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Ash fusion characteristics of bamboo, wood and coal

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ABSTRACT

Ash fusion characteristics of bamboo, masson pine and coal were investigated using X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). XRF results showed that the major components of bamboo ash were K_2O, SiO_2 and SO_3. Masson pine ash mainly included Fe_2O_3 and CaO. Coal ash was comprised of SiO_2, Al_2O_3, CaO, Fe_2O_3 and SO_3. The variation of major components resulted in different fusion characteristics, such as the low fusion temperature of bamboo ash and the high thermal conductivity of masson pine ash. XRD results confirmed chemical compositions transformation because six main chemical reactions occurred during thermal treatment process. SEM and TEM results showed that the elongated grains or plates of various sizes of all thermal treated ashes disappeared and they had less pores and denser structure on the surface, indicating structure transformation. The results from this research will be helpful to promote utilization of masson pine and bamboo for fuel in power station of China.

1. Introduction

Coal is one of the main fossil fuels used around world. The utilization of coal as energy products has resulted in some environmental problems such as acid rain and ozone depletion [1]. Biomass is considered as an alternative to coal because it is sufficiently "green" renewable and CO_2-neutral energy source. In China, 1000 MW of electricity will be generated from biomass, replacing 2.1 million tons of coal in 2020 [2]. Combustion or co-firing is also considered as a simple and feasible way to use biomass as energy products for power generation. However, ash fusion is also one of the most important issues, such as alkali-induced slagging [3], silicate melt-induced slagging [4], agglomeration [5] and corrosion [6], which reduces the thermal efficiency of a boiler and increases fouling of superheaters and economisers [7]. Ash fusion of fuel has widely been investigated around world. Li and Fang found that the formation of high-melting-point mullite and change in its content were the main reason for ash fusion temperature fluctuation during co-firing of coal and biomass [8]. Rizvi et al. found that there was not any clear trend between fusion temperature and high alkali content of biomass [9]. Reinmöller et al. found that the mineral phases were assigned to main mineral groups and related to the experimentally determined ash fusion temperatures [10]. Chen et al. evaluated ash fusion behaviour of eucalyptus bark/lignite blends and suggested that biomass blending ratio should be controlled within 40% to reduce the possibility of sintering for eucalyptus bark/lignite blends [11]. Robinson et al. found that co-firing of coal and wood had the lower deposition rates than coal due to the low ash content and its low alkalis content of wood [12]. Priyanto et al. investigated ash transformation by co-firing of coal with high ratios of woody biomass. They observed that significant changes generated in the properties of the ash and the ash deposition ratio increased with increasing biomass ratio for co-firing [13].

Bamboo and masson pine are the main forestry plants with its fast-growing, rich cultivation and the high economic value. To date, China has more than six million hectares of bamboo and 2 million Km^2 of masson pine now, which have great potential as a bioenergy resource of the future. Authors reported combustion and co-firing process and characteristics of bamboo, masson pine and coal [14–17]. To the best of our knowledge, there is a lack of sufficient information concerning ash fusion characteristics of bamboo and masson pine. Despite these previous researches are very helpful in understanding ash characteristics of fuels, bamboo and masson pine are two different types of forestry resource. Ash fusion

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such as alkali-induced slagging and silicate melt-induced slagging depend on the components of fuel ash. Authors also found that there had different chemical components in bamboo, masson pine and coal ash. To further evaluate combustion properties of bamboo and masson pine, ash fusion characteristics of bamboo, masson pine and coal were therefore investigated by X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Results from this research will be provide ash-related information to power station and promote utilization of masson pine and bamboo for energy products in China.

2. Material and methods

2.1. Materials

Phyllostachys praecox *(CV.Ventricousinternode)* and masson pine *(Pinus massoniana Lamb.)* were used in this study. Bamboo materials aging with 4 years were taken from a bamboo plantation located in Zhejiang Province, China. The initial moisture content was about 8.1%. Masson pine aging with 20 years was taken from Anhui Province, China. The initial moisture content was about 9.5%. Coal was taken from Hebei Province, China. They were broken down to particles using a Wiley Mill. Samples were screened to get 250–425 μm particles and dried at temperature 105 °C until the mass stabilized.

The ash of bamboo and masson pine was prepared using muffle furnace according to Chinese standard (GB/T 28731-2012). Similar, coal ash was also prepared according to Chinese standard (GB/T212-2001). In order to investigate transformation of chemical composition, the ash of bamboo, masson pine and coal was respectively thermal treated to the initial deformation temperature. All treated samples were placed into a desiccator to cool them to room temperature.

2.2. Determination of ash characteristics

(1) The main chemical composition of biomass and coal ashes was determined by an X-ray fluorescence spectrometer (XRF), produced by Shimadzu in Japan. Five replicates of each experiment were performed.
(2) The X-ray Diffraction (XRD) analysis was applied to identify the crystalline compounds present in the ashes using an X-ray diffractometer, produced by Philip in Holland, with an X-ray generator and a Cu target ($\lambda = 0.1540598$ nm) with Kα (40kv, 40 mA) radiation at room temperature and the scan rate at 2.50/min. Data were recorded each 0.020 (2θ) for the angle range of $2\theta = 5–90°$. Five replicates of each experiment were performed.
(3) The morphology of all ashes was determined by Scanning Electron Microscopy (SEM) using an XL30 ESEM-FEG Scanning Electron Microscope. Furthermore, TEM measurement was conducted with a high resolution Tecnai G212, operating at 80 kV.
(4) The fusibility analysis was performed by a YX-HRD. Ash fusion temperatures, including DT, ST, HT, FT were identified from the ash cones with video camera. Five replicates of each experiment were performed.

For predicting the ash behaviour, deposition tendencies and thermal conductivity coefficient, the empirical indices were showed in Eqs. (1)–(4) [18,19]:

$$R_{B/A+P}=(Fe_2O_3+CaO + MgO + Na_2O + K_2O + P_2O_5)/(SiO_2+Al_2O_3+TiO_2) \quad (1)$$

Where, $R_{B/A+P}$ is base-to-acid of ash, used to characterize ash fouling tendency.

$$R_B=(Fe_2O_3+CaO + MgO + Na_2O + K_2O) \quad (2)$$

Where, R_B is basic constituents of ash (%).

$$Fu = R_{B/A}(Na_2O + K_2O) \quad (3)$$

Where, Fu is fouling index of ash.

$$\lambda = 0.773 \lg R_{B/A+P} + 0.673 \quad (4)$$

Where, λ is thermal conductivity of ash (W/m K).

3. Results and discussion

3.1. Chemical compositions and fusion characteristics

The chemical compositions of mineral matters in biomass and coal ashes often existed in oxide forms. The chemical compositions of all ashes were showed in Table 1. The major components were K_2O (34.23%), SiO_2 (24.32%) and SO_3 (14.05%) in the bamboo ash. There were also some amounts of CaO (3.99%) and MgO (6.69%). The chemical compositions were obtained from ash of masson pine showing an abundance of Fe_2O_3 (33.60%) and CaO (21.70%), although the amounts of K_2O (7.55%), SiO_2 (4.34%) and MgO (4.14%) were relatively little. The coal ash was mainly comprised of SiO_2 (47.77%), Al_2O_3 (18.44%), CaO (12.83%), Fe_2O_3 (9.80%) and SO_3 (6.22%), although there were some amounts of K_2O (0.88%), Na_2O (0.41%), MnO_2 (0.23%) and TiO_2 (0.87%). The main components of biomass ashes included potassium, silicates, carbonates, slufates and phosphates, resulting in corrosion and slagging risk of biomass ash [20]. Especially for alkali metals, it played an important role in ash fusion and deposition by vaporization and condensation [21]. Alkali metals could be released such as $KOH_{aerosol}$, $KCl_{aerosol}$, $K_2SO_{4aerosol}$, $NaCl_{aerosol}$, $Na_2SO_{4aerosol}$ during combustion process. These components formed submicron ash particles when flue gas temperature decreased, ultimately condensed on the heating surface and formed a sticky initial slagging layer [22]. It was found that bamboo ash had higher content of K and Na, indicating that bamboo ash was easier to slag than masson pine and coal. It was also confirmed that there were three types of oxides in the ash of fuel. The basic oxides included Na_2O, K_2O, MgO, CaO and MnO_2. The acid oxides included SiO_2, P_2O_5, TiO_2. The amphoteric oxides included Al_2O_3 and Fe_2O_3 [23]. The acid oxides increased ash fusion temperatures and the basic oxides decreased them. Al_2O_3 was considered as an acid oxides in the chemical components analysis. However, Fe_2O_3 acted as a basic oxide. According to the results from Table 2, the base-to-acid ratio ($R_{B/A+P}$) of masson pine ash was

Table 1
Chemical composition of bamboo, masson pine and coal ashes.

Oxide content (%)	Bamboo	Masson pine	Coal
SiO_2	24.32 ± 0.34	4.34 ± 0.03	47.77 ± 8.48
Al_2O_3	2.80 ± 0.02	3.94 ± 0.05	18.44 ± 3.20
Fe_2O_3	2.38 ± 0.08	33.60 ± 2.68	9.80 ± 1.32
TiO_2	0.20 ± 0.01	2.77 ± 0.08	0.87 ± 0.01
CaO	3.99 ± 0.02	21.70 ± 3.68	12.83 ± 3.23
MgO	6.69 ± 0.02	4.14 ± 0.03	0.98 ± 0.02
K_2O	34.23 ± 0.94	7.55 ± 0.06	0.88 ± 0.02
Na_2O	1.14 ± 0.02	0.25 ± 0.01	0.41 ± 0.01
MnO_2	1.03 ± 0.02	2.42 ± 1.00	0.23 ± 0.01
SO_3	14.05 ± 0.43	4.84 ± 0.03	6.22 ± 0.04
P_2O_5	2.58 ± 0.01	1.38 ± 0.05	1.11 ± 0.03