Computational Modeling of CO/CO$_2$ Ratio Inside Single Char Particles during Pulverized Coal Combustion

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Received January 9, 2003. Revised Manuscript Received July 12, 2003

A recently developed model was used to study the CO/CO$_2$ ratio inside a burning pulverized coal particle, to better understand the effect of bulk gas composition on the equilibrium partial pressure of reduced metal species at the surface of ash inclusions. The motivation was to improve the ability to model submicrometer particle formation by ash vaporization, as a function of furnace conditions. Assumptions for the CO/CO$_2$ ratio that have been made in previous studies are compared to predictions from a psuedo-steady-state model for a single porous particle that considers homogeneous and heterogeneous reaction kinetics and mass transfer both in particle pores and in the boundary layer. This is the first publication of model predictions for the CO/CO$_2$ ratio as a function of radius for a coal char particle in a furnace with a bulk gas CO$_2$ concentration in the range of 0%−79%. A method is proposed for summarizing the effects on the CO/CO$_2$ ratio that are due to changes in the bulk furnace gas O$_2$ and CO$_2$ concentration, furnace temperature, and particle size, using an empirical equation that is suitable for incorporation as a submodel into comprehensive computational fluid dynamics-based codes for combustion simulation. Trends from the model simulations show general agreement with experimental data; however, the accuracy of the predictions is limited by the lack of fuel-specific input data.

Introduction

The formation of submicrometer-sized ash in coal combustion systems affects the emissions of toxic metals and the formation of boiler deposits. The formation of submicrometer-sized aerosol during coal combustion is known to be due to ash vaporization under locally reducing conditions inside the char particle.[1−8] Summarizing the model that was originally developed by Quann and Sarofim,[1,2] the refractory metal oxides in the ash are reduced to more-volatile suboxides or elemental metal species that diffuse from the inclusion inside the particle through the boundary layer to the oxidizing bulk gas. Here, the reduced species is oxidized and forms a supersaturated vapor that nucleates and condenses to form submicrometer-sized particles. The metal oxide (MO$_n$) reacts with carbon monoxide (CO) as

$$\mathrm{MO}_n(s) + \mathrm{CO}(g) \leftrightarrow \mathrm{MO}_{n-1}(g) + \mathrm{CO}_2(g) \qquad (1)$$

Reaction 1 is assumed to be in equilibrium at the inclusion surface:

$$K_\mathrm{e} = \frac{P^\mathrm{e}_{\mathrm{MO}_{n-1}} P_{\mathrm{CO}_2}}{a_{\mathrm{MO}_n} P_\mathrm{CO}} \qquad (2)$$

where K_e is the equilibrium constant for the metal of interest and is determined from thermodynamics. $P^\mathrm{e}_{\mathrm{MO}_{n-1}}$ is the equilibrium partial pressure of the metal vapor at the surface of the inclusion; P_{CO_2} and P_CO are the local partial pressures of CO$_2$ and CO, respectively; and a_{MO_n} is the activity of the solid metal oxide (which is assumed to be ∼1). The rate of metal vaporization is controlled by $P^\mathrm{e}_{\mathrm{MO}_{n-1}}$ and by mass transfer through the char and the surrounding boundary layer. When reporting data, Quann assumed that the amount of refractory elements that were vaporized was equal to the quantity of experimentally measured submicrometer-sized fume. Quann back-calculated the partial pressures of the reduced metal species at the coal particle surface from measurements of the amount and composition of the collected submicrometer-sized ash, assuming external diffusion to be the rate-limiting process.

Quann's model assumed that the only source of CO$_2$ inside the particle was the reaction with a metal oxide (eq 1). Therefore, P_{CO_2} was set equal to $P^\mathrm{e}_{\mathrm{MO}_{n-1}}$. Given this assumption and eq 2, we get

$$P^\mathrm{e}_{\mathrm{MO}_{n-1}} = (K_\mathrm{e} P_\mathrm{CO})^{0.5} \qquad (3)$$

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10.1021/ef030006k CCC: $25.00

Table 1. Assumptions for Gas Composition Inside the Particle Used in Previous Studies of Metal Vaporization during Coal Combustion

reference	objective	CO composition	CO_2 composition	comments
Quann (1982)[2]	explain drop tube submicrometer fume data in terms of mechanism	stoichiometry $P_{CO} = 2P_{O_2}/1 + P_{O_2}$	$P_{CO_2} = P^{e}_{MO_{n-1}}$	single gas composition; laminar flow furnace
Lee (2000)[13]	couple Quann's model with CFD code to study ash vaporization and the effect of low NO_x retrofit	bulk gas composition from the results of CFD modeling	bulk gas composition from the results of CFD modeling	CFD model of power plant boiler
Yousif (1998)[10]	predict size distributions of lead and cadmium	equilibrium bulk gas composition; not explicitly stated	equilibrium bulk gas composition; not explicitly stated	vaporization proportional to burning rate; no kinetic model for metals
Sandelin (2000)[9]	trace element partioning between fly ash, bottom ash, and flue gas	bulk gas composition	bulk gas composition	two-reactor model

On the basis of stoichiometric reasoning, Quann estimated the CO concentration to be

$$P_{CO,surface} = \frac{2P_{O_2,bulk}}{1 + P_{O_2,bulk}} \tag{4}$$

This gives a value of $P_{CO} = 0.33$ atm for combustion with 20% O_2 in the bulk gas.

The Quann model used a single temperature and gas composition to represent the furnace conditions. More recently developed models for ash vaporization allow for varying conditions along a particle trajectory.[9,10] Advances in computational fluid dynamics (CFD)-based simulations of reacting flows provide detailed particle temperature and gas-phase composition data, as a function of time, during char burnout.[11,12] Lee[13] combined CFD simulations with the Quann model by assuming that the CO and CO_2 values applicable to the ash inside the particle were the local bulk gas composition. Lee showed large differences in metal vaporization, depending on the detailed gas compositions and temperatures along the particle trajectory. Table 1 summarizes the assumptions that were made for the CO/CO_2 ratio at the surface of the ash inclusion used by Quann,[1,2] Sandelin,[9] Yousif,[10] and Lee.[13]

The focus of this study was to consider the effects of particle size, bulk gas composition, and furnace temperature on the CO/CO_2 ratio, as a function of radius from the particle center out through the boundary layer. A motivation for considering these effects was to study the formation of submicrometer-sized particles for proposed coal-fired power-plant configurations (for instance, O_2-enriched coal combustion with CO_2 recycle[14,15]). The vaporization of SiO was studied, because this is a volatile suboxide for which both experimental data and previous simulation data[13,16] were available, and SiO_2 is a major component of submicrometer-sized ash from practical combustion systems.

Methods

A pseudo-steady-state code was used to develop algebraic expressions for the CO/CO_2 ratio at the surface of the ash inclusions for various coal particle sizes, bulk gas compositions, and furnace temperatures using detailed reaction kinetics, thermodynamics, and mass-transfer calculations. SKIPPY (Surface Kinetics in Porous Particles) is a FORTRAN code (provided by Dr. Brian S. Haynes at the University of Sydney, Australia) that calculates species and temperature profiles for the reaction of a porous solid with a reacting gas at pseudo-steady state.[16] The SKIPPY program incorporates homogeneous and heterogeneous reaction kinetics and mass transfer in both pores within the particle and in the boundary layer. The SKIPPY program is based on data and subroutines from the CHEMKIN, SURFACE CHEMKIN, and Sandia transport packages.[17−19] The SKIPPY program was validated by comparing model predictions to published laboratory furnace experimental data, as documented by Haynes.[16]

For this study, simulations used gas compositions that spanned the range of both practical combustion and the laboratory experiments that were used to develop the Quann model. Cases included no CO_2 in the bulk gas (which was representative of drop tube experiments in artificial atmospheres), 10% CO_2 (which was representative of combustion products after volatile combustion in a coal-fired boiler), and 50%−79% CO_2 (which was representative of the furnace gas that results from blending oxygen with dry recycled CO_2 from the combustion products). The simulations were performed using the default reaction kinetics constants and species thermodynamic data included in the SKIPPY program. The code has the option of either using an energy balance to predict particle temperature or using a specified particle temperature, such as an experimentally measured value from two-color pyrometry. User-input values for the various cases that were used to generate data for this paper appear in Table 2.

The ash inclusions where metal vaporization occurs are dispersed throughout the char volume; therefore, the detailed radial profiles of CO and CO_2 inside the particle—$P_{CO}(r)$ and $P_{CO_2}(r)$, respectively—calculated by the SKIPPY program were converted to volume-average values of the CO/CO_2 ratio, calculated as

$$\left(\frac{P_{CO}}{P_{CO_2}}\right)_{volumeaverage} = \frac{4\pi\int_0^R r^2 (P_{CO}(r)/P_{CO_2}(r))\, dr}{4\pi\int_0^R r^2\, dr} \tag{5}$$

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Table 2. SKIPPY Inputs for Cases Used to Generate Data for Figures and Tables in This Paper

	Figure 1	Figure 2	Figure 3, Table 3	Figure 4
furnace temperature (K)	1750	1750	1750, 2000, 2250	1750
amount of bulk gas component (%)				
O_2	5, 10, 20, 35, 50, 75, 100	20	5, 20	20, 35, 50
CO_2	0	0, 10, 20, 50, 79	0, 10, 20, 50, 79	0, 25
H_2O	0, 1	1	1	0
N_2	difference	difference	difference	difference
particle diameter (μm)	100	100	20, 50, 100	138
particle temperature (K)	SKIPPY[a]	SKIPPY[a]	SKIPPY[a]	experimental values[b]
void fraction	0.8	0.8	0.8	0.8
tortuosity	5	5	5	5
area density (m^2 pore surface/m^3 of external volume)	5×10^6	5×10^6	5×10^6	5×10^6
solid-phase thermal conductivity (J/(m s K))	1.33	1.33	1.33	1.33

[a] Calculated using SKIPPY simulation data. [b] Experimental values from Quann.[2]

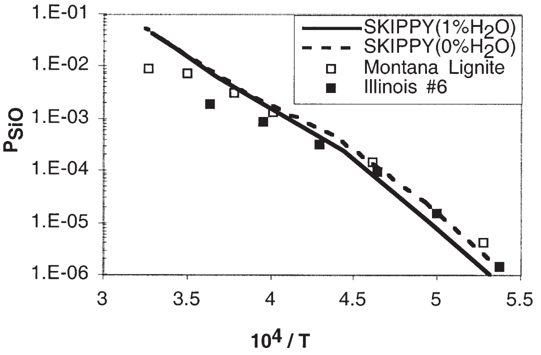

Figure 1. Comparison of model prediction for P_{SiO} at the particle surface with Quann's calculated values based on experimental data[2] for two fuels in a laminar-flow drop tube furnace. The effect of water vapor is small, compared to the uncertainty in fuel-specific input values.

This study compared the SKIPPY predictions for 0% and 25% CO_2 in the bulk gas to experimental data found in Quann's thesis.[2] Quann reported vaporized metal in terms of micrograms of metal per gram of coal; however, the SKIPPY program gives the P_{SiO} value at the particle surface. For low fraction of total ash vaporized, one would expect a linear relationship between the P_{SiO} value and the fraction of ash vaporized. Quann's data for P_{SiO}, as a function of O_2, and for the number of micrograms of metal per gram of coal, as a function of O_2 for the 0% CO_2, was plotted and determined to fit a linear equation that was then used to estimate the P_{SiO} value for the 25% CO_2 experiments.

Results

The predictions by the SKIPPY code for the P_{SiO} value are compared with experimental values in Figure 1 for cases with 0% and 1% water vapor. The SKIPPY inputs that are listed in Table 2 give a reasonable fit to the experimental values of SiO at the char particle surface for both Illinois No. 6 and Montana lignite. The presence or absence of water, which affects the rate of CO oxidation, has a small effect on the predicted P_{SiO} value, compared to the uncertainty in the coal-specific input values.

Model results for the CO and CO_2 from the center of a 100-μm-diameter char particle out to the bulk gas are shown in Figure 2. The model predictions can be compared to the assumptions in Table 1. Sandelin,[9] Yousif,[10] and Lee[13] all apparently assumed that the CO and CO_2 partial pressures inside the particle represented the local bulk gas composition; however, Figure 2 shows that the CO_2 content decreases inside the particle and the CO content has a steep gradient across the boundary layer between the particle and the bulk gas. Quann's stoichiometric equation gives a CO partial pressure of $P_{CO} = 0.33$ atm, which is within the range of the SKIPPY predictions. However, Quann's assumption that the only source of CO_2 inside the particle was the reaction with metal oxides suggests greater CO/CO_2 ratios than those predicted by the SKIPPY program.

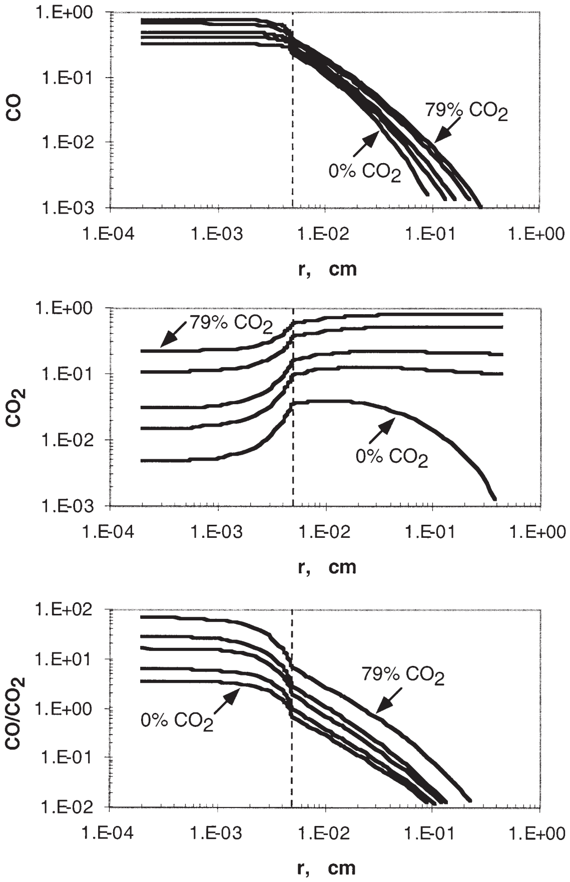

Figure 2. CO and CO_2 partial pressures (atm) and the CO/CO_2 ratio, as a function of radius from the center of the particle through the boundary layer. Vertical dotted lines correspond to the surface of the particle. Values calculated by the SKIPPY program are for a 100-μm-diameter char particle burning in a furnace with 1750 K walls with 0%, 10%, 20%, 50%, and 79% CO_2 in the bulk gas. Quann's estimate of $P_{CO} = 0.33$ inside the particle is within the range of the predictions; however, the SKIPPY code predicts much higher P_{CO_2} values inside the particle than given by $P_{CO_2} = P^{e}_{MO_{n-1}}$.

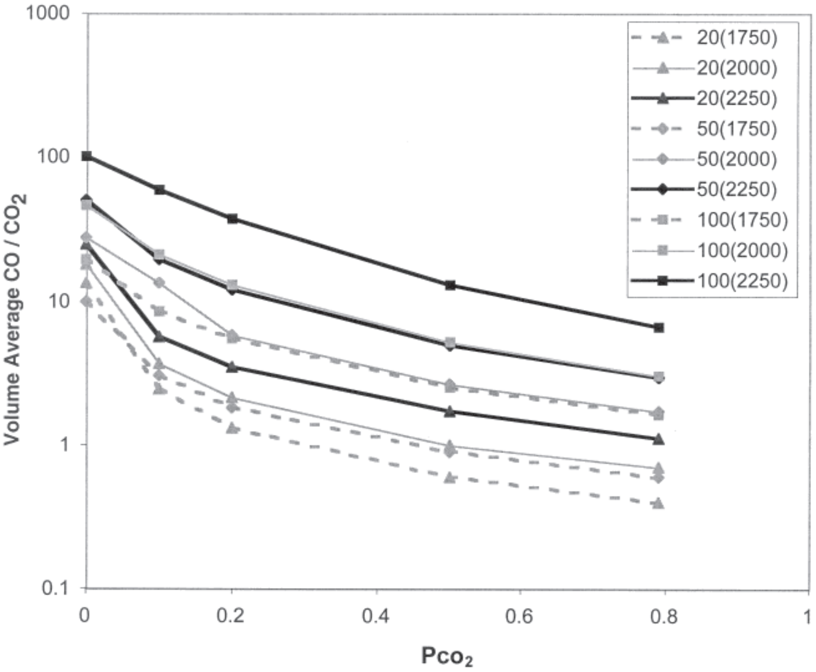

Figure 3. Model predictions for the volume-averaged CO/CO_2 ratio inside the char particle where furnace temperature and particle size were varied while holding the O_2 content at 20%. Legend gives the particle diameter in micrometers and the furnace temperature in degrees Kelvin. The CO/CO_2 ratio varies by 2 orders of magnitude over a reasonable range of combustion conditions, which indicates that increased CO_2 in the bulk gas will change the metal-vapor equilibrium at the ash inclusion surface and, therefore, will change the rate of formation of submicrometer-sized ash.

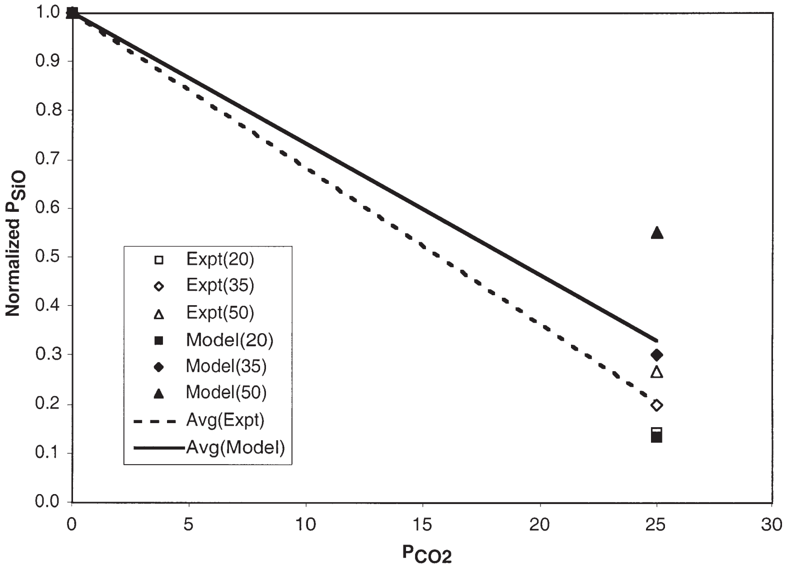

Figure 4. Experimental data (solid symbols) and model predictions (open symbols) for the effect of increased P_{CO_2} on the normalized partial pressure of SiO at the char surface. Cases are shown for 20%, 35%, and 50% O_2. Experimental points for the 25% CO_2 case were calculated by the authors from data in Quann.[2]

This SKIPPY program includes additional CO_2 that is formed by other reactions within the particle.

Figure 3 summarizes the results of a series of cases where the particle size, furnace temperature, and bulk gas CO_2 concentration were systematically varied. The CO/CO_2 ratio varies by 2 orders of magnitude over a reasonable range of combustion conditions, which indicates that an increased amount of CO_2 in the bulk gas will change the metal vapor equilibrium at the ash inclusion surface and, therefore, will change the rate of formation of submicrometer-sized ash. A method for incorporating the type of information provided by Figure 3 into a CFD-based model of particle combustion is presented in the Discussion.

Equilibrium reasoning that has been applied to eq 1 implies that the increased CO_2 in the bulk gas will result in reduced metal vaporization. Figure 4 compares the decrease in P_{SiO} at the char surface that is predicted by the SKIPPY code to data that have been calculated by the authors from experimental data documented by Quann.[2] Results for 20%, 35%, and 50% O_2 cases were combined in a single graph by normalizing the P_{SiO} values at 25% CO_2 by the P_{SiO} value at 0% CO_2 for the same O_2 concentration. The average values for the model and experiment follow the same trend, but, as indicated by the scatter in the 25% CO_2 data, suggest that the SKIPPY program predicts more change in the P_{SiO} value, relative to changes in bulk gas O_2, than that observed in the experimental data.

Discussion

The general agreement, shown in Figure 4, suggests that the SKIPPY code, or a similar kinetics and mass-transfer model, can provide useful insights into the effect of changing the bulk gas CO_2 content on the formation of submicrometer-sized ash. However, it is not feasible to perform a series of pseudo-steady-state simulations for every particle size at every grid cell in a CFD-based code when modeling combustion. The success in simulating CO and NO_x formation that was achieved by replacing detailed chemical kinetic models with global reactions suggests a similar approach for ash vaporization. The results of detailed SKIPPY simulations, such as that shown in Figure 3, can be efficiently represented by an empirical equation fit to the data.

The predicted CO/CO_2 ratio can be represented by a function of the form

$$\frac{P_{CO}}{P_{CO_2}} = Kf(T - T_{ref})g(P_{CO_2} - P_{CO_2,ref})h\left(\frac{d_p}{d_{p,ref}}\right) \quad (6)$$

where K is the predicted CO/CO_2 ratio at the reference conditions, and f, g, and h are functions of furnace temperature (T), bulk gas CO_2 (P_{CO_2}), and particle diameter (d_p), respectively. Tognotti[20] suggested an algebraic model in which the CO/CO_2 ratio varied as an exponential function of the temperature of the bulk gas (T_{gas}) and as a power function of the O_2 concentration. Various empirical equation forms were tested, and the following form was determined to fit the data with an acceptable correlation coefficient:

$$\frac{P_{CO}}{P_{CO_2}} = K \exp\left(\frac{A}{T_{ref}} - \frac{A}{T}\right) \exp[B(P_{CO_2,ref} - P_{CO_2})]\left(\frac{d_p}{d_{p,ref}}\right)^C \quad (7)$$

where A, B, and C are fitting constants. These 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. For the 20% O_2 cases used for Figure 3 and for a similar set of 5% O_2 cases, the values are given in Table 3.

Table 3. Coefficients for eq 7, Based on Multiple Linear Regression, Using Results from SKIPPY Cases

	5% bulk O_2	20% bulk O_2
equilibrium constant, K	1.28	5.36
reference temperature, T_{ref} (K)	1750	1750
partial pressure of CO_2, $P_{CO_2,ref}$ (atm)	0.12	0.12
reference particle diameter, $d_{p,ref}$ (μm)	50	50
constants from eq 7		
A (K)	3.78	3.33
B (atm^{-1})	11614	11370
C	0.87	0.96
goodness of fit, R^2	0.73	0.90

The empirical eq 7 and the values in Table 3 illustrate the approach that can be used to incorporate improved estimates of CO/CO_2 ratios into comprehensive CFD codes. The coefficient values were obtained from simulations where the inputs were selected to generate predictions that matched the laboratory data used for code validation. Testing the applicability of these coefficients to other combustion conditions will require experimental data that are not currently available.

Conclusions

This computational study applied a recently developed single particle kinetics and mass-transport model to obtain insights into the gas composition as a function of radius. The model predictions differ from the assumptions used in previous studies of ash vaporization. The empirical eq 7 gives an estimate of CO/CO_2 ratio inside a burning char particle that can be used to incorporate the effect of bulk gas composition, temperature, and particle size into ash-formation simulations.

Acknowledgment. We are very thankful to Dr. Brian S. Haynes (University of Sydney, Australia) for providing us with the SKIPPY program and Dr. Adel F. Sarofim for his useful feedback and invaluable suggestions. This study was supported by the U.S. Department of Energy (Contract No. DE-FG26-00NT40828).

EF030006K

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