



K–Cl–S chemistry in air and oxy-combustion atmospheres

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Abstract

This paper studies the consequences on high temperature corrosion when biomass is co-fired with coal in oxy-fuel combustion, a concept that would enable negative CO₂ emissions by combining renewable fuels with CO₂ capture. The particular focus of the work is the sulphation of alkali chlorides which is studied by means of experiments and modelling. The melting point of alkali sulphates is higher than for alkali chlorides and a high degree of alkali sulphation is hence a measure to reduce issues related to high-temperature corrosion. In the experiments a propane flame was doped with SO₂ and KCl (in solution) in air and oxy-fuel atmospheres. Two alternative measurement principles were applied to quantify potassium sulphation and the paper thereby contributes with a novel experimental approach as well as unique experimental data for turbulent diffusion air and oxy-fuel flames. The degree of sulphation of the injected KCl increases substantially in oxy compared to air combustion conditions, a fact which favours the use of biomass in oxy-combustion. This is mainly due to the increased concentration of SO₂ due to flue gas recycling in oxy-combustion, but also chemical effects introduced by the CO₂ as well as a small effect resulting from an increased residence time in the combustor.

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1. Introduction

The anthropogenic use of fossil fuels is widely accepted to be the main reason for global warming. The interest in alternative energy resources, such

as biomass and waste derived fuels, has therefore increased in recent years. An alternative path to reduce the emission of carbon dioxide (CO₂) from fossil fuels is to apply the concept of carbon capture and storage (CCS). The present work will focus on one of the main CCS technologies, oxy-fuel combustion, in which the fuel is combusted in a mixture of pure oxygen and recycled flue gas in order to obtain a high CO₂ concentration in the flue gas. The use of biomass in CCS processes

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(BECCS) has been discussed in the literature as an option to create a carbon sink in order to reduce the atmospheric concentration of CO_2 , see e.g. Ref. [1]. With this background, the present work studies the use of biomass in oxy-fuel combustion; in particular, the K-Cl-S chemistry is studied by means of modelling and experiments.

In relation to coal, biomass is usually considered as a fuel of lower quality, e.g. with respect to lower heating value and higher contents of alkali metals (sodium and potassium) and chlorine [2,3]. The alkali metals tend to react with chlorine and the product may cause issues with high temperature corrosion (HTC) on heating surfaces in a boiler. Compounds containing alkali metals and chlorine are among the most problematic HTC related compounds. Due to this, HTC is primarily a problem for power plants fired with biomass rather than coal [4]. One way of mitigating the HTC related issues is to introduce sulphur, for example by means of a second fuel with higher sulphur content. In such an environment, in which significant amounts of sulphur is present, the alkali chlorides can be converted into sulphates, whose melting temperatures are higher and which are less problematic from a HTC perspective [3,5]. It is therefore of interest to study how the degree of sulphation can be controlled both with respect to fuels and fuel mixtures as well as combustion parameters and design.

In oxy-fuel combustion the replacement of nitrogen with recirculated flue gases causes a difference in flue gas composition. As a consequence, the SO_2 concentration is typically more than three times higher in oxy-fuel combustion compared to air combustion [6,7]. As discussed in our previous modelling work, the increase in SO_2 will influence the homogenous sulphation process and in general the sulphation of alkali is substantially enhanced in oxy-fuel compared to air-fuel combustion [8]. The present work aims to examine this process further by means of a combined experimental and modelling approach; the overall aim is to assess the gas phase K-Cl-S chemistry including the overall degree of potassium sulphation. The sensitivity to CO_2/N_2 atmospheres, sulphur to potassium ratios injected to the combustor and residence time is analysed and discussed.

2. Theory

In a solid-fuel fired combustion system, both potassium (K) and sodium (Na) are typically present but potassium is usually the main alkali specie. In addition, sodium has been reported to follow a similar reaction mechanism as potassium [3,9]. In this work, potassium was therefore chosen to represent both alkali metals. Potassium and chlorine are released from the fuel to the gas phase during devolatilization and combustion. The chlorine is mainly released as HCl, KCl or chlorinated hydrocarbons. The chlorinated hydrocarbons react

soon after the release with subsequent formation of HCl during combustion. As long as chlorine is present, the potassium is released as KCl, otherwise it is released either as atomic potassium (K) or as hydroxide (KOH) [10–12]. Due to the number of reactions and general complexity, the release of inorganic compounds and ash reactions are neglected in this work, which instead focuses entirely on the gas phase chemistry and its potential to convert potassium chloride into potassium sulphate. The chlorinated form of potassium, KCl, is the main potassium compound released to the gas phase. KCl may, however undergo sulphation during combustion to form potassium sulphate (K_2SO_4). At temperatures lower than $450\text{ }^\circ\text{C}$, sulphated potassium may be found as pyrosulphate ($\text{K}_2\text{S}_2\text{O}_7$) [13]. Such low temperatures are however not relevant for this work. The sulphation of potassium chloride is suggested to follow one of two possible paths: homogenous sulphation where the sulphates are formed in the gas phase (and are condensed after its formation), or heterogeneous sulphation which includes surface reactions of non-gaseous chloride particles. The heterogeneous sulphation of KCl was proposed by Steinberg and Schofield [14] as a surface reaction phenomenon taking place under post flame conditions. In their work with hydrogen and propane flames, they concluded sodium sulphate to be too unstable during flame conditions to be responsible for the observed sulphation [14,15]. Experimental results presented by others have, on the other hand, showed that the heterogeneous path is too slow to describe the sulphation typically occurring in industrial scale boilers [16,17]. Therefore, this work focuses entirely on homogenous sulphation of KCl.

The theory which suggests that gas phase reactions control the sulphation process is in agreement with several experimental studies [16–18]. In the present work, we aim to examine if the homogeneous chemistry can explain the potassium sulphation also in an 80 kW turbulent propane diffusion flame. The sulphation of KCl may follow one of the reaction routes available including reactions with both SO_2 and SO_3 (see Table 1). Regardless of the route, the final step is the condensation of gaseous K_2SO_4 , which first is formed in reaction between KHSO_4 and KCl or KOH (R1 and R2). There are mainly four routes which concerns the formation of KHSO_4 including either SO_2 or SO_3 . SO_3 may react directly with KOH (R3) or through a two-step reaction starting with KCl (R4 and R5). KHSO_4 may then also be formed via SO_2 in a three-step reaction starting with K (R6–R8) or starting with KSO_3 (R9), which may form from either KO (R10) or K (R11) involving SO_2 and SO_3 , respectively. KCl, KOH, KO and K are key components in the sulphation process. These compounds are coupled via several reactions; the most important ones are listed in Table 1. This list is based on the result in our previous work [8]. KOH may form from

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