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Full Length Article

Emission factors of mercury and particulate matters, and in situ control of mercury during the co-combustion of anthracite and dried sawdust sludge

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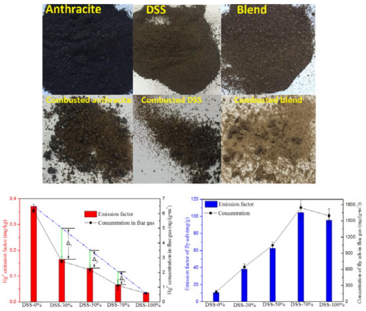
GRAPHICAL ABSTRACT



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ABSTRACT

Anthracite and dried sawdust sludge (DSS) were demonstrated as a complementary combination. Since air pollution has attracted great concern, this paper studies the emission characteristics of mercury and particulate matters (PMs) during the co-combustion process. The results indicated that no Hg^{2+} was produced in all cases. The Hg^0 emission factor decreased significantly with the increasing of DSS. The rising temperature from 800 to 900 °C slightly promoted the Hg^0 emission, but the further increasing temperature caused a decreasing of Hg^0 emission. Oxygen-enrich atmosphere accelerated the release of Hg^0 from anthracite, but the DSS combustion was independent on the atmospheric conditions. The emission factor of PMs for DSS was 10.5 ± 1.7 mg/kg which was 9 times higher than that of anthracite combustion (95.2 ± 7.7 mg/kg). The results of in situ control of Hg^0 demonstrated the co-combustion of fuel and Ca-based additives could not deeply reduce Hg^0 emission, however the integrated approach of gas phase oxidation combined with wet absorption was satisfactory in terms of Hg^0 control, and the way of post-combustion injection was better, the oxidation efficiencies of Hg^0 reached 62.5%. The main existing forms of mercury were determined as $HgSO_4$ and HgX_2 (X: Br or Cl) by XPS, the reaction mechanism of Hg^0 removal was proposed accordingly.

1. Introduction

Co-combustion of sludge and coal is a desirable method for treating sludge, with the merits of the decreasing of the sludge volume, thermally decomposing the organic/toxic components in sludge, recovering the energy from sludge [1–5]. During the co-combustion process, a number of volatile compounds in sludge are released and combusted in the early stage of co-combustion [6]. The heat generated from the volatile combustion increases the local temperature and promotes the further release of volatile compounds from coal, which then results in an acceleration of fix carbon combustion [7,8]. In turn, the high temperature owing to fix carbon combustion is also beneficial for the

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burnout of sludge [9,10], thus the co-combustion of coal and sludge can reduce the harmful effects of sludge on the environment and improve the combustion performance of coal.

The cases of co-combustion of tannery sludge and bituminous coal [2], pulp mill sludge and bituminous coal [11], dried sewage sludge pellets and coal gangue [12], semi-anthracite and paper mill sludge [13], rice husks and coal [14], pine sawdust and coal had demonstrated the co-combustion way was a secure treatment. While in terms of practical application, the feasibility of co-combustion technology not only depends on the combustion behaviors but also is determined by the emission characteristics of the air pollutants. Hence, the emission factors of air pollutants for the co-combustion process should be systematically studied. Dong et al. [2] revealed that the fraction of sludge contributed to the emissions of NO_x and some trace elements. Yang et al. [12] determined the emission factors of SO_2, NO_x and the trace elements during co-combustion of sewage sludge and coal gangue. Zhang et al. [15] studied the emissions of SO_2, NO_x, HF, HCl and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) during co-combustion of bituminous coal and pickling sludge in a drop tube furnace. It had been reported [16,17] that the emissions of SO_2 and NO_x might be affected by the composition of fuels and the combustion temperature.

Most of the sludges also contain a number of heavy metals (HM), in which mercury is the most concern as a result of its bad characteristics of bioaccumulation, long distance migration and biotoxicity. Therefore, the study on mercury emission and its distribution is of significance. Several studies [18–21] have examined HM emission behaviors during the co-combustion of sewage sludge (SS) and coal, and bituminous coals were mostly used in these studies, however anthracite was rarely involved. SS is actually produced in the biological wastewater treatment facilities and contains lots of organic, inorganic and even toxic substances and pathogens [22], the calorific value of SS was low and not so proper to be used to co-combust with coal. Compared with SS, dried sawdust sludge (DSS), with high content of organic combustibles and less inorganic compounds and toxic substances, possesses relatively high calorific value and low ignition temperature [23], which is suitable to be used as a combustion improver for anthracite since anthracite has a high calorific value but a very high ignition temperature. However, few papers studied the emission characteristics of mercury and particulate matters (PMs) during the combustion of biomass-based DSS. Thus in consideration of these differences in the fuel and sludge, the research on the emission characteristics of mercury and PMs in the co-combustion of DSS and anthracite is meaningful. Circulating fluidized bed (CFB) combustion has been verified to be an efficient way to conduct the co-combustion of coal and sludge. Hence, the combustion temperature and O_2 contents selected in the current study were based on the operational parameters of CFB system. Normoxic and oxygen-enriched atmospheres (21% and 30%) were commonly used in the combustion of coal and solid waste or sludge [24,25], thus three atmospheric conditions, i.e. oxygen-leaned, normoxic and oxygen-enriched, were adopted. The typical combusted temperature for CFB boilers were 850–950 °C [26,27], thus the investigated temperatures were determined as 800, 900 and 1000 °C. Finally, the in situ control of mercury, the determination of mercury existing forms in the removal product and the reaction mechanism relating to mercury removal were also studied.

2. Experimental

2.1. Materials

The anthracite and DSS used in the experiments were obtained from Longyan coal district and some sawmill in Fuzhou (Fujian province). Anthracite and DSS were dried at 105 °C for at least 24 h, then both of anthracite and DSS were ground into powders with the particle size of 200-mesh. The generated Hg^{2+} in the flue gas was initially removed by NaOH (since most of industrial boilers have installed alkaline scrubbers to remove acidic gas of SO_2), then the residual Hg^{2+} was completely absorbed by 1.0 mol/L of KCl, the generated Hg^0 was completely absorbed by H_2SO_4-$KMnO_4$ (10%v/v–4%w/w). The pipe lines used after the furnace were made by Teflon.

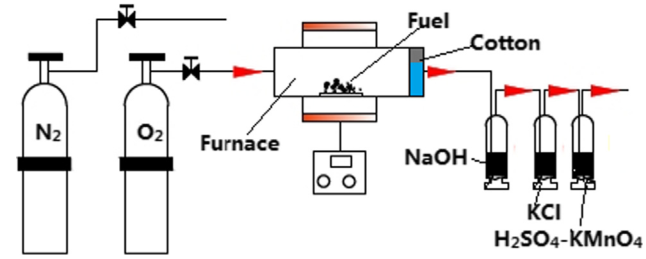

Fig. 1. Schematic diagram of the experimental apparatus.

2.2. Equipment and procedures

The combustion experiments of anthracite, DSS and their blends were carried out in a horizontal tube furnace (SK-2-13, Yong Guang Ming Medical Instrument Company, Beijing, China) with a temperature precision of ± 3 °C, as shown in Fig. 1. In real working conditions of coal-fired boilers, the fuels are burned at a relative stable temperature. Thus in the current study, the temperature of the tube furnace was firstly increased to the desired value, then the sample was pushed into the tube furnace (Fig. 1a). This method can avoid the increasing of the furnace temperature as a result of the sample is burned in the combustion chamber. When the burning reaction was terminated, the sample was pulled out from the tube furnace to the cooling position (Fig. 1b), as described in Wang's method [6].

During the combustion process, the feeding gas composed of N_2 and O_2 controlled by mass flowmeter controller entered into the tube furnace. A sample of 2 g (± 0.01 g) was used for each test, in which, the blends of anthracite and DSS (1:1) were prepared by physically mixing the powders of DSS and anthracite. The total gas flow was 1.0 L/min. After the combustion, the flue gas firstly passed through a weighted cotton that was used to retain the PMs, after where, the flue gas entered sequentially into the solutions of NaOH, KCl and H_2SO_4-$KMnO_4$. The mercury concentrations in NaOH, KCl and H_2SO_4-$KMnO_4$ were detected by a cold atom fluorescence spectrometry (AFS-9230, Jitian company, China). The effects of DSS proportion (0, 30, 50, 70, 100%), O_2 content (10%, 21% and 30%) and combustion temperature (800, 900 and 1000 °C) on the emission of Hg^0 were studied. Since the PMs emission was mainly affected by the DSS proportion, we just assessed the effect of DSS proportion on the emission factor of PMs.

2.3. Mercury control methods

Two methods were employed to in situ control of Hg^0. The first method is the co-combustion of blend and Ca-based additives such as $CaCO_3$, $CaCl_2$ and $CaBr_2$ with the mass proportions of 10% and 30%. The other method is a combined approach of pre- or post-combustion injection of vaporized complex oxidant with wet absorption. The used oxidants included H_2O_2 (15%), UV/H_2O_2-g, H_2O_2/$Na_2S_2O_8$ (15: 0.5% w/w), H_2O_2/NaClO (15: 1.0%w/w), H_2O_2/$NaClO_2$ (15: 0.5%w/w) and H_2O_2/HBr (15: 0.5%w/w) [28–33].

2.4. Analysis and characterization methods

In order to clearly reveal the combustion characteristics of anthracite and DSS, TG analyses were performed in a thermo-gravimetric analyzer (Mettler-Toledo TGA/SDTA851e). The air dried samples of 20 mg were used for each analysis. N_2 or air was used as a reaction gas with a flow rate of 80 mL/min. The heating rate was set to 10 °C/min,