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Alkali metals association in biomass and their impact on ash melting behaviour

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ABSTRACT

Selected agricultural and energy crop biomass ashes represented by two mixed cereal straws, corn straw, *Miscanthus* × *Gigantus* and *Salix Viminalis* were chosen for ash behaviour investigation and prediction of operating problems during biomass combustion. The presence of aggressive species in the ash generate operational problems of heat exchanging surfaces in power boilers connected with slagging and fouling processes, limiting the use of biomass direct combustion for energy production. In this work, thermal behaviour characteristics, transformation properties of the inorganic components and ash fusion temperatures of biomass ashes were investigated using thermal analysis (STA), X-ray diffraction (XRD) and high-temperature microscope. The special attention was focused on the evaluation of potassium compounds presented in ashes. Potassium was detected as KCl, K_2SO_4, K_2CO_3 and K_3PO_4. It was noted, that presence and concentration of alkali metals, silicon and calcium compounds has the major impact on fusion temperatures of studied ashes. Leaching process of ash elements using water, ammonium acetate and hydrochloric acid solutions was performed to determine the association of alkali metals in the raw material. Based on the results, a mineral matter composition recalculation model was proposed to predict alkali compounds concentration in the fuel. The model might be also used to determine the risk of eutectics formation, which have the strongest influence on ash melting behaviour.

1. Introduction

The necessity of environmental protection, decreasing of fossil fuel resources and EU regulations promote renewable fuels use in energy and heat production. The European Union has an ambitious goal for renewable energy production to achieve at least 27% of final energy consumption leading to 40% reduction of greenhouse gas emissions [1]. Biomass is one of the major renewable energy resources and energy production from biomass is expected to be further increased. Based on EUCO27 scenario, it is expected that by 2030, the share of biomass will be around 50% of overall renewable energy production. Biomass is mainly supplied from forest and agriculture industries and urban waste resources. The origin of biomass is directly associated with its advantages like, renewable form enables to reduce amount of wastes with neutral CO_2 emission. The application of biomass as environmental friendly fuel for energy production still faces new challenges which require sustainable solutions and has to be managed [2].

Thermal utilization technologies of different kind of biomass go into a good direction. Biomass is successfully combusted via direct combustion and co-combustion technologies [3,4], as well as gasification and pyrolysis installations attempt to use biomass [5,6]. Unfortunately, during the thermal processes of biomass conversion the ash related problems frequently came up. The biomass ash contains wide range of inorganic elements which form complex compounds in gaseous, liquid and solid phases during thermal conversion of the fuel.

The mineral matter transformation is crucial phenomenon in biomass combustion. The presence of aggressive species in the ash generate operational problems of heat exchanging surfaces in power boilers connected with slagging and fouling processes [7]. Although the amount of ash generated during biomass combustion in comparison to coal is significantly lower, the biomass ash generates more damages and needs more attention these days then coal ash. The nature of biomass is characterised by huge heterogeneity and depends on biomass origin and processing, it is also difficult to systematise and predict to prevent the unwanted effects in combustion system. The generation of deposit layers on heat exchanger surfaces depends on many factors mainly, chemical composition of the fuel, combustion temperature and residence time of the fuel samples.

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The biomass ash mainly consists of calcium, silicon, potassium and phosphorus as well as noticeable amounts of chlorine. The alkali metals like K and Na together with chlorine are the most important elements in biomass ash affecting unwanted processes. During fuel combustion reactive compounds evaporate and alkali metals might form aerosols (KOH, KCl, K_2SO_4, NaCl, Na_2SO_4) in the gas phase. When the exhaust gases temperature decreases, aerosols can condensate on fly ash particles and form deposits - small agglomerates of ash particles leading to preliminary slag layer. Additionally, aerosols of alkali metals can react with each other or other ash components like SiO_2 and Fe_2O_3 to form eutectic mixtures [8]. Si, K and Ca are the main elements responsible for agglomeration process, based on the knowledge of SiO_2–CaO–K_2O system the fusibility tendencies can be predicted [9]. Alkali metals can exist also in solid phase in the form of silicates (e.g. $K_2Si_2O_5$, Na_2SiO_3) and aluminosilicates (e.g. $KAlSi_3O_8$, $KAlSiO_4$, $NaSi_3AlO_8$) [10].

Beside of some disadvantages associated with ash related issues in power boilers, biomass ash is characterised by appropriate chemical composition for its further application. The amount of ash generated during combustion depends on the origin of the fuel and it is in the range of c.a. 1% (woody biomass) up to more than 10% (agriculture biomass) [11]. Silica-rich ash can be used as a substrate for both calcium silicate hydrate-based and sodium aluminosilicate-based binders and in consequence can be successfully applied in ceramic and cement sectors [12].

There are many studies concerning the formation and transformation of the mineral phases during thermal processes depending on the process parameters [11,13,14]. Many methods used in previous studies including: simultaneous thermal analysis [10,15,16], XRD [16,17] and chemical fractionation [18] were incorporated in this study to find most appropriate combination of laboratory scale methods used to predict potential ash related operating problems associated with direct biomass combustion. Such combination of procedures is essential for prediction of the potential problems before introduction of the new, unknown fuel in the existing unit. This paper has to offer a multifaceted analysis of five biomass ashes using combination of chemical and instrumental methods. The leaching process was investigated to predict the behaviour of ash elements during combustion process. Based on the results, a modified recalculation model was proposed to predict alkali compounds concentration in the fuel. The model can be used to predict the risk of low-melting eutectic mixtures formation in the ash phase. For deeper studies the ash fusion temperatures and its thermal behaviour were in detail investigated using thermal analysis and high-temperature microscope. Additionally, achieved results can help in developing the biomass ash utilization methods and its appropriate management.

2. Material and methods

2.1. Materials

In the study more than 15 kinds of biomass (woody, energy crops and samples of agricultural origin) were collected from Polish market. The mineral matter composition was determined for all studied materials. The main aim of this study was to determine the influence of alkali metals on ash melting behaviour. Therefore, only five kinds of biomass, characterised by the highest concentration of potassium and varying concentration of chlorine and sulphur were chosen for further analysis. Three samples of herbaceous biomass of agricultural origin (two mixed cereal straw and one corn straw samples) and two energy crops were selected and denoted as MCS1 – mixed cereal straw 1, MCS2 – mixed cereal straw 2 (fuel sample collected from Polaniec Power Plant), CS – corn straw, MxG – *Miscanthus* × *Giganteus* and SV – *Salix Viminalis*.

2.2. Methods

2.2.1. Mineral matter composition

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used for detection of inorganic elements in raw biomass and ash samples using ICP-AES-JY 2000 apparatus. The concentration of the following elements was determined: Na, Mg, Al, Si, P, K, Ca, Ti and Fe. The method is very useful for low content elements concentration measurements in the liquid samples, but it can be also used for elements present in higher concentrations in the sample. Solid samples prior analysis are mineralised in acid mixtures. In the study, raw biomass and ash samples were dissolved using the acid digestion method with a mixture of nitric (HNO_3) and hydrofluoric (HF) acids.

The ash analysis including carbon, hydrogen, nitrogen and sulphur concentrations was carried out using an Elemental Analyser Truespec CHN and S Leco (CHNS628). The method is dedicated to raw biomass samples analysis, but with some restrictions it might be used in case of ashes as well. The analysed sample is heated up in pure oxygen at 950 °C, for C, H, N and 1350 °C for S determination. The chlorine content was measured using chemical analysis (titration method) based on PN-EN 196-2:2013-11 standard.

2.2.2. Chemical fractionation

The fundamental assumption of the chemical fractionation method is that a given element will be dissolved in water or acidic solvent according to its association in the fuel matrix. First, the procedure was developed and applied for determination of coal inorganic behaviour [19,20], later on it was adapted for biomass studies as well [21–23].

The overall concept of the method was shown in Fig. 1 and the procedure applied in this study was determined in Fig. 2. A consecutive

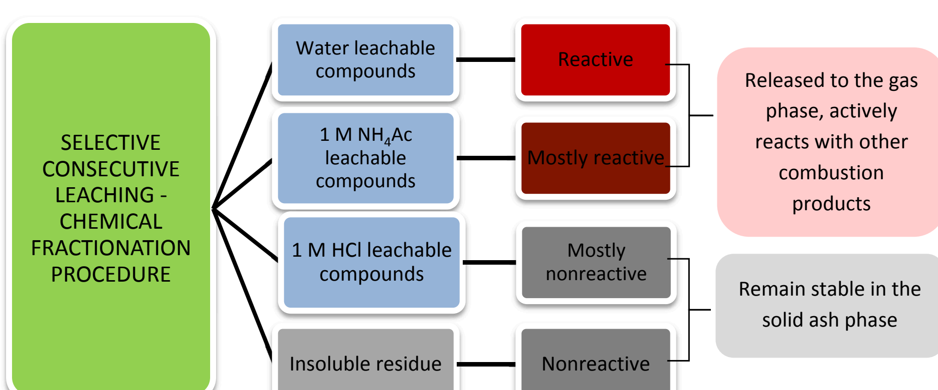

Fig. 1. Chemical fractionation general concept [24].