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Bio- and hydrochars from rice straw and pig manure: Inter-comparison

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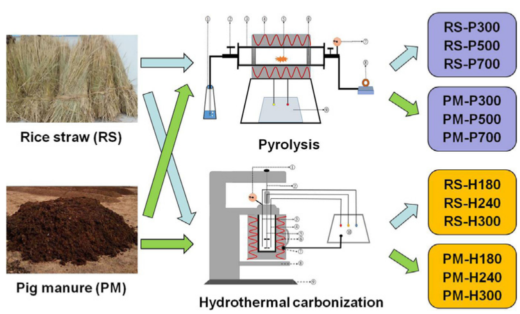
HIGHLIGHTS

- Bio- and hydrochars were obtained by thermal treatment of rice straw and pig manure.
- Higher temperatures resulted in lower bio-/hydrochar yields.
- Biochars showed lower H/C ratios than hydrochars due to their greater stability.
- Rice straw is suited for carbon sequestration by pyrolysis/hydrothermal carbonization.
- Pig manure is suitable for use as a soil amendment substrate.

GRAPHICAL ABSTRACT



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ABSTRACT

Conversion of rice straw (RS) and pig manure (PM) into chars is a promising disposal/recycling option. Herein, pyrolysis and hydrothermal carbonization were used to produce bio- and hydrochars from RS and PM, affording lower biochar (300–700 °C) and hydrochar (180–300 °C) yields at higher temperatures within the specified range. The C contents and C/N ratios of RS chars were higher than those of PM ones, with the opposite trend observed for yield and ash content. C and ash contents increased with increasing temperature, whereas H/C, O/C, and (O + N)/C ratios decreased. The lower H/C ratio of biochars compared to that of hydrochars indicated greater stability of the former. KCl was the main inorganic fraction in RS biochars, whereas quartz was dominant in PM biochars, and albite in PM hydrochars. Thus, RS is more suitable for carbon sequestration, while PM is more suitable for use as a soil amendment substrate.
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1. Introduction

Rice is a staple food for more than 3.5 billion people worldwide, i.e., for around half of the world population. In 2008, about 620 million tons of rice straw was produced in Asia alone, with this quantity increasing every year. In most places, this waste has no commercial value and is disposed of in various ways. Rice straw contains about 0.6% (w) N, 0.1% P and S (each), 1.5% K, 5% Si, and 40% C (Ponnamperuma, 1984), being a convenient source of plant nutrients due to its on-the-spot availability in amounts varying from 2 to 10 t/ha. Although residue retention is essential for the sustainable soil management of non-rice crops and mixed cropping (rice-upland crops), direct incorporation of rice straw into soil usually causes methane emissions due to its anaerobic breakdown. The alternative (where practiced) burning of rice straw in fields results in airborne emissions hazardous to humans and the ecosystem. Therefore, the development of a proper rice straw treatment method preceding its incorporation into soil is urgently required.

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Moreover, another important issue concerns waste management in the livestock industry. Livestock production, mainly comprising pig and poultry farming, has developed rapidly in China, especially after the launch of economic reforms (Zheng et al., 2014). The intensive industrial livestock production has resulted in a high density of animals in relatively small areas, with large quantities of manure produced in recent years (Ko et al., 2008). As a result, the nitrogen- and phosphorus-containing manure constituents contaminate soil and water bodies, also resulting in odor pollution, particularly in and around production buildings, storage areas, and during pig manure spreading (Makara and Kowalski, 2015). Therefore, the need for more environmentally friendly methods for the treatment and utilization of pig manure has become imperative, making the significance of establishing an integrated crop-livestock system hard to overstate.

Biochar refers to carbon-rich solid particles produced from biomass by pyrolysis under oxygen-limited conditions at a relatively low temperature (<700 °C) (Chen et al., 2008; Lehmann, 2007), typically exhibiting a well-developed pore structure, very large surface area, high stability, and exceptional adsorption properties (Kei et al., 2004). The increasing attention enjoyed by biochar in recent years is ascribed to its beneficial use for carbon sequestration, climate change mitigation, soil amendment, and contaminant removal (Chan et al., 2007; Mohan et al., 2014; Tan et al., 2015). Hydrochar refers to the solid products of hydrothermal carbonization, which is a promising alternative waste management strategy for biomass residuals, especially those with high water content (up to 80%) (Catalkopru et al., 2017). In terms of structure, hydrochar is closer to coal than biochar produced by dry pyrolysis (Berge et al., 2013), being potentially suitable for a wide range of applications such as carbon sequestration, adsorbents, container nurseries, fuels, and even soil additives (Guo et al., 2015). Extensive efforts have been directed at the production of energy-rich hydrochars from a wide range of lignocellulosic biomasses, digestate, and manure. Generally, the characteristics of bio- and hydrochars mainly depend on the type of feedstock and pyrolysis/carbonization processes. However, the effects of pyrolysis/carbonization conditions on the properties of bio-/hydrochars derived from the same biomass are yet to be thoroughly assessed. Therefore, in the present work, rice straw and pig manure were chosen as pyrolysis and hydrothermal carbonization precursors, and the corresponding bio- and hydrochars were produced under a series of thermal conditions. The characteristics of these chars were determined to investigate the differences between the above thermochemical processes at various temperatures, as well as those between rice straw and pig manure. Thus, this study provides a basis for the disposal and utilization of biowaste produced by agriculture and the livestock industry.

2. Materials and methods

2.1. Preparation of bio- and hydrochars

Rice straw (RS) and pig manure (PM) were collected as raw biomasses and used to produce bio- and hydrochars utilizing two types of thermochemical processes. RS was collected from Haining City, Zhejiang Province, China, shredded into pieces of less than 5 mm, and air-dried. The compositional analysis of RS yielded the following results: cellulose 38.2 wt%, hemicellulose 20.1 wt%, and lignin 21.4 wt%. PM was collected from Tongxiang City, Zhejiang Province, China, and also air-dried. The dried RS and PM samples were sealed in a plastic container for further use.

Pyrolysis was performed in a programmable tube furnace (Hangzhou Lantian Instrument Co., Ltd., China), whose schematic is shown in Fig. 1. Typically, the prepared biomass was slowly pyrolyzed under anaerobic conditions at a heating rate of 25 °C min^{-1} and a residence time of 1.5 h. Final temperatures of 300, 500, and 700 °C were used, and the produced biochars were allowed to cool to room temperature after pyrolysis.

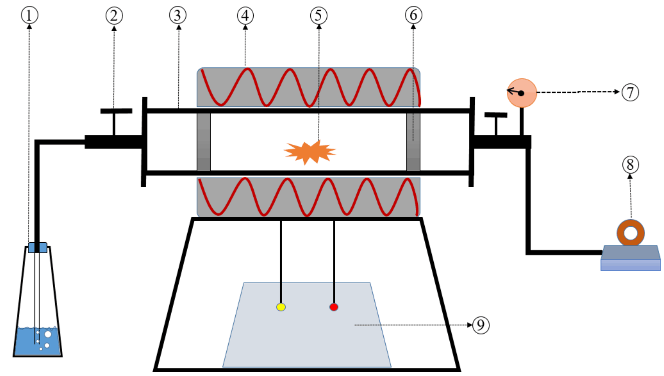

Fig. 1. Schematic diagram of pyrolysis setup. 1) Exhaust gas absorber; 2) valve; 3) quartz tube; 4) heating jacket; 5) biomass; 6) filter plug; 7) pressure meter; 8) vacuum pump; 9) temperature controller.

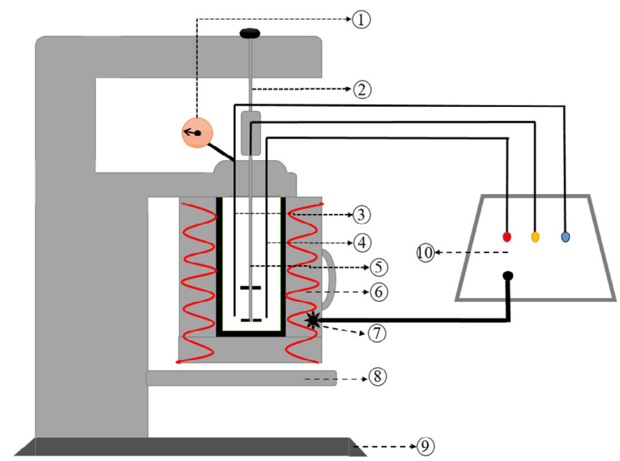

Fig. 2. Schematic diagram of hydrothermal carbonization setup. 1) Pressure meter; 2) magnetic stirrer; 3) pressure sensor; 4) temperature sensor; 5) magnetic stirrer; 6) heating jacket; 7) power port; 8) protection platform; 9) support base; 10) PID controller.

Hydrothermal carbonization was performed in a 2-L stainless steel pressure reactor, as shown in Fig. 2. The reaction temperature was controlled at 180, 240, and 300 °C by a single-display proportional – integral – derivative (PID) controller. In this temperature range, biomass components become more reactive: hemicellulose is degraded at ~200 °C, cellulose starts to react above 230 °C, and lignin is partially decomposed above 260 °C (Funke and Ziegler, 2010). For each run, 50 g of RS or 150 g of PM and 1 L of distilled water were loaded into the reactor, heated to the desired temperature at 3 °C min^{-1}, and held at the final temperature for 1.5 h. During the process, the mixture of water and biomass was continuously stirred by a magnetic stirrer at 150 rpm to ensure uniform heating. After 1.5 h, the reactor was allowed to air-cool, and the gaseous products were released into the atmosphere. The solid and liquid products were separated by gravity filtration using 150-mm qualitative filter circles. The obtained hydrochar samples were air-dried in a ventilated fume cupboard for 48 h.

For simplicity, the bio-/hydrochars derived from RS were denoted as RS-P300, RS-P500, RS-P700, RS-H180, RS-H240, and RS-H300, and those derived from PM were denoted as PM-P300, PM-P500, PM-P700, PM-H180, PM-H240, and PM-H300, where

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