3-2 Development of Technologies for the Utilization of Agricultural and Forestry

Wastes: Preparation of Biochar from Coconut Husk and Rice Husk

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ABSTRACT

In this study biochar was prepared by pyrolysis of coconut and rice husks. The effect of pyrolysis temperature (400, 450 and 500 °C) and the rate of heating (10 °C/min or °50 °C /min) on the yield and properties of the biochars were investigated. The char yield decreases with increase of heating rate and increases with the decrease of pyrolysis temperature. Higher pyrolysis temperatures resulted in higher surface area with a maximum at 450 °C for rice husk biochar and the specific surface areas of coconut husk biochar (CHBC) was lower than the rice husk biochar (RHBC). Rapid heating resulted in slightly higher water adsorption capacity, however no correlation of pyrolysis temperature with the water adsorption capacity of biochar was observed. Water adsorption capacity of CHBC was higher than the RHBC. Higher pyrolysis temperature and faster heating rate resulted in slightly higher pH of the biochars in water. CHBC has higher pH than the RHBC due to higher alkali metal content in CHBC. The highest biochar-induced CO₂ emissions were observed from the samples containing the CHBC prepared at lower temperatures and decreasing emission with increasing pyrolysis temperatures.

KEYWOEDS

Agricultural Waste, Biochar, Rice Husk, Coconut husk, Corn Stover

INTRODUCTION

Biochar is considered a potential climate change mitigation technology because it removes CO₂ and simultaneously release energy. It would be carbon negative if its use sequesters more carbon than it emitted. 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 (Joseph 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 husk and coconut husk under various preparation conditions. The main purpose of this study is to investigate the effect of type of feedstock and preparation conditions such as pyrolysis temperatures and heating rates on the char yields and the biochar properties such as specific surface area, water (vapor) adsorption capacity, pH, cation exchange capacity and their stability in soil, etc.

MATERIALS AND METHODS

1. Biochar Feedstock

Two different types of agricultural residues, namely, rice husk and coconut husk were studied for the production biochar. Rice husk was collected from the rice farmers of Okayama Prefecture and the coconut husk was received from Hue, Vietnam. The feedstocks were first sundried and kept in plastic bags inside well-sealed plastic containers for long time room-temperature storage.

2. Biochar Preparation

The biochars were 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 in a stainless steel mesh basket and the basket was placed inside a tubular ceramic reactor. The reactor was purged with dry N₂ (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 or 50 °C/min from room temperature to a predetermined pyrolysis temperature (400 °C~500 °C) in a nitrogen flow of 1L/min and kept at final temperature 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. In this report, the biochars prepared from coconut husk will be denoted as "CHBC" and the rice husk biochars as "RHBC".

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. For pH measurement, biochar was soaked in water in a weight ratio of 1:100 and stirred for 3h at room temperature. Surface area was determined by nitrogen adsorption using BET method (Micromeritics Gemini 2375). H₂O 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.

Biochar stability experiment included 4 samples, i.e. soil amended with three different biochar produced at different pyrolysis temperatures (400, 450, and 575°C) and slow a heating rate (10 °C/min) in a weight ratio of 40 (soil):1(biochar). The incubation period was 5days days. During the incubation period the soil-biochar mixture in a glass container (50 ml) was kept at constant temperature of 25°C and mixed with a rotary mixer. The carbon dioxide (CO₂) emission from each container was measured using gas chromatograph mass spectrometer (Shimadzu QP2010)). The overall degradation of biochar was calculated using simple difference, i.e. CO₂ emission from the treatment soil minus emission from the reference soil (no biochar added).

RESULTS AND DISCUSSION

Figure 1 shows the effect of pyrolysis temperature and heating rate on the yield of biochar. It can be seen that the pyrolysis temperature has greater effect on the yield of biochar than the heating rate. The yield of biochar decreased with the increase of pyrolysis temperature from 400°C to 450°C, however it decreased slightly with the increase of temperature from 450°C to 500°C. Furthermore slow heating rate (10°C/min) resulted in higher char yield for both coconut husk biochar (CHBC) and rice husk biochar (RHBC). Although the low temperature pyrolysis resulted in higher char yield, however the biochar may contain an unconverted biomass fraction, which will mineralize rapidly in soil.

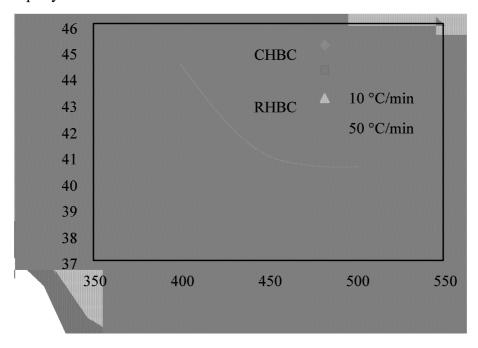


Fig. 1 Yield of coconut husk and rice husk biochar prepared under various conditions

Table 1 summarizes the results of specific surface area of the CHBC and RHBC prepared under various pyrolysis conditions. Higher pyrolysis temperatures resulted in higher surface area with a maximum at 450°C for RHBC and the specific surface areas of CHBC was lower than the RHBC. The higher specific surface area of RHBR may be due to

Table 1: Specific surface area

Biochar Sample	Specific surface area (m ² /g)			
(Heating rate, °C/min)	400°C	450°C	500°C	
CHBC (10)	3.8	7.3	19.5	
CHBC (50)	9.7	11.6	7.6	
RHBC (10)	52	74	65	
RHBC (50)	53	97	68	

the partial contribution of the high surface area of the rice husk ash.

Table 2 shows the C, H, N composition of the biochars prepared under various pyrolysis conditions. Type of feedstock or raw materials has greater impact on the chemical composition of the resulting biochars: carbon content of coconut husk biochar was higher than the rice husk biochar due to the difference in carbon contents in the raw materials. The carbon content of both CHBC and RHBC increased with the increase of pyrolysis temperature. The rate of heating also affected the composition of the biochar: Fast heating resulted in increase of carbon content at 400°C and 450°C, however it was decreased at 500°C. The reason for this behavior is not know at this stage. The percent of original carbon content retained in the biochar is also shown in Table 2. It was found that about 48-61 % of the carbons of coconut husk were retained in the product biochars and 38-47 % for rice husk, depending on the conditions of preparation such as pyrolysis temperature and heating rate. These results indicate the potential of sequestering a high portion (i.e. about 50 %) of the carbon of agricultural wastes if the biochars are produced from these wastes and used as a soil

Table 2: Elemental composition

		Elemental composition (wt%)					Carbon retained in		
Eleme	ent	С		Н		N		biochar (%)	
Sample		Coconut	Rice	Coconut	Rice	Coconut	Rice	Coconut	Rice
		husk	husk	husk	husk	husk	husk	husk	husk
Raw ma	terial	48.09	40.73	4.85	4.57	0.51	0.51	biochar	biochar
10 °C/min	400 °C	62.61	47.77	2.74	2.38	0.61	0.49	57.7	45.4
	450 °C	64.68	49.75	2.52	2.13	0.44	0.60	55.0	43.0
	500 °C	70.38	50.92	2.47	1.71	0.44	0.49	59.9	43.9
50 °C/min	400 °C	67.29	50.15	2.43	2.39	0.47	0.50	60.7	45.8
	450 °C	70.41	47.87	2.44	2.01	0.70	0.55	49.2	40.0
	500 °C	58.91	45.40	1.85	1.72	0.64	0.40	46.9	37.7

conditioner. The biochar with high nitrogen content could be a suitable soil ameliorant to improve the nutrient content of the soil.

Table 3 shows water adsorption capacity of CHBC and RHBC prepared under various pyrolysis conditions. Although the specific surface area of CHBC is much lower than the rice

husk biochars, however Table 3: Water adsorption capacity

its	water	ads	orption				
capac	city is	much	higher				
than	the	RHBO	C. No				
corre	lation	of py	rolysis				
temp	erature	witl	n the				
water adsorption capacity							
of biochar was observed.							
Fast	heating	g resu	lted in				
slight	tly h	igher	water				

		After 12 h (wt%)		After 24 h (wt%)		
Biochar sample		RHBC	RHBC	CHBC	RHBC	
400 °C	10 °C/min	36.9	12.2	49.4	11.6	
450 °C		36.3	7.8	47.1	7.2	
500 °C		39.8	11.9	51.3	11.8	
400 °C	50 °C/min	44.7	10.2	53.6	10.2	
450 °C		39.9	7.6	49.2	7.8	
500 °C		43.4	10.6	51.6	10.2	

adsorption capacity. High surface area of biochar is desirable for retaining water in the soil, however surface chemistry i.e. surface hydrophilic/hydrophobic characteristics of the char is also determining factor for the water adsorption capacity of the biochar. Further investigation on the surface properties of the CHBC and RHBC is needed.

Figure 2 shows the pH of the biochar when soaked in water (in a ratio of 1:100) for 12h and 24 h. Table 4 shows the ash content of the CHBC and RHBC. It is evident in Fig. 2 that CHBC has higher pH than the RHBC, most probably due to higher alkali metal content in coconut husk than in the rice husk. It is shown in Table 4 that the ash content of RHBC is much higher that the CHBC which in agreement with reported results [Yalcin eta al., 2001] and the fact that rice husk conation a large quantity of silicon and during pyrolysis the amount of silicon is enriched in the resulting biochar. It has been reported that coconut husk contains a significant amount of potassium and chlorine which could be a source of macreo and micro nutrients when coconut husk biochar would be used as a soil conditioner (Bonneau eta al., 2010). The high silicon content of RHBC could be of beneficial in the case of rice production.

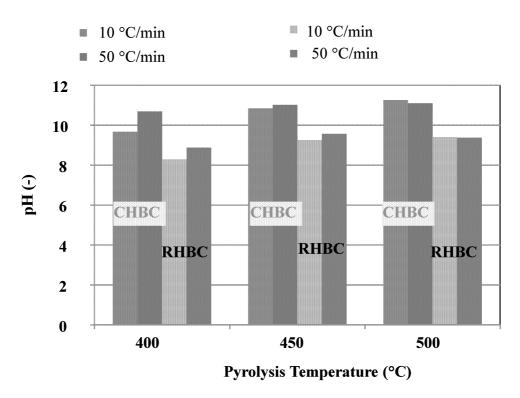


Fig. 2 pH of the biochars in water

Table 4: Ash content of the biochars

Sample	Heating rate	Ash content (wt%)			
	(°C/min)	400 °C	450 °C	500 °C	
CHBC	10	11.3	16.1	10.6	
	50	13.6	10.2	12.4	
RHBC	10	37.4	39.7	41.8	
	50	37.7	39.8	41.1	

Figure 3 shows the biochar-induced CO₂ emissions when CHBC was treated with soil in a ration of 1:40 in an incubator at 25 °C for 5 days. In this experiment, the concentration of CO₂ emitted by decomposition is plotted against the lapse of time. The results in this figure indicate the relative stability of biochar prepared under various conditions when amended with soil. It is evident the concentration CO₂ remained almost unchanged with the passage of time from soil only. However in the case of soil mixed with CHBC prepared under different conditions, the concentration of CO₂ increased with the lapse of time initially for 3-4 days and then slightly changed with the passage of time. Furthermore, the highest biochar-induced CO₂ emissions were observed from the samples containing the biochars prepared at low temperatures and decreasing

emission with increasing pyrolysis temperatures. These results indicate that the biochar prepared at lower temperature is relatively unstable than biochar prepared at lower temperature.

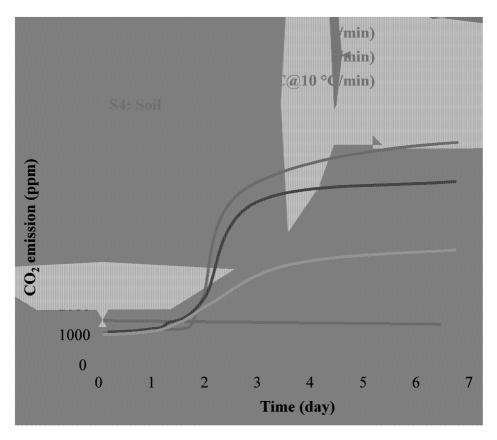


Fig. 3 CO₂ emission from Soil-biochar mixture at 25 °C

CONCLUSIONS

In this study biochars were prepared by pyrolysis of agricultural residues such rice husk and coconut husk. The effect of pyrolysis temperature (400, 450 and 500°C) and the heating rate (10 and 50°C/min) on the yield and properties of char were investigated. The following results were obtained: Both the carbon yields and properties of the biochar varied with the type of raw materials used and their preparation conditions: Biochar yield decrease with the increase of heating rate and increase of pyrolysis temperature. Higher pyrolysis temperatures resulted in higher surface area and the specific surface areas of coconut husk biochars were lower than the rice husk biochars. Water adsorption capacity of coconut husk biochars was much higher than the rice husk biochars. Higher pyrolysis temperature and faster heating rate resulted in slightly higher pH of the biochar in water. Coconut husk biochar had higher pH than the rice husk biochar due to higher alkali metal content. About 40-60 % of the carbons of raw materials were retained in the product biochars depending on the conditions of preparation such as pyrolysis temperatures and heating rates and the type of raw materials. The highest biochar-induced CO₂ emissions were observed from the samples containing the biochars prepared at low temperatures and decreasing emission with increasing pyrolysis temperatures.

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