



Research paper

Biomass ash interactions with a manganese ore used as oxygen-carrying bed material in a 12 MW_{th} CFB boiler

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ABSTRACT

Oxygen carrier aided combustion (OCAC) is a combustion concept which utilises oxygen carriers as bed material in existing fluidised bed boilers. In this study, a manganese ore was used in a 12 MW_{th} CFB boiler. During the experimental session with the manganese ore, the boiler was operated with wood chips as fuel for more than a week without replacement of the bed material. Bed samples were extracted each day in order to investigate interactions between the manganese ore and the wood ash components. The samples were examined with SEM/EDX to follow the chemical distribution of ash elements in the bed particles. Physical properties such as density, size distribution and attrition resistance were followed as well. The impact on the reactivity of the oxygen-carrier bed particles was examined in a batch fluidised bed reactor at laboratory scale with gaseous fuels.

Elemental composition analysis of the samples showed that common ash elements such as silicon, calcium, potassium, magnesium and sulphur had been accumulated in the manganese ore. Silicon, calcium and potassium were found throughout the particles as well as in formed surface layers. Sulphur was only found at the surface of the particles. The reactivity of the oxygen-carrying particles was affected during operation and showed a continuous decrease with increasing residence time in the boiler. The decrease in reactivity could be coupled to the layers of ash formed. Thus, this is an important issue when developing novel combustion concepts, such as OCAC and chemical-looping combustion (CLC), for biomass fuels.

1. Introduction

Bioenergy with carbon capture and storage (BECCS) has been put forward as a necessary implementation to meet the climate targets [1]. Biomass is, however, known to contain very reactive ash components and to interact with for example silica sand, which is the conventionally used bed material in fluidised bed boilers [2].

Carbon capture with chemical-looping combustion (CLC), using metal oxides with the ability to be oxidised or reduced at combustion conditions depending on the surrounding oxygen partial pressure, has been studied extensively [3]. Numerous metal oxides, referred to as oxygen carriers, have been operated in chemical-looping units ranging from small lab-scale units up to a 1 MW_{th} reactor unit [4].

Furthermore, the use of oxygen carriers in conventional combustion in fluidised bed boilers has been proposed as a measure to even out the oxygen availability and temperature in the boiler. This technology has been referred to as oxygen carrier aided combustion (OCAC) and promising results have been reported [5]. The concept has been successfully operated for more than 12,000 h using ilmenite as bed material in full industrial scale [6]. The replacement of conventional bed materials

in fluidised beds boilers with oxygen carriers gives rise to new areas of investigation. One issue is whether ash components in the fuel will interact with the oxygen carrier and how this will affect the performance of the oxygen carrier. Consequences of interactions between conventional bed materials and biomass ashes have been widely studied. However, the interactions between oxygen carriers and ashes is an almost unexplored field.

1.1. Biomass combustion in fluidised beds

The amount and composition of ash varies widely depending on the fuel used. Biomass usually contains an ash fraction between 0.1 and 40%; the lower ash fractions can be found in wood and the highest in rice husks and water milfoil [7]. The ash contains inorganic matter that remains after the fuel is combusted. The most common elements in biomass ash are calcium, potassium, silicon, magnesium, aluminium, sulphur, iron, phosphorous, chlorine, sodium and trace elements [8].

The characterisation of the ash components is important for the operation of fluidised bed boilers. Potassium, which is most often the main alkali source in biomass ashes, is regarded as a specifically

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| Nomenclature | | | |
|-----------------|---|------------------------|---|
| CFB | circulating fluidised bed | \dot{n} | molar flow rate at the reactor outlet (mol/s) |
| CLC | chemical-looping combustion | OCAC | oxygen carrier aided combustion |
| EDX | energy dispersive X-ray spectroscopy | SEM | scanning electron microscopy |
| m_{ox} | mass of fully oxidised oxygen carrier (g) | x_i | gas concentration of species i (mol.%) |
| M_{O} | molar mass of oxygen (g/mol) | γ_{CO_2} | CO ₂ yield (–) |
| | | ω | mass-based oxygen carrier conversion (–) |

problematic ash component. Potassium is known to react with chlorine, forming gaseous potassium chloride. This compound can cause problems such as corrosion and fouling in the convection path of the boiler. The formation of alkali chloride compounds also promotes the reaction of alkali with silicates since the mobility of alkali increases when present in gaseous form [2,9]. When the potassium reacts with the commonly used silica sand, sticky ash compounds are formed on the surface of particles. It is thereby being the cause of particles merging together to larger clusters, a phenomenon commonly referred to as agglomeration [10].

Agglomeration has been studied widely and occurs due to the formation of sticky alkali silicate complexes of low melting temperature. Morris et al. [10] reviewed the possible mechanisms for agglomeration and divided them into three categories; coating-induced agglomeration; melt-induced agglomeration and physical agglomeration. Coating-induced agglomeration is characterized by layer formation on the particles. The layers are frequently reported to be divided in an “inner” more homogeneous and an outer heterogeneous layer. The outer layer is distinguished by its similarity to the fuel ash composition, while the inner layer consists of mainly calcium and silica. For fuels rich in potassium, an “inner-inner” layer has been reported as well, which is composed of mainly potassium and silica [10].

To understand the ash interactions on bed material is imperative to maintain durable operating conditions. As agglomeration of bed material is generally caused by merger of ash layers on bed particles [9,11,12], the formation of these layers are of importance to understand. Zevenhoven-Onderwater et al. [12] proposed three mechanisms for ash-layers to form on bed material: 1) The bed particle is considered to be inert and acts only as a carrier of the layer. In this case the layer grows outward on the surface of the particle and consists of elements originating from the fuel. 2) The formation is considered to be caused by a reaction between the bed particle and elements from the fuel or additives. In this case the layer grows inwards on the particle. 3) There is a mixed mechanism where the layer is formed by a combination of 1) and 2). Studies covering bed materials including quartz, olivine and ilmenite have reported mechanism 3) to be the most commonly occurred one [12–15].

The mechanism for layer formation on olivine used for fluidized bed gasification with woody biomass as fuel was studied by Kuba et al. [16] It was observed that the well documented Ca-rich layer on olivine [13,14], was formed through the incorporation of Ca²⁺ into the crystal structure by the replacement of either Fe²⁺ or Mg²⁺. The released Mg²⁺ formed MgO which was found in distinguishable zones between the main particle layers.

The alkali balance in the boiler, and thus its effects on the operation, is affected by the interaction between these species and the bed material. By applying other bed materials than the commonly used silica sand, the tendency for agglomeration formation may be significantly reduced [17]. Consequently, it could increase the issues related to deposition of alkali on heat-transfer surfaces if more alkali will be left in gaseous form. Furthermore, the composition and amount of ash in the fuel affects the risk of agglomeration and, thus, decides the possible operation parameters such as temperature.

1.2. Interactions between ash and oxygen carriers

As discussed above, interactions between ash and bed material can cause agglomeration of the bed. When an oxygen carrier is used as bed material in order to transport oxygen within the bed or between multiple beds, ash interaction could cause additional effects. Ash components attaching to the surface of the particles may either decrease or increase the oxidation and reduction rates of the oxygen carrier. The reaction rate can be reduced if gas diffusion is hindered by an ash layer on the surface of particles. It is also possible that attaching ash components could have a catalysing effect on the reaction or even have oxygen carrier properties. Ash components reacting with the oxygen carrier and altering the composition could either increase or decrease the oxygen transport capacity depending on the compounds formed.

The research on interactions between ash and oxygen carriers has so far mainly been focused on coal ashes. A study on the effect of coal ash on iron oxide oxygen carriers was carried out in a thermal gravimetric mass spectrometer (TGMS) and the reactivity of the oxygen carriers was found not to be decreased by the ash in this case [18]. Azis et al. [19] concluded that a small addition of coal ash to ilmenite reduced the reactivity of the oxygen carrier, but a further addition of ash substantially increased the gas conversion. Keller et al. [20] published a study on interactions between minerals commonly found in ashes and oxygen carriers, including ilmenite. It was concluded that the mineral pyrite had the most deteriorating effect on the oxygen carrier reactivity due to formation of sulphides. It was, however, shown that ilmenite did not form any sulphides [20]. Bao et al. [21] investigated the effect of common coal ash components on iron oxygen carriers and found that most of the ash components decreased the reactivity, except calcium sulphate which can function as an oxygen carrier itself. A recent study showed that brown coal ash, which is rich in silica, iron and magnesium, reacted both with iron ore and with ilmenite [22]. Gong et al. [23] found that the solid conversion during oxygen uncoupling was lowered when a copper oxygen carrier was mixed with coal ashes.

Even though most studies have been carried out with respect to coal ashes, interactions between biomass ash and oxygen carriers have been studied. It has been concluded that ash rich in silica caused sintering and agglomeration of an iron ore, while potassium-rich ash increased the reduction reactivity of the ore [24]. Ilmenite has been examined as oxygen-carrying bed material for OCAC. When studying ilmenite particles that had been operated in a 12 MW_{th} CFB boiler with biomass as fuel, it was seen that a segregation of iron to the surfaces and an enrichment of titanium in the particle core had taken place. A calcium-rich double layer on the particle had also been formed, which surrounded the iron layer [25].

1.3. Aim of study

The use of biomass in chemical-looping is increasing, which can clearly be seen in the recent review article by Adánez et al. [26] For example, a 1 MW_{th} chemical-looping pilot plant has been operated with a fuel mix of hard coal and torrefied biomass [27]. The manganese ore examined in this paper has also been used as oxygen carrier in two pilot scaled chemical-looping pilots, 10 kW_{th} and 100 kW_{th}, with wood char and pellets as fuels [28]. However, these studies did not include any examinations of how the oxygen carrier was affected by the ash present

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