars should be a function of the moisture content and composition of the source biomass. Indeed, the biochars with the highest C contents are those derived from woody (PSD) or predominantly woody