

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

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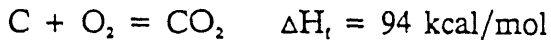
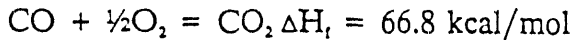
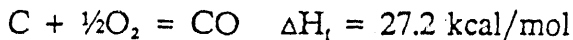
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Introduction

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 better understand the temperature history of char particles in conventional pulverized-coal-fired boilers in order to better understand the processes governing the formation of pollutants and the transformation of mineral matter.

The temperature of a char particle burning in an oxygen containing atmosphere is the product of a strongly coupled balance between particle size and physical properties, heat transfer from the particle, surface reactivity, CO_2/CO ratio and gas phase diffusion in the surrounding boundary layer and within the particle. In addition to its effects on burning rate, particle temperature has major effects 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, do not allow direct determination of the CO_2/CO ratio produced at the char surface or the catalytic effects of mineral matter in the individual char particles and it has generally been assumed that CO is the only product of the carbon-oxygen reaction and that CO_2 is formed by subsequent gas phase reaction. More recent work, however, has pointed out the need to take CO_2 production into consideration in order to account for observed particle temperatures.

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



The heat released by formation of CO₂ is a factor of 3.5 higher than for CO so the temperature of a particle will depend strongly on the CO₂/CO ratio produced. If gas diffusion through the boundary layer is fast, increased direct production of CO₂ 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 CO₂ consumes half as much carbon as production of CO so carbon consumption rate is reduced even though temperature may be somewhat higher. Models of these complex interactions have been developed; however, the CO₂/CO ratio produced by the carbon-oxygen reaction must, at present be assumed or inferred from measurement of particle temperature.

CO₂/CO ratios can be strongly influenced by catalytic material in the carbon and by the char temperature. In this program we are measuring the CO₂/CO ratio for both catalyzed and uncatalyzed chars over a wide range of temperature. These results will then be used to develop predictive models for char temperature and burning rates.

In this report progress on modeling particle temperature under conditions where ignition occurs is reported. A comparison of preliminary modeling results with experimental results is also reported.

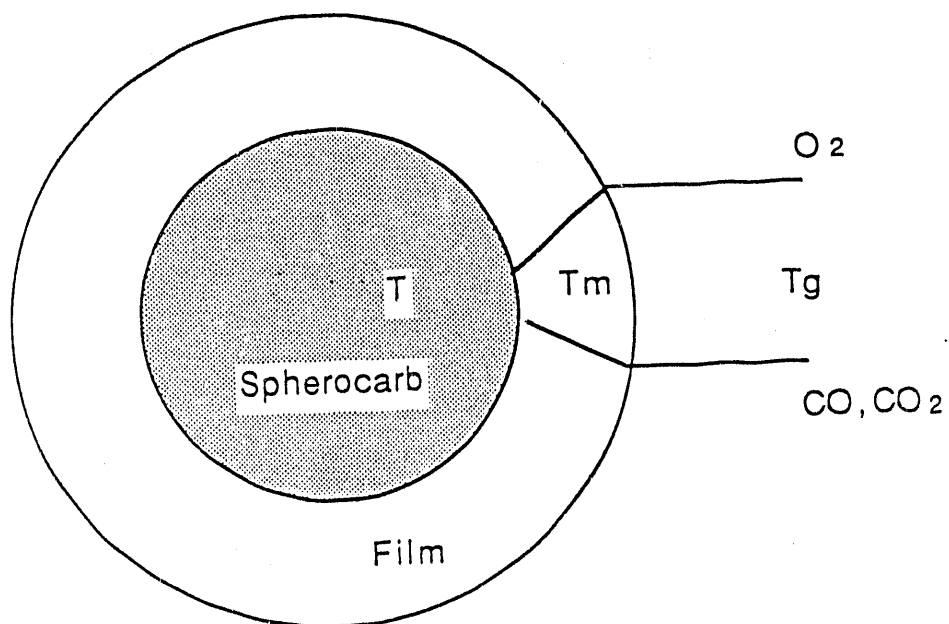


Figure 1: Modeling environment ($T_m = \frac{T+T_g}{2}$)

Results

A. Theory and Modeling of Spherocarb Ignition

Ignition and extinction of char particle combustion is of major importance in coal combustion. These phenomena are being studied in this program where particle can be laser heated in our electrodynamic balance with time resolved measurement of particle temperature. The temperature at which combustion continues to increase after termination of laser heating is defined, in this work, as ignition temperature. In this section progress in developing a model for ignition and for post-ignition particle temperature and combustion rate are reported.

1 Theory

[Assumptions]

1. Temperature is uniform inside the particle.
2. The gas temperature is constant.
3. The natural convection is negligible.
4. First order intrinsic reaction rate
5. There is a power law relationship between density and diameter.

These assumptions enable us to use a simple lumped parameter model instead of using complex PDEs. As we can see in Fig. 1, oxygen is transferred through the gas film, and it diffuses inside the particle. Until ignition, laser heating is a major heat source. As usual, T_m is assumed to be the mean temperature T and T_g . The main energy balance can be set up as in the following equation:

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

where m is the mass of the particle, T is the particle temperature, t is time, Q_{abs} is the absorption efficiency of laser heating flux, A_c is the cross-sectional area of the particle, I is

the laser heating flux, r_c is the carbon consumption rate [gC/cm²s], $(-\Delta H)$ is the heat of reaction [J/g], A is the external surface area, T_m is the mean temperature of T and T_a , h is the convective heat transfer coefficient, σ is the Stefan-Boltzman constant, and ϵ is the emmissivity of the particle.

(1) Intrinsic reaction rate

The intrinsic reaction rate [gC/cm²s] was measured by many researchers, but the difference between the data is very broad. Furthermore the order of the reaction is not clear. I assume here first order reaction kinetics, and get the data from the results of Tognotti(1990) for spherocarb carbon.

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

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

$$\chi = \frac{\text{gC consumed}}{\text{mole } O_2 \text{ transferred}} = M_C(1 + X_{CO}) \quad (4)$$

$$k'_s = k_s RT / \chi \quad (5)$$

$$k_s = 0.184 \exp(-33000/RT) \quad [gC/cm^2 \text{ atm}] \quad (6)$$

(2) External mass transfer rate

The external mass transfer rate is expressed [gC/cm²s], which is based on the particle external surface area. The Nusselt number for mass transfer is 2 for the sphere. The temperature used is film temperature.

$$r_g = k'_g (C_b - C_s) \chi \quad (7)$$

$$= k_g (P_b - P_s) \quad (8)$$

where χ is the reaction fraction(refer to section (3))

$$k'_g = \frac{2D_b}{d} \quad (9)$$

$$= 2.0 \times 10^{-5} T^{1.75} / d \quad (10)$$

The factor that comes from Stefan flow is calculated by Graham (Graham,1990).

$$f_m = \frac{1}{1/\psi - 1} \ln \left[\frac{1 + y_b(1/\psi - 1)}{1 + y_s(1/\psi - 1)} \right] \quad (11)$$

where

$$\psi = \frac{\text{mole } O_2 \text{ reacted}}{\text{mole } C \text{ consumed}} \quad (12)$$

$$= 1 - \frac{X_{CO}}{2} \quad (13)$$

When the mass transfer reaction is a limiting step, the surface concentration of oxygen can be assumed as 0, and the bulk concentration here is 100% oxygen, so $y_s = 0$ and $y_b = 1.0$ in this case. Therefore, for this limiting case, mass transfer coefficient based on oxygen pressure is:

$$k_g = \frac{k'_g \chi f_m}{RT} \quad (14)$$

(3) Overall reaction rate

Overall reaction rate r_c [gC/cm²s] can be calculated by

$$r_c = \frac{[P_{O_2}]}{(1/k_g + 6/\eta k_s S_g \rho d)} \quad (15)$$

Where η is the effectiveness factor

S_g is the internal surface area cm²/g

ρ is the particle density gm/cm³

The structure of spherocarb consists of a network of large pores which provide access to relatively small microporous domains which are responsible for a large fraction of the surface area. Estimation of effectiveness factor for this structure remains to be done. Here, the limiting case of $\eta = 1$, which corresponds to all the internal surface in contact with oxygen at the particle surface concentration P_s was used.

(4) Reaction fraction

The concentration ratio between CO_2 and CO was measured by Tognotti (1990). The equation which represents the fraction of CO reaction between the two competitive reactions can be developed using this concentration ratio.

$$X_{\text{CO}} = (1 + A_o P_{\text{O}_2})^{-n} \exp(E/RT) \quad (16)$$

$$A_o = 0.02 \quad n = 0.21 \quad R = 1.987 \quad E = 6000$$

(5) Heat of Reaction

We can calculate the heat of reaction if we use the reaction fraction, and we can calculate the temperature dependence from C_p data.

$$(-\Delta H) = \{(-\Delta H_{\text{CO}})X_{\text{CO}} + (-\Delta H_{\text{CO}_2})(1 - X_{\text{CO}})\}4.184/M_C \quad (17)$$

(6) Density and diameter

The relationship between normalized apparent density and normalized particle density can be represented as a power law. (Waters, 1988)

$$\frac{\rho}{\rho_o} = \left(\frac{m}{m_o}\right)^a \quad (18)$$

$$\frac{d}{d_o} = \left(\frac{m}{m_o}\right)^b \quad (19)$$

$$a + 3b = 1 \quad (20)$$

From earlier studies of spherocarb combustion (Dudek (1989), the values of a,b were found to be equal to 0.25.

(7) Convective heat transfer coefficient

We can assume $Nu = 2$ in the case of a sphere. The thermal conductivity of oxygen from Perry's is

$$\overline{k_{O_2}} = 9.36 \times 10^{-6} + 6.147 \times 10^{-7} T \quad (21)$$

$$h = \frac{2\overline{k_{O_2}}}{d} \quad (22)$$

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

$$f_h = \frac{B}{\exp(B) - 1} \quad (23)$$

$$B = -\frac{X_{CO} r_c d C_{p,g}}{4M_c \overline{k_{O_2}}} \quad (24)$$

(8) Conversion

The conversion of spherocarb can be calculated by integration of reaction rate.

$$x = \frac{1}{m_o} \int_0^t -\frac{dm}{dt} dt = \left(1 - \frac{m}{m_o}\right) \quad (25)$$

$$= \frac{1}{m_o} \int_0^t -r_c S_{ex} dt \quad (26)$$

(9) Emmissivity, absorption efficiency, and heating flux

The data of emmissivity and absorption efficiency of laser heat flux as function of conversion and temperature is not available, but it is reasonable to assume this value as 0.85 if we refer to other literature. The heating flux Tognotti used is not clear because he controlled the power to achieve a certain temperature. In the program $300W/cm^2$ was used and turned off when the temperature went up to 1300K.

In Figure 2 calculated particle temperature for first order reaction and an effectiveness factor of 1 is shown. Here, laser heating was terminated when particle temperature reached 1300 K. Ignition is demonstrated by the rapid increase of temperature in the absence of laser heating and temperature rises to a maximum of 3000 K.

Figure 3 presents conversion as a function of time with complete burnout predicted at $.075 - .028 = .047$ seconds after termination of external heating. Very little conversion before ignition is predicted.

In Figure 4 experimental results (Tognotti 1990) are shown. The shape of the temperature-time curve corresponds well to the model results of Figure 2 with the time to burnout of approximately .04 seconds. Maximum temperature is 2260-2400 K -- somewhat lower than predicted. This difference could be due to a lower effectiveness factor, lower reaction rate or other approximations in this highly simplified model. The correspondence of the results for effectiveness factor of 1.0 with experimental observations indicated that internal oxidation is significant. The product of effectiveness factor and carbon reactivity must apparently be maintained at approximately the level used in Fig. 2. Further study of effectiveness factor and reactivity is needed to separate these effects.

B. Construction of Upgraded TGA

Work on this phase of the program has been delayed due to a back injury suffered by Mr. Lee.

Future Program

During the next quarter construction of the laser heating and the laser power control systems will be resumed. Work on modeling will continue.

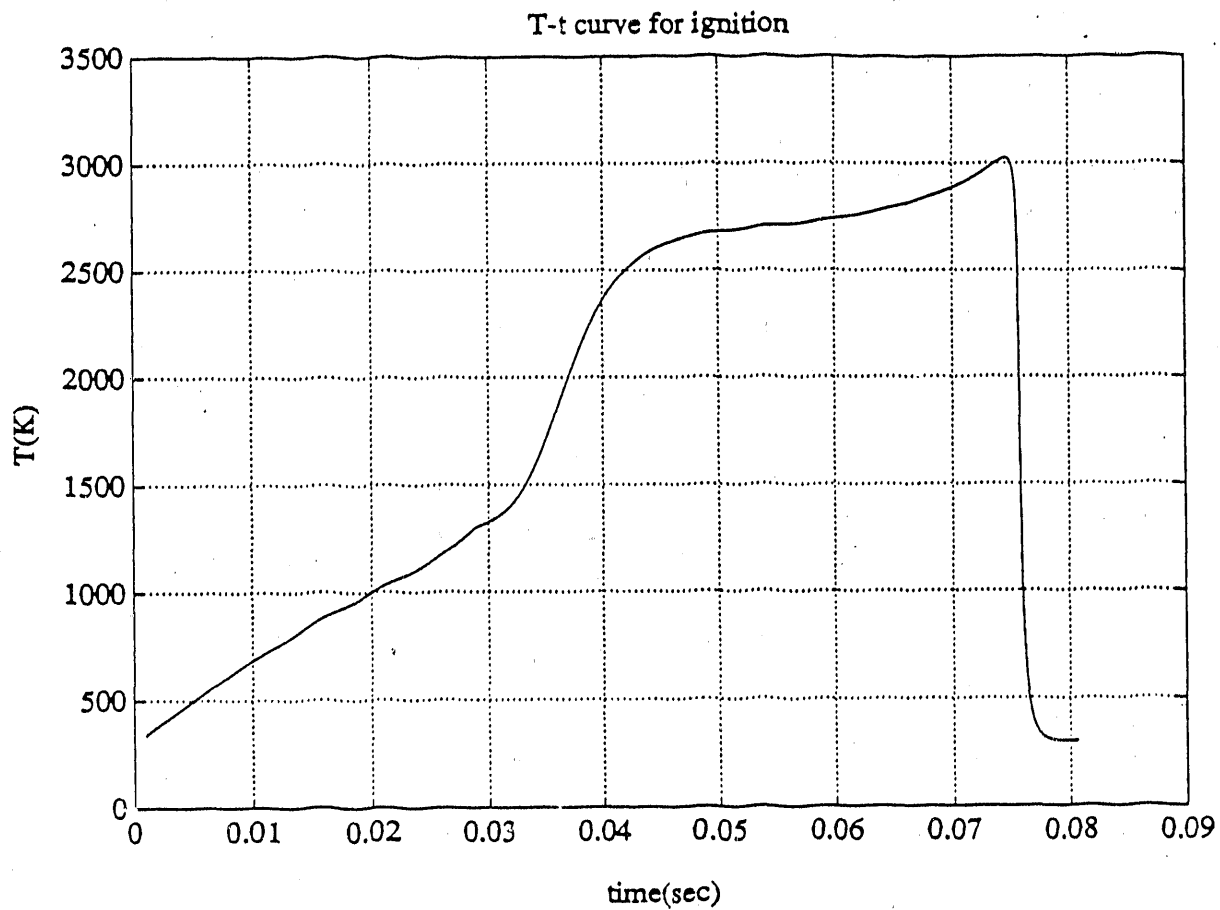


Figure 2: Temperature as a function of time. (Laser turned off at 1300K. $I = 300W/cm^2$. 1 st order intrinsic reaction. Effectiveness factor = 1)

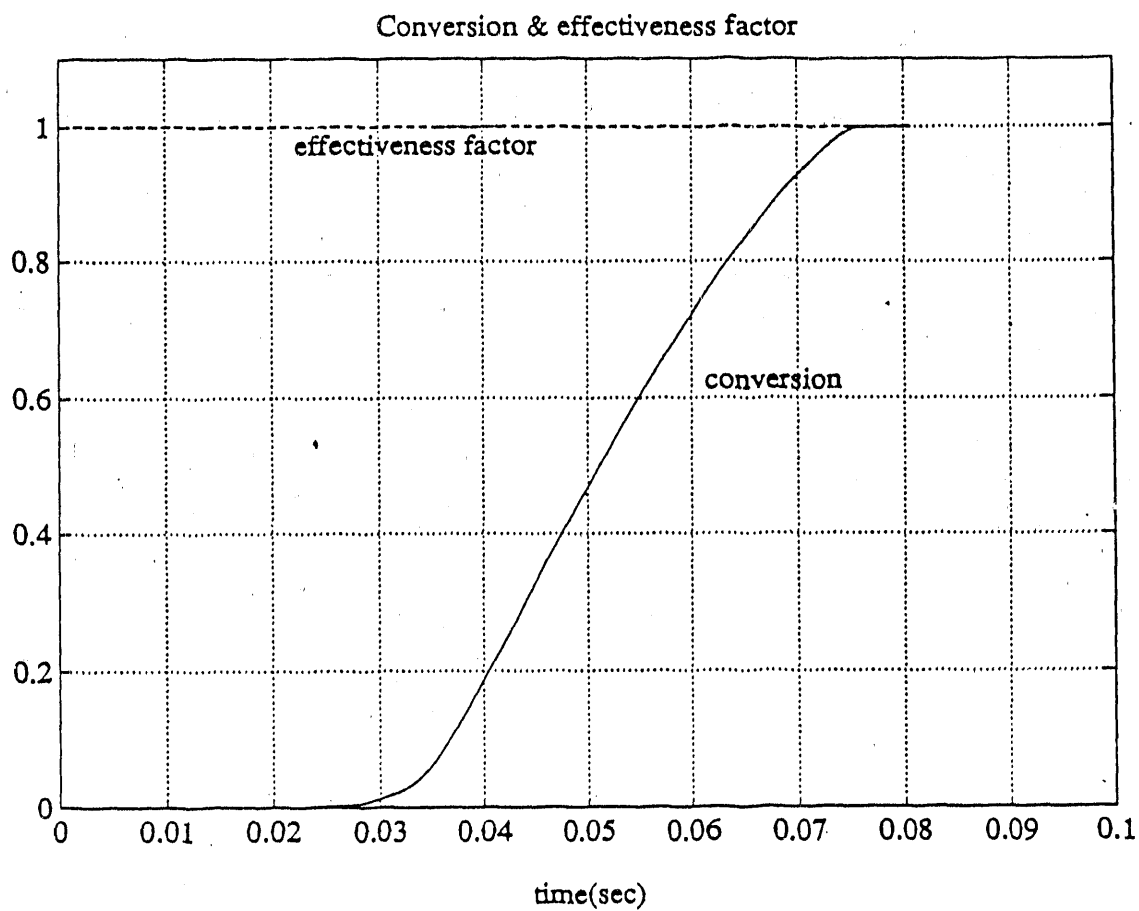


Figure 3: Effectiveness factor and conversion as a function of time. (Laser turned off at $1300K, I = 300W/cm^2$. 1 st order intrinsic reaction. Effectiveness factor = 1)

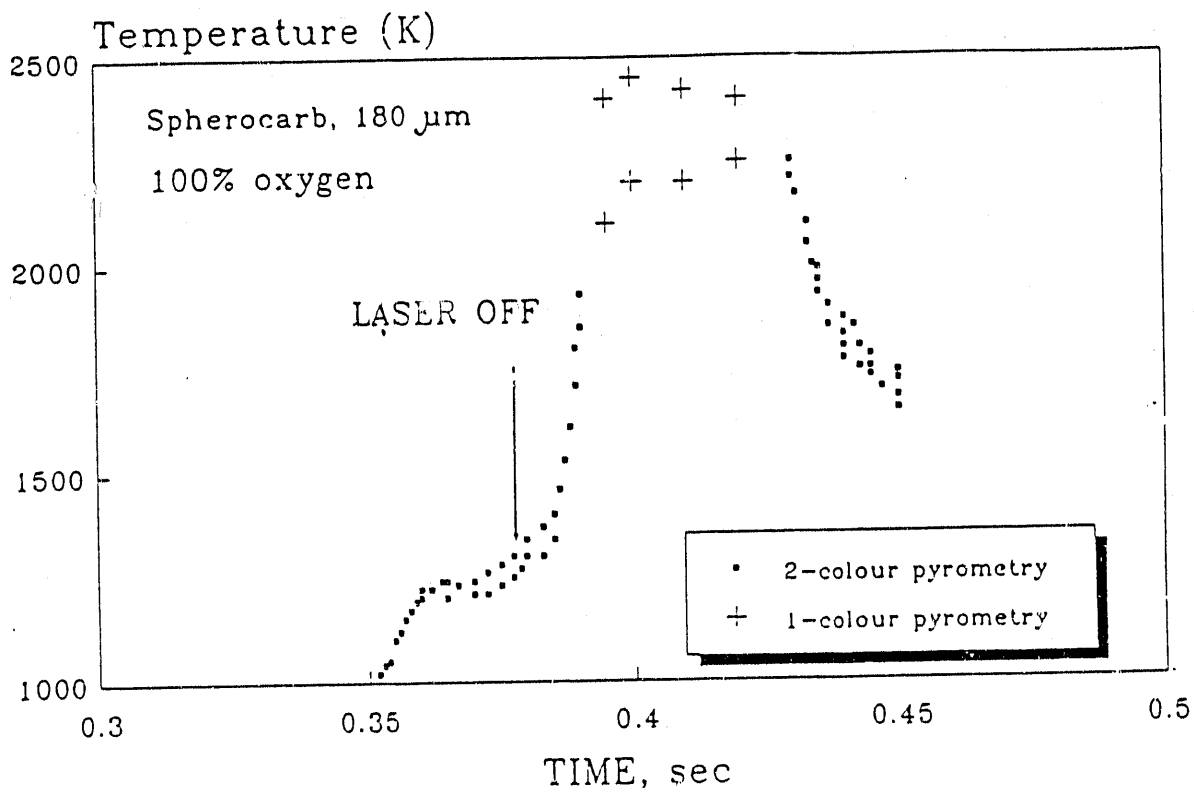


Figure 4: Particle temperature as a function of a time for 100 % oxygen under ignition condition. (from Tognotti, 1990)

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