



Emission of particulate matter during the combustion of bio-oil and its fractions under air and oxyfuel conditions

Chao Feng, Xiangpeng Gao¹, Hongwei Wu*

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

Received 4 December 2015; accepted 18 August 2016

Available online xxx

Abstract

The study reports the emission of inorganic particulate matter (PM) with aerodynamic diameters $<10\ \mu\text{m}$ (PM_{10}) during the complete combustion of bio-oil in a drop-tube-furnace (DTF) system at $1400\ ^\circ\text{C}$ under air and two oxyfuel conditions (i.e., $21\%\text{O}_2/79\%\text{CO}_2$ and $30\%\text{O}_2/70\%\text{CO}_2$, by volume). Three bio-oil samples were studied, i.e., a raw bio-oil, a filtrated bio-oil (prepared from the raw bio-oil after fine char particles were removed via filtration), and the water-insoluble fraction of the filtrated bio-oil (blended with ethanol). The total inorganic species of the raw bio-oil are distributed dominantly (74.7%) in the water-soluble fraction but minorly in the water-insoluble fraction (10.4%) and suspended fine char particles (14.9%). The results from the combustion experiments show that the PSDs of PM_{10} from the complete combustion of the raw and filtrated bio-oils have a bimodal distribution, with a fine mode at $\sim 0.03\ \mu\text{m}$ and a coarse mode at $\sim 2.0\ \mu\text{m}$. The water-insoluble fraction and the fine char particles suspended in the raw bio-oil have insignificant contributions to PM_{10} emission during the combustion of the raw bio-oil. It is the water-soluble fraction that plays a key role in the emission of PM_{10} during the combustion of the raw bio-oil. The data also show that PM_{10} emission during the complete combustion of bio-oil is insensitive to combustion atmosphere (air or oxyfuel) because complete bio-oil combustion is dominated by gaseous-phase reactions and the contribution of solid combustion is minimal. However, the excessive CO_2 under oxyfuel conditions leads to more Fe being partitioned into $\text{PM}_{0.1-1}$.

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Keywords: Bio-oil; Water-insoluble fraction; Combustion; Oxyfuel; PM_{10}

1. Introduction

Bio-oil produced from biomass fast pyrolysis is considered as a potential fuel for stationary combustion applications [1,2]. Bio-oil addresses the key issue of high logistic cost associated with biomass and is suitable for transport due to its considerably higher volumetric energy density [3,4]. As a fuel, bio-oil has high acidity, poor stability, high

* Corresponding author. Fax: +61 8 92662681.

E-mail address: h.wu@curtin.edu.au (H. Wu).

¹ Present address: Discipline of Electrical Engineering, Energy and Physics, School of Engineering and Information Technology, Murdoch University, 90 South Street, Murdoch, WA 6150, Australia.

water content, and high viscosity [4,5]. During biomass fast pyrolysis, a small proportion of inorganic species in biomass can partition into bio-oil [6]. While the concentrations of such inorganic species are low in bio-oil, the ash-related issues during bio-oil combustion may not be overlooked. On the other hand, oxyfuel combustion technology replaces air combustion with O_2/CO_2 combustion and consequently produces a CO_2 -dominant and sequestration-ready flue gas [7]. Therefore, bio-oil combustion under oxyfuel conditions becomes very attractive as it enables the renewable carbon in bio-oil to be readily captured for sequestration, potentially enabling power generation with negative carbon emission. However, there has been little investigation into ash transformation and the emission of particulate matter with aerodynamic diameters of $<10\ \mu\text{m}$ (PM_{10}) during bio-oil combustion under oxyfuel conditions. Furthermore, it is known that bio-oil contains suspended fine char particles, water-soluble fraction and water-insoluble fraction [6,8]. In particular, fine char particles suspended in bio-oil contribute significantly to the emission of PM_{10} from the incomplete combustion of the bio-oil [9]. However, the roles of different bio-oil fractions (especially fine char particles) in PM_{10} emission during the complete combustion of bio-oil under air and oxyfuel conditions are largely unknown. Consequently, the objective of this study is to investigate the emission of PM_{10} from the complete combustion of a fast pyrolysis bio-oil or its fractions using a laboratory-scale drop-tube furnace (DTF) at $1400\ ^\circ\text{C}$ under both air and oxyfuel conditions.

2. Experimental section

2.1. Bio-oil samples

The raw bio-oil was supplied by a commercial supplier. It was produced by fast pyrolysis of pine wood at $500\ ^\circ\text{C}$ and then stored in a fridge at $\sim 4\ ^\circ\text{C}$ prior to use. A filtrated bio-oil was prepared via filtering the raw bio-oil through a $0.45\ \mu\text{m}$ polyvinylidene difluoride (PVDF) syringe filter to remove suspended fine char particles. The filtrated bio-oil was further washed by water (water/bio-oil = 1/1, by volume). After phase separation, the bottom fraction of the water/bio-oil mixture was separated and air dried as the water-insoluble fraction of the bio-oil. The mass ratio of water/water-insoluble fraction/water-soluble fraction in the filtrated bio-oil is 1.0/1.2/1.8. For the purpose of spraying, the water-insoluble fraction was blended with ethanol (to the same proportion as it is in the filtrated bio-oil) into a solution. The three bio-oil samples (the raw bio-oil, the filtrated bio-oil, as well as the mixture of bio-oil water-insoluble fraction and ethanol) were used in the experimental program.

2.2. Bio-oil combustion and PM collection

A laboratory-scale DTF system with the details given elsewhere [10], was employed to conduct a set of bio-oil combustion experiments at $1400\ ^\circ\text{C}$ in air, 21% O_2 –79% CO_2 and 30% O_2 –70% CO_2 atmospheres. The atomization of bio-oil samples was achieved via an air-assist nozzle set (model: VLA-3, VLT-1 and VLB, Paasche Airbrush) under optimized conditions. In each experiment, via a stainless steel syringe powered by a syringe pump (model: KDS LEGATO 210), $\sim 20\ \text{ml}$ bio-oil sample was injected at a flow rate of $\sim 0.2\ \text{ml/min}$ into an inner tube and then atomized through the air-assist nozzle (atomization gas flow rate: $7\ \text{l/min}$). Using a previous method [11], the mean droplet diameters of the spray from the raw bio-oil, the filtrated bio-oil, as well as the mixture of bio-oil water-insoluble fraction and ethanol were determined as 46, 40 and $42\ \mu\text{m}$, respectively. The inner tube and the nozzle were cooled by double jackets (water-cooled and gas-cooled) to maintain the temperature at the outlet of the nozzle below $70\ ^\circ\text{C}$ in order to prevent bio-oil coking. The total flow rate of the combustion gas, including atomization gas and protection gas, was $8.35\ \text{l/min}$. The values of λ (i.e., the ratio of the actual gas/fuel ratio to the stoichiometric gas/fuel ratio) were estimated to be ~ 8 –13. Complete combustion was achieved in all experiments. PM samples were collected for $\sim 100\ \text{min}$ using a sampling system that consists of a cyclone and a Dekati low pressure impactor (DLPI) [10]. All experiments were at least conducted in duplicate to ensure repeatability. The temperature of flue gas at the outlet of sampling probe and also that of the PM sampling system was kept at $115\ ^\circ\text{C}$ in order to avoid the condensation of acidic gases (e.g., SO_3 and HCl) in the flue gas.

2.3. Sample analysis and characterization

Following a procedure detailed elsewhere [5], the water contents of the bio-oils were analyzed using Karl–Fischer titration. The ash contents of the bio-oils were determined via ashing the samples in a muffle furnace at $600\ ^\circ\text{C}$, following a temperature program that was detailed elsewhere [12]. Ultimate analysis of the three bio-oils was carried out using a CHNSO elemental analyzer (model: PerkinElmer 2400 series II). The contents of alkali and alkaline earth metallic (AAEM) species (mainly Na, K, Mg and Ca) in the three bio-oils were determined using a method recently developed [12]. The Al, Si and Fe in the bio-oils were quantified using a method detailed elsewhere [13]. The concentrations of Cl and S in the bio-oils were quantified via an improved Eschka method that was developed recently [14]. Table 1 lists the properties of the three bio-oil samples.

Fig. 1 presents the concentrations of major inorganic elements (Na, K, Cl, S, Mg, Ca, Al, Si,

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