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Research article

Does blending the ashes of chestnut shell and lignite create synergistic interaction on ash fusion temperatures?

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ABSTRACT

The ashes of twelve different Turkish lignites were blended with the ash of chestnut shell (20 wt.%) to investigate the effects of the biomass ash on the ash fusion temperatures (AFTs) of the ashes of coal/biomass blends. Fusion characteristics of ashes were studied according to ASTM D1857. Calculated values (theoretical values) of AFTs were compared with the experimental ones to evaluate the existence of additive behavior or synergistic/antagonistic interactions between the ashes. It was found that the presence of the ash of chestnut shell led to more or less lowering trends in AFTs in eleven of the twelve lignite ashes and this is an undesirable interaction. Although, the chestnut shell contains high amount of Ca, it was concluded that the improving effect of Ca on ash fusion temperatures are overtaken by the lowering effect of K. Alumina-silicate minerals in lignite ashes may show interaction with K to form new phases with low melting temperatures. Consequently, it was found out that the increasing acidic oxides ($SiO_2 + Al_2O_3 + TiO_2$) in ash leads to high levels of deviations from the calculated values (additive behavior) of AFTs and particularly the Al content is the key parameter.

1. Introduction

Co-combustion of coal with biomass has widely been considered to mitigate CO_2 emissions, to take advantage of the energy potential of biomass, and to dispose waste materials effectively.

Most of the biomass species, however, have drawbacks compared to coal because of low density, low calorific value in unit mass, high moisture content, and easily decomposition by biological activity [1]. Moreover, biomass ashes are typically in basic character because of high concentrations of alkaline (K, Na) and alkaline-earth (Ca, Mg) elements, and this feature creates an additional problem that is known ash-related deposit formation [2]. Namely, alkaline constituents in biomass ash cause slagging and fouling that lead corrosion [3]. Especially some biomass species such as agricultural wastes, biosolids, and municipal solid wastes (MSW) cause severe deposit problems in combustion systems since their ashes are highly basic together with the presence of chlorine that worsens the trouble [4].

Na and K are likely to form volatile compounds which show condensation on metallic surfaces to form a sticky layer that is the initial stage of deposition [5]. In this stage, these elements in biomass tend to form Na/K-silicates that have low melting temperatures, causing accumulations on boiler tubes and inner surfaces of combustor [6,7]. Then, fly ash particles are sintered on this sticky layer to worsen the deposit formation problem [8]. For this reason, a fluidized-bed may be wholly agglomerated as a result of melting of the alkaline compounds in biomass ash [9]. Agglomeration prevents air from reaching the fuel particles, and likewise sintered ash reduces the heat transfer capacity of heat exchangers seriously. Also, removal of such deposits from the surfaces is usually troublesome [9]. It is reported that a typical coal-fired boiler needs cleaning after an operation period of 2000 h, while it is only 400 h for those burning waste biomass species such as RDF (refuse derived fuel) [10].

Thus, the alkaline content of a fuel is regarded as a reliable indicator to predict the level of deposit-related problems [8]. On the other hand, some special biomass types such as rice husk are not rich in alkaline compounds, and acidic SiO_2 accounts for almost all of the inorganics [11]. Accordingly, ash from rice husk cannot show melting below 1600 °C so it does not create any ash-related problems in combustion systems [12]. Actually, when sum of SiO_2 and Al_2O_3 exceeds 90% in ash composition, such ashes are regarded as refractory ashes [13].

International standards such as ASTM D1857, DIN 51730, AS 1038.15, BS 1016, ISO 540, JIS M8801, etc. usually base on measurement of four different temperatures to characterize the ash fusion. These temperatures are initial deformation temperature (IDT), softening temperature (ST), hemi-sphere formation temperature (HFT), and flow temperature (FT). IDT is the temperature at which the top of a standard ash pyramid rounds upon heating under controlled conditions (5–10 °C/min). As heating continues, melting of ash begins and it gets rather a spherical shape, from which ST is determined. HFT is the temperature at which the height of standard ash pyramid becomes just the half of its

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length, and this is the strong evidence of melting. When it reaches to FT, the height of pyramid is only 1/16 of its length [13].

Various parameters including the inorganic composition of ash, particle size and its distribution, bed temperature, and the atmosphere under which the operation takes place affect the agglomeration behavior of ash. IDT corresponds to an initial deformation of ashes (shrinkage, expansion, agglomeration, sintering, softening, stickiness) as a result of mineral transformations [14]. Although, IDT is very helpful to predict the ash-related deposition problems, results of the studies in the pilot plant of Exxon showed that agglomeration can occur at temperatures several hundred temperatures lower than IDT [15,16].

On the other hand, co-presence of different types of fuels in the same combustion medium often leads to unforeseen circumstances. Therefore, some indexes have been derived to predict the ash fusibility. Of which, ash fusibility index (AFI) can be used to compare the fusibility trend of ashes basing on IDT and HFT values:

$$\mathrm{AFI} = [4 \cdot (\mathrm{IDT}) + (\mathrm{HFT})]/5. \tag{1}$$

The relation between AFI value and the severity of the ash fusion problem is as follows [17]:

AFI < 1149 °C	: Very high
1149 °C ≤ AFI < 1232 °C	: High
1232 °C ≤ AFI < 1343 °C	: Medium
AFI ≥ 1343 °C	: Low

Ash composition in oxide form also offers a rapid screening opportunity for slagging potential of ash, and the ratio of basic oxides to acidic oxides yields the slagging index [18]:

$$\text{Slagging Index} = (\mathrm{CaO} + \mathrm{MgO} + \mathrm{Na_2O} + \mathrm{K_2O} + \mathrm{Fe_2O_3})/(\mathrm{SiO_2} + \mathrm{Al_2O_3} + \mathrm{TiO_2}). \tag{2}$$

High values of this ratio mean that basic oxides are abundant and it predicts that the ash fusion temperature (AFT) is comparatively low, causing deposit formation in combustion systems.

The ash melting behavior of a biomass that contains mainly alkaline-earth elements in the mineral matter has not been investigated purposefully, and effects of blending directly the ashes of lignite and biomass have not been determined without considering the carbon contents of the samples. In this context, chestnut shell was chosen as the biomass material since the alkaline earth elements in this biomass are more abundant than the alkaline elements. The ashes obtained according to ASTM standards were blended to check the effects of biomass ash on the ash fusion temperatures of the lignite ashes. The direct blending of ashes from different fuels and the possible interactions which are relevant to AFTs have not been studied in literature yet.

2. Material and methods

Twelve lignite samples used in this study are Turkish lignites located in the western part of the country where a number of power plants have been operated to generate electricity from these lignites. The lignites were coded between L1 and L12, and their origins and locations can be summarized as follows: L1 (Canakkale-Can), L2 (Seyitomer A19), L3 (Karanlikdere-Eynez), L4 (Eskihisar-Yatagan), L5 (Seyitomer-S48), L6 (Tavsanli), L7 (Karanlikdere-Imbat), L8 (Can-2), L9 (Tuncbilek-Tavsanli), L10 (Tinaz-Yatagan), L11 (Orhaneli), and L12 (Orhaneli-Gumuspinar). Accordingly, the ashes from these lignites will be denoted hereafter as A1–A12. Chestnut shell was provided from Turkish food industry. Actually, China is the top country in chestnut production, and Turkey and Korea Republic follow China according to FAO statistics [19]. Accordingly, thousands of tons of chestnut shells are evolved yearly in Turkey after processing in food industry. Both lignite samples and chestnut shell were sampled, prepared, and analyzed. That is, samples were spread onto the open trays in laboratory, and kept for one week to get air-dried samples. Then, the lignites were crushed and milled using pilot scale equipment, while a special grinder that had been designed for leafy materials was used to chop and grind the chestnut shell. The particles lower than 250 μm were used in analyses as well as in the subsequent experiments.

Proximate analyses of lignites and chestnut shell were performed according to ASTM standards, while ultimate analyses were conducted using an elemental analyzer (Leco TruSpec® CHN model with S module). Calorific value measurements were carried out using IKA C2000.

Ashes of the lignites and chestnut shell were obtained by simply burning of each sample in a muffle furnace at temperatures specified by ASTM standards. For this, 10 g of ground sample (<250 μm) was heated in porcelain crucibles with a heating rate of 10 °C/min under static air atmosphere from ambient to 750 °C for lignites (ASTM D3174 — ash in coal) and 600 °C for chestnut shell (ASTM D1102 — ash in wood). This differentiation in final temperatures comes from the fact that determination of the ash yields of coal and biomass are performed at 750 and 600 °C for coal and biomass, respectively, according to the mentioned standards. The ashes were cooled down to room temperature and then kept for subsequent experiments. The ash blends were prepared by adding the chestnut shell ash into lignite ashes to form blends in which the ratio of chestnut shell ash is 20 wt.%.

Atomic Absorption technique was performed to measure the concentrations of the elements in ashes. For this, Perkin Elmer AAnalyst 800 was used. Besides, the mineral phases found in the ashes were tested by X-ray diffraction (XRD) method using PANalytical — X'Pert Pro PW 3040/60 model device.

AFTs were determined according to ASTM D 1857 standard procedure by LECO AF600 ash fusion determinator that operates up to 1600 °C. This equipment makes it possible to monitor the changes in the ashes upon heating, and from which IDT, ST, HFT, and FT values can be specified. AFT tests have been repeated several times to get results which are repeatable within (+/—) 1% deviation.

3. Results and discussion

3.1. Sample characterization results

Proximate and ultimate analyses results of the lignites and chestnut shell are given in Table 1.

Table 1 shows that the lignite samples used in this study are highly different lignites from several aspects. That is, the ash yields of the lignites change in a wide range of 3.3–42.6 wt.%, and this indicates that the samples range from low-ash coals to high-ash coals. Similarly, C contents and HHV values vary so remarkably that they are between 45.3–76.9 wt.%, and 8.2–23.0 MJ/kg, respectively. On the other hand, these HHV results correspond to 20.5–30.0 MJ/kg on dry-ash-free basis. Besides, chestnut shell possesses the typical features of woody biomass that has higher yield of volatiles and lower content of sulfur compared to the lignites. Also, chestnut shell has an ash yield which is lower than those for lignites except L5. These differences between chestnut shell and lignites mean that the reactivities and the chemical properties of them are different from each other, and it will also possibly affect the ash-related characteristics.

Results given in Table 2 present the comparison of the elemental compositions of ashes, and it makes clear that the lignite ashes are highly rich in acidic oxides, while the ash from chestnut shell consists mainly of basic oxides. Namely, silicon and aluminum contents of lignite ashes that contribute to the acidic character were at least ten times as rich as the biomass ash. On the other hand, calcium is the dominant element followed by potassium and magnesium in the biomass ash, which contributes to the basic character. Besides, the biomass ash contains higher amounts of calcium and potassium than those in lignite ashes, while sodium content is comparable with those in lignite ashes. Although, typical biomass species contain mostly potassium and sodium in their