Sub Topic: Coal, Biomass, and New Devices

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Nitrogen Oxide Evolution in Oxy-Coal Combustion

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Abstract: This paper investigates emissions of NO_x from pulverized coal burning in O_2/CO_2 environments. Such environments are pertinent to oxy-coal combustion, a promising "clean-coal" technology. The replacement of the inert nitrogen gas in air with carbon dioxide, which has different physical properties, alters the combustion conditions in the furnace. Hence, the purpose of this work is to theoretically examine the effects of (a) the oxygen concentration in the O_2/CO_2 gases, and (b) the resulting combustion temperatures, on the evolution of NO_x. To achieve these goals a previously published kinetic model was used, which assumes that fuel-bound nitrogen is released along with the tars during coal devolatilization and converts mostly to hydrogen cyanide. A sizable fraction of hydrogen cyanide is then converted to NO. Flame simulations were performed using Cantera to investigate the relative impacts of temperature and oxygen mole fraction, and to understand the causes of the observed trends.
Keywords: Coal, NOx, Fuel-Nitrogen, Hydrogen Cyanide, Oxy-Combustion.

1. Introduction

Combustion-generated pollutants, such as acid gases, particulates, and air toxics, as well as greenhouse gases such as carbon dioxide, are a serious concern. Technologies to capture the pollutants, with various degrees of efficiency, have been developed and implemented [1]. One promising approach is carbon capture and sequestration (CCS) or carbon capture and utilization (eg. for underground oil recovery)[2]. Oxy-coal combustion, where coal combustion occurs in neat oxygen provided by an air separation plant, can greatly facilitate CCS as, upon drying, flue gases consist mainly of carbon dioxide. To reduce temperatures, flue gases are recycled, so the oxidizer stream is essentially a mixture of O_2 and CO_2.

In addition to facilitating carbon dioxide capture, oxy-coal combustion can drastically reduce the generation of nitrogen oxides, NO_x, which consist of mostly NO and little NO_2[3]. Since combustion takes place in the absence of atmospheric N_2 no thermal NO_x is generated; the detected amount of NO_x originates from fuel nitrogen. It has been shown that increasing the concentration of O_2 increases the NO_x generation during coal oxy-combustion, but it remains unclear whether this is driven by the increased temperature, increased oxygen concentration, or both. This study aims to separate the effects of temperature and oxygen partial pressure. This separation was investigated by first assuming that fuel-bound nitrogen is released along with the tars during coal devolatilization and converts mostly to hydrogen cyanide, HCN. Then to assess the conversion

of HCN to NO a published kinetic model for HCN oxidation was used. This model was developed by Dagaut and Glarborg [4] and enhanced with reactions pertinent to CO_2 by Glarborg and co-workers; see Alzueta et al.[5] and Hashemi et al. [6].

Hashemi et al.[6] have worked on developing the nitrogen chemistry of coal oxy-combustion along with a model for different reaction mechanisms. According to the model, differences in the NO yield between the oxy-fuel combustion and the conventional combustion of pulverized coal can mostly be attributed to the recycling of NO (re-burning effect) and to changes in the mixing patterns between fuel and oxygen. Alzueta et al.[5] formulated the model for calculating NO_x concentration by combustion of HCN as intermediate. It was also found that the higher availability of oxygen increases the HCN conversion, due to the increased radical formation. The kinetic and stoichiometric data for modeling is collected from various research papers and theses on nitrogen chemistry and mechanisms in coal oxy-combustion [7–11].

2. Methods

2.1 Kinetic Model

Hashemi et al. [6] published a detailed kinetic model in CHEMKIN format but the transport data of species which is required to perform flame simulations was not made available in their published model. Transport data was found by comparing the species names using RMG-models [12] database and the transport data for pseudo species in Hashemi model were found in Ergut et al [13].

2.2 Thermogravimetric analysis of coal

The volatilization temperature of an HVA bituminous black coal (Pittsburgh No.8 from Pennsylvania (PSOC-1451)) was determined by thermogravimetric analysis(TGA), using TA instruments' Q500 Series thermogravimetric analyzer. A sample of bituminous coal was loaded on a platinum sample pan which was further loaded on a sensitive thermobalance in the analyzer. The volatilization temperature was determined by ramping the temperature to 900 °C at the rate of 20 °C/min while recording the weight change. The weight change data with increasing temperature was analyzed using TA Universal Analysis software.

2.3 Counter current diffusion flame simulations

Upon injection of a bituminous coal particle in a furnace, it heats up and devolatilizes. Upon ignition of the volatiles, an envelope diffusion flame appears surrounding the particle, as depicted in Fig. 1. This flame was simulated herein as a one-dimensional counter-current diffusion flame. Simulations were carried out using the open-source software Cantera[14] via the Python interface. The solutions are converged on approximately 120 grid points with convergence criteria `set_refine_criteria( ratio=3.0,slope=0.1,curve=0.1,prune=0.04)`, without radiation, and a domain width of 0.02 m. The simulations are carried out for bituminous coal by varying oxidizer inlet temperature and oxidizer composition. The inlet fuel composition is assumed to be composed of the coal volatile matter composition determined by Hashemi et al. Table 1 shows the molar composition of bituminous coal.

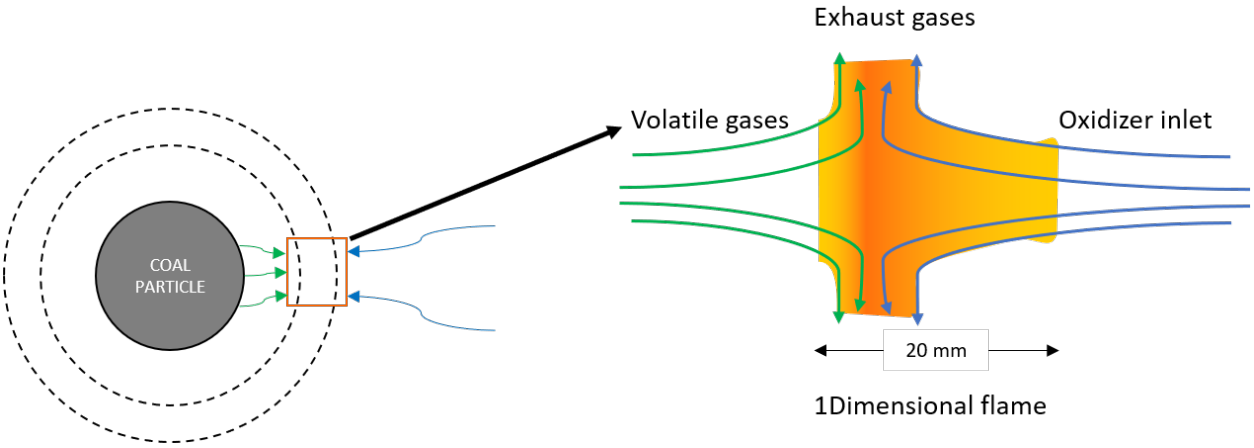


Figure 1: Schematic of simulated counter-current diffusion flame

Species	SOOT	H_2	CO_2	CO	CH_4	C_2H_4	H_2O	HCN
Molar composition	28.36	38.52	3.26	8.53	3.76	1.76	14.56	1.25

Table 1: Estimated molar composition of volatiles for bituminous coal

3. Results

3.1 Thermogravimetric analysis

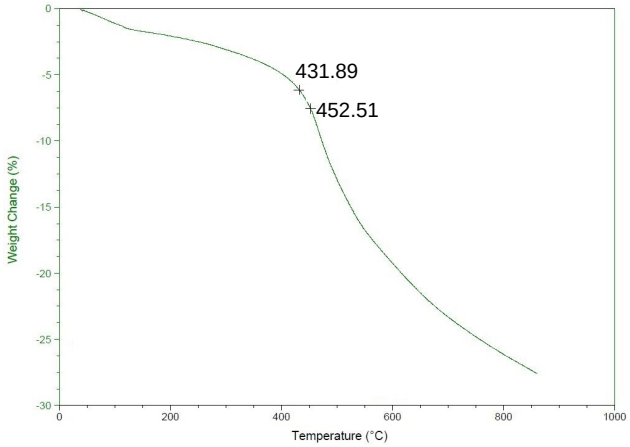
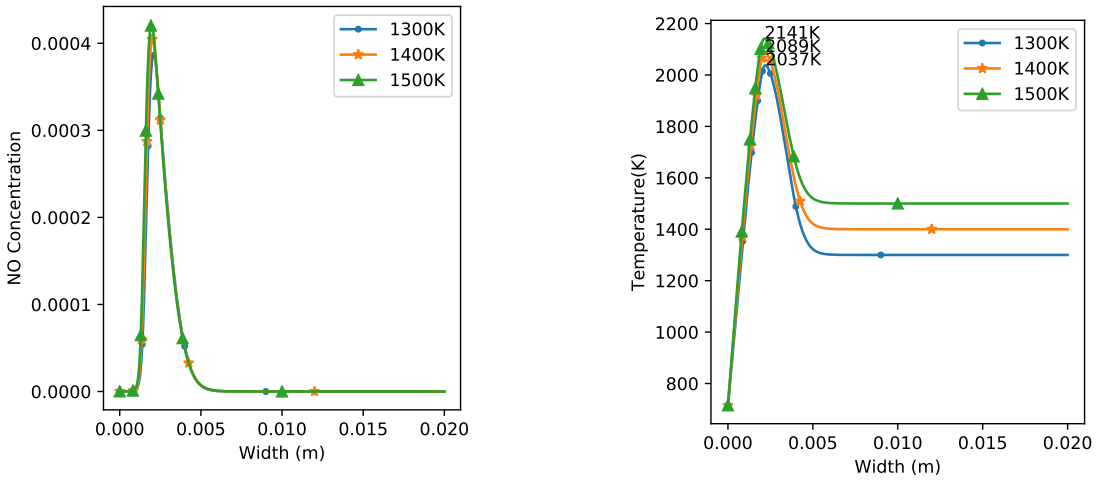


Figure 2: Weight change profiles for bituminous coal

As shown in Figure 2, during the thermogravimetric analysis, the weight of coal decreases with temperature. Initially the weight drops due to evaporation of water in both coals. The weight of bituminous coal sample starts to decrease sharply between 430 °C and 450 °C. Such behavior can be attributed to volatilization of gases from this coal. Hence we assumed the devolatilization temperature of the bituminous coal to be 442 °C. This determines the fuel feed temperature in the flame simulations.

3.2 Effect of inlet oxidizer temperature on NO concentration in flame

Counter-current diffusion flame simulations were carried out by changing the oxidizer inlet temperature, which is the furnace gas temperature, but keeping the oxidizer composition constant. This was done to quantify the effect of furnace gas temperature on NO generation and particle flame temperature. The oxidizer composition was kept constant at $O_2:0.20, CO_2:0.80$ while the inlet temperatures of the oxidizer gas were set at `[1300, 1400, 1500]` in K. Figure 3.a, shows the effect of oxidizer inlet temperature on the NO concentration in the diffusion flame. Figure 3.b shows the effect of the oxidizer inlet temperature on the flame temperature across the width of flame and the peak temperatures in the flame are reported.



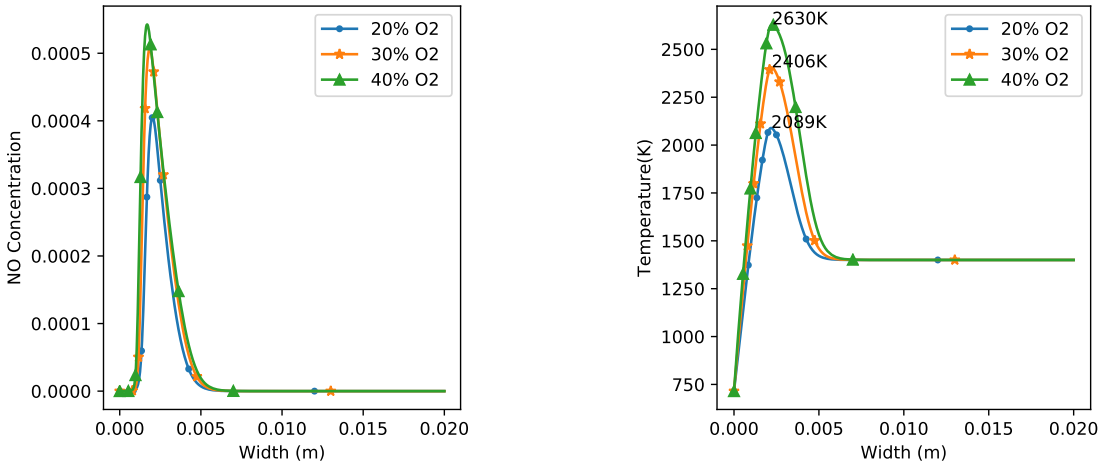
(a) NO concentration profile

(b) Flame temperature profile

Figure 3: NO species and flame temperature profiles by varying oxidizer inlet temperature

3.3 Effect of oxidizer inlet composition on NO concentration in flame

Counter-current diffusion flame simulations were carried out by changing the oxidizer inlet composition but keeping the oxidizer inlet temperature, which is the furnace gas temperature, constant to quantify the effect of oxidizer composition on NO generation and flame temperature. The oxidizer inlet temperature is kept constant at 1400 K while the O_2 and CO_2 concentrations at inlet were set at `[0.20,0.30,0.40]`, `[0.80,0.70,0.60]` respectively. Figure 4.a shows the effect of the oxidizer inlet temperature on the NO concentration in the flame. Figures 4.b shows the effect of the oxidizer inlet composition along the width of the flame and the peak temperatures in the flame are reported. The difference between the peak temperatures in the flames is considerable when the oxidizer composition is changed as shown in 4.b .



(a) NO concentration profile

(b) Flame temperature profile

Figure 4: NO species and flame temperature profiles by varying oxidizer inlet composition

A comparison of the results shown in Figures 3 and 4 shows that the change in oxygen mole fraction in the range of `[0.20-0.40]` is more influential on both the flame temperature and on the NO formation than the gas temperature variation in the range of 1300-1500 K.

4. Conclusions

From the theoretical investigation of the NOx concentrations in a diffusion flame and of the temperature profile of this flame, it can be concluded that the oxidizer inlet temperature has a significant effect on the peak NO concentration during oxy-combustion of coal at a fixed oxidizer inlet composition as shown in figure 3, whereas the oxidizer inlet composition has a more significant effect on flame temperatures as shown in 4. These conclusions are valid for the ranges of the two parameters (gas temperature and oxygen concentration) input to this model. Further theoretical and experimental work is needed to determine what type of reactions and at what temperatures are producing more NOx and how to minimize the production on NO while also retaining combustion efficiency.

Acknowledgments

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