**Oxygen-Enriched Coal Combustion with Carbon Dioxide Recycle and
Recovery: Simulation and Experimental Study**

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Parametric Modeling of Metal Vaporization During Coal Combustion

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Abstract

An accurate estimation of the CO/CO₂ ratio at the surface of an ash inclusion in coal during combustion is necessary to predict the equilibrium partial pressure of volatile reduced metal species inside the burning particle and the rate of vaporization of metal oxides. Assumptions that have been made previously for the CO/CO₂ ratio at the surface of mineral inclusions are compared to those obtained from a steady state detailed kinetics code for a single porous particle (SKIPPY). The detailed kinetic simulations from SKIPPY for varying particle sizes and bulk gas compositions were used to develop algebraic expressions for the CO/CO₂ ratio that can be incorporated into metal vaporization sub-models run as a post processor to detailed furnace simulations.

Introduction

The formation of sub-micron ash in coal combustion systems has been extensively studied due to concerns regarding the effects of advanced combustion technologies on boiler deposits, the particle size distribution at the inlet of air pollution control systems and the emissions of toxic metals. The formation of sub-micron aerosol during coal combustion is known to be due to the phenomena of coal ash vaporization under locally reducing conditions inside the char particle [1-8]. The refractory metal

oxides in the ash are reduced to more volatile sub-oxides or elemental metal that diffuse from the particle through the boundary layer to the oxidizing atmosphere in the bulk gas. Here the reduced species is oxidized forming a supersaturated vapor that nucleates and condenses to form sub-micron particles. The rate of vaporization of a metal (M) from an ash particle depends on the partial pressure of metal vapor at the surface of individual mineral inclusions inside the char. The metal oxide (MO) reacts with carbon monoxide as:

The above reaction is assumed to be in equilibrium at the inclusion surface.

$$K_e = \frac{P_M^e P_{CO_2}}{a_M P_{CO}} \quad (2)$$

K_e is the equilibrium constant for the metal of interest and is determined from thermodynamics. The activity of the metal oxide in the inclusion, a_M , is generally set to 1. P_M^e is the equilibrium partial pressure of the metal vapor at the surface of the inclusion, P_{CO_2} and P_{CO} are the partial pressures of CO_2 and CO respectively. The temperature of the burning char particles and the gas composition at the surface of char inclusions controls the equilibrium partial pressure P_M^e of the volatile reduced metal species. In summary, the amount of sub-micron ash formed depends on the ash vaporization rate, which in turn depends on the temperature dependant equilibrium constant and on the ratio of CO to CO_2 .

An accurate estimation of the CO/CO₂ ratio at the surface of the ash inclusion inside the char is therefore necessary to predict the equilibrium partial pressure P_M^e of the volatile reduced metal species.

Quann [1,2] developed a model for metal vaporization that was able to correlate the results of experiments in a laminar flow laboratory furnace with no ambient CO₂ present. The model developed by Quann to analyze the data from drop tube experiments assumed that the only source of CO₂ inside the particle was the reaction with metal oxide. Therefore, P_{CO_2} was set equal to P_M^e .

Given the Quann's assumption and equation (2) we get

$$P_M^e = (K_e P_{CO})^{0.5} \quad (3)$$

Based on stoichiometric reasoning, Quann estimated the CO concentration to be

$$P_{CO} = \frac{2P_{O_2}}{1 + P_{O_2}} \quad (4)$$

This gives a value of 0.35 atm for P_{CO} for combustion with 21% O₂ in the bulk gas.

Table 1 summarizes the assumptions made for the CO/CO₂ ratio at the surface of the mineral inclusion used in previous studies of metal vaporization during coal combustion.

Table 1: A summary of assumptions made for the CO/CO₂ ratio at the surface of the mineral inclusion in previous studies of metal vaporization during coal combustion.

Model	Objective	CO Composition	CO ₂ Composition
Quann (1982)	Explain drop tube data in terms of mechanism.	Stoichiometry $P_{CO} = \frac{2P_{O_2}}{1 + P_{O_2}}$	P _{CO₂} = P _M
Lee (2000)	Couple Quann's model with CFD code.	Bulk gas composition from the results of CFD modeling.	Bulk gas composition from the results of CFD modeling.

The Quann model only considers the effect of oxygen in the bulk gas and does not include the effect of varying bulk CO₂ concentration. The Quann model was based on constant gas temperature and composition. More recent models have been developed to better predict ash vaporization in furnaces [9-11]. Advances in computational fluid dynamics (CFD) based simulations of reacting flows provide the tools to obtain detailed particle temperature and gas phase composition as a function of time during char burnout [12,13]. The temperature-time histories of the char particles as well as the composition of the bulk gas can be obtained from the 3-D CFD simulations and can be used as an input to the metal vaporization model. The metal partial pressure is determined by the equilibrium constant and by the gas composition [1]. Lee [14] modified the Quann model to allow for varying temperature and gas composition history along a streamline. Lee assumed that the change in gas composition across the boundary layer was small and that

the CO and CO₂ values applicable to the particle were the local bulk gas composition computed by the CFD code. Lee showed large differences in metal vaporization depending on the detailed gas composition and temperature along the particle trajectory.

The focus of this study was to consider the effects of particle size, bulk gas composition, and furnace temperature on the concentrations of gas phase species especially the CO/CO₂ ratio as a function of radius from the particle center out through the boundary layer. SKIPPY [15,16], a steady state detailed kinetics code for a single porous particle has been used to develop expressions for the CO/CO₂ ratio at the surface of the metal inclusions. But it is time consuming to combine a pseudo-steady state simulation of individual particles with the statistical distributions of particle trajectories calculated by CFD-based codes. The detailed kinetic simulations for varying particle size bulk gas composition and furnace temperatures were used to develop algebraic expressions that can be incorporated into the model developed by Quann et al., [1] and can be used in a metal vaporization sub-model run as a post processor to detailed furnace simulations.

Methods

SKIPPY is a FORTRAN code that calculates species and temperature profiles for the reaction of a porous solid in a reacting gas at pseudo steady state. Dr. Brian S. Haynes at University of Sydney, Australia provided the code. Details of the SKIPPY code are documented [15,16]. SKIPPY has previously been validated by comparing predictions to experimental data for chemically controlled combustion of Spherocharb and with coal chars of specific ranks, Illinois #6 in particular.

The simulation cases in this study were used to determine the general trends and to test the sensitivity of the results to input assumptions. This study was also aimed at

obtaining correlations for the CO/CO₂ ratios inside the char particles even if they are burnt in atmospheres different from those present in conventional boilers. For instance, during oxygen enriched coal combustion, the bulk gas composition and the temperature-time histories to which the particles are exposed to are quite different from those prevalent during coal combustion with air. Consequently, in our simulations, the CO₂ concentration in the bulk gas was zero, representative of drop tube experiments in artificial atmospheres; 10%, representative of combustion products after volatile combustion in a coal-fired furnace; and 50-79%, representative of the oxidant stream resulting from blending oxygen with dry recycled flue gas. Oxygen was kept constant at 20% that represented one of the experimental conditions used to develop the Quann model. A void fraction of 80% was used and all the voidage was assumed to be located in mesopores and macropores that are assumed to have an area density of $5 \times 10^4 \text{ cm}^2/\text{cm}^3$. The tortuosity was maintained at 5. SKIPPY was validated for the Illinois #6 char using these values as input [16]. Figure 1. compares the values of lifetime-mean partial pressure of SiO (P_{SiO}) at the surface of Illinois #6 char determined experimentally by Quann with the values calculated by SKIPPY. The initial diameter of the particles in the experiment was 125 μm while the lines are calculated for 100 μm diameter. The furnace temperature was maintained at 1750 K and the partial pressure of oxygen in the air stream (rest of which is nitrogen) was varied to generate different particle temperatures.

Figure 1. Comparison of P_{sio} calculated from SKIPPY runs with Quann's experimental data [15,16].

The simulations were aimed at studying the validity of the composition assumptions listed in Table 1, examine the parameters that influence the metal vaporization and come up with correlations for CO/CO₂ ratio existing at the surface of the mineral inclusion at different combustion conditions.

Results

Figure 2 shows the partial pressure profile of CO₂ calculated by SKIPPY for a 100 μ m diameter Illinois # 6 char particle burning in a furnace maintained at 1750 K with various concentrations of CO₂ in the bulk gas. The curve for 0% CO₂ corresponds to the experimental conditions maintained by Quann for 20% O₂. The concentration of CO₂

inside the particle approaches a constant value that varies with the CO_2 concentration in the bulk gas.

Figure 2: Partial pressure profile of CO_2 calculated by SKIPPY for a 100 μm diameter Illinois # 6 char particle burning in a furnace maintained at 1750 K with various concentrations of CO_2 in the bulk gas. The vertical dotted line corresponds to the surface of the particle.

Figure 3 shows the species partial pressure profile of CO calculated by SKIPPY for a 100 μm diameter Illinois # 6 char particle burning under the same conditions as those in Figure 2. The concentration of CO inside the char also approaches a constant value that varies with the bulk CO_2 gas concentration. The simulations assumed zero CO in the bulk gas.

Figure 3: Partial pressure profile of CO calculated by SKIPPY for a 100 μm diameter Illinois # 6 char particle burning in a furnace maintained at 1750 K with various concentrations of CO_2 in the bulk gas. The vertical line corresponds to the surface of the particle.

Figure 4 shows CO/CO_2 calculated by SKIPPY for a 100 μm diameter Illinois # 6 char particle burning in a furnace maintained at 1750 K with various concentrations of CO_2 in the bulk gas. Since both the CO and CO_2 inside the char depend on bulk gas CO_2 the ratio also shows a similar behavior.

Figure 4: CO/CO₂ ratio calculated by SKIPPY for a 100 μm diameter Illinois # 6 char particle burning in a furnace maintained at 1750 K with various concentrations of CO₂ in the bulk gas. The vertical line corresponds to the surface of the particle.

Figure 5 compares the calculated values of SiO at the surface of the char particle (P_{SiO}) with the particle energy balance equation (PEBL) in SKIPPY turned off and on. The calculations were carried for a 100 μm diameter Illinois #6 char particle. The simulations with the energy balance turned off used a fixed particle temperature. The difference between the prescribed temperature and energy balance calculated temperature cases are small.

Figure 5: P_{sio} calculated with the particle energy balance (PEBL) turned off and on.

Figure 6 shows the P_{sio} data that was generated from SKIPPY for a 100 μm diameter Illinois #6 char particle burning in (20% O_2 , 1% H_2O) with the balance being CO_2 and N_2 in a furnace maintained at 1750 K. The runs were carried out by turning off the particle energy balance equation in SKIPPY and specifying a particle temperature of 2280 K (2280 K is the validated temperature for SKIPPY when 20% O_2 is in the bulk). With prescribed temperature the effect of varying P_{CO_2} on P_{sio} is small relative to the effect of changing P_{O_2} .

Figure 6: P_{sio} calculated at different CO_2 concentrations and using a fixed particle temperature of 2280 K.

Figure 7 shows the effects of CO_2 and temperature that decrease P_{sio} at the surface of the char. These runs were carried out for a 100 μm diameter Illinois #6 char particle burning in (20% O_2 , 1% H_2O) and the balance being CO_2 and N_2 in a furnace maintained at 1750 K. Here the model predicts that the temperature and P_{sio} decrease when the P_{CO_2} in the bulk gas increases. Figure 8 shows the partial pressure profile of O_2 calculated by SKIPPY for a 100 μm diameter Illinois # 6 char particle burning in a furnace maintained at 1750 K with various concentrations of CO_2 in the bulk gas. The depth of penetration of the O_2 inside the char also corresponds to the increase in CO_2 concentrations inside the char close to the surface as seen in Figure 2. This is due to reaction of O_2 with the carbon resulting in the production of CO_2 .

Figure 7: The effects of decrease in particle temperature and increase in CO_2 concentration in the bulk towards suppressing the metal vaporization (P_{sio})

Figure 8: Partial pressure profile of O_2 calculated by SKIPPY for a 100 μm diameter Illinois # 6 char particle burning in a furnace maintained at 1750 K with various concentrations of CO_2 in the bulk gas. The vertical line corresponds to the surface of the particle.

Discussion

Combustion with 20% O₂ in the bulk gas results in a particle temperature between 2200 and 2300 K for the Illinois #6 char. Now, according to Quann's assumption (P_{CO_2} set equal to P_M^e) this would mean that the concentration of CO₂ at the surface of the metal inclusion at this temperature is in the range 1×10^{-4} to 3×10^{-4} . It can be seen from Figure 2 that SKIPPY predicts CO₂ partial pressures 2 orders of magnitude higher than what was originally assumed by Quann. The volume average of the CO₂ within the char was calculated to be 2×10^{-2} .

From Figure 3 we notice that Quann's assumption for the CO partial pressures from stoichiometric reasoning agrees with SKIPPY predictions. However, from Figures 2 and 3 we see that his calculation of the CO/CO₂ ratio are quite different from those predicted by SKIPPY. According to Quann's assumptions for a zero bulk CO₂ concentration the CO/CO₂ is 2000 versus a range within the particle from 6 to 70 predicted by SKIPPY as shown in figure 4.

As previously mentioned in Table 1, Lee (14) assumed that the change in gas composition across the boundary layer of the particle was small and that the CO and CO₂ values applicable to the particle were the local bulk gas composition computed by the CFD code. From Figure 2 we find that this assumption is a good one for CO₂ concentrations whereas from Figure 3 it seems that it is not so for CO concentrations as seen by the steep concentration gradients that exist across the boundary layer. According to Lee's assumption the ratio is close to zero for the conditions in Figure 4. SKIPPY results show that the volume averaged CO/CO₂ ratio is about 20 at these conditions.

The validation of SKIPPY in figure 1 [16] with Quann's experimental data was carried out by disabling the energy balance equation in SKIPPY. This means that the calculations were carried out with a specified particle temperature. Since we do not know the particle temperatures in a CO₂ atmosphere, we had to turn on the particle energy balance equation while carrying out our computations. Figure 5 shows that there is little difference between the values of partial pressure of SiO on the particle surface (P_{SiO}) that was calculated using the two methods.

Metal vaporization

The SKIPPY runs seemed to indicate that during coal combustion under oxygen enriched conditions with flue gas recycle (or in other words high CO₂ in the bulk) two effects tend to suppress the amount of metal vaporized from the char. The high CO₂ concentration tends to cause the endothermic gasification reaction to occur that causes the temperature of the char to decrease. This was also observed in the temperatures of the coal particles from our 3-D CFD simulations of a coal-fired boiler operating at oxygen enriched combustion conditions. Secondly the high CO₂ concentration also reduces the equilibrium partial pressure of the metal vapor at the inclusion surface (P_M^e , which is determined from equation 2) to decrease.

How each of these two effects individually suppresses the amount of metal vaporized can be studied by turning off the energy balance equation in SKIPPY (Figures 6 and 7). The metal vaporization is thus shown to be highly temperature dependent. The primary effect is through the exponential temperature dependence of the equilibrium constant (K_{eq}) of the reduced metal species. The equilibrium constant can be calculated from thermodynamics provided that the Gibbs free energy data are available for all the

metal oxide species of interest and provided that the particle temperature can be estimated from heat balance. SKIPPY includes thermodynamic data for 28 Si species. The coupling of CO and CO₂ reactions inside the particle with a particle heat balance is provided by SKIPPY but a parametric study of particle temperature was outside the scope of this project. The dependence of CO-CO₂ equilibrium on particle temperature is implicitly included in the data used to generate the empirical coefficients used in the approximate algebraic model of gas composition.

Macropores and Micropores

Quann assumed that the diffusion of the volatile metal oxide inside the char particle was by Knudsen diffusion through the micropores in the char. Quann's model was modified by replacing the micropore or Knudsen diffusivity with macropore or binary diffusivity. SKIPPY performs its calculations using macropore diffusivity. This resulted in about 2 orders of magnitude increase in the SiO vaporization rate. The rate of vaporization is directly proportional to the effectiveness factor. Table 2 compares the effectiveness factor that is obtained by assuming all micropores and all macropores in the Quann's model for a 100 μm diameter Illinois #6 char burning in 20% O₂ with the temperature of the furnace maintained at 1750 K. Since SKIPPY has been validated for and matches the Quann's experimental data, the effectiveness factor calculated by SKIPPY is also shown as an indicator of the actual experimental effectiveness factor in Quann's experiments.

Table 2: Calculation of effectiveness factor using various pore models

Pore Model for Char	Effectiveness Factor
All micropores	1.92E-03
All macropores	6.38E-01
SKIPPY	2.42E-01

In reality the diffusion of the vaporized metal inside the char occurs both through the micropores as well as the macropores. This is what is shown in Table 2 with the actual measured effectiveness factor (the one that corresponds to SKIPPY) lying between the two extremes. SKIPPY was validated by comparison to Quann's P_{sio} values back calculated from ash vaporization measurements. But SKIPPY predicts very different CO/CO₂ ratios than assumed by Quann. A possible explanation is that the effect of the micropores assumed by Quann offset the effect of the low P_{co2} at the inclusion surface in Quann's model.

Incorporating Metal vaporization in Comprehensive Codes

Closed form algebraic equations that can approximate the results of detailed simulations are a useful and computationally efficient way to improve the accuracy of comprehensive combustion models. An example is the success achieved in using simplified global kinetic equations to approximate the results of detailed kinetic modeling of the elementary reactions involved in CO oxidation and NO_x formation.

Since metal inclusions are dispersed throughout the char volume, the concept of estimating a volume average CO/CO₂ ratio inside the particle is a reasonable approximation. The volume average ratio is calculated as:

$$\frac{P_{CO}}{P_{CO_2 \text{ vol avg}}} = 4\pi \int_0^R r^2 \frac{P_{CO}(r)}{P_{CO_2}(r)} dr \bigg/ \text{Particle Volume} \quad (5)$$

This study suggests that an algebraic model of the form

$$\left(\frac{P_{CO}}{P_{CO_2}} \right)_{\text{vol avg}} = f(T_{\text{gas}}, P_{\text{bulk CO}_2}, d_p) \quad (6)$$

(where T_{gas} is the temperature of the bulk gas in Kelvin, $P_{\text{bulk CO}_2}$ is the CO_2 partial pressure in the bulk gas and d_p is the diameter of the particle in meters) can be used to incorporate the information available from a detailed solid phase kinetic and mass transport model such as SKIPPY into a comprehensive combustion model.

The temperature, bulk gas composition and particle diameter dependent coefficients can be calculated by multiple linear regression from a reasonable number of single particle simulations using the appropriate input data for the coal and furnace conditions of interest. Single particle simulations were carried out for 20, 50 and 100 μm diameter particles burning in 20% O_2 , 1% H_2O and the furnace temperature maintained at 1750K, 2000K and 2250K respectively. The composition of the rest of the bulk gas was 0%, 10%, 20%, 50% and 79% CO_2 with the balance being N_2 .

Figure 9 shows the volume average CO/CO_2 ratio data points plotted as a function of CO_2 concentration in the bulk. As previously mentioned, at each CO_2 concentration there are 3 different particle size data points each of which is burning at 3 different furnace temperatures.

Figure 9: Volume average CO/CO₂ ratio data points plotted as a function of CO₂ concentration in the bulk. The first number in the legend is the particle diameter in microns and the number inside the brackets is the furnace temperature in Kelvin.

A simplified algebraic equation for the volume average CO/CO₂ ratio has been suggested below

$$\left(\frac{P_{CO}}{P_{CO_2}} \right)_{volavg} = 7.14 \times 10^7 e^{-3.33 P_{bulk CO_2} - (11370 / T_{gas})} d_p^{0.96} \quad (7)$$

The R² value for the regression coefficients is close to 0.9 indicating that the selected functional form gives a reasonable approximation to the SKIPPY output data.

Conclusions

This computational study using SKIPPY applied a recently developed single particle kinetic and mass transport model to obtain insights into the relevant gas composition to be used in calculating the vaporization of mineral ash inside a burning coal particle. The results suggest a way of combining the output of CFD-based particle trajectory data with a metal vaporization sub-model.

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