Applied Thermal Engineering 104 (2016) 678–686

Contents lists available at ScienceDirect

Applied Thermal Engineering

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

Research Paper

Effects of hydrothermal treatment temperature and residence time on characteristics and combustion behaviors of green waste

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HIGHLIGHTS

- The hydrothermal treatment of green waste was studied.
- Effects of temperature and time on product characteristics were evaluated.
- The energy density and combustion performance of hydrochar was improved.
- The optimum reaction temperature and residence time of were selected.
- The activation energy of the main combustion process was calculated.

ARTICLE INFO

Article history:
Received 17 February 2016
Revised 25 April 2016
Accepted 19 May 2016
Available online 20 May 2016

Keywords:
Hydrothermal treatment
Green waste
Waste-to-energy
Combustion behavior
Kinetic study

ABSTRACT

The hydrothermal treatment of green waste was investigated to elucidate the effect of different temperature and residence time on the combustion behaviors and properties of hydrochar. The higher heating value of the hydrochar after the hydrothermal treatment was enhanced by 1.00–1.58 times (energy content per mass). The combustion performance was also significantly improved. The reaction temperature of 210 °C was the most suitable temperature of hydrochar production compared with different temperature. It was found that the energy recovery efficiency was decreased with the residence time increased. The oxygen/carbon atomic ratio indicated that the upgrading process converted the green waste near to clean solid fuel with high energy density. The thermal gravimetric analysis showed that the temperature and residence time had a significant impact on combustion behavior and activation energy of hydrochar. The consecutive first order reaction model could well describe the combustion process.

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1. Introduction

With the speeding up of urbanization in China, the urban afforestation plays a very significant role in improving urban environmental quality, relieving the urban heat island effect, and maintaining ecological balance. However, the amount of green waste (GW) becomes increasingly larger. Zhang and Sun [1] reported that GW is the biodegradable organic fraction of municipal solid waste and generally consists of grass, leaves, tree trimmings, and other similar constituents. Meanwhile, there was much moisture, oxygen and alkaline earth metals in the GW, which is unfavorable for burning. What's more, direct combustion of GW can cause a large amount of smoke, and lead to the air pollution. As a consequence, disposal of GW is a major problem affecting the environment and sustainable development of cities [2]. The conversion of GW to solid fuel for combustion may be a feasible GW treatment scheme from the standpoint of restraint of the environmental pollution as well as relief of fossil fuels depletion. The problems are solved by hydrothermal treatment of the GW to produce hydrochar [3]. Recently, hydrothermal treatment (HT) has received a great deal of attention as a simple, sustainable and effective management pre-treatment technique for the efficient conversion of biomass wastes (e.g. biomass, municipal waste, macroalgae, and fruit bunches, etc.) to useful biocarbons [4]. This innovative treatment process can convert GW to value-added energy such as coal-like clean solid fuel.

This study represents the application of HT on GW to generate powdered solid products with good combustion performance. The HT was a heat treatment in hot-compressed water and was a promising way to pretreat biomass energy [5–7]. This HT process of biomass was carried out in the subcritical water, at which water

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http://dx.doi.org/10.1016/j.applthermaleng.2016.05.111
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was still in a liquid phase and acts as a non-polar solvent enhancing the solubility of organic compounds of biomass [8]. These conditions produce a highly reactive solvation environment and avoid an energetically costly phase change associated with feedstock drying [9]. It narrowed the differences in fuel properties among different biomass feedstocks [10]. On the other hand, HT was a promising technology for biomass with high water content (up to 80%) [11]. The present study showed that HT was a promising conversion process for the production of the hydrochar which had increased fuel qualities compared to raw biomass [3,10,12]. The Ref. [13] has reported HT can be defined as combined dehydration and decarboxylation of a fuel to raise its carbon content with the aim of achieving a higher calorific value. Within the range 180–240 °C, the reaction was given priority to with hydrolysis, the hydrothermal effect greatly weakened the role of hydrogen bonds in hemicellulose and cellulose crystal. The chemical bonds of hydrochar broke and reformed [12], and then released in the form of volatile gas. HT reaction path of GW was found as follows: GW – glucose – decomposition product [14]. The reactions also lead to the loss in volatile matter and the carbonization results in the gain in fixed carbon of residual hydrochar [4]. What's more, the hydrochar has a lower moisture uptake content compared with the raw GW after HT process, which is easy for storage and transportation.

The previous works have concentrated on the HT of municipal solid waste and sewage sludge, the investigations on the HT of GW have rarely been studied. The objective of this preliminary work was to develop a HT that can be applied to convert GW into high energy density and heating value fuel in a relatively short reaction time and moderate reaction temperature. Three parts of research contents were studied to research the effects of HT temperature and residence time: hydrochar characteristics, thermal combustion behavior and combustion kinetics mechanism. The results could provide a detailed investigation on HT of GW, thus providing reference opinions for the implementation and optimization of the energy upgrading technology for GW.

2. Experimental

2.1. Materials

In this work, the GW selected from a garbage treatment station in southern china that mainly contains deciduous trees, bushes and bamboo and so on, was adopted as raw material. The collected GW was screened, and the non combustible materials such as small stones were removed. The retained branches, barks and leaves were shattered into small particles of less than 1 mm for subsequent HT, and then over-dried in an drying oven at 105 °C for 24 h. The treated samples were placed in a desiccator.

2.2. Hydrothermal treatment

The HT experiments of GW were carried out by using an autoclave 250 ml reactor (Model SLM250, Beijing Shi Ji Sen Lang Experimental Instrument Co., Ltd., Beijing, China) as shown in Fig. 1. GW was subjected to the hydrothermal treatment at the temperature gradient at 30 °C, range from 150 °C to 300 °C, residence time was 60 min. To analyze the effect of residence time (stay at a certain pre-set reaction temperature) on GW, under the same temperature of 240 °C, six desired residence times (30 min, 45 min, 60 min, 90 min, 120 min and 180 min, respectively) were adopted. Before each experiment, 5 g of GW feedstock was mixed with approximately 100 ml deionized water and was manually stirred for 5 min to ensure complete mixing. The reactor was heated up to the pre-set reaction temperature in an external electric heating device which was operated under nitrogen gas. Then the reactor maintained at the reaction temperature for desired residence time (60 min) at a stirring rate of 500 rpm. The residence time was defined as the period of the reactor was remained at the preset temperature, except for preheating and cooling time. After complete reaction, the pressure relief valve was open and the reactor was immediately cooled to room temperature, and the gaseous products escaped rapidly. The solid products (hydrochar) of small size and liquid products were separated by using quantitative filtration (3 mm), washed with deionized water. Then the hydrochar samples were dried in a drying tunnel at 105 °C for 24 h and crushed into the particle size of less than 1 mm before analysis. All the experiments were carried out three times to ensure reproducibility and consistency. The hydrochars were denoted as *X*–*Y*, where *X* and *Y* represent temperature (°C) and time (min) for the HT respectively.

2.3. Fuel analysis

To understand the HT process characteristics and optimum experimental conditions for the energy balance, the combustion process analysis, energy densification, hydrochar yield, and energetic recovery efficiency were calculated by the following equations [4]:

$$\text{Energy densification} = \text{HHV of hydrochar}/\text{HHV of feedstock} \quad (1)$$

$$\text{Hydrochar yield} = \text{Mass of hydrochar}/\text{Mass of feedstock} \quad (2)$$

$$\text{Energetic recovery efficiency} = \text{Hydrochar yield} \times \text{Energy densification} \quad (3)$$

where HHV was the higher heating value of sample, kJ/kg. It was measured by oxygen bomb calorimeter in this study.

2.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was widely used to study biomass kinetics as they are high-precision methods and provide quantitative methods for examination of processes [15]. It was regarded as an effective way to analyze combustion behavior by using TGA system attributed to its ability in fast assessment of different kinds of materials like coal, biomass and their blends [16]. In this study, thermal gravimetric analysis were carried out by a thermal gravimetric analyzer (TGA, METTLER TOLEDO). Thermal gravimetric analysis was conducted in the range of room temperature to 1000 °C at the heating rate of 20 °C/min. Air was adopted to reaction gas. The flow rate of reaction gas was controlled to be 100 ml/min. About 10 mg sample was selected and placed in an alumina crucible. Each sample was detected three times to ensure good reproducibility.

The methods how to define the ignition combustion temperature (T_i) and burnout temperature (T_f) could found in Ref. [12]. A combustibility index *S* was used as a evaluation criteria for fuel combustion characteristic, and the definition was as follows [17]:

$$S = ((dW/dt)_{max} \times (dW/dt)_{mean})/(T_i^2 \times T_f) \quad (4)$$

where $(dW/dt)_{max}$ was the maximum weight loss rate, %/min. $(dW/dt)_{mean}$ was the average weight loss rate, %/min. T_i and T_f were respectively the ignition temperature and the burnout temperature (°C). The index *S*, which includes the ease of ignition, the burning velocity and the burnout temperature, was a comprehensive combustion parameter. The higher the values of the comprehensive combustion characteristic index *S*, the more vigorous the combustion was.

The conversion rate (α) was defined as [18,19]:

$$\alpha = (m_0 - m_t)/(m_0 - m_\infty) \quad (5)$$

where m_0, m_t and m_∞ were initial sample mass, sample mass at time *t* and sample mass at the end of reaction, respectively.

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