

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

Final Report

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Abstract

Two computational problems were worked on for this study. The first chapter examines the option of coal combustion using oxygen feed with carbon dioxide recycle to control the adiabatic flame temperature. Computer simulations using an existing state-of-the-art 3-dimensional computer code for turbulent reacting flows with reacting particles were employed to study the effects of increased carbon dioxide mole fraction on the char burnout, radiant heat transfer, metal partitioning, and NO_x formation.

The second chapter compares assumptions for the CO/CO₂ ratio at the surface of mineral inclusions made in previous studies to predictions obtained from a pseudo-steady state kinetic model (SKIPPY) for a single porous particle. 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. Vaporization rate controls the formation of metal-enriched sub-micron particles in pulverized coal fired power plants.

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Chapter 1: Oxygen Enriched Coal Combustion with Flue Gas Recycle

Introduction

Concerns over the role of greenhouse gases in forcing global warming have led to international agreements like the Kyoto Protocol, that have set targets for controlling carbon dioxide emissions. Achieving these goals will require emissions trading, increasing energy efficiency, fuel substitution, and changes in combustion practice. Coal is an abundant, low cost fuel but with a high ratio of carbon to hydrogen, making CO₂ control a major concern for the future use of coal. In lieu of our growing energy demands, carbon sequestration provides an alternative to sharply reducing coal use. Carbon sequestration can be defined as the capture and secure storage of the carbon that is emitted as a result of human activities as well as the carbon that is already present in the atmosphere. However, it is necessary that the concentration of CO₂ in the gas or liquid stream be more than 90% before it can be injected into the oceans or deep underground geological formations. Concentrated high pressure CO₂ can also be injected into oil wells to dissolve the CO₂ in the oil, this not only causes the oil to expand but also decreases its viscosity and surface tension resulting in enhanced oil recovery.

Ordinarily coal combustion results in only about 15% CO₂ in the flue gas. The capture of CO₂ from the flue gas for sequestration is made difficult due to its relatively low concentration and the presence of other gaseous species like sulfur oxides that interfere with its separation. As an alternative, nitrogen can be separated from the air stream prior to combustion. However, combustion with pure oxygen results in very high flame temperatures that the current materials of construction cannot withstand. A novel method of using enriched oxygen for coal combustion with flue gas recycle to control the adiabatic flame temperature is being investigated so that the new technology can easily be applied as a retrofit to existing boilers. This method results in more than 90% CO₂ in the flue gas.

Experimental and 1-D computer modeling studies [1-4] have shown that dry and wet recycle conditions do exist at which the heat transfer rates are similar to those in conventional boilers. This project will involve carrying out 3-D computer simulations of the coal-fired boiler employed by [4] in their study at the base (combustion with air) condition, a dry (remove water by condensation) and a wet (not removing water by condensation) recycle conditions. The results obtained from the simulations will be compared with the experimental and modeling results of [4] to find out if the applicability of the CFD software that is being used can be extended to study combustion under these novel conditions. The study will progress by first carrying out similar simulations on natural gas fired boilers for simple geometries and then gradually proceeding towards coal-fired boilers and actual boiler geometries and conditions. The results obtained from the modeling studies will be used to design future experimental studies on two research furnaces located at the University of Utah.

The formation of sub-micron aerosol during coal combustion is known to be due to the phenomena of coal ash vaporization. Sub-micron particles are not easily captured by air-pollution control devices and have long atmospheric residence time thereby raising atmospheric and health concerns. The results from the modeling will be given as input to a metal vaporization model [10,11] in order to study and compare the extent of metal vaporized from coal under the different operating conditions.

Summary of literature search on O₂-CO₂ Combustion

A 1-D model was developed by Argonne National Laboratory to simulate and compare the heat transfer characteristics of burning coal in a mixture of CO₂ and O₂ rather than air [1]. Their results showed little differences between the predicted theoretical values and experimental values of the exit temperature and the amount of heat transferred and that CO₂/O₂ ratios between 2.23:1 and 2.42:1 imitate heat transfer characteristics of a conventional air burn. In a subsequent paper [2] they made comparisons for the axial distributions of the component mass fractions of coal, axial temperature, O₂, CO, CO₂ concentrations and combustion efficiencies between experimental and modeling studies with a 1-D model (1-DICOG). This study confirmed that the combustion of pulverized coal could be completed in a CO₂/O₂ atmosphere over a range of mole ratios between 2.23 and 3.65. Pilot scale experiments and the use of a boiler performance model were able to demonstrate the feasibility of recovering CO₂ by using flue gas recycle to control the temperature [3]. Studies have also been carried out

that employed pressurized combustion and combined cycles to increase the efficiency of the combustion process in different concentrations of O₂ and CO₂ [5]. However O₂/CO₂ – pulverized coal burners are associated with reduced ignition stability and simulation studies by [6] have shown that the addition of an oxygen injection nozzle to the burner improves the ignition stability. Studies have also shown reduced emissions of NO_x in enriched oxygen combustion with flue gas recycle [7]. Design, economics and life cycle analysis of a power plant operating under these conditions have also been previously done [8-9].

Experimental: Setup of Model Using Best-Available Data

Simulations of a coal-fired boiler with a capacity of 10 Mbtu/hr were carried out. Details of the furnace are available elsewhere [4]. The current version of GLACIER, a three-dimensional code for turbulent reacting flows and reacting particles provided by Reaction Engineering International is being used to carry out the simulations. GLACIER solves the continuity and Navier-Stokes equations in an Eulerian framework with particle source terms representing the coupling between the particle phase and the fluid phase. The k-ε model is used to model the turbulence and the differential equations are Favre-averaged and the resulting Reynolds-stress terms are modeled with an eddy diffusivity. This code assumes that the chemical reaction rates are limited by turbulent mixing and not by kinetics, local equilibrium is assumed for fast reacting gas phase based on the mixture fraction and is used to calculate the local gas concentrations. A metal vaporization model [10-11] is being used as a post processor to study ash vaporization.

A brief description of the furnace is given below [4]:

Boiler Type: Tower Furnace (indirectly fired)

Boiler Capacity: 10 Million Btu/hr

Geometry: 4 ft* 4ft*16.5 ft (internal dimensions)

Burner: Single, variable swirl coal burner. Fired from the top. The burner is being fed by two streams.

Mixture of oxygen and recycled flue gas.

Pulverized coal entrained in recycle flue gas.

A swirl number of 0.75 is currently being used.

Boiler Walls: 3" Refractory with 1" Water Jacket (to reproduce typical boiler temperature histories).

Coal: Sub-Bituminous coal from Wyoming (Black Thunder).

Size(μm)	Mass Fraction
400	0.075
250	0.075
200	0.1
125	0.1
100	0.1
65	0.05
50	0.05
30	0.45

Test Conditions: Boiler operating at full capacity with 3.5% O₂ (dry basis) in the exit flue gas.

Table 1-1 lists the different modeling studies that were carried out.

Table 1-1: List of Simulations carried out

Table 1-1a: Device				
Furnace	Geometry (in meters)	Nodes	Operation	Comments
Hot Box	10*1*1	24,150	5 MBtu/hr, Natural Gas and Air	
Hot Box	10*1*1	24,150	5 MBtu/hr, Natural Gas CO ₂ /O ₂ =2.92	A comparative study carried out.
Hot Box	4.95*1.2*1.2	3168	10 Mbtu/hr, Coal and Air	
Hot Box	4.95*1.2*1.2	3168	10 Mbtu/hr, Coal and (CO ₂ +H ₂ O)/O ₂ =2.94	A comparative study carried out
Argonne Furnace	4.95*1.2*1.2	135,000	10 Mbtu/hr, Coal and Air	
Argonne Furnace	4.95*1.2*1.2	135,000	10 Mbtu/hr, Coal and (CO ₂)/O ₂ =2.66	
Argonne Furnace	4.95*1.2*1.2	135,000	10 Mbtu/hr, Coal and (CO ₂ +H ₂ O)/O ₂ =3.00	A comparative study in progress

Table 1-1a: Device (continued)				
Configured Furnace Simulator (CFS)	58*15*11	30,000	Full Scale Boiler	A comparative Study of Base case and CO2 recycle case in progress
	43*13*8	506,660	Full Scale Boiler	A comparative Study of Base case and CO2 recycle case in progress

Table 1-1b: Flow conditions			
Stream	Air	Dry Recycle = 2.66	Wet Recycle = 3.0
Coal feed rate (Kg/sec)	0.127	0.127	0.127
Primary Stream	Air at 530.2 K, 0.2284 Kg/sec, O2 = 21%, N2 = 79%	Oxidant at 362.4 K, 0.2328 Kg/sec, O2 = 10%, N2 = 5%, CO2 = 68%, H2O = 16%	Oxidant at 511.3 K, 0.2395 Kg/sec, O2=9%, N2=6%, CO2=53%, H2O=32%
Secondary Stream	Air at 530.2 K, 0.9136 Kg/sec O2 = 21%, N2 =79%	Oxidant at 362.4 K, 1.1481 Kg/sec, O2 = 17%, N2 = 4.7%, CO2 = 63.4%, H2O = 14.9%	Oxidant at 511.3 K, 1.204 Kg/sec, O2=16.7%, N2=5.4%, CO2=48.5%, H2O=29.3%

Table 1-1c: Grid Size	150*30*30 (135,000 nodes)
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Results

Figure 1-1 shows the results of axial gas emissivities obtained for dry recycle and base case for “Preliminary studies” carried out on a 10m*1m*1m Natural Gas Fired Furnace. Notice the higher emissivity for the CO₂ Recycle case due to the higher concentration of CO₂ within the furnace (Polar molecules like CO₂, H₂O and CH₄ have distinct absorption bands associated with their vibrational and rotational modes and radiation is able to escape through windows between these strongly absorbed wavelengths. This explains the higher emissivity of the gases for the CO₂ recycle case).

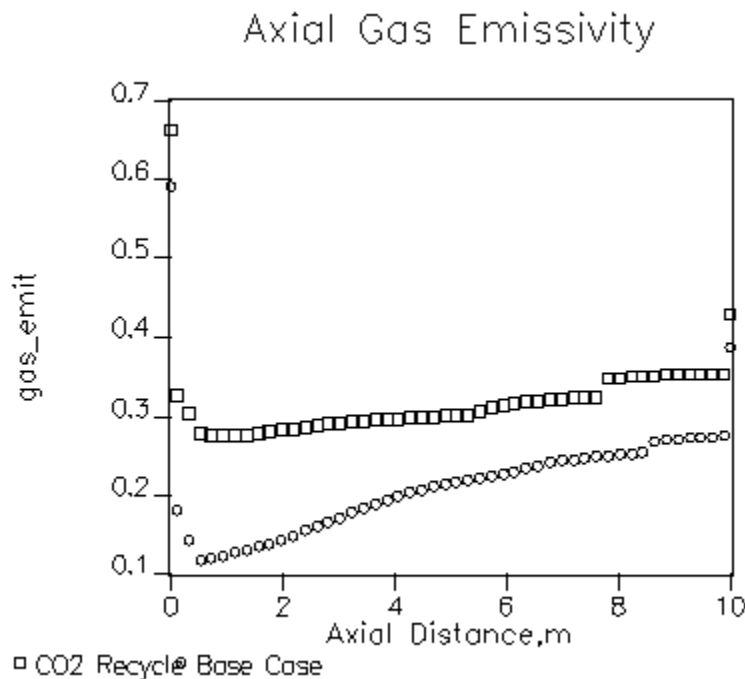
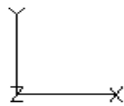
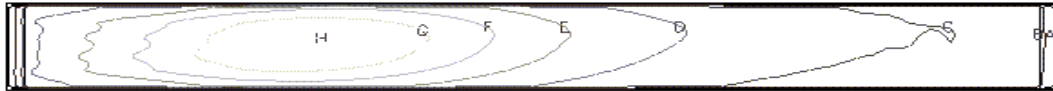


Figure 1-1: A comparison of axial gas emissivity for dry CO₂ recycle with the air combustion case as calculated by GLACIER for natural gas combustion.

A comparison of the net heat transferred to the wall (Figure 1-2), in our preliminary study with the natural gas fired furnaces also shows that heat transfer rates are comparable at certain recycle conditions. The recycle condition shown here is CO₂/O₂ molar ratio of 2.92 in the oxidant.

A	-10000.000
B	0.000
C	10000.000
D	20000.000
E	30000.000
F	40000.000
G	50000.000
H	60000.000



A	-10000.000
B	0.000
C	10000.000
D	20000.000
E	30000.000
F	40000.000
G	50000.000
H	60000.000

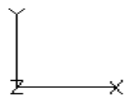
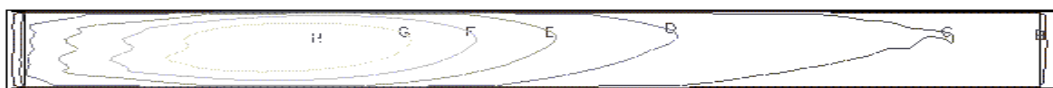


Figure 1-2: Net Heat Transferred to the wall of a natural gas fired furnace (flue gas recycle).

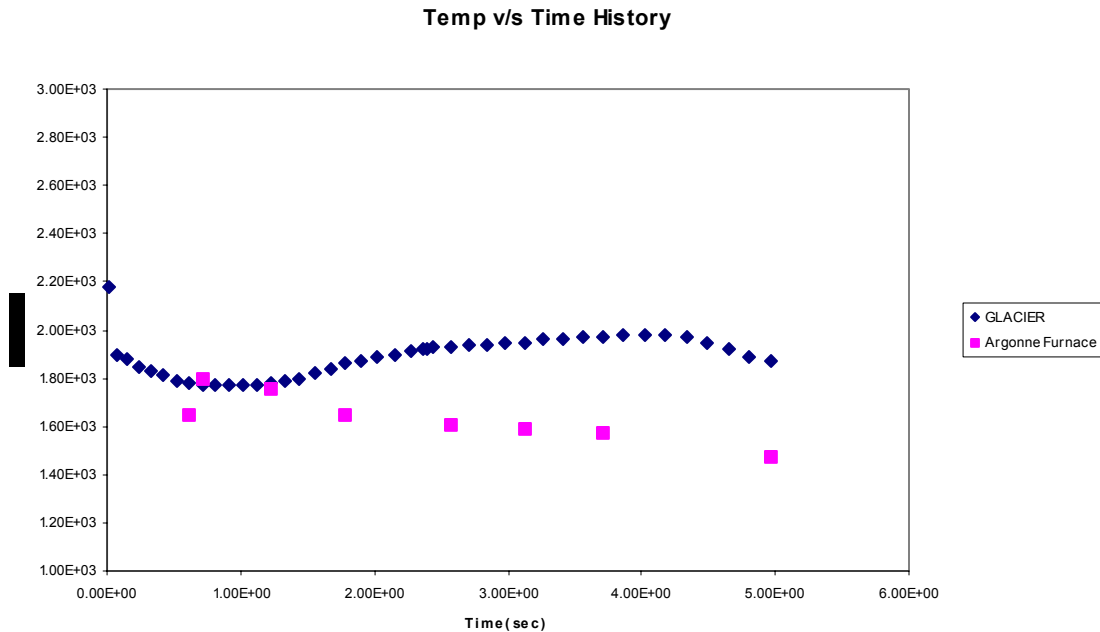


Figure 1-3: Shows a comparison of the axial gas temperature profile for our model (base case) with that of the Argonne Furnace.

When runs were conducted with a wall heat resistance of $0.001 \text{ m}^2\text{-K/W}$ throughout the furnace the outlet temperature (1427.3K) was comparable to the experimentally obtained temperature (1355 K).

At present we are getting about 70% CO_2 (on a dry basis).

SO_2 (expected) = 560 ppm

Obtained = 1965 ppm

Oxygen concentration in the exit is not 3.5%, CO_2 concentration lower than expected and CO concentration higher (0.1%).

Temperature-Time History

Figure 1-4 shows a comparison of the temperature-time histories and the temperature profiles of the GLACIER simulations with the Argonne furnace. Our models temperature –time history is that tracked for a single coal particle whereas the experimental and model profile for the furnace is the gas temperature.

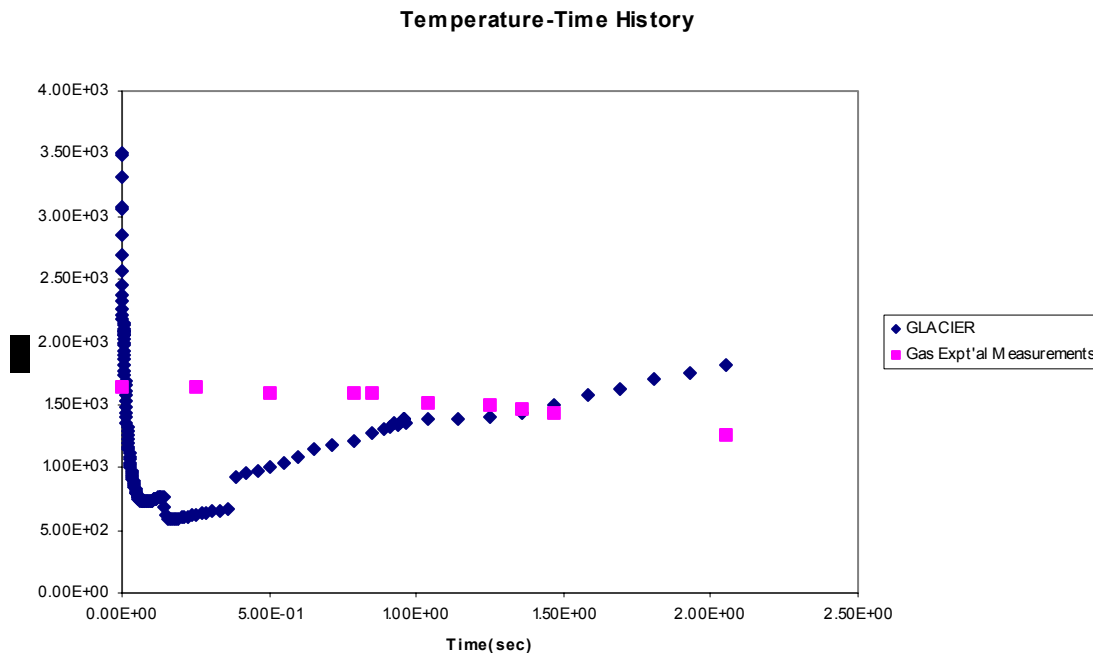


Figure 1-4: A Comparison of the Temperature-Time Profile of the Argonne boiler with our model

Areas for future study: Key Metal Vaporization Variables

Vaporization of metal oxides from a burning char occur as a result of the reducing conditions occurring within a char particle and are suspected to proceed according to the carbothermal reduction reactions $MO + CO \rightarrow M + CO_2$. The volatile sub-oxide formed vaporize and diffuse to the surface of the char where they re-condense to form the original metal oxide upon contact with oxygen and form the nucleus of the sub-micron vapor.

Sub-micron particles are not easily captured by air-pollution control devices and have long atmospheric residence time thereby raising atmospheric and health concerns. The results from the modeling will be given as input to a metal vaporization model [10,11] in order to study and compare the extent of metal vaporized from coal under the different operating conditions.

Areas for future study: Metal Vaporization Model

The formation of sub-micron aerosol during coal combustion is believed to be due to the phenomena of coal ash vaporization. Coal char contains various metal oxides. Under, combustion conditions these metal oxides form volatile sub-oxides as a result of the reducing conditions found within the char particle. These sub-oxides vaporize easily (as a result of their higher vapor pressure) and diffuse to the surface of the char. On encountering oxygen in the bulk gas phase, the sub-oxide is re-oxidized to form the original oxide that condenses and forms the nuclei of the sub-micron particle. This study will involve making modifications to a metal vaporization model in order to get an accurate measure of the reducing conditions within the burning char and then use the model as a post processor to study and compare the metal vaporization that occurs under flue gas recycle conditions with that under conventional firing. It is suspected that the increased concentration of CO_2 under recycle conditions would suppress ash vaporization.

In order to study this phenomenon it is important to have an accurate prediction of the reducing conditions within a char particle. The mathematical model developed by Quann and Sarofim [12] assumed that CO was the only primary product of the heterogeneous reaction of carbon, however CO_2 is also produced and this affects the metal-metal oxide equilibrium at the surface of the mineral inclusion. Efforts are on to determine the CO/ CO_2 ratio within char particles at different temperatures. The temperature of the burning particle will also have to be corrected since the formation of CO_2 releases much more heat than when CO alone is the primary product of combustion. Also, the CO_2 diffusing out will affect the rate of diffusion of oxygen, and hence the burning rate. The following figure shows that if we account for the formation of CO_2 , the calculated particle temperature is much more than the predicted temperature without accounting for CO_2 formation. As a result of the increased temperature the vaporization rates should also increase. However, the presence of CO_2 tends to suppress the amount of metal vaporized. Hence, it would be interesting to find out how the vaporization phenomena are affected by these two opposing effects. Efforts are on in this direction.

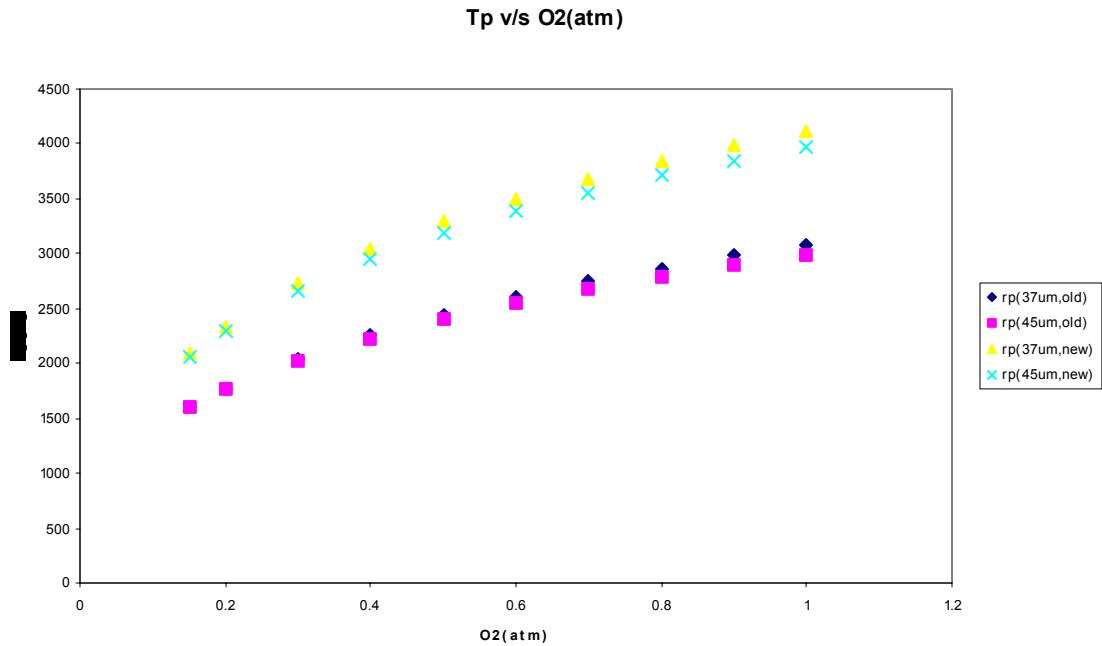


Figure 1-5: The temperature of a burning char particle with and without accounting for the formation of CO₂ as a product of the heterogeneous reaction. (old = CO is the only product of heterogeneous carbon reaction, new = Both CO and CO₂ are products of the heterogeneous reaction of carbon, rp = radius of the particle)

Figure 1-6 compares the amount of Aluminum vaporized experimentally (FV(exp)) with the calculated amount of Aluminum vaporized by the old model (FV(calc)) for different types of coals (labeled in the x-axis). It can be seen that for inclusion sizes between 1 and 5 microns the model fits the experimental data. Figure 1-7 compares the amount of Aluminum vaporized experimentally (FV(exp)) with the calculated amount of Aluminum vaporized by the new model (FV(calc)) that accounts for the increased temperature rise resulting from CO₂ formation for different types of coals (labeled in the x-axis). It can be seen that for inclusion sizes close to 40 microns the model fits the experimental data.

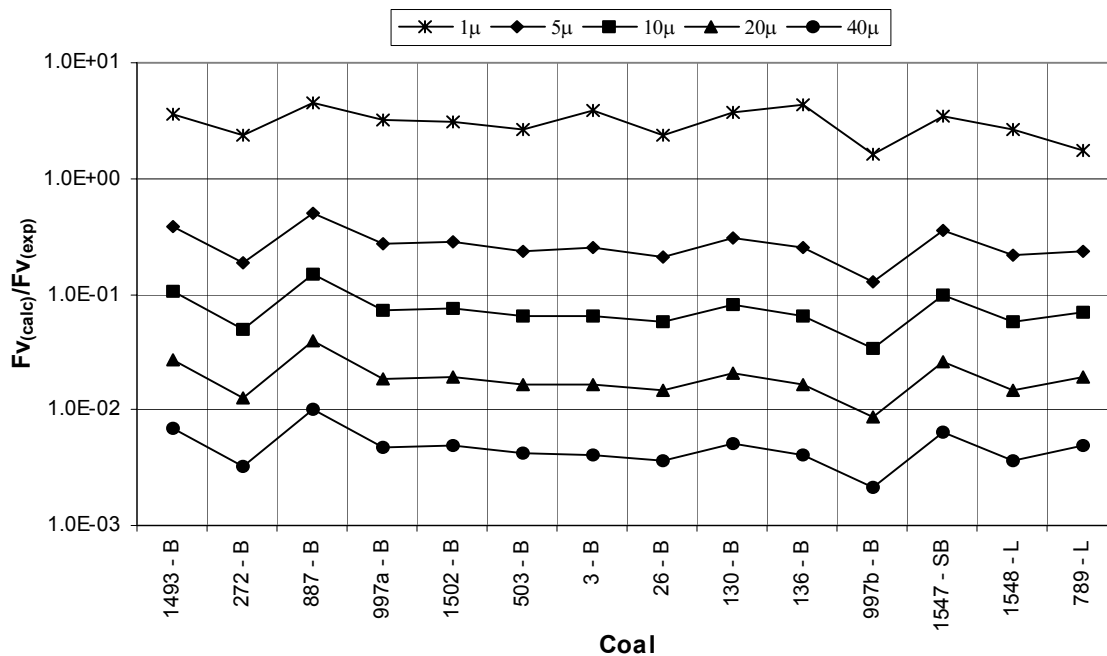


Figure 1-6: A comparison of the amount of Aluminum vaporized experimentally (FV(exp)) with the calculated amount of Aluminum vaporized by the old model (FV(calc)) for different types of coals (labeled in the x-axis).

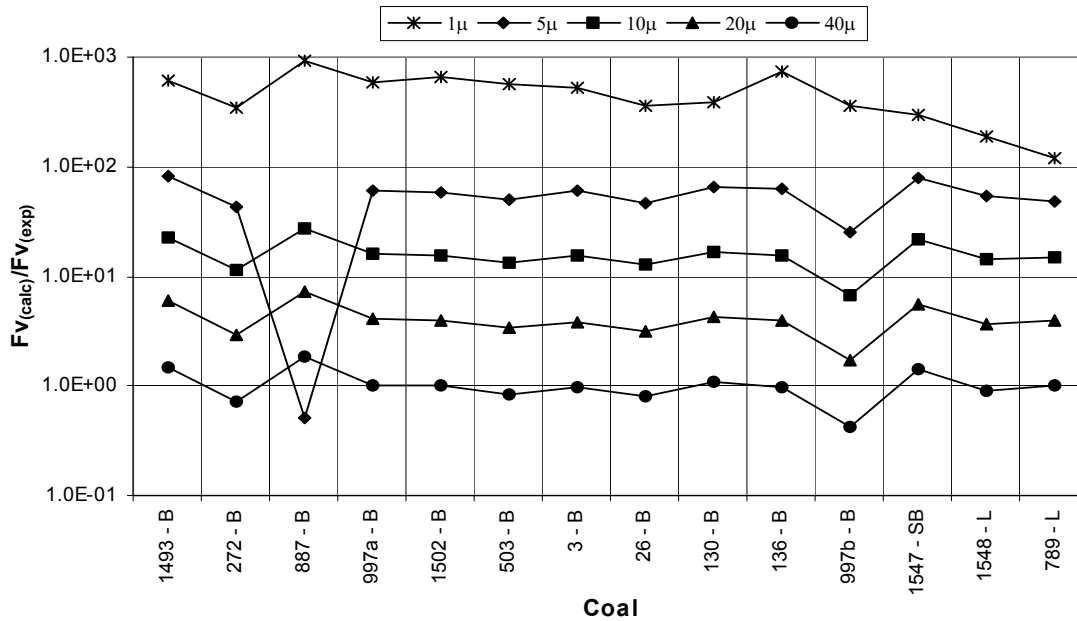


Figure 1-7: A comparison of the amount of Aluminum vaporized determined experimentally(FV(exp)) with the amount of aluminum vaporized as calculated by the improved model (FV(calc))

Attention then switched to the related field of parametric modeling of CO/CO₂ ratio inside single char particles during pulverized coal combustion, as being likely to be more productive during the remaining time available.

Chapter 2: Parametric Modeling of CO/CO₂ Ratio Inside Single Char Particles During Pulverized Coal Combustion

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 [10,12-18]. 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/CO_2 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 [10,12] developed a model for metal vaporization that was able to correlate the results of experiments in a laminar flow laboratory furnace with no ambient CO_2 present. The model developed by Quann to analyze the data from drop tube experiments assumed that the only source of CO_2 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% O_2 in the bulk gas.

The Quann model only considers the effect of oxygen in the bulk gas and does not include the effect of varying bulk CO_2 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 [19-21]. 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 [22,23]. 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. Lee [24] 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 predicted large differences in metal vaporization from different burner locations in a boiler based on CFD output for the gas composition and temperature along the particle trajectory.

Table 2-1 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.

Model	Objective	CO Composition	CO ₂ Composition
Quann (1982)	Explain drop tube data in terms of mechanism.	Stoichiometry $P_{CO} = \frac{2P_{O_2}}{1 + P_{O_2}}$	$P_{CO_2} = P_M$
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.

Table 2-1: 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.

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 [25,26], 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., [12] and can be used in a metal vaporization sub-model run as a post processor to detailed furnace simulations.

Experimental 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. SKIPPY incorporates homogenous kinetics in the pores and boundary layer, heterogeneous kinetics in the pores and gas-phase mass transport in the char pores and boundary layer. Dr. Brian S. Haynes at University of Sydney, Australia provided the code. Details of the SKIPPY code are documented [25,26]. 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, power plants based on oxygen-enriched combustion with flue gas recycle have been proposed as a technology to produce concentrated CO₂ for sequestration [3,4,8]. 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 [26]. Figure 2-1. 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.

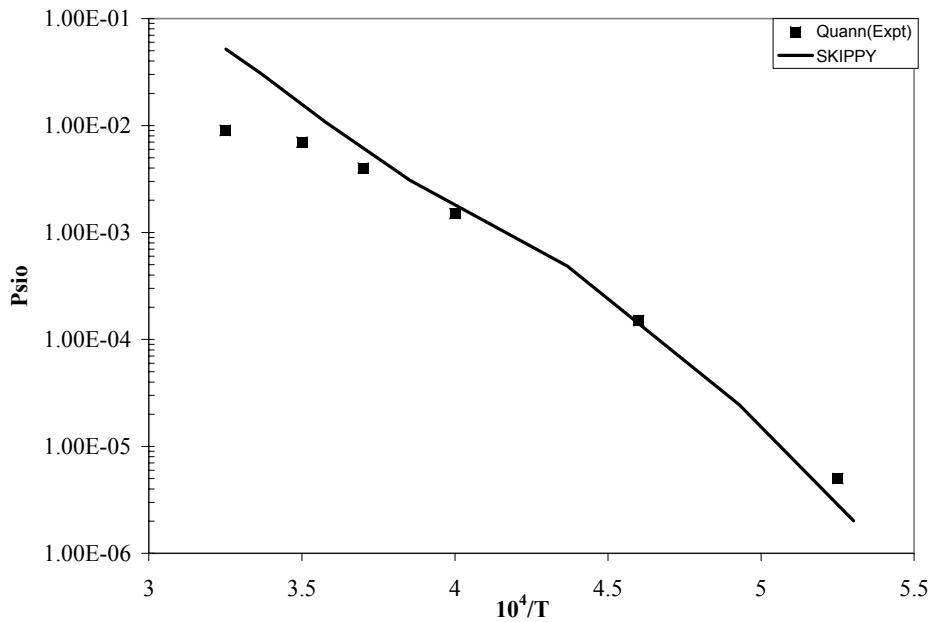


Figure 2-1. Comparison of P_{SiO} calculated from SKIPPY runs with Quann's experimental data [25,26]

Results

A series of simulations were aimed at studying the validity of the composition assumptions listed in Table 2-1, 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. All results shown in Figures 2-8 were calculated by SKIPPY assuming a 100 (micron) char particle from Illinois #6 coal with a void fraction of 80% and with the furnace temperature set at 1750 K.

The curve for 0% CO₂ in Figure 2-2a 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 CO₂ concentration in the bulk gas.

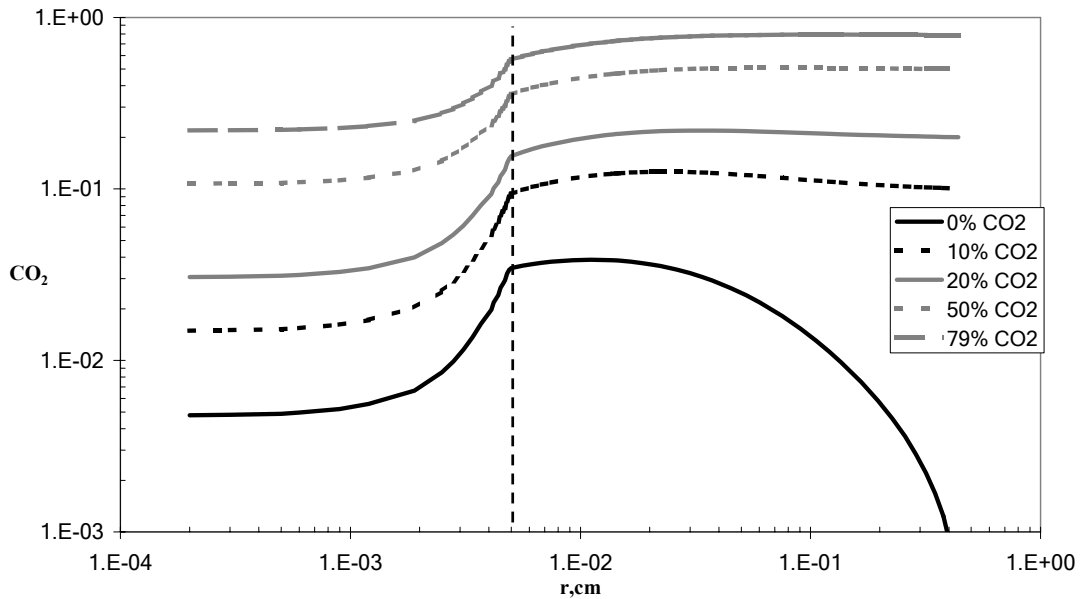


Figure 2-2a: Partial pressure profile of CO₂ calculated by SKIPPY for a 100 μm diameter Illinois # 6 char particle burning in a furnace maintained at 1750 K with various concentrations of CO₂ in the bulk gas. The vertical dotted line corresponds to the surface of the particle.

The concentration of CO inside the char in Figure 2-2b also approaches a constant value that varies with the bulk CO₂ gas concentration. The simulations assumed zero CO in the bulk gas.

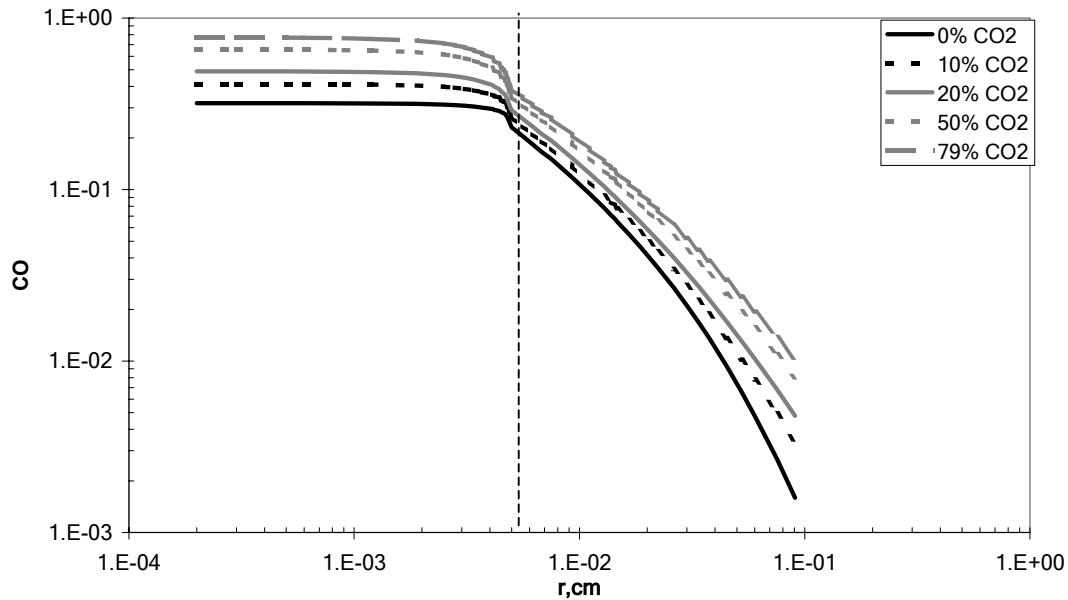


Figure 2-2b: Partial pressure profile of CO calculated by SKIPPY for a 100 μm diameter Illinois # 6 char particle burning in a furnace maintained at 1750 K with various concentrations of CO₂ in the bulk gas. The vertical line corresponds to the surface of the particle.

Figure 2-2c shows that since both the CO and CO₂ inside the char depend on bulk gas CO₂ the CO/ CO₂ ratio also shows a similar behavior.

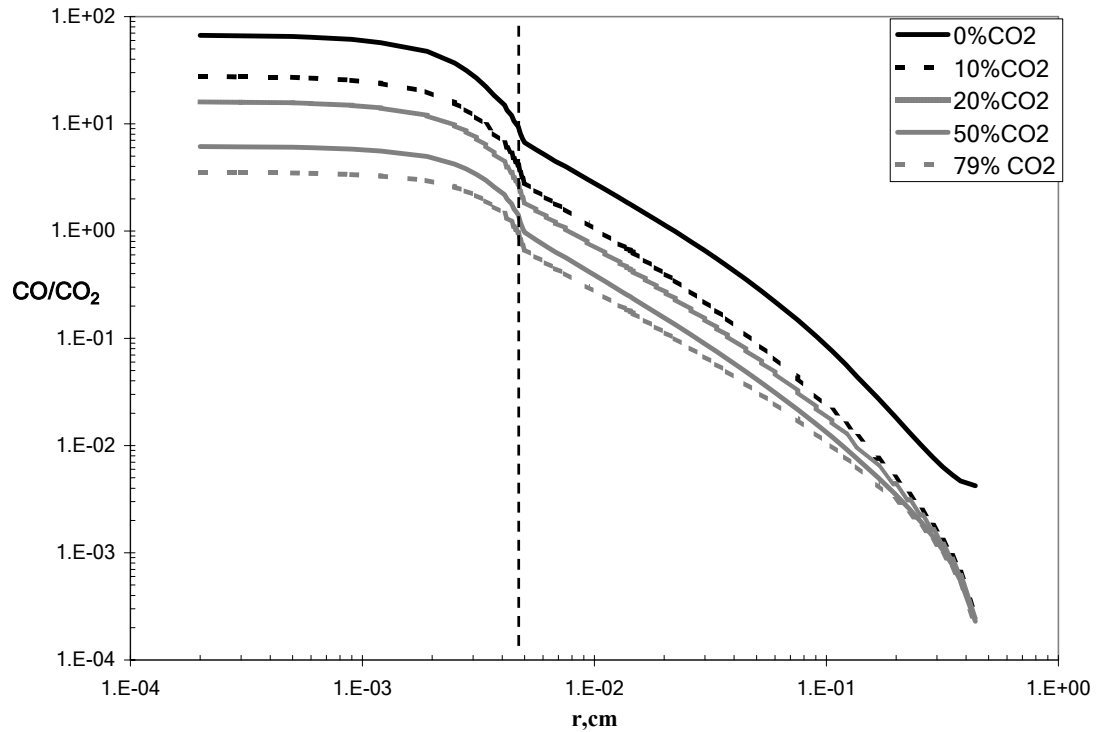


Figure 2-2c: CO/CO₂ ratio calculated by SKIPPY for a 100 μm diameter Illinois # 6 char particle burning in a furnace maintained at 1750 K with various concentrations of CO₂ in the bulk gas. The vertical line corresponds to the surface of the particle.

Figure 2-3 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 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 2-3: P_{SiO} calculated with the particle energy balance (PEBL) turned off and on.

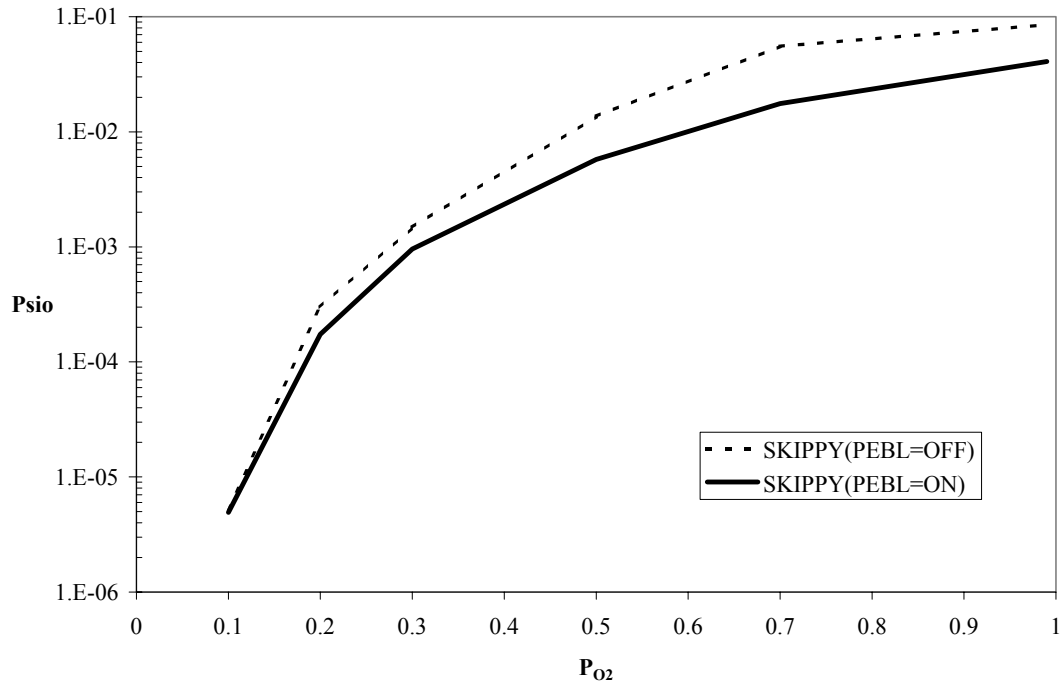


Figure 2-4 shows the P_{seo} data that was generated by turning off the particle energy balance equation in SKIPPY and specifying a particle temperature of 2280 K (2280 K is the validated temperature for SKIPPY when 20% O_2 is in the bulk). With prescribed temperature the effect of varying P_{co2} on P_{seo} is small relative to the effect of changing P_{O_2} .

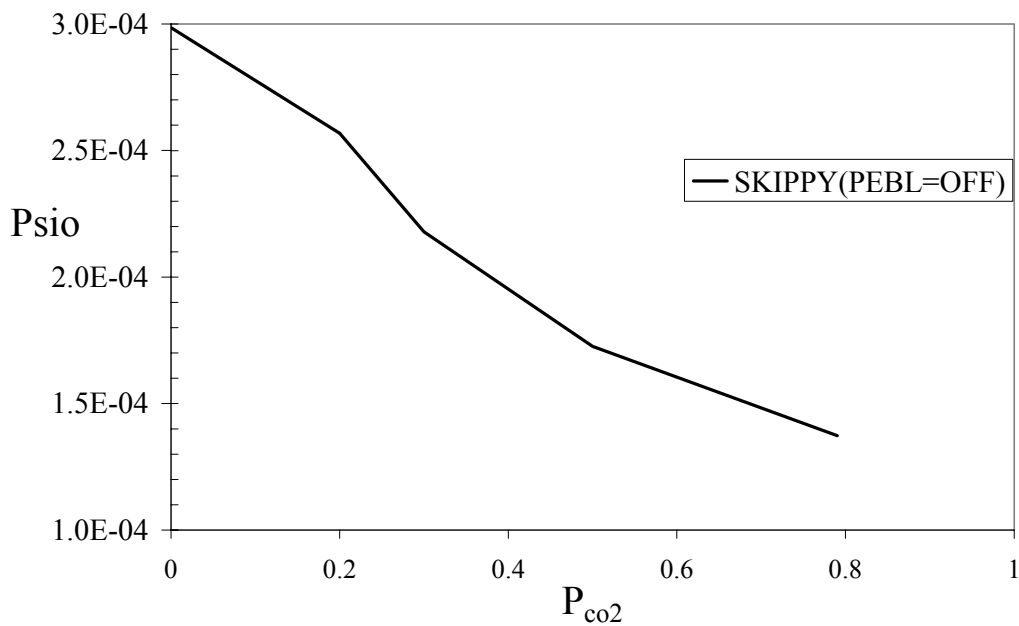


Figure 2-4: P_{seo} calculated at different CO_2 concentrations and using a fixed particle temperature of 2280 K.

Figure 2-5 shows the effects of CO_2 and temperature that decrease P_{sid} at the surface of the char. Here the model predicts that the temperature and P_{sid} decrease when the P_{co_2} in the bulk gas increases. Figure 2-6 shows the partial pressure profile of O_2 calculated by SKIPPY. 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 2-2a. This is due to reaction of O_2 with the carbon resulting in the production of CO_2 .

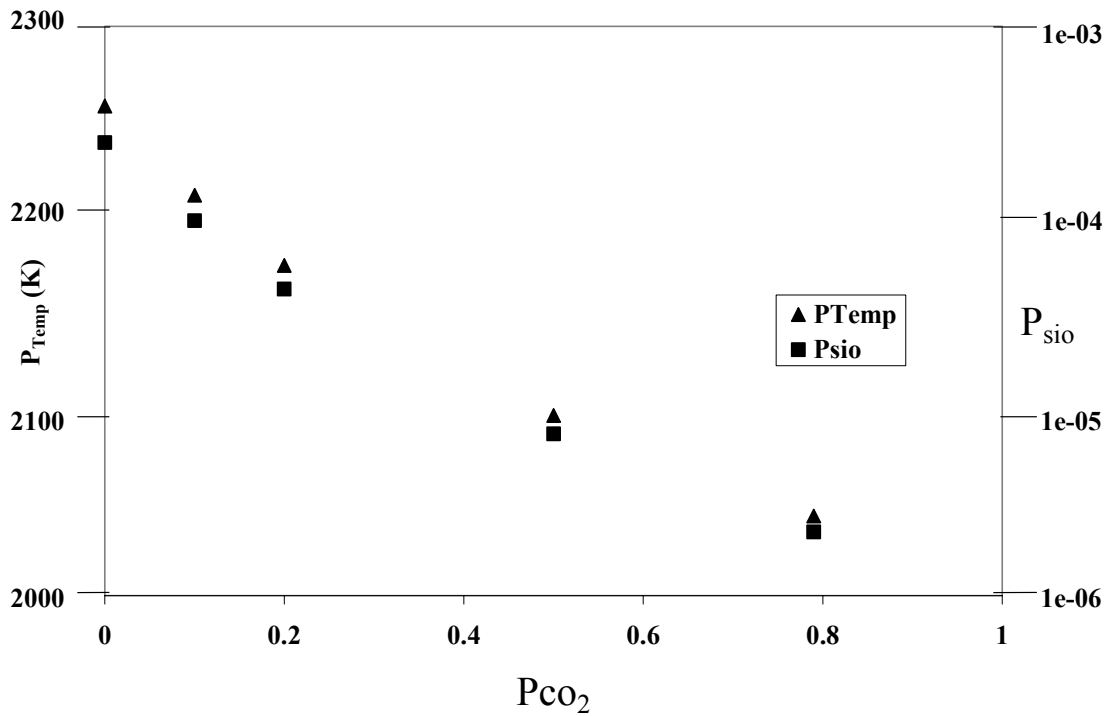


Figure 2-5: The effects of decrease in particle temperature and increase in CO_2 concentration in the bulk towards suppressing the metal vaporization (P_{sid})

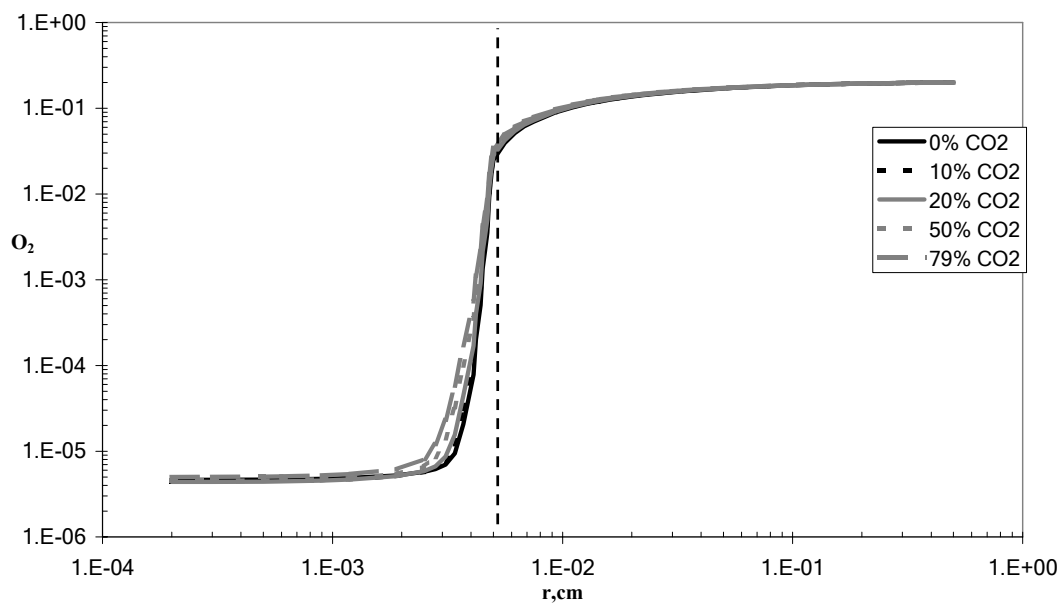


Figure 2-6: Partial pressure profile of O_2 calculated by SKIPPY for a 100 μm diameter Illinois # 6 char particle burning in a furnace maintained at 1750 K with various concentrations of CO_2 in the bulk gas. The vertical line corresponds to the surface of the particle.

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 CO_2 in the bulk) two effects tend to suppress the amount of metal vaporized from the char. The high CO_2 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 CO_2 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 4 and 5). 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 2-2 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 2-2: 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 2-2 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_{tio} 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:

$$\frac{P_{\text{CO}}}{P_{\text{CO}_2 \text{ vol avg}}} = 4\pi \int_0^R r^2 \frac{P_{\text{CO}}(r)}{P_{\text{CO}_2}(r)} dr / \text{Particle Volume} \quad (5)$$

This study suggests that an algebraic model of the form

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

(where T_{gas} is the temperature of the bulk gas in Kelvin, $P_{bulk CO_2}$ 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 2-7 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.

The current version of SKIPPY predicts a large decrease in temperature due to the endothermic carbon gasification reaction (Figure 2-5). However, pilot scale studies with high bulk gas CO_2 [4] show little effect on char burnout suggesting that the reaction rate in SKIPPY is too high. An alternative set of cases was run with the carbon gasification reaction turned off. The correlation that was obtained from these runs is shown in equation 8.

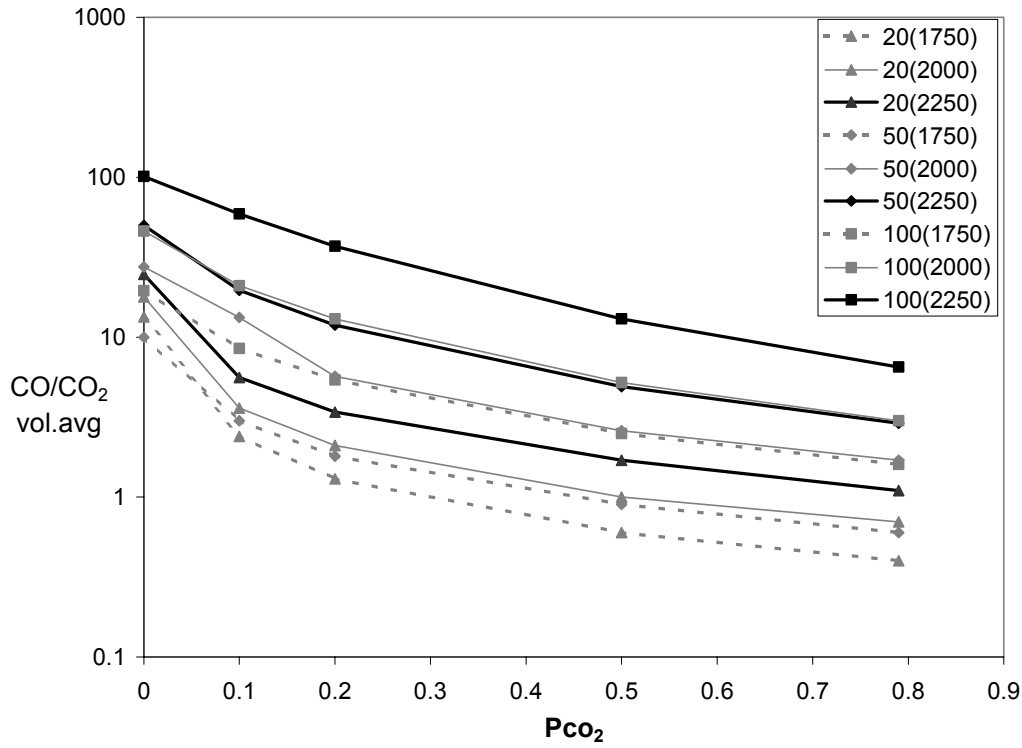


Figure 2-7: Volume average CO/CO₂ ratio data points plotted as a function of CO₂ concentration in the bulk. The first number in the legend is the particle diameter in microns and the number inside the brackets is the furnace temperature in Kelvin.

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

$$\left(\frac{P_{CO}}{P_{CO_2}} \right)_{vol\,avg} = 5.36 e^{3.33(0.12 - P_{bulk\,CO_2})} e^{\left(\frac{11370}{1750} - \frac{11370}{T_{gas}} \right)} \left(\frac{d_p}{50 \times 10^{-6}} \right)^{0.96} \quad (7)$$

The algebraic correlation that we arrived at when the carbon gasification turned off was

$$\left(\frac{P_{CO}}{P_{CO_2}} \right)_{vol\,avg} = 2.54 e^{3.25(0.12 - P_{bulk\,CO_2})} e^{\left(\frac{708}{1750} - \frac{708}{T_{gas}} \right)} \left(\frac{d_p}{50 \times 10^{-6}} \right)^{-0.183} \quad (8)$$

The R^2 value for the regression coefficients in equations (7) and (8) was 0.9 and 0.82 respectively indicating that the selected functional forms give a reasonable approximation to the SKIPPY output data.

Discussion

Combustion with 20% O_2 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) and from Figure 2-1 this would mean that the concentration of CO_2 at the surface of the char at this temperature is in the range 1×10^{-4} to 3×10^{-4} . It can be seen from Figure 2-2a that SKIPPY predicts CO_2 partial pressures 2 orders of magnitude higher than what was originally assumed by Quann. The volume average of the CO_2 within the char was calculated to be 2×10^{-2} .

From Figure 2-2b we notice that Quann's assumption for the CO partial pressures from stoichiometric reasoning agrees with SKIPPY predictions. However, from Figures 2a and 2b we see that his calculation of the CO/ CO_2 ratio are quite different from those predicted by SKIPPY. According to Quann's assumptions for a zero bulk CO_2 concentration the CO/ CO_2 is 2000 versus a range within the particle from 6 to 70 predicted by SKIPPY as shown in Figure 2-2c.

As previously mentioned in Table 2-1, Lee (14) assumed that the change in gas composition across the boundary layer of the particle was small and that the CO and CO_2 values applicable to the particle were the local bulk gas composition computed by the CFD code. From Figure 2-2a we find that this assumption is a good one for CO_2 concentrations whereas from Figure 2-2b 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 2-2c. SKIPPY results show that the volume averaged CO/ CO_2 ratio is about 20 at these conditions.

The validation of SKIPPY in Figure 2-1 [26] 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 CO_2 atmosphere, we had to turn on the particle energy

balance equation while carrying out our computations. Figure 2-3 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.

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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List of Acronyms and Abbreviations

CFD: Computational Fluid Dynamics

CFS: Configured Furnace Simulator

FV: volume fraction (volume aerosol/volume gas)

PEBL: particle energy balance equation