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Effects of Catalytic Mineral Matter on CO/CO₂
Temperature and Burning Time for Char Combustion

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I. Introduction

The high temperature oxidation of char is of interest in a number of applications in which coal must be burned in confined spaces. These include: the conversion of oil-fired boilers to coal using coal-water slurries, the development of a new generation of pulverized-coal-fired cyclone burners, the injection of coal into the tuyeres of blast furnaces, the use of coal as a fuel in direct-fired gas turbines and in large-bore low-speed diesels, and entrained flow gasifiers. In addition, there is a need to understand the temperature history of char particles in conventional pulverized-coal-fired boilers to better explain the processes governing the formation of pollutants and the transformation of mineral matter.

The temperature of char particle burning is the product of a strongly coupled balance between particle physical properties, heat and mass transfer, surface reaction, and CO/CO₂ ratio. Particle temperature has major effects not only on the burning rate but also on ash properties and mineral matter vaporization. Measurements of the temperature of individual burning char particles have become available in recent years and have clearly demonstrated large particle-to-particle temperature variations which depend strongly on particle size and on particle composition. These studies, done with pulverized coal, can not determine the CO/CO₂ ratio produced at the char surface or the catalytic effects of mineral matter in the individual char particles. Consequently, it has generally been assumed that CO is the only product of the carbon-oxygen reaction and that CO₂ is formed by subsequent gas phase reaction. More recent work, however, has pointed out the need to take CO₂ production into consideration in order to account for observed particle temperatures.

The importance of the CO/CO₂ ratio of carbon oxidation products is illustrated by examination of the heats of reaction for formation of these two products:

$$\Delta H_f = 94 \text{ kcal/mol}$$

The heat released by formation of CO_2 is a factor of 3.5 higher than for CO so the temperature of a particle will depend strongly on the CO/CO_2 ratio produced. If gas diffusion through the boundary layer is fast, increased direct production of CO_2 produces a higher temperature and a higher burning rate. If the supply of oxygen to the surface is limited by diffusion through the boundary layer, production of CO_2 consumes half as much carbon as production of CO so carbon consumption rate is reduced even though temperature may be somewhat higher.

This report consists of two major parts. In the first part, experimental measurements of CO/CO_2 ratio for a single spherocarb particle is presented along with a kinetic model which allows estimation of CO/CO_2 generated at a carbon surface for temperatures higher than those reported in the experimental work. In the second part, modeling of a temperature profile during a char combustion is reported, and also progress in modeling the complex sets of coupled phenomena involving full gas phase reaction kinetics, heat and mass transfer is summarized.

In the appendix progress on construction and testing of an improved electrodynamic balance is presented.

II. Measurements of CO/CO₂ and Temperature profile in an Electrodynamic Balance

II.1 CO₂/CO ratio in the primary combustion product

The carbon oxidation reaction is a very complex reaction, which has many steps. Usually it can be separated into two main categories. First, the coal is heated, undergoing physical and chemical changes as it is thermally decomposed into volatile matter and a solid, porous, char particle. Second, the char reacts with oxygen diffusing to the surface at temperature between 1000K and 2500K, progressively burning away.

It has generally been assumed that the CO is the only product of the carbon-oxygen reaction and that CO₂ is formed by subsequent gas phase reactions. More recent work (Mitchell et al. 1990), however, has pointed out the need to take CO₂ production at the surface into consideration in order to explain the observed particle temperature. Our measurements using the electrodynamic balance show that both CO and CO₂ are formed in the heterogeneous reaction. CO₂/CO ratio showed an Arrhenius type dependence according with temperature variation and an activation energy of 5.9 ~ 6.1 kcal/mol as shown in Fig.1. The CO₂/CO ratio decreases as the temperature increases. This ratio increases suddenly after a threshold temperature of 1200K, because of the additional CO oxidation in the gas phase boundary layer or in the pores as the temperature goes above the threshold temperature. The homogeneous CO oxidation at high temperature was confirmed by adding water vapor to catalyze the gas phase oxidation reaction. The resultant decrease observed in the threshold temperature is consistent with the expected effects of gas phase oxidation of CO. Oxygen concentration was varied and the CO₂/CO ratio was found to increase with the 0.21 power of oxygen concentration.

In parallel with the work supported on this program, Du (Du et al.1990) studied oxidation of an uncatalyzed carbon and carbon catalyzed by Calcium oxide at different

temperatures and several oxygen partial pressures. The catalytic effect of Ca on the carbon oxidation was also examined.

It was found that both CO and CO₂ are primary products during carbon oxidation, but they are generated via different mechanisms. The separate examination of the CO and CO₂ formation brought new insights about the carbon oxidation.

CO formation is composed of a wide range of activation energies due to the complex structure of carbon. The rate of CO formation was found to be of fractional order with respect to the oxygen partial pressure, and to be insensitive to Ca catalysis.

The rate of CO₂ formation was found to be first order with respect to the oxygen partial pressure and can be effectively catalyzed by Ca. The observed increase in CO/CO₂ ratio with reaction temperature can be explained by the activation energy difference between the rates of CO and CO₂ formation. In general, the apparent activation energy for CO production is about 35 kcal/mol within the temperature range of 773-873 K, but the activation energy of CO₂ production was found to be 28.6 kcal/mol. Since the CO production has a stronger dependence on temperature than that of CO₂, the CO/CO₂ will increase as the reaction temperature rises. The rate expressions developed in this program are consistent with the single particle measurements, and are used to calculate heat generation from heterogeneous reaction and also to determine the boundary condition for the gas phase model. The results of this work are reported in greater detail in Tognotti et al. (1990), Du et al. (1991) and in the quarterly report DOE/PC/89774-1.

II.2 The temperature-time history of a burning particle

In addition to the constant temperature measurements of CO/CO₂, time resolved measurements of particle surface temperature were made under conditions where ignition took place with a resulting rapid rise in particle temperature which was measured by fast response pyrometer. (Tognotti, 1990).

In these studies, the particles were heated by laser irradiation. When the particle reached a temperature of 1300K, the laser was turned off and the particle temperature typically rose to over 2000K until burnout resulted in extinction. The results of such a run in 100% oxygen is shown in Fig.2. In this run the pseudo steady state at 2300-2500K lasted about 0.04 seconds, after which burnout resulted in extinction and a sharp temperature drop.

The particle temperature is the result of the particle heat balance which depends on generation of heat, by reaction, at the particle surface and in the surrounding gas phase, heat losses by radiation and conduction through the gas and also upon heat added to the particle to increase its temperature.

The model derived in the following section is aimed at simulating this strongly interacting set of processes and these temperature measurements provide a quantitative test of the validity of the model.

III. Modeling of temperature profile during a char combustion

IV.1 Theory

The temperature history of carbon particle ignition is quite difficult to model because of the rapid temperature increase. The difficulties are due to the large variation in property values as the temperature increases. Our objective is to develop a model to reproduce the major features in the experiments. The assumptions made in the model are: (1) Uniform temperature inside the particle. (2) Constant ambient gas temperature. (3) A power law relationship between density and diameter. These assumptions enable us to use a simple lumped parameter model. Heat or mass transfer due to gas phase reaction adjacent to the solid-gas interface are not considered for this model. The main energy balance can be set up as in the following equation:

$$mC_p \frac{dT_p}{dt} = Q_{abs} A_c I + r_c (-\Delta H) A - hA(T_p - T_m) - \sigma \epsilon A(T_p^4 - T_g^4) \quad (1)$$

The left hand side represents the temperature change of the particle as the time changes. The first term and second term of the right hand side represent the heat gain from the laser and reaction respectively, and third and fourth term represent heat loss via convective and radiative heat transfer. The following sections include the theories and the equations for each of the parameters and variables.

III.1.1 Intrinsic reaction rate

The intrinsic reaction rate [$\text{gC}/\text{cm}^2\text{s}$] has been measured by many researchers, but the difference between the data is very broad. Furthermore the order of the reaction is uncertain. We will assume here first order reaction kinetics.

$$r_s = k'_s C_s \chi \quad (2)$$

$$= k_s P_s \quad (3)$$

where χ represents grams of carbon consumed per mole of O_2 reacted. This χ can be calculated from X_{CO} (reaction fraction, refer to section (3)).

$$\chi = M_c(1+X_{CO}) \quad (4)$$

where M_c is molecular weight of carbon.

III.1.2 External mass transfer rate

The external mass transfer rate [gC/cm^2s] is based on the particle external surface area. The Nusselt number of the sphere for mass transfer is 2. The film temperature is used to calculate bulk gas diffusivity.

$$r_g = k'_g(C_b - C_s)\chi \quad (5)$$

$$= k_g(P_b - P_s) \quad (6)$$

$$k'_g = \frac{2D_b}{d} \quad (7)$$

where d is the diameter of the particle. The factor that comes from Stefan flow is derived by Graham (Graham, 1990).

$$f_m = \frac{1}{1/\psi - 1} \ln \frac{1+y_b(1/\psi-1)}{1+y_s(1/\psi-1)} \quad (8)$$

where ψ is moles of O_2 reacted per one mole C consumed, and which is related to reaction fraction by

$$\psi = 1 - \frac{X_{CO}}{2} \quad (9)$$

Therefore, the mass transfer coefficient based on oxygen partial pressure is

$$k_g = \frac{k'_g \chi f_m}{RT_m} \quad (10)$$

III.1.3 Reaction fraction

The concentration ratio of CO₂ and CO was measured earlier in this program by Tognotti. Du (Du et al., 1991) also reported CO/CO₂ ratio based on activation energy distribution model, which shows similar temperature dependence. The equation which represents the fraction of CO reaction between the two competitive reactions can be developed using this concentration ratio.

$$X_{CO} = (1 + A_O P_{O_2}^n \exp(E/RT_p))^{-1} \quad (11)$$

where $A_O = 0.02$ $n = 0.21$ $R = 1.987$ $E = 6000$.

III.1.4 Heat of reaction

We can calculate the heat of reaction [J/g] if we use the reaction fraction, and we can calculate the temperature dependence from C_p data.

$$-\Delta H = [(-\Delta H_{CO}) X_{CO} + (-\Delta H_{CO_2})(1 - X_{CO})] 4.184/M_c \quad (12)$$

III.1.5 Density and diameter

The relationship between normalized apparent density and normalized particle density can be represented as a power law (Waters, 1988). Because $m = \frac{\pi}{6} \rho d^3$, following equations can be derived if we divide the both side with $m_o = \frac{\pi}{6} \rho_o d_o^3$.

$$\frac{\rho}{\rho_o} = \left(\frac{m}{m_o}\right)^a \quad \frac{d}{d_o} = \left(\frac{m}{m_o}\right)^b \quad (13)$$

$$a + 3b = 1 \quad (14)$$

From the experimental results of Sphero carb oxidation (Waters, 1988), the values of a , b were found to be equal to 0.25.

III.1.6 Surface area

The surface area [cm²/gC] which is responsible for the reaction is not yet clear. Micropore surface area measured by CO₂ adsorption (Dudek, 1989) or BET N₂ method are generally used. The measurement of surface area variation during the reaction is available

from Dudek and also from Waters. These data can be represented by third order polynomial of conversion to be used in modeling.

$$S_g = (4.85x^3 - 5.5566x^2 + 0.8215x + 0.8688) 10^7 \quad (15)$$

where 'x' is the conversion of Sphero carb.

III.1.7 Effectiveness factor

In order to calculate the effectiveness factor, we need to know the tortuosity and porosity as a function of conversion. Here we assume tortuosity to have a constant value of 3 during the reaction. Porosity as a function of conversion can be calculated from the power law relationship of density to the mass. The Thiele modulus is calculated using the following equation.

$$\phi = \frac{d}{6} \sqrt{\frac{\rho S_g k_s R T_p}{D_e \chi}} \quad (16)$$

The mean diffusivity is calculated from bulk gas diffusivity and Knudsen diffusivity. Then effective diffusivity can be calculated by multiplying the porosity to the mean diffusivity and dividing it by the tortuosity. The effectiveness factor is calculated from the following equation.

$$\eta = \frac{1}{\phi} \left(\frac{1}{\tanh(3\phi)} - \frac{1}{3\phi} \right) \quad (17)$$

III.1.8 Overall reaction rate

The overall reaction rate r_c [gC/cm²s] is determined by the relative rate between intrinsic reaction and oxygen transfer. Pore diffusion effects can be expressed by the effectiveness factor. With the assumption of 1st order reaction, the overall reaction rate is given as:

$$r_c = \frac{P_{O_2}}{(1/k_g + 6/\eta k_s S_g \rho d)} \quad (18)$$

III.1.9 Convective heat transfer coefficient

We can assume $Nu = 2$ in the case of a sphere. The convective heat transfer coefficient can be calculated from the thermal conductivity of gas phase.

$$h = \frac{2k_b}{d} \quad (19)$$

The additional convective heat transfer factor coming from Stefan flow was calculated by Bird et al.(1960) and Waters et al.(1988).

$$f_h = \frac{B}{\exp(B)-1} \quad (20)$$

$$B = - \frac{X_{CO} r_c d C_p}{4M_c k_b} \quad (21)$$

III.1.10 Emissivity, absorption efficiency, and heating flux

Data on emissivity and absorption efficiency of laser heat flux as a function of conversion and temperature are not available, A value of 0.85 seems to be most appropriate based on the available literature. A heating flux of $300W/cm^2$ was assumed and turned off when the temperature reached 1300K.

III.2 Modeling results

The major uncertainties in the modeling of Spherocarb ignition are the intrinsic reaction order and the pore size which participate in the reaction. First, we assume 1st order reaction kinetics and micropore surface area. If we set effectiveness factor as 1.0, which means no diffusion limitation to the micropore, the result is Fig.4.

If we compare Fig.4 to Fig.2, we discover the similarity between the two curves. The durations of steady state burning are almost same in both cases. For Fig.2 it is 0.038

second, and it is 0.034 second for Fig.4. This means the carbon oxidation rate calculated from the model is close to the experimental case. But there exist differences we need to consider. The maximum temperature rise in Fig.4 is about 500K higher, and the extinction curve is steeper. This behavior is caused by the total conversion of carbon particle, which is due to the underestimation of the heat loss term. We can explain this by O_2 disassociation in the high temperature environment. This effect increases the thermal heat conductivity, and therefore the heat loss. Oxygen begins to disassociate significantly at temperature as low as 2200K at 1 atm of pressure. Graham (Graham, 1990) calculated the effective thermal conductivity of mixture of oxygen, and found out the O_2 disassociation increased the conductivity factor of 2~5. This is another reason for a complete gas phase reaction model to explain heat transfer to the particle.

The use of an effectiveness factor of close to one was found be necessary to get an ignition, which can be explained in two different ways. First one is Hurt's micrograin idea, which considers the Spherocarb as a conglomerate of small micrograins. If we assume no oxygen diffusion limitations to the micrograin, we get an ignition curve similar to the experimental result. But if we calculate the effectiveness factor of intergrain and coupled it to the intragrain effectiveness factor, this model need more data on macropore structure. The other idea which can explain this high effectiveness factor is that only the macropores participate in the reaction. Because the macropore surface area is about 1% of total surface area and macropore volume fraction is about 0.4, the effectiveness factor retains the value about 0.1~1.0 which can ignite the particle. The detailed process of macropore surface area or volume evolution during the reaction is uncertain yet, and needs to be studied. There is controversy over this surface area issue. Many explanations, like different reactivity of pores or activated diffusion, have been proposed. The average diameter of Spherocarb's micropores is order of 1nm. So, at the temperature of ignition, it is questionable that oxygen could diffuse freely into the micropores in very short time available. The answer to this issue could be aquired through both simulation and experiment.

Gas phase model which includes CO oxidation in the boundary layer (Gas phase model will be discussed in the following section) will be necessary to study the effects of gas phase reaction, because the CO_2/CO ratio deviates from the pseudo Arrhenius plot due to the homogeneous reaction of CO after ignition. The heat of reaction of CO oxidation is 66.8 kcal/mol, therefore, the heat feedback to the particle may not be neglected. A standard kinetic code (including reactions of H, H_2 , H_2O , HO, HO $_2$, H_2O_2 , HCO, CO, CO_2 , O, O_2 , and N_2) will be used to estimate this effect.

IV. Modeling of CO oxidation in the gas phase

IV.1 Theory

To confirm the experimental results of CO oxidation in gas phase reaction, it is necessary to make a gas phase reaction model. There are two possibilities of CO₂ generation: One is in the macro or meso pores inside the char particle, and the other is in the gas phase. Until recently, most of the modeling studies assume quasi-steady state, constant gas thermodynamic and transport properties, and global reaction kinetics. By incorporating all elementary reactions and species and using time dependent approach, this modeling study will predict the heat feedback to solid and gas species and temperature distribution around the particle more accurately. CO/CO₂ ratio obtained from heterogeneous reaction will be extrapolated base on Du's model to be used as an initial condition for the gas phase model. Essential boundary conditions for the temperature were set as surface temperature and bulk gas temperature for each boundary. O₂, CO, CO₂ flux were calculated and used as flux boundary conditions at the particle surface and essential boundary conditions were used for the infinite boundary. From the results we can deduce what amount of CO will be oxidized to CO₂ and this will be compared with the experimental value, and we can decide how much CO₂ was produced from gas phase reaction. This information coupled with temperature and concentration profile will be used to calculate the amount of heat feedback to the particle, and the importance of radicals to the heterogeneous reactions.

IV.1.1 Governing equations

The governing equations for conservation of species and energy are listed as follows:

(i) Conservation equation for species i

$$\rho_g \frac{\partial Y_i}{\partial t} + \rho_g v_r \frac{\partial Y_i}{\partial r} = -\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho_g Y_i V_i) + R_i$$

(ii) Energy balance equation for the gas phase

$$\rho_g C_{p,g} \frac{\partial T}{\partial t} + \rho_g C_{p,g} v_r \frac{\partial T}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \lambda_g \frac{\partial T}{\partial r}) - \rho_g \sum_{i=1}^n (Y_i V_i C_{p,i}) - \sum_{i=1}^n R_i H_i$$

(For symbols, refer to nomenclature.)

IV.1.2 Basis function

To calculate the spatial dependence of temperature and concentration, it is necessary to use a numerical method capable of spatial discretization. Among many methods Galerkin finite elements method is well established for solving partial differential equations. First we need to define basis functions. The solution can be represented as a linear combination of these basis function. For higher accuracy, we can use higher order basis functions. Here, linear basis functions will be used for the simplicity and faster computation time. The space domain will be divided by N elements and N+1 basis functions can be defined as in Fig. 5. These functions have a value of one at each node, but are zero at the other nodes.

By multiplying these basis functions to the governing equations and integrating these equation, we can get simple tridiagonal matrices. During integration, natural boundary conditions can be easily incorporated. Essential boundary conditions can be added by changing conditions at that node to satisfy condition.

IV.1.3 Evaluation of parameters

During the process of partial integration of Eq(i) and Eq(ii), we need to evaluate terms like following.

$$\int f(T(r), Y_i(r)) * \alpha_i(r) \Phi^i \Phi^j r^2 dr$$

To solve the problem, it is essential to evaluate these terms. The difficulty is, however, f is highly dependent on temperature and mass fractions of each species. If the function f represents terms like $\rho_g, \lambda_g, C_p, H_i$, and v_r , we can think of these as continuous piecewise constants.

Therefore, if the temperature and mass fraction distribution are given by initial guesses, $f(r)$ can be calculated at each point and the averaged value of $f(r)$ will be used for corresponding interval. $Y_i(r)$, $T(r)$ can be calculated, and new values will be used to update $f(r)$.

If $f(r)$ represents a reaction term, it needs special consideration due to the exponential dependence on temperature. If a linear combination of temperature or mass fraction is used to represent nodal value of reaction rate, the whole integration simplifies to be following by using the fact that only $\Phi^k(r_k) = 1$.

$$\begin{aligned}
& \int R \left(\sum_{i=1}^N \alpha_i(r) \Phi^i \right) * \Phi^j r^2 dr \\
&= \int \sum_{k=1}^N R \left(\sum_{i=1}^N \alpha_i(r_k) \Phi^i(r_k) \right) \Phi^k * \Phi^j r^2 dr \\
&= \int \sum_{k=1}^N R(\alpha_k(r_k)) \Phi^k * \Phi^j r^2 dr
\end{aligned}$$

This interpolation approach not only proved to be convenient but also gave numerical results that appear to be consistent with the behavior that would be expected.

IV.1.4 Stiffness matrices

Based on the governing equations and Galerkin finite elements method we can construct tridiagonal matrices. Matrices for species conservation equation are

$$\begin{aligned}
\underline{M} \frac{dY_i}{dt} &= -\underline{A} Y_i + \underline{B} \\
\text{where } \underline{A} &= \rho v_r \int_{R_o}^{R_-} \Phi^i \frac{d\Phi^k}{dr} r^2 dr - \rho V_i \int_{R_o}^{R_-} \frac{d\Phi^i}{dr} \Phi^k r^2 dr, \quad \underline{B} = R_i \int_{R_o}^{R_-} \Phi^i r^2 dr, \quad \text{and} \\
\underline{M} &= \rho_g \int_{R_o}^{R_\infty} \Phi^k \Phi^i r^2 dr
\end{aligned}$$

Boundary conditions for O₂, CO, and CO₂ should be considered at the solid-gas interface. The term of $\rho v_r \int_{R_o}^{R_-} R_o^2$ is added to the diagonal element of $\underline{A}$ and $R_o^2 * flux$ is added to the corresponding element of residual vector. The values for the flux of O₂, CO, CO₂ are $r_c \frac{4}{3}(f_{co} - 2)$, $r_c \frac{7}{3} f_{co}$, and $r_c \frac{11}{3}(1 - f_{co})$.

A matrix for an energy conservation equation is

$$\begin{aligned}
\underline{M} \frac{dT}{dt} &= -\underline{A} T + \underline{B} \\
\text{where } \underline{A} &= \rho(v_r C_{p,g} + \sum Y_i V_i C_{p,i}) \int_{R_o}^{R_-} \Phi^i \frac{d\Phi^k}{dr} r^2 dr + \lambda_g \int_{R_o}^{R_-} \frac{d\Phi^k}{dr} \frac{d\Phi^i}{dr} r^2 dr
\end{aligned}$$

$$\underline{B} = -(R_i H_i) \int_{R_o}^{R_i} \Phi^l r^2 dr, \text{ and } \underline{M} = \rho_g C_{p,g} \int_{R_o}^{R_i} \Phi^t \Phi^l r^2 dr$$

Essential boundary conditions can be incorporated by setting a diagonal element as one, and changing the corresponding value of residual vector to the essential condition value.

IV.1.5 Diffusion velocity

The diffusion velocity V_i is calculated by following.

$$V_i = -\frac{1}{X_i} D_{im} \frac{dX_i}{dr} - \frac{D^T}{\rho Y_i T} \frac{dT}{dr}$$

There are two ways of calculating multi-component diffusion coefficient D_{im} . One is mixture-average formulation based on the binary diffusion coefficient, and the other is using ordinary multi-component diffusion coefficients.

$$D_{im} = \frac{1 - Y_i}{\sum_{j \neq i}^K X_j / D_{ji}}$$

$$D_{im} = -\frac{\sum_{j \neq i}^K M_j D_{ij} \nabla X_j}{\bar{M} \nabla X_i}$$

A problem with mixture averaged formulation is that it is not well defined if the mixture goes to a pure species. To satisfy the constraint of $\sum_{i=1}^K V_i Y_i = 0$, a corrective term V_c defined by $V_c = -\sum_{i=1}^K V_i Y_i$ is used. And updated value of V_i satisfying the restriction condition is obtained by $V_i(\text{new}) = V_i(\text{old}) + V_c$. An alternative approach can be used if one species is present in excess. An excess component mass fraction is computed simply by subtracting the sum of the remaining mass fractions from one.

Because it has a differential term, the formulation of diffusion velocity reduces the order of differential equation from second to first. When we solve the equations, we first evaluate the diffusion velocities from initial guess mass fractions and temperature distribution. Then the diffusion velocities are updated from the computed values. If we can

neglect the thermal diffusion related term, the structure of the stiffness matrices reduces to the form which is similar to the one from energy conservation equation.

Because this thermal diffusion effect is not negligible if the temperature gradient is substantial, it is necessary to include this term for this case.

IV.1.6 Modeling approach

For calculation of thermodynamic and transport properties including specific heat, enthalpy, multicomponent diffusion coefficient, thermal diffusion coefficient and thermal conductivity, it is necessary to develop subroutines to calculate these. But there exist well built libraries for this purpose, we are going to use packages called CHEMKIN II and TRANSPORT from Sandia National Laboratory.

The integration of a set of differential-algebraic ODEs after Galerkin finite elements methods are performed using DASSL, a package from Lawrence Livermore National Laboratory. This package uses a combination of Backward Differentiation Formula methods, which is known to be a very stable and efficient implicit integration method.

IV.2 Modeling results

To model gas phase reaction, 28 elemental reactions and 12 species were considered. Reaction kinetics data were from Yetter et al..

[Table 1] Reaction mechanism rate coefficients (units are mole/cm³, sec, K, cal/mol)

REACTIONS CONSIDERED	(k = A T ^b exp(-E/RT))		
	A	b	E
1. CO+O+M=CO ₂ +M	2.51E+13	0.0	-4540.0
2. CO+O ₂ =CO ₂ +O	2.51E+12	0.0	47690.0
3. CO+OH=CO ₂ +H	1.51E+07	1.3	-765.0
4. CO+HO ₂ =CO ₂ +OH	6.03E+13	0.0	22950.0
5. H+O ₂ =OH+O	1.91E+14	0.0	16440.0
6. O+H ₂ =OH+H	5.13E+04	2.7	6290.0
7. OH+H ₂ =H ₂ O+H	2.14E+08	1.5	3430.0
8. O+H ₂ O=OH+OH	1.23E+04	2.6	-1878.0
9. H+O ₂ +M=HO ₂ +M	6.76E+19	-1.4	0.0
10. H+HO ₂ =H ₂ +O ₂	6.61E+13	0.0	2130.0
11. HO ₂ +H=OH+OH	1.70E+14	0.0	870.0

12.	$O+HO_2=O_2+OH$	1.74E+13	0.0	-400.0
13.	$H+HO_2=H_2O+O_2$	1.45E+16	-1.0	0.0
14.	$H+M=H+H+M$	4.57E+19	-1.4	104380.0
15.	$O+O+M=O_2+M$	6.17E+15	-0.5	0.0
16.	$O+H+M=OH+M$	4.68E+18	-1.0	0.0
17.	$H+OH+M=H_2O+M$	2.24E+22	-2.0	0.0
18.	$HO_2+HO_2=H_2O_2+O_2$	3.02E+12	0.0	1390.0
19.	$H_2O_2+M=OH+OH+M$	1.20E+17	0.0	45500.0
20.	$H_2O_2+H=H_2O+OH$	1.00E+13	0.0	3590.0
21.	$H_2O_2+H=HO_2+H_2$	4.79E+13	0.0	7950.0
22.	$H_2O_2+O=OH+HO_2$	9.55E+06	2.0	3970.0
23.	$H_2O_2+OH=H_2O+HO_2$	7.08E+12	0.0	1430.0
24.	$HCO+M=H+CO+M$	1.86E+17	-1.0	17000.0
25.	$HCO+O_2=HO_2+CO$	4.17E+12	0.0	0.0
26.	$HCO+H=CO+H_2$	7.24E+13	0.0	0.0
27.	$HCO+O=OH+CO$	3.02E+13	0.0	0.0
28.	$HCO+OH=CO+H_2O$	3.02E+13	0.0	0.0

The gas phase model is still in development. The current program stopped after 2.0×10^{-5} second due to improper mesh positions. In the beginning of the reaction the steepest temperature gradient exists adjacent to the particle surface. However, as the reaction progresses the CO oxidation begins to take off and the temperature maximum moves from the surface to the gas phase. Therefore, putting the grids densely right next to the particle is not adequate to resolve the steepest temperature gradient propagating to the gas phase.

The plot of the temperature and mass fraction distribution up to this point is shown in Fig. 6 a & b. The concentration of water vapor in the gas phase is 3.5 wt %, and surrounding gas phase temperature is set as 1500K. The important feature of Fig. 6 a is the generation of CO_2 from gas phase reaction. The initial condition of the simulation was that CO and CO_2 mass fraction profile was given from the CO_2/CO ratio extrapolated from heterogeneous reaction. The boundary conditions were set as no in or out flux at the solid gas interface to isolate gas phase reaction. The resultant CO_2/CO ratios are already over 0.5 much more than 0.085 of initial condition from heterogeneous reaction. Considerable amount of OH and O radical was also built near the particle surface as we can see in Fig. 6 b. Based on the intermediate modeling results, we can deduce that the CO_2/CO ratio

measured by Tognotti were strongly influenced from gas phase oxidation, although this needs to be further verified by a completed version with various temperatures.

Summary

In this program experimental measurements of CO_2/CO ratio were carried out in the electrodynamic balance. This ratio was found to decrease as temperature was increased but, at a transition temperature, suddenly shifted to a higher CO_2/CO ratio. A kinetic model, based on reactions at the char surface, was developed to describe the lower temperature regime.

The sudden transition to a high CO_2/CO ratio is attributed to oxidation in the gas phase, and much of the effort in this program was devoted to modeling the combination of gas phase and surface reactions. This model is still under development.

Work was also started to enhance the performance of the electrodynamic balance. This work, however, was not completed during this program.

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VII. Nomenclature

[subscript]

'b'	means bulk property
'e'	means effective property
'g'	means gas mixture in the boundary layer
'i'	means the i-th species in the gas mixture
's'	means surface
'o'	means at time equals zero

[symbol]

A	external surface area
A_0	pre-exponential factor
A_c	cross-sectional area of the particle
$C_{p,i}$	specific heat of 'i' th species
$C_{p,g}$	gas mixture specific heat at constant pressure
C	concentration
D	gas diffusivity
D_{ij}	binary diffusion coefficient
D_{im}	multi-component diffusion coefficient
D^T	thermal diffusivity
d	diameter of the particle
E, E_a	activation energy
f_h	factor in heat transfer due to Stefan flow
f_m	factor in mass transfer due to Stefan flow
H_i	specific enthalpy
$-\Delta H$	heat of reaction [J/g]
h	convective heat transfer coefficient
I	laser heating flux
k_b	thermal conductivity at the gas phase
k'_g	mass transfer rate coefficient based on concentration
k_g	mass transfer rate coefficient based on partial pressure
k'_s	intrinsic reaction rate coefficient based on concentration
k_s	intrinsic reaction rate coefficient based on partial pressure
m	mass of the particle

M	molecular weight
$\bar{M}$	mean molecular weight
M_c	molecular weight of carbon
P	pressure
Q_{abs}	absorption efficiency of laser heating flux
R	gas coefficient
R_i	mass production rate
R_o	particle radius
r	radial coordinate
r_c	carbon consumption rate (based on the external surface area) [gC/cm ² s]
r_s	intrinsic reaction rate (based on internal surface area) [gC/cm ² s]
S_g	BET surface area [m ² /g]
T	temperature
T_g	ambient gas and wall temperature
T_m	mean temperature of T_p and T_g
T_o	temperature at $t=0$
T_p	particle temperature
t	time
v_r	fluid velocity in 'r' direction
V_i	diffusion velocity of 'i' th species
V_c	corrective diffusion velocity
X_{CO}	reaction fraction of CO = (CO ₂ /CO + 1) ⁻¹
X_i	mole fraction of 'i' th species
Y_i	mass fraction of 'i' th species

αβχδεφγηιφκλμνοπθρστυωξψζ

α	nodal value
χ	grams of carbon consumed per mole of O ₂ reacted
ϵ	emissivity of the particle.
Φ	basis function for Galerkin finite element method
ϕ	Thiele modulus
η	effectiveness factor
ϕ	moles of O ₂ reacted per one mole carbon consumed
λ_g	thermal conductivity
ρ_g	density of the gas mixture in the boundary layer
σ	Stefan-Boltzman constant

Fig.1. CO_2/CO ratio as a function of inverse temperature for 100% oxygen for dry gas and in the presence of 3.5 mol % water

Fig.2. Particle temperature as a function of time for 100% oxygen under ignition condition.

Fig.3 Schematic diagram of an electrodynamic balance

Fig.4. Temperature as a function of time (Laser turned off at 1300K
1st order intrinsic reaction. Effectiveness factor is one. 100% oxygen)

Fig.5 Cumulative pore size distribution on volume basis (dashed line)
and on surface basis (solid line)

I XY Coordinate

$$\Phi^1 = (1 - \epsilon)/2$$

$$\Phi^2 = (1 + \epsilon)/2$$

I Spherical Coordinate

$$\Phi^{i(+)}(r) = \frac{R_i(R_{i+1} - r)}{r(R_{i+1} - R_i)}$$

$$\Phi^{i(-)}(r) = \frac{R_i(r - R_{i-1})}{r(R_i - R_{i-1})}$$

Fig.6 Basis functions

Fig.7 a Temperature and mass fraction distribution

Fig.7 b Mass fraction distribution of O , OH , H , H_2

Appendix

A. Reconstruction of an Electrodynamic Balance

The electrodynamic balance has been rebuilt to improve its performance including:

1. Better control of gas flow and composition
2. High pressure operating capability
3. Advanced imaging system for size measurement and position determination
4. Capability of high and low temperature measurement
5. Better position control
6. Fast computation and memory facilities
7. Better laser power control

A schematic diagram of an electrodynamic balance system is shown in Fig.3.

A.1 Position control system

The improved control system for the electrodynamic balance is based on the development of Bar-Ziv et al. (1990). This control system comprises three parts:

- (1) An electro-optical sensing system.
- (2) A data acquisition system and an on-line tracing algorithm that determines the particle position.
- (3) A PID controller.

A schematic diagram is shown in Fig.3. A He-Ne laser beam passes horizontally through the center of an electrodynamic balance (through the hole in the ring electrode) then traverses a diverging lens and finally is projected onto a

linear photo diode array (PDA) that was placed vertically. A shadow image of the particle is processed to determine its position by the PID program in the computer. Then the corresponding control signal is calculated, amplified, and sent back to the DC electrodes to adjust the DC voltage to maintain the same position.

The major advantages of this system are (1) elimination of specific devices, digital or analog, for the position control system and (2) flexibility in the operation of the system since it is based on software rather than hardware.

A.2 Size measurement using imaging system

The spherocarb particles vary in size and density. The usual method of measuring the size of the particle is to use measurements of aerodynamic drag and particle weight in the EDTGA. That method requires calibration by particles of known size and density, and the accuracy is not high. By development of the high resolution imaging system, it is now possible to measure the diameter of the particle directly.

The method is simple. A fine microscope scale (AZI Co. 100 parts/ 10mm) was inserted in the center of the chamber. A 3-way adjustable stand with a holder is used for centering. Also the microscope was used to verify that the scale was centered. The one scale of the picture is equal to 100 μm . The Image-Pro Plus program (Media Cybernetics) and AT386 have been used for image processing. The accuracy of this method can be estimated. The error from centering the scale is less than 1 mm and the focal length of the convex lens is 10 cm, so the relative error is about 1 %. Because the image of the particle is not perfectly sharp, the measurement by the imaging program results in 1-3 pixels uncertainty. The number of the pixels over the diameter is about 120. We can reduce the uncertainty by trying as many measurements as we want. On the average, the error coming from the imaging program is about 2%. Therefore, the total error is about 2.24%

maximum, which is comparable to the one from the aerodynamic method. But this method is much quicker and easier.

A.3 Laser heating of a particle

The laser power control system consists of three components. As we can see in Fig.3, the temperature of the particle is measured by the two color pyrometer. The signals go through the set of amplifiers to remove noise and AC components. One of the signals comes into the computer for recording, and the other signal comes into the laser power control box, which goes through the circuits to generate the control signal of the laser power by the algorithm of Proportional, Integral, and Differential control. And the TTL (a series of 0-5V square wave signal) signal generated goes into the power supply of the CO₂ Laser to control the laser power. The variable resistance for each control needs to be set by calibration.

A laser power control system has been successfully installed to control the temperature of a thermocouple. The schematics of this system has been reported at Quarterly Progress Report No.8. But, in the process of heating a spherocarb particle, we discovered a few difficulties which prevent the laser heating.

When the laser (CO₂ laser 20W) was turned on, instability of the spherocarb particle was observed and particle would disappear as soon as the laser was turned on. The method of laser heating was vertical compared to the previous method of heating horizontally by splitting laser beam. The main cause of the instability is believed to be the photophoretic effects. Photophoresis is a phenomena in which a particle moves due to uneven radiation on the surface of the particle. Based upon earlier calculations of Dudek (Dudek, 1989) , the photophoretic force on a particle was estimated to be very small compared to the gravitational force. But the actual force seems to be greater than the calculated value.

The other difficult is a force moving the particle sideways due to the Gaussian distribution of laser flux. Because the only stabilizing force acting upon a particle horizontally is the AC field which is too weak to hold the particle in the center. Therefore the particle tends to move sideways due to the laser flux gradient. One possible solution is weakening the flux gradient by focusing the laser beam much wider, but this will lower the maximum temperature. Another solution is using a beam which has a minimum in the center. Simulating a doughnut shape beam has been tried by putting a beam block in the center of the laser beam before the convex lens, which stabilized the particle much better.

This modification gave improved particle stabilization, however, the vertical movement of the particle makes it difficult to record the mass change of the particle continuously. The vertical movement seems to be closely related to the laser modulation frequency, and the current position system is unable to follow that vertical oscillation. The maximum control frequency of the current position control system is 500-800 Hz, and the laser modulation frequency is about 8000 Hz. The current system, therefore, needs a faster control system or perhaps a return to the conventional method of horizontal heating to perform kinetic studies.

END

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