



Evaluation on ash fusion behavior of eucalyptus bark/lignite blends



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ABSTRACT

One of the most crucial problems in using biomass fuel is the amount of solid wastes produced, which will cause serious deposition and corrosion. This work is mainly focused on an evaluation of ash fusion characteristics of eucalyptus bark, lignite and their blends by using thermal analysis technique. The ash deformation temperatures of eucalyptus bark and lignite were 1181 °C and 1320 °C. The differences between ash softening temperature and hemispherical temperature were 31 °C and 13 °C for biomass/lignite blends with biomass blending ratios of 20% and 80%. Also, the influences of blending ratio and heating rate on the co-fusion kinetics of eucalyptus bark and lignite were revealed based on two-stage scheme, which referred to pre-peak and post-peak around maximum reaction rate point in the main ash fusion region. The activation energy of ash fusion for eucalyptus bark/lignite blends in the pre-peak stage and the post-peak stage was in the range of 419–828 kJ/mol, and 322–702 kJ/mol, respectively. The biomass blending ratio should be controlled within 40% in order to reduce the possibility of sintering for eucalyptus bark/lignite blends. The ash fusion kinetic characteristics of mixture samples had no linear relation with blend ratios due to interaction between biomass and coal.

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1. Introduction

The co-firing of biomass and coal would reduce CO₂ emissions, NO_x and SO_x levels [1,2], and reduce the dependency on fossil fuels [3]. Biomass fuels also contain mineral matter, generally in proportions strongly different from those found in coal [4]. However, inorganic species in biomass fuels such as alkali oxides and salts can aggravate agglomeration, deposition and corrosion problems on heat transfer surfaces in boilers [5]. The ash fusion characteristics of biomass are mainly dependent on the high-temperature molten material built up of quartz, potassium iron oxide and silicates [6]. Initial deformation temperatures of Capsicum stalks ashes, cotton stalks ashes and wheat stalks ashes increase with decreasing K₂O and go up with increasing MgO, CaO, Fe₂O₃ and Al₂O₃ [7]. SiO₂ and Al₂O₃ of biomass fuels are all favorable to increase the ash fusion temperature, and the Al₂O₃ is more effective than SiO₂ in reducing the slagging tendency [8]. The initial deformation temperature decreases with the base to acid ratio increasing if the base to acid ratio is less than 1.4. When co-fired with coal, biomass fuels may significantly lower the ash melting temperature [9]. The formation of low temperature eutectics is considered as the initiator of agglomerates, and the ash fusibility test has been the most accepted

method of assessing whether an ash will foul or slag on the heat transfer surfaces of boilers [10]. Due to the diversity and variable amount of biomass combusted with coal in industrial processes, produced ash has different characteristics and composition compared to coal ash and has not been characterized to date [11]. Blends of straw with coal contents between 5 wt.% and 15 wt.% are able to inhibit ash and reduced ash quantity [12]. When lignite is blended with some agro residues in proportions 95:5, 90:10, 80:20, Ca and Fe levels in fly ash are reduced, whereas Al and Si levels are increased, suggesting lower deposition and corrosion problems, in comparison to the combustion of lignite alone [13]. Ash melting temperatures for co-combustion of corn straw with coal firstly decrease and then increase with the content of the corn straw increase [14]. Combustion of each fuel alone for lignite or agro residue can provoke medium or high deposition problems. Biomass causes a significant decrease in the content of some metals in fly ash from co-combustion of coal and biomass including Al₂O₃, Fe₂O₃, SiO₂, K₂O, TiO₂, and CaO [11].

By blending potassium-rich hazelnut shell with lignite in the ratios of 5 or 10 wt.%, the sintering temperatures are reduced to 919 and 730 °C, respectively [10]. The antagonistic influence of hazelnut shell on the thermal behavior of ash is attributed to the interaction of potassium from biomass with silicon compounds found in mineral matter of lignite. The softening temperature of the biomass fuels examined is substantially lower than that of a brown coal [15]. Switching from pure coal combustion to co-firing herbaceous biomass fuels with coal will require lowering the operation temperature of the boiler, otherwise

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softening deformation of the composite ash can form deposits and slagging, with potential damage to the heat exchange surfaces. Therefore, extensive research is needed to reduce the operational costs and improve the reliability of the existing and newly built co-fired and/or biomass-fired power plants [16].

Rice straw, pine sawdust and leaf show serious slagging/fouling due to their high alkali content, and the ash content decreases with the increase in ashing temperature, and the alkali metals are relatively more volatile with the increase in ashing temperature [17]. Addition of straw into coal lowers the viscosity of the produced ash fractions, and the stickiness of the produced ash particles increases at lower temperatures with increasing the percentage of straw in the blends [16]. There is a great deal of eucalyptus bark for woody waste biomass species in south China. Eucalyptus is a short period of growth of industrial timber tree species. All countries tend to increase the share of biomass in the process of industrial combustion, e.g. the EU has introduced regulations to increase its amount in the process of the combustion of coal (hard bituminous coal and lignite) from 7.5% (2010) to 14% (2020) [11]. Lignite has some advantages over higher rank coals such as lower mining cost, high volatile matter content, high reactivity and low amount of pollution-forming impurities such as sulfur, nitrogen, and heavy metals [18]. Lignite resources in China are more than 1.3×10^{14} tons, which is about 13% of the total world coal reserves [19].

The properties of ash material formed during combustion of a blend cannot be predicted from the known characteristics of the ash formed from each fuel, and interaction between ashes from different fuels is poorly understood [13,20]. Therefore, knowledge of the influences of the mixtures on the ash fusion properties can make it possible to avoid fuel combinations with unwanted properties.

Despite the extensive research on melting developments of biomass and coal ash, little attention is placed on their kinetic aspect of melting transition. An assessment about the effect of blending ratio in the fuel blends on the ash fusion kinetics is also scarce. In this paper, the ash melting kinetics of a typical biomass (eucalyptus bark), lignite and eucalyptus bark/lignite blends based on the two-period scheme are investigated using thermal analysis experiments at heating rates of $10 \text{ }^\circ\text{C min}^{-1}$, $15 \text{ }^\circ\text{C min}^{-1}$ and $20 \text{ }^\circ\text{C min}^{-1}$. Furthermore, the ash analyses and ash fusing temperatures of eucalyptus bark, lignite and eucalyptus bark/lignite blends are determined.

2. Methods

2.1. Experimental facility and test samples

A kind of Chinese pulverized lignite and a typical biomass sample, eucalyptus bark were selected. Table 1 illustrated proximate analyses and ultimate analyses of coal and biomass. Proximate analyses of the samples were performed in a thermogravimetric analyzer (TGA/SDTA851, Mettler Toledo) with a precision of 0.001 mg, the detailed measuring methods were reported in Refs. [21,22]. The heating values in Table 1 were estimated by using the method reported in Ref. [23]. The ultimate analyses of eucalyptus bark and lignite were conducted in an Element Analyzer (EA3000, Leeman). There were no specific standards for biomass ash analysis in China, so the standards for coal ash analysis were usually used to determine the property of biomass ash [17]. The samples were dried at $50 \text{ }^\circ\text{C}$ and crushed into powder with diameters less than 0.2 mm. Then, these samples were ashed in a muffle furnace. 1 g of sample in a corundum crucible was placed into

a muffle furnace below $100 \text{ }^\circ\text{C}$ and then heated up to the temperature of $500 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C min}^{-1}$ heating rate. The sample was kept on being heating up to $815 \text{ }^\circ\text{C}$ after $500 \text{ }^\circ\text{C}$ was maintained for 30 min, and the samples burnt for 2 h under $815 \text{ }^\circ\text{C}$ to ensure complete ashing. The ash sample was removed from the muffle furnace, and then it was placed in a dryer to be cooled down to room temperature after being cooled in the air. The sample was again burnt by above procedure, until the final ash sample was obtained up to two consecutive mass difference of sample less than 0.001 g. The residual ash was respectively milled to smaller particles ($<0.1 \text{ mm}$) in an agate mortar. The eucalyptus bark/lignite ash blends were prepared and homogenized with biomass ash mass percentages of 20%, 40%, 60% and 80%, respectively.

Ash fusion temperatures of samples were measured according to GB/T 219-2008 (Chinese norms). A triangular ash cone with a bottom of 7 mm equilateral triangle and a height of 20 mm was made. The triangular ash cone was heated in weak reducing atmosphere. The sample was heated at the heating rate of $15 \text{ }^\circ\text{C min}^{-1}$ before $900 \text{ }^\circ\text{C}$ and $5 \text{ }^\circ\text{C min}^{-1}$ after it. The shape change of the ash cone was detected in the furnace by using a thermal microscope (BYTHR-9F, Boyuntian), and the deformation temperature (DT), softening temperature (ST), hemispherical temperature (HT) and flow temperature (FT) were measured.

TG/DTG/DSC experiments were carried out by a synchronous thermal analyzer (SDT-Q600, TA) with a precision of $\pm 2\%$. The samples were heated in nitrogen (80 ml/min) in a Pt crucible (using Al_2O_3 as a reference material), in the temperature range between 30 and $1450 \text{ }^\circ\text{C}$, with heating rates of 10, 15 and $20 \text{ }^\circ\text{C min}^{-1}$. To ensure reproducibility, the experiments were repeated three times. The results indicate that a good reproducibility is maintained for each run because the relative deviation was generally within $\pm 1.5\%$.

The uncertainties of the measurement in the experiment were dependent on the experimental conditions and the measurement instruments. The uncertainties of the measured parameters were estimated by using the method in Refs. [24–26].

The uncertainty of temperature was determined by

$$\pm \frac{\delta T}{T} = \pm \frac{0.01/2\sqrt{3}}{20} = \pm 0.01\%$$

where T is the minimum value of the temperature during the experimental process, δT the standard resolution uncertainty of the temperature.

Similarly, the uncertainty of the mass is given by

$$\pm \frac{\delta m}{m} = \pm \frac{0.001/2\sqrt{3}}{5} = \pm 0.006\%$$

where m is the minimum value of the sample mass during the experimental process, δm the standard resolution uncertainty of the mass.

Powder X-ray diffraction was utilized to determine the inorganic compounds in the ashes, using a S4 Explorer diffractometer (Bruker AXS). The ash analyses of samples were shown in Table 2.

Compounds in ashes can be divided into two groups by ionic potential difference [27]. One is acidic group compounds with high ionic potential like SiO_2 , Al_2O_3 , and TiO_2 which function as network formation agents. The other is basic group compounds with low ionic potential like Fe_2O_3 , CaO , MgO , and so on. They can damage polymers in ash and help melting.

Table 1
Proximate analyses and ultimate analyses of samples.

Samples	Proximate analysis (wt.%)				Ultimate analysis (wt.%)					HHV (MJ/kg)
	M_{ar}	V_{ar}	A_{ar}	FC_{ar}	C_{ar}	H_{ar}	O_{ar}	N_{ar}	S_{ar}	
Lignite	6.84	39.12	31.61	22.43	41.40	3.14	54.46	0.68	0.32	14.97
Eucalyptus bark	7.79	84.16	3.60	4.45	43.94	5.27	50.36	0.42	0.01	15.94

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