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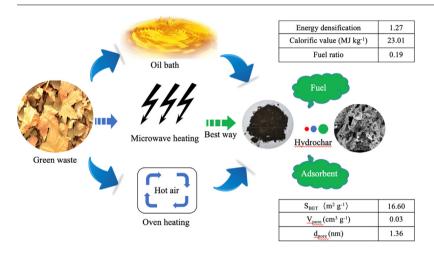
Full Length Article

Synthesis of improved hydrochar by microwave hydrothermal carbonization of green waste

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G R A P H I C A L A B S T R A C T



ARTICLE INFO

Keywords: Microwave hydrothermal carbonization Hydrochar Green waste Energy property Adsorption property

ABSTRACT

Green waste (GW), a typical biomass waste, was used to produce hydrochar using microwave hydrothermal carbonization (MHTC). The results indicate that MHTC promotes the dehydration of GW to a greater extent than traditional oven or oil bath heating under the same hydrothermal conditions. The hydrochar obtained from the MHTC process showed an energy densification factor of 1.27 and a fuel ratio of 0.19, both of which exceeded those produced by traditional hydrothermal processes. Thermogravimetric data also demonstrated that hydrochar obtained using MHTC had better incineration properties. Moreover, the material possessed a high specific surface area and a more porous structure, resulting in improved adsorption properties. The result of value and potential evaluation demonstrated that the MHTC process also displays the lower energy consumption of operation. Hydrochar generated from GW is a potential environmentally friendly functional material, and MHTC appears to be a suitable means of producing this substance.

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https://doi.org/10.1016/j.fuel.2020.117146

Received 30 September 2019; Received in revised form 22 December 2019; Accepted 19 January 2020 0016-2361/ © 2020 Elsevier Ltd. All rights reserved.







Nomen	clature	MHTC	microwave hydrothermal carbonization				
A1.1		P	power				
Abbrevia	ation	SSA	specific surface areas				
		TGA	thermogravimetric analysis				
BET	Brunauer-Emmett-Teller						
Ed	energy densification	Variable	<i>'S</i>				
Ei	energy input						
Er	energy recovery efficiency	He	heating time				
FT-IR	Fourier transform infrared spectroscopy	Но	holding time				
GW	green waste						
HHV higher heating value		Subscrip	t				
HTC	hydrothermal carbonization						
Μ	mass	f	feedstock				
Hy	hydrochar yield	h	hydrochar				

1. Introduction

Green waste (GW) is a generic term for waste biomass, including wood, bark, leaves, grass clippings and soil, originating from sources such as parks, gardens, reserves and domestic dwellings [1,2]. With increasing worldwide urbanization, the impact of such waste will become more important. As an example, GW accounts for approximately 50% of the municipal solid waste generated in Beijing, China [3]. It is therefore vital to examine the disposal and treatment of this waste. One option is the combustion of GW to generate electricity, which provides economic value. However, this disposal method has limited potential or may even be unsuitable in the case that the GW has a high water content, low heating value and/or is heterogeneous [4]. Traditionally, GW is also often placed in landfills but this means of disposal uses valuable land and also does not take advantage of the value of the material. Composting has become a widely accepted strategy for GW disposal. During composting, aerobic microorganisms convert organic matter into hygienic, biostable products that can be used as soil additives, organic fertilizers, or substitutes for soilless cultivation peat [5]. However, compositing still has disadvantages, including the discharge of odorous gases, and is readily affected by seasonal temperature fluctuations [6]. Moreover, composting requires long time spans, especially if high concentrations of cellulose and hemicellulose present [7].

Recently, hydrothermal technology has been shown to be an efficient approach to biomass waste treatment [8-10]. Compared with the methods discussed above, this technique can dispose of biomass having high levels of moisture, cellulose and hemicellulose, because dehydration and decarboxylation occur during the associated reactions. In addition, the reaction period is extremely short. According to the pressure-temperature phase diagram of water, hydrothermal processes can proceed via carbonization [11,12], liquefaction [13–15] or gasification [16,17], all of which lead to different main products. To date, hydrothermal carbonization (HTC) has been the most widely researched. HTC is performed at low temperatures in the range of 160-270 °C, with the biomass waste immersed in water and heated in a confined system under pressures of 2-6 MPa for 5-240 min [18,19]. HTC can convert biomass waste into a carbon rich solid product that may be used as a fuel [20], soil additive [21], carbon-based catalyst [22] or adsorbent [23]. A previous study reported that hydrochar has significant potential as a clean fuel and can be obtained using microwave hydrothermal carbonization (MHTC) [24]. MHTC appears to offer superior dewaterability and shortens the reaction time by providing rapid heating so as to improve processing efficiency and reduce energy consumption [25]. However, there has been minimal research comparing MHTC to the more traditional HTC processes. The superiority of MHTC on enhance the physical and chemical properties of biomass waste are not very clear. Therefore, it is worthwhile to investigating performance of microwave in resource recycling of biomass waste to make up for the lack of current research in this area.

The present study used GW as a raw material and subjected this substance to heating by oven, oil bath or microwaves. The physical and chemical properties of the hydrochar, derived from GW employing these different hydrothermal processes at various temperatures, were investigated and compared. The goal of this work was to assess the potential for the valorization of GW via MHTC.

2. Materials and methods

2.1. Material preparation

The GW comprised dead leaves with a small proportion of deadwood and was collected from green belts in Hangzhou, China. This material was first washed with deionized water to remove inorganic substances such as pebbles and dust, then heated in an oven overnight at 105 °C. Finally, the GW was crushed into particles smaller than 1 mm and stored in sealed plastic bags before use.

2.2. Hydrothermal conditions

An electrothermal blast drying oven (GZX-9240MBE, Shanghai Boxun Industrial Co., Ltd.), a collector-type thermostatic heating magnetic stirrer equipped with silicone oil (DF-101S, Gongyi Yuhua Instrument Co., Ltd.) and a microwave digestion instrument (MarsXpress, CEM, USA) showing in Fig. S1 were used to examine the effects of various hydrothermal conditions. The samples heated in the oven and oil bath were contained in a 25 ml Teflon hydrothermal vessel, while special microwave digestion tubes were used to hold the samples treated using MHTC. The trials were performed by initially adding 0.5 g GW and 4 ml deionized water to a hydrothermal vessel or microwave digestion tube, after which the container was covered and transferred into the corresponding heating apparatus. Following the reaction, the container was removed and placed in an ice water bath for cooling, then suction-filtered through a Bush funnel. The solid hydrochar was subsequently dried at 105 °C to constant weight.

The characteristics of each hydrothermal process were examined by determining the energy balance, hydrochar yield, energy density and energy recovery efficiency using the equations [26]:

$$Hy = M_h/M_f,$$
(1)

$$Ed = HHV_h/HHV_f \tag{2}$$

and

$$Er = Hy \times Ed,$$
 (3)

where *Hy* is the hydrochar yield (%), M_h is the hydrochar mass after drying (g), M_f is the mass of the feedstock after drying (g), *Ed* is the energy densification, *Er* is the energy recovery efficiency (%), *HHV*_h is the high heating value (HHV) of the hydrochar (MJ kg⁻¹), and *HHV*_f is the high heating value of the feedstock (MJ kg⁻¹).

2.3. Raw GW and hydrochar characterization

According to ASTM-D1762-84, the analysis of raw GW and hydrochar should include volatile matter, ash content and fixed carbon. The high heating values of the GW and the hydrochar were determined using an oxygen bomb calorimeter (XRY-1A, Shanghai Shjingmi, China), while thermogravimetric analysis (TGA) was performed using a TGA Q500 instrument (TA Instruments, USA). These analyses were conducted over the temperature range from ambient to 1000 °C at a heating rate of 20 °C/min under a N2 flow of 100 ml/min. Elemental analysis of the raw GW and hydrochars was carried out using a combustion method (vario EL cube, Elementar, Germany). The surface morphology of raw GW and each hydrochar was studied using a scanning electron microscope (SEM, Phenom G2 Pro, Phenom, Switzerland) with a magnification of $1000 \times$ to $5000 \times$. The functional groups on the surfaces of the raw GW and hydrochars were identified by Fourier transform infrared spectroscopy (FT-IR, VERTEX 70, Bruker, Germany) over the wavelength range of 400 to 4000 cm^{-1} , summing 64 scans to produce each spectra at a resolution of 4 cm⁻¹. The Brunauer-Emmett-Teller (BET) specific surface areas (SSAs) were determined by adsorbing N₂ at the temperature of liquid N₂, using a Quantachrome instrument (Quadrasorb EVO, USA). All experiments were repeated at least three times to establish reproducibility.

3. Results and discussion

3.1. Feasibility of applying microwaves to a hydrothermal reaction

Fig. 1 summarizes the hydrochar yields obtained from microwave, oven and oil bath heating while applying various conditions. As the hold temperature was increased from 130 to 190 °C, the yield obtained from the microwave system decreased, and the reduction rate was significantly higher than those obtained using the other HTC processes. It is well known that both the dehydration and decarboxylation

reactions of biomass waste are enhanced as the temperature of a hydrothermal system is increased [27]. Therefore, this study indicates that microwave heating could further enhance the hydrothermal reactions. The FT-IR results in Fig. 2 also provided evidence for this effect. The peaks appearing in these spectra at approximately 3430 and 3140 $\rm cm^{-1}$ were attributed to O-H stretching vibrations associated with hydroxyl groups [28]. These peaks obtained from the sample treated using oven and oil bath heating methods were hardly changed as the holding temperature was increased, laterally indicating the poor hydrothermal efficiency of traditional heating methods. In contrast, the intensity of peaks from hydrochar under MHTC were lower, and weakened more significantly as the holding temperature increased, showing a greater degree of this reaction during the hydrothermal process. Furthermore, Fig. 3 demonstrates that the H/C and O/C ratios exhibited a linear relationship ($R^2 = 0.83$) with respect to different hydrothermal treatments, also suggesting that the microwave process maximized the hydrothermal reactions, especially dehydration. However, this figure does not show a difference in the progress of the decarboxylation reaction between MHTC and the traditional HTC processes at 190 °C. The FT-IR spectra in Fig. 2 also indicate that the peak at approximately 1700 cm^{-1} (attributed to the C=O stretching vibration) was not significantly changed [29]. Therefore, the dehydration reaction rather than the decarboxylation reaction was dominant under these reaction conditions when using these hydrothermal systems.

3.2. Effects of microwave processing on the energy properties of the hydrochar

The relationship between the hydrochar yields and the energy recovery efficiency values shows the same trends for each of the three HTC processes as described above (Fig. 1). Specifically, a higher hold temperature increased the energy recovery efficiency, indicating that the energy densification was improved. This effect appeared earlier when using the microwave hydrothermal system, establishing that

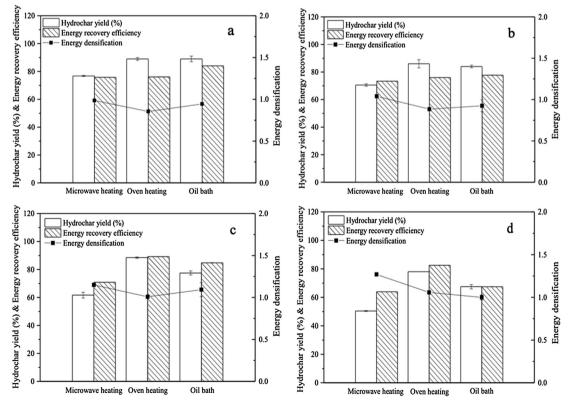


Fig. 1. Effect of microwave heating, oven heating and oil bath heating on energy densification, hydrochar yield and energetic recovery efficiency at holding temperature of (a) 130 °C, (b) 150 °C, (c) 170 °C and (d) 190 °C.

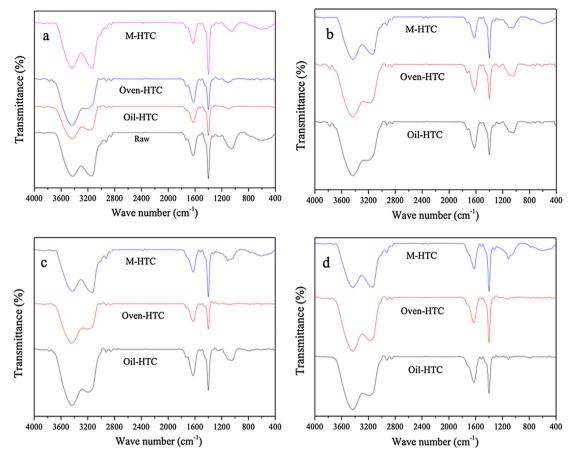


Fig. 2. FT-IR of hydrochar under microwave heating (M-HTC), oven heating (Oven-HTC) and oil bath heating (Oil-HTC) at holding temperature of (a) 130 °C, (b) 150 °C, (c) 170 °C and (d) 190 °C.

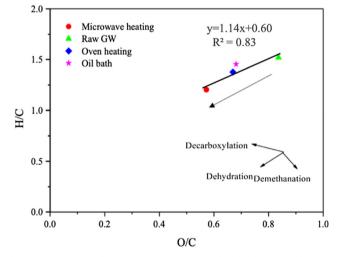


Fig. 3. Van Krevelen diagram of the raw GW and hydrochar at holding temperature of 190 $^\circ\text{C}.$

MHTC produced the fastest improvement in energy densification. This outcome is also attributed to the stronger hydrolysis reaction during MHTC. Hydrolysis decreases the amounts of cellulose and hemicellulose in the hydrochar while simultaneously increasing the relative amount of lignin [30]. Research has shown that the calorific value of lignin is $23.3-26.6 \text{ MJ kg}^{-1}$, and so is much higher than the values for cellulose and hemicellulose (17–18 MJ kg⁻¹), such that a higher lignin content will result in greater energy densification [31].

Table 1 summarizes the HHV data obtained from the raw GW and

hydrochar produced by the three different methods at 190 °C. The HHV of the hydrochar generated by microwave heating was 23.01 \pm 0.06 MJ kg⁻¹, which was much higher than that of the original GW. In contrast, there were only slightly improvements in the HHV following oil bath and oven heating. Comparing with other similar researches, for instance, Zhu et al obtained the hydrochar with the HHV of 20.39 MJ kg⁻¹ at the hydrothermal temperature of 200 °C and the holding time of 4 h under HTC, whose feedstock is cotton stalk with its HHV of 19.09 MJ kg⁻¹ [32]. Also, Yan et al gained the bamboo particles hydrochar with its calorific value of 19.80 MJ kg $^{-1}$ at the HTC temperature of 220 °C and the holding time of 1 h, which is only slightly higher than that of raw material (19.17 MJ kg^{-1}) [33]. These results demonstrate that MHTC was superior to the more traditional HTC methods under the situation of similar or even more energy input. In addition, the ultimate analysis results showed that higher carbon concentrations and lower oxygen concentrations were present in the hydrochar obtained from the microwave hydrothermal system. The proportions of these elements will affect the HHV of the hydrochar [34]. Table 1 presents the data obtained from the proximate analyses of the initial GW and the hydrochars obtained by using the three HTC methods. These results indicate that the ash content of the hydrochar produced using MHTC was 7.55 \pm 0.66%, and so was significantly lower than that of the original GW. Similar results were obtained using the other two processes. This outcome was ascribed to the removal of large quantities of impurities and metallic species from the raw material by extraction into the aqueous phase during each HTC [35]. The fuel ratio, calculated based on the amounts of volatile matter and fixed carbon, determines the ease with which a solid fuel can be gasified or converted by combustion [36]. As shown in Table 1, the highest fuel ratio of 0.19 was acquired after microwave heating, although improved Table 1

Proximate and ultimate analysis of the GW and the hydrochar obtained by (a) oil bath heating, (b) oven heating and (c) microwave heating at 190 °C.	Proximate and ultimate analysis of the GW and	the hydrochar obtained by (a)	oil bath heating, (b) oven heating	and (c) microwave heating at 190 °C.
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Sample (dry basis)	Proximate analysis					Ultimate analysis			
	Volatile matter (wt%)	Ash (wt%)	Fixed carbon ^d (wt%)	Fuel Ratio ^e	C (wt%)	H (wt%)	0 (wt%)	N (wt%)	
Raw GW	87.96 ± 1.22	10.59 ± 0.13	1.45 ± 1.35	0.02	44.10	5.59	49.19	1.12	18.15 ± 0.09
Hydrochar ^a	82.09 ± 0.79	9.16 ± 0.08	8.75 ± 0.79	0.11	49.35	5.66	44.05	0.94	18.77 ± 0.01
Hydrochar ^b	87.93 ± 1.01	8.89 ± 0.05	3.18 ± 1.01	0.04	48.80	5.91	44.31	0.98	19.20 ± 0.12
Hydrochar ^c	77.45 ± 2.95	7.55 ± 0.66	15.00 ± 3.61	0.19	53.15	5.33	40.57	0.95	23.01 ± 0.06

^d Fixed carbon (wt%) = 100-Volatile Matter (wt%) – Ash content (wt%).

^e Fuel ratio = Fixed carbon (wt%)/Volatile matter (wt%).

fuel ratios were also provided by the other HTC processes. Hence, the hydrochar obtained from MHTC was more suitable for use as a clean fuel.

Fig. 4 represents the TGA data and the corresponding differential thermogravimetric (DTG) profiles for the raw GW and the hydrochar produced from the different hydrothermal systems at a hold temperature of 190 °C. From room temperature to 105 °C (Fig. 4a), a weak mass loss peak was produced by each sample, attributed to the loss of moisture. As shown in Fig. 4b, the highest mass loss occurred within the temperature range of 300-400 °C, likely due to the decomposition of organic substances such as cellulose and hemicellulose. Another small mass loss appeared between 650 and 700 °C, attributed to the decomposition of lignin because lignin degradation has been shown to begin at approximately 600 °C under ambient pressure [19]. Compared with the raw GW and the hydrochars obtained from the traditional hydrothermal systems, the hydrochar produced via MHTC exhibited superior combustion characteristics, based on a relatively high mass loss and lower residue. Previous studies found that MHTC employing similar hydrothermal conditions produced hydrochar having the highest HHV when using several different wastes, with these hydrochars having the potential to act as fuels [24]. Therefore, MHTC is more suitable for the conversion of GW to hydrochar fuel than other traditional HTC processes.

3.3. Hydrochar adsorption properties

The adsorption properties of the raw GW and the hydrochars obtained by oil bath, oven and microwave heating at 190 °C were analyzed in this work, and Table 2 presents the SSA, pore volume and pore diameter values. These results show that the hydrochars produced using oven, oil bath and microwave heating all had increased SSA values that were approximately three, six and ten times that of the raw GW. Chu et al. reported that biochar derived from pine sawdust had an SSA of 9.15 m² g⁻¹ after heating at 350 °C, which is lower than the values obtained in the present study [37]. Thus, hydrothermal process can effectively improve adsorption performance while saving energy, Table 2

BET surface area and pore characteristics of raw material and hydrochar obtained by (a) oil bath, (b) oven heating and (c) microwave heating at 190 °C.

			-			
Sample	$S_{BET} (m^2 g^{-1})$	V_{pore} (cm ³ g ⁻¹)	d _{pore} (nm)			
Raw material Hydrochar ^a Hydrochar ^b Hydrochar ^c	$\begin{array}{rrrr} 1.62 \ \pm \ 0.04 \\ 9.06 \ \pm \ 0.07 \\ 5.49 \ \pm \ 1.06 \\ 16.60 \ \pm \ 0.72 \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$			

especially in the case of microwave hydrothermal technology. In addition, Yan et al. indicated the trend of hydrochar SSA improved first and then decreased with the reaction temperature increasing from 220 °C to 300 °C during HTC [33]. It proves that not the higher the energy input is, the better the adsorption performance of hydrochar is. Fu et al. [38] evaluated the SSA values of biochars and hydrochars produced from food wastes, and reported that these values were generally low (mostly within the range of 0.01 to 2.17 m² g⁻¹), similar to the value determined by Ul Saqib et al. (1.45 m² g⁻¹) [39]. Therefore, the type of raw material is also an important factor limiting the adsorption characteristics of pyrolytic or hydrothermal products.

The pore volumes of the hydrochars were also increased compared with that of the GW, and the largest volume was obtained with the microwave hydrothermal system. The microstructures of the raw GW and the hydrochars at various hydrothermal conditions are presented in Fig. 5. Compared with the GW microstructure, the hydrochars showed highly porous structures, especially those produced using oil bath and microwave heating. Therefore, a porous structure was positively correlated with improved adsorption characteristics. Moreover, the porosity of the hydrochar increased as the hold temperature was increased (Fig. 5). Therefore, the optimal adsorption properties were obtained at 190 °C.

Fig. 6 provides the N_2 adsorption-desorption isotherms and pore size distributions for the raw GW and the hydrochars from the three methods. The volume adsorbed by the hydrochar was found to increase along with the relative pressure up to a value of 1.0, indicating the

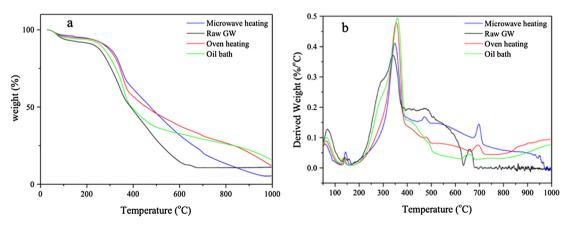


Fig. 4. (a) Thermogravimetric (TG) and (b) corresponding derivative thermogram (DTG) profiles of samples in nitrogen atmosphere.

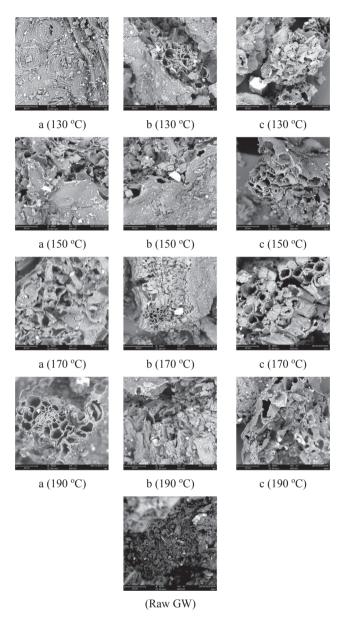


Fig. 5. Microstructural analysis of raw GW and hydrochar produced under (a) oil bath heating, (b) oven heating and (c) microwave heating at various holding temperature.

existence of micropores and mesopores. This phenomenon was not exhibited by the raw GW, thus confirming that the HTC processes effectively improved the adsorption performance of the biomass waste. In addition, a hysteresis loop was observed in the data acquired from these hydrochars over the relative pressure range from 0.0 to 1.0, providing further evidence for the existence of such pores [40,41]. The hydrochar treated by MHTC adsorbed a greater volume and showed an increased pore volume compared to the other hydrochars, demonstrating improved ash removal during the formation of new pores and enhancement of existing pores [42]. The pore size distributions of these samples as shown in Fig. 6b lead to the same conclusion. Therefore, hydrochar produced using MHTC has more potential to act as an absorbent.

3.4. Value and potential evaluation of the MHTC process

This study also evaluated the value and potential of the MHTC process to demonstrate the superiority of microwave hydrothermal technology. The optimal hydrothermal temperature of 190 °C was chosen for these calculations, and several other studies employing similar hydrothermal conditions were examined for the sake of comparison. Table 3 provides the simple evaluation of each process, including energy input of hydrothermal reaction and water consumption, and takes into account the value of the resulting hydrochar. Because electricity is the primary energy input, this work used Joule's law to evaluate the process energy consumption, via the equations

$$E_i = P \times (He + Ho) \times 0.6, \tag{4}$$

where P is power (W), He and Ho are the heating times and hold times, respectively (min), Ei is the energy input per ton substrate (dry basis), the constant having a value of 0.6 is a conversion factor based on the units of Ei, P, He and Ho.

Comparing the energy consumption values of hydrothermal reaction under similar conditions, the microwave process requires only 4.8 MJ per 0.1 kg substrate, which is much lower than the majority of traditional hydrothermal technologies (Table 3). Water consumption was also considered in these deliberations, and compared with the other processes, MHTC was found to involve reduced water consumption according to the liquid-to-solid ratios in Table 3. The fuel and adsorption properties of the hydrochar produced via MHTC in this work were similar or even superior to the values obtained in other studies, and so MHTC is evidently an economically viable approach to biomass waste treatment.

4. Conclusions

The characteristics of GW hydrochar under HTC and MHTC were evaluated. The hydrochar yield obtained from MHTC decreased as the holing temperature increasing from 130 $^{\circ}$ C to 190 $^{\circ}$ C and the reduction

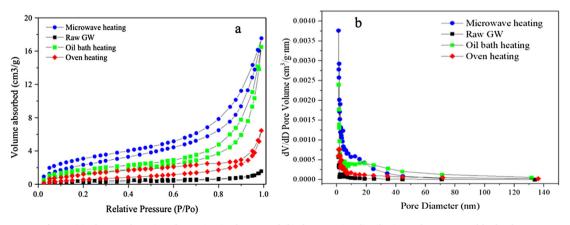


Fig. 6. (a) The N₂ adsorption-desorption isotherms and (b) the pore size distributions of raw GW and hydrochar.

Table 3

Economic analysis of hydrothermal processes under similar conditions.

Substrate (dry	Hydrothermal conditions ^a			Heating	Consumption ^b		Potential application ^c			Yield (%)	Reference	
basis)		Heating up	Heating up Holding time (min) time (min)	Holding temperature (°C)	—method	Energy (MJ)	Liquid-to- solid ratio	Fuel		Adsorbent	-	
		time (min)						Ed	Fuel ratio	SSA ($m^2 g^{-1}$)		
Pinewood sawdust	2000	60	20	250	Autolave	9.6	10	1.36	0.70	/	/	[43]
Rice husk								0.98	0.32			
Coconut fiber								1.29	0.74			
Coconut shell								1.02	0.28			
Food waste			60	200	High-pressure batch reactor	14.4	13	1.83	0.47	5.2	7.0	[39]
			120		Stainless steel	21.6	20	/	0-0.66	0.01 - 2.17	/	[38]
Leather waster			30		reactor	10.8	10	1.10	0.11	/	82.9	[20]
Green waste	1700	40	60	190	Oven	10.2	8	1.06	0.04	5.5	78.0	This study
	800				Oil bath	4.8		1.04	0.11	9.1	67.5	
					Microwave			1.27	0.19	16.6	50.4	

^a Hydrothermal conditions including power, heating up time, holding time and holding temperature were obtained from references above or website [20,38,39,43–45].

^b Consumption of energy and water was simple calculated in this study. The energy consumption to process 100 g of substrate was calculated according to Joule's law.

^c Potential application was analyzed and compared in this study. The energy densification (Ed) showed in Eq. (2) and fuel ratio were selected as the fuel characteristic parameters. And the specific surface area (SSA) was selected as the typical adsorbent characteristic index.

rate was significantly higher than those obtained using the other HTC processes. MHTC was found to promote the dehydration reaction of GW based on analyses using FT-IR and on C/O and C/H ratios. The hydrochar generated via MHTC process exhibited an energy densification factor of 1.27, a carbon content of 53.15% and a fuel ratio of 0.19, all of which exceeded those produced by traditional hydrothermal processes. In addition, TGA confirmed that the MHTC hydrochar showed the best combustion characteristics, based on a relatively high mass loss. The hydrochar obtained from MHTC also had superior adsorption properties according to SSA and microstructure data. Finally, value and potential evaluation of the MHTC process demonstrated that the MHTC process involves lower energy input of hydrothermal reaction and water consumption, which can provide reference for future industrial applications.

CRediT authorship contribution statement

Yuchao Shao: Conceptualization, Methodology, Software, Validation, Investigation, Data curation, Writing - original draft. Hao Tan: Validation, Formal analysis, Visualization, Software. Dongsheng Shen: Validation, Formal analysis, Visualization. Ying Zhou: Resources, Writing - review & editing, Supervision, Data curation. Zhiyuan Jin: Resources, Writing - review & editing, Supervision, Data curation. Dan Zhou: Writing - review & editing. Wenjing Lu: Writing review & editing. Yuyang Long: Conceptualization, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (grant no. 51778579) and the University Students' Science and Technology Innovation Activity Plan and New Miao Talent Program of Zhejiang province (2019R40858). We thank Liwen Bianji, Edanz Editing China (www.liwenbianji.cn/ac), for editing the English text of a draft of this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2020.117146.

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