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Co-hydrothermal carbonization of corn stalk and swine manure: Combustion behavior of hydrochar by thermogravimetric analysis

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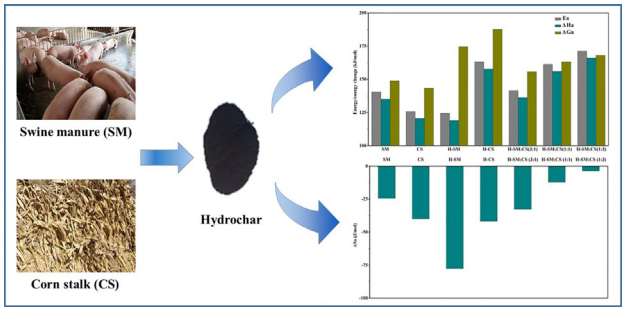
GRAPHICAL ABSTRACT



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ABSTRACT

The combustion behavior of the hydrochar from co-hydrothermal carbonization (HTC) of corn stalk (CS) and swine manure (SM) was thermogravimetrically investigated. Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) were used for kinetic analysis, and the thermodynamic parameters were determined. Results showed that HTC decreased the combustion property and stability of SM, while co-HTC with CS significantly improved the combustion performance of the hydrochar including the increased ignition temperature and decreased burnout temperature. HTC of SM decreased the average activation energy (E_a) value from 140.40 and 137.31 KJ/mol to 124.40 and 120.17 KJ/mol by FWO and KAS, respectively, and increasing proportion of CS during co-HTC increased the E_a value of the hydrochar to 141.53–171.23 and 138.35–169.66 KJ/mol, respectively. The thermodynamic parameters confirmed the enhanced combustion reactivity of the hydrochar from co-HTC of CS and SM. These findings demonstrated that co-HTC with CS benefited the hydrochar production from SM with improved combustion performance.

1. Introduction

With the fast-growing animal husbandry, more than 2.7 billion tons of animal manure is annually generated in China (Chen et al., 2017). Anaerobic digestion and composting of animal manure are time-consuming and usually release a lot of greenhouse gases (Lin et al., 2018). In addition, the potential risk of antibiotics and heavy metals in animal manure is not effectively eliminated during these processes (Anjum

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et al., 2017; Feng et al., 2017). Considering the gradual depletion of fossil fuel reserve and subsequent environmental pollution, animal manure is regarded as an alternative and sustainable fuel owing to its carbon-neutral nature. It is estimated that the annual amount of thermal energy generated from animal manure combustion is appropriately equal to 150,300 tons of coal in China (Shen et al., 2015). However, there are some drawbacks for direct combustion of animal manure including its poor grindability, high moisture content and low heating value (Bach and Skreiberg, 2016), easily resulting in low combustion efficiency and high operation cost.

Hydrothermal carbonization (HTC), a facile, environmentally friendly and cost-effective pretreatment method, has been extensively used to upgrade biomass to the coal-like hydrochar for combustion (Cai et al., 2016; Chen et al., 2018; Peng et al., 2016b). The antibiotics and heavy metals in biomass were greatly decomposed and immobilized by HTC (Lang et al., 2018; Wang et al., 2018), and the homogeneous hydrochar from HTC had improved fuel properties including higher calorific value and lower oxygen, nitrogen and sulfur contents than raw biomass (Cai et al., 2016; He et al., 2013; Lin et al., 2016; Yao et al., 2016). More importantly, compared to raw biomass, the reduced toxic polycyclic aromatic hydrocarbons were released during hydrochar combustion (Peng et al., 2016b). Therefore, converting biomass into the hydrochar has multiple benefits prior to combustion. Nevertheless, the remarkably increased ash content of the hydrochar by HTC (Park et al., 2018) resulted in the low efficiency, high slagging and fouling tendency during combustion (Bach and Skreiberg, 2016). Additionally, previous studies demonstrated that high HTC temperature increased the higher heating value and fuel ratio of the hydrochar, while the energy yield was significantly reduced with increasing temperature, ascribing to the decreased hydrochar yield (Cai et al., 2016; Park et al., 2018).

At present, several studies found that co-HTC of protein-based biomass and lignocellulosic biomass was a novel and promising approach for the hydrochar production with low ash content and high energy recovery (Lang et al., 2018; Zhai et al., 2017; Zhang et al., 2017). For instance, the presence of corncob during HTC of sewage sludge dramatically decreased the ash content of the hydrochar from 60.32% to 33.66%, and significantly increased the energy recovery rate from −4.76% to 37.56% (Zhai et al., 2017). Moreover, our previous study reported the synergistic effects between animal manure and lignocellulosic biomass during co-HTC, contributing to the increased hydrochar yield, fixed carbon content and energy yield of the hydrochar (Lang et al., 2018). As a consequence, co-HTC of animal manure and lignocellulosic biomass offered an alternative approach for hydrochar production towards solid fuel with high quality.

Thermogravimetric analysis (TGA) is essential to evaluate the combustion behavior of solid fuel in order to deeply understand the kinetic behavior and design the combustion equipment at industrial scale (Fernandez-Lopez et al., 2016). To our knowledge, no systematic study is available about the combustion behavior of the hydrochar from co-HTC of animal manure and lignocellulosic biomass. Therefore, the primary objectives of this study were: 1) to investigate the characteristic combustion parameters of the hydrochar from co-HTC of animal manure and lignocellulosic biomass; 2) to determine the kinetic and thermodynamic parameters of combustion process of the hydrochar.

2. Material and methods

2.1. Hydrochar preparation

Swine manure (SM) and corn stalk (CS) were selected as the typical animal manure and lignocellulosic biomass in this study, and the detailed procedure for the hydrochar preparation can be found elsewhere (Lang et al., 2018). Briefly, the blend of SM and CS at different mixing ratios (1:0, 3:1, 1:1, 1:3 and 0:1, respectively) was treated by HTC at 220 °C for 10 h in a 50-mL stainless autoclave. Afterwards, the obtained hydrochar by centrifugation at 10000 rpm for 15 min was immediately dried at 60 °C, and crushed to homogeneous powders with the diameter less than 100 mesh. The hydrochars from HTC of individual SM and CS were denoted as H-SM and H-CS, respectively, and the hydrochar from co-HTC was labeled as H-SM:CS (X), where X referred to the mixing ratio of SM and CS.

2.2. Thermal analysis

The combustion experiment was carried out with a thermogravimetric analyzer (TG 209, F3, Netzsch, Germany) under atmospheric pressure. Around 5 g of sample placed in a Al_2O_3 crucible was heated from 40 to 900 °C with an air flow rate of 100 mL/min at different heating rates (10, 20, 30 and 40 °C /min, respectively). For each sample, the TGA experiment was repeated at least twice for accuracy.

2.3. Characteristic combustion parameters

The thermogravimetric (TG) and differential thermogravimetric (DTG) data provide the characteristic combustion parameters including ignition temperature (T_i), burnout temperature (T_b), mass residue (R_m), maximum weight loss rate (DTG_m) and corresponding temperature (T_m) to evaluate the combustion behavior of all samples. Specifically, T_i indicates the temperature the fuel starts to burn, and T_b denotes the temperature for the complete combustion of fuel, and they are determined by the TG-DTG tangent method (Mureddu et al., 2018). With respect to T_m, it is defined as the temperature at which the weight loss rate reaches the maximum. Additionally, the comprehensive combustion index (CCI) and combustion stability index (R_w) are calculated using the following equations (Chen et al., 2018; Xie et al., 2018), respectively.

$$CCI = \frac{DTG_m \times \mathrm{DTG_{mean}}}{T_i^2 \times \mathrm{Tb}} \quad (1)$$

$$R_w = 8.5875 \times 10^7 \times \frac{\mathrm{DTG_m}}{\mathrm{T_i} \times \mathrm{Tm}} \quad (2)$$

where DTG_m and DTG_{mean} indicate the maximum and average weight loss rate, respectively; T_i and T_b represent the ignition temperature and burnout temperature, respectively; and T_m is the peak temperature.

2.4. Kinetic analysis

The decomposition characteristics with increasing temperature during combustion are revealed by kinetic analysis using model-free methods of Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS). The data obtained from TG curve are calculated using the following equations:

$$\frac{d\alpha}{dt} = \mathrm{kf}(\alpha) \quad (3)$$

$$\alpha = \frac{m_0 - \mathrm{m_t}}{m_0 - \mathrm{m_f}} \times 100\% \quad (4)$$

where t is the reaction time; k is the reaction rate constant; α refers to the conversion rate; f (α) represents the model function; and m_0, m_t and m_f indicate the initial mass, the mass at time t, and the final mass of sample, respectively.

In addition, the reaction rate constant (k) is described by the Arrhenius equation:

$$k = \mathrm{A}e^{\frac{-\mathrm{E}}{\mathrm{RT}}} \quad (5)$$

where A refers to the pre-exponential factor (s^{-1}); E is the activation energy (KJ/mol); R is the gas constant (8.314 J mol^{-1} K^{-1}); and T is the reaction temperature (K).

The reaction rate of a solid-state is described by the following equation: