2-2 Development of Technologies for the Utilization of Agricultural and Forestry Wastes: Preparation of Biochar from Agricultural Residues

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ABSTRACT

In this study biochar was prepared by pyrolysis of various agricultural residues such as rice straw, wheat straw and corn stover. The effect of pyrolysis temperature (400, 450 and 500 °C) on the yield and properties of the biochars was investigated. Yields of rice straw, wheat straw and corn stover biochars decreased with the increase of temperature. Specific surface area of rice straw biochar decreased with the increase of pyrolysis temperature, however the same trend was not observed for wheat straw and corn stover biochars. The pH and water adsorption capacity and extractable phosphorous contents of rice straw and corn stover biochars were much higher than the wheat straw biochar. All of the biochars produced are comparatively moderate in carbon content, and corn stover biochar was high in nitrogen content. This means that rice straw and corn stover biochars have properties that provide water retention, acidic soil neutralization and direct nutrition benefits.

KEYWOEDS

Agricultural Waste, Biochar, Rice Straw, Wheat Straw, Corn Stover

INTRODUCTION

Plants and crops-derived agricultural wastes or residues are lignocellulosic biomass which can be used as animal food, compost, plowing back into soil, cattle house flooring, and covering material for field, etc. Recently, utilization of biomass as a source of renewable energy is attracting considerable attention. Since biomass is carbon neutral as a source of energy, bioenergy is seen as one of the primary possibilities for preventing global warming. Pyrolysis is a thermochemical technique in which the biomass is heated in inert or oxygen deprived atmosphere to produce fuels (gas, liquid and solid). During pyrolysis, syngas and/or bio-oil are produced along with a char residue (biochar). Biochar is highly resistant to microbial degradation upon land application and has a number of positive effects relating to soil fertility. The approach i.e., the application of biochar as a soil ameliorant, is considered carbon-negative because carbon is sequestered in the soil in the form of biochar, thus releasing less carbon than do carbon-neutral technologies. Production and application of biochar to the soil is rapidly gaining recognition as a viable option in permanent carbon storage, while its benefits to soil fertility continue to emerge (Renner, R., 2007). Biochar is thought to have some common features regardless of feedstock source or synthesis, in particular, potential soil quality benefits which include increases in the water holding capacity, cation exchange capacity, and carbon content of amended soils (Lehmann et al., 2008). In addition, biochar may enhance soil fertility (Van Zwieten et al., 2010) and soil aggregation (Novotny et al., 2009). Generally, biochar additions to soil may increase the soil carbon and nitrogen pools but the accompanying nitrogen addition may have little added benefit for plant nutrition (Granatstein et al., 2009).

Biochar is a product that can be manufactured from almost any uncontaminated organic matter, such as crop residues, bark, stem timber (logs), non-stem logging residues (bark, branches, tree-tops), various grasses and agricultural plant residues. The main processes for char production are fast or slow pyrolysis (biomass heating without air or oxygen) or gasification (run in the regime that leaves charcoal residue). Biochar production is typically self sufficient in energy requirements and can produce surplus energy as heat or biofuel for use in various energy conversion processes, including transportation and electricity production. The properties of biochar depend on the type of feedstock, pyrolysis temperature and other preparation conditions. In this study, biochar is prepared from agricultural residues such as rice straw, wheat straw and corn stover under various preparation conditions. The main purpose of this study is to investigate the effect of type of feedstock and preparation conditions on the char yields and the biochar properties such as specific surface area, water (vapor) adsorption capacity, pH and extractable phosphorus contents, etc.

MATERIALS AND METHODS

1. Biochar Feedstock

Three different types of agricultural residues, namely, rice straw, wheat straw and corn stover were selected for the production and evaluation of biochar. All feedstocks were collected from the farmers of Okayama Prefecture, Japan. The feedstocks were first sundried and kept in plastic bags inside well-sealed plastic containers for long term room-temperature storage.

2. Biochar Preparation

A series of initial experiments were conducted using all three biochar feedstocks by thermogravimetric (TGA) method with a thermobalance (SHIMADZU TG-30S) to compare the effect of pyrolysis temperature on the pyrolysis behavior of the feedstocks. The biochar feedstock was initially dried to constant weight at 110 °C and a 5~7mg aliquot was loaded into a platinum wire mesh basket suspended in a sealed quartz tube reactor inside a tubular electric furnace of the thermobalance. The quartz tube reactor was constantly purged with dry nitrogen gas at 0.2 L min^{-1} and then heated at a constant rate of 10 °C/min from 100 °C to 500 °C. The change in sample weight due to pyrolysis of feedstock was monitored against the pyrolysis temperature via a thermocouple inserted directly into the reactor close to the sample.

The biochar was prepared by pyrolysis of the feedstocks in a tubular electric furnace in constant nitrogen flow. In a typical run, a bundle (7 cm long) of dried feedstock was loaded on a ceramic tray and the tray was placed inside a tubular ceramic reactor. The reactor was purged with dry N_2 (99.99%) gas flow for 3 hours to remove any oxygen remaining in the reactor. Then the reactor was heated at a heating rate of 10 °C/min from room temperature to a predetermined pyrolysis temperature (400 °C~500 °C) in a nitrogen flow of 1L/min or 2.5 L/min and the final hold temperature was maintained for 1 min after which time the reactor was cooled down to the room temperature over a period of 2~3 h. Finally the biochar sample was removed from the furnace and the biochar thus produced was immediately weighed. The yield of a biochar was determined from the initial weight of the dry feedstock and the final weight of the biochar sample.

3. Biochar Characterization

The biochars produced in this study were subjected to a range of analyses in order to provide a basic physio-chemical characterization of each raw and pyrolyzed material. Carbon, nitrogen and hydrogen contents of the biochar sample were determined by dry combustion using a Perkin Elmer Elemental Analyzer 2400II with routine analytical uncertainty better than ± 5% of the measured value. In addition, ash content of biochar was determined by combustion of biochar sample at 550 °C for 2 h. pH was determined in 20 ml de-ionized H_2O: 0.05g biochar mixtures after shacking for 6h at room temperature. Extractable phosphorus was determined in biochar(~0.05g): water (20 ml) mixture and biochar (~0.05g):HCl (3N/L HCl (5ml) + de-ionized H_2O(15 ml)) mixtures by colorimetric method using molybdenum blue reagent with a UV-VIS spectrophotometer (SHIMADZU UV 260) in the wavelength range around 885 nm. Surface area was determined by nitrogen adsorption using BET method (Micromeritics Gemini 2375). H_2O adsorption capacity of biochar sample was determined gravimetrically by adsorbing saturated water vapor at 25 °C for 24 h in a desiccator inside an incubator.

RESULTS AND DISCUSSION

A series of initial experiments were conducted using all three biomass feedstocks by thermo gravimetric (TGA) method with a thermobalance (SHIMADZU TG-30S) to compare the effect of pyrolysis temperature on the pyrolysis behavior of the feedstocks. Figure 1 shows the results of thermo gravimetric analysis of each feedstock. It is evident from this figure that the change (loss) in sample weight due to pyrolysis commenced at around 250 °C for rice straw and wheat straw, whereas corn stover started to pyrolyze at a much lower temperature (150 °C). It is worth mentioning that the weight loss in N_2 flow in the temperature range of ~250 °C to ~400 °C is due to the evolution of volatile matters (gas and liquids) from the biomass. The remaining sample weight (residual amount) up to the final pyrolysis temperature is generally attributed to the combined weight of char + ash. We will refer the combined weight of char + ash as the weight of biochar in this paper. It is also observed in Figure 1 that the residual amount (char + ash) of rice straw is much higher than that of wheat straw and corn stover. The high residual amount for rice straw pyrolysis is due to the high ash content of rice straw compared to wheat and rice straw (Worasuwannarak et al., 2007). From the above TGA results, we decided to investigate the effect of pyrolysis temperature on the efficiency of biochar production in the temperature range of 400 °C to 500 °C.

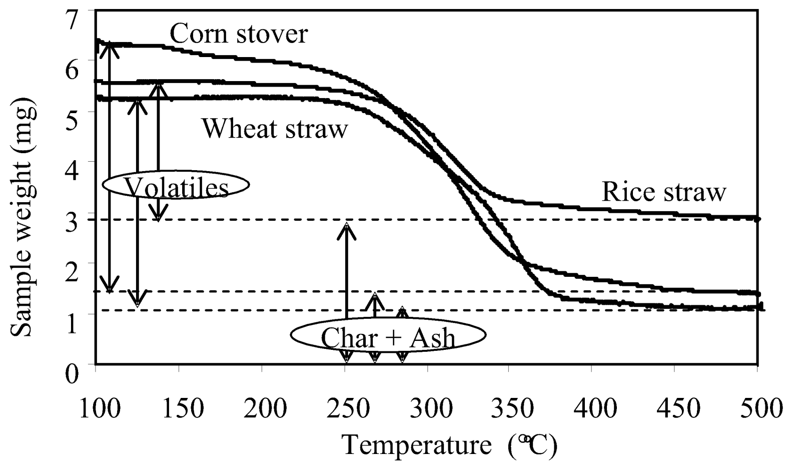

Fig. 1. Pyrolysis behavior of rice straw, wheat straw and corn stover studied by TGA

Table 1 summarizes the results of char yield and specific surface area of the biochar produced from rice straw, wheat straw and corn stover. The yield of biochar from all three types of feedstock studied decreased with the increase of pyrolysis temperature. Char yield of rice straw biochar was higher than corn stover and wheat straw biochars. These results are reasonable because the mineral (particularly silica) content of rice straw is higher than that of wheat straw and corn stover which resulted in a higher char yield for rice straw (Worasuwannarak et al., 2007). Specific surface area of rice straw biochar was also higher than the other two biochars, particularly the corn stover biochar. Specific surface area of rice straw biochar increased with the increase of char yield and the decrease of pyrolysis temperature. This trend, i.e., increase of specific surface area with char yield, was not observed for corn stover and wheat straw biochars. The higher specific surface area of rice straw biochar may be due to the partial contribution of the high surface area of the rice straw ash. Further investigation is needed to clarify these results.

Table 1 Yield and specific surface area of biochar obtained form various agricultural residues at different temperatures.

Feedstock	Pyrolysis Temperature (°C)	Heating Rate (°C/min)	Char Yield (wt %)	Specific Surface Area (m^2/g·biochar)
Rice straw	400	10	43.1	70
	450	10	42.0	48
	500	10	40.7	42
Wheat straw	400	10	33.8	21
	450	10	31.8	11
	500	10	28.4	34
Corn stover	400	10	41.7	8
	450	10	39.6	25
	500	10	35.7	10

Table 2 shows the ash content and C, H, N composition of the biochars prepared from various feedstocks at 500 °C. Although the ash content of rice straw is much higher than the corn stover and wheat straw, the ash content of the rice straw biochar (38 wt %) is slightly lower that of corn stover biochar (40 wt%). Rice straw biochar has the highest carbon content (about 54 wt%), and wheat straw biochar the lowest (about 42 wt%). Another noticeable difference in the composition is the nitrogen content of the biochars: Corn stover biochar has quite a high nitrogen content compared to wheat and rice straw biochar. These results suggest that corn stover biochar with high nitrogen content could be a suitable soil ameliorant to improve the nutrient content of the soil. Assuming that the carbons in these biochar are stable under the microbial conditions, the biochar obtained from rice straw, wheat straw and corn stover with moderate carbon contents have potential for greenhouse gas reduction by carbon storage in agricultural soil.

Table 2 Char yield, ash content and elemental composition(C, H, N) of biochar obtained form pyrolysis of various agricultural residues at 500 C.

Biochar	Char Yield (wt %)	Ash Content (wt %)	C, H, N, Composition (wt %)		
			C	H	N
Rice straw	40.7	38	53.49	2.31	0.39
Wheat straw	28.4	34	41.46	1.77	0.58
Corn stover	35.7	40	49.18	2.21	2.12

Table 3 shows the water adsorption capacity, pH and extractable phosphorous content of the biochars prepared from various feedstocks at 500 °C. Water adsorption capacities of both rice straw (about 40 %) and corn stover biochars (about 30 wt%) are much higher than the wheat straw biochar (about 3 wt%), suggesting that the rice straw and corn stover biochars can be used as a soil ameliorant to improve the water retention of the soil. However the reason for the difference in water adsorption capacity of these biochar cannot be explained by their specific surface area data only (see the data for 500 °C in Table 1). It may be possible that the hydrophilicity of these samples is different due to the difference in their chemical nature, such as the presence of different amounts and different types of mineral matter and the presence or absence of hydrophilic carbon surface groups. The above results indicate that rice straw and corn stover biochars have properties that provide water retention benefits to the soil.

The pH of the water treated with various biochars is also reported in Table 2 and the relative order of the measured pH is as follows:

Corn stover biochar > Rice straw biochar >> Wheat straw biochar.

It is evident that the pH of all of the samples is greater than 7 indicating that all of the biochars prepared in this study are alkaline in nature to some extent. The higher pH of the biochar treated water is an indication of the presence of water soluble inorganic and organic bases in the biochars. However, the relative contribution of inorganic and organic bases in these biochars can not be discussed from the above results. It can be suggested that the biochars from rice and corn stover have properties that provide acidic soil treatment benefit.

The amount of extractable phosphorous from biochar (~0.05g): water (20 ml) mixture and biochar (~0.05g): HCl (3N/L HCl (5ml) + de-ionized H_2O (15 ml)) mixtures is shown in the last two columns of Table 1. The results are shown as the extractable phosphorous content of each biochar with a unit of mg/g·biochar. From Table 3 it is evident that the extractable phosphorous

Table 3 Water adsorption capacity, pH and extractable phosphorous content of biochar obtained form pyrolysis of various agricultural residues at 500 °C.

Biochar	Water adsorption capacity (wt %)	pH of biochar-treated water	Extractable phosphorous content (mg /g·biochar)	
			With H_2O	with HCl
Rice straw	41	9.63	6.7	7.4
Wheat straw	3	7.46	0.2	1.3
Corn stover	32	10.87	13.3	14.5

content of corn stover biochar is particularly high (about 14.5 mg/ g·biochar). On the other hand, the extractable phosphorous content of wheat straw biochar was very low. Rice straw biochar has an intermediate value. Use of HCl solution for phosphorus extraction resulted in a very slight increase in extractable amounts indicating that most of the extractable phosphorous compounds in the biochar are water soluble.

Poultry litter biochar made under similar conditions has been reported to have a carbon content of ~38%; nitrogen content of 2%; pH of 9.9; and an available phosphorous concentration of 11,600 mg kg^{-1} (Chan et al., 2009). Togoe et al. produced biochar at 500 °C from poultry litter with 12.3% C, 2.6% N, pH of 9.93, and a P content of 18,170 $mgkg^{-1}$ (Tagoe et al., 2008). In contrast, ligno-cellulosic (wood) biochar tends to have much higher carbon contents, and cation exchange capacities compared to the poultry litter biochar, with pH values below 7 and significantly lower ash and available nutrient contents (Chan et al., 2009; DeLuca et al., 2009; Ozcimen et al., 2010). Therefore, carbon contents of the biochars produced from rice straw, wheat straw and corn stover in the study are higher than poultry litter biochar but lower than woody biochar. The extractable phosphorous content from corn stover biochar in this study is comparable to the poultry litter biochar and sewerage sludge biochars (Chan et al., 2009). The extractable phosphorous content of corn stover biochar is very promising because phosphorus is one of the inorganic nutrients essential for crops growth and sources of phosphorous are limited globally.

CONCLUSIONS

In this study biochar was prepared by pyrolysis of various agricultural residues such rice straw, wheat straw and corn stover. The effect of pyrolysis temperature (400, 450 and 500 °C) on the yield and properties of char was investigated. The following results were obtained:

Yields of all biochars decreased with the increase of temperature. Surface area of rice straw biochar decreased with the increase of pyrolysis temperature, however the same trend was not observed for wheat straw and corn stover biochars. The pH and water adsorption capacity of rice straw and corn stover biochars was much higher than the wheat straw biochar. Extractable phosphorous contents of the biochars were in the following order: Corn stover char (14.5 mg/ g·biochar) ≥ Rice straw char (7.4 mg/ g·biochar) >> wheat straw char (1.3 mg/ g·biochar). All of the biochars produced were comparatively moderate in carbon content, and corn stover biochar was high in nitrogen content. This means that rice straw and corn stover biochars have properties that provide water retention, acidic soil neutralization and direct nutrition benefits.

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