

Fusion characteristics of blended ash from Changzhi coal and biomass

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Abstract: The blended ash fusion characteristics and its fusion mechanism of biomasses (peanut husk (PH) and rice husk (RH)) and Changzhi (CZ) coal with high melting point (MP) were investigated by ash fusion temperature (AFT) detector, X-ray fluorescence, X-ray diffraction, and FactSage software. The results show that the AFTs of CZ ash mixtures decrease with addition of biomass ash, and the fluxing effect of PH ash is better than that of RH ash, which mainly depends on their ash chemical compositions and elements existing form. The formations of low MP minerals anorthite, albite, and leucite are responsible for the decrease in AFT of PH and CZ mixtures. With RH ash addition, feldspar and eutectics are generated, resulting in a decrease in AFT of their mixtures. In the presence of Na₂O, CaO, or K₂O, SiO₂ and Al₂O₃ would firstly react with them to form low MP aluminosilicate from the perspective of thermodynamic calculation, inhibiting formation of high MP mullite. The mixed ash fusion process could be divided into two major stages: fusion of K- and Ca-bearing minerals, respectively.

Key words: Changzhi coal; biomass; blended ash; ash fusion temperature; mineralogical property

The utilization of renewable and clean energy sources has attracted more attention in the world because of the excessive depletion of fossil fuels and environmental pollutions^[1]. Biomass plays a significant role in energy system for its carbon-neutral, wide distribution, and cheapness, and its consumption increases year by year. However, biomass has some other characteristics, such as high moisture content, low calorific value, high transportation and storage costs, and seasonal supply, restricting its large-scale utilization to a certain extent^[2,3]. Fortunately, the co-gasification of coal and biomass provide a good way to utilize biomass on a large-scale. It mitigates excessive dependence on fossil fuels and reduces the air pollutants emission (e.g., SO_x and NO_x); coal gasification reactivity is improved, and seasonal shortage problem can be avoided during biomass utilization alone^[4,5]. Entrained-flow (EF) bed gasification is considered as a promising technology in comparison with fixed- and fluidized-bed gasification for its feedstock flexibility, low pollutants emission, and high quality of synthetic gas^[6]. During EF gasification process, organic matters are converted into synthesis gas, meanwhile, inorganic matters transfer into ash/slag and discharge from slag outlet in

molten state. For high ash fusion temperature (AFT) coal, it is easy to cause ash deposition and slag blocking, resulting in shutdown of gasification system. Improving operation temperature of gasifier can meet the requirement of liquid slag discharge, however, too high temperature will directly affect the lifetime of refractory^[7]. In industrial practice, ash fluid temperature (FT) of 1400°C is generally selected as a key parameter to evaluate whether a feedstock can be applied to EF gasification directly. Blending coal and adding flux are the main methods to reduce coal AFT (FT > 1400°C)^[8]. In co-gasification, biomass can not only supply feedstock, but also modify ash fusibility characteristics of coal for its abundant alkaline and alkaline earth elements.

Enormous discrepancies of ash fusion characteristics exist between blended and pure ash. Several researchers have investigated blended ash fusion characteristics of biomass with different rank coals. Haykiri-Acma et al^[9] studied the mixed ash fusion characteristics of chestnut shell and Turkey lignite, and compared the theoretical and experimental AFT; the results showed that the higher content of acid oxides in ash, the greater deviation between theoretical and experimental AFT.

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Table 1 Proximate and ultimate analyses of coal and biomasses

Sample	Proximate analysis $w_{ad}/\%$				Ultimate analysis $w_{daf}/\%$				
	<i>M</i>	<i>A</i>	<i>V</i>	FC	C	H	O ^a	S ^b	N
CZ	1.46	18.03	9.72	70.79	86.20	3.08	2.62	3.96	4.14
PH	3.08	7.18	69.48	20.26	70.86	6.95	20.99	1.07	0.13
RH	2.21	10.12	62.03	25.64	60.46	7.22	32.15	0.10	0.07

^a: calculated by difference; ^b: total sulfur

Table 2 Chemical compositions of coal and biomass ashes

Sample	Content $w/\%$										
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	TiO ₂	P ₂ O ₅	Cl
CZ	48.32	35.20	4.03	5.78	1.59	1.3	1.24	0.31	1.39	0.84	–
PH	30.22	8.45	3.63	15.78	4.31	1.98	24.13	5.60	0.35	3.37	2.18
RH	69.30	2.00	1.29	8.11	1.53	0.40	10.76	2.06	0.43	1.01	3.11

Fang et al^[10] investigated influence of corn straw on bituminous coal AFT and found with increasing mass ratio of corn straw the blended AFT decreased initially and then increased. For mixture of biomass (cotton stalk or sargassum natans) with high-rank Jincheng coal, Chen et al^[11] found that the mixed AFT was lower than that in each single case with AFT >1400°C, meeting the requirements of slagging for EF gasifier at appropriate biomass ratio. Tang et al^[12] showed that the mixed ash of Changping coal and rice straw formed low viscosity melt at high temperatures; with increasing the melt fluidity, decomposition rate of high melting point (MP) minerals was accelerated, leading to a decrease in AFT. The mineral compositions of biomass ash is complex, and more than 200 minerals have been detected^[13], therefore great differences exist in the effect of biomass on AFT of coal. The mineral reaction mechanism in mixed ash of coal and biomass under weak reducing atmosphere is not very clear. It is difficult to select biomass and determine blending ratio during co-gasification process. Thus, the mineralogical property of mixed ash at high temperature need to be explored further.

In this work, the blended ash fusion characteristics of biomass, peanut husk (PH) and rice husk (RH), and Changzhi coal (CZ) with high AFT were investigated. The blended ash melting mechanism was explored from variation in mineralogical property using X-ray fluorescence (XRF), X-ray diffraction (XRD), and FactSage software. The results might supply the basic data and theoretical references for developing co-gasification technologies using high AFT coal and biomass.

1 Experimental

1.1 Characteristics of raw materials

Two biomasses (PH and RH) and CZ were selected as the raw materials which were pulverized and sieved to a particle size < 0.200 mm. The results of proximate (GB/T212—2008

and GB/T28731—2008) and ultimate analyses (GB/T476—2001) are listed in Table 1. The ash content of CZ is higher than that of PH and RH, while the volatile matter content of PH and RH is higher evidently than that of CZ. Meanwhile, PH and RH have a higher amount of oxygen and a lower amounts of nitrogen and sulfur than CZ.

1.2 Preparation of ash samples

Biomass ash is rich in alkaline elements (Na and K), therefore, volatilization and sintering will emerge at a higher ashing temperature. The ashing temperature of 500–600°C can better reflect the biomass ash chemical properties for a small amount of alkaline elements evaporation^[14]. Thus, the ASTM E1755-01 was selected to prepare the biomass and coal ash samples. They were ashed in muffle furnace with the following procedure: the temperature was increased from room temperature to 250°C at 10°C/min and hold for 30 min, then rose to 575°C within 30 min and kept for 3 h (6 h for CZ to ensure the organic matters were combusted completely)^[11]. As shown in Table 1, the ash contents of two biomasses are highly different. To compare influence of two biomass ashes on ash fusion characteristics of CZ and their fluxing mechanisms, mixed ash samples with different biomass ash mass ratios (10%, 20%, 30%, 40%, and 50%) were prepared.

Ash samples at high temperature were prepared through the following steps: a mixture of active carbon and graphite powder (mass ratio of 7:4) was added to a corundum boat placed in AFT detector to create a weak reducing atmosphere. Ash sample was heated in a small porcelain boat. When temperature reached the preset value, the porcelain boat was taken out and immersed in ice water quickly to prevent the crystal segregation and mineral phase transformation of ash sample. The quenched samples were placed in a vacuum drying oven at 105°C for 36 h, and crushed to a particle size < 0.075 mm for further measurement.

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