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Effects of binders on the properties of bio-char pellets

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HIGHLIGHTS

- Bio-char was densified with four binders of varying content (5–20%).
- The rheological characteristics of pellets were analyzed.
- Starch pellets showed good hydrophobicity, but low volume density and poor mechanical strength.
- NaOH pellets showed highest compressive strength and hydroscopicity among all pellets.
- Lignin and $Ca(OH)_2$ pellets exhibited more desirable characteristics for use as biofuels.

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ABSTRACT

Bio-char, produced from biomass pyrolysis, can be pelletized to improve its undesirable characteristics, such as low bulk and energy densities, poor transportation and storage properties, and troublesome to co-fire with coal. In this study, rice husk char was compressed into pellets with four kinds of binders (lignin, starch, calcium hydroxide and sodium hydroxide). The compressive process, mechanical strength, basic fuel properties, and combustion characteristics were investigated to elucidate the effect of binders on the properties of bio-char pellets. Results showed that starch pellets had good hydrophobicity, but low volume density and poor mechanical strength. The softening and morphological transition of lignin during compression may account for the high elastic modulus and good bonding of lignin pellets. The low saturated moisture content of $Ca(OH)_2$ pellets is mainly ascribed to its hydration. NaOH pellets showed the highest compressive strength among all pellets, and also exhibited the highest moisture uptake that may worsen the handling and storage treatment of bio-char. Compared with raw bio-char, bio-char pellets had a lower ignition temperature, wider temperature interval, and higher oxidation activity according to the thermogravimetric analysis. The lignin and $Ca(OH)_2$ pellets showed lower compression energy consumption and moisture uptake, enhanced mechanical strength and promoted combustion performance, which demonstrated more desirable properties for utilization as biofuels.

1. Introduction

The development of biomass has been an important issue for the past several decades and would remain to be attractive in the future due to its clean, renewable, and carbon–neutral properties [1]. Among the plentiful conversion and utilization technologies applied to biomass, pyrolysis is one of the most promising ways to convert biomass into bio-char, pyrolysis gas, and liquid oil [2,3]. Many upgrading methods, such as catalytic reforming, filtration, and purification [4,5], have been investigated extensively to improve the effective utilization of pyrolysis gas and bio-oil despite the ineluctable shortcomings faced in application [6]. Bio-char, with the properties of high calorific value, concentrated carbon content, excellent grindability, porosity, and species homogeneity [3,7], showed the potential to be used in firing plants, barbecues, steelmaking, and soil amendment to replace conventional coal partially and mitigate the environment burden. Therefore, it is very attractive to explore efficient ways to upgrade bio-char into high value-added bioenergy.

Whereas, the application of bio-char suffers from its low bulk density, low energy density, and high transportation and storage cost [8]. It has been reported that densification can improve feedstock uniformity and enhance the handling and conveyance efficiencies [9]. In addition, with pretreatment technologies such as torrefaction [10,11], steam treatment [12], and SO_2-catalyzed steam pretreatment [13], the resulted densified biomass has considerable density, desirable hardness, and good hydrophobicity. Low rank coal or biomass can be compressed into pellets (briquettes) with enhanced density and considerable mechanical

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strength, thus improve the logistics of pellet fuel and benefit the following utilization processes. Therefore, it is potentially possible to treat bio-char using densification technology in order to overcome the inherent disadvantages mentioned above and enable a wider range of application.

Densification, a well proved technology [14–16], shows the splendid practical prospects in converting coal, biomass, and torrefied biomass into pellets (briquettes). It was found that the materials properties (e.g. particle size, shape, moisture content, and composition) and processing conditions (e.g. compressing speed, temperature, pressure, and die size and shape) were the main factors affecting the densification results [9,11,17]. Poddar et al. [18] found that the density of lignocellulosic biomass pellet increased radically at first and then gradually with the increase of the applied pressure. Jiang et al. [19] recommended the optimum moisture content was 10–15% for co-pelletization of sewage sludge and biomass. Peng et al. [10] pointed out that the quality of torrefied pellets was improved at the die temperature of 230 °C and moisture content of about 10%. Fine torrefied sawdust particles (less than 0.25 mm) was demonstrated to produce pellets with prior water hydrophobicity and hardness compared with coarse ones [17]. Furthermore, the densification, hardening, and activation methods were developed to produce high-value added coal/biomass briquettes [11,20,21]. Han et al. [14] and Massaro et al. [22] found that high energy density and low ash content briquettes could be obtained with the densification of low rank pulverized coal. Diez et al. [23] established a method for compressing carbon-containing wastes into briquettes for metallurgical coke production. Rubio et al. [21] pressed char and pitch at 125 MPa to form briquettes, followed by curing, carbonization, and activation to obtain briquettes with enhanced surface areas and pore volumes.

Compared with raw biomass, the derived pyrolytic bio-char has different features, such as decreased moisture and volatile matter content, increased friability, cracked fiber component, and enhanced surface area and pore structure [3,7], which inevitable changed the forming characteristics during densification process and even might impede the deformation of particles and reduce their adherence among each other, thus making it difficult to form pellets. For this very reason, a few studies have been conducted on the densification behavior of pyrolytic bio-char. Bazargan et al. [24] pointed out that compacting palm kernel shell bio-char without addition of water resulted in weak bonding products. And bio-char pellets formed with water and soluble starch showed promoted tensile crushing strength, impact resistance, and water resistance compared with no-binder pellets. Kong et al. [8] investigated the conversion of sawdust into bio-char pellets through pyrolysis and densification. Results showed that the mixture of $Ca(OH)_2$ and lignin added in bio-char had water resistant effect on reducing moisture adsorption percentage during storage of bio-char pellets. Haykiri-Acma et al. [25] found that sulfide liquor, molasses, and Linobind could be used as binding agents to improve the durability of the briquettes when pelletizing carbonized brown seaweed. Accordingly, binder addition assisted bio-char particles bonded together and improved the densification characters of bio-char, especially for which was hard to form strong pellets without water and binder, in terms of energy saving and quality upgrading in industry. However, to the best of authors' knowledge, there are very limited studies focused on the effects of binders on the properties of bio-char after densification. This raise two questions when densification of bio-char for the promising quality briquette bioenergy. One is why binders are needed to form bio-char into bio-char pellets in order to enhance the quality. The other is how binders affect the pelletization process of bio-char and the properties of the derived pellets. The solution of these questions will then guide for binders selection and application when compacting bio-char in the industrial production process.

Concerns of the description above, the representative organic binders, lignin and starch, as well as the inorganic binders, $Ca(OH)_2$ and NaOH, were selected for use in this study. The densification process was described and the properties of the derived bio-char pellets were characterized. The effects of binders on densification of bio-char were investigated and the mechanical properties, basic fuel properties, and combustion characteristics of the pellets derived from different binders were explored. Especial attention was paid to explore the optimum densification condition with the binders, which may be helpful for future binder selection and application in the bio-char densification industry.

2. Materials and methods

2.1. Materials

The raw material of rice husk bio-char was collected from the biomass pyrolysis poly-generation demonstration plant in E'zhou, Hubei province, China. The results of the proximate and ultimate analysis of the bio-char are shown in Table 1. The bio-char sample has more fixed carbon and ash content, lower O content and higher calorific value compared with the original rice husk sample.

Bio-char was ground in a blade mill (XY-1000A, Songqing Hardware Company, China) for 3 min and then the particle size distribution was analyzed using a laser particle-size analyzer (MS2000, Malvern Instruments Ltd., U.K.). The results are shown in Fig. 1. It was found that the bio-char particles were uniform in size with an average particle size of about 0.1 mm, and about 98% of the ground bio-char was less than 0.3 mm in size, indicating the good grindability of the bio-char as previously reported [7,26]. Bio-char was dried in an oven at 105 °C overnight and kept in a desiccator before further analysis. Two organic binders (alkaline lignin and starch) and two inorganic binders ($Ca(OH)_2$ and NaOH) were selected. Alkaline lignin, a dark brown powder, was purchased from Sigma–Aldrich Co., Ltd (USA). The starch, $Ca(OH)_2$, and NaOH were purchased from the Tianjin Chemical Reagent Factory (China). All the chemicals used in this study were analytical grade and were not further purified.

3. Experimental method

The densification of bio-char was carried out in a universal material testing machine (CMT5205, MTS, China) with binder and water added at room temperature. The pellet device of the

Table 1
Proximate and ultimate analysis of the rice husk and bio-char (dry material).

Sample	Proximate analysis (d, wt.%)			Ultimate analysis (d, wt.%)					HHV (MJ/kg)
	V	A	FC	C	H	N	S	O[a]	
Rice husk	67.70	16.22	16.08	41.78	5.35	0.30	0.08	36.31	15.44
Bio-char	7.29	33.19	59.52	56.46	2.14	1.14	0.63	6.44	19.69

[a] Calculated by difference.

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