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QUARTERLY PROGRESS REPORT

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Reporting Period: August 1, 1990 - October 31, 1990

Project Title: Thermally Induced Structural Changes in Coal Combustion

Identification Number: DE-FG22-88PC88911

Institution: California Institute of Technology

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I. Project Objectives

The project objectives are (1) to measure the effect of devolatilization temperature and time on the properties of the char and (2) characterize and quantify the effect of thermal annealing on char reactivity during char burnout under conditions of pulverized combustion.

II. Work Done During Reporting Period

1. Coal Devolatilization/Char Generation

Coal devolatilization runs continued during the reporting period. However, one heating element (Super-Kanthal) burned out and three others were found to have deteriorated. The flow reactor had to be shut down for several weeks until the elements were replaced. Currently the flow reactor is functioning normally and char generation and combustion runs are proceeding at a fast pace.

2. Char Characterization

Elemental analysis and N_2 BET surface areas measurements were carried out on the three chars produced in the devolatilization runs (see previous quarterly report). The results are presented in Table 1. The char produced by 100 ms devolatilization has considerably lower carbon content and higher hydrogen content. Oxygen, by difference, is also substantially higher than in the other two chars. The two chars prepared in 200 ms devolatilization (one in pure N_2 , the other in 1% O_2-N_2) are quite similar in elemental composition.

More drastic differences are observed in the N_2 BET surface areas of the three chars. The 100 ms char had area below the sensitivity of the instrument, the 200 ms (N_2) char had $10.7 \text{ m}^2/\text{g}$ and the 200 ms (1% O_2-N_2) char had $3.7 \text{ m}^2/\text{g}$. The lack of measurable area in the 100 ms char is evidently due to blocking of pore mouths. With additional devolatilization time a fraction of these pore mouths was evidently opened up as evolution of volatiles continued and some consolidation occurred. The lower area of the char devolatilized in 1% O_2 could be due to chemisorption of oxygen resulting again in some constriction of the pore mouths.

3. Experiments in the Electrodynamic Balance

Our previous quarterly report described our initial results from intermediate temperature oxidation experiments in the electrodynamic balance. That series of experiments provided temperature traces which could be used to estimate oxidation rate parameters, assuming knowledge of particle size and density, and laser intensity. But because of irregular particle

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shape, variable density, and variable laser intensity from experiment to experiment, it was not possible to separate the rate parameters from the other unknowns. A direct measurement of particle mass is necessary for this purpose. Work during the reporting period was focused on developing ways to measure the particle mass loss and, therefore, the reaction rate directly. This work is summarized in the attached Appendix.

4. Considerable modeling work has been carried out during the reporting period on the effect of particle shape and surface roughness on combustion and on the proper interpretation of combustion rate measurements. This work will be summarized in the next quarterly report.

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Table 1. Elemental analysis and N₂ BET surface area of chars from a hvA bituminous coal (Pittsburgh No. 8) devolatilized at 1600 K (coal particle size 38-74 μm , char particle size 53-90 μm).

Elemental Composition (%)	Devolatilization Time and Atmosphere		
	100 ms, N ₂	200 ms, N ₂	200 ms, 1% O ₂ -N ₂
C	69.9	75.6	76.6
H	1.9	1.0	1.0
N	1.3	1.1	1.3
Ash	21.6	22.6	21.3
N ₂ -BET Area (m ²)	too low to measure	10.7	3.7

Appendix

Summary of Electrodynamic Balance Experiments for the quarter 8/90 to 10/90

Previous results in the single particle electrodynamic thermogravimetric analyzer have shown that pulse heating a char particle in varying levels of oxygen could be used to estimate the apparent Arrhenius rate parameters for the carbon--oxygen reaction. However, the range of pre-exponential factors and activation energies which fit the data within a certain error is fairly broad, hence, an experiment which would provide more specific numbers was sought. A direct method to measure the apparent rate parameters requires a knowledge of the mass of the particle to be able to determine the burning rate of the particle. Thus, the main effort has been devoted to developing the methodology to determine the mass of the single particle in the electrodynamic balance.

Several techniques have been developed for determining the mass of a particle in the electrodynamic balance. One technique is termed "Electron Stepping", in which a short pulse of UV light is used to change the charge on the particle by one electron, and the resulting balancing voltage recorded. The balancing voltages for the electron steps are then used to calculate the mass and charge of the particle (Philip, et al, 1983).

$$m = \frac{C e V_n V_{n+1}}{g z_0 V_n - V_{n+1}} \quad 1$$

where C is the electrode geometrical constant, V_n and V_{n+1} are the balancing voltages, e is the charge of an electron, and z_0 is the interelectrode distance. This technique is suitable only for small particles, which hold tens or hundreds of charges. Large particles, such as char, may hold millions of charges, and distinguishing the loss of a single electron is extremely difficult.

Another technique measures the aerodynamic drag on a particle. The DC voltage required to suspend a particle is determined, then a flow of air is axially directed through the electrodynamic balance. The particle is rebalanced. The difference in balancing voltages corresponds to the aerodynamic drag force (Davis, et al, 1987). Implementing this technique would require extensive modifications to the chamber and extensive calibration work.

The sedimentation velocity of a particle has also been used to determine its mass in the electrodynamic balance. The AC and DC voltages are turned off, and the particle is allowed to fall. After waiting a sufficient amount of time, the terminal velocity of the particle is measured (Sageev, et al, 1986). This technique is most easily applied to small particles of a few microns in diameter, with a low terminal velocity and very fast relaxation time.

An alternative method was considered in which the difference between the driving AC voltage and particle motion is measured. When a particle which is balanced in the electrodynamic balance is displaced, the AC voltage causes the particle to oscillate. The aerodynamic drag on the particle induces a phase lag in the particle motion with respect to the driving AC voltage (Fuchs, 1964).

$$V = V_0 \sin (\omega t - \varphi) \quad 2$$

$$\varphi = \tan^{-1} \left(\omega \frac{\rho_p d_p^2 C_c}{18 \eta} \right) \quad 3$$

where V is the particle velocity, ω is the angular driving frequency, ρ_p is the particle density, d_p is the particle diameter, C_c is the Cunningham slip correction factor, and η is the gas viscosity.

A phase meter was obtained (Wavetek, Model 740. This model is no longer in production). After setting up equipment and electronics to obtain phase information, it was determined that the phase meter could not be calibrated satisfactorily, hence a phase meter was constructed from IC's. After the meter was constructed and calibrated, it was determined that the phase measurement did not correlate very well with the estimated mass, based on average properties of the particles being used. The phase that was measured was also highly dependent on the displacement of the particle. It is hypothesized that the phase measurement is different from expected and dependent on the particle displacement because of non-linearities in the AC electrical field, or because the driving waveform is not a pure sinusoid.

A variation of the sedimentation velocity technique was adopted. Electronics were constructed to switch off the AC and monitor the position of the particle as it fell. The AC field is turned on after .13 seconds. The velocity is calculated, and the portion where the velocity becomes terminal is plotted against the DC voltage.

$$\nu = \frac{2}{9} \frac{r_p^2 \rho_p g C_c}{\eta} \left(\frac{V_0 - V_{DC}}{V_0} \right) \quad 4$$

where ν = particle velocity, r_p = particle radius, V_0 = DC voltage when particle is balanced, and V_{DC} = DC voltage leading to the velocity ν .

Figure 1a shows three smoothed velocity traces for a spherocarb particle, 156 μm in diameter. Each point on the time axis actually represents 0.5msec, so the total time span represented is 0.128 seconds. Figure 1b shows several pairs of velocity--voltage measurements. A linear regression was performed. The intercept, as indicated in equation 4 contains

information about density and size. The size of the particle was measured by an eyepiece micrometer. The resulting density was calculated to be 0.623 g/cm^3 , similar to densities found by others. An error analysis has not yet been completed.

References

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b

Figure 1. Smooth velocity traces of a 156 μm spherocarb particle (a); velocity vs. voltage measurements (b).

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