Fuel 199 (2017) 488–496

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

The pyrolysis of biomass briquettes: Effect of pyrolysis temperature and phosphorus additives on the quality and combustion of bio-char briquettes

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HIGHLIGHTS

- A novel bio-char briquettes production of bio-char briquettes is developed.
- The physico-chemical quality of bio-char briquettes were studied.
- Thermal and kinetic analysis of bio-char briquettes were studied.
- Influences of pyrolysis temperature and P-based additives were investigated.

ARTICLE INFO

Article history:
Received 29 August 2016
Received in revised form 10 February 2017
Accepted 7 March 2017
Available online 15 March 2017

Keywords:
Bio-char
Briquette
Pyrolysis temperature
Quality
Phosphorus additives

ABSTRACT

The influences of pyrolysis temperature and phosphorus additives on physico-chemical quality and combustion property of bio-char briquettes were investigated in this research. Bio-char briquettes were obtained from directly pyrolysis of maize straw briquettes. Pyrolysis temperature were from room temperature to 250–650 °C with a heating rate 10 °C/min. Combustion tests were performed in a thermal-gravimetric analyzer. Results showed that with the increased pyrolysis temperature, volume density decreased initially and subsequently turned flat. While durability rating and mass yield sustained to decline. The optimal pyrolysis temperature was estimated to be 550 °C, gave the higher heating value 21.05 MJ/kg, energy-mass co-benefit (EMCI) 8.14. The volumetric energy densities were mainly in the range of 10–14 GJ/m^3. Combustion feature of bio-char acquired at 250 °C was significantly different. Both the index S and D_i at the first stage were obviously higher; the S was improved by addition of $Ca(H_2PO_4)_2$ at a suitable pyrolysis temperature. The E generally showed increasing trend with enhanced pyrolysis temperature. In the same pyrolysis temperature, the sequence of E from high to low is: E_{MS}, $E_{MS\text{-}CPM}$ and $E_{MS\text{-}ADP}$. The performance of $NH_4H_2PO_4$ on combustion characteristics was worst.

1. Introduction

Considering extensive worldwide focus on global warming problems originating mainly from fossil fuels, biomass is regarded as a renewable energy resource alternative to fossil fuels in recent years. Approximately 60 exajoules of total energy demand were supplied from biomass in 2015, and biomass resources contributed about 9–13% of the total global energy supply [1]. The bioenergy conversion of biomass is also regarded to keep increasing in the future. However, the inferior properties of biomass such as high moisture content and low volumetric energy density made the costs in fuel transportation storage and processing to be high, those inhibit biomass market promotion, especially directly use for combustion [2,3].

Densification can improve physical and combustion behavior, which are benefit for using larger variety of lignocellulosic materials as fuels [4]. Biomass briquettes can be used in both the grate and fluidized bed furnaces combustion. Recently, there has been increasing focus on producing biomass briquettes for both domestic and industrial utilization of briquettes. In addition to easy storage and transport properties of densified biomass briquettes [5], Rhén et al. [6] have pointed out that pellets had the possibility for automation and optimization similar to petroleum, with low residuals amounts and high combustion efficiencies.

In addition to densification, other pre-treatment methods such as pyrolysis (torrefaction and carbonization) can achieve high quality biofuels. Pyrolysis can improve better combustion

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http://dx.doi.org/10.1016/j.fuel.2017.03.011
0016-2361/

characteristic, lower pollutant emissions of biomass. Due to the decomposition of cellulose and hemicellulose, there was a decrease in volatile matter, promoting the homogenization of biomass [7]. And during the transformation of N content in volatiles to NH_3, an obvious reduction in emissions of NO_2 was observed for torrefied biomass [8]. Carbonization of biomass in low temperature was different to that acquired from torrefaction in the aspect of mass and energy yields [9]. Fuel properties such as calorific value and fixed carbon content were improved with increased pyrolysis temperature [10]. Pyrolysis temperature and time were two crucial parameters, the optimum biochar fuel yield and energy yield reached 47.29% and 56.55% under optimal pyrolysis condition [11]. Except to transform the biomass into the energy fuel, bio-char also was appropriate to be used in soil application as well as carbon sequestration [12]. Thus, no matter in large industrial installation, the individual farm or even at the domestic level, bio-char can be utilized at a wide range scales, making it suitable for extensive applications [13,14].

In general, numerous beneficiations existed in densification and pyrolysis, and these pretreatments possessed great potentials for expanding biomass in a variety of socioeconomic situations. However, previous studies were mainly focused on pyrolysis or densification separately, only a little study provided a research on properties of torrefied briquettes. Considering the properties such as higher heating values, better water-resistivity and durability, bio-char briquettes enjoy a significant potential to be applied in metallurgical processes and thermal power plants to replace the traditional fossil fuel. Currently torrefied wood pellets have been considered as the 2nd generation of wood pellets [15–17]. The production cost per GJ of torrefied wood pellets will be 6% lower than that of traditional pellets, and the transportation cost will be saved by more than 40% [18]. Typically, the value chain of a torrefied biomass pellets were usually torrefying firstly before densifying [19]. However, due to the change of fiber structure and moisture content in pyrolysis, the densification of pyrolyzed biomass samples was more difficult than pretreatment in the same operating situation of untreated biomass [20]. The cohesiveness and flowability went worse during pyrolysis, bio-char had worse compaction characteristic compared to parent materials. Therefore, bio-char was not ideal feedstocks for densification [21]. As a result, reversing the chain order between pyrolysis and densification, taking advantages of cohesiveness of biomass briquettes itself, may be an alternative method to improve quality of bio-char briquettes.

Except the deficiency of low energy density during the traditional thermal utilization process of raw biomass, the relative high content of alkali metals such as potassium, especially in herbaceous plants cannot be neglected [22]. Problems such as bed agglomeration, fouling and corrosion in combustion devices are related to alkali species [23–25]. Mixing mineral based additive is an attractive solution to mitigate these problems. Phosphorus rich additives have benefit influences on capturing potassium and improving ash melting points [26–29]. During the powder combustion, $NH_4H_2PO_4$ decreases gaseous potassium release ratios during the carbonization of rice straws [30]. And the bio-char acquired from co-pyrolysis of external phosphates and biomasses can be acted as an effective fertilizer [31,32]. Calcium (Ca) element contribute to the formation of high temperature melting calcium potassium phosphate and silicates [33]. Combination of calcium and phosphorus as additives (such as $Ca(H_2PO_4)_2$) had benefit influences on capturing potassium and improving ash melting points. In addition, $Ca(H_2PO_4)_2$ slows nutrient release problems and stabilize heavy metals in soil when it was co-pyrolyzed with biomass [34,35]. Moreover, $Ca(H_2PO_4)_2$ is effective in increasing carbon retention and strengthening bio-char stabilization [36]. However, the influence of phosphorous additives on bio-char briquettes physical property and combustion patterns still needs to be further researched.

Thus, this research is aim to explore the fuel characterizations for bio-char briquettes. The bio-char briquettes are derived from directly pyrolysis of biomass briquettes in a fix bed pyrolysis system, rather than densification of biomass powder char with binders in previous research. Effect of pyrolysis temperature and two kinds of phosphorous additives on qualification and combustion behavior of bio-char briquettes was determined. Thermal and kinetic analysis on combustion behavior of maize straw (MS) char was investigated by a thermogravimetric apparatus. The results may provide guidance for bio-char briquettes technology and benefit to the efficient pyrolysis and densification application of biomass.

2. Materials and methods

2.1. Materials and preparation

The raw maize straw (MS) in this research was obtained from the suburb of Shandong province in China. Prior to analysis, the raw materials were milled and sieved into 80 meshes. The basic properties of maize straw and the carbonized products were measured based on air dried basis. The sieved particles were put in a drying system at 105 °C for at least 24 h prior to use. Proximate and ultimate analysis results of maize straw were listed in Table 1. The proximate analysis was undertaken according to GB/T 28731-2012 (Proximate analysis of solid biofuels, China). The C, H and N contents in ultimate analysis were measured by an elemental analyzer (Leco tru spec), the S was analyzed by a sulfur analyzer (Leco S144DR) and the O was calculated by differences. The measurement of potassium ratio was carried out by inductively coupled plasma–atomic emission spectrometry (ICP–AES, Thermo Fisher Scientific, IRIS). The content of chlorine was determined by titration method according to GB/T 3558-2014 (Solid mineral fuels-Determination of chlorine using Eschka mixture, China). Fuel blends were prepared by mixing maize straws with two different powder additives: Ammonium dihydrogen phosphate ($NH_4H_2PO_4$, ADP in abbreviation) and Calcium phosphate monobasic ($Ca(H_2PO_4)_2$, CPM in abbreviation) (Kemiou Chemical Reagent Co.), with a P/K molar ratio of 1.5.

2.2. Briquetting process

Accurate weighted (5 ± 0.1) g raw or mixed powder materials were put into a cylindrical mold. All the samples were pressed in a laboratory compaction apparatus and kept at a working pressure of 15 MPa in 60 s. The produced briquettes presented to be a cylindrical shape with 24 mm in diameter and 8–9 mm in length as shown in Fig. 1a.

Biomass were mainly composed by cellulose, hemicellulose and lignin. The cellulose and lignin acted as natural binder in the raw bio-material [37]. The pressure in this research (15 Mpa) was high enough for briquetting, no external binders or heat source were needed for briquetting. Fig. 2 illustrated detailed morphology information of acquired briquettes by the scanning electron microscopy (SEM, FEI QuantaFEG250). Due to the biomass network was full of abundant hemicellulose, the surfaces remained the branched fiber configurations with compact and smooth flatten structures due to the high pressure.

2.3. Pyrolysis experimental system and procedure

The experimental system was composed by a gas feeding unit and a horizontal pyrolysis reaction unit as shown in Fig. 1b. The