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**CHAR PARTICLE FRAGMENTATION AND ITS EFFECT
ON UNBURNED CARBON DURING PULVERIZED COAL
COMBUSTION**

Quarterly Report for the Period

October 1, 1993 - December 31, 1993

Grant DE-FG22-92PC92528

Prepared for

THE UNITED STATES DEPARTMENT OF ENERGY

**James Hickerson
Project Officer
Pittsburgh Energy Technology Center
Pittsburgh, PA 15236**

Submitted by

Mr. Ruben Diaz and Professor Reginald E. Mitchell

February 1994

**HIGH TEMPERATURE GASDYNAMICS LABORATORY
Mechanical Engineering Department
Stanford University**

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February 1994

High Temperature Gasdynamics Laboratory
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REPORTED BY: Reginald E. Mitchell and Ruben Diaz

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RESEARCH OBJECTIVES

This document is the fifth quarterly status report of work on a project concerned with the fragmentation of coal char particles that is being conducted at the High Temperature Gasdynamics Laboratory at Stanford University, Stanford, California. The project is intended to satisfy, in part, PETC's research efforts to understand the chemical and physical processes that govern coal combustion. The work is pertinent to the char oxidation phase of coal combustion and focuses on how the fragmentation of coal char particles affects overall mass loss rates and how char fragmentation phenomena influence coal conversion efficiency. The knowledge and information obtained will allow the development of engineering models that can be used to predict accurately char particle temperatures and total mass release rates. In particular, the work will provide insight into causes of unburned carbon in the ash of coal-fired utility boilers and furnaces. Work is to be performed over the three-year period from September 1992 to September 1995.

The proposed study has relevance to char particle fragmentation and its effect on mass loss rates during pulverized coal combustion. Depending on coal type, a significant number of char particles are formed during devolatilization that are categorized as being cenospheres or mesospheres -- particles that have relatively large void volumes within them. Large voids at the outer surfaces of particles allow oxygen to consume the inner particle material. As a consequence, particles may fragment. Fragments burn at rates governed by their individual sizes and not at rates determined by the sizes of their parent char particles. Thus, the overall mass loss rates of char particles that fragment extensively can not be predicted accurately without accounting for the effects of fragmentation. In this study, to eliminate the complications associated with the complex

composition of coals, combustion tests are performed using synthetic chars having particle morphologies similar to those of the char particles formed during coal devolatilization.

The overall objectives of the project are: (i) to correlate char particle porosity with fragmentation phenomena, (ii) to determine if mineral matter in the coal affects fragmentation patterns, and (iii) to relate the effects of fragmentation events to unburned carbon in ash. The knowledge obtained during the course of this project will be used to predict accurately the overall mass loss rates of coals based on the mineral content and porosity of their chars. The work will provide a means of assessing reasons for unburned carbon in the ash of coal fired boilers and furnaces.

The project is divided into four research tasks. Specific objectives associated with each task are as follows:

Task 1: Production and Characterization of Synthetic Chars

Objective: The objective of this task is to produce and characterize synthetic chars with controlled macroporosity and known mineral content. Densities, porosities, pore size distributions, and total surface areas will be measured. Chemical analyses will be performed to determine the composition of chars that have been laden with pyrites, calcites, silica, and gypsum.

Deliverables: Results of this task will yield well-characterized materials for use in combustion and fragmentation studies associated with Tasks 2 and 3 of this project. Particles in the size ranges 75 - 90 μm , 90 - 106 μm and 106 - 125 μm that have porosities up to 75% will be produced.

Task 2: Baseline Char Combustion Experiments

Objectives: The objectives of this task are to design and fabricate an entrained flow reactor and a solids extraction probe and to determine gaseous conditions for diffusion-limited combustion of the synthetic chars. The extent to which particles fragment during the extraction process will be characterized.

An additional objective is to employ thermogravimetric analysis to determine the extent to which the overall particle burning rates of the mineral-laden synthetic chars are catalyzed in the gaseous environments that will be used in the fragmentation studies.

Deliverables: The following will result after completion of this task:

- An entrained flow reactor capable of simulating environments typical of pulverized coal combustors and a solids extraction probe that permits sampling of partially reacted chars at different residence times in the reactor.
- Characterization of the extent to which particles fragment during the extraction process.
- Oxygen concentrations and gas temperatures that yield diffusion-limited burning of the synthetic chars produced.
- Characterization of the extent of catalysis in the gaseous environments employed due to mineral constituents of the synthetic chars.

Task 3: Char Fragmentation Studies

Objective: The overall objective of this task is to obtain the data necessary to understand how the porosity of char particles affects their fragmentation behavior and how the minerals in char particles influence their fragmentation patterns.

Deliverables: The following will result after completion of this task:

- A measure of fragmentation events that result as a consequence of burning at diffusion-limited rates in various gaseous environments as a function of particle porosity.
- A measure of how the type of mineral and the mineral content of char affects its fragmentation patterns.

Task 4: Fragmentation Modeling

Objective: The objective of this task is to develop and validate a fragmentation model that can be incorporated into a char oxidation model.

Deliverable: The successful completion of this task will yield a char fragmentation model that describes the results of Task 3 experiments. The model will be capable of accurately predicting significant fragmentation events in gaseous environments typical of pulverized coal combustors. When combined with a char oxidation model, the extent to which fragments might extinguish and hence, contributes to unburned carbon in ash can be predicted.

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TECHNICAL PROGRESS DURING THIS QUARTER

SUMMARY

The information reported is for the period October 1 to December 31, 1993. During this quarter, activities were undertaken in Task 2. Oxygen concentrations were measured in the post-flame region of the entrained flow reactor. The sampling probe was used for the hot gas tests to sample the gas stream. Samples were injected into a gas chromatograph to determine the oxygen concentration. Results agreed with thermoequilibrium calculations that yield equilibrium compositions based on the stoichiometry of the feed gases. The axial temperature distribution along the reactor centerline was measured using a silica-coated platinum-rhodium thermocouple. Two coating techniques were tested and it was found that flame-plating silica to the thermocouple wires produced a thinner coating than a ceramic adhesive technique and therefore a smaller radiation correction.

Other activities this quarter included the fabrication of a solids sampling probe support assembly and thermocouple support assembly. The reactor mass flow controllers and probe rotameters were calibrated. A control system for the stepper motor was built and tested.

TASK 2: BASELINE CHAR COMBUSTION EXPERIMENTS

Solids Sampling Probe and Particle Capture

A probe support assembly was designed and constructed. The assembly can hold the probe in a stable vertical position within the reactor post-flame environment, and it allows the ability to swing the probe to and from the reactor with little loss in reactor-to-probe alignment. The assembly also holds a thermocouple support assembly with identical capabilities. The rotameters for the probe coolant water, particle quench gas, and sample gas were calibrated. A recently repaired and recalibrated wet test meter was used in the calibration of the latter two rotameters. A faulty pump, that was to be used for particle capture, was replaced.

The probe coolant system was tested under hot gas conditions. With a flow of about 0.1 lpm of water, the probe was swung into position above the hot reactor environment. The reactor was raised until it was about 8 cm below the probe tip. As the burner was raised, water vapor in the post-flame gas mixture condensed onto the probe. Although condensation indicated the probe was not overheating, condensation near the probe tip led to water droplets falling onto

the burner surface. Lower flow rates of coolant water were used to raise the condensation line on the probe and prevent the water from falling. In later experiments, the water flow rate was raised in such a way as to prevent both water droplets and overheating of the probe. Coolant flow rates for proper operation of the sample probe were established.

A particle capture filter housing and filter material were purchased. The filter housing was a neoprene screw-type filter holder that can hold the 47 mm diameter 1 μ m-pore Nuclepore filters. The filters and filter housing were tested using the solids sampling probe, pump and particle feeder. Particles were fed directly into the solids sampling probe and captured by the filter housing. Although 99% of the material fed into the probe was captured by the filter assembly, about 18% of the material had to be recovered from the walls of the container and especially the O-ring used to seal the holder. This large percentage of particles adhering to the housing and O-ring makes this filter holder inadequate. The filter itself was deemed adequate and will be used in a replacement filter holder.

Laminar Flow Reactor

All five reactor mass flow controllers were calibrated with a wet test meter and adjustments were made. The controller system for the stepper motors used in the reactor translator and the particle feeder was built and tested. The controller system consists of a stepper motor driver electronics circuit, a PC containing an I/O board and a program to send the specified number of pulses to either stepper motor. Both motor translation systems were tested and repeatability of position was excellent.

The feeding capabilities of the particle feeder were tested with samples of synthetic char. The feeder syringe was filled with the char, placed into the feeder flask, and sealed. The syringe plunger was pushed by the motor translator and falling particles were entrained by nitrogen through the feed tubes and into a weighing pan. Initial tests showed that the particles fed through the Tygon tubing clogged due to moisture on the particles. All subsequent tests were preceded with drying of the particles in a vacuum oven under nitrogen at 100 °C for 3 hours. The dried particles did not stick to the tubing and flowed continuously through. Over 99% of the particles that were poured into the syringe were fed through the system. The feeder system was deemed satisfactory.

Prior to the hot gas tests with the sampling system, the burner was tested at various flow conditions and a safe operating procedure was developed. The procedure assures the safety of the

operator and prevents the fuel tubes and oxidizer honeycomb cells from overheating during the startup transients. With this in hand, experiments were performed to measure the post-flame gas concentrations and gas temperatures at various flow conditions.

Post-flame gas concentration measurements

Oxygen concentration determinations were performed using a Perkin Elmer Sigma I gas chromatograph. In gas chromatography (GC), constituents of a flowing gas mixture are separated using a packed bed of material and then an appropriate detector gives a response proportional to the concentration of each gas. The response is in the form of a chromatogram, which is a series of peaks for each species. The material used to separate the oxygen from the gas mixture consists of a six foot long, 1/8 inch OD stainless steel column packed with washed molecular sieve 5A of mesh range 80/100. Before the column was used, it was conditioned at 250 °C for 12 hours. The detector used was a thermal conductivity detector that responds to any gas component whose thermal conductivity is different from the carrier gas. Because of its high thermal conductivity and chemical inertness, helium was chosen as the carrier gas. The manufacturer of the molecular sieve column recommended a flow rate of 30 cc/min and GC oven temperature of 35 °C.

Utilizing these conditions in oxygen calibration tests (described later) resulted in chromatograms with oxygen peaks resolved from nitrogen peaks. However, since water vapor is a major component in the post-flame region (up to 20%), it condenses onto the molecular sieve column at 35 °C and causes problems with elution of gases from the column. Tests with the hot gas stream confirmed difficulties at these conditions. Raising the temperature to 130 °C eliminated all condensation onto the column but resulted in decreased resolution of the oxygen and nitrogen peaks, due to increased elution velocities. Comparison of two oxygen calibrations at these two temperatures showed no difference in linearity with a small increase in slope. Therefore, decreased resolution is not a problem.

The oxygen calibrations were performed using the reactor and flow system, and the sampling probe. The sampling probe was positioned about 8 cm above the center of the burner surface. The volumetric flow rates of oxygen and nitrogen were varied to achieve the desired oxygen concentration while maintaining a total flow rate of 60 lpm, (the flow rate used in flame experiments). The pumping rate was set at 11 lpm air and the helium quench rate was set at 21 lpm. After five minutes of pumping gas through a sampling bottle placed downstream of the probe pump, the container was sealed. One end of the bottle contained a cap with a silicone rubber

septum through which a 100 ml of sample gas was drawn with a gas-tight syringe. The gas was subsequently injected into the GC. Plots of the resultant area of the oxygen peaks as a function of oxygen mole fraction are shown in Fig. 1 for both calibrations at different temperatures. As mentioned above, use of 130 °C rather than 35 °C has little affect on the calibration.

The conditions used in the hot gas concentration measurements (labelled gas conditions 1 and 2) are shown in Table 1. These two conditions produce comparable adiabatic flame temperatures yet, yield oxygen mole fractions that vary by a factor of over two. These equilibrium mole fractions and flame temperatures are included in Table 1 and were calculated using STANJAN, a versatile computer program developed by Professor W. C. Reynolds of Stanford University (Reynolds, 1987). STANJAN can determine equilibrium concentrations of a mixture of gases and mixed-phase reactants for a variety of problems. From the measurements of the hot gas stream, the average areas of the O₂ peaks were found to be 1.17 and 2.18, respectively, for gas conditions 1 and 2. Using the calibration curve, the values of the oxygen mole fraction are 0.052 and 0.115 respectively, and are found in Table 1. The calculated and measured mole fractions are within 4%. This validates flow meter calibrations.

Figure 1. Calibration curves relating the mole fraction of oxygen in a 100 μ l sample to the corresponding peak area found with a gas chromatograph and a stainless steel column of molecular sieve 5A. The above temperatures are the GC oven temperatures used. A helium carrier gas was set at 30 cc/min.

Table 1. Gas conditions used in the oxygen concentration measurements. The adiabatic flame temperature and equilibrium oxygen mole fractions were calculated using STANJAN.

Gas condition number	Reactant molar ratios			Adiabatic Flame Temperature (K)	Calculated and measured oxygen mole fraction	
	CH ₄ /O ₂	H ₂ /O ₂	N ₂ /O ₂		calculated	measured
1	0.15	0.75	4.11	1839	0.054	0.052
2	0.12	0.56	2.84	1827	0.113	0.115

Axial Temperature Measurements

In all of the fragmentation experiments, the post-flame environment will be at temperatures exceeding 1500 K and highly oxidizing. Noble metal thermocouples containing platinum and rhodium are appropriate for these hostile conditions. A commercially available standard thermocouple type is Type S, whose composition is platinum/platinum-10% rhodium. Type S thermocouples and wires with these compositions were used in the fabrication of a thermocouple probe used in the temperature measurements.

A sketch of the probe is shown in Fig. 2. Fine wire thermocouples of diameter 5 mils were spot welded to Y-shaped 20 mil wire tines and kept under tension. The reason for this suspended thermocouple arrangement was to reduce the temperature error due to conduction. Within the reactor post-flame region, the radial temperature distribution near the centerline is fairly uniform. Aligning the 5 mil thermocouple wires along a radial isotherm within the reactor minimizes the conduction from the wire tines to the thermocouple bead. The difference in the bead temperature and the desired gas temperature was further minimized by using a fine diameter wire because radiation heat losses decrease with smaller diameters. Larger diameter tines are used because of the fragility of the fine wires and the need for accurate location of the thermocouple junction bead. The thicker wires are inserted into a two-hole alumina ceramic insulator that acts as an electrical insulator and a heat-resistant mechanical support for the whole assembly. On the opposite end of the insulator, the wires are connected to a ceramic connector that supported the insulator and joined the thermocouple probe to the thermocouple support assembly.

Figure 2. Sketch of thermocouple probe used in axial temperature measurements.

To protect the thermocouple from chemical attack and to prevent catalytic heating of platinum wires, thin coatings are necessary. Two coatings were tested, a ceramic adhesive and a silica coating. Use of aluminum oxide-based ceramic coatings is described by Burton *et al.* (1992). In this method, a powder consisting of magnesium and aluminum oxides is mixed at a fixed ratio with a silicate liquid solution. The thermocouple is then dipped into the mixture and the resultant coating is cured at various temperatures. It was found that the size of the thermocouple

bead tripled in size from 11 mils to 35 mils giving an unacceptable radiation correction of over 300 K. The alternative technique, flame plating silica to the wire, has been described by Madson and Theby (1984). In this technique hexamethyldisiloxane is burned in a propane diffusion flame using a Meker burner. The silica particles produced are plated onto the thermocouple wire passed into the flame zone where the temperature is about 1800 K. Care must be taken to assure a uniform coating of SiO₂ onto the junction bead. This method increased the bead diameter from 11.4 mils to 12.6 mils, which results in a radiation correction of about 100 K. This correction is acceptable, however the correction can be further reduced by using 2 mil diameter wires.

For temperatures over 1000 K, the thermocouple bead temperature becomes significantly lower than the gas temperature primarily due to radiation losses from the bead to the cooler quartz chimney walls and room walls. As mentioned above, the heat losses due to conduction were minimized by the thermocouple probe design. To account for the difference in the two temperatures the approximate temperature correction for the gas temperature measurements was calculated. The following expression relating the two temperatures was derived from an energy balance of convective heat transfer from the gas to the bead and radiation from the bead to the cooler surroundings

$$T_{gas} = T_{bead} + \frac{\sigma \epsilon_b}{h} (T_{bead}^4 - T_{wall}^4)$$

where h is the heat transfer coefficient, σ is the Stefan-Boltzmann constant, and ϵ_b is the bead emissivity. The heat transfer coefficient is found from

$$h = \frac{Nu\lambda}{d}$$

where Nu is the Nusselt number, λ is the thermal conductivity of the gas mixture, and d is the diameter of the spherical thermocouple bead. Because the thermal conductivity is evaluated at the unknown gas temperature, an iterative solution is necessary.

The value of the Nusselt number is taken as to be constant and equal to 2.45. A discussion of the choice of this value is found in the Appendix. The value of the emissivity of the coated thermocouple is taken as 0.3. Bradley and Entwistle (1966) experimentally determined that the emissivity of silica-coated Type S thermocouples dropped from about 0.35 at 800 K to about 0.25 at 1700 K. An average value within this range was chosen for the radiation calculations. The

bead diameter was determined with a 100X magnification microscope and found to be 12.6 mils. The gas mixture thermal conductivity was determined using the major species mole fractions calculated by STANJAN, and the gas mixing rules and property data found in Mitchell (1980). The wall temperature was set at 300 K, the room temperature, although the bead radiates to both the room walls and hot quartz walls. The measured quartz wall temperature was approximately 500 K and, calculations show little difference in the correction when using either temperature.

The results of the thermocouple measurements of the gas temperature distribution along the centerline for gas condition number 3 ($\text{CH}_4/\text{O}_2:0.09$, $\text{H}_2/\text{O}_2:0.47$, $\text{N}_2/\text{O}_2:2.04$) and the corrected temperatures are plotted in Fig. 3. For the measurements, a laser was used to accurately position the bead above the burner surface. The agreement between two sets of data taken at various heights is good. Overall, due to heat losses to the room and quartz walls the gas temperature drops about 9 K/cm in the range measured.

Figure 3. Uncorrected and corrected thermocouple measurements of the axial gas temperature as a function of height above the burner surface. Measurements are for gas condition #3, where the adiabatic flame temperature is 1852 K. The solid and dashed curves represent two different data sets.

PLANS FOR NEXT QUARTER

- Characterization of the flow reactor environments will be completed.
- The solids sampling probe will be used to extract char samples subjected to reactor post-flame environments having oxygen levels in the ppm range and temperatures of about 1400 K. At these conditions, particle burning is minimal, permitting assessment of the extent of fragmentation during feeding and sample collection.

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APPENDIX

As mentioned earlier, the Nusselt number is set equal to 2.45. In general the Nusselt number is a function of the flow velocity, the transport properties of the gas, and a characteristic length scale. Because the flow velocity distribution along the burner axis has not been measured at this time, it is advantageous to remove it from the calculation of the gas temperature. A form of this relationship is from Eckert and Drake (1972) as follows

$$\overline{Nu}_d = 2 + 0.236 Re_d^{0.606} Pr^{1/3}$$

where Re_d is the Reynolds number and Pr is the Prandtl number. The Reynolds number is defined as follows

$$Re_d = \frac{\rho v d}{\mu}$$

where ρ is the density, v is the velocity, d is the bead diameter and μ is the dynamic viscosity. The Prandtl number is defined as follows

$$Pr = \frac{\mu c_p}{\lambda}$$

where c_p is the specific heat at constant pressure and λ is the thermal conductivity. The gas properties were evaluated as mixture properties. The gas mixture was found from STANJAN calculations and the four major species: N_2 , O_2 , H_2O , and CO_2 were assumed to be the only species contributing to the properties. The mixture rules and property information used were those found in Mitchell (1980).

The total flow of gases through the burner is about 60 lpm. With a burner cross-sectional area of about 26.8 cm^2 , the flow velocity is about 0.4 m/s. Just downstream of the flame front the gas temperature has been raised from about 300 K to around 1800 K. From continuity and assuming the area change to be minimal, the flow velocity has achieved about 2.3 m/s. Measurements by Mitchell *et al.* (1984) using a similar burner and flow conditions found the flow velocity to vary from about 2 m/s at the flame to about 3.5 m/s at 37 cm above the burner surface. The increase in velocity with height above the burner is due to a decrease in the cross-sectional area for flow as a result of the boundary layers along the reactor walls. Using a similar

range of velocities (2-5 m/s) and temperatures in the range of 1500 K to 1800 K the following ranges of Reynolds number, Prandtl number and Nusselt number were found:

$$2.0 < Re < 6.0$$

$$0.671 < Pr < 0.679$$

$$2.3 < Nu < 2.6$$

Using extreme Nusselt numbers within this range changed the radiation correction no more than 7 K, therefore using a constant value of the nominal value of 2.45 seems reasonable.

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