

Effects of hydrothermal carbonization temperature on carbon retention, stability, and properties of animal manure-derived hydrochar

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Abstract: Hydrothermal carbonization of animal manure is being increasingly recognized as a green process for hydrochar production. Temperature obviously affects the properties of hydrochar especially with respect to carbon retention and stability. These properties determine the carbon sequestration potential of hydrochar but related researches are limited. In this study, chicken, dairy, and swine manures were collected and hydrothermally carbonized under different temperature conditions, aiming to study the fuel characteristics, carbon retention, and stability of hydrochar influenced by temperature. Results show that high temperature led to low yield and declined H/C, O/C, and volatile matter of hydrochar. While high temperature caused high fixed carbon, fuel ratio, and heating value of hydrochar, indicating that animal manure hydrochar can be adopted as an alternative of fuel. After hydrothermal carbonization, less than half of carbon from animal manure was retained in hydrochar: 22.70%-46.71% for chicken manure, 39.36%-49.72% for dairy manure, and 36.24%-64.21% for swine manure. The carbon retention decreased with the increase of temperature. Conversely, high temperature improved the aromatic and strengthened the resistance to thermal oxidation of hydrochar, which was evidenced by FTIR and TGA analysis. Moreover, the carbon sequestration capacity of animal manure hydrochar was less than a third of total carbon (originated from animal manure) and relatively low temperature (no more than 250°C) was beneficial to produce hydrochar for carbon sequestration.

Keywords: livestock manure, carbon sequestration, hydrochar, hydrothermal temperature

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1 Introduction

With the continuous development of animal husbandry, a large amount of animal manure is discharged. For example, the production of livestock manure in China is nearly 3 billion t/a^[1]. Many environmental and ecological problems including greenhouse gas emissions, water, and soil pollution are emerging^[2-4]. Hence, how to handle this manure is becoming urgent. In China, composting is a widely adopted method to treat animal manure. However, composting cannot effectively remove or immobilize antibiotics and heavy metals, which presents

potential environmental and ecological risks and limits its utilization^[5-7].

In the past decade, pyrolysis is considered a good approach for treating animal manure aiming to resolve the defects of compost^[8-10]. The antibiotics are broken down and heavy metals are immobilized after pyrolysis^[11-13]. Besides, manure-based biochar addition into soils brings extra environmental ecology benefits including soil quality improvement and soil pollution mitigation^[14-18]. However, pyrolysis requires a large amount of energy input and financial load^[19,20], in particular, for the pre-drying requirement of high-wet manure. Besides, many nutrients in manure are lost during the pyrolysis process under high-temperature conditions^[21,22]. Moreover, the cost associated with the treatment and disposal of gas and liquid produced during the pyrolysis process limits its wide application^[23]. Thus, developing a novel and efficient method for the disposal of animal manure is becoming an urgent issue.

At present, hydrothermal carbonization (HTC) conversion is gradually proved as a great method for the treatment of waste biomass. It is conducted at mild temperatures^[23-25]. The necessity and advancement of HTC are 1) low energy input due to no pre-drying requirement for high-moisture waste biomass including sewage sludge and animal manure^[26,27]; 2) clean production technology due to its smoke-free process and low hazardous gas discharge^[28,29]; 3) mitigating environmental health risks by eliminating pollutants including pathogens, antibiotics and antibiotic resistance genes^[30,31]; 4) multifunctional and high added

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value production including hydrochar and liquid^[32,33].

Hydrochar exhibits many advantages including high carbon and nutrient content, abundant functional groups, strong recalcitrance, high mass and energy density, etc. Hydrochar was widely applied including bioenergy production, wastewater pollution remediation, and exhaust gas purification^[34-36]. Besides, hydrochar with high calorific values can serve as a potential fuel source^[37,38]. Moreover, the liquid as a by-product can be recycled and/or as a raw material for CH₄ or fertilizer production^[39,40]. In summary, HTC is an economically viable, environmentally friendly technology of hydrochar production for waste biomass disposal.

Feedstock and temperature greatly affect hydrochar properties^[35,41]. Many studies have focused on plant-based and slurry feedstock for hydrochar production^[24,25,42]. Limited studies have considered animal manure including chicken, horse, rabbit and swine manures, etc. as a potential feedstock for HTC^[43,44]. They have investigated the nutrients recovery and fixation, heavy metals species change and fuel characteristics of hydrochar. However, only a few studies have examined the carbon retention and stability of hydrochar influenced by temperature, especially with respect to its proposed use for carbon sequestration^[45]. Hence, in this study, three animal manures were selected as feedstock at four temperatures for hydrochar production. The aims of this study include 1) study the temperature influenced the properties of hydrochar; 2) evaluate the energy potential of hydrochar; 3) determine the carbon retention, stability and carbon sequestration of hydrochar.

2 Materials and methods

2.1 Materials

Chicken manure, dairy manure, and swine manure were obtained from the suburbs of Bengbu City (China) as feedstock, air-dried, ground through a 20-mesh sieve for analysis and hydrochar production. The properties of the manure are shown in Table S1.

2.2 Hydrochar production

To obtain the animal manure based hydrochar, 20 g of each animal manure material and 200 mL of deionized water were placed in a 500 mL hydrothermal reactor (GS-0.5, Shandong Chemical Machinery Co., Ltd., China). Then the mixture in the reactor was stirred well, adjusted to approximately pH=7, sealed with stainless steel cover, heated at a rate of 5°C/min until it reached the four settled gradient temperatures from 200°C to 350°C and kept for 2 h. After the hydrothermal reactor cooled down to room temperature through circulating water, the solid product was obtained by separating from the mixture in the reactor, dried at 105°C and labeled as hydrochar. For simplicity, the hydrochar was labeled as initial capital letters of feedstock and temperature, for example, C200 represents hydrochar derived from chicken manure under 200°C.

2.3 Characterization of hydrochar

The element content, specific surface area, surface functional group distribution, morphology, and stability of hydrochar were analyzed using the authors' reported Methods [46-48].

2.4 Calculation

Carbon retention (CR) is defined as the quantity of carbon originated from carbon in feedstock and retained in the hydrochar and expressed as Equation (1)^[49,50]

$$CR = \frac{C_{\text{hydrochar}}}{C_{\text{feedstock}}} \times \text{Yield} \quad (1)$$

where, $C_{\text{hydrochar}}$ and $C_{\text{feedstock}}$ are carbon content of hydrochar and animal manure, respectively, %; Yield is the hydrochar yield, %.

R_{50} is an index used to express the recalcitrance of carbon in the hydrochar as Equation (2).

$$R_{50} = \frac{T_{50, \text{hydrochar}}}{T_{50, \text{graphite}}} \quad (2)$$

where, $T_{50, \text{hydrochar}}$ and $T_{50, \text{graphite}}$ are the temperature values when 50% weight of hydrochar and graphite loss based on TGA analysis^[45,51].

The high heating value (HHV, MJ/kg) was calculated using Equation (3).

$HHV = 0.3491C_w + 1.1783H_w - 0.1034O_w - 0.0151N_w - 0.211Ash$ (3)
where, C_w , H_w , O_w , and N_w are the mass percentages for C, H, O and N of hydrochar or its feedstock, respectively; Ash is the mass percentages of hydrochar or its feedstock.

The energy densification (ED) and the energy yield (EY) were calculated using Equations (4) and (5), respectively.

$$ED = \frac{HHV_{\text{hydrochar}}}{HHV_{\text{feedstock}}} \quad (4)$$

$$EY = ED \cdot \text{Yield} \quad (5)$$

where, $HHV_{\text{hydrochar}}$ and $HHV_{\text{feedstock}}$ are the high heating values of hydrochar and its feedstock, respectively.

3 Results and discussion

3.1 Yield and ultimate analysis

As shown in Table 1, the yield of hydrochar declined with the temperature increase. The C contents of hydrochar were high and increased with the temperature rise indicating that HTC played an important role in carbon enrichment depending on the temperature. It is consistent with other reported results^[52,53].

Table 1 Elemental compositions of animal manures and their hydrochar

Sample	Yield/%	C/%	H/%	N/%	O/%	Ash/%	H/C	O/C
Chicken manure	--	41.27	6.43	3.55	37.15	11.60	1.87	0.68
C200	42.41	46.34	5.82	2.70	21.58	23.56	1.51	0.35
C250	20.97	48.69	5.53	2.86	10.68	32.24	1.36	0.16
C300	18.41	50.87	5.77	2.72	5.87	34.76	1.36	0.09
C350	21.46	53.71	5.83	2.81	6.63	31.02	1.30	0.09
Dairy manure	--	35.99	4.98	0.67	47.61	10.75	1.66	0.99
D200	41.77	42.84	5.11	1.12	31.12	19.82	1.43	0.54
D250	32.74	48.21	4.18	2.01	16.45	29.15	1.04	0.26
D300	29.75	48.47	3.73	2.14	11.78	33.87	0.92	0.18
D350	25.66	55.22	4.46	2.37	10.04	27.91	0.97	0.14
Swine manure	--	39.22	5.47	1.37	41.36	12.58	1.67	0.79
S200	55.52	45.36	5.23	1.28	29.46	18.67	1.38	0.49
S250	37.37	48.99	4.80	1.86	17.05	27.30	1.18	0.26
S300	30.89	49.62	4.30	2.11	10.72	33.25	1.04	0.16
S350	25.64	55.45	4.43	2.30	8.47	29.35	0.96	0.11

Note: O=100-C-H-N-Ash. For simplicity, the hydrochar was labeled as initial capital letters of feedstock and temperature, for example, C200 represents hydrochar derived from chicken manure under 200°C. D: Dairy; S: Swine.

Noticeably, the oxygen content of hydrochar sharply decreased with the rise in temperature from 21.85% to 6.63%, 31.12% to 10.04%, 29.46% to 8.47% for chicken, dairy, and swine manure based hydrochar, respectively. Moreover, the oxygen content of hydrochar much lower than that of its feedstock indicates that during the HTC process the oxygen-containing component probably broken down and its products diffused into liquid phase and/or escaped into the gas phase. The phenomenon is consistent with other reports^[23,35].

The hydrogen contents of hydrochar somewhat declined with the temperature increase (200°C-300°C). When the temperature reached 350°C, its contents increased. However, the trend of nitrogen content with temperature depended on the type of animal manure. On one hand, for the chicken manure hydrochar, its nitrogen content decreased slightly. On the other hand, for dairy and swine manure hydrochar, their nitrogen contents gradually increased and enriched.

H/C and O/C ratios are two indexes for evaluating the carbon aromaticity of carbon-based material^[25,54]. With the rise of temperature, the H/C ratio and O/C ratio of hydrochar gradually decreased, which is consistent with findings of other studies^[55,56], indicating that high temperature promoted the aromaticity of hydrochar.

3.2 Proximate analysis and energy content

In this study, the ash content of hydrochar gradually increased from 200°C to 300°C. While it decreased at temperatures over 300°C (Table 1) probably due to the mineral matter, decomposing under high temperature and/or promoting the mineral diffuse into liquid. As temperature increased, the labile organic component originated from feedstock decomposed and formed some fragments dissolving in the liquid phase, meanwhile, these fragments could also turn into insoluble solids by polymerization^[23], which led to decreased volatile matter (VM) and increased fixed carbon (FC) (Table 2). Moreover, the FC of chicken manure-based hydrochar was much lower than that of the other two manure-based hydrochar, in particular, when the hydrothermal temperature was over 200°C, indicating that the FC of hydrochar depended on feedstock type.

Table 2 Proximate analysis and thermal dynamic properties of animal manures and their hydrochar

Sample	VM /%	FC /%	Fuel ratio	HHV /MJ·kg ⁻¹	ED	EY /%	CR /%	R ₅₀
Chicken manure	82.54	5.86	0.07	15.64	--	--	--	0.45
C200	67.20	9.24	0.14	15.79	1.01	42.81	47.61	0.50
C250	56.44	11.32	0.20	15.56	0.99	20.86	24.74	0.55
C300	49.50	15.74	0.32	16.58	1.06	19.52	22.70	0.60
C350	54.36	14.62	0.27	18.34	1.17	25.17	27.93	0.64
Dairy manure	88.00	1.25	0.01	11.24	--	--	--	0.44
D200	74.67	5.51	0.07	13.55	1.21	50.37	49.72	0.46
D250	38.36	32.49	0.85	13.88	1.23	40.42	43.85	0.60
D300	32.42	33.71	1.04	12.93	1.15	34.21	40.07	0.64
D350	30.57	41.52	1.36	17.56	1.56	40.09	39.36	0.63
Swine manure	82.97	4.45	0.05	13.18	--	--	--	0.42
S200	65.60	15.73	0.24	14.99	1.14	63.15	64.21	0.48
S250	50.71	21.99	0.43	15.21	1.15	43.12	46.68	0.55
S300	38.01	28.74	0.76	14.23	1.08	33.36	39.08	0.61
S350	33.39	37.26	1.12	17.47	1.33	33.98	36.24	0.62

Note: FC=100-VM-Ash; Fuel ratios=FC/VM. VM: Volatile matter; FC: Fixed carbon; HHV: High heating value; ED: Energy densification; EY: Energy yield; CR: Carbon retention; R₅₀ is an index used to express the recalcitrance of carbon in the hydrochar.

As shown in Table 2, the fuel ratio of animal manure was too low to be used as an alternative of fuel. However, after it was hydrothermal carbonization, the fuel ratio of hydrochar showed an increasing trend, in particular, it was over 1 when the temperature was over 300°C for dairy and swine manure-based hydrochar, implying high temperature was beneficial for improving the fuel ratio and these two kinds of hydrochar could be an alternative fuel. However, the fuel ratios of all the chicken manure-based hydrochar were too small to fit as an alternative to fuel.

The HHV of hydrochar depended on the feedstock and temperature. For the chicken-manure hydrochar, the HHV

slightly changed, until the temperature reached 350°C, increased 16.15%, compared to C200. For the dairy and swine manure-based hydrochar, the HHV gradually increased with the rise of temperature except under 300°C, which had the lowest HHV. During the hydrothermal, with the temperature increase, hemi-cellulosic components relatively rich in O content decreased and lignin relatively rich in C content components increased in hydrochar led to HHV gradually increased^[52,57]. Then temperature reached a critical temperature, due to the increase of mineral content and some carbon loss, the HHV sharply decreased. When temperature continued to rise, the density and aromaticity of carbon strengthened by polymerization to the highest HHV^[26,58]. Moreover, the trend of ED and EY was as similar as that of HHV. The EY of dairy and swine manure-based hydrochar was much higher than that of chicken-manure hydrochar. All of these indicate that chicken-manure was unfit to be turned into hydrochar with the purpose of fuel alternative.

3.3 SEM analysis

Scanning electron microscope (SEM) images were used to investigate surface morphology evolutions of hydrochar at different hydrothermal carbonization temperatures from 200°C to 350°C. The morphology of hydrochar from low temperatures (especially for C200, D200, and S200) was of the tight block structure and clustered aggregates originating from animal manure feedstock without porous structure or pathways (Figure S1). With the temperature rising, the fragmentation and porosity of hydrochars increased especially for the highest temperature derived hydrochars (C350, D350, and S350). High temperature promoting the release of volatile matter by devolatilization and chemical bond decomposition of animal manure matrix led to its porous structure formation^[59].

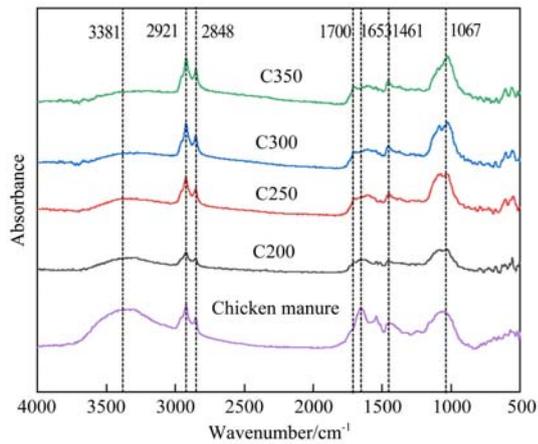
3.4 FTIR analysis

The Fourier Transform Infrared Spectroscopy (FTIR) of animal manure hydrochar is presented in Figure 1. There were five main vibration regions as follows: 3381-3425 cm⁻¹, 2845-2924 cm⁻¹, 1692-1720 cm⁻¹, 1455-1661 cm⁻¹, 1067-1103 cm⁻¹, which correspond to -OH, C-H_s, C=O, C=C, and C-O vibrations, respectively^[60-62]. With the temperature increasing, the -OH sharply decreased and even up to disappear probably attributed to the dehydration during the HTC, which is in accord with other reports^[23,45]. However, the C-H_s and C=O vibration strength improved, as the temperature rose. Besides, a similar trend was found for C=C vibrations, indicating that the aromatic nature of hydrochar improved that is in accord with the O/C and H/C atomic ratio changing trendy (Table 1). Usually, the higher the aromatic degree is, the more stable is the hydrochar^[49,63]. Hence, the stability of hydrochar was strengthened by increasing temperature. Moreover, the C-O vibrations improved with increased temperature for chicken and dairy manure hydrochar, while the opposite result was for swine manure hydrochar (Figure 1). The FTIR spectra showed hydrochar was rich in oxygen-containing functional groups.

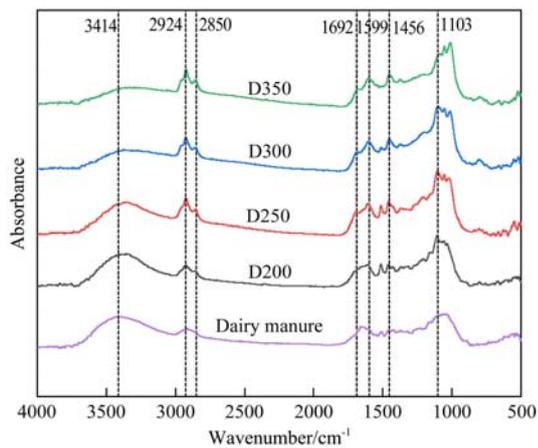
3.5 TGA analysis

As shown in Figure 2, when the temperature was below 220°C, there was an obvious weight loss peak of the chicken-manure and its hydrochar, the opposite to that of the other two kinds of hydrochar. During the hydrothermal process, some small and liable molecule organics and/or some undecomposed hemicellulose are sequestered in hydrochar, usually, the weight loss of hemicellulose mainly happens at 220°C-315°C^[64], and they can release and/or decomposition from the hydrochar under heated with

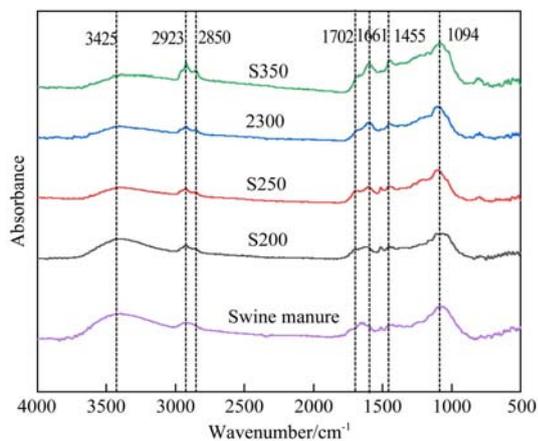
air. It was further supported by proximate analysis (Table 2) that chicken manure hydrochar showed high VM content. From 220°C to 500°C, the majority weight loss of the hydrochar happened. The stage can be divided into two main regions, one was below about 375°C and the other was over 375°C which can be ascribed to the oxidation of volatile matter fixed carbon, respectively^[30]. Moreover, hydrochar derived from over 300°C showed little weight loss in the region below 375°C, the weight loss of cellulose mainly happens during this region^[64]. Moreover, the weight loss of the modified hydrochar was much lower than that of pristine hydrochar. When the temperature was over 500°C, there was no obvious change in hydrochar weight loss.



a. Chicken manure and its hydrochar



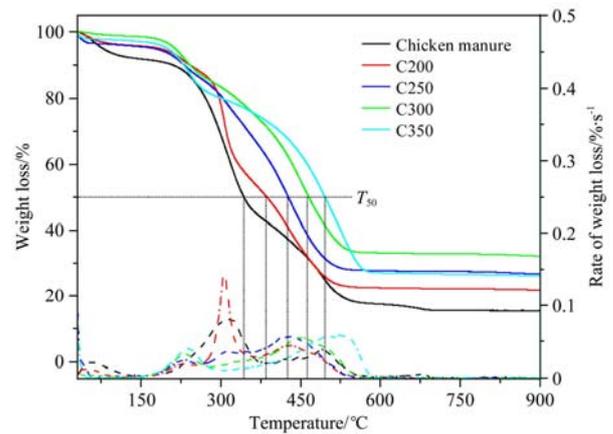
b. Dairy manure and its hydrochar



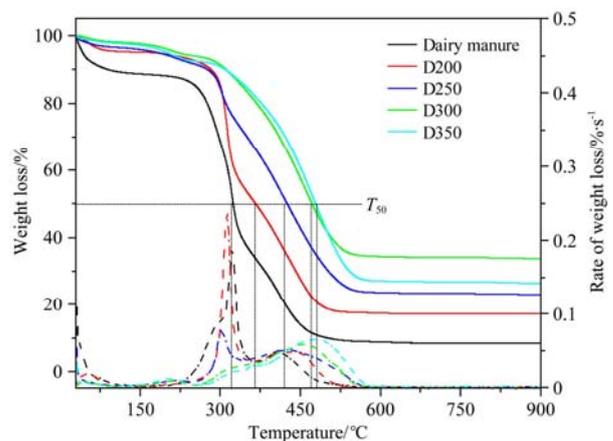
c. Swine manure and its hydrochar

Note: For simplicity, the hydrochar was labeled as initial capital letters of feedstock and temperature, for example, C200 represents hydrochar derived from chicken manure under 200°C. D: Dairy; S: Swine.

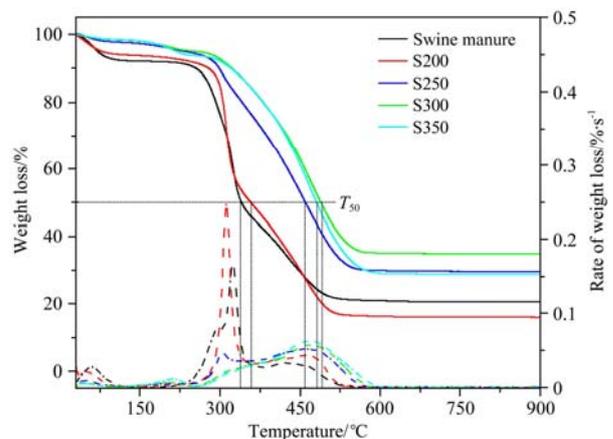
Figure 1 FTIR of animal manure and its hydrochar



a. Chicken manure and its hydrochar



b. Dairy manure and its hydrochar



c. Swine manure and its hydrochar

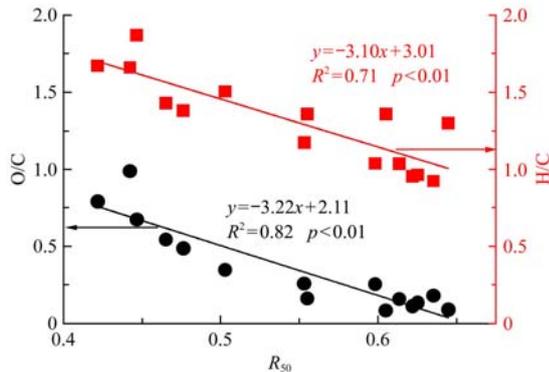
Figure 2 TGA of animal manure and its hydrochar

3.6 Carbon retention and stability

Carbon retention was a very important characteristic of hydrochar meaning that the carbon element from feedstock was retained after turning into hydrochar. The more carbon sequestered in the hydrochar, there is less greenhouse gas emission (CO, CO₂, and CH₄) and organic liquid discharge. In this study, low temperature was beneficial for the increase of carbon retention (Table 2) and it decreased with the increase of temperature (except C350). When the temperature was 200°C, over half of carbon was retained in the hydrochar (except C200), and the temperature was over 200°C, the average of carbon retention was about 25% for chicken manure hydrochar and 40% for dairy manure and swine manure hydrochar. Moreover, the carbon retention also depended on the type of animal manure. The chicken manure hydrochar contained much lower carbon retention than that of the others, in

particular, hydrochar obtained under high temperature due to its high volatile matter content (Table 2).

Carbon stability is another key characteristic of hydrochar that determined its life cycle. Because the H/C and O/C can reflect the aromatic nature of biochar and high aromatic means strong stability, they are widely adopted as an index to evaluate the stability of biochar^[65,66]. Hydrochar belongs to biochar. R_{50} , another index, is used to express resistance to thermal oxidation of biochar and shows its stability^[51]. In this study, with temperature increased, the R_{50} of hydrochar gradually rise. Moreover, there was a significant ($p < 0.01$) relationship between the R_{50} and H/C and O/C (Figure 3), indicating that R_{50} was a simple and effective index to estimate carbon stability.



Note: The black arrow means the linear equation between the O/C and R_{50} ; the red arrow means the linear equation between the H/C and R_{50} .

Figure 3 Correlations between R_{50} of hydrochar and elemental composition characteristics of hydrochar (H/C and O/C)

Hydrothermal carbonization of animal manure into hydrochar is considered a promising method for sequestering carbon to alleviate climate change when returned to the soil^[67,68]. Usually, hydrochar with high carbon retention and strong carbon stability exhibits excellent carbon sequestration potential, which depends on the temperature and feedstock^[33,49]. However, in our study, carbon retention of hydrochar decreased with the temperature increase while the opposite change trend for carbon stability (Table 2). In order to accurately evaluate the effect of temperature on the carbon sequestration potential of hydrothermal carbon, the carbon sequestration (CS) index was adopted^[51].

$$CS = CR \cdot R_{50} \quad (6)$$

Carbon sequestration was calculated in Figure S2. It showed that with the temperature increased, the carbon sequestration varied from 13.6% to 23.8% for chicken manure-derived hydrochar, 22.9% to 26.3% for dairy manure-derived hydrochar and 22.5% to 30.8% for swine manure-derived hydrochar, respectively. Moreover, the optimal processing temperature for maximum carbon sequestration in hydrochar was 200°C for chicken manure and swine manure, and 250°C for dairy manure, indicating that low temperature was beneficial for carbon sequestration and hydrothermal carbonization of animal manure into hydrochar was a promising tool for carbon sequestration.

4 Conclusions

The properties of hydrochar derived from animal manure varied at different temperatures. With increasing temperature, the yield, H/C, O/C, and VM of hydrochar decreased, however, the fixed carbon, HHV, and fuel ratio increased. High temperature improved the aromaticity of hydrochar and strengthened its stability but reduced carbon retention. R_{50} was an effective index to estimate the carbon stability of animal manure hydrochar. In

addition, relatively low temperature ($\leq 250^\circ\text{C}$) was beneficial for hydrochar production to sequester carbon.

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Appendix

Table S1 Properties of animal manure

Properties	Chicken manure	Dairy manure	Swine manure
Water content/%	8.59	9.74	5.83
Organic matter/%	20.12	18.40	22.31
P/g·kg ⁻¹	8.13	5.44	26.31
K/g·kg ⁻¹	26.14	3.02	6.35
Na/g·kg ⁻¹	6.02	5.92	3.49
Ca/g·kg ⁻¹	109.80	20.08	60.60
Mg/g·kg ⁻¹	17.29	4.46	12.55
Zn/g·kg ⁻¹	0.40	0.43	1.36
Cu/mg·kg ⁻¹	60.24	61.41	317.20
Pb/mg·kg ⁻¹	23.93	12.69	29.35
Cd/mg·kg ⁻¹	0.28	0.45	15.23

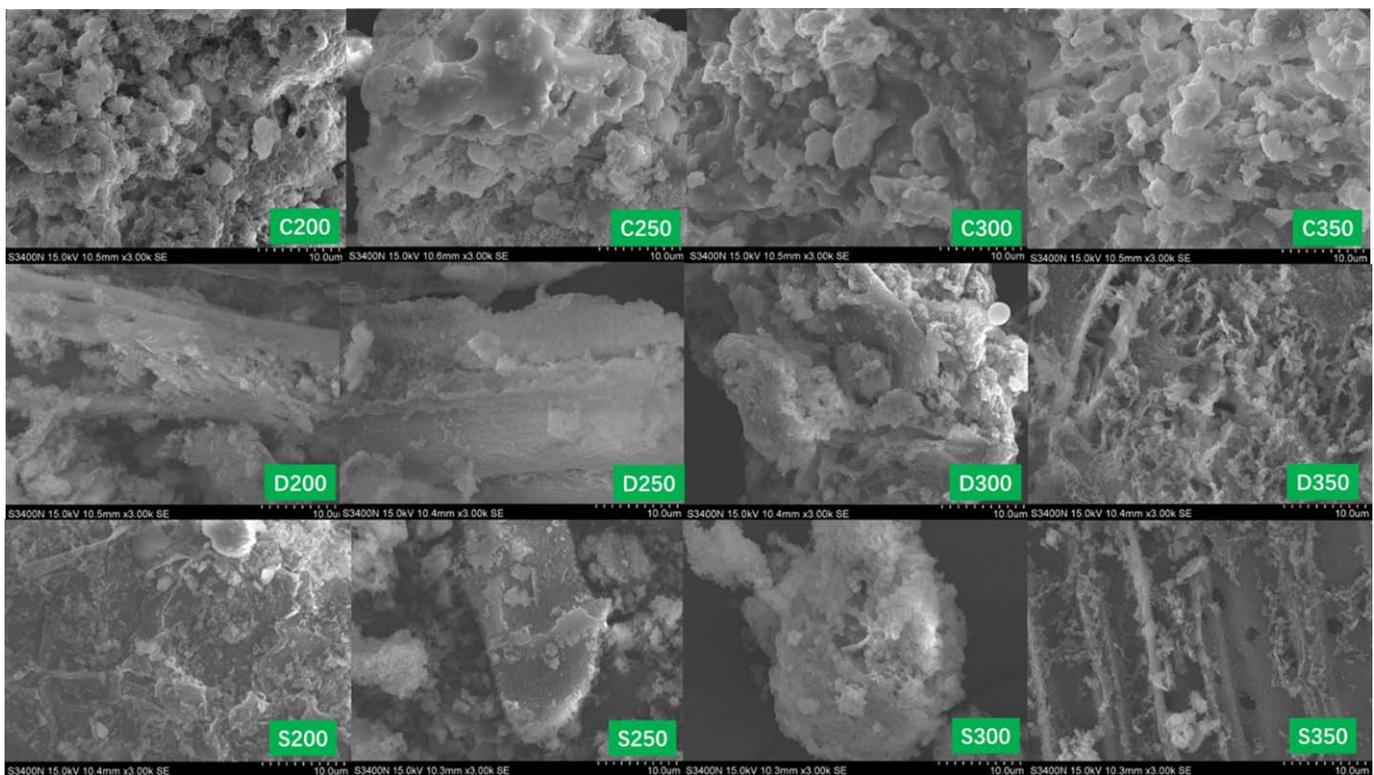


Figure S1 Scanning electron micrographs (SEM) images of hydrochar

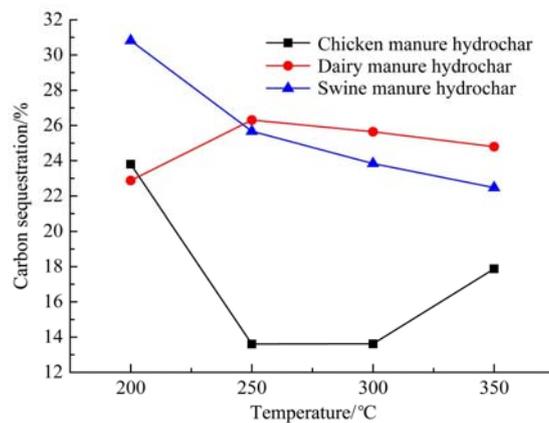


Figure S2 Effects of hydrothermal carbonization temperature on the carbon sequestration of animal manure hydrochar