Fuel 214 (2018) 546–553

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Synergy on particulate matter emission during the combustion of bio-oil/biochar slurry (bioslurry)

Chao Feng, Hongwei Wu[*]

Department of Chemical Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

ARTICLE INFO

Keywords:
Bioslurry
Bio-oil/biochar slurry
Combustion
Synergy
Particulate matter (PM)

ABSTRACT

Bio-oil/biochar slurry (i.e. bioslurry) is a new type of fuel that is prepared by suspending fine biochar particles into fast pyrolysis bio-oil. This study reports the synergy on PM_{10} emission during bioslurry combustion in a laboratory-scale drop-tube-furnace in air at 1400 °C. The experimental results show that the PM_{10} emission from the direct combustion of bioslurry (with 5 or 10% biochar loading level) is higher than the sum of those from separate bio-oil and biochar combustion, clearly indicating the existence of synergy. It is evident that at least two mechanisms are responsible for such synergistic effects. One mechanism is the leaching of inorganic species from biochar by acidic bio-oil in the bioslurry system. This is demonstrated by the direct comparisons between PM_{10} emissions from the combustion of bio-oil or biochar before and after bioslurry preparation. The experimental results show that such a leaching effect leads to both an increase in PM_1 and a decrease in PM_{1-10} during combustion, because of the redistribution of inorganic species between the bio-oil and biochar fractions of bioslurry. The other mechanism is the synergy between the bio-oil and biochar fractions that takes place during bioslurry combustion. This is demonstrated by the comparison between PM_{10} emissions from the direct bioslurry combustion and the sum of PM_{10} from the separate combustion of bio-oil and biochar fractions separated from bioslurry. The interactions between the combustions of bio-oil and biochar fractions lead to an increase in PM_1 and a decrease in PM_{1-10} during bioslurry combustion. The results further show that the second mechanism (i.e. interactions between the combustions of bio-oil and biochar fractions) accounts for ~ 80% of the total increase in PM_1 and ~ 60% of the total decrease in PM_{1-10}.

1. Introduction

Bio-oil/biochar slurry (i.e. bioslurry) is prepared by suspending fine biochar particles into fast pyrolysis bio-oil [1–4]. It offers a series of advantages including high energy density, low production cost, low energy and carbon footprints, suitable for transport, and adaptable to conventional combustion devices for stationary applications such as combustions in boilers [2–4]. Particulate matter (PM) emission especially those with aerodynamic diameter size less than 1, 2.5 and 10 μm (hereafter referred to as PM_1, $PM_{2.5}$ and PM_{10}, respectively) during fuel combustion, are important considerations for stationary power generation. These PMs are notorious due to high capture cost [5] and adverse impact to human health. Once emitted to the atmosphere, PM particles may easily pass through the human respiration system, deposit in the lung and cause related diseases [6]. While extensive investigations were carried out on PM emissions from the combustion of coal [7–11], biomass [12–17], bio-oil [18] and biochar [19], the studies on PM emission during bioslurry combustion is scarce [20].

The two-phase nature of bioslurry dictates that the combustion process of such a fuel and the related PM emission may be complicated. It is known that when biochar is mixed with bio-oil, inorganic species in biochar may be leached from biochar into bio-oil phase [21,22]. During combustion, reactions between bio-oil and biochar particles may potentially influence the transformation of inorganic species in bioslurry. For example, during bioslurry pyrolysis, the primary biochar may be deposited with coke produced from bio-oil cracking [23]. Both indirect and direct [24,25] evidences show that volatiles may react with char to enhance PM_1 emission during biomass combustion. Clearly, synergy is likely to take place during bioslurry combustion to influence PM emission but little investigation has been undertaken to study such an important aspect that is largely unknown.

Consequently, the objectives of this study are to carry out a systematic set of experiments to investigate the synergy on PM_{10} emission during the combustion of bioslurry in a laboratory-scale drop-tube furnace (DTF) in air at 1400 °C. To investigate the potential synergy, a series of fuel samples are considered, including bio-oil, biochar, bioslurry prepared from the bio-oil and biochar, bio-oil and biochar fractions filtered from bioslurry after its preparation and storage. Direct

---

[*] Corresponding author.
E-mail address: h.wu@curtin.edu.au (H. Wu).

https://doi.org/10.1016/j.fuel.2017.11.057
Received 18 June 2017; Received in revised form 15 November 2017; Accepted 16 November 2017

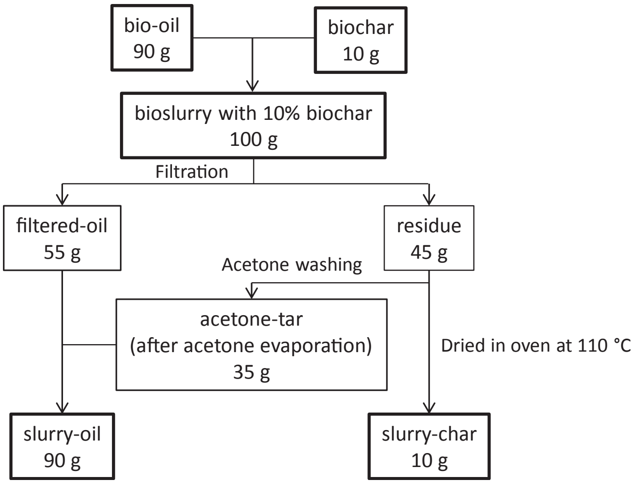

Fig. 1. Flow chart of sample preparation of bioslurry and its different fractions, i.e., slurry-oil and slurry-char.

experimental evidences are obtained to demonstrate the synergy, and key mechanisms responsible for such synergy are discussed.

2. Experimental section

2.1. Sample preparation

A bio-oil (produced from fast pyrolysis of pine wood at 500 °C) was supplied by a company. The biochar was produced from fast pyrolysis of an Australian pine wood at 500 °C via a quartz drop-tube/fixed-bed reactor (detailed description of the procedure can be found elsewhere [19]). To study the potential synergy on PM emission during bioslurry combustion, various samples were prepared and used according to the sample preparation flow chart illustrated in Fig. 1. The biochar was ground and sieved to the size fraction less than 75 μm for preparing bioslurry, according to a procedure described elsewhere [21]. Two bioslurry samples (at 5 and 10 wt% biochar loading levels) were prepared, hereafter referred to as "bioslurry with 5% biochar" and "bioslurry with 10% biochar", respectively. The bioslurry samples were stored for 1 week to achieve the equilibrium of inorganic species [21] prior to combustion experiments. Additional samples were also prepared via separating bio-oil and biochar fractions from the bioslurry with 10% biochar via a 0.45 μm polyvinylidene difluoride syringe filter. Briefly, the bioslurry was firstly separated into the filtered-oil and the residue via filtration. The residue, i.e. biochar particles soaked with the residue fraction of bio-oil, was further washed using acetone followed by filtration. Acetone was chosen because as a solvent it leaches little inorganic species from biochar [22]. The solid residue after filtration was then collected and dried in an oven at 110 °C to evaporate residue solvent, yielding a new biochar sample that is hereafter referred to as "slurry-char". The bio-oil fraction in the acetone solution was also collected after acetone evaporation in an oven at 45 °C and mixed with the filtered-oil to make as a new bio-oil sample hereafter referred to as "slurry-oil". The mass balance of these samples is presented in Fig. 1 for the bioslurry with 10% biochar.

2.2. Combustion experiments and collection of PM samples

Experiments on the combustion of bio-oil, biochar, bioslurry, slurry-oil and slurry-char were carried out in a laboratory-scale DTF (description given elsewhere [14]) in air at 1400 °C. Different feeders were deployed for these fuels. The solid samples (including biochar and slurry-char) were fed into the DTF via an entrained-flow feeder (description given elsewhere [19]). A stream of air flow (1.0 L/min) was used as carrier gas to entrain the fuel particles into the furnace at ~0.05 g/min. The liquid or slurry fuels (including bio-oil, slurry-oil, and bioslurry) were fed into the DTF via a spray nozzle set that consists of a pump syringe system (model: KDS LEGATO 210), a two-fluid nozzle set (model: VLA-3, VLT-3 and VLB, Paasche Airbrush) and water-cooling jacket. The feeding system was protected by both a water-cooling jacket and a stream of cooling gas (helium, 1.35 L/min) to maintain the temperature of the feeder below 70 °C. The atomisation conditions were adjusted to spray each fuel into droplets with similar mean droplet size (~50 μm) that was measured using a previous method [26]. The values of λ (the ratio of the actual air/fuel ratio to the stoichiometric air/fuel ratio) for all experiments were > 8 for achieving complete combustion.

PM_{10} samples were collected using a PM collection system that including a cyclone connected to a subsequent 13-stage Dekati low pressure impactor (DLPI) and a backup filter. The temperature of the sampling probe outlet and the PM sampling system was kept at 115 °C to avoid the condensation of acidic gases (e.g., SO_3 and HCl) in the flue gas [14]. All experiments were carried out at least in triplicates. Complete combustion was achieved in all experiments as thermogravimetric analysis suggested no unburned carbon was detected in the PM samples and the total organic carbon analysis showed no organic carbon was detected in the leachates from these samples washed by deionized water.

2.3. Characterisation and analysis of samples

The water contents of bio-oil, slurry-oil, and bioslurry were determined via Karl–Fischer titration [27]. The proximate analysis was conducted via thermogravimetric analysis (TGA, model: Mettler TGA/DSC 1 STAR). Elemental compositions were determined using a CHNS analyser (model: Perkin-Elmer 2400 Series II), with the oxygen content calculated by difference. The viscosity of a liquid/slurry sample was measured by a rheometer (model: Haake Mars II) fitted with acone-plate C35/4 sensor system and a Haake Thermocontroller TC501 according to a method detailed elsewhere [21]. The concentrations of inorganic elements, i.e. Na, K, Mg, Ca, Al, Si and Fe were measured via a previous method [28,29] that consists of ashing, fusion and quantification using either ion chromatography (IC, model: Dionex ICS-3000) or inductively-coupled plasma optical emission spectrometry (ICP-OES, model: PerkinElmer Optima 8300). The contents of Cl and S were quantified via an improved Eschka method [30]. The lower heating value was calculated via a previous correlation based on fuel chemistry [31]. The properties of bio-oil, biochar, bioslurry samples with 5 and 10% biochar, slurry-oil and slurry-char are listed in Table 1.

For the PM_{10} samples, the mass-based particle size distribution (PSD) was determined by measuring the mass of PM_{10} collected in each stage of DLPI and backup filter using a microbalance (model: Mettler MX5) with an accuracy of 0.001 mg. At least two batches of PM_{10} were prepared for measuring the concentrations of the inorganic elements. One is the analyses of Na, K, Mg, Ca, Al, Si and Fe in PM_{10} via a previous method [28] of multiple steps including ashing, fusion, digestion followed up by analysis using the ICP-OES. The other is for washing by Milli-Q water for 24 h to yield solutions that was analysed by IC (model: Dionex ICS-1000) for determining the concentrations of Cl and S in PM_{10} in the forms of Cl^- and SO_4^{2-} [14].

3. Results and discussion

3.1. Direct evidence for the presence of synergy on PM emission during bioslurry combustion

Fig. 2 compares the experimentally-measured particle size distributions (PSDs) of PM_{10} from the combustions of the bioslurry with 5% biochar and bioslurry with 10% biochar with the predicted values via the addition of the PM_{10} emission from the separate combustion of bio-oil and biochar. Evidence can be clearly seen for synergy on PM_{10}