



Full Length Article

Experimental and theoretical methods for evaluating ash properties of pine and El Cerrejon coal used in co-firing



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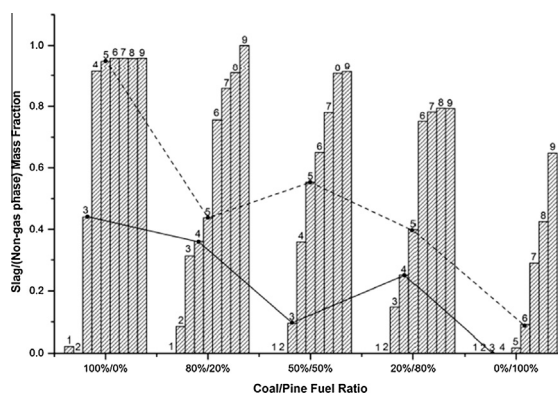
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HIGHLIGHTS

- Reliability of XRF analysis of fuel ashes improved by wet chemical analysis.
- Ash melting behaviour of different coal-pine blends assessed via laboratory methods.
- Indices and viscosity models tested for El Cerrejon-Pine blends.
- Thermodynamic modelling usefully predicts slag formation.

GRAPHICAL ABSTRACT



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ABSTRACT

There has been an increase in the use of biomass for power generation by means of co-firing with coal as well as by the combustion of 100% biomass. Despite the advantages of biomass in reducing carbon emissions from the electricity sector, the co-firing of high percentages of biomass can potentially aggravate ash related problems in the boiler. In order to develop mitigation strategies for the formation of deposits, an understanding of the ash behaviour during the combustion of high percentages of biomass is required. In this work, ash samples from El Cerrejon coal and pine biomass were characterised for their inorganic composition by X-ray fluorescence and wet chemical methods. Relationships between these two methods were found. Furthermore, the melting behaviour of ashes from pure coal, pine, and their blends were studied through ash fusion tests (AFT) and via a method using a simultaneous thermal analyser coupled to mass spectrometer (STA-MS) for the evolved gas analysis. Pine ash has lower slagging potential than El Cerrejon coal ash and results show that for 20:80 and 80:20 pine:coal ash blends the characteristic ash fusion temperatures increase with increasing pine ash content. There is unusually higher slagging potential (lower ash fusion temperatures) at a 50:50 blend ratio. Viscosity models produced sensible results for coal and coal/pine blends, but further refinement is required for modelling the viscosity of pure biomass ash. Thermodynamic modelling of slag formation was undertaken using the FactSage model. This model was successful in predicting the changes of gas, solid and liquid phases during pure pine, coal and co-combustion.

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1. Introduction

To reduce the use of fossil fuels and to help meet emission targets for CO₂ and, it is now common practice to burn 100% biomass or to co-fire with coal for the large scale generation of electricity using pulverised fuel combustion. Biomass combustion is also advantageous in many cases in terms of lowering SO_x and NO_x compared to using coal. However, biomass is not an ideal alternative to coal using current technologies, because of the differences in physical and chemical characteristics. The nature of the inorganic content of biomass results in ash particles which may adhere on the heat transfer surfaces, accumulate on the inside walls of the burners to form deposits or slags, and also induce boiler fouling in the convective pass. Alkali metals present may lower the melting temperature of the ash [1,2] but this is also dependent on the other metal oxides present particularly calcium. Generally, slagging takes place in the hottest parts of the boiler whilst fouling deposits occur as the flue gases and ash particles cool down [3]. Several approaches have been taken to study the formation and chemistry of these deposits. Vassilev et al. [4] used optical microscopy, X-ray diffraction (XRD) and Differential Thermal Analysis-Thermogravimetric analysis (DTA-TGA) to examine ash formation and behaviour during biomass heating and identified several steps associated with different temperature ranges: (i) fragmentation of particles <500 °C; (ii) agglomeration: initial (700–900 °C), significant (700–1100 °C) and extensive (700–1300 °C); (iii) ash melting: initial (700 °C), extensive (900–1100 °C) and complete (1100–1500 °C); (iv) phase crystallization between 500 and 1500 °C; and (v) glass liquid formation between 700 and 1500 °C.

There has been some success in relating biomass ash behaviour to the nature of the inorganic components. In this approach, the inorganics are classified into four types: (i) water soluble salts, (ii) elements associated with the inorganic fraction of the biomass, (iii) minerals included in the fuel structure, (iv) inorganic material incorporated within the biomass from extraneous sources. Removal of the water-soluble salts (alkali chlorides, sulphates, etc.) has been shown to increase the ash melting temperature in many agricultural residues and straws [5], and also to reduce fouling by alkali salts. Washing also impacts on the combustion behaviour of the fuel. In a previous study [6], water-washed and demineralised (acid wash) biomass samples were investigated to determine the effect of potassium on their devolatilisation behaviour. The influence of alkali metals on the kinetics of the thermal decomposition of biomass has also been investigated by other researchers using a similar approach [7–9]. Because of the difference in ash composition between coal and biomass, there are different classifications and amounts of inorganics present. Hence, there are possible consequences when firing blends of coal and biomass, and improvement in either char burnout behaviour and/or ash behaviour is possible. The current work examines the impact on ash behaviour.

Another approach to predicting, biomass ash behaviour and deposition tendencies is through the use of empirical coal ash indices. Under complex combustion conditions, the changes in the boiler and heat transfer passes are predicted using indices; this is a widely used approach, but their reliability when applied to coals from around the world, or when applied to blends, (coal-coal or coal-biomass) is still an issue. Also, their value is limited for biomass because there is less experience in using biomass than coal, hence validation becomes important. However, some indices have proved popular, for example the alkali index is a useful guide to fouling, and the base-to-acid ratio a guide for biomass slagging, although interpretation is different from coal [10]. These indices as well as others are evaluated in this study of pine blended with El Cerrejon coal in different ratios.

There are few reports on ash composition and deposition behaviour of El Cerrejon coal. López and Ward [11] studied the composition and mode of occurrence of mineral matter as they vary for different coal seams and also with particle size. Their studies showed that the mineral phase from El Cerrejon coal contains a high proportion of pyrite (14%) and a significant proportion of coquimbite (3.5%) on hydrated aluminium sulphate, and ~54% of quartz, and lower proportions of the clay minerals, kaolinite, and illite. The deposition behaviour of El Cerrejon coal during combustion has been studied experimentally and evaluated by a numerical simulation of its slagging propensity by Wieland et al. [10]. These authors compared El Cerrejon to Pittsburgh 8. The Watt-Fereday model (also utilised in this current study) gave reasonable prediction of deposition of El Cerrejon. The higher deposition propensity of El Cerrejon was then modelled using sticking criteria derived from a thermodynamic model (FactSage) and DTA-TGA, giving reasonable, although slightly different predictions.

Pine wood has been widely investigated for 100% combustion and also for co-firing with coal, and favourable properties have been reported [12,13]. Compared with rice husk, straw and coffee husk, pine branches shows a low ash content—with especially low SiO₂ content, but with the highest Na₂O content. Furthermore, the ash from pine resulted in higher melting and ash fusion temperatures, thereby reducing their slagging propensity. During the large-scale co-firing tests pine also showed a different behaviour from other biomass, as it resulted in a low degree of adherence to furnace surfaces.

Co-firing adds further complexity to ash behaviour because of possible interactions; these interactions are studied in this work. For example, vapour phase inorganics from the biomass ash, particularly, potassium salts, interact and react in both the gas phase and also with coal char and ash particles. These interactions take place at high temperature and can result in surface layers potassium-alumina silicate on the coal fly ash [14]. Alternatively, the coal ash can act as surface for deposition of aerosols of potassium salts. In fact, some authors have studied the addition of coal pulverised fly-ash to biomass boilers to mitigate fouling by potassium salts [15]. In this paper the ash behaviour of two fuels, El Cerrejon coal and pine, are examined in as well as blends of the two which might be used for co-firing. For this purpose, the inorganic composition of the fuels are characterised by both X-ray Fluorescence and wet chemical methods and the results obtained by both methods compared. The ash melting behaviour and ash fusion temperatures of the ash from the coal and pine and their ash blends are determined using the characteristic temperatures SST (shrinkage starting temperature), DT (deformation temperature), HT (hemisphere temperature) and FT (flow temperature) previously described [16,17]. The results are also verified with simultaneous thermal analysis coupled to a mass spectrometer for evolved gas analysis (STA-MS). This work is an expansion of earlier work [17] and uses thermodynamic modelling of slag formation in different ratios of coal and pine via the FactSage software package. Factsage has previously been used successfully to model the behaviour of coal and biomass [18,19]. The modelling results obtained here are compared with the experimental data obtained from the ash fusion tests and thermal analyses.

2. Experimental methods

2.1. Sample preparation

Ash was prepared from the pine wood and El Cerrejon coal samples according to the British Standard DD CEN/TS 15370-1:2006 and BS 1016-104.4:1998, respectively. Each sample was ashed in air at two final temperatures, namely 550 °C and 800 °C for 14 h

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