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Transformation and release of potassium during fixed-bed pyrolysis of biomass

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A B S T R A C T

To study the release and transformation of fuel K during rapid pyrolysis of biomass, wheat straw, corn stalk and rice hull are pyrolyzed in a fixed-bed reactor system during 400–1000 °C, and weight measurement, elemental composition analysis, and chemical fractionation analysis are performed. The effects of fuel type, pyrolysis temperature, co-pyrolysis of different fuels, and water washing pretreatment are discussed. The results show that for all biomass fuels, the released K is far less than the water-soluble K and a sudden increase occurs in the fraction of ion-exchangeable K at 400 °C, whereas a significant increase happens in the fraction of insoluble K above 800 °C. Wheat straw releases less than 5% of K at 400 and 500 °C. As temperature rises, the K release increases abruptly and around 40% of K enters the gas phase at 1000 °C. Rice hull has a slow and linear K release with increasing pyrolysis temperature. Corn stalk has the lowest K release during 400–800 °C. Co-pyrolysis of wheat straw and rice hull reduce the K release at 1000 °C, and the biggest decrement is 0.76 mg g^{-1}. Water washing removes all the water-soluble K of corn stalk and part of ion-exchangeable K enters the gas phase during pyrolysis of the washed sample. Water washing decreases the K release from 2.77 to 0.18 mg g^{-1} at 1000 °C.

1. Introduction

In recent years, biomass has been attracting increasing attention because of its renewable and environmentally friendly characteristics [1–4]. Utilizing biomass for heat and/or power production would significantly reduce CO_2, NO_x and SO_x emissions that are caused by combustion of fossil fuels [5]. It is believed that taking biomass as a combustion feedstock of boiler is a prospective scheme for utilization of biomass [1–5]. In North America and Europe, biomass-fired boilers have been serving for more than two decades [6,7]. Among these boilers, the grate-fired boiler has been broadly employed. In China, a few biomass-fired boilers have been successively built and operated during last ten years [8], and grate firing is still the most widely used firing method. However, the grate-fired boiler has been experiencing serious problems of fouling, slagging and high-temperature corrosion according to the foreign experiences [6,9–12]. In China, although the operational time of the grate-fired boiler was relatively short, the tube bursting of superheaters began to occur due to the deposit-induced high-temperature corrosion [13–16]. These problems appeared in biomass-fired boilers have been considered to originate from the release of K, Cl and S during combustion of biomass.

The occurrences of ash deposition and high-temperature corrosion on superheaters have experienced three processes. First, parts of K, Cl and S go into the gas phase to form HCl, Cl_2, SO_2, SO_3, KOH, KCl or K_2SO_4 during combustion of biomass [7,17–19]. Second, gaseous potassium salts condense in the gas phase and on the surface of superheater to form sticky particles and condensed layer, respectively. Then the ash deposition occurs when fly ash particles are trapped by the sticky condensed layer [9–11,16]. Finally, the ash deposit (mainly composed of KCl and K_2SO_4) and metallic matrix react with HCl, Cl_2, SO_2 or SO_3, which would cause the growth of ash deposit and high-temperature corrosion [9,12,20–23]. Obviously, potassium is involved in all three processes and plays a crucial role. Compared with coal, biomass generally has much higher potassium content [5,24]. Although pyrolysis is different from combustion with regard to the surrounding environment and temperature fields, it is still meaningful to investigate the transformation and release of potassium during biomass

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pyrolysis, because pyrolysis happens at the primary stage of combustion. The investigation will be significantly helpful to understand the origin of ash deposition and high-temperature corrosion occurred on superheaters and find methods to solve these problems. It can also be useful to the design of biomass-fired boilers or other thermal conversion equipment.

Many studies [17–19,25–32] have been carried out to investigate the release of potassium during pyrolysis of various biomass fuels. Among these studies, Olsson et al. [29], Davidsson et al. [30,31], and Kowalski et al. [32] applied the surface ionization method to evaluate the time-resolved potassium release from wheat straw, wood waste, birchwood, or wood saw dust. Unfortunately, these evaluations were qualitative. In the other studies [17–19,25–28], the potassium release was quantified on the basis of weight measurements and elemental composition analyses of raw biomass, char and ash. In the studies of Okuno et al. [25] and Keown et al. [26], to quantify the potassium contents of raw biomass and char, samples were burnt and then the resultant ashes were analyzed. Deviations would be introduced because part of potassium could release although the ash may be prepared at a low temperature. Thus, the better choice for potassium analysis should be directly pressurized acidic digestion combined with inductively coupled plasma spectrometry [17–19,27,28]. It is well known that the release behavior of potassium is closely related to its occurrence mode in biomass [7]. However, the focus on the transformation of occurrence mode of potassium during biomass pyrolysis was extremely limited [19]. The pretreatment of water washing seems to be an effective method to remove potassium and has the potential to alleviate the deposition and corrosion problems in biomass-fired boilers [33–35]. To date, the quantitative assessment on the effect of water washing on potassium release is still lacking. Sometimes the feedstock of the biomass-fired boiler consists of several different biomass fuels [13–15,20,36]. Interaction between these fuels may affect the potassium release during the co-firing, especially when a certain fuel has relatively high silicon content [6,7,17]. To our knowledge, the effect of interaction between different biomass fuels on potassium release during pyrolysis has seldom been reported.

In this study, a fixed-bed reactor system is built up to simulate the conditions on the grate of the biomass-fired boiler. The release of potassium is evaluated quantitatively during rapid pyrolysis of wheat straw, corn stalk and rice hull in a wide temperature range. The transformation of occurrence mode of potassium in raw biomass and char is investigated at different temperatures through chemical fractionation analysis. The effects of fuel type, pyrolysis temperature, co-pyrolysis of different fuels, and water washing, are discussed in detail.

2. Materials and methods

2.1. Sample preparation

In this study, three biomass fuels are used for investigation, including wheat straw, corn stalk and rice hull. These biomass fuels are all collected from the rural areas of Xi'an, Shaanxi Province, China. After being cut by an herb shredder, all the samples are sieved to 280–450 μm [35]. Washing pretreatment is performed on corn stalk samples, and the details about washing are described in our earlier studies [34,35]. The corn stalk sample is submerged and soaked in the deionized water with a temperature of 30 °C for 3 h. The biomass mass-to-water ratio is the sample of 12.5 g to the deionized water of 1 L. All the raw and washed biomass samples are sent to the Comprehensive Laboratory of Coalfield Geological Bureau (Xi'an, Shaanxi Province) for proximate and ultimate analyses, and ash composition analysis [34,35]. The ash preparation is followed ASTM E830 at 575 °C. Parts of potassium, sulfur and chlorine may release when the ash is prepared [7,28]. Thus for the contents of sulfur and chlorine, the determinations are performed directly on the raw or washed sample according to the relevant standard methods, rather than on the ash sample [35]. For the potassium content, the raw or washed sample is directly dissolved by pressurized acidic digestion and then analyzed by inductively coupled plasma spectrometry in this study. The smaller the sample size, the easier the dissolution of sample in acid. In addition, although the chemical fractionation analysis is a nonstandard method, a smaller sample size is inclined to be used to ensure the complete permeation of sample by the leaching agents [6,37]. Thus in this study, all the raw and washed biomass samples of 280–450 μm are further cut and sieved to 150–250 μm. After air-drying at 105 °C for 24 h, samples are analyzed for potassium content and sent to the pyrolysis experiment and the chemical fractionation analysis.

The fuel properties of raw and washed biomass samples are listed in Table 1 [35]. For the potassium content, the standard deviation is calculated from the three replicates of measurements. For the other results, the standard deviations are provided by the Comprehensive Laboratory of Coalfield Geological Bureau.

To examine the possible interaction between different biomass fuels on potassium release, some samples are prepared by mixing dry samples of wheat straw and rice hull. The chosen mass fractions (hereinafter denoted as *MF*) of rice hull in the mixed sample are 10%, 30%, 50%, 70% and 90%.

2.2. Pyrolysis experiment

Pyrolysis experiments are conducted in a fixed-bed reactor system, which is illustrated in Fig. 1. A quartz reactor that has an inner diameter of 39 mm is located in an electric heating furnace. A dry biomass sample of 2 ± 0.02 g is placed in a quartz cup with an external diameter of 35 mm. An alumina filter is laid on the quartz grating, which can avoid the leakage of biomass sample and ensure the penetration of the carrier gas. The height of the sample bed ranges from 10 to 21 mm, depending on the sample density. The quartz tube that has a smaller diameter than the quartz reactor is movable and an inner frosted surface is manufactured on its top end. Thus, the quartz cup that has an external frosted surface on its bottom end can be equipped on the top of the quartz tube. A water chamber is surrounded at the bottom end of the quartz reactor for cooling the biomass samples. Water with a temperature of 20 °C will go through the water chamber during the pyrolysis experiments.

The pyrolysis experiments are performed from 400 to 1000 °C. First, the quartz reactor is heated to a preset temperature. Then, the quartz cup and the movable quartz tube are inserted into the quartz reactor, and the dry biomass sample is cooled by the water chamber. After that, the mass flow meter No. 1 and the inlet tube are opened, and the quartz reactor is purged by the pure N_2 to make sure the whole reactor is in a nitrogen atmosphere. Later, the mass flow meter No. 1 is closed and the mass flow meter No. 2 is opened, and carrier gas (pure N_2) of 200 mL min^{-1} goes through the reactor from the top to the bottom. The quartz cup is moved forward to the constant temperature zone (in the middle of the electric heating furnace), and the biomass sample is pyrolyzed for 30 min and turns into char. At last, the quartz tube is

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