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Investigation of representative components of flue gas used as torrefaction pretreatment atmosphere and its effects on fast pyrolysis behaviors

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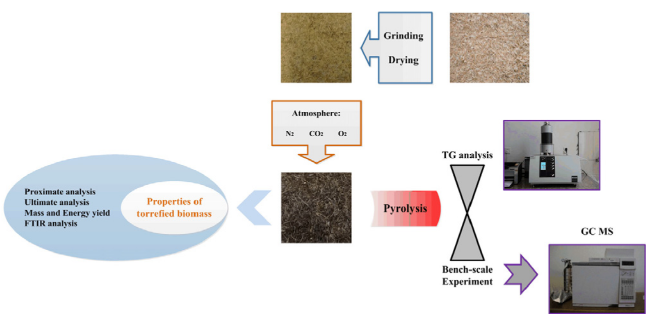
GRAPHICAL ABSTRACT



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ABSTRACT

In this study, three torrefaction atmosphere (N_2, CO_2 and 2 vol% O_2 with N_2 balance) were used to study effects of representative main components of flue gas during torrefaction and subsequent pyrolysis. Torrefaction pretreatment was carried out in a fixed-bed reactor at 230 °C and 250 °C, respectively. Results showed after torrefaction, torrefied samples from oxygenated atmosphere presented severer hemicellulose decomposition. And its effects on fast pyrolysis were investigated in thermogravimetry analysis and bench-scale fixed-bed reactor. It was found that oxygenated atmosphere preferred to give higher relative content of phenols at 230 °C and furans at 250 °C. For CO_2, higher relative content of ketones and lowest phenols were got. The result also indicated that it's the O_2 in flue gas which significantly improved the char yield. These results will be beneficial reference to predict and interpret alterations of pyrolysis behaviors when flue gas constitution changes in industrial application.

1. Introduction

Due to characteristics of renewability, wide abundance and CO_2 neutral, lignocellulosic biomass has been used as an alternative selection for energy and chemicals production worldwide. Fast pyrolysis is one of the most promising thermo-chemical technologies to convert biomass into value-added products (including char, bio-oil and bio-gas). In fast pyrolysis, biomass is rapidly heated to temperature range of 450–600 °C in inert atmosphere (Daniel Carpenter et al., 2014). However, for its high water content, low energy density and low grindability, original biomass is normally considered as a low-grade feedstock. That is unsuitable to be utilized directly. Torrefaction pretreatment prior to fast pyrolysis is an effective method to improve the physicochemical characteristics and pyrolysis behaviors.

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Torrefaction is a thermo-chemical process normally under inert atmosphere at the temperature range of 200–300 °C. Ben and Ragauskas (2012) used NMR analysis demonstrated the decomposition of hemicellulose, cellulose and lignin during torrefaction. These reactions, such as dehydration, deoxygenation, and dehydrogenation during torrefaction, transform original biomass to be a low-oxygenic, hydrophobic and higher bulk density and energy density feedstock (Chen et al., 2012). Wang et al. (2017) found that temperature is the most important torrefaction variation in spouted bed reactor, and particle size affects torrefaction process as well. Correia et al. (2017) confirmed the reduced volatile content, O/C and H/C ratios of the biomass after torrefaction. Inorganic species also significantly affect torrefaction process. When most AAEMs were leached out, the solid product yield was decreased and the gas product yield was increased as well (Zhang et al., 2018a).

Exhaust flue gas is normally used in industrial torrefaction system. Sellappah et al used a mixture gas consisted of N_2, CO_2, O_2, CO and H_2 at percentages of 75.5, 16.4, 4.0, 3.5 and 0.3 vol% to simulate the flue gas in torrefaction process (Sellappah et al., 2016). Despite of temperature, the component of flue gas can also intensify the torrefaction process. Uemura et al. (2017) pointed out that due to the decomposition enhanced by O_2 and CO_2 in combustion gas, a decreased solid yield and increased HHV were obtained after torrefaction. Chen et al. (Chen et al., 2013; 2015a) researched effects of torrefaction temperature, O_2 concentration and superficial velocity on torrefied biomass.

Influence of torrefaction pretreatment under pure N_2 atmosphere on fast pyrolysis behavior has been studied in numerous works (Chen et al., 2017a,b; Zhang et al., 2018b). However, the influence of different flue gas component on fast pyrolysis behaviors was rarely reported and just a few literatures only focused on TG/DTG analysis (Mei et al., 2015). It's well-known that composition of flue gas isn't constant, sometimes changed, especially in industrial system. Study of individual representative component from flue gas will be a beneficial reference to predict and interpret alterations of pyrolytic products. In this study, bamboo particle was used to research effects of three representative components of flue gas (pure N_2, pure CO_2 and 2 vol% O_2 with N_2 balance) during torrefaction. And effects of these changes on pyrolytic products distribution and bio-oil components. Flowchart of the torrefaction pretreatment and subsequent pyrolysis process is presented in Fig. 1.

2. Materials and methods

2.1. Feedstock

Bamboo was collected from a mill in Ji'an City, Jiangxi Province, China. Before experiment, bamboo was first ground and screened to obtain a particle range varying from 0.15 to 0.3 mm. And then dried further at 105 °C for night to achieve a constant weight. The dried bamboo particle was denoted as B.

2.2. Torrefaction pretreatment and fast pyrolysis procedure

Torrefaction pretreatment was carried out in a vertical drop fixed-bed reactor system, which has been described in our previous work (Zhang et al., 2016). Bamboo particles (10 g) were fed into the fixed-bed reactor by the influence of gravity. Torrefaction atmosphere with a flow rate of 300 ml/min purged the reactor for 15 min. After that, the reactor was heat up to the predetermined torrefaction temperature (230 °C and 250 °C, respectively) with a heating rate of 10 °C/min. Three different torrefaction atmospheres used in this experiment were pure N_2, pure CO_2 and 2 vol% O_2 with nitrogen balance. After stabilized to the set temperature for 60 min, the quartz reactor was removed from the heating furnace to cool to ambient temperature and pure N_2 was introduced into the system. Then the solid residue was poured out and weighed. TB230-N_2, TB230-CO_2 and TB230-2%O_2 denoted the bamboo particles after the torrefaction pretreatment at the temperatures of 230 °C in pure N_2, pure CO_2 and 2 vol% O_2, respectively. And so as the TB250-N_2, TB250-CO_2 and TB250-2%O_2 represented the torrefaction temperature of 250 °C.

Fast pyrolysis experiment was carried out in the same fixed-bed reactor. Normally, bamboo particles (5 g) were dropped into the vertical drop fixed-bed reactor under pure N_2 atmosphere at the pyrolytic temperature of 550 °C and maintained for 5 min. After experiment, pyrolytic products in forms of char, bio-oil, and pyrolytic gas were collected from the reactor, condenser, and gas sampling bags, respectively.

2.3. Product analysis

The proximate analysis of original and torrefied samples was carried out based on GB212-91 standard. The ultimate analysis was determined with a Vario MACRO cube elementary. The higher heating value (HHV) was analyzed by the SDACM3000 calorimeter. Surface functional groups of samples were conducted with a Fourier transform infrared spectroscopy (FTIR) analyzer (Perkin-Elmer Spectrum GX).

Thermogravimetry analysis (TGA) was carried out in the TA Q600 SDT analyser for studying the thermal degradation behaviors of original and pretreated samples. Approximately 5 mg of bamboo particle samples were analyzed at a heating rate of 20 °C/min from ambient temperature to 600 °C under nitrogen protection with a flow of 70 ml/min.

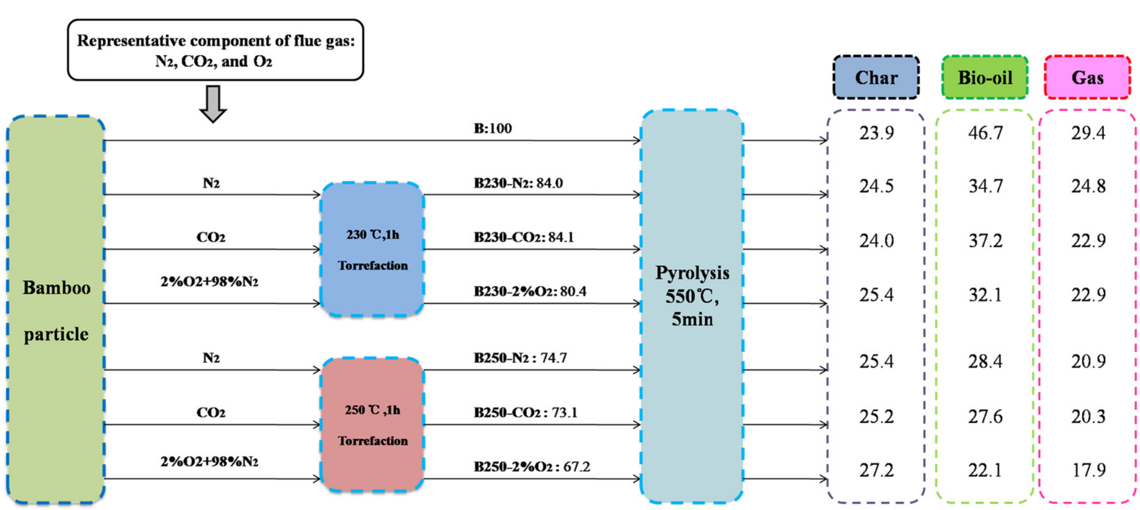

Fig. 1. Flowchart of bamboo particles torrefaction pretreatment and pyrolysis.