INVESTIGATION OF SO_X AND NO_X CHEMISTRY IN OXY-COMBUSTION FLUE GAS

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Abstract

This study focuses on revealing the influences of different combustion parameters on sulfur trioxide (SO_3) formation during oxy-coal combustion through detailed gas-phase kinetic modeling. Dominant reaction pathways for SO_3 formation were determined by conducting sensitivity analysis. By applying different reaction sets, the interaction between nitrogen oxide (NO_x) and sulfur oxide (SO_x) species has also been investigated. Temporal profiles of SO_3 and NO_x concentrations under a variety of operating conditions have been collected by conducting combustion experiments. The presented comparisons between the model prediction and the experimentally collected data demonstrate the need for improvements in the oxy-combustion models including sulfur chemistry.

Keywords

Oxy-combustion, Kinetic modeling, SO_3 detection, NO detection, FTIR

Introduction

In oxy-coal combustion, oxygen (O_2) is used as the oxidizer instead of air to eliminate nitrogen (N_2) in the flue gas. In an oxy-fired coal power plant, the coal is burned in an oxygen-rich environment and the flue gas is recycled back to the boiler, which in the end produces a highly concentrated CO_2 stream that can be captured at relatively low-cost. As the combustion medium is changed, significant changes in the combustion chemistry is expected. The lowered volume of flue gas along with the recycle process can result in higher concentrations of pollutants such as sulfur trioxide (SO_3). The presence of SO_3 in parts per million (ppmv) levels can cause severe corrosion damage both at high and low temperature regions. In addition, emissions of nitrogen oxide (NO_x) species are expected to reduce due to the absence of N_2 and the reburn reactions occurring in the flame as a result of recycling. Oxy-combustion thus has the potential to reduce the overall NO_x emissions from power plants. To gain an understanding of the sulfur and nitrogen chemistry, a comprehensive study focused on pollutant formation during oxy-combustion is crucial to reduce the emissions.

In the present study, a combined approach of kinetic modeling and experiments has been adopted to elucidate the sulfur and nitrogen chemistry in oxy-combustion flue gas. Experiments have been performed in a unique lab-scale setup with a time-temperature history similar to actual boiler conditions. Flue gas samples have been collected from different points to obtain the temporal profiles of SO_3. Speciation of nitric oxide (NO) and nitrogen dioxide (NO_2) will also be examined under various combustion conditions. Kinetic simulations have been performed by applying two different combustion mechanisms. Also, the interaction between sulfur and nitrogen species has been studied computationally by integrating different reaction sets to the existing combustion mechanisms and a comparison has been made to the experimentally collected data.

Kinetic Simulations

The kinetic simulations have been conducted using Chemkin IV software. The kinetic model layout consists of a perfectly stirred reactor (PSR) for simulating the flame followed by a plug flow reactor (PFR). The PFR has been subjected to a temperature profile collected from the lab-scale reactor and it is representative of the plant boiler condition. The gas-phase model developed by Alzueta et al. (2001) based on the research of Glarborg et al. (1994) has been applied for the simulation studies. The Leeds combustion model (Hughes et al., 2001) has also been applied as a comparison between the two models. In the simulated cases, influences of different parameters have been examined by changing equivalence ratio (0.8-0.98), O_2 percentage (28-34%) and inlet sulfur dioxide (SO_2) concentration (1000-3200 ppmv). Decreasing the equivalence ratio resulted in a raise in the SO_3 concentration due to the availability of O, OH and H radicals. A higher amount of SO_3 was generated with higher inlet SO_2 amount but a declining trend in

conversion was observed. Minimal influence of O_2 percentage on SO_3 formation was observed in the simulated cases.

Significant increase in SO_3 generation was observed with NO introduction into the reactor. Four different reaction sets were integrated into the kinetic model and the results demonstrated complex interaction between NO_x and SO_x species through direct and indirect pathways. Sensitivity analysis in the absence of NO revealed the radicals to be rate controlling in SO_3 generation. In the presence of NO, the reactions that influence SO_3 formation were determined by performing sensitivity analysis. Comparing different reaction sets, similar reactions were found to be effective; however, the extent of the effect was different based on the reaction set applied.

Gas Phase Experiments

Gas phase experiments have been performed in a lab-scale combustion setup of 0.5kW firing rate. The setup includes a burner, where methane is burned with an O_2/CO_2 mixture in a laminar premixed flame, followed by a quartz reactor. The first part of the reactor is heated within a furnace to ignite the fuel/oxidizer mixture and the second part is exposed to a certain quenching rate to mimic the temperature profile of a boiler. This second segment of the reactor contains 15 sampling ports from which samples can be collected and analyzed for quantification of SO_3, NO and NO_2.

For quantification of SO_3 under various operating conditions, salt method has been used. For each experimental run, samples have been collected twice form each port and reproducibility of the data has been checked. The temporal profile of SO_3 presented in Figure 1 demonstrates an increasing trend of the generated SO_3 with the decline in temperature and this is contrary to the model prediction with the Alzueta mechanism. Although the model predicted the reactor exit concentration, it was not able to capture the profile throughout the reactor. Influences of equivalence ratio, inlet SO_2 concentrations and O_2 percentage were also investigated experimentally. For various equivalence ratio and inlet SO_2 concentrations, comparison between experimental data and simulation results revealed good agreement for final SO_3 concentrations. Increase in inlet O_2 concentrations exhibited significant increase in the SO_3 concentration, while the model showed a slight increase.

To investigate the influence of NO, various concentrations of NO were introduced into the system in the presence of SO_2 and an interesting trend was observed from the collected data. A sharp increase in the amount of SO_3 was observed with increasing NO concentration from 200 to 500 ppmv; however, with further increase in the NO concentration, SO_3 concentration exhibited a declining trend. These experiments indicated relatively poor reproducibility while applying the salt method indicating that an alternative method may need to be implemented for SO_3 measurements in the presence of NO.

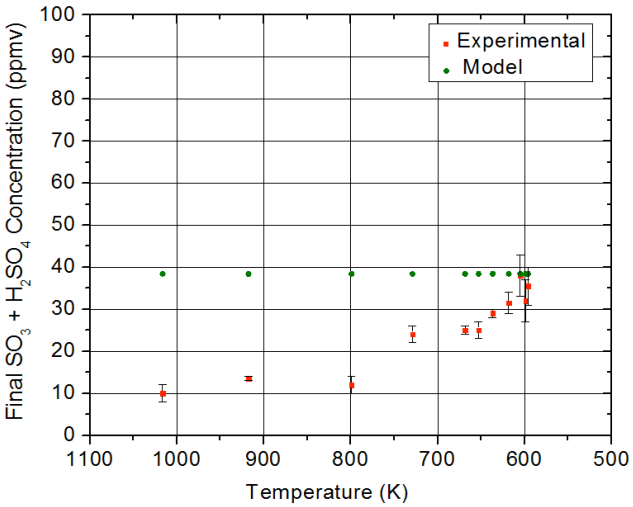

Figure 1. Temporal Profile of SO_3 and Comparison with Model Prediction

As more investigations are required to clarify the speciation of NO_x species in oxy-combustion, similar experimental approach will be adopted in the course of this study to elucidate the profiles of NO and NO_2. FTIR spectroscopy will be applied to measure concentrations of NO and NO_2 present in the combustion flue gas.

Conclusions

In this comprehensive study, the sulfur chemistry within an oxy-combustion system has been investigated by conducting kinetic simulations and combustion experiments. SO_3 formation has been found to be affected by the combustion parameters, such as equivalence ratio, O_2 percentage, inlet SO_2 concentration, and the presence of NO. Reasonable agreement between the model predictions and experimental results have been observed in most cases, but the study indicated the need of further improvements to the existing oxy-combustion models including sulfur chemistry.

Acknowledgements

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