DOE/PC/89774--T3

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

DE-FG22-89PC89774

Prof. John P. Longwell
Prof. Adel F. Sarofim

DOE/PC/89774--T3

DE92 011581

Chun-Hyuk Lee
A.J. Modestino
C. Cho

Quarterly Progress Report No. 9

October - December 1991

Prepared for

Norey B. Laug
U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940, MS 921-165
Pittsburgh, Pennsylvania 15236-0940

by

Massachusetts Institute of Technology
Department of Chemical Engineering
Cambridge, MA 02139-4307

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

100-1-1002

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 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/CO₂ 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/CO₂ 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 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

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 CO/CO₂ 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 CO/CO_2 ratio produced by the carbon-oxygen reaction must, at present be assumed or inferred from measurement of particle temperature.

CO_2/CO ratios can be strongly influenced by catalytic material in the carbon and by the char temperature. In this program we are measuring the CO_2/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. The electrodynamic balance has been successfully used to make such measurements for single 200 μm spherocarb particles. In this report, progress on the laser heating and the theoretical modeling are reported.

Results

A laser power control system has been successfully installed to control the temperature of the particle. The temperature calibrations using a thermocouple in place of the suspended particle were performed.

In Figs 1 and 2 the response of the $2\mu\text{m}$ and $4\mu\text{m}$ infrared detectors are plotted as a function of the inverse temperature. Each data point is an average of 4,000 observations, and the empirical equations representing the data will be used to calculate particle temperature from the infrared data.

Quarterly Progress Report No. 8 presents a schematic drawing of this system. In this system, the heating CO_2 laser beam is along the vertical axis, in contrast to the horizontal beam used in earlier work. Unfortunately, when

the 20 W CO₂ laser was turned on, at a power level sufficient to heat the particle to the temperatures of interest in this work, the particle was lost. While increasing the power very gradually sometimes allowed retention of the particle, performance could not be considered satisfactory. The CO₂ laser has a gaussian energy-radius distribution. The radial energy gradient will produce a radial photophoretic force which will tend to move the particle away from the center of the beam. Similarly, a small vertical force is expected. The Horizontal stabilization is provided by the ac field which is apparently too weak to hold the particle in the center of the field. Based on earlier calculations (Dudek 1989) this force is expected to be small compared to gradational force. These forces are illustrated in Fig. 3.

One possible solution is weakening the flux gradient by focusing the laser beam much wider, however, this will lower the maximum temperature. Another solution is to use a doughnut shape beam energy distribution which has a minimum in the center. A simulated doughnut shape beam has been tested by putting a beam block in the center of the laser beam before the convex lens. This greatly improves particle stabilization. Although this modification prevented loss of the particle, vertical movement of the particle makes it difficult to record the mass change of the particle continuously. This 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 capable control frequency of the current position

control system is 500-800 Hz, and the laser modulation frequency is about 8000Hz. The current system needs a faster control system or a change to the conventional method of horizontal heating to allow continuous weight measurement needed for kinetic studies.

A preliminary model of the ignition temperature profile of a single particle was presented in Progress Report No. 4. A more precise model should include CO oxidation in the boundary layer. The heat of reaction of CO oxidation is 66.8 kcal/mol, therefore, the heat generation may not be neglected.

A set of equations describing the heat balance in the boundary layer is added in the Appendices. A standard kinetic code (including reactions of H, H₂, H₂O, HO, H₂O₂, HCO, CO, CO₂, O, O₂ and the effect of N₂) will be used to estimate this effect. Surface concentration of oxygen needs to be calculated to get an accurate value of Stefan flow effect. This requires many iteration for each temperature, and may need the capability of a super computer like the MIT Cray II.

Future Program

During the next quarter detailed equations, describing the boundary layer reactions will be set up, and the programmed for the FEM (finite elements method) in order to study the temperature - time behavior of the char oxidation kinetics. Modifications of the control system or the laser heating method will be tested.

IR_calib2_2m.dat

Fig.1 Calibration curve of 2μ IR detector

IR_calib2_4m.dat

Fig.2 Calibration curve of 4μ IR detector

Fig.3. Forces acting on the particle in an electrodynamic balance

APPENDICES

Governing equations for gas phase reaction in the boundary layer

Continuity equation

$$\frac{\partial \rho_g}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho_g v_r) = 0 \quad (\text{A.1})$$

Continuity equation for species i

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

Energy balance equation for the gas phase

$$\begin{aligned} \rho_g C_{p,g} \frac{\partial T}{\partial t} + \rho_g C_{p,g} v_r \frac{\partial T}{\partial r} = & \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \lambda_g \frac{\partial T}{\partial r} \right) - \rho_g \sum_{i=1}^n (Y_i V_i C_{p,i}) \frac{\partial T}{\partial r} \\ & - \sum_{i=1}^n Y_i H_i \end{aligned} \quad (\text{A.3})$$

where subscript 'g' means gas mixture in the boundary layer, and subscript 'i' means the i-th species in the gas mixture. Also ρ_g is the density of the gas mixture in the boundary layer, $C_{p,g}$ is the specific heat at constant pressure, λ_g is the thermal conductivity, Y_i is the mass fraction, H_i is the specific enthalpy, R_i is the mass production rate, v_r is the fluid velocity in 'r' direction, V_i is the diffusion velocity of the 'i' th species and T is the temperature of the gas phase.

END

DATE
FILMED

6/09/92