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Online corrosion measurements in small- and mid-scale during pulverised biomass/coal co-combustion

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Abstract

The partial substitution of coal with biomass in the existing power plant fleet can reduce the carbon dioxide pollution in a cost effective way at high efficiencies. The goal of this study was to identify suitable co-firing ratios during co-combustion of straw and three different coal types (0, 10, 25, 40, 60, 100% straw on energy basis in fuel blend) minimizing the corrosion risk. An online corrosion monitoring systems based on the linear polarisation resistance method has been used for measurements in two pulverised fuel co-firing systems: An externally heated entrained flow reactor at the Technical University of Munich and a 300 kW_{th} drop down fired reactor at University of Stuttgart. The experiments at the entrained flow reactor have been conducted for 8 h per blend at 1200 °C with an excess oxygen of 3-5 vol-%. Online corrosion measurements were performed at a flue gas temperature of about 700 °C – 900 °C representing the superheater region of a power plant. Material temperature was set to 530 °C utilizing 10CrMo9-10 as the examined alloy. The pilot scale tests were performed for 0, 25, 40, 60% e.b. straw content. Each blend was combusted for 24 hours. At lab scale tests a constant sensor signal was measured for 0, 10, 25, 40% e.b. straw content which increased steeply after changing the ratio to 60%, indicating a corrosive atmosphere. This phenomenon was found for all three different coals, however the overall corrosion signal was lower for coal from South Africa and El Cerrejon. Nevertheless, all series of measurements showed an increasing signal for a higher share of straw in the fired fuel blend. These tendencies were also confirmed at the pilot scale test with El Cerrejon coal. Deposition and fuel analysis show correlations between the Cl-content in fly ash, Al₂O₃ content in the fuel and the corrosion signal.

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1. Introduction

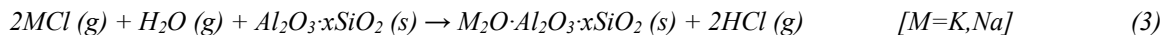
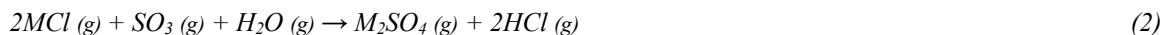
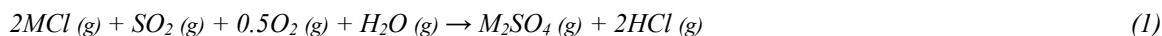
The world community has recently renewed its ambitious climate goal in Paris: reducing the CO₂ emissions to reach only 1.5 °C global warming. To reach this goal, the use of fossil fuels has to be strongly reduced until 2050. To promote this plan the states are advised to tighten their laws for emissions to reach this goal [7, 23]. These days power plant owners and energy supplier are already facing challenges of reducing emissions. One possibility is to add renewable fuels. As an alternative the use of non-conventional materials such as herbaceous biomass or agriculture waste products have shown a large potential for the heat and power production. Besides the reduction of CO₂ also other emission such as SO₂, NO_x, N₂O, NH₃, dioxins and furans are influenced positively. In the last years the investigation of co-firing of biomass with coal has become more and more relevant. Likewise, the focus of the research lies on ash formation, deposition built up, high temperature chlorine induced corrosion and emissions. The main aim is to increase the share of biomass in co-firing while maintaining power plant efficiency. Power plants designed for fossil fuels are not automatically suitable for the use of biomasses. Especially herbaceous fuels such as straw or bio-waste materials are labelled as problematic and can cause ash related problems due to their fuel composition. The ash melting behaviour leads to slagging and fouling while high chlorine contents induce corrosion. Mostly the high content of potassium and chlorine, bound in the fuel matrix as salts, causes these problems. Plant shutdowns and expensive maintenance are the results.

1.1. Challenges

Many publications focus on the co-combustion of straw and coal [10–12, 17]. However biofuels aren't homogenous and differ strongly in their fuel composition. For biomasses and bio-waste, the S/Cl-ratio in the fuel can give a good forecast to predict their corrosion risk [18]. This ratio is based on the sulphating process between alkali salts and released sulphur, which appears as SO₂ or SO₃. Hard coal also has a high amount of sulphur in their fuel matrix but the embedding reactions of alkali metals with aluminium silicates are dominating the mitigation of corrosion products. Fuel indices like K/(Al+Si) or K/(Si+S) [9, 24] (based on embedding reactions) are well known but not as strong as the S/Cl-ratio. One objective in the OnCord project is to predict corrosion by combining online corrosion measurement systems with advanced fuel characterisation to maximise coal-biomass shares.

1.2. High temperature chlorine induced corrosion and its mitigation measures

Straw has a high content of alkali chlorides bound as salts in the fuel matrix. These alkali chlorides are volatile at high temperatures in the flue gas. If the gaseous KCl has contact with cold boiler internals, such as superheater tubes the alkali chlorides condense at the tubes and generate a sticky initial layer. This layer enhances the deposit built up. The KCl in the deposit reacts with SO₂. At this reaction pure chlorine appears, diffuses to the layer surface and reacts with iron to ferric chloride. This diffuses into higher layers to react with oxygen to ferric oxide and releases chlorine. Under specific conditions such as special partial pressure and availability of the single gaseous components the chlorine can diffuse backwards and a circular corrosion process starts that leads to heavy loss of metal. In the coal biomass co-combustion two mitigation reactions mainly take place both in flue gas: the sulfation of potassium chloride and the embedding reaction with aluminium silicates from the coal ash.



All reactions need the KCl in the gas phase to be effective. Therefore the mitigation processes has only a small temperature frame with suitable conditions: for the sulfation process with SO₂ (1) or SO₃ (2) the temperature has to be in a range between 900 – 1100 °C [1, 22]. For higher temperatures above 1100°C the sulfating process is thermodynamically not preferred. In this temperature frame the embedding reactions with aluminium silicates take place [6]. Aluminium silicates can absorb the KCl as chemi- or physisorption dependent on the temperature, partial

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