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Measuring gaseous HCl emissions during pulverised co-combustion of high shares of straw in an entrained flow reactor

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Abstract

The co-firing of biomass with coal in retro-fitted pulverised fuel power stations is seen as one cost-effective opportunity to reduce carbon dioxide emissions. Currently either higher shares of high quality biomass (e.g. wood) or limited ratios of low quality biomass (e.g. straw) are co-fired. Ash-related problems, namely fast deposit built-up and corrosion due to high potassium-chloride content in low-quality biomass, have limited the amount of co-fired difficult biogenic materials. Therefore, a measurement campaign in an externally heated entrained flow reactor co-firing two types of bituminous coal with straw at elevated shares was performed. The goal was the investigation of the release and the reaction path of chlorine during co-combustion of blends with a share of 0, 10, 25, 40, 60, 100 % straw on dry energy basis. Therefore, the HCl amount in the flue gas was quantified using conventional IR-methods and wet-chemical analysis according to DIN EN 1911. Extensive fuel and ash analysis comprising of proximate & ultimate analysis, ash analysis, computer-controlled scanning electron microscopy and chemical fractionation were implemented. Combustion experiments were conducted at 1200 °C reactor temperature and an excess oxygen ratio of 3 – 5 vol-% resembling power plant conditions. Fuel input was kept constant at 8 kW_{th} for every fuel blend. The HCl content in the flue gas was measured at one position in the heated zone of the reactor and in the flue gas duct at approx. 350 °C. Gaseous HCl emissions measured by IR method in the flue gas duct increased from 9,6 mg/Nm³ dry 6 % O₂ for pure coal combustion to a maximum 215,3 mg/Nm³ dry 6 % O₂ for the 40 % Straw/Columbian coal blend, dropping to 170,2 mg/Nm³ dry 6 % O₂ for pure straw combustion. This indicates a higher release of KCl during straw combustion and therefore decreasing alkali capture by chemisorption in alumina-silicates for blends with a straw share exceeding approx. 40 %. For the second fuel blend of South African coal and straw the maximum HCl content in the flue gas is 245,7 mg/Nm³ dry 6 % O₂ at 60 % straw. Therefore, a better alkali capture at higher straw shares during co-combustion with South African Coal is assumed. Additionally, chemical equilibrium calculations have been performed using the Software package FactSage 7.0 ®. Calculated concentrations of HCl are in good agreement with the measured values.

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1. Introduction

The co-combustion of difficult solid fuels with coal in existing power stations with state-of-the-art efficiencies is seen as one cost-effective possibility to reduce the share of coal in the energy sector. Especially the utilisation of currently unused biomass materials (e.g. agricultural residues in many European countries) offers a large potential to increase the amount of biofuels in heat and power production [1]. The substitution of coal by biomass can make a significant contribution to decrease CO₂ emissions as well as lower the SO₂ and NO_x emissions [2, 3]. Co-firing activities in PF systems are primarily performed with woody materials, sewage sludge and straw [4]. Denmark has taken a leading role worldwide in the utilisation of cereal straw for energy production. During a long-term demonstration project from 1996 – 1998 conducted at Unit 1 of Studstrup power station the co-firing of straw with bituminous coal was studied extensively [5]. The maximum amount of co-fired straw during the campaign was limited to approx. 20 % of the fuel input on an energy basis. Therefore, current research projects aim to further increase the share of straw and to widen the fuel range co-fired while maintaining high availability and assuring highest efficiencies. Several challenges highlighted in the next chapter have to be overcome to realise this goal.

1.1. Challenges

Biobased fuels differ largely in their composition [6]. Especially herbaceous fuels such as straw can contain high shares of volatile alkali compounds and chlorine. The release of those components to the gas phase can lead to several disadvantageous effects on operation and performance. High concentrations of gaseous alkali salts in the flue gas can cause enhanced deposit formation and high temperature chlorine induced corrosion in the superheater area [3]. Volatilised alkali-salts may form deposits via direct condensation on heat exchanger surfaces or by the formation of fine aerosol particles, which then deposit via thermophoresis, eddy deposition and/or diffusion. These mechanisms have been described in detail in the literature and are well-understood [5]. Usually deposition rates are lower for straw-coal blends compared to pure straw combustion because of the beneficial interaction between both fuels described in chapter 1.2.

A high share of chlorine in the deposits can further lead to a corrosive atmosphere on the surface of the superheater tubes. This process is usually referred to as high-temperature chlorine induced corrosion or active oxidation. Nielsen et al. describe the process extensively with other possible corrosion phenomena occurring during co-firing of biomass with coal [7].

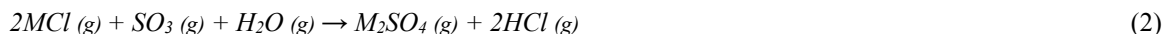
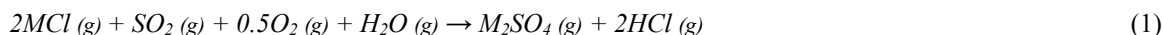
Both introduced challenges are related to the presence of gaseous alkali salts in the flue gas. Therefore, the reduction of alkali chloride concentrations has been a major goal of the research conducted in the field of combustion science.

1.2. Preventing gaseous alkali chlorides

The prevention of the aforementioned problems has been investigated thoroughly for both co-firing of low shares of biomass and pure biomass combustion in all common firing systems (Grate firing systems, FB systems and PF systems) [2, 8, 9, 10, 11]. The goal is the limitation of the amount of gaseous alkali chlorides in the flue gas. Two main ways of alkali reduction taking advantage of the chemical reactions in the flue gas have been established.

a) Sulphation of alkali chlorides to alkali sulphates in the gas phase by adding sulphur to the system.

Gaseous alkali chlorides can react to alkali sulfates according to the following reactions (1) and (2):



where M is Na or K. Both reactions convert alkali salts to less dangerous alkali sulphates and gaseous HCl. Reaction (2) is reported to be by a magnitude faster than reaction (1) [10]. The gaseous oxidation of SO₂ to SO₃ is a required step in order to achieve a satisfying sulphation. Wu et. al. point out the narrow temperature window enabling the

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