



A comprehensive experimental and modeling study of sulfur trioxide formation in oxy-fuel combustion



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ABSTRACT

This study focuses on the sulfur chemistry occurring within an oxy-combustion system by adopting a combined approach of detailed kinetic modeling and experiments. Influences of variable combustion parameters on SO₃ generation have been investigated computationally by implementing different combustion mechanisms. Results indicated significant influences of the equivalence ratio, inlet SO₂ concentration and presence of NO on SO₃ formation while the inlet O₂ concentration exhibited minimal effect. Presence of NO demonstrated different degrees of direct and indirect interactions between NO_x and SO_x species for different reaction sets. Sensitivity analysis indicated radicals to be playing a dominant role in SO₃ formation. Collected temporal profiles of SO₃ from the lab-scale combustion setup showed evidence of significant SO₃ formation at temperatures as low as 650 K under realistic boiler temperature conditions. The equivalence ratio and the concentrations of SO₂, O₂ and NO were found to influence the SO₃ formation. Predictions of final SO₃ concentration from different mechanisms were comparable with the experimental data; however, the trend of the temporal profiles could not be anticipated by the models. Experiments conducted in the presence of NO indicated the existence of interactions between NO_x and SO_x species and also the requirement of modifications to the existing oxy-combustion models.

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1. Introduction

38% of the carbon dioxide (CO₂) emissions in the United States are caused by power plants (US, 2011), which are still dominated by the usage of coal as fuel, and they are expected to remain as the main source of electricity generation for many years to come. Advancements in carbon capture and storage (CCS) technology are necessary in order to keep the CO₂ level acceptable while continuing to use fossil fuels. Post-combustion, pre-combustion and oxy-combustion are the three currently available options for CCS (Gibbins and Chalmers, 2008; Toftgaard et al., 2010; Wall et al., 2009; Wall, 2007). Oxy-coal combustion is a promising option as it inherits the flexibility of being retrofitted to existing power plants (Toftgaard et al., 2010), which will work as an advantage for the power generation sector. As the name suggests, oxy-coal combustion is the process of burning coal in oxygen (O₂) instead of air while also introducing a recycle stream into the boiler to stabilize the flame and lower the temperature. The flue gas evolved from this process is rich in CO₂ and 80% lower in volume (Buhre et al., 2005),

which can be easily compressed for storage or sequestration. But as the combustion medium is changed from nitrogen (N₂) to CO₂-rich environment, significant changes in the combustion chemistry is expected while the lowered volume of flue gas along with the introduction of the recycle stream in the boiler can result in higher concentrations of different corrosive species. One of the concerns of adopting this technology involves the corrosion problem caused by increased sulfur oxide (SO_x) species concentrations (Stanger and Wall, 2011). During the devolatilization and char oxidation process, most of the sulfur content of the coal gets released in the form of sulfur dioxide (SO₂) while a certain percentage (0.1–1% in air combustion) converts to form sulfur trioxide (SO₃) (Brady and Holm, 1988) through reactions (R1)–(R3).



(R1) occurs at high temperature (>1150 K) while (R2) and (R3) are active at lower temperature ranges (<1150 K) and are termed as the secondary formation pathway (Brady and Holm, 1988; Fleig et al., 2012a; Hindiarti et al., 2007). The generated SO₃ can later easily convert to sulfuric acid (H₂SO₄) below 700 K by going

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through reaction (R4), while around 450 K all the SO₃ is likely to be in the form of H₂SO₄ (Hardman et al., 1998).



There is no restriction on SO₃ or H₂SO₄ emissions placed by the Environmental Protection Agency (EPA). But emission of H₂SO₄ through the stack will produce a visible blue plume with an opacity greater than 20%, which is in violation of the EPA emission standards (Srivastava et al., 2004). Under the acid dew point, condensation of the generated H₂SO₄ can cause severe corrosion damage in the subsequent units after the boiler. The situation will get aggravated as higher concentrations of SO₃ have been observed in oxy-combustion experiments (Duan et al., 2015; Monckert et al., 2008; Tan et al., 2006). SO₂ emissions in terms of unit energy produced in oxy-coal combustion has been shown to decrease, which was attributed to the increased conversion to SO₃ and higher sulfur retention by ash (Croiset and Thambimuthu, 2001; Maier and Dhungel, 2008; Tan et al., 2006). An experimental study (Ahn et al., 2011) conducted using two different kinds of coal in a pulverized coal boiler revealed higher SO₂ concentration (in terms of volume) in oxy-fuel cases comparing to air-test cases and almost 4 times higher SO₃ concentration (in terms of volume) with the maximum being at 800 K. However, on a normalized mass basis (mass SO₃ per unit energy input), air-fired pulverized coal tests showed higher SO₃ emissions while air-fired circulating fluidized bed tests exhibited similar emissions compared to oxy-firing. Another study (Chamberlain et al., 2013) examining emissions of sulfur species from eight different types of coal revealed the SO₂ concentration (in terms of volume) to be 3 times higher in oxy-combustion environment. The collected experimental data also showed the SO₃ generation to be closer to air-combustion, which was attributed to the fact that SO₃ could be frozen near the equilibrium concentration in the high temperature range. Comprehensive studies (Fleig et al., 2013, 2012a, 2011a, 2011b, 2012b) conducted by Fleig et al., involving experiments and simulations, revealed that combustion parameters such as, equivalence ratio (ϕ), SO₂ content and O₂ percentage in the oxidizer to influence the formation of SO₃ under oxy-combustion environment. Sensitivity analysis, performed in the post combustion zone (Fleig et al., 2013) by Fleig et al., showed the dependency of SO₃ formation on oxygen (O) and hydroxyl (OH) radicals and that higher concentrations of SO₃ was found to form in the burnout regions of carbon monoxide (CO). As the concentration of SO₃ has been found to be higher in oxy-combustion cases, the acid dew point is anticipated to be higher resulting in condensation of H₂SO₄ at higher temperatures than that in air combustion units. To anticipate the evolution of SO₃ under different plant conditions a complete temporal profile of SO₃ under realistic boiler condition is required. But such profiles of SO₃, especially extending to the lower temperature region, under variable operating conditions are yet to be reported.

Alongside the sulfur chemistry, nitrogen chemistry in oxy-combustion has also been a focus of several studies (Croiset and Thambimuthu, 2001; Gimenez-Lopez et al., 2010; Glarborg et al., 2003; Kimura et al., 1995; Kuhnemuth et al., 2010; Liu et al., 2005; Mackrory and Tree, 2009, 2012; Mendiara and Glarborg, 2009; Normann et al., 2009, 2010, 2011; Obras-Loscertales et al., 2015; Okazaki and Ando, 1997; Watanabe and Okazaki, 2011). Experiments revealed the emission of nitrogen oxides (NO_x) to be significantly lowered in oxy-combustion comparing to that of air-combustion (Croiset and Thambimuthu, 2001; Kimura et al., 1995; Liu et al., 2005). Reburn mechanism (Mendiara and Glarborg, 2009) is a dominant reaction pathway for NO destruction, which mostly contributes to the NO_x reduction in the oxy-coal environment, as recycling a part of the flue gas to the boiler increases the exposure of nitric oxide (NO) to the hydrocarbon radicals. Also, removal of N₂ eliminates the possibility of the occurrence of the Zeldovich mech-

anism (Zeldovich, 1946), provided air ingress is negligible, thus contributing to lower NO emissions. Even though experimental and kinetic studies have been performed to study NO emissions in oxy-combustion, there is still a gap remaining regarding the interaction between SO_x and NO_x species. There have not been kinetic simulations performed to observe the effect of recycled NO on SO₃ generation in oxy-combustion cases with detailed chemistry and no experimental data on such matter is available.

The objective of this study is to elucidate the evolution trends of SO₃ in oxy-coal combustion flue gas and compare the experimental data with simulated cases using kinetic mechanisms available in the literature. For this purpose, experiments in a unique lab-scale combustion system, which represents the actual plant temperature conditions, have been conducted. The setup has the advantage of sampling from different points and obtaining the temporal profile of SO₃ under varied operating conditions. Kinetic simulations have been performed using different combustion mechanisms and these have been compared to the experimental results. Also, the interaction between sulfur and nitrogen species has been studied computationally by integrating the available reaction sets to the existing combustion mechanisms and a comparison has been made to the experimentally collected data.

2. Kinetic simulations

Previously, simulation studies (Alzueta et al., 2001; Giménez-López et al., 2011; Hindiyarti et al., 2007) focused on sulfur and nitrogen chemistry of oxy-combustion environment have been conducted by applying a combustion mechanism that has been developed and modified for CO₂-rich environment. The sulfur chemistry subset of this mechanism was developed by Alzueta et al. (2001) based on the studies of Glarborg et al. (1996) and it consists of 91 reactions. Modifications were later implemented into the mechanism to acquire better agreement with available experimental results. Hindiyarti et al. (2007) conducted ab-initio calculations to investigate the SO₃ consumption and generation routes and the resultant reaction network with new rate parameters were employed to simulate different conditions. The computationally obtained results on SO₂ oxidation by applying new parameters were then compared to the experimentally available results and it was concluded that only the influence of (R5) was significant among the other reactions under investigation, ((R6)–(R7)).



To investigate the effect of high CO₂ concentration on CH₄ combustion, a reaction subset consisting of 14 reactions was applied by Glarborg and Bentzen (2008). It was found that CO₂ has a significant influence on the radical pool and CO burnout through reaction (R8).



Such effect of CO₂ was taken into consideration and implemented into the reaction mechanism by Giménez-López et al. (2011). This updated combustion mechanism, containing 110 species and 747 reactions, was implemented by Fleig et al. (2013, 2012a, 2011b) in a comprehensive study to computationally elucidate the sulfur chemistry occurring during oxy-combustion. The study revealed that the equivalence ratio, O₂, NO and SO₂ concentrations in the oxidizer affected the SO₃ formation significantly under a linear temperature profile extending from 1800 to 500 K (Fleig et al., 2012a, 2011b). The influence of various combustibles like CH₄ and CO at the post combustion zone was also investigated

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