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Effect of volatile–char interactions on PM_{10} emission during the combustion of biosolid chars under air and oxyfuel conditions

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ABSTRACT

This study reports the significant effect of volatile–char interactions on the emission of particulate matter (PM) during the combustion of biosolid chars in drop-tube furnace at 1300 °C under air and oxyfuel conditions. Slow and fast heating chars were prepared from biosolid pyrolysis and then interacted with the volatiles produced *in situ* from the pyrolysis of polyethylene (PE) and double acid-washed biosolid (DAWB) in a novel two-stage quartz reactor at 1000 °C (limited by the operating temperature of quartz). The results clearly show that under the experimental conditions, the interactions between chars and small non-oxygenated reactive species in both volatiles substantially decrease the yield of PM with aerodynamic diameter < 1 µm (i.e. PM_1), dominantly PM with aerodynamic diameter < 0.1 µm ($PM_{0.1}$) during char combustion. The interactions between oxygen-free volatiles (produced from PE pyrolysis) and char also reduce char macroporosity, leading to a reduction in the yield of PM with aerodynamic diameter between 1 µm and 10 µm (i.e. $PM_{1\text{-}10}$). However, the interactions between O-containing reactive species (produced from DAWB pyrolysis) and char significantly increase char macroporosity. Higher heating rate with shorter aging process during pyrolysis significantly weakens the effect of volatile–char interactions on PM_1 emission but intensifies its effect on $PM_{1\text{-}10}$ emission during char combustion. The combustion atmospheres have little effect on the net yield of PM contributed by volatile–char interactions. Combustion of chars interacted with the oxygen-free volatiles lead to a reduction in the yield of refractory elements (i.e. Mg, Ca, Al, Si, Fe, Ni, Co, Cu, Mn, V and Zn) in $PM_{1\text{-}10}$ but those interacted with the O-containing volatile resulted in an enhanced yield of these elements in $PM_{1\text{-}10}$. Furthermore, the interactions between O-containing reactive species and chars significantly decrease Cr yield in $PM_{0.1}$ due to formation of volatile chromium oxyhydroxides. In addition, volatile–char interactions have little influence on the forms of alkali and alkaline earth metallic (AAEM) species and P in PM_{10}, i.e. as $(Na, K)PO_3$ in PM_1 and $(Mg,Ca)_3(PO_4)_2$ in PM_{10}.

1. Introduction

Biosolid is by far the largest in volume amongst the by-products of wastewater treatments, and its processing and disposal is one of the most critical environmental problems [1,2]. Biosolid combustion or co-combustion with coal in stationary applications (e.g. fluidised-bed or pulverised fuel combustion) is considered as one of important technologies for not only volume reduction and toxic matter destruction but also recovering useful energy from biosolid [3–6]. However, the abundant inorganic and notorious trace elements in biosolid can be transformed into and emitted as particulate matter (PM) with the aerodynamic diameter smaller than 0.1, 1, 2.5 and 10 µm ($PM_{0.1}$, PM_1, $PM_{2.5}$ and PM_{10}) [5,7,8]. These fine particulates may escape into the environment and pose a high risk to both human health and the environment [9–11]. Therefore, PM emission is an important consideration in the design and operation of thermochemical processing of biosolid.

Practically, once subjected into a combustor/boiler, solid fuel particles such as biosolid would first experiences rapid devolatilisation and generate volatiles and char. Conventional approaches generally assume volatiles combustion and char combustion proceed independently and the potential interactions between volatiles and char are not considered [12,13]. However, such volatile–char interactions may potentially take place under various conditions. For example, in a fluidised-bed boiler (typically operates at 850–1000 °C [13]), the pyrolysing char particles are continuously fluidised, leading to volatile–char interactions for an extensive period in the bed. In a pulverised fuel (PF) boiler,

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volatile–char interactions can take place in the flame zone where the temperature of such interactions is very high (1500 °C or above [14]). Even through the time for such interactions under PF conditions is short, the potential role of volatile–char interactions may not be neglected. Extensive investigations have been done on the transformation of inorganic species in fuels into ash and PM_{10} [11,15–26] including the roles of S, Cl and alkali vapours [22,24,25] as well as the effect of temperature, oxygen concentration and sampling method [21,26]. Previous experimental results [27,28] implicitly suggest that the interactions between reactive volatiles and char particles may have an effect on PM_{10} emission during solid fuels combustion. A subsequent study [29], which deployed an innovative three-stage reactor system, further provided direct experimental evidence for demonstrating the significant role of volatile–char interactions in enhancing the emission of PM with aerodynamic diameter < 0.1 µm (i.e. $PM_{0.1}$) from the combustion of biosolid volatiles.

The potential volatile–char interactions may also influence the transformation of inorganic species in char and the structure of char hence PM_{10} emission during char combustion. The fundamental research question is “Does the exposure of char to reactive volatiles potentially influence the transformation of inorganic species in and the structure of char hence PM_{10} emission during the subsequent combustion of the char?” of which the answer is largely unknown.

To answer this fundamental research question, the research program needs to design a volatile–char interaction reactor that is capable of generating and separating fresh volatiles *in situ* then allowing the volatiles react with char under well-controlled conditions. It is also highly desirable to conduct the experiments at a high temperature with short interaction time. Unfortunately, the conventional reactors made from materials such as mullite or alumina are not suitable because those reactors can only be heated/cooled at a very slow rate (typically < 3 °C/min). Such lengthy (several hours) heating/cooling processes lead to significant experimental artefacts because of the extensive thermal effect on the chars before sample collection. In this study, these shortcomings have been overcome by the design of an innovative quartz volatile–char interaction reactor with the use of quartz frits for successfully conducting volatile–char interaction experiments to answer the aforementioned research question. However, the working temperature of quartz limits the volatile – char interaction reactor be only operated at temperatures below 1050 °C. Therefore, in this study, all experiments on volatile–char interactions have been conducted at 1000 °C with long interaction time. The experimental parameters have also been carefully chosen for the combustion of chars with or without volatile–char interactions in order to achieve the complete combustion, including small particle size (90–150 µm), excessive oxygen supply (with an O_2/fuel ratio of 30) and high temperature (1300 °C).

Therefore, this study is a fundamental investigation to answer the aforementioned key research question, i.e. providing experimental evidence to demonstrate that exposure of chars to reactive volatiles produced *in situ* from rapid pyrolysis can influence char properties hence PM_{10} emission during subsequent char combustion. Despite the constraints of the quartz reactor, nevertheless, the experimental results in this study show that volatile–char interactions not only enhance the release of the inorganic species from char particles, but also alter the pore structures of the chars, both of which affect PM_{10} emission during char combustion.

2. Experimental section

2.1. Samples

Biosolid (a different batch of biosolid sample from our previous study [29]) was sourced from a waste water treatment plant in Western Australia. The bulk biosolid sample was dried for 12 h in an oven at 105 °C, crushed and then sieved to yield the biosolid sample with a size fraction of 90–150 µm for use in subsequent experiments. To study the effect of volatile–char interactions on PM_{10} emission during char combustion, two chars were prepared, including a slow-heating char (SHC) and a fast-heating char (FHC). The SHC was prepared using a fixed-bed quartz reactor under slow pyrolysis conditions at 1000 °C. Briefly, 5 g of the biosolid was loaded onto the frit of a quartz fixed-bed reactor with an internal diameter of 60 mm. The reactor was then heated in a vertical tube furnace to 1000 °C at 10 °C/min using argon (1 L/min) as the sweep gas. The reactor was held at 1000 °C for a further 15 min before it was lifted from the furnace and allowed to cool to ambient temperature with the argon flow continuing to flow through the reactor. The FHC was prepared using a fixed-bed/drop-tube reactor (detailed elsewhere [30]) under fast pyrolysis conditions at 1000 °C. Briefly, the reactor with a pulse feeder was preheated in a vertical tube furnace with 1 L/min of argon as sweep gas. When the reactor temperature reached 1000 °C, ~0.4 g of biosolid was fed into the reactor in one shot. While the char remained on the quartz frit, the volatiles rapidly passed through the frit and were rapidly swept out of the reactor. Therefore, the pulse feeding achieved the minimisation of the interactions between char and volatiles during the preparation of fast heating char. The reactor was further held for 15 min then lifted from the furnace for cooling to ambient temperature with the argon flow continue to flow through the reactor. The pyrolysis experiments were repeated at least three times. The char yields of SHC and FHC are ~28.2% and ~22.4% on a dry basis (db), respectively.

Polyethylene (PE) and demineralised biosolid were used to generate oxygen-free and oxgen-containing volatiles *in situ*, respectively, to interact with SHC and FHC chars. Granular PE purchased from Sigma-Aldrich was crushed and sieved to size fraction of < 200 µm. The demineralised biosolid was prepared through a series of acid washing. First, the prepared biosolid was leached with 1 M HCl solution at solid to liquid ratio of 1:200 for 24 h before it was filtrated. The recovered solid was leached with 20 wt% HF solution at 80 °C in a sealed PFA vial for 12 h then the acid solution was evaporated. The recovered sample was once again subjected to leaching with HCl and HF before it was repeatedly rinsed with deionised water and filtrated until no Cl^- and F^- is detected in the filtrate (via Ion Chromatograph, Dionex ICS-1100 equipped with IonPac AS22-fast column and suppressed conductivity detector). The recovered solid sample was dried at 105 °C to yield double acid-washed biosolid (thereafter, termed as DAWB). Table 1 lists the properties of the biosolid, PE, DAWB, SHC and FHC samples used in this study. The DAWB has a low ash content of 0.3 wt% (on a dry basis) and contains little S and Cl. As shown in Table 1, PE only contains C and H, while DAWB also contains 14.51% of O and 2.77% N.

2.2. *Experiments on volatile–char interactions and char combustion*

As shown in Fig. 1a, the chars interacted with PE and DAWB volatiles were prepared using a two-stage quartz reactor which simultaneously permits generation of volatiles in Stage I and *in situ* volatile–har interactions in Stage II. Briefly, 0.3 g of SHC or FHC was loaded onto the frit of the outer reactor (Stage II) before loading the reactor into a vertical furnace pre-heated to 1000 °C. Upon reaching the reaction temperature, 1 g of PE or DAWB was fed into the inner reactor (Stage I) via an entrained sample feeder with argon (1 L/min) as entrain gas at a feeding rate of 0.05 g/min. The frit in the inner reactor of Stage I retained the char formed while the volatiles passed through the inner reactor to interact with the char (SHC or FHC) particles that were preloaded onto the frit of