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High-strength charcoal briquette preparation from hydrothermal pretreated biomass wastes

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ABSTRACT

The waste cotton stalk (CS) and wood sawdust (WS) biomass samples pretreated by two different thermal methods (dry torrefaction (DT) and hydrothermal treatment (HT) at 200, 230, 260 °C, respectively) were densified to prepare biomass briquette and then carbonized at 400 °C to prepare charcoal briquette without any binders. The physical properties and combustion characteristics of the derived charcoal briquettes were investigated to assess the feasibility of its application as barbecue charcoal. The results indicate that the physical properties including the mass densities and compressive strengths of HT charcoal briquettes are better than those of DT and unpretreated charcoal briquettes, even those of the commercial barbecue charcoal with binder addition. Moreover, the fixed carbon and ash yields of the resulted HT charcoal briquettes meet the European Standard on commercial barbecue charcoal. Especially HT charcoal briquettes has far lower ash yield than the commercial barbecue charcoal. HT charcoal briquettes have similar combustion character index (*S*) with the commercial barbecue charcoal. In the research, CS and WS hydrothermal pretreated at 230 °C are the best materials for the charcoal briquette preparation process.

1. Introduction

As a plentiful renewable energy source, bioenergy has great contribution to increase energy diversity and reduce carbon emissions. Having 2.8×10^8–3.0×10^8 t/a of wood waste energy and 7.7×10^8 t/a of crops straw, etc., China is in possession of good resource condition for the development of bioenergy industries [1]. Biomass wastes can be densified to prepare solid biofuels, which is one of the main ways of bioenergy utilization [2]. There are lots of researchers focusing on the preparation of briquette with high mass density and calorific value from the biomass wastes [3–7].

Dry torrefaction is one of pretreatment methods, which is defined as a mild pyrolysis process that occurs below 350 °C and the desired result is a material with low moisture content and higher heating value (HHV) [3]. Shang et al. have recently reported that the dry torrefaction of Scots pine pellets at 230–270 °C could increase HHV from 18.37 MJ/kg to 24.34 MJ/kg but showed a rapid decrease in mechanical compressive strength [4]. Sylvia H. Larsson et al. have produced the biomass briquettes from Norway spruce torrefied at 270–300 °C, but their mass densities are only 630–710 kg/m^3 [5]. Wolfgang Stelte et al. found that the spruce samples torrefied at 300 °C could not be densified successfully and the pellets prepared from the spruce samples torrefied at 275 °C exhibited many defects [6]. The carbohydrates break down after dry torrefaction, which strongly reduces the ability to establish hydrogen bonds between polymer chains of adjacent particles. So the mass density and compressive strength of the biomass briquette prepared from dry torrefied biomass are poor and even lower than those prepared from raw biomass, making the transport and storage economically challenging [5,7].

As mentioned above, it is quite difficult to bound dry torrefied biomass particles together especially treated at high dry torrefaction temperature. To obtain high-strength biomass briquette, the binders have to be employed to improve the particle adhesion of the dry torrefied biomass. However, the binders such as wheat flour and starch could reduce HHV and fixed carbon yield of the products [8]. Other binders like microalgae and biosolids would increase ash yield of biomass briquette and the biosolids are the residues by anaerobic digestion of waste activated sludge from municipal wastewater [9]. And coal tar residue also could be used as a binder but that lead to pollutant emissions of NO, SO_2, polycyclic aromatic hydrocarbons (PAHs) and dioxins (PCDD/Fs) during the combustion process of biomass pellets [10]. Those behaviors have resulted in great difficulties in green biochar preparing.

A new treatment approach is to employ wet torrefaction as biomass

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pretreatment, which is usually called as hydrothermal treatment (HT). During HT process, biomass is treated with hot compressed subcritical water (200–260 °C) for 5 min–8 h, resulting in three products, including gases, aqueous chemicals, and solid fuels [11,12]. In contrast to the raw and DT biomass briquette, HT biomass briquette has higher mass density and compressive strength and the bonding bridges between HT pellet particles are more stable. Moreover, HT pellets also has higher HHV [13,14].

HT biomass briquette is excellent boiler fuel but it can't be used as barbecue charcoal. However, barbecue charcoal has higher economic value and broader market prospects. The fixed carbon yield of HT biomass is still lower compared to European Standard on barbecue charcoal (EN 1860-2:2005, dry basis > 60%). Hence, it is indispensable for preparing qualified barbecue charcoal to remove volatile materials by carbonization at high temperature. Nevertheless, no evidence is available on the properties of charcoal briquette prepared from HT biomass briquette by high temperature carbonization. Moreover, the aqueous phase from HT process can be used as the feedstock for biogas production by anaerobic digestion [15].

In our laboratory, the technology of barbecue charcoal production from biomass wastes has been developed for many years and the application for Chinese inventive patents about the process has been accepted. During the process, the biomass briquette is prepared from the hydrothermal pretreated biomass wastes by densification and then carbonized to produce high-strength charcoal briquette without any binders. The products of biomass briquette and charcoal briquette can be used as the feedstock for boilers and the charcoal briquette also can be used as barbecue charcoal. Moreover, high-valued wood vinegar can be obtained from the aqueous phase from the hydrothermal process. Thus, it is very necessary for the utilization of the biomass wastes to investigate the properties of the charcoal briquette.

Chinese pine wood sawdust (WS) and cotton stalk (CS), two typical woody and herbaceous biomass wastes, were used as raw materials for the investigation in the present work. The two wastes employed for the charcoal briquette preparation can protect precious forest resource and promote the effective utilization of the biomass wastes. The biomass samples experiencing dry torrefaction or hydrothermal treatment were densified into biomass briquette and then carbonized to prepare barbecue charcoal. Then, the physicochemical properties of the derived charcoal briquette were determined to assess the feasibility of its application as barbecue charcoal according to the European Standard EN 1860-2:2005 and the properties of commercial barbecue charcoal.

2. Material and methods

2.1. Material

Two agricultural and forestry wastes, cotton stalk (CS) and pine wood sawdust (WS), were used as the raw materials for the investigation. The proximate and ultimate analyses are shown in Table 1. The ash analyses are shown in Table 2. The samples were milled with a grinding machine and sieved to the particle size of 0.5–1 mm.

Table 2
Ash analyses of the biomass wastes.

Samples	Ash analysis (wt.%)									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	SO_3	K_2O	Na_2O	P_2O_5
CS	11.7	1.8	1.1	30.8	13.9	1.4	6.3	18.9	10.0	4.1
WS	40.6	6.8	11.6	27.5	4.7	0.9	3.8	1.8	0.9	0.8

2.2. Biomass dry torrefaction pretreatment (DT)

Dry torrefaction was performed in a bench-scale electrically heated furnace (GR-AF1216, Shanghai GUIER Company). The sample was loaded in the reactor and a flow of nitrogen (200 mL/min) was purged into the reactor to provide an inert atmosphere. Meanwhile, a gas chromatograph (GC2014, Japan SHIMADZU Company) was used to test the oxygen content of the outlet gas. When there was no oxygen detected in the outlet gas, the reactor was heated from room temperature to the desired final temperature (200, 230, 260 °C) at rate of 5 °C/min and held for 20 min. Then the reactor was cooled down to room temperature under nitrogen atmosphere. The CS and WS samples after dry torrefaction pretreatment were marked as CS-DT200/230/260 and WS-DT200/230/260.

2.3. Biomass hydrothermal pretreatment (HT)

The hydrothermal pretreatment of the biomass was carried out in a 500 mL autoclave. Nitrogen of 200 mL/min was firstly flowed through the reactor for 20 min to exhaust oxygen. 20 ± 1 g of the biomass waste mixed with 100 mL de-ionized water was loaded into the reactor and heated to different final temperatures (200, 230, 260 °C) at 5 °C/min. After holding for 20 min, the reactor was cooled down to room temperature. The resulted samples were collected and washed with de-ionized water. Then the samples were stored in a dry, ventilated place under room temperature. The CS and WS samples after hydrothermal pretreatment were marked as CS-HT200/230/260 and WS-HT200/230/260.

2.4. Densification

3.5 ± 0.2 g of the raw or pretreated biomass sample was placed manually into a die of 16 mm diameter to prepare biomass briquette. A band heater was used to heat the sample with a controller maintaining the temperature of the sample at about 75 °C for 3 min. A compressive force of 80 MPa was applied to the sample by a piston-cylinder briquetting apparatus. After a holding time of 30 s, the pressure was released and the heater was turned off simultaneously. The derived biomass briquette was removed and stored at room temperature for the subsequently experiment. The briquettes of CS and WS samples were marked as CS/WS-Raw/DT/HT-B and here "Raw" represents the unpretreated biomass.

2.5. Biomass briquette carbonization

The carbonization experiment of the biomass briquette was carried

Table 1
Proximate and ultimate analyses of the biomass wastes.

Samples	Proximate analysis (wt.%, ad)				Ultimate analysis (wt.%, ad)					HHV (MJ/kg)
	M	*A*	*V*	*FC*	*C*	*H*	*O*	*N*	*S*	
CS	10.7	2.9	75.1	11.3	47.6	3.2	40.0	0.86	0.40	17.5
WS	8.9	3.1	78.6	9.4	53.6	2.8	38.9	0.96	0.03	17.6

M = moisture content; *A* = ash yield; *V* = volatile yield; *FC* = fixed carbon yield; ad = air-dried basis; HHV = higher heating value.