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"ADVANCED COMBUSTOR DESIGN CONCEPTS
TO CONTROL NOX AND AIR TOXICS"

SUBMITTED BY

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1.0 Program Overview

Direct coal combustion must be a primary energy source for the electric utility industry and for heavy manufacturing during the next several decades because of the availability and economic advantage of coal relative to other fuels and because of the time required to product major market penetration in the energy field. However, the major obstacle to coal utilization is a set of ever-tightening environmental regulations at both the federal and local level. It is, therefore, critical that fundamental research be conducted to support the development of low-emission, high efficiency pulverized coal power systems.

The University of Utah, Massachusetts Institute of Technology (MIT), Reaction Engineering International (REI) and ABB/Combustion Engineering have joined together in this research proposal to develop fundamental understanding regarding the impact of fuel and combustion changes on ignition stability and flame characteristics because these critically affect: NO_x emissions, carbon burnout, and emissions of air toxics., Existing laboratory and bench scale facilities are being used to generate critical missing data which will be used to improve the NO_x and carbon burnout submodels in comprehensive combustion simulation tools currently being used by industrial boiler manufacturers. to ensure effective and timely transfer of This technology, a major manufacturer (ABB) and a combustion model supplier (REI) have been included as part of the team from the early conception of the proposal.

ABB/Combustion Engineering is providing needed fundamental data on the extent of volatile evolution from commercial coals as well as background information on current design needs in industrial practice. Since they will ultimately be a recipient of the enhanced design methodology, they are also providing ongoing review of the practical applicability of the tools being developed. MIT is responsible for the development of an improved char nitrogen oxidation model which will ultimately be incorporated into an enhanced NO_x submodel. Reaction Engineering International is providing the lead engineering staff for the experimental studies and an overall industrial focus for the work based on their use of the combustion simulation tools for a wide variety of industries. The University of Utah is conducting bench scale experimentation to (1) investigate alternative methods for enhancing flame stability to reduce NO_x emissions and (2) characterize air toxic emissions under ultra-low NO_x conditions because it is possible that such conditions will alter the fate of volatile and semivolatile metal species and the emission of heavy hydrocarbons. Finally the University of Utah is responsible for the development of the improved NO_x and carbon burnout submodels.

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2.0 Progress During The Last Quarter

2.1 Char Collection System

One goal of the study is to develop improved NO_x and carbon burnout submodels. Improvements to the NO_x submodel include modeling the fate of char nitrogen (char-N). Hence, both the carbon burnout and NO_x submodel development and validation will require experimental data obtained from coal chars. These coal chars should be prepared under conditions similar to those in a pulverized coal combustor to yield the most accurate and relevant data. Commercially-obtained chars are usually produced at temperatures and heating rates unlike those found in a combustor, so it was necessary to devise a way to collect significant quantities of char from a pulverized coal combustor.

A char collection system has been designed to collect char produced from a pulverized coal flame in the U furnace located at the University of Utah. The U furnace has been described in a previous report. It has a nominal firing rate of 29 kW and is refractory lined. Opposing sample ports are located along the length of the furnace. The collection system serves to quench oxidation at the sampling point and to collect the desired particulate matter. Figure 1 is a schematic drawing of this system.

A water-cooled plate is inserted into a sample port in the furnace. This plate extends across the diameter of the furnace and essentially plugs the furnace so that the particle-laden flue gas can be diverted out the opposing port and through a vacuum system. A distribution plate is welded to the water-cooled plate at right angles. Dilution gas will pass through a series of tubes to holes located in the distribution plate. This gas will then blow across the surface of the water-cooled plate and mix with the flue gas as it enters the opposing port. The dilution gas serves two purposes: one, to quench oxidation in the flue gas and two, to prevent excessive slag buildup on the water-cooled plate. It is anticipated that the ratio of dilution gas to flue gas will be 1:1 in order to adequately quench oxidation.

The mixture of dilution gas and particle-laden flue gas will then exit the sample port and enter a water-cooled section where temperatures will be reduced to approximately 590 K. The flue gas mixture then enters a cyclone which is designed to collect particles 5 mm and above. Partially burned char particles are in the range of 5 mm to 250 mm, so the cyclone should collect the desired particles. Once the particles are removed in the cyclone, the flue gas mixture enters a long horizontal pipe where gas flowrate is measured using an Accutube and a thermocouple. This flow measurement is necessary to verify that the cyclone is being operated at the flowrate for which it was designed. The final step is to spray water into the flue stream to cool it sufficiently before entering the vacuum. Because the entire flue gas stream from the furnace will be diverted through this system, it is estimated that 0.9-1.4 kg/hr of char will be collected using this system.

Fabrication is almost complete on the various components of this char collection system and testing will begin within the next two weeks.

2.2 Char Nitrogen Modeling

In the quarterly report covering the period 1/95-3/95, a detailed description was given of a new char nitrogen model developed at MIT. It was desired to compare the kinetic reaction rates in this new model to those obtained by other researchers. This comparison proved difficult because the reaction rates in the MIT model are pseudo-homogeneous with units of moles per unit volume per second while most other researchers report heterogeneous reaction rates with units of moles per unit area per

second. Thus, a comparison of the reaction rates becomes a function of the model used to convert from heterogeneous rates to pseudo-homogeneous rates or vice versa.

A comparison of reaction rates is also difficult because of the complex processes that occur during char nitrogen oxidation. These processes include mass transfer in porous particles, heterogeneous reactions, homogeneous reactions, and changes in the physical structure of the char as a function of burnout. Some published reaction rates are actually pseudo kinetic rates because the effects of mass transfer are lumped into the kinetic rate. Other important factors which vary from experiment to experiment are temperature and char type. Table 1 compares various published rates for the reduction of NO on the surface of char. An attempt has been made to correlate all rates using the same units. To convert from heterogeneous rates to pseudo-homogeneous rates, a pore diameter of 50 nm was chosen. Complete references for all entries in Table 1 are included in this report.

Reference	Rate (mol/m ³ -s)	Type of char	Temp. range, K
Goel, S. and Sarofim, A. F.	$1.7e+06\exp(-11155/T)$	Newlands	1023-1123
De Soete, G. G.	$3.0e+03\exp(-16900/T)$	HV bituminous	500-1300
Rodriguez-Mirasol, J. et al.	$2.8e+07\exp(-20100/T)$	HV bituminous	673-1223
Chan, I. K. et al.	$1.68e+07\exp(-13100/T)$	lignite	723-1123
Levy, J. M.	$3.3e-07\exp(-17500/T)$	lignite	1250-1750
Song, Y. H. et al.	$4.0e+06\exp(-16500/T)$	lignite	1250-1750

Table 1

It is clear from this table that there is not much consistency between various reported rates. Therefore, the kinetic reaction rates used in the char nitrogen model of Goel and Sarofim appear to be as valid as any other published rates. Since the work of Goel and Sarofim includes a set of self-consistent rates for both char oxidation and char nitrogen reactions, modeling work will continue using these rates.

3.0 Plans for Next Quarter

The char collection system will be used to collect realistic chars from four different coals: lignite and subbituminous coals from the Powder River Basin, a Utah high-volatile bituminous coal, and Illinois No. 6 (also a bituminous coal). Once the chars have been collected, they will be reintroduced to the furnace at pulverized coal firing conditions, and detailed experimental measurements will be taken using the solid and gas sampling systems which have been developed.

4.0 References

- Chan, L. K., Sarofim, A. F., Beer, J. M., *Combust. Flame* 52:37-45 (1983).
- De Soete, G. G., *Twenty-Third Symposium (International) on Combustion*, The Combustion Institute, pp. 1257-1264 (1990).
- Goel, S. K., Sarofim, A. F., Quarterly Report for DOE Contract No. DE-FG22-94PC94223, 1/95-3/95.
- Levy, J. M., Chan, L. K., Sarofim, A. F., Beer, J. M., *Eighteenth Symposium (International) on Combustion*, The Combustion Institute, pp. 11-120 (1981).

Rodriguez-Mirasol, J., Ooms, A. C., Pels, J. R., Kapteijn, F., Moulijn, J. A., *Combust. Flame*, to be published.

Song, Y. H., Beer, J. M., Sarofim, A. F., *Combust. Sci. Tech.* 25:237-240 (1981).

MODELING OF CO OXIDATION IN THE BOUNDARY LAYER OF A SINGLE PARTICLE AT PULVERIZED FUEL CONDITIONS

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Abstract

A single particle model is developed for modeling the kinetics and the transport properties pertinent to CO oxidation in the boundary layer of a single particle. A 56 elementary gas phase kinetic scheme is coupled with the diffusive properties of the 12 species involved in the CO oxidation. The model is successfully calibrated against the experimental data of Tognotti and co-workers. Studies on the effect of water concentration show that significant CO oxidation occurs even at low temperatures but only with increases in the surrounding water concentration. Release of bound hydrogen both at a rate proportional to carbon consumption or instantaneously is characterized by high degree of CO oxidation. There is a minimum temperature, however, below which CO oxidation does not occur irrespective of how high the water concentration is. The model has been applied to predict the effects of changing parameters. The addition of calcium leads to both a high particle temperature overshoot and significant levels of CO oxidation during char gasification/combustion itself. Large amounts of CO are oxidized to CO_2 even at low oxygen concentration levels which would otherwise be impossible in absence of calcium. The effects of ambient gas temperature, oxygen concentration and initial particle size have also been studied. High ambient temperatures are conducive to CO oxidation even at lower oxygen levels. This is due to a decrease in the loss of CO generated at the particle surface to the cold ambient *via* the diffusive processes. A maximum is observed in particle temperature with decreases in particle size at high oxygen concentrations. The latter observation is a consequence of changes in particle density, carbon conversion, and char gasification rates, all of which are a function of initial particle size.

1 INTRODUCTION

In order to develop combustors with high combustion efficiency, a good understanding of the char oxidation process is very important. The temperature history of a burning char particle is important for predicting the carbon consumption rate, the relative ratio of CO_2 to CO , the burning time, and the combustion efficiency. Moreover, pollutant emissions and ash formation are severely affected by the particle temperature. Since NO can be destroyed by CO on the particle surface [9], a good understanding of the oxidation characteristics of CO is necessary. Earlier experimental studies on this aspect include the measurement of particle temperature history in an electrodynamic balance [2] [18], and the CO_2/CO ratio as a function of particle temperature [15][16] [18]. With regard to modeling, particle temperature profiles have been modeled [10] by assuming pure heterogeneous reactions.

During char combustion the two most important products are CO and CO_2 . CO so formed is further oxidized to CO_2 either in the pores (macro and meso) of the particle or in the gas phase, affecting the energy balance in and around the particle. Modeling of CO oxidation around the particle has been complicated due to high temperatures involved, complex coupling between the partial differential equations governing mass and energy conservation, and the stiff gas phase chemistry. Most of the modeling studies to date have either assumed quasi-steady state, constant gas thermodynamic and transport properties, or global reaction kinetics. Amundson and co-workers [17] using global kinetics and average gas and solid properties, estimated CO oxidation as a function of temperature, particle size and moisture content. They concluded that CO oxidation is not accelerated in the presence of water for small particles ($< 200 \mu m$) but for large particles it is. Essenhigh and co-workers [8] studied the effect of reactions inside a large particle ($\sim 1 cm$). Using a finite element code they showed that at high temperatures more CO burned in the boundary layer, and that the temperature profile was highly dependent on the penetration depth of the gases into the particle. Mitchell [14], using an elaborate reaction set concluded that CO oxidation in the boundary layer could be neglected at 1500-1700 K and 12% oxygen, and that a simple one film model was applicable for particles burning at pulverized fuel conditions. Recently, Dryer and co-workers [5] [12] used a general transient approach to solve the carbon combustion problem. Using a 5 step surface reaction mechanism and an elementary gas phase mechanism, they found that only moist air enhanced CO oxidation in the gas phase. They also concluded that small particles ($\sim 200 \mu m$) did not burn at quasi-steady state after ignition. However, the formation of CO_2 during char gasification was not considered in their heterogeneous reaction scheme, and the pore diffusion effects were neglected. Although a lot of modeling results were presented, comparisons of the model predictions with the experimental data were not done. In this paper a fully time dependent approach to model the physical

and kinetic processes occurring in the boundary layer of a burning char particle has been presented. The spatial discretization of the mass and energy conservation was done using orthogonal collocation on finite elements [4]. The transient partial differential equations were then solved implicitly allowing for the variation in the transport, kinetic, and thermodynamic properties at all time steps. The primary aim of this study was to explain the observed data of Tognotti *et al.* [18] and develop a better understanding of the CO_2 formation or, alternatively, the CO oxidation process during char combustion.

The following sections discuss the development of the single particle boundary layer (SPBL) model and its solution procedure, comparison of the model predictions with the experimental observations, and a study on the effect of mineral matter in char, ambient temperature, oxygen concentration, and the initial particle size on the peak particle temperature both a laboratory conditions and at practical pulverized fuel combustion (PFC) conditions.

2 MODEL DEVELOPMENT

Physical and kinetic processes occurring in the concentration boundary layer of a single particle can be described by using continuity and coupled mass and energy conservation equations of the form given by Equations 1 and 2.

$$\rho_g \frac{\partial Y_i}{\partial t} + \rho_g U_r \frac{\partial Y_i}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left\{ r^2 \rho_g D_{im} \frac{Y_i}{X_i} \frac{\partial X_i}{\partial r} + r^2 \frac{D_i^T}{T} \frac{\partial T}{\partial r} \right\} + \omega_i \quad (1)$$

$$\begin{aligned} \rho_g C_{p,g} \frac{\partial T_g}{\partial t} + \rho_g C_{p,g} U_r \frac{\partial T_g}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \lambda_g \frac{\partial T_g}{\partial r} \\ + \sum_{i=1}^n \left\{ C_{p,g,i} \left(\rho_g D_{im} \frac{Y_i}{X_i} \frac{\partial X_i}{\partial r} + \frac{D_i^T}{T} \frac{\partial T}{\partial r} \right) \right\} \frac{\partial T_g}{\partial r} - \sum_{i=1}^n \omega_i H_{g,i} \end{aligned} \quad (2)$$

Since 12 species, *viz.*, O_2 , CO , CO_2 , O , H_2 , H , OH , HO_2 , H_2O_2 , H_2O , HCO and N_2 , govern the CO oxidation chemistry, there are 13 (12 mass and 1 energy) second order, non-linear, non-homogeneous partial differential equations (PDEs) which should be solved simultaneously due to their coupled nature. The initial and the boundary conditions are given by Eqs. 3 - 7.

- Initial Conditions at any location, r :

$$Y_{g,i}(0, r) = Y_{g,i,\infty} \quad T_g(0, r) = T_{g,\infty} \quad (3)$$

- Boundary Condition at $r = \infty$ at any instant of time, t :

$$Y_{g,i}(t,r)|_{r \rightarrow \infty} = Y_{g,i,\infty} \quad T_g(t,r)|_{r \rightarrow \infty} = T_{g,\infty} \quad (4)$$

- Boundary Condition at the particle surface, $r = R_p$ at any instant of time, t (At the particle surface flux continuity conditions must apply):

$$R_{s,i} = \rho_g Y_{g,i} \left(U_r - \frac{1}{X_i} \mathcal{D}_{im} \frac{\partial X_i}{\partial r} - \frac{D_i^T}{\rho_g Y_{g,i} T} \frac{\partial T}{\partial r} \right) \quad (5)$$

$$-\rho_c \frac{\partial R_p}{\partial t} = w_c \quad (6)$$

$$\lambda_g \frac{\partial T_g}{\partial r} = -\omega_c H_c + \epsilon \sigma (T_s^4 - T_{g,\infty}^4) + \frac{\rho_c C_{p,c} R_p}{3} \frac{\partial T_s}{\partial t} \quad (7)$$

In the last boundary condition equation (Eq. 7), the term $\frac{\rho_c C_{p,c} R_p}{3} \frac{\partial T_s}{\partial t}$ replaces $\lambda_c \frac{\partial T_c}{\partial r}$. This assumes that the particle temperature is not a very strong function of particle radius. Conduction limit analysis on the char particle confirmed the validity of this assumption [12]. The diffusive transport coefficients are calculated using the transport software package developed at Sandia [11]. Instead of solving for the diffusion velocities, second order derivative terms describing the fickian diffusion and thermal transport were used in the conservation equations. The elementary chemistry governing the CO oxidation in the gas phase was taken from the work of Dryer *et al.* [19]. There are several surface reaction mechanisms which describe char gasification [3] [13]. However, uncertainty still persists in the rate constants of these mechanisms and further work needs to be done in this area to develop a better understanding of the surface phenomena. For the present study, the mechanism suggested by Tognotti *et al.* [18] as given below was used.

where,

$$f_{co} = \frac{1}{1 + 0.02 p_{O_2}^{0.21} e^{3000/T}} \quad (9)$$

The decision to use this mechanism was corroborated by the fact that several other researchers [6], [15], [16] have found similar expressions for f_{co} originating from pure heterogeneous chemistry.

3 Numerical Procedure

The PDEs described above are stiff in nature due to large differences in the magnitudes of the rate constants, which in turn, affects the characteristic time scales for different reactions. Therefore, a numerical tool which is both robust and fast is required to solve the system of PDEs discussed earlier. In the present work orthogonal collocation on finite elements [4] with Legendre Polynomial of third order as basis functions is used for the spatial discretization. A simple finite difference approach is used to discretize the transient term. The resulting equations are then solved implicitly using the Newton-Raphson method by updating the transport, kinetic, and thermodynamic properties at each Newton iteration to determine the concentration and temperature profiles in the boundary layer of the particle. In other words, if the calculations were done for the time step $k + 1$, the gas and solid properties used were also evaluated at the current time step and not the previous one. The resulting discretized mass conservation equations are given below.

1. At nodes within elements:

$$\begin{aligned}
 S_{i,j}^{k+1} = & \frac{(Y_{g,i,j}^{k+1} - Y_{g,i,j}^k)}{\Delta t D_{i,m,j}} (R_{\infty} - R_p)^2 + \left\{ \frac{\sum_{l=1}^{N_p} \sum_{m=1}^{N_p} b_{l,m,p} Y_{g,i,j}}{h_j^2} + \frac{Y_{g,i,j}}{X_{g,i,j}} \frac{\sum_{l=1}^{N_p} \sum_{m=1}^{N_p} a_{l,m,p} X_{g,i,j}}{h_j} \right. \\
 & \left(\frac{2(R_{\infty} - R_p)}{r} + \frac{\sum_{l=1}^{N_p} \sum_{m=1}^{N_p} a_{l,m,p} D_{g,i,m,j}}{h_j D_{i,m,j}} + \frac{\sum_{l=1}^{N_p} \sum_{m=1}^{N_p} a_{l,m,p} \rho_j}{h_j \rho_j} - \frac{U_{r,j}}{D_{i,m,j}} (R_{\infty} - R_p) \right) \\
 & + \frac{D_{i,j}^T}{\rho_j D_{i,m,j} T_j} \frac{\sum_{l=1}^{N_p} \sum_{m=1}^{N_p} b_{l,m,j} T_j}{h_j^2} + \\
 & \frac{D_{i,j}^T}{\rho_j D_{i,m,j} T_j} \frac{\sum_{l=1}^{N_p} \sum_{m=1}^{N_p} a_{l,m,p} T_j}{h_j^2} \left(\frac{2(R_{\infty} - R_p)}{r} - \frac{\sum_{l=1}^{N_p} \sum_{m=1}^{N_p} a_{l,m,p} T_j}{h_j T_j} \right. \\
 & \left. + \frac{(\sum_{l=1}^{N_p} \sum_{m=1}^{N_p} a_{l,m,p} D_{i,j}^T)(\sum_{l=1}^{N_p} \sum_{m=1}^{N_p} a_{l,m,p} T_j)}{h_j^2 T_k \rho_j D_{i,m,j}} \right) \\
 & \left. + \frac{\omega_{g,i,j}}{D_{i,m,j} \rho_j} (R_{\infty} - R_p)^2 \right\}^{k+1}
 \end{aligned} \quad (10)$$

2. Continuity of flux and concentration profiles is maintained at the boundaries of the elements.

$$S_{i,j}^{k+1} = \frac{\sum_{l=1}^{N_p} \sum_{m=1}^{N_p} a_{m,l,p-1} Y_{g,i,j}}{h_{j-1}} \Big|_{p-1}^{k+1} - \frac{\sum_{l=1}^{N_p} \sum_{m=1}^{N_p} a_{m,l,p-1} Y_{g,i,j}}{h_j} \Big|_p^{k+1} \quad (11)$$

3. Boundary conditions:

Surface:

$$S_{i,1}^{k+1} = \left\{ \frac{-U_{r,1} Y_{i,1} (R_{\infty} - R_p)}{D_{1,1}} + \frac{\sum_{l=1}^{N_p} a_{1,m} Y_{1,j}}{h_1} + \frac{R_i (R_{\infty} - R_p)}{D_{1,1} \rho_1} + \frac{D_{1,1}^T \sum_{l=1}^{N_p} a_{1,l} T_j}{h_1 T_{1\rho_1}} \right\}^{k+1} \quad (12)$$

At ∞ :

$$S_{i,Nt}^{k+1} = Y_{i,Nt} - Y_{i,\infty} \quad (13)$$

Following a similar approach, the energy conservation equation can also be discretized. Solution of the differential equations using the Newton-Raphson method requires the evaluation of the Jacobian. Since such calculations can be numerically expensive, first order derivatives should be calculated with respect to those variables which affect the dependent variable the most. The numerical scheme employed here is given by Eq. 14.

$$F = F_{rxn} + F_{transp} \quad (14)$$

where, F is the function whose first order derivative needs to be estimated. The function is broken down into two terms representing the reaction kinetics (F_{rxn}) and the transport (F_{transp}) terms. Reaction rates are a strong function of both the concentration of the species and gas temperature. Since the calculation of reaction rates is not computationally expensive, the calculation of derivatives is also fast. The calculation of transport properties such as diffusivity coefficients and thermal conductivity require expensive matrix operations. The derivative of F_{transp} , therefore, was calculated only with respect to temperature as perturbations in temperature affect the transport properties the most. This approach gives the matrix approximation of the jacobian.

Having developed the single particle model and discussed its solution strategy our next step was to test its prediction ability against the experimental data. The next section describes the model calibration results, effect of ambient oxygen concentration and temperature and practical ramifications of this study.

4 RESULTS AND DISCUSSION

4.1 Model Calibration

Tognotti *et al.* [18] obtained the particle temperature history profile as a function of combustion time and the CO_2/CO ratio as a function of instantaneous particle temperature for oxygen concentrations of 100% and 21% both in absence and presence of water. The ambient gas temperature was maintained at 300 K for their experiments. For temperatures below 1300 K and at 100 % oxygen, the CO_2/CO ratio could be attributed to a certain known particle temperature. Since the particle had not ignited for these conditions, it was possible to obtain time resolved data for CO and CO_2 . At temperatures above 1300 K when the ignition occurred the temperature rise was so steep that the CO_2/CO ratio reported could only be an average over a temperature range of 1500-2500 K (The peak surface temperature was around 2500 K). However, at 21% oxygen the combustion was not rapid and averaging the CO_2/CO ratio over a

temperature range could be avoided. Equations 15 and 16 were used to calculate the ratio at the steady and unsteady state combustion conditions, respectively.

$$\left. \frac{[CO_2]}{[CO]} \right|_{ss} = \frac{\int_{r_{cf}}^{R_{\infty}} [CO_2] r^2 dr}{\int_{r_{cf}}^{R_{\infty}} [CO] r^2 dr} \quad (15)$$

$$\left. \frac{[CO_2]}{[CO]} \right|_{us} = \frac{\int_{t|T=1500K}^{t|T=2500K} \int_{r_{cf}}^{R_{\infty}} [CO_2] r^2 dr dt}{\int_{t|T=1500K}^{t|T=2500K} \int_{r_{cf}}^{R_{\infty}} [CO] r^2 dr dt} \quad (16)$$

The primary of aim this paper is to calibrate the model by comparing the modeling results with the experimental data and explain the following characteristics.

1. Match the steep rise in the temperature profile above 1300 K and the combustion time of 0.06-0.07 sec.
2. Decrease in the CO_2/CO ratio with increases in temperature in absence of water.
3. An upward curvature in the CO_2/CO ratio at 100% oxygen and at very high temperatures. Water was apparently absent under these conditions.
4. Ignition at lower temperatures both for 100% and 21% oxygen but now in presence of water.

Figure 1 shows the comparison between the model predicted particle temperature profile obtained by performing transient analysis, and the experimentally observed profile in an electrodynamic balance. The predictions are very close to the experimental observations both in terms of the combustion time and the particle temperature overshoot. This supports the predictive ability of the model to some extent. In order to test the model further our next step was to explain the observations 2-4 on mass conservation listed above.

Oxidation of CO does not occur under bone dry conditions and the presence of water is imperative towards its conversion to CO_2 [1]. Water supplies the OH radicals which are known to control CO oxidation *via* the following reaction:

The OH radicals so generated react with O radicals to form HO_2 radicals. HO_2 so generated further leads to the oxidation of CO .

Another source of OH radicals is the emanation of hydrogen flux from the surface of the burning spherocarb (the spherocarb particle under investigation contained 0.74% hydrogen by weight). The H radicals so released, in turn, generate the OH radicals. Therefore, the task of model comparisons for the CO_2/CO ratio was undertaken for the following possibilities.

1. Absence of any water, H , and OH radicals in the surroundings.
2. Absence of water but release of H radicals from the particle at a rate proportional to carbon consumption.
3. Instantaneous release of all of hydrogen present in the spherocarb assuming fast pyrolysis. This phenomenon will lead to water concentration of the order of few ppm in the surroundings.
4. Supplying water externally and building its concentration to the order of few percents.
5. Slow pyrolysis of hydrogen contained in the spherocarb in addition to supplying external water.

Comparisons of the CO_2/CO ratio as a function of instantaneous particle temperature are shown in Figures 2 and 3. For 100% oxygen the particle combustion is at quasi-steady state for temperatures below 1300K. Above 1300K the particle temperature rises rapidly suggesting ignition and the particle combustion now occurs at unsteady state conditions. This transition from steady state to unsteady state conditions was taken into account using Eq. 16 while performing model comparisons 16. The figures show that the model predictions for all of the 5 possibilities discussed above are close to the experimental data and any deviations are within the experimental error. The model can also explain the change in curvature of the CO_2/CO profile at very high temperatures ($> 1600K$) or in presence of moisture in the surroundings. There is no upward curvature at 1600 K and 100% oxygen when there is neither any water available in the surroundings nor there is any flux of hydrogen radicals from the particle surface. This suggests that presence of H and/or the OH radicals is imperative to CO oxidation. Since water acts as a source of OH radicals its presence is very important. In its absence, ignition does not occur, and the CO_2/CO ratio continuously decreases with increases in temperature. The release of hydrogen radicals from the particle surface (and, hence, the formation of OH ($H + O = OH$)) at a rate proportional to carbon consumption helps in igniting CO . On the other hand, one needs only a few ppm of water to ignite CO at high temperatures and high oxygen concentrations. This small water concentration can be easily achieved if the spherocarb undergoes rapid pyrolysis releasing all the bound hydrogen at once. If water is supplied externally (3.5%) then the concentration of OH radicals increases. This concentration is high enough even at low temperatures ($\sim 1000 K$) such that CO can now be ignited in the gas phase.

Consequently, an upward curvature in the CO_2/CO profile is obtained at 1250 K. Figure 2 also shows that by changing the water concentration one can control the ignition temperature of the particle. There is, however, a lower limit on surface temperature below which ignition does not occur even on further increasing the water concentration. This limit is set due to a reduction in the dissociation rate of H_2O , and the OH radicals generated are not sufficient to compensate for the decrease in the rate constant for the $CO + OH$ reaction. Figure 3 shows similar results but for an ambient oxygen environment of 21%.

Figure 4 presents the OH , HO_2 , and the O profiles in the boundary layer at particle temperatures of 800 and 1250 K for the cases when there is (a) only hydrogen flux from the particle surface, and (b) when water is also present in the surroundings. There is a significant difference in the concentration levels of the radicals for the two cases at 1250 K. Figure 4a shows that the OH mass fractions are higher at 1250 K and 3.5% water as compared to when water is absent (1250 K), or when water is present but the temperature is 800 K. This suggests that the OH concentration is sufficiently high at 1250 K and 3.5% water to ignite CO in the boundary layer. Similar trends are observed for the HO_2 profile. The trends, however, are reversed for the O radical profile meaning that OH radicals scavenge out O to form HO_2 . Now both the OH and the HO_2 radicals control CO oxidation. At 800 K the OH concentration is more than 1000 times lower than that at 1250 K even in presence of moisture. If one further augments the water concentration in the surroundings, CO oxidation still cannot occur.

4.2 Effect of Mineral Matter

Under naturally occurring conditions coal is a complex agglomerate of mineral matter, carbon, hydrogen, and oxygen, and other elements. In other words, its composition is significantly different from that of a spherocarb. A study on the catalytic effect of mineral matter like ion exchange calcium on particle temperature overshoot and CO oxidation, therefore, is of practical relevance. Several earlier experimental studies have shown that ion exchange calcium acts as a catalyst in oxidizing CO heterogeneously. Du *et al.* [7] report the following equation for the relative conversion of carbon to CO heterogeneously in presence of Ca ,

$$\frac{CO}{CO_2} = 0.28 p_{O_2}^{-0.21} e^{-2575/T}$$

Our next step, therefore, was to conduct model simulations to predict the particle temperature overshoot, and determine the minimum oxygen concentration at which ignition will occur. Figure 5 shows the particle temperature profiles as a function of combustion time for different oxygen concentrations. It can be seen that the particle temperature is much higher in presence of calcium and combustion time lower

as compared to the case when calcium is not present in char. Moreover, ignition occurs for an oxygen concentration level as low as 21%. Ignition did not occur at 21% when calcium was absent (this is true when the surrounding gas temperature is 300 K. At higher ambient temperatures ignition may occur even in absence of calcium). The presence of calcium is particularly important for practical combustion conditions like those of pulverized fuel combustion when the ambient oxygen concentration is very low and still significant amounts of CO oxidation occurs due to the availability of calcium within the char particle itself.

Another possible reason for CO oxidation in practical combustors even at low temperatures could be the elevated levels of ambient gas temperature. This is discussed in the next section.

4.3 Effect of Ambient Gas Temperature and Oxygen Concentration Levels, and Initial Particle Radius on Peak Particle Temperature

There are several operating parameters which influence the oxidation of CO to CO_2 . Some of the important variables discussed here are ambient gas temperature, oxygen concentration, and particle radius. Figures 6a and 6b show the contour plots of peak particle temperature obtained by performing transient model simulations as a function of ambient oxygen concentration and gas temperature. The studies have been done both at laboratory conditions, where it is possible to have high oxygen concentrations and ignition at low surface temperatures, and the practical conditions where the surface temperatures are high and the oxygen concentrations are low. The peak temperature increases and the extinction diameter decreases with increases in ambient temperature and oxygen levels. At high oxygen concentration the char gasification rate is high, leading to a greater release of thermal energy and an increase in the particle temperature. If the ambient temperature is also increased, the temperature gradient decreases resulting in a decrease in the loss of radicals to the surroundings. Moreover, there is also a decrease in the radiative heat loss which further elevates the particle temperature. The particle is now able to maintain the high temperature for a longer period of time leading to a very high degree of carbon conversion, that is, reduced extinction diameters.

In the above analyses, the surface area, particle density, and the gasification rates were assumed to be a strong function of carbon conversion. Since the carbon conversion at any given instant of combustion time is a function of initial particle radius, a study on the effect of initial particle size on peak particle temperature was necessary. The results of the study are presented in Figs. 7a and 7b for different oxygen concentrations but constant ambient temperature. The figures show that the peak particle temperature exhibits a maximum with decreases in the initial particle size. A small particle has lesser thermal inertia

and, therefore, the energy released during combustion is able to heat up the particle more. As the particle size decreases, however, its total surface area also decreases. The decrease in the char consumption rate due to a decrease in the surface area is compensated by an increase in the particle temperature. If the particle size decreases further the magnitude of the decrease in surface area, and, thus, the char consumption rate prevents any increase in the particle temperature. There is a competition between the diffusive and the reaction time scales, denoted as τ_d and τ_{rxn} , respectively. The ratio of the two time scales is given by Eq. 17.

$$\frac{\tau_d}{\tau_{rxn}} = \frac{k}{D_e/R_p^2} \quad (17)$$

As the particle size decreases, the diffusive time scale decreases algebraically. Since the particle temperature increases with decreases in particle size, the reaction time scale decreases exponentially. This suggests that the CO produced at the particle surface is converted to CO_2 before it can diffuse out to the bulk. For a certain particle size the two time scales will be of comparable magnitude. Below this size the particle temperature will start decreasing.

5 SUMMARY and CONCLUSIONS

A single particle model for CO oxidation in the boundary layer characterized by 12 species and 56 elementary reactions is developed. The model is successfully calibrated against the experimental data. Modeling results show that water concentration or in other words the O , HO_2 , and the OH radical concentration is critical in determining ignition temperatures. However, at very low temperatures CO oxidation does not occur even at large water concentrations. Presence of mineral matter in form of ion-exchange calcium leads to significant amounts of CO oxidizing at and near the particle surface. Consequently, the particle temperature overshoot is considerably higher and combustion time lower than when calcium is not present. A parametric study shows that the particle temperature increases with increases in ambient gas temperature and oxygen concentration. This is primarily due to a decrease in the loss of radicals by thermal diffusion and a decrease in the radiative heat losses. CO oxidation occurs very close to the particle surface leading to elevated particle temperatures. Also a decrease in the extinction diameter results for the same conditions. The particle temperature passes through a maximum as the particle size decreases for constant ambient oxygen concentration and gas temperature.

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6 Nomenclature

a, b	=	Coefficient for the derivatives used in the Collocation approach
C_p	=	Specific heat capacity
$\mathcal{D}$	=	Diffusivity
f_{CO}	=	Conversion of char carbon to CO
h_j	=	Length of the element j
H_g	=	Heat of formation
k	=	Gas phase rate constant
N_e	=	Number of elements
N_p	=	Number of nodes in an element including the end points
N_t	=	Total number of nodes in the numerical domain = $N_e(N_p - 1) + 1$
p_{O_2}	=	Partial pressure of oxygen
r	=	radial position
r_{cf}	=	Radius after which the fluxes of CO and CO_2 are constant
R_p	=	Particle radius
R_s	=	Rate of surface reaction
R_∞	=	Numerical domain
S	=	Residual of the differential equations obtained after spatial discretization
t	=	Time
T	=	Temperature
U	=	Velocity
X	=	Mole fraction
Y	=	Mass fraction

6.1 Greek symbols and sub/super scripts

ϵ	=	Emissivity
σ	=	Stefan-Boltzmann constant
ρ	=	Mass density
ω	=	Gas phase reaction rate
λ	=	Thermal conductivity
g	=	Gas phase
i	=	Species index
j	=	Element index = $(p - 1)(N_p - 1) + l, (1..N_t)$
k	=	Time step index
l, m	=	Index for the node in a given element j , $(1..N_p)$
p	=	Element index or particle
p	=	Particle
s	=	Surface
ss	=	Steady state
us	=	Unsteady state

References

- [1] Adomeit, G., Mohiuddin, G., and Peters, N., *Sixteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, pp. 731- (1977).
- [2] Bar-Ziv, E., Jones, D. B., Spjut, R. E., Dudek, D., Sarofim, A., and Longwell, J. P., *Comb. Flame*, 75:81-106 (1989).
- [3] Bradley, D., Dixon-Lewis, G., El-Din, H., and Mushi, E., *Twentieth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, pp. 931-940 (1984).
- [4] Carey, G. F., and Bruce, A. F., 1975, "Orthogonal Collocation on Finite Elements", *Chem. Engng Sci.*, 30:587-596 (1974).
- [5] Cho, S. Y., Yetter, R. A., and Dryer, F. L., *Journal of Computational Physics*, 102: (1992).
- [6] Du, Z.: PhD thesis, *Kinetic Modeling of Carbon Oxidation*, Massachusetts Institute of Technology (1990).

- [7] Du, Z., Sarofim, A. , and Longwell, J., *Energy and Fuels*, 5:214-221 (1991).
- [8] Kurylko, L. and Essenhigh, R. H., *14th Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, pp. 1375-1386 (1973).
- [9] Goel, S., Morihara, A., Tullin, C., and Sarofim, A., *25th Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, pp. 1051-1059 (1994).
- [10] Jones, D. B., "Ph.D. Thesis: *Carbon Oxidation in an Electrodynamic Balance*", Department of Mechanical Engineering, M.I.T. (1989).
- [11] Kee, R., Warnatz, J., and Miller, J., *Sandia National Laboratories Report, SAND83-8209* (1983).
- [12] Lee, C., Yetter, R., and Dryer, F., *Comb. Flame*, 101:387-398 (1995).
- [13] Mitchell, R. E., *Twenty-Second Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, pp. 69-78 (1988).
- [14] Mitchell, R. E., Glarborg, P., and Coltrin, M. E., *23rd Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, pp. 1169-1176 (1990).
- [15] Otterbain, M. and Bonnetain, L., *Carbon*, 6:877 (1968).
- [16] Phillips, R., Vastoal, F., and Walker, P., *Carbon*, 8:205 (1970).
- [17] Sunderasen, S. and Amundson, N. R., *AIChE J.*, 27:679-686 (1981).
- [18] Tognotti, L., Longwell, J. P., and Sarofim, A. F., *23rd Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, pp. 1207-1213 (1990).
- [19] Yetter, R. A., Dryer, F. L., and Rabitz, H., *Combust. Sci. Technol.*, 79:97-128 (1991).

Fig 1

CO2/COcomp100%.cht

Fig 3

Fig 4a

Fig 4c.

Fig 5

Fig. 6a.

Oxygen Concentration [%]

Fig. 7a

Fig. 7b.