

## Accepted Manuscript

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PII: S0960-8524(17)30384-X  
DOI: <http://dx.doi.org/10.1016/j.biortech.2017.03.103>  
Reference: BITE 17807

To appear in: *Bioresource Technology*

Received Date: 28 January 2017  
Revised Date: 11 March 2017  
Accepted Date: 17 March 2017

Please cite this article as: Liu, Y., Yao, S., Wang, Y., Lu, H., Kaur Brar, S., Yang, S., Bio- and hydrochars from rice straw and pig manure: Inter-comparison, *Bioresource Technology* (2017), doi: <http://dx.doi.org/10.1016/j.biortech.2017.03.103>

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

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10

11 **Abstract:** Conversion of rice straw (RS) and pig manure (PM) into chars is a promising disposal/recycling option. Herein, pyrolysis and  
12 hydrothermal carbonization were used to produce bio- and hydrochars from RS and PM, affording lower biochar (300–700 °C) and hydrochar  
13 (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  
14 ones, with the opposite trend observed for yield and ash content. C and ash contents increased with increasing temperature, whereas H/C, O/C,  
15 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  
16 the main inorganic fraction in RS biochars, whereas quartz was dominant in PM biochars, and albite in PM hydrochars. Thus, RS is more  
17 suitable for carbon sequestration, while PM is more suitable for use as a soil amendment substrate.

18 **Keywords:** biowaste; biochar; hydrochar; pyrolysis; hydrothermal carbonization

19

## 20 **1 Introduction**

21 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  
22 rice straw was produced in Asia alone, with this quantity increasing every year. In most places, this waste has no commercial value and is  
23 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),  
24 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  
25 essential for the sustainable soil management of non-rice crops and mixed cropping (rice-upland crops), direct incorporation of rice straw into  
26 soil usually causes methane emissions due to its anaerobic breakdown. The alternative (where practiced) burning of rice straw in fields results in  
27 airborne emissions hazardous to humans and the ecosystem. Therefore, the development of a proper rice straw treatment method preceding its  
28 incorporation into soil is urgently required.

29 Moreover, another important issue concerns waste management in the livestock industry. Livestock production, mainly comprising pig and  
30 poultry farming, has developed rapidly in China, especially after the launch of economic reforms (Zheng et al., 2014). The intensive industrial  
31 livestock production has resulted in a high density of animals in relatively small areas, with large quantities of manure produced in recent years  
32 (Ko et al., 2008). As a result, the nitrogen- and phosphorus-containing manure constituents contaminate soil and water bodies, also resulting in

33 odor pollution, particularly in and around production buildings, storage areas, and during pig manure spreading (Makara and Kowalski, 2015).  
34 Therefore, the need for more environmentally friendly methods for the treatment and utilization of pig manure has become imperative, making  
35 the significance of establishing an integrated crop-livestock system hard to overstate.

36 Biochar refers to carbon-rich solid particles produced from biomass by pyrolysis under oxygen-limited conditions at a relatively low temperature  
37 (< 700 °C) (Chen et al., 2008; Lehmann, 2007), typically exhibiting a well-developed pore structure, very large surface area, high stability, and  
38 exceptional adsorption properties (Kei et al., 2004). The increasing attention enjoyed by biochar in recent years is ascribed to its beneficial use  
39 for carbon sequestration, climate change mitigation, soil amendment, and contaminant removal (Chan et al., 2007; Mohan et al., 2014; Tan et al.,  
40 2015). Hydrochar refers to the solid products of hydrothermal carbonization, which is a promising alternative waste management strategy for  
41 biomass residuals, especially those with high water content (up to 80%) (Catalkopru et al., 2017). In terms of structure, hydrochar is closer to  
42 coal than biochar produced by dry pyrolysis (Berge et al., 2013), being potentially suitable for a wide range of applications such as carbon  
43 sequestration, adsorbents, container nurseries, fuels, and even soil additives (Guo et al., 2015). Extensive efforts have been directed at the  
44 production of energy-rich hydrochars from a wide range of lignocellulosic biomasses, digestate, and manure. Generally, the characteristics of  
45 bio- and hydrochars mainly depend on the type of feedstock and pyrolysis/carbonization processes. However, the effects of

46 pyrolysis/carbonization conditions on the properties of bio-/hydrochars derived from the same biomass are yet to be thoroughly assessed.  
47 Therefore, in the present work, rice straw and pig manure were chosen as pyrolysis and hydrothermal carbonization precursors, and the  
48 corresponding bio- and hydrochars were produced under a series of thermal conditions. The characteristics of these chars were determined to  
49 investigate the differences between the above thermochemical processes at various temperatures, as well as those between rice straw and pig  
50 manure. Thus, this study provides a basis for the disposal and utilization of biowaste produced by agriculture and the livestock industry.

51

## 52 **2 Materials and methods**

### 53 **2.1 Preparation of bio- and hydrochars**

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

59 Pyrolysis was performed in a programmable tube furnace (Hangzhou Lantian Instrument Co., Ltd., China), whose schematic is shown in Fig. 1.  
60 Typically, the prepared biomass was slowly pyrolyzed under anaerobic conditions at a heating rate of  $25\text{ }^{\circ}\text{C min}^{-1}$  and a residence time of 1.5 h.  
61 Final temperatures of 300, 500, and 700  $^{\circ}\text{C}$  were used, and the produced biochars were allowed to cool to room temperature after pyrolysis.  
62 Hydrothermal carbonization was performed in a 2-L stainless steel pressure reactor, as shown in Fig. 2. The reaction temperature was controlled  
63 at 180, 240, and 300  $^{\circ}\text{C}$  by a single-display proportional – integral – derivative (PID) controller. In this temperature range, biomass components  
64 become more reactive: hemicellulose is degraded at  $\sim 200\text{ }^{\circ}\text{C}$ , cellulose starts to react above  $230\text{ }^{\circ}\text{C}$ , and lignin is partially decomposed above  
65  $260\text{ }^{\circ}\text{C}$  (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  
66 desired temperature at  $3\text{ }^{\circ}\text{C min}^{-1}$ , and held at the final temperature for 1.5 h. During the process, the mixture of water and biomass was  
67 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  
68 products were released into the atmosphere. The solid and liquid products were separated by gravity filtration using 150-mm qualitative filter  
69 circles. The obtained hydrochar samples were air-dried in a ventilated fume cupboard for 48 h.  
70 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  
71 those derived from PM were denoted as PM-P300, PM-P500, PM-P700, PM-H180, PM-H240, and PM-H300, where the letters P/H stand for

72 pyrolysis/hydrothermal carbonization, respectively, and the numbers represent the final temperature. All biochars were milled to a homogenous  
73 fine powder using a ball mill and dried overnight at 105 °C prior to being analyzed.

## 74 **2.2 Analytical methods**

75 Yields of bio- and hydrochars were calculated as fractions of raw material mass, and the char properties, such as pH, were investigated at a  
76 solid:water ratio of 1:20 (w/v). The suspension was first shaken and equilibrated for 5 min, and pH measurements were performed in triplicate  
77 using a pH meter (Mettler-Toledo, Switzerland). Electric conductivity (EC) was measured by an EC meter. The moisture content of chars was  
78 determined from the sample mass loss at 105 °C, whereas ash and volatile matter contents were calculated from the residual weight obtained  
79 after heating at 815±1 °C for 2 h and 900±1 °C for 7 min, respectively, in a muffle furnace (National Standard of the People's Republic of China,  
80 GB/T 212-2008). Fixed carbon content was calculated by subtracting the ash and volatile matter content from 100% on a dry basis. C, H, N, and  
81 S contents of bio- and hydrochars were determined using an elemental analyzer (Vario EL/micro cube, Elementar, Germany). The oxygen  
82 content was calculated by subtracting C, N, H, S, and ash contents from the total char mass. The specific surface area, total pore volume, and  
83 mean pore size of biochar were measured with a BET surface area analyzer (ASAP2020, Micromeritics, USA) using N<sub>2</sub> adsorption. Inorganic  
84 components of chars were identified based on their X-ray diffraction (XRD) patterns obtained using an X-ray diffractometer (D8 Advance,

85 Bruker, Germany) equipped with a graphite-monochromatized Cu  $K_{\alpha}$  radiation source ( $\lambda = 1.541841 \text{ \AA}$ ) and employing a scan rate of  $0.01^{\circ} \text{ s}^{-1}$  in  
86 a  $2\theta$  range of  $10\text{--}70^{\circ}$ . The surface functional groups of biochars were characterized by Fourier transform infrared (FTIR) spectroscopy (Varian  
87 640-IR, USA) in a wavelength range of  $400\text{--}4000 \text{ cm}^{-1}$  using KBr pellets at room temperature. SigmaPlot 10.0 software was used for drawing  
88 figures.

89

### 90 **3 Results**

#### 91 **3.1 Basic physical and chemical properties of bio- and hydrochars**

92 The yields, atomic ratios, pH, ECs, specific surface areas, total pore volumes, and mean pore sizes of bio- and hydrochars derived from RS and  
93 PM at different temperatures are listed in Table 1, whereas their elemental compositions and ash contents are shown in Fig. 3. For each feedstock,  
94 higher temperatures resulted in lower bio-/hydrochar yields, which equaled  $25.6\text{--}57.7\%$  for RS and  $38.0\text{--}57.8\%$  for PM. At the same  
95 temperature, the yields of PM-derived bio-/hydrochars were higher than those of RS-derived chars. The ash contents of RS- and PM-derived bio-  
96 and hydrochars increased with increasing temperature, equaling  $24.4\text{--}42.8\%$  and  $6.59\text{--}35.4\%$  for chars obtained by pyrolysis and hydrothermal  
97 carbonization, respectively. The ash contents of PM-derived bio- and hydrochars were higher than those of RS-derived chars under the same

98 conditions. The C contents of bio- and hydrochars derived from both RS and PM increased with increasing temperature, whereas their H and O  
99 contents, as well as H/C, O/C, and (O + N)/C ratios decreased. For each feedstock, the C/N ratio of biochar increased with increasing  
100 temperature, while it decreased for hydrochar. The C contents and C/N ratios of bio-/hydrochars derived from RS (44.1–61.7% and 51.8–91.4,  
101 respectively) were much higher than those of PM-derived chars (43.3–46.4% and 18.0–39.4, respectively) at the same temperature. Furthermore,  
102 the H/C ratios of hydrochars derived from both RS (0.94–1.47) and PM (0.91–1.18) were higher than those of RS- and PM-derived biochars  
103 (0.37–1.04 and 0.31–1.00, respectively).

104 The pH of RS- and PM-derived biochars increased with increasing temperature, equaling 7.15–10.6 for thermal treatment temperatures of  
105 300–700 °C (Table 1). A similar tendency was observed for the pH of hydrochars derived from RS and PM (except for RS-H180), which equaled  
106 5.43–5.99 at 180–300 °C. The ECs of both RS- and PM-derived biochars increased with increasing temperature, with RS-derived biochar  
107 exhibiting much higher values (4.36–5.89 mS cm<sup>-1</sup>) than PM-derived biochar (0.543–0.919 mS cm<sup>-1</sup>). Conversely, the ECs of hydrochars  
108 decreased with increasing temperature, with PM-derived hydrochar (0.051–0.147 mS cm<sup>-1</sup>) exhibiting higher values than RS-derived hydrochar  
109 (0.040–0.062 mS cm<sup>-1</sup>).

110 The specific surface areas of most bio- and hydrochars were very low (2.57–32.9 m<sup>2</sup> g<sup>-1</sup>, Table 1). Under pyrolytic conditions, the specific

111 surface areas and total pore volumes of RS- and PM-derived biochars increased with increasing temperature, whereas their mean pore sizes  
112 decreased. The specific surface area of RS-derived biochar ( $3.35\text{--}32.9\text{ m}^2\text{ g}^{-1}$ ) was higher than that of PM-derived biochar ( $3.32\text{--}20.5\text{ m}^2\text{ g}^{-1}$ ),  
113 and the mean pore size of RS-derived biochar ( $59.2\text{--}151.3\text{ nm}$ ) was lower than that of PM-derived biochar ( $88.4\text{--}229.9\text{ nm}$ ). However, the  
114 specific surface areas, total pore volumes, and mean pore sizes of RS- and PM-derived hydrochars exhibited an initial increase and a subsequent  
115 decline with increasing temperature. The specific surface area and total pore volume of PM-derived hydrochar ( $10.7\text{--}15.6\text{ m}^2\text{ g}^{-1}$  and  
116  $0.0728\text{--}0.1212\text{ cm}^3/\text{g}$ , respectively) were higher than those of RS-derived hydrochar ( $2.57\text{--}4.46\text{ m}^2\text{ g}^{-1}$  and  $0.0128\text{--}0.0382\text{ cm}^3/\text{g}$ , respectively).

### 117 **3.2 Composition of char ash determined by XRD**

118 Typical XRD patterns of bio- and hydrochars are shown in Fig. S1 (Supplementary data). For RS-derived biochars, sylvite (KCl) and quartz  
119 ( $\text{SiO}_2$ ) were the main crystalline phases detected after pyrolysis at  $300\text{ }^\circ\text{C}$ , with calcite ( $\text{CaCO}_3$ ) also detected at temperatures above  $500\text{ }^\circ\text{C}$ . For  
120 PM-derived biochars,  $\text{CaCO}_3$  and  $\text{SiO}_2$  were the major inorganic crystalline phases observed at  $300\text{ }^\circ\text{C}$ , with magnesium silicate ( $\text{MgSiO}_3$ )  
121 detected at  $500\text{ }^\circ\text{C}$ , and dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ] and albite ( $\text{NaAlSi}_3\text{O}_8$ ) observed at  $700\text{ }^\circ\text{C}$ . Furthermore, only small amounts of crystalline  
122 phases were detected at  $180\text{--}300\text{ }^\circ\text{C}$  for RS-derived hydrochars. In contrast,  $\text{SiO}_2$  and  $\text{NaAlSi}_3\text{O}_8$  were the main inorganic crystalline phases  
123 observed at  $180\text{--}300\text{ }^\circ\text{C}$  for PM-derived hydrochars, with  $\text{CaCO}_3$  observed at  $240\text{ }^\circ\text{C}$  and [ $\text{CaMg}(\text{CO}_3)_2$ ] detected at  $300\text{ }^\circ\text{C}$ .

### 124 **3.3 Surface property analysis by FTIR**

125 Functional groups of bio- and hydrochars were analyzed by FTIR spectroscopy, with the obtained spectra presented in Fig. S2 (Supplementary  
126 data). For RS-derived biochars, the intensity of peaks at 3397, 2920, 1110, and 789  $\text{cm}^{-1}$  decreased with increasing temperature, and some peaks  
127 disappeared at 700 °C. For PM-derived biochars, peaks at 3397, 2920, 2358, 1092, and 769  $\text{cm}^{-1}$  were well preserved at 300 and 500 °C, but lost  
128 intensity at 700 °C, whereas peaks at 1591 and 1350  $\text{cm}^{-1}$  exhibited an intensity decrease with increasing temperature. Conversely, for both RS-  
129 and PM-derived hydrochars, peaks at 2928, 2360, 1600 and 800  $\text{cm}^{-1}$  became sharper with increasing temperature, and those at 2850 and 1114  
130  $\text{cm}^{-1}$  appeared at 300 °C for RS-derived hydrochars.

131

## 132 **4 Discussion**

### 133 **4.1 Basic characteristics of bio- and hydrochars**

134 During thermochemical processing, the char yield (defined as the mass ratio of dry bio-/hydrochar to that of input dry feedstock) usually  
135 decreases with increasing temperature due to the formation of liquid and gaseous by-products (Libra et al., 2011). The reduced yields of RS- and  
136 PM-derived bio-/hydrochars with increasing treatment temperature (Table 1) are mainly associated with the removal of cellulosic and

137 hemicellulosic components (Kambo and Dutta, 2015).

138 The high ash content of individual bio-/hydrochars directly correlates with yield reduction. For both RS and PM, the ash content of biochar was  
139 usually higher than that of hydrochar at the same treatment temperature (Fig. 3), in agreement with the results of Dai et al. (2015), who  
140 concluded that hydrothermal carbonization can be employed to dissolve and wash out some inorganic components from hydrochar.  
141 As reported in numerous previous researches (Chen et al., 2008; Ghanim et al., 2016; Keiluweit et al., 2010; Smith et al., 2016), thermal  
142 treatment temperature is the primary factor determining bio-/hydrochar properties. Elevated temperatures favored higher C contents, which  
143 increased for all bio-/hydrochars produced from RS and PM (Fig. 3). Conversely, H and O contents markedly decreased with increasing  
144 temperature, indicating the occurrence of decarboxylation, decarbonylation, and dehydration during pyrolysis and hydrothermal carbonization of  
145 biomass (Ghanim et al., 2016). The H/C atomic ratio was proposed as an index of aromaticity and resistance of bio-/hydrochars to microbial and  
146 chemical degradation (Crombie et al., 2013). This ratio significantly decreased with increasing temperature for all chars, suggesting an increase  
147 of their aromaticity. The lower H/C ratio of biochar compared to hydrochar indicates the greater stability of the former.  
148 The decrease of the polarity index  $(O + N)/C$  and the O/C atomic ratio with increasing temperature indicated a reduction of polarity and the  
149 number of oxygen-containing functional groups. This agrees with previous reports, suggesting that pyrolysis and hydrothermal carbonization of

150 biomass result in removal of hydroxyl groups via dehydration, loss of carboxyl and carbonyl groups via decarboxylation, cleavage of ester and  
151 ether bonds via hydrolysis, and, for lignocellulose-based biomass, in increased aromatization due to the dehydration of lignin and aromatization  
152 of carbohydrates (Funke and Ziegler, 2010; Smith et al., 2016).

153 It should be noted that bio-/hydrochar properties varied greatly with biomass type. The C content of RS-derived bio-/hydrochars was much  
154 higher and exhibited a more obvious increase upon pyrolysis than that of PM-derived ones (Fig. 3), indicating that RS is more suitable for  
155 carbon sequestration than PM. Similar to the C content, the O content of RS-derived bio-/hydrochars markedly decreased with temperature.  
156 Unlike RS, PM is a sort of livestock manure, commonly containing a large number of inorganic elements (e.g., K, Ca). PM contains abundant  
157 porcine metabolites, being easily decomposable in comparison to plant biomass. The C/N ratio of RS-derived bio-/hydrochars was much higher  
158 than that of PM-derived ones (Table 1), indicating that PM is more suited for use as a soil amendment substrate than RS, since an overly high  
159 C/N ratio that goes against decomposition by microbes will result in excessive consumption of available soil nitrogen.

#### 160 **4.2 Composition of bio- and hydrochars**

161 XRD was used to detect the short-range ordered structures of bio- and hydrochars and the crystalline structures of the present minerals (Wang et  
162 al., 2016). The observed strong and sharp peaks indicated the presence of crystalline inorganic phases in bio- and hydrochars derived from RS

163 and PM. The speciation and abundance of inorganic constituents were determined by thermal treatment temperature and feedstock properties.  
164 Under the same conditions, the peaks of RS-derived bio- and hydrochars were less abundant than those of PM-derived chars, indicating the  
165 lower ash content of the former and being in agreement with the results presented in Table 1. For example, the weak peaks observed for  
166 RS-derived hydrochars demonstrated their low inorganic content, whereas quartz and albite were detected in PM-derived hydrochars. Peaks at  
167  $28^\circ$  and  $41^\circ$  confirmed the presence of sylvite in RS-derived biochars, whereas those at  $27^\circ$  were indicative of quartz in PM-derived biochars.  
168 In addition, the results showed that a larger amount of crystalline inorganic fractions was formed in both RS and PM at high temperatures during  
169 pyrolysis and hydrothermal carbonization. For RS-derived biochars, the peak of calcite at  $29^\circ$  was observed only above  $500^\circ\text{C}$ . In contrast, for  
170 PM-derived biochars, peaks at  $28^\circ$ ,  $31^\circ$ ,  $36^\circ$ , and  $43^\circ$  indicated that  $\text{MgSiO}_3$  was formed above  $500^\circ\text{C}$ , and albite ( $22^\circ$  and  $28^\circ$ ) and dolomite  
171 ( $31^\circ$  and  $41^\circ$ ) were formed at  $700^\circ\text{C}$ . For PM-derived hydrochars, the peak at  $29^\circ$  confirmed the formation of calcite during hydrothermal  
172 carbonization at  $240^\circ\text{C}$ , and that at  $31^\circ$  was due to the formation of dolomite at  $300^\circ\text{C}$ .  
173 Li et al. (2017) found that the type and amount of inorganic crystalline phases in biochar depend on the feedstock and temperature. However,  
174 their results demonstrated that KCl formed at relatively low pyrolysis temperature ( $200\text{--}300^\circ\text{C}$ ), while carbonates generally formed above  
175  $400^\circ\text{C}$ .

### 176 4.3 Surface property of bio- and hydrochars

177 As demonstrated by the FTIR spectra, the band at  $3397\text{ cm}^{-1}$ , attributed to the stretching vibrations of hydrogen-bonded hydroxyl groups of  
178 water (Droussi et al., 2009), lost intensity with increasing temperature and disappeared at  $700\text{ }^{\circ}\text{C}$  for both RS- and PM-derived biochars. For all  
179 biochars, peaks at  $2920$ ,  $2850$ , and  $1458\text{ cm}^{-1}$  (aliphatic  $\text{CH}_2$ ) (Xiao et al., 2014) gradually disappeared with increasing temperature. The intense  
180 bands of aromatic  $\text{C}=\text{C}$  and  $\text{C}=\text{O}$  groups ( $1591\text{--}1601\text{ cm}^{-1}$ ) (Chun et al., 2004) were well preserved between  $180$  and  $500\text{ }^{\circ}\text{C}$ , but lost intensity at  
181  $700\text{ }^{\circ}\text{C}$  in the case of PM-derived biochar. Peaks of aliphatic  $\text{C}\text{--}\text{O}\text{--}\text{C}$  fragments at  $1092\text{--}1114\text{ cm}^{-1}$  (Li et al., 2017) disappeared at temperatures  
182 above  $500\text{ }^{\circ}\text{C}$  for PM-derived biochar, being better preserved for RS-derived biochar. Peaks observed at  $3397$ ,  $2920$ ,  $2850$ ,  $1591$ ,  $1458$ ,  $1355$ ,  
183 and  $1100\text{ cm}^{-1}$  indicated that a large number of organic residues (e.g., polymeric  $\text{--CH}_2\text{--}$ , fatty acids, lignins, and polysaccharides) were  
184 preserved in RS- and PM-derived hydro- and biochars at low temperature ( $300\text{ }^{\circ}\text{C}$ ), whereas some of them disappeared in biochars pyrolyzed at  
185 high temperature, e.g., above  $500\text{ }^{\circ}\text{C}$ . The changes observed in the range of  $1000\text{--}1400\text{ cm}^{-1}$  ( $\text{C}\text{--}\text{O}$ ) and at  $1591\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ) indicated that  
186 oxygen-containing functional groups might have been oxidized during hydrothermal carbonization and pyrolysis.

187

### 188 5 Conclusions

189 High temperature resulted in lower bio-/hydrochar yields. C and ash contents increased with increasing temperature, while H/C, O/C, and  
190 (O+N)/C ratios decreased. Higher C contents and C/N ratios of RS chars compared to those of PM chars indicate that RS is more suitable for  
191 carbon sequestration, whereas PM is suitable for soil amendment. Biochars showed lower H/C ratios than hydrochars due to their greater  
192 stability. KCl was the main inorganic fraction in RS biochars, while SiO<sub>2</sub> was dominant in PM biochars, and NaAlSi<sub>3</sub>O<sub>8</sub> was detected in PM  
193 hydrochars. The number of surface groups in biochars gradually decreased with increasing temperature.

194

#### 195 **Acknowledgements**

196 This research was financially supported by the International Science & Technology Cooperation Program of China (2014DFE90040), the  
197 Science and Technology Project of Zhejiang Province (2015C03004), and the Zhejiang Provincial Natural Science Foundation (LY16D010004  
198 and LQ17D020002).

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#### 200 **References**

201 [1] Berge, D.N., Kammann, C., Ro, K., Libra, J., 2013. Environmental applications of hydrothermal carbonization technology: biochar

- 202 production, carbon sequestration, and waste conversion. In: Titirici, M.M. (Ed.), Sustainable Carbon Materials from Hydrothermal Processes.  
203 John Wiley & Sons, Ltd., United Kingdom, p. 297.
- 204 [2] Catalkopru, A.K., Kantarli, I.C., Yanik, J., 2017. Effects of spent liquor recirculation in hydrothermal carbonization. *Bioresour. Technol.* 226,  
205 89–93.
- 206 [3] Chan, K.Y., Van Zwieten, L., Meszaros, I., Downie, A., Joseph, S., 2007. Agronomic values of greenwastebiochar as a soil amendment. *Aust.*  
207 *J. Soil Res.* 45, 629–634.
- 208 [4] Chen, B., Zhou, D., Zhu, L., 2008. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine  
209 needles with different pyrolytic temperatures. *Environ. Sci. Technol.* 42, 5137–5143.
- 210 [5] Chun, Y., Sheng, G.Y., Chiou, C.T., Xing, B.S., 2004. Compositions and sorptive properties of crop residue-derived chars. *Environ. Sci.*  
211 *Technol.* 38, 4649–4655.
- 212 [6] Crombie, K., Mašek, O., Sohi, S.P., Brownsort, P., Cross, A., 2013. The effect of pyrolysis conditions on biochar stability as determined by  
213 three methods. *GCB Bioenergy* 5, 122–131.
- 214 [7] Dai, L., Tan, F., Wu, B., He, M., Wang, W., Tang, X., Hu, Q., Zhang, M., 2015. Immobilization of phosphorus in cow manure during

- 215 hydrothermal carbonization. *J. Environ. Manage.* 157, 49–53.
- 216 [8] Droussi, Z., D’orazio, V., Provenzano, M.R., Hafidi, M., Ouattmane, A., 2009. Study of the biodegradation and transformation of olive-mill  
217 residues during composting using FTIR spectroscopy and differential scanning calorimetry. *J. Hazard. Mater.* 164, 1281–1285.
- 218 [9] Funke, A., Ziegler, F., 2010. Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process  
219 engineering. *Biofuels Bioprod. Bior.* 4, 160–177.
- 220 [10] Ghanim, B.M., Pandey, D.S., Kwapinski, W., Leahy, J.J., 2016. Hydrothermal carbonisation of poultry litter: Effects of treatment  
221 temperature and residence time on yields and chemical properties of hydrochars. *Bioresour. Technol.* 216, 373–380.
- 222 [11] Guo, S., Dong, X., Wu, T., Shi, F., Zhu, C., 2015. Characteristic evolution of hydrochar from hydrothermal carbonization of corn stalk. *J.*  
223 *Anal. Appl. Pyrol.* 116, 1–9.
- 224 [12] Kei, M., Toshitatsu, M., Yasuo, H., Nishihara, K., Nakanishi, T., 2004. Removal of nitrate-nitrogen from drinking water using bamboo  
225 powder charcoal. *Bioresour. Technol.* 95, 255–257.
- 226 [13] Keiluweit, M., Nico, P.S., Johnson, M.G., Kleber, M., 2010. Dynamic molecular structure of plant biomass-derived black carbon (biochar).  
227 *Environ. Sci. Technol.* 44, 1247–1253.

- 228 [14]Ko, H.J., Kim, K.Y., Kim, H.T., Kim, C.N., Umeda, M., 2008. Evaluation of maturity parameters and heavy metal contents in composts  
229 made from animal manure. *Waste Manage.* 28, 813–820.
- 230 [15]Lehmann, J., 2007. A handful of carbon. *Nature* 447, 143–144.
- 231 [16]Li, J., Liang, N., Jin, X., Zhou, D., Li, H., Wu, M., Pan, B., 2017. The role of ash content on bisphenol A sorption to biochars derived from  
232 different agricultural wastes. *Chemosphere* 171, 66–73.
- 233 [17]Libra, J.A., Ro, K.S., Kammann, C., Funke, A., Berge, N.D., Neubauer, Y., Titirici, M.-M., Fühner, C., Bens, O., Kern, J., Emmerich, K.H.,  
234 2011. Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry  
235 pyrolysis. *Biofuels* 2, 71–106.
- 236 [18]Makara, A., Kowalski, Z., 2015. Pig manure treatment and purification by filtration. *J. Environ. Manag.* 161, 317–324.
- 237 [19]Mohan, D., Sarswat, A., Ok, Y.S., Pittman, C.U. Jr., 2014. Organic and inorganic contaminants removal from water with biochar, a  
238 renewable, low cost and sustainable adsorbent – A critical review. *Bioresour. Technol.* 160, 191–202.
- 239 [20]Ponnamperuma, F.N., 1984. Straw as a source of nutrients for wetland rice. *Organic matter and rice. Manila (Philippines): International Rice*  
240 *Research Institute*, p. 117–136.

- 241 [21]Smith, A.M., Singh, S., Ross, A.B., 2016. Fate of inorganic material during hydrothermal carbonisation of biomass: Influence of feedstock  
242 on combustion behaviour of hydrochar. *Fuel* 169, 135–145.
- 243 [22]Tan, X.F., Liu, Y.G., Zeng, G.M., Wang, X., Hu, X.J., Gu, Y.L., Yang, Z.Z., 2015. Application of biochar for the removal of pollutants from  
244 aqueous solutions. *Chemosphere* 125, 70–85.
- 245 [23]Wang, Y., Lu, H., Liu, Y., Yang, S., 2016. Ammonium citrate-modified biochar: An adsorbent for La(III) ions from aqueous solution. *Colloid.*  
246 *Surface. A: Physicochem. Eng. Aspects* 509, 550–563.
- 247 [24]Xiao, X., Chen, B., Zhu, L., 2014. Transformation, morphology, and dissolution of silicon and carbon in rice straw-derived biochars under  
248 different pyrolytic temperatures. *Environ. Sci. Technol.* 48, 3411–3419.
- 249 [25]Zheng, C., Bluemling, B., Liu, Y., Mol, A.P.J., Chen, J., 2014. Managing manure from China's pigs and poultry: The influence of ecological  
250 rationality. *AMBIO* 43, 661–672.

251

252 Table 1. Basic physical and chemical properties of bio- and hydrochars obtained from RS and PM at different temperatures.

Biochar	Yield (%)	Moisture (%)	VM* (%)	FC* (%)	H/C	O/C	(O+N)/C	C/N	pH	EC* (mS/cm)	SSA* (m <sup>2</sup> /g)	TPV* (cm <sup>3</sup> /g)	MPS* (nm)
RS-P300	57.7	6.29	45.0	24.3	1.04	0.379	0.396	56.9	7.15±0.01	4.36±0.13	3.35	0.0127	151.3
RS-P500	33.8	5.93	14.6	51.0	0.58	0.178	0.193	67.2	10.4±0.05	4.54±0.06	7.47	0.0202	108.1
RS-P700	30.7	7.15	7.40	56.6	0.37	0.083	0.097	71.3	10.6±0.09	5.89±0.16	32.9	0.0486	59.2
PM-P300	57.8	6.15	31.4	34.2	1.00	0.354	0.410	18.0	7.53±0.04	0.543±0.022	3.32	0.0191	229.9
PM-P500	42.9	4.52	14.9	40.2	0.59	0.171	0.215	22.3	7.97±0.03	0.586±0.033	6.30	0.0291	184.5
PM-P700	38.0	4.68	7.62	44.9	0.31	0.146	0.171	39.4	8.98±0.04	0.919±0.050	20.5	0.0454	88.4
RS-H180	56.0	5.73	68.9	18.8	1.47	0.735	0.746	91.4	5.69±0.08	0.062±0.005	2.57	0.0202	314.1
RS-H240	37.6	3.43	58.2	24.3	1.08	0.335	0.352	58.2	5.58±0.07	0.055±0.004	4.46	0.0382	342.5
RS-H300	25.6	3.00	52.2	26.4	0.94	0.165	0.184	51.8	5.92±0.10	0.040±0.006	2.94	0.0128	174.3
PM-H180	56.7	5.04	44.2	20.6	1.18	0.340	0.382	24.2	5.43±0.01	0.147±0.005	15.5	0.0907	233.5
PM-H240	46.8	3.37	35.8	31.3	1.04	0.264	0.309	22.1	5.76±0.05	0.092±0.003	15.6	0.1212	310.6
PM-H300	43.7	2.40	26.8	35.4	0.91	0.187	0.236	20.2	5.99±0.02	0.051±0.005	10.7	0.0728	272.7

253 \* VM, volatile matter; FC, fixed carbon; EC, electric conductivity; SSA, specific surface area; TPV, total pore volume; MPS, mean pore size.

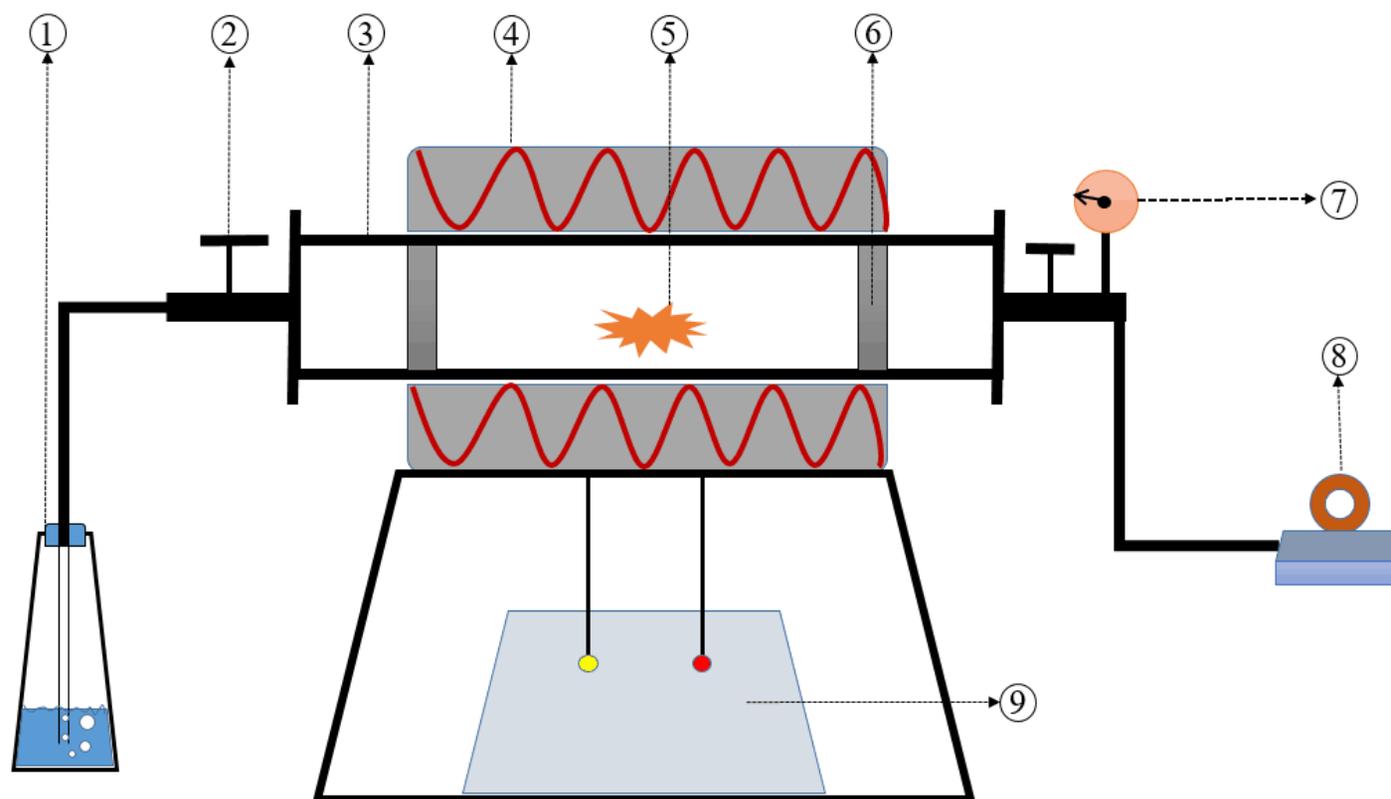
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255 **Figure captions**

256 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)  
257 pressure meter; 8) vacuum pump; 9) temperature controller.

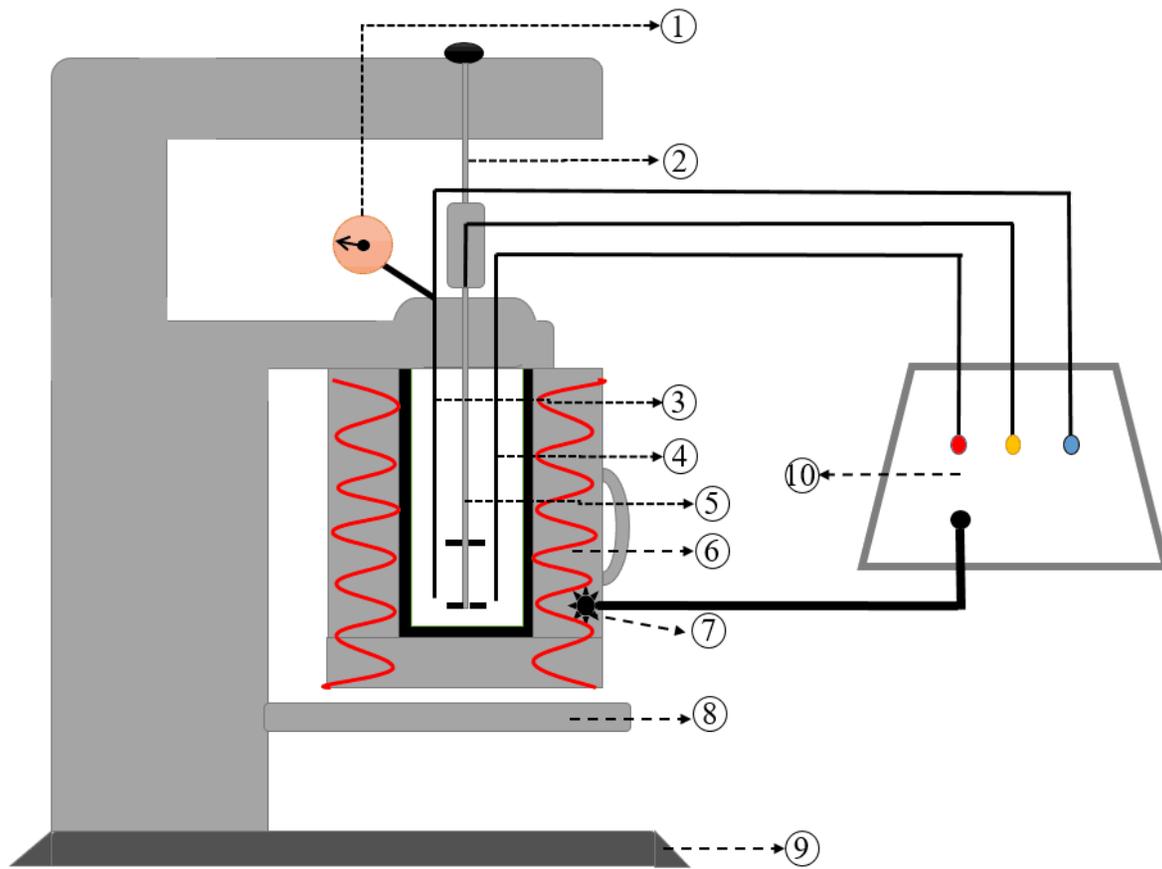
258 Fig. 2. Schematic diagram of hydrothermal carbonization setup. 1) Pressure meter; 2) magnetic stirrer; 3) pressure sensor; 4) temperature sensor;  
259 5) magnetic stirrer; 6) heating jacket; 7) power port; 8) protection platform; 9) support base; 10) PID controller.

260 Fig. 3. C, H, N, S, O and ash content of biochars and hydrochars.



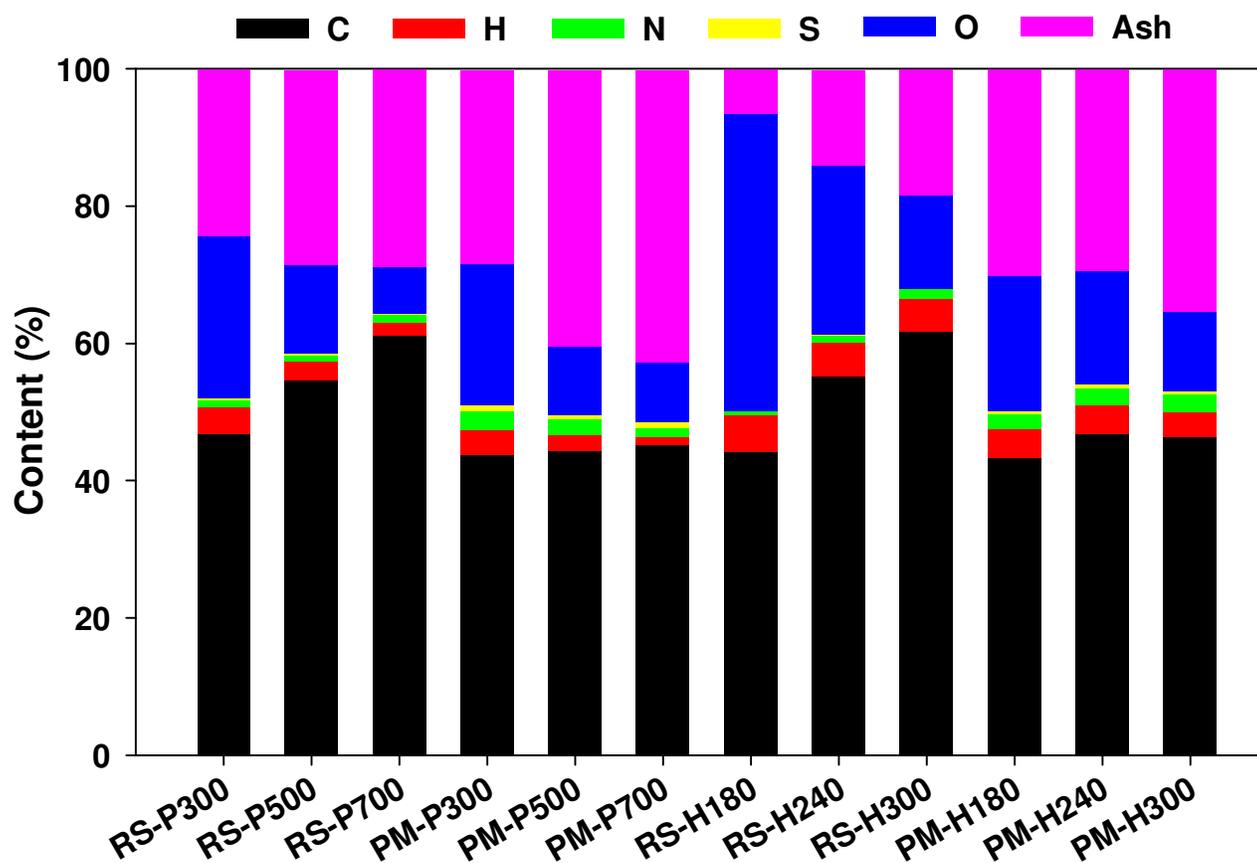
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262 Fig. 1.



263

264 Fig. 2.



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266

267 Fig. 3.

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ACCEPTED

269 **Highlights:**

270 • Bio- and hydrochars were obtained by thermal treatment of rice straw and pig

271 manure

272 • Higher temperatures resulted in lower bio-/hydrochar yields

273 • Biochars showed lower H/C ratios than hydrochars due to their greater stability

274 • Rice straw is suited for carbon sequestration by pyrolysis/hydrothermal

275 carbonization

276 • Pig manure is suitable for use as a soil amendment substrate

277

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