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Mineral phase transformation of biomass ashes – Experimental and thermochemical calculations

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ABSTRACT

The paper is focused on the thermal characterisation of biomass ashes especially of mineral phase transformation. Ash generated during combustion (with high alkali metal concentration) can deposit and consequently cause serious operating problems such as slagging, fouling and corrosion of metal surface limiting heat transfer. Four biomass ashes with different origin were investigated. The chemical composition of the mineral matter of ashes varied between the samples, but CaO, SiO_2, K_2O, MgO, P_2O_5 and Al_2O_3 are the main compounds of the ashes. The thermal behaviour of ashes was studied using TG-DSC and Ash Fusion Temperatures (AFTs) techniques. In order to describe and understand the mineral matter transformation at high temperatures the FactSage Thermodynamics Model was used. FactSage calculations allowed to predict chemical composition in equilibrium, showed amount of liquid slag and solid phases, and gave information about slagging properties of ashes. A corrosion study of the metal surface used for heat transfer biomass ashes was undertaken. The corrosion behaviour of steel X10CrMoVNb9-1 in the present of biomass ash at 650 °C in 1000 h in furnace. The degradation of the metal surface was investigated by observation of surface morphology using the SEM method. The presence of potassium and chlorine in deposits causes the acceleration of oxidation. They break and peel off the surface easily, thus evidently accelerating corrosion.

1. Introduction

Recently, fossil fuels have been the basis for the production of energy. The use of biomass as a fuel has been increasing. The development of processing technologies and energy use of renewable fuels is taking place. The number of power plants using biomass is on the increase, too. The thermal conversion techniques of biomass are varied such as combustion, co-combustion, gasification and pyrolysis. Combustion and co-combustion go in pulverised coal boilers, fluidised bed boilers, and a grate furnace, whilst further technologies are still developing. Biomass fuel is defined as a green and zero CO_2 – a natural energy source. The variety of biomass is very wide; there are those that are wood-based (e.g. forest and landscaping residues), agricultural (straw, grass, food industry) and waste derived. Although biomass and sewage sludge combustion processes are applied with good efficiency, ash deposit is a new problem, which requires new solutions. The mineral part of the fuel causes a serious problem in the combustion process of biomass [1–3] (Fig. 1).

The inorganic part of the fuel accelerates the risks associated with the formation of ash deposits on the heating surface of the boiler. The most important phenomena affecting the work conditions of biomass and sewage sludge combustion devices are slagging, bed agglomeration, fouling, and corrosion in the combustion devices, which degrade their performance and severely damage the firing equipment [4–9]. The deposit of ash on the heat transfer surfaces of the boiler depends on the chemical composition of the fuel and the combustion process parameters. The presence of ash reduces the heat transfer and combustion efficiency, and damages combustion chambers when large particles break off. The term slagging is used to describe the formation and accumulation of slags on the furnace sections (refractory walls, water walls and grates). The structural forms of slags and bed agglomerations can vary [10]. Their reactivity depends on the chemical reaction between ash components and other inorganic compounds present in the environment. The term fouling is used to indicate the formation of ash deposits on heat transfer surfaces in the convective parts of

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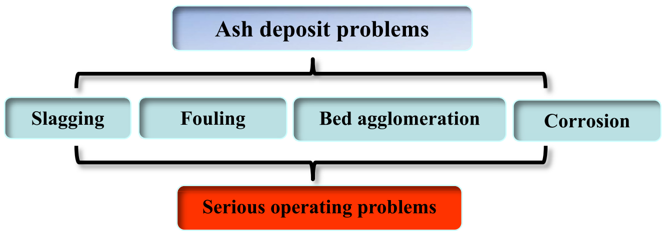

Fig. 1. The scheme of biomass ash deposit problems.

the furnace. It causes insulation of the convection tubes and reduces heat transfer. Different correlations and methodologies have been used for predicting the slagging and fouling tendencies of solid fuel ashes. There are some empirical indices correlating the standardized chemical composition of ashes, thus making it possible to predict the ash behaviour and deposition tendencies. The works of Pronobis [11,12] present empirical indices for the co-combustion of coal and biomass from indices concerning coal combustion.

The main elements in the biomass ash are calcium, silicon, magnesium and potassium as well as sulphur, chlorine, and phosphorus. However, the biomass source determines the chemical composition of ash, meaning that the generalisation of ash contents and their composition is not possible and variable. The alkali metals play an essential role in biomass combustion and next in slagging, fouling and corrosion processes. The potassium content is important because it indicates potential ash fusion and deposition by vaporization and condensation. In biomass combustion K and Cl can be released in gas such as HCl, KCl and potassium exists as potassium silicate, aluminosilicate and sulphate ($K_2Ca(SO_4)_2$, $K_3Na(SO_4)_2$). Depending on the temperature potassium can exist in different forms; K_2SO_4 condenses on high temperature heating surfaces, whereas KCl condenses on lower ones [1]. KCl is the most stable gas-phase alkali metal that influences biomass slagging. It should be emphasized that all forms of potassium play a significant role in slagging and fouling. This was reported in experimental and numerical calculations [2,13]. Additionally, in studies [10,14] $K_2Ca(SO_4)_2$ and $K_3Na(SO_4)_2$ significant phases in slagging were found.

The chemical and mineral compositions strongly influence on the ash melting and fusion temperatures. Thermal techniques are well known to study the characteristics of biomass and other fuels [15,16] during the pyrolysis, gasification and combustion processes. The thermal behaviour of ash can be successfully studied by thermal analysis (TGAs: TG and DSC) connected with mass spectrometry (MS), as well, to obtain information on ash melting, phase transformation and release of gaseous phase [17,18]. TG and DSC curves show the mass change via temperature and thermic effects (endo-, exothermic) associated with the change of enthalpy. Determination of ash fusion temperatures is important to study ash deposit problems. Therefore, four temperatures are identified in describing the ash melting process: initial deformation temperature (IDT), softening temperature (ST), hemispherical temperature (HT) and flow temperature (FT) [19,20].

Generally, corrosion is the phenomenon of the destruction of materials under the influence of the environment. The reaction of the corrosion process is described in the following equation:

$$M_{(s)} + a/2\, X_{2(g)} \leftrightarrow MX_{a\ (s,g)} \qquad (1)$$

where X can be: O_2, Cl_2, S.

Taking into account the corrosion which appears in the combustion process, the most important is the degradation of the metallic material of the boiler as well as the protective oxide scales which take place under combustion and its associated products (solid, liquid and gas) [21]. A high temperature corrosion process influences negatively on the efficiency of the energy systems during renewable fuels combustion. The mechanism of corrosion depends on interactions between ash elements as well as the conditions of the combustion process. The most aggressive agents existing in biomass ashes are alkali metal compounds, especially potassium and sodium. The reaction between the compounds in the ash lead to products which can cause operating problems during combustion. Detail description of this process have been widely studied in the papers [22–25]. Some possible reactions (2–8) are listed below:

$$2KCl_{(g)} + SO_{2(g)} + 1/2O_{2(g)} + H_2O_{(g)} \leftrightarrow K_2SO_{4(g)} + 2HCl_{(g)} \qquad (2)$$

$$K_2CO_{3(g)} + SO_{2(g)} + 1/2O_{2(g)} \leftrightarrow K_2SO_{4(g)} + CO_{2(g)} \qquad (3)$$

$$KOH_{(g)} + HCl_{(g)} \leftrightarrow KCl_{(g)} + H_2O_{(g)} \qquad (4)$$

$$K_2SO_{4(g)} + SiO_{2(s,liq.)} \rightarrow K_2O \cdot SiO_{2(s,liq.)} + SO_{3(g)} \qquad (5)$$

$$K_2SO_4(g) + SiO_{2(s,\ liq.)} \rightarrow K_2O \cdot SiO_{2(s,liq.)} + SO_{3(g)} \qquad (6)$$

$$2KCl_{(g)} + (2Al_2O_3 \cdot SiO_{2(s,liq.)}) + H_2O_{(g)} \rightarrow 2KAlSiO_{4(s,liq.)} + HCl_{(g)} \qquad (7)$$

$$2KCl_{(s,liq)} + SO_{2(g)} + 1/2O_{2(g)} + H_2O_{(g)} \leftrightarrow K_2SO_{4(s,liq.)} + 2HCl_{(g)} \qquad (8)$$

High-temperature heating surface corrosion during the combustion of renewable fuels is due to chlorine deposition and reactions between chlorine and metal [26,27]. That is why the chemical composition of metallic material plays a major role in corrosion during combustion. In this context, stainless steel with a high amount of chromium is advised. Chromium steel is characterized by its high resistance of corrosion. Besides the chromium other additions such as Ni, Nb, Ta and Mo are added to improve the corrosion resistance [28,29].

The knowledge concerning the formation and transformation of the mineral part of biomass ash is necessary to control problems associated with fouling and slagging in boilers during biomass combustion. In order to provide a deeper description of biomass ash's thermal behaviour, TGA analysis was conducted, ash fusion temperatures were examined under oxidizing atmosphere conditions, and additionally the mineral phases were determined by thermochemical calculations (FactSage). Additionally, a corrosion study of the metal surface used for heat transfer under renewable fuel ashes was undertaken. The work presents the character of biomass ashes and the study of metallic surface morphology after ashes influence. The tested steel was the type which is being considered for use in super-heaters of stream boilers fired for renewable fuel combustion.

2. Experimental

2.1. Material

Four different types of biomass ashes with different origin (three wood and straw) were used in this study. The biomass materials are typical renewable fuels used in energy units in the combustion process. The ash samples have reflected biomass ashes in general. The ash samples were denoted as: OS – oat straw (agriculture biomass) ash, BS – beech sawdust ash, LS - larch sawdust ash and WS – wood sawdust ash (mixture of different kind of wood biomass), respectively. The results and knowledge obtained in this study can provide a better understanding of ash formation

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