Hydrochar Derived from Anaerobic Solid Digestates of Swine Manure and Rice Straw: A Potential Recyclable Material

Hongmei Jin,[a,b,c,*] Enhui Sun,[a,b,c] Yueding Xu,[a,b,c] Ruihua Guo,[a] Mengjie Zheng,[d] Hongying Huang,[a,b,c] and Songhe Zhang [d]

Hydrothermal carbonization (HTC) is an efficient conversion process that treats solid digestates from anaerobic digestion plants and converts it into valuable solid products. In this study, digestates of swine manure (DS_M) and rice straw (DS_S) were HTC-treated at 190 °C with biomass-to-water ratios of 1:4 and 1:9. The hydrochars were characterized physically and chemically to elucidate their potential as a valuable resource. The hydrochars from the solid digestates were acidic, and the dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and Brunauer-Emmett-Teller surface area (S_{BET}) were significantly ($P < 0.05$) higher compared with that of the feedstocks and pyrochars. Mesopores were dominant in the hydrochars, where the pores had slit-type holes and a stratified structure. The hydrochars possessed more O functional groups and aromatic C=C and C-H band than the feedstocks and pyrochars. The hydrochars derived from solid digestates were better as a solid fuel because of their combustion property. The increase in the crystallinity of the hydrochars enhanced their stability. The hydrochars produced from the DS_M were more acidic than those from the DS_S. The HTC_{DS_S} had a better adsorptive effect on pollutants than the HTC_{DS_M} because of the higher S_{BET} and optimal functional groups.

Keywords: Hydrochar; Solid digestates; Swine manure; Rice straws

Contact information: a: Circular Agriculture Research Center, Jiangsu Academy of Agricultural Sciences, Nanjing 210014, China; b: Jiangsu Agricultural Waste Treatment and Recycle Engineering Research Center, Nanjing 210014, China; c: East China Scientific Observing and Experimental Station of Development and Utilization of Rural Renewable Energy, Ministry of Agriculture, Nanjing 210014, China; d: College of Environment, Hohai University, Nanjing 210098, China;
** Corresponding author: hmjin@jaas.ac.cn*

INTRODUCTION

It has been widely accepted that biogas production with agricultural residues plays an important role in energy supply, environmental protection, and the promotion of agricultural development in rural areas (CRES 2012). As the largest agricultural and developing country in the world, China has the largest amount of agricultural waste (Zhang *et al*. 2015). Every year 809 million tons of crop straw and 1629 million tons of animal manure are collected as biomass resources, which has the biogas potential of 33.5×10^{10} m^3 (Wang *et al*. 2016a). Over 40 million household-scale reactors and 30,000 large-scale digesters (volume of 500 m^3) were built in China in 2010 (Song *et al*. 2014). The total biogas production of all of the provinces in China reached 1.58×10^{10} m^3 in 2012, which can save 1.12×10^{10} tons of coal equivalent (Wang *et al*. 2012).

Biogas technology not only reduces greenhouse gas emissions when compared with fossil fuel electricity production (Chen *et al*. 2017), but also offers grid services by making electricity production from the combined heat and power units more flexible. This technology also generates solid and liquid by-products, which can be used as fertilizer and soil amendment. Clearly, the benefits of biogas for the economy, society, and environment link most closely to agricultural areas (Wang *et al*. 2016a). Therefore, biogas utilization is a promising strategy for reducing fossil fuel energy consumption and greenhouse gas emissions in rural China (Zheng *et al*. 2012). Rural household biogas (RHB) has drawn increasing attention worldwide as one of the most prominent bioenergy technologies for biomass utilization. The RHB is important for rural development in China because it functions as the connecting chain among livestock breeding, agricultural production, and energy supply (Yang *et al*. 2012). In addition, anaerobic digestion (AD) technology is considered to be an effective way to treat organic waste in scale livestock farming, which is in a rapid development stage worldwide, especially in China over the past few years.

The AD process yields a wet solid residue, known as a digestate. The digestate is rich in nitrogen, phosphorous, and organic matter, which is conventionally applied as a fertilizer or soil amendment (Teglia *et al*. 2011a,b). Excessive amounts of digestate can lead to nutrient leaching, resulting in severe water pollution, *e.g.*, algal blooms (Teglia *et al*. 2011a,b). The production of AD digestate has reached over 0.12 billion tons every year in China, which is expected to grow remarkably with the prosperity of the biogas industry because of the National Rural Biogas Development for the 13th Five Year Plan (National Development and Reform Commission, and Ministry of Agricultural of the People's Republic of China 2017). However, improperly managed digestates could create other environmental problems, including greenhouse gas emissions and the volatilization of ammonia. Additionally, high contents of heavy metals, such as Cu, Zn, and As, and residual antibiotics, such as sulfadiazine, sulfadimidine, and sulfachloropyridazine, in digestates derived from animal manures increases the risk of those problems when they are spread on fields (Jin and Chang 2011; Jin *et al*. 2017). Thus, a more effective method is urgently needed for the treatment of digestates and utilization of value-added products.

Hydrothermal carbonization (HTC) is a thermal conversion process that can be used to treat high-moisture biomass and convert it into a valuable solid product called hydrochar. Compared with pyrolysis, the HTC process requires shorter reaction times (1 h to 12 h) at a relatively low temperature range (180 °C to 250 °C) with corresponding pressures of up to 30 bar (He *et al*. 2008; Guo *et al*. 2016). Additionally, the water in HTC processes is reported to contain some phenolic, organic, and furan derivative compounds, such as acetic acid, formic acid, glycolic acid, levulinic acid, 2-furfural, and 2,5-hydroxymethylfurfural (HMF), that are formed *via* the degradation of biomass polymers and causes the acidic nature of the hydrochars (Mukherjee *et al*. 2011). Some studies reported that hydrochars possess excellent properties, which are more efficient for water treatment and soil remediation. For example, Dai *et al*. (2015) used HTC at 200 °C for 2 h to 24 h to produce hydrochar for immobilizing phosphorus from cow manure. Hydrochar was also prepared from swine manure *via* HTC at 250 °C for 20 h, and it was concluded that the HTC process depends on the hydrolysis and condensation polymerization reactions (Cao *et al*. 2011). Mumme *et al*. (2014) investigated the behavior of hydrochar in an AD reactor with regards to the degradability and effects on the biogas production and ammonia inhibition. It was found that the addition of hydrochar increased the methane yield 32% because of the larger fraction of anaerobically degraded carbon (10.4% of total carbon) in the hydrochar.

However, stronger inhibitions (3.1 g TAN/kg to 6.6 g TAN/kg) were not mitigated by the hydrochar.

The feedstocks for HTC are derived from a wealth of sources, including straw, manure, sludge, and algae. However, there are a limited number of studies on the use of digestates as feedstocks for HTC. The physicochemical properties of digestates are different dependent upon the lignocellulosic biomass it was produced from, and the material itself needs to be evaluated for its biochar properties through individual characterization and reaction (Reza *et al*. 2015). To illuminate the characteristics of hydrochar derived from digestates is useful for better understanding the potential applications and environmental risk assessment, and creates a rational basis for the design of more suitable modifications to enhance the application performance and prevent toxic elements from entering the environment.

The main objectives of this study are to determine the physicochemical characteristics of the hydrochars and pyrochars derived from digestates of swine manure and rice straw, including elemental composition, pH, dissolved organic carbon (DOC) and nitrogen (DON) contents, Brunauer-Emmett-Teller surface area (S_{BET}), stabilization, functional groups, and morphology. The intent of the present study is to obtain fundamental knowledge of the conversion of digestates into hydrochar. The findings of this work will be helpful in designing experiments and the scaling-up of HTC units.

EXPERIMENTAL

Materials

Feedstock

The feedstocks used for HTC were solid digestates that were anaerobically digested from swine manure (SD_M) and rice straw (SD_S). These solid digestates were obtained from three bench-scale completely stirred tank reactors (CSTRs). Two CSTRs were continuously run for 210 d. The swine manure was obtained in one batch from a commercial swine farm in Jintan City, south of Jiangsu Province, China, and stored at -18 °C. The rice straw was collected from the Liuhe Experimental Base of Jiangsu Academy of Agricultural Sciences (Nanjing, China), and then air-dried and cut to pieces approximately 2 mm in length. The experiments used swine manure and rice straw with feeding total solid (TS) concentrations of 8% and 6%, respectively. The experiments were operated at 37 °C ± 1 °C with a hydraulic retention time (HRT) of 20 d, which are the conditions that are widely used in large-scale biogas plants on livestock farms. The inoculums were digested swine manure slurries taken from an on-farm biogas plant, which used swine manure at a loading rate of 4.31 kg COD/m^3/d and was operated at 37 °C ± 1 °C. The basic characteristics of the feedstocks and inoculum are listed in Table 1.

Table 1. Physical and Chemical Characteristics of the Feedstocks and Inoculum for Anaerobic Digestion

Feedstock and Inoculum	TS	VS	TOC	TN	C/N	pH
	(%)					
Swine manure	24.3	79.9	34.6	2.0	17.3	7.18
Rice straw	87.4	82.0	45.8	0.8	57.3	7.15
Inoculum	3.28	39.4	-	-	-	7.78

VS – volatile solids; TOC – total organic carbon

The solid digestates were collected and dewatered on-site by a screw press and belt dryer (70 °C for 8 h) for further application.

Hydrothermal carbonization

Each HTC experiment used 2 g of solid digestates and 8 mL of deionized (DI) water, and 1 g of solid digestates and 9 mL of DI water to maintain the constant biomass-to-water ratios of 1:4 and 1:9, respectively. Both mixtures were transferred to a 20-mL PTFE reactor connected to a temperature controller (Jinan Henghua Technology Ltd., Jinan, China). After heating the mixture to the desired temperatures of 190 °C and 250 °C at a heating rate of 3 °C/min, the temperatures were maintained for 4 h. After the reaction period, the heater was turned off and the reactor was cooled down naturally. The residual overpressure from the gaseous products was released to the hood. The resulting slurry was filtered using 58-μm cellulose filter paper (type 113 P filter, Carl Roth GmbH, Karlsruhe, Germany). The solid hydrochar was dried overnight at 105 °C, and then stored in an air-tight container. The solid hydrochars are hereafter referred to as $HTC_{\text{DS\_M1:4}}$, $HTC_{\text{DS\_M1:9}}$, $HTC_{\text{DS\_S1:4}}$, and $HTC_{\text{DS\_S1:9}}$. Each experiment was conducted four times, and the products from each run were mixed to obtain enough sample for the analyses.

Pyrolysis

Pyrolysis was performed in a bench-scale horizontal tubular furnace (TL1200, Nanjing Boyuntong Science & Technology Co., Ltd., Nanjing, China) at 500 °C. For each run, 10 g of digestates were placed into a small crucible made of stainless steel. Three crucibles were then placed inside the furnace. Prior to starting each run, the reactor was purged with N_2 gas at a rate of 5 L/h to generate an oxygen-free atmosphere. The reactor was heated under a 100 mL/min N_2 gas flow rate until the desired temperature was attained. After heating the mixture to the desired temperature of 500 °C at a heating rate of 17 °C/min, the temperature was maintained for 30 min. Then, the heater was shut down and the inside of the reactor was cooled to room temperature. After cooling, the pyrochars from swine manure and rice straw were stored in air-tight containers, and hereafter are referred to as $BC_{\text{DS\_M}}$ and $BC_{\text{DS\_S}}$, respectively. Each experiment was conducted at least four times to generate enough sample (> 10 g) for the analyses. The samples from the repetitions were mixed prior to further use.

Methods

Product characterization

The determination of TS, volatile solids (VS), and pH was performed as described by Reza *et al*. (2015). The pH values were analyzed with a pH meter (Accumet model 25 pH/ion meter, Thermo Fisher Scientific, Waltham, MA, USA) and a liquid-to-solid ratio of 20.

The surface areas of the digestates, hydrochars, and pyrochars were measured from N_2 isotherms at 77 K using a gas sorption analyzer (ASAPTM 2020, Micromeritics Instrument Corp., Atlanta, GA, USA). The samples were degassed for 6 h under vacuum at 473 K prior to conducting the adsorption measurements. The N_2 adsorbed per gram of sample was plotted *versus* the relative vapor pressure (P/P_0) of the N_2 ranging from 0.02 to 0.2, and the data was fitted to the Brunauer–Emmett–Teller (BET) equation to calculate the surface area. The total pore volume was estimated from the N_2 adsorption at a P/P_0 of approximately 0.5. The Barret–Joyner–Halender (BJH) method was used to determine the pore size distribution from the N_2 desorption isotherms.

The surface morphology was examined using a scanning electron microscope (JSM-6400-SEM, JEOL, Akishima-shi, Tokyo, Japan). Samples were placed on double-sided platinum-coated tape, and images were recorded of a 50 m^2 area with the scanning mode. An energy dispersive spectrometer (EDS) was used to analyze the element distribution in a micro region of the feedstocks, hydrochars, and pyrochars.

A Fourier transform infrared (FT-IR) spectroscope (J200, Thermo Fisher Scientific) was used to evaluate the structural properties of the digestates, hydrochars, and pyrochars. The infrared spectra were collected in the range of 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1}. In order to minimize the sampling error, five subsamples were selected at random from each sample of the digestates, hydrochars, and pyrochars for measurement by FT-IR, and the average of the measurements was taken.

Thermogravimetric analysis (TGA) was the high-precision method used to study the combustion characteristics of the biomass (Mishra *et al*. 2015). In this study, TGA was performed using a SII EXSTAR TG/DTA 7200 thermogravimetric analyzer (Seiko Instruments Inc., Chiba Prefecture, Japan). Air was used as the reaction gas with a flow rate of 15 mL/min. Approximately 5.0 mg of sample were selected and placed in an alumina crucible. The weight loss of the samples was carried out continuously under nonisothermal conditions from 50 to 800 °C with a heating rate of 20 °C/min. Each sample was analyzed three times to ensure good reproducibility, and the average was determined.

Statistical analysis

An analysis of variance (ANOVA) was used for assessing the variations in the pH, DOC, and DON between the feedstocks, hydrochars, and pyrochars. These statistical analyses were performed using SPSS (v. 13.0, SPSS Inc., Chicago, USA). Multiple means were compared with the least significant difference (LSD) test at a P-value of 0.05.

RESULTS AND DISCUSSION

pH and Dissolved Carbon and Nitrogen

Consistent with the results of previous studies (He *et al*. 2008; Fuertes *et al*. 2010; Fang *et al*. 2015), all of the hydrochars were slightly acidic (Table 2). Compared with the pyrochars derived at a higher temperature, the acidity of the hydrochars was similar to that of low temperature biochars, which had both a lower mineral content and higher level of volatile organic matter (Mukherjee *et al*. 2011). In this study, the hydrochars produced from the DS_M were more acidic than those from the DS_S. The pH of the hydrochars was inversely proportional to the inorganic mineral contents of the feedstocks (Parshetti *et al*. 2014). Although the mineral content of the DS_S was higher than that of the DS_M, the pH may have also been dependent upon the higher organic acid content (Mukherjee *et al*. 2011). The trend of pH changes between the hydrochars produced from the biomass-to-water ratios of 1:4 and 1:9 corresponded to their mineral contents. Thus, although the hydrochars would not be useful for neutralizing soil acidity, the pH buffering capacity may help reduce ammonia emissions and retain nutrients in soils (Mumme *et al*. 2014). In addition, the pH of the hydrochars could impact pollutant adsorption (Liu and Zhang 2009; Dong *et al*. 2011).

The HTC treatment significantly ($P < 0.05$) enhanced the DOC and DON. The contents of DOC and DON in the HTC products were 50 to 200 times higher compared with the pyrochars (Table 2), which indicated that the labile carbons in the hydrochars had a higher bioavailability than that in the pyrochars (Mumme *et al*. 2011). The higher contents of dissolved organic matter (*i.e.*, DOC and DON) in the hydrochars were because of a lower loss of volatile matter in the feedstocks at 190 °C, and the decomposition of cellulose and hemicellulose to oligosaccharides and monosaccharides during the HTC process (Kumar *et al*. 2011; Libra *et al*. 2011). The higher degradability of the hydrochars as compared to the pyrochars was related to a lower extent of carbonization, including less ash content and higher H/C and O/C ratios (Bai *et al*. 2013). Additionally, Mumme *et al*. (2014) found that hydrochars possessed the ability to catalyze anaerobic digestion by the mitigation of mild ammonia inhibition, and support archaea growth and methanization of labile carbon in the hydrochar.

Table 2. Physical and Chemical Characteristics of the Feedstocks and their Derived Hydrochars and Pyrochars

Samples	pH		DOC (%)(mg/g)		DON (%)(mg/g)	
DS_M	6.93 ± 0.02	b	13.32 ± 1.81	b	1.26 ± 0.34	b
$HTC_{\mathrm{DS\_M1:4}}$	5.77 ± 0.02	c	49.21 ± 3.20	a	3.60 ± 0.24	a
$HTC_{\mathrm{DS\_M1:9}}$	6.98 ± 0.06	b	12.16 ± 1.79	b	0.71 ± 0.24	b
$BC_{\mathrm{DS\_M}}$	10.16 ± 0.04	a	0.21 ± 0.02	c	-	
DS_S	8.21 ± 0.03	b	16.35 ± 0.82	c	0.64 ± 0.10	c
$HTC_{\mathrm{DS\_S1:4}}$	6.07 ± 0.02	c	44.13 ± 2.01	b	3.23 ± 0.30	b
$HTC_{\mathrm{DS\_S1:9}}$	5.96 ± 0.02	d	50.95 ± 2.18	a	4.10 ± 0.32	a
$BC_{\mathrm{DS\_S}}$	10.63 ± 0.03	a	0.51 ± 0.02	d	-	

Morphology and Structural Properties of the Hydrochars

The surface area and porosity characterization of the digestates, hydrochars, and pyrochars are shown in Table 3. Kambo and Dutta (2015) reported that the specific surface area and porosity of the hydrochar typically increased for reaction temperatures of up to approximately 200 °C, and a further increase in the temperature had a negative response. After the HTC process at 190 °C, the S_{BET} of the $HTC_{\mathrm{DS\_M}}$ and $HTC_{\mathrm{DS\_S}}$ was more than 4.5 and 13.5 times higher, respectively, than for the feedstocks, which were also slightly higher than that of the pyrochars, except for $HTC_{\mathrm{DS\_S1:4}}$ (Table 3). Although the pore volumes in the $HTC_{\mathrm{DS\_M}}$ and $HTC_{\mathrm{DS\_S}}$ were distinctly higher than those in the feedstocks, the micropore volumes were lower. This indicated that mesopores ($S_{\mathrm{BET}} < 10$ m^2/g) were dominant in the HTC products (Fang *et al*. 2015). The N_2 adsorption and desorption isotherms also demonstrated this point (Fig. 1). According to the standard determination reported by IUPAC (2015), the pore structures were type II for the digestates and the derived hydrochars and pyrochars. This isotherm type shows no holes or adsorption isotherms of macroporous materials, where multilayer adsorption usually occurs after monolayer absorption (turning point). The presence of hysteretic rings (H3) indicated that the pores had slit-type holes and a stratified structure. The average pore sizes of the HTC products were consistent with changes in the micropore volume. An increase in the surface area could have been due to the formation of nanoparticles caused by the high content of hemicellulose, and new pores caused by the loss of volatile matter (Donar *et al*. 2016). This phenomenon was shown by the SEM images of the hydrochars, which indicated that the surface of the hydrochars was rougher compared with that of the feedstocks and pyrochars (Fig. 2). Results from Fang *et al*. (2015) showed that hydrochars with the highest surface area and pore volume were produced at 200 °C, regardless of the feedstock (Fang *et al*. 2015). In this study, the HTC products derived from the higher biomass-to-water ratio possessed a higher S_{BET} and pore volume (Table 2), which indicated that water was a crucial factor that affected the characteristics of the hydrochars. The S_{BET} and pore volume are considered to be connected with adsorption, and a higher S_{BET} improves adsorption (Jin *et al*. 2014). It was concluded that the HTC_{DS_S} had a better adsorptive effect on pollutants than the HTC_{DS_M} because of the higher S_{BET}.

Table 3. Surface Area and Porous Characterization of the Feedstocks and their Derived Hydrochars and Pyrochars

Samples	S_{BET} (m^2/g)	Total Volume (cm^3/g)	Micropore Volume (cm^3/g)	Average Pore Size (nm)
DS_M	0.4501	0.0030	0.0011	26.82
$HTC_{DS\_M1:4}$	2.9439	0.0163	0.0004	23.16
$HTC_{DS\_M1:9}$	2.8176	0.0150	0.0011	20.32
BC_{DS_M}	2.2489	0.0157	0.0011	27.92
DS_S	0.7059	0.0117	0.0009	66.32
$HTC_{DS\_S1:4}$	9.4864	0.0581	0.0001	24.51
$HTC_{DS\_S1:9}$	10.3457	0.0617	0.0005	23.85
BC_{DS_S}	9.5162	0.0414	0.0025	17.40

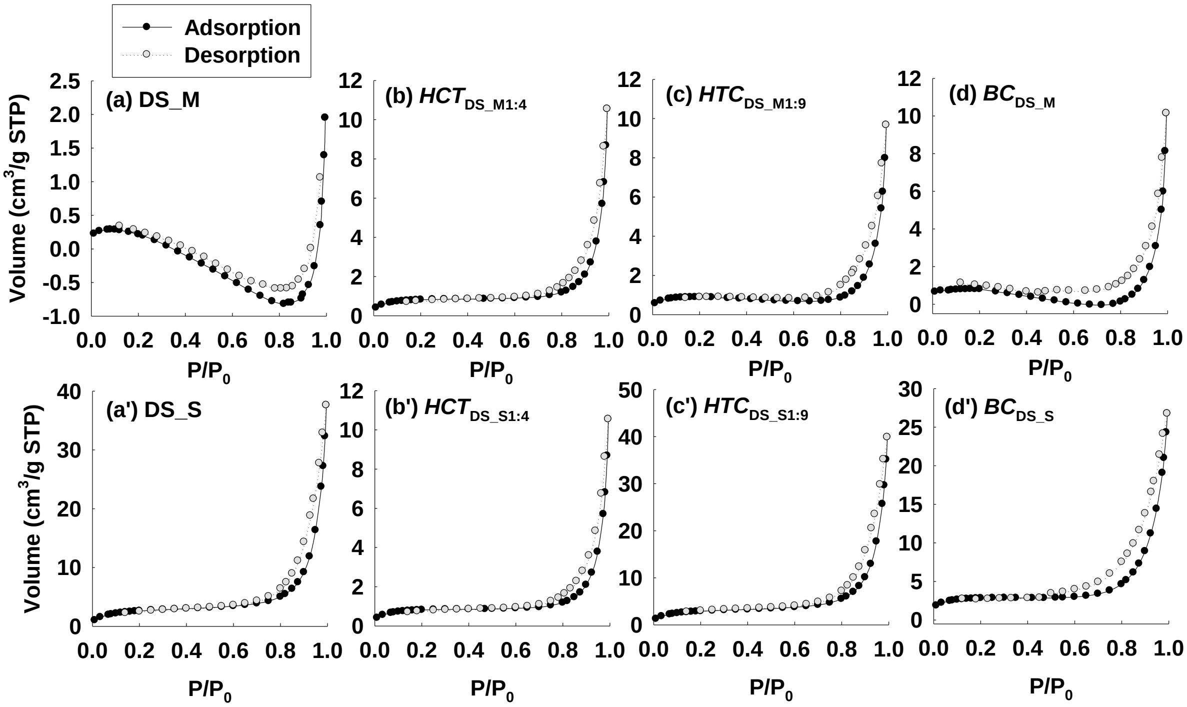

Fig. 1. N_2 adsorption and desorption isotherms of the feedstocks and their derived hydrochars and pyrochars

The SEM images of the hydrochars and pyrochars are presented in Fig. 2, and illustrate the potential structural differences caused by the HTC treatment. The SEM images of the HTC products (Figs. 2b, 2c, 2b', and 2c') revealed porous structures with disorganized structural cracks, channels, and microspheres for both digestates. From these figures, it was obvious that the surface of the hydrochars was rougher compared with that of the feedstocks (Figs. 2a and 2a') and pyrochars (Figs. 2d and 2d'). This was ascribed to the removal of impurities from partially blocked pores and the generation of microspheres after the HTC treatment (Donar *et al*. 2016). In HTC process, water has a role of solvent, reactant or catalyst, which could be manipulated during HTC reactions to enhance reaction selectivity to desired products, such as density, hydrogen bonding, etc. (Pavlovič *et al*. 2013). In this study, HTC with higher biomass-to-water ratios was able to form micropore structure in hydrochars (Table 3).

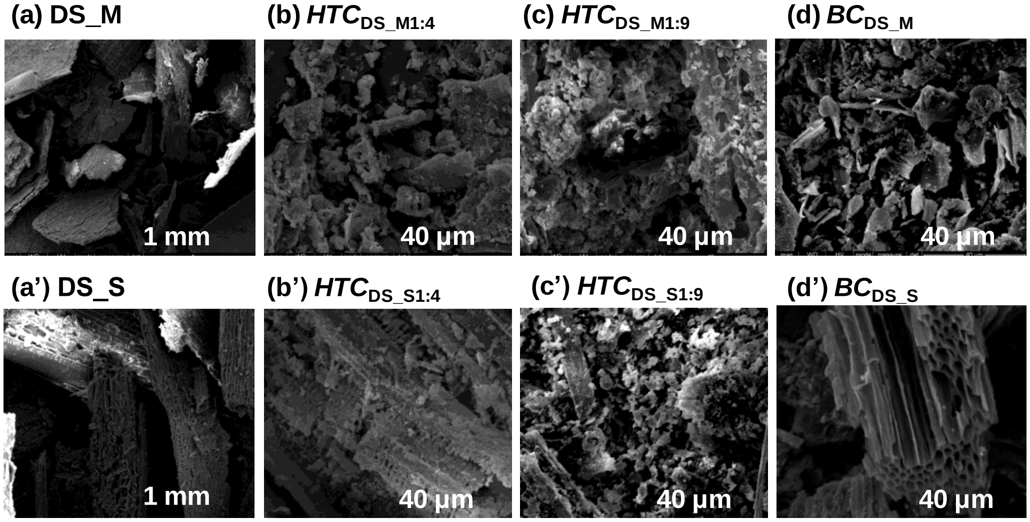

Fig. 2. SEM images of the selected feedstocks and their derived hydrochars and pyrochars

Functional Groups on the Surface of the Hydrochars and Pyrochars

The IR spectra of the feedstocks, hydrochars, and pyrochars in the near IR region (*i.e.*, wavenumber: 3500 cm^{-1} to 600 cm^{-1}) are shown in Fig. 3. At 190 °C, hydrolysis was given priority in the reaction, and the hydrothermal effect greatly weakened the hydrogen bonds in the hemicellulose and cellulose crystal (Parshetti *et al*. 2013). The organic compounds in the hydrochars derived from the digested swine manure included the O-H stretching vibration of alcohols and phenols (3429 cm^{-1}), C-H stretching vibration of aliphatics (2920 cm^{-1}), C=O stretching vibration of non-conjugated β-carbonyls (at 1704 cm^{-1}), C-H vibration of aromatic rings (1457 cm^{-1}), C-H in-plane bending vibration of aromatic rings and/or the C-O-C stretching vibration of cellulose and β-glycoside bonds of hemicellulose and/or the C-O vibration of phenols (1036 cm^{-1} to 1110 cm^{-1}), and C-H out-of-plane bending vibration of cellulose and β-glycoside bonds of hemicellulose and/or Si-O stretching vibration (878 cm^{-1}) (Fig. 3a). The organic compounds in the hydrochars derived from the digested rice straw were a little bit different from those in the digested swine manure (Fig. 3b). The HTC_{DS_S} also had C=C aromatic ring frame vibration of lignin (1510 cm^{-1}) and C-H stretching substitutes on benzene (782 cm^{-1}), while the C-O-C stretching vibration of cellulose and β-glycoside bonds of hemicellulose and/or C-O vibration of phenols completely disappeared (Ábrego *et al*. 2009; Chen *et al*. 2013).

After the HTC treatment, the peaks at 3429 cm^{-1}, 1704 cm^{-1}, and 1110 cm^{-1}, which were attributed to the O-H vibrations of hydroxyl groups and the C=O stretching vibration of primary and/or alkyl substituted ethers, became more apparent (Fig. 3). This suggested that the HTC products had more O functional groups than the feedstocks and pyrochars, *i.e.*, more electron donating sites for pollutants, such as heavy metals. Hence, the hydrochars had an increased adsorption ability (Wang *et al*. 2015; Donar *et al*. 2016;

Petrović *et al*. 2016). Moreover, the peak at 1510 cm^{-1}, attributed to aromatic C=C bonds in the hydrochars, was more prominent in the $HTC_{DS\_S1:4}$ and $HTC_{DS\_S1:9}$ (Fernández *et al*. 2015), which played a major role in the interaction between the surface of the hydrochars and heavy metals, like Pb^{2+} (Hamid *et al*. 2014). Additionally, an increase in and shifting of C-H bands (782 cm^{-1}) after the HTC of the digested rice straw suggested that metals could interact with the hydrochars through π-electron interactions (Wang *et al*. 2016b). Namely, heterocyclic compounds easily bonded with metals through the formation of coordination bonds between the d-electrons of metals and C=C (π-electron) bonds in the unsaturated and aromatic systems. Based on the functional groups on the surfaces of the hydrochars, it was concluded that the HTC_{DS_S} had a better adsorptive effect on pollutants than the HTC_{DS_M}.

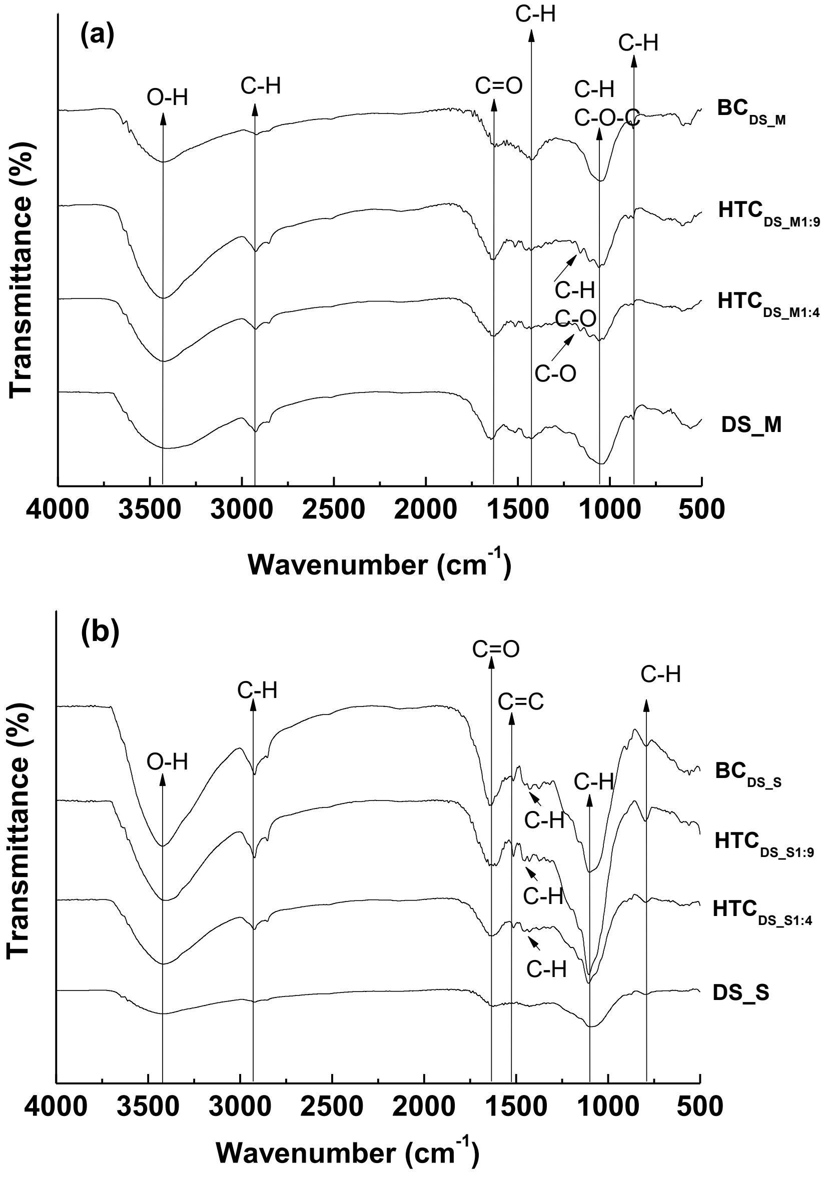

Fig. 3. FT-IR spectra of the digestates of swine manure (a) and rice straw (b) and their derived hydrochars and pyrochars

Combustion Behavior and Thermal Characteristics

Figure 4 shows the combustion profiles of the original digestates and the corresponding hydrochars and pyrochars obtained from the different operating conditions. Compared with the pyrochars, the hydrochars derived from the HTC process at 190 °C could improve the combustion performance (Fig. 4). The TGA profiles of the hydrochar were similar to the original digestates, which showed three distinct weight loss stages as the temperature rose. The first stage was a small mass loss peak that occurred within the temperature range of 50 °C to 105 °C, which was due to the loss of absorbed and capillary water. The second stage was the strongest mass loss peak, and occurred within the temperature range of 150 °C to 400 °C. This peak was ascribed to the loss of bound water and the composition of the organic matter, *i.e.*, cellulose, hemicellulose, and their degradation products (Liu and Balasubramanian 2012). The third stage was a burning process that occurred within the temperature range of 400 °C to 800 °C, which resulted in the formation of a stable carbon structure (Yao *et al*. 2016).

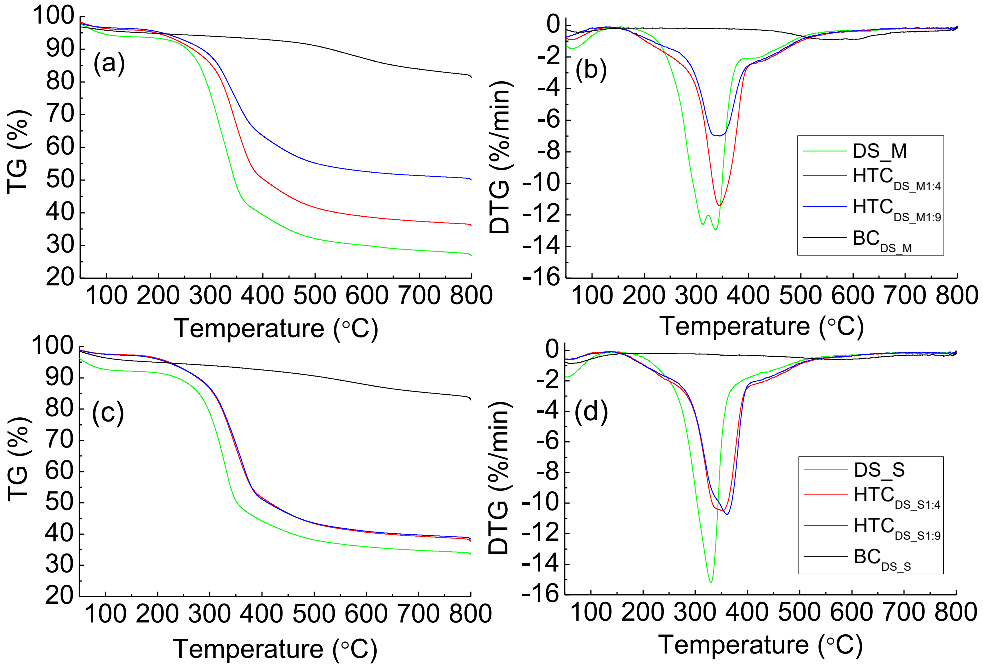

Fig. 4. Thermogravimetric analysis of the digestates of swine manure (a, b) and rice straw (c, d) and their derived hydrochars and pyrochars

The HTC process caused a significant change in the combustion behavior of the original digestates, especially for the $HTC_{DS\_M1:4}$ (Figs. 4a and 4b). The weight loss for the $HTC_{DS\_M1:4}$ during combustion was much lower than that for the original digestate derived from swine manure, which indicated that the hydrochar went through complete combustion. The reason for the above phenomenon was that there was a higher content of volatile matter, which could have improved the flame burning (Yao *et al*. 2016). In this study, the contents of dissolved matter (*i.e.*, DOC and DON in Table 2) in the $HTC_{DS\_M1:4}$ were significantly higher than those in the corresponding feedstock and pyrochars, which suggested that the hydrochars were better as a solid fuel. An additional reason for the lower weight loss phenomenon was that the larger specific surface area and porosity increased the flammability of the materials (Yao *et al*. 2016). The $HTC_{DS\_M1:4}$ possessed a better S_{BET}

and excellent pore structure (Table 2), which were beneficial to combustion. The HTC products from the digested rice straw showed similar combustion characteristics to those of the digested swine manure (Figs. 4b and 4c). However, the weight losses of the $HTC_{DS\_S1:4}$ and $HTC_{DS\_S1:9}$ were lower than those of the corresponding feedstock, *i.e.*, DS_S. This differed from the $HTC_{DS\_M1:4}$, although the contents of the dissolved matter and surface areas were significantly ($P < 0.05$) higher for $HTC_{DS\_M1:4}$ than for the DS_S. The porosity of the DS_S was the major cause of this phenomenon. However, the effect of the volatile compounds on the combustion still needs further analysis because the volatile matter, surface area, and porosity often had a synergistic effect (Wang *et al*. 2016b). The combustion behaviors of the $HTC_{DS\_S1:4}$ and $HTC_{DS\_S1:9}$ were almost identical, which indicated that the different biomass-to-water ratios had a subtle impact on the combustion profile of the HTC products.

Crystal Texture

The X-ray diffraction (XRD) patterns of the feedstocks, hydrochars, and pyrochars are shown and compared in Fig. 5. The digestates derived from swine manure and rice straw and their hydrochars usually had a combination of crystalline and amorphous structures (semi-crystalline). The feedstocks and their hydrochars showed two XRD peaks at approximately 15° and 22°, and these peaks corresponded to amorphous cellulose structures (Zhang *et al*. 2015), which suggested that cellulose was not completely degraded after HTC at 190 °C (Falco *et al*. 2011). The crystal cellulose structure in the hydrochars was confirmed by a distinct sharp peak at 22.7°, which was assigned to the (002) interlayer reflection (Figs. 5a and 5b) (Parshetti *et al*. 2013). In contrast, the cellulose peak was weakened in the pyrochars as a result of the partial decomposition of cellulose because of the high temperatures.

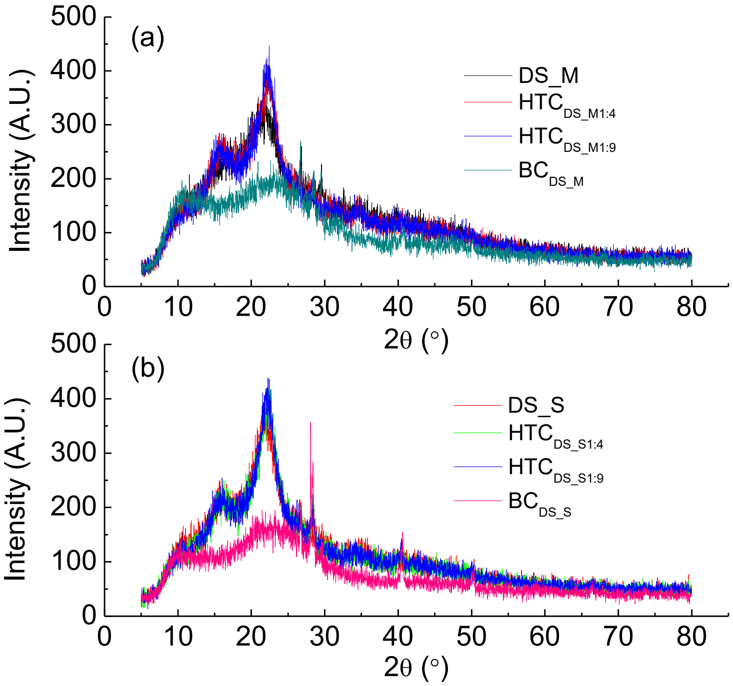

Fig. 5. X-ray diffractograms of the digestates of swine manure (a) and rice straw (b) and their derived hydrochars and pyrochars

A new sharp peak appeared at 26.5° in the pyrochars, which corresponded to 002 lattice spacing and indicated a graphitic structure and p-p/ transitions (Navarro-Suárez *et al*. 2014). The crystalline structure of the cellulose was preserved at 190 °C in the digestates because of the protective lignin layer, which was the most robust and resistant component compared to the cellulose and hemicellulose (Mosier *et al*. 2005). Compared with the feedstocks, an increase in the crystallinity for the hydrochars was induced by a partial removal of the amorphous constituents of cellulose (Sghaier *et al*. 2012). In addition, the 2θ peaks moved backwards, which indicated that the stability of the hydrochars was enhanced, especially for the $HTC_{\mathrm{DS\_M}}$.

CONCLUSIONS

1. The hydrochars from solid digestates were acidic, and their contents of DOC and DON were 50 to 200 times higher compared to pyrochars. The S_{BET} of the hydrochars was 4.5 to 13.5 times higher than that of the feedstocks. Mesopores were dominant in the hydrochars, where the pores had slit-type holes and a stratified structure.
2. The hydrochars possessed more O functional groups and aromatic C=C and C-H band shifting than the feedstocks and pyrochars, *i.e.*, more electron donating sites for the adsorption of pollutants. The hydrochars derived from solid digestates were favorable as a solid fuel because of their combustion property. An increase in the crystallinity of the hydrochars enhanced their stability. The hydrochars produced from the DS_M were more acidic than those from the DS_S.
3. The application of HTC on digestates was found to be a promising way to pretreat solid digestates with high water contents. It was concluded that the $HTC_{\mathrm{DS\_S}}$ might have a better adsorptive effect on pollutants than the $HTC_{\mathrm{DS\_M}}$ because of the higher S_{BET} and optimal functional groups. Different biomass-to-water ratios during the HTC process had a distinct impact on the physical and chemical characteristics of the $HTC_{\mathrm{DS\_S}}$ and $HTC_{\mathrm{DS\_M}}$.

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