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Investigation on the fusion characterization and melting kinetics of ashes from co-firing of anthracite and pine sawdust

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ABSTRACT

Co-firing of biomass and coal adds further complexity to variations in ash fusion temperature (AFT), which is regarded as a key parameter reflecting ash agglomerations. This study is focused on evaluating the ash fusion behaviour and kinetics of blends of pine sawdust (PS) and Jincheng anthracite (JC). The ash properties, ash transformation and evolution behaviours during the co-firing were determined. The AFT variations of JC/PS blends did not show a linear variation with a rising biomass ratio. The PS addition promoted the reaction of potassium with quartz to form muscovite, leading to a reduction of arcanite. As the ashing temperature was elevated, the most perceptible effect was the increasing agglomerate size due to adhesion of fine powders. For a given temperature, with a rising PS ratio, the total weight loss, maximum weight loss rate and the exothermic peak distinctly increased, and their relevant peaks shifted to a higher temperature zone. Herein, for different blends, the blending ratio of 30 wt% JC and 70 wt% PS was suggested as optimal for preventing ash-related problems. The ash fusion of blends requires less energy than pure ash at a certain temperature, which can be explained in terms of first-order-reaction with Arrhenius theory.

1. Introduction

In recent years, the declining energy supplies, severe greenhouse effect, environmental constraints and fossil energy depletion, have increased the interest in exploring clean energy sources, and among such sources, biomass is a carbon-neutral and renewable energy source [1–3]. Presently, all countries are showing a tendency to increase the percentage share of biomass usage in primary energy consumption. By 2050, 33–50% of the world's energy consumption will be met by biomass [4,5]. From an economic point of view, co-firing of biomass and coal is of growing interest, since apart from its environmental benefits, biomass extends the range of available coal. It also offers technical and economic benefits by increasing the amount of energy supply options as well as avoiding seasonal supply difficulties, allowing for the use of existing infrastructure [6].

However, the co-firing of biomass and coal also has certain drawbacks, such as ash deposition, fouling and slagging, resulting in ash agglomeration, sintering and corrosion as well as reductions of combustion efficiencies in boilers [7–9]. Co-firing adds further complexity to the ash characteristics due to possible interactions between the minerals of biomass and coal. Ash fusion behaviour is one of the crucial parameters for assessing ash sintering and agglomeration propensity. Generally, the ash fusion temperature (AFT) is considered as an important parameter to reflect the difficulty level of ash agglomeration and sintering, which strongly affects ash deposition and slag formation. The AFT of biomass and coal blends was different from that of ash from single biomass and coal [8]. Apart from the own minerals in coal and biomass affecting the blends AFT, the new minerals generated by reactions of the minerals in coal and biomass can also affect it. And there were clear differences in the mineral contents between biomass and coal [9].

The investigation of ash fusion provides a better understanding of the mechanisms of subsequent ash deposition, fouling and slagging. Previous studies [10,11] confirmed that the AFTs can be greatly influenced by the process temperature during ash formation. Knowledge of ash fusion behaviour and the influence of temperature and blending ratio can help reduce ash-related problems and avoid fuel combinations with unwanted characteristics. Therefore, understanding the ash fusion behaviours of these fuels both together and separately is important, since coupling reactions can occur between the reactions that can influence the efficiency of

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combustion boilers.

As a type of fast-growing forestry plant, masson pine has been widely cultivated and used to produce wood products in China. China has more than 2 million km^2 of masson pine [8]. During its utilization process, large amounts of pine sawdust (PS) are inevitably generated, thus showing great potential as a bio-energy residue of the future. A study conducted by Xiao et al. [11] indicated that the PS showed a serious slagging/fouling tendency due to its high alkali content. When PS was combusted under different temperatures, its ash content negatively correlated with temperature, and the alkali metals became more volatile. To the best of our knowledge, despite the fusion behaviours of the ash from coal and biomass blends having been widely investigated, due to the diversity and variable amount of PS co-fired with coal, the formed ash shows different properties in comparison with pure fuel ash, and it has not been characterized [12].

To date, investigations on the fusion developments of ashes from biomass and coal blends are limited. There is a lack of sufficient information concerning the ash fusion properties of PS and coal blends, as well as a detailed evaluation about the effects of ashing temperatures and blending ratios on ash fusion properties and kinetics. This study evaluates the ash fusion properties and kinetics during PS co-firing with a Chinese anthracite at different temperatures and with various blending ratios. The ash analyses and ash transformation during the combustion of PS, coal as well as blends of the two were also determined. Results from this study will provide useful information that can be used to reduce ash-related problems and promote the wide utilization of co-firing of masson pine and coal for heat and power production.

2. Experimental section

2.1. Materials

Jincheng coal (JC), which is a type of representative anthracite from Shanxi Province, China, is selected as a coal sample in this study. As a major woody biomass residue from masson pine, PS has abundant reserves in China and is chosen for this study. The PS is taken from the countryside of Shenyang, Liaoning province, northeast China. Prior to the tests, the as-received coal samples were air-dried, and then crushed and sieved by a 100-mesh sieve to a size fraction of <0.154 mm. The PS samples were firstly dried at 105 °C ± 0.5 °C for 24 h in an oven. Then, the samples were grinded and pulverized using a high-speed rotary cutting mill. Finally, they were sieved with a 100-mesh sieve. The materials that passed through the sieve (<0.154 mm in size) were gathered in a closed container and kept for analysis. Coal and biomass blends were prepared, with 30 wt%, 50 wt% and 70 wt% PS mass additions. For convenience throughout this manuscript, the blends were denoted in a general form of JC*x*PS*y*, with *x* and *y* indicating the mass percentages of JC and PS in the blends, respectively. Table 1 shows the proximate and ultimate analysis of prepared samples.

2.2. Ash preparation

There are no specific standards available in China for the preparation of biomass ash. In this study, the ashing temperature of 600 °C during biomass ash preparation was chosen since the volatilization of some alkali chlorides (such as KCl, NaCl) in biomass ash may occur above 700 °C; meanwhile, 500 °C was too low of a temperature to prepare biomass ash due to the high contents of combustible substances in the ash [11–13]. Thus, the temperature range of 500–700 °C best reflects the chemical characteristics of biomass ash. The ashing temperature of the prepared samples was set at 600 °C according to the ASTM E1755-01 standard [14]. This temperature can minimize the evaporation of alkali metals and avoid the possible volatilization of inorganic elements due to flame burning during the ashing process [15]. For individual coal and biomass/coal blends, an ashing temperature of 815 °C was chosen according to the standards for coal ash preparation in China (GB/T212-2008) [16], offering an opportunity to obtain information on proceeding temperature-induced mineral formations in coal ash and likewise details about the starting decomposition of carbonates, sulfates, and other mineral phases [17].

To maintain the consistency of the ashing temperature for different fuel samples and to better understand the properties of the relative ashes, the preparation of ashes from individual coal, biomass and their blends by combustion in a muffle furnace (SX2-15-12, Dongtai Shuangyu Instruments Co., Ltd., Jiangsu, China) followed the previously described standards. The differentiation in the final temperatures comes from the ash compositions of coal and biomass being performed at 815 °C and 600 °C, respectively, as based on the standards. The storage interval of the muffle furnace was 1 °C, and the atmosphere was air. Note that the ashes prepared using this method were not intended to represent real boiler ashes, but to serve as a standard fuel and as an ash testing method to predict the ash fusion behaviour in boilers. A real-world ash boiler is highly variable in nature [18].

In this study, about 10 g of each sample (including the single coal, biomass and their blends) was thinly spread onto a aluminium mullite crucible and heated in a muffle furnace in air at a heating rate of 10 °C/min from room temperature to 250 °C and hold for 30 min, then increasing the temperature to 600 °C or 815 °C within 30 min, and kept at this temperature for 2 h to burnout the inorganic matter in those samples. The ashing procedure is used to produce ash samples under controlled temperatures and to avoid the volatilization of inorganic elements due to flame burning. Finally, the muffle furnace was switched off and the ash was removed and cooled to room temperature. All the ash samples were collected in an airtight container for further analysis.

2.3. Determination of ash characteristics

The ash fusibility was determined using an ash fusion determination meter (5E-AFIII, Kaiyuan Instruments Co, Ltd., Changsha, China). The test involved heating a sample cone of specified geometry at 5 °C/min in air, up to about 1500 °C and recording the temperatures that characterize ash melting, *i.e.*, deformational temperature (DT), softening temperature (ST), hemispherical temperature (HT) and fluid temperature (FT).

The ash chemical composition was measured by X-ray fluorescence (XRF) (ZSX100e. Rigaku Co. Ltd, Japan). The ash morphology

Table 1
Proximate and ultimate analysis of prepared samples (on air dried basis).

Materials	Proximate Analysis (wt.%)				Ultimate Analysis (wt.%)				
	Volatile Matter	Moisture	Fixed Carbon	Ash	C	H	O	N	S
Jincheng coal	8.11	2.29	72.00	17.85	71.27	3.025	4.95	0.92	0.86
Pine sawdust	77.67	7.89	14.34	0.71	49.55	6.11	41.08	0.25	0.33