Short communication

Interaction between sodium vapor and reactor wall during biomass combustion and its influence on measurement of particulate matter emission

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HIGHLIGHTS

- Na vapor interacts with alumina reactor wall during biomass combustion.
- The interaction results in the presence of instable water-soluble Na in the reactor tube.
- The interaction is dependent on the occurrence forms of Na in the combustion feedstock.
- Release of Na retained in the reactor tube via surplus Cl distorts PM measurement.

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ABSTRACT

A mallee bark (75–150 µm) was washed with 0.1 M sulfuric acid, followed by preparing a Na-exchanged bark via ion-exchange process and a NaCl-loaded bark via wet impregnation. The Na-exchanged bark and the NaCl-loaded bark were then combusted at 1300 °C in air using a novel laboratory-scale drop-tube furnace (DTF) which consists of an inner reactor tube cascaded into an outer heating tube. The results demonstrate the retention of water-soluble Na in the reactor tube after the combustion of the Na-exchanged bark and the NaCl-loaded bark, confirming the interaction between Na vapor and the reactor tube during biomass combustion. Such interaction is dependent on the occurrence forms of Na (or the availability of chlorine, Cl) in the combustion feedstock. In the absence of Cl (i.e., the Na-exchanged bark combustion), the amount of water-soluble Na retained in the reactor tube is ~4 times higher than that in the presence of Cl (i.e., the NaCl-loaded bark combustion). The data provide new insights into the roles of Cl in the emission of Na in the particulate matter (PM) with aerodynamic diameters of <10 µm (PM10). The retained water-soluble Na is instable and can be released again during the combustion of Cl-surplus polyvinyl chloride (PVC) particles, contributing to PM10 emission and thereby distorting the measurement of its emission.

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1. Introduction

The high contents of alkali metals, namely sodium (Na) and potassium (K), of lignocellulosic biomass are responsible for various ash related problems such as ash deposition, corrosion and emission of fine particulate matter (PM) during its combustion [1,2]. Extensive experimental studies were conducted on the transformation of these inorganic species during the combustion of solid fuels [3–14]. One-dimensional combustion reactors including down-fired combustor or drop-tube furnace (DTF) [3,4] are widely used because such reactors can achieve high temperatures (up to 1800 °C) and rapid heating rates (>1000 K/s). The reactor tubes in such combustion reactors are often made from high-purity dense alumina (Al2O3) due to its easy availability and excellent thermal properties [15–19]. However, during biomass combustion at high temperatures (e.g., ≥ 1300 °C), it is inevitable that alkali vapors from biomass combustion may interact with the alumina reactor tube of these one-dimensional combustion reactors. If the products of such interaction are instable, the alkali species may be released again into the flue gas (e.g., in presence of excessive Cl) in subsequent
combustion experiments. This can have some important implications to distorting experimental data on the transformation of inherent alkali metals and the measurement of PM emission during the subsequent biomass combustion. Unfortunately, little previous work has noticed such interaction, and in particular, its implications in the emission of PM with aerodynamic diameters of $<10 \mu m$ (PM$_{10}$) from biomass combustion. This motivates the work presented in this communication, in which the interaction between Na vapor and the alumina reactor tube during biomass combustion was successfully identified. Na was chosen because it behaves similarly with K during biomass combustion [20]. Two biomass samples with known Na occurrence forms were studied to further understand the effects of Na forms on such interaction. Its implications to inorganic PM$_{10}$ emission were also discussed.

2. Experimental section

Two sets of experiments were designed and conducted to provide indirect evidence and direct evidence, respectively, on the interaction between Na vapor and alumina reactor tube during biomass combustion. For the first set of experiments, $\sim 10 \, g$ mallee bark (Na content: 0.255 wt%, dry basis) was firstly burned at 1300 °C in air, using a DTF that equipped with a clean alumina reactor tube. Subsequently, $\sim 1 \, g$ Collie coal loaded with 1.23 wt% (dry basis) bromine (Br) was combusted in the same reactor tube under same conditions. The PM$_{10}$ produced from the coal combustion was collected and analyzed for Na content. The details on coal preparation, combustion experiments and PM$_{10}$ sampling are presented in Section 1 of the Supplementary Material.

The second set of experiments employed two key innovations to enable an in-depth investigation, providing direct evidence on the interaction of Na vapor and reactor wall during biomass combustion. One is the use of a series of purposely-prepared biomass samples with simplified Na occurrence forms, i.e., organically-bound Na ions (e.g., carboxylates) and water-soluble Na salts, which are known as main occurrence forms of Na presented in biomass [21]. The mallee bark was first washed with 0.1 M sulfuric acid ($H_2SO_4$) to prepare an acid-washed bark with very low Na content (0.027 wt%, dry basis). Basic fuel properties of the acid-washed bark are presented in Table S1 of the Supplementary Material. The acid-washed bark was then added to sodium acetate (NaOAc) solution prepare a Na-exchanged bark via ion-exchange process, which mainly contains organically-bound Na. The acid-washed bark was also mixed with sodium chloride (NaCl) solution prepare a NaCl-loaded bark via wet impregnation. The Na contents in the Na-exchanged bark and the NaCl-loaded bark are 0.496 and 0.498 wt% (dry basis), respectively. Whereas no chlorine (Cl) is found in the Na-exchanged bark, its content in the NaCl-loaded bark is 0.77 wt% (dry basis). The Na-exchanged bark and the NaCl-loaded bark were then used for combustion experiments. Details on sample preparation, combustion experiments and PM$_{10}$ sampling are presented in Section 1 of the Supplementary Material. The other innovation is to employ a novel DTF system that consists of two annularly-arranged alumina tubes (see Fig. 1). It is modified from the one used previously [9,14] via annually cascading a small inner alumina reactor tube (ID: $\sim 26 \, mm$, termed as “reactor tube” hereafter) into a big outer alumina heating tube (ID: $\sim 54 \, mm$, termed as “heating tube” hereafter). The reactor tube can therefore be disassembled easily for quantifying Na retained in it.

All combustion experiments were conducted at 1300 °C in air. Details on combustion experiments and PM sampling are described in Section 3 of the Supplementary Material. After an experiment, the DTF was cooled down to room temperature and the reactor tube was disassembled and washed with ultra-pure water. The leachate was then analyzed using ion chromatography (IC, model Dionex ICS 3000) to quantify water-soluble Na retained in the reactor tube. Detailed procedures for the analyses of the combustion feedstock, the PM produced and the leachate from washing the reactor tube are presented in Section 4 of the Supplementary Material.

3. Results and discussion

Indirect evidence on the interaction between Na vapor and alumina reactor tube is implied via the results presented in Fig. S1 of the Supplementary Material, which compares the mass of Na in the PM$_{10}$ from the Br-loaded coal combustion and that of Na in the input feedstock. It demonstrates that the measured Na mass in the PM$_{10}$ substantially exceeds the total amount of Na input from the feed, implying additional Na sources existing in the combustion system. To identify the possible Na sources, a section of the clean alumina reactor tube was cut into pieces and the chips were digested in a mixture of nitric acid and hydrofluoric acid, followed by quantification using the IC. No Na was detected in the clean reactor tube. Thus, the additional Na in the PM$_{10}$ must be from that retained in the reactor tube during the previous mallee bark combustion, due to interaction between Na vapor and the reactor tube.

To provide direct evidence on the interaction between Na vapor and the reactor tube during biomass combustion, the Na-exchanged bark and the NaCl-loaded bark were combusted in the purposely designed DTF that consists of two annularly-arranged alumina tubes. As depicted in Fig. 2a, $\sim 0.22$ and $\sim 0.97 \, mg/g$ dry feedstock of water-soluble Na, corresponding to $\sim 4.5$ and $\sim 19.6 \, wt\%$ of total Na in the feedstock, are retained in the reactor tube after the combustion of the NaCl-loaded bark and the Na-exchanged bark, respectively. As aforementioned, there is no Na found in the clean reactor tube. In addition, it is well-established that Na is easily released into gas phase during biomass combustion [13,14] and the collision of fuel particles with the reactor wall is unlikely in the laminar-flow DTF. Therefore, the water-soluble Na retained in the reactor tube is most likely...