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QUARTERLY PROGRESS REPORT

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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

Following the devolatilization procedure described in the preceding quarterly report, one additional char was generated from the hvA bituminous coal (Pittsburgh No. 8, PSOC 1451). The temperature employed was 1600 K, the carrier gas was 1% O₂-N₂ and the residence time 200 ms.

2. Char Oxidation in the TGA

Char oxidation rates at about 500°C is one means of characterizing chars produced under different temperature-time schedules. These measurements are conducted with a DuPont 951 thermogravimetric analyzer (TGA) interfaced with a personal computer for on-line acquisition of temperature and sample mass. Oxidation was conducted at 500°C in a 5% O₂-N₂ mixture at 150 cm³/min flowrate. Under these conditions external and intraparticle diffusional limitations were negligible. Three chars obtained from the Pittsburgh No. 8 coal under conditions defined in Table 1 were used in the experiments.

Figure 1 shows the weight loss during three oxidation runs with a char prepared by devolatilization at 100 ms (char A). Each run started with flow of N₂ for 20 minutes followed by the flow of the 5% O₂-N₂ mixture. A slight weight loss occurred during the flow of N₂ suggesting evolution of a small amount of residual volatile material. Figure 2 shows three runs, obtained under the same conditions as Figure 1, but with the char prepared by 200 ms devolatilization (char B). The traces are similar to those of Figure 1 except for a much smaller, in fact negligible, mass loss during the 20 minutes exposure in nitrogen.

Figure 3-5 are plots of conversion during oxidation. Conversion is defined by $(W_o - W)/(W_o - W_f)$ where W, W_o, W_f are instantaneous, initial, and final sample weights. After the completion of oxidation at 500°C for about two hours, the temperature is raised to 800°C to complete the oxidation of small residues of relatively unreactive carbon. The residue after oxidation at 800°C which consists solely of inorganic components is what we have used for W_f. The carbon remaining after two hours of oxidation is 5-10% of the mass of the residue. Because of the definition of W_f adopted here, conversion does not reach 1 even after two hours

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oxidation at 500°C. Each of Figures 3-5 show duplicate or triplicate runs designated by I, II, and III. Reproducibility is very good.

A comparison of the conversion-time behavior of the three chars is shown in Figure 5 with duplicate runs for each char. Oxidation rate in the order char A > char B > char C. The difference is larger between char A and char B than between B and C. In any case it is less than 12-13%. The slightly higher reactivity of char A is probably due to different intrinsic reactivity rather than higher surface area. In fact the initial surface area of char A was lower than that of the other two chars. The higher intrinsic reactivity of char A could be due to chemical factors such as higher content of hydrogen and aliphatic carbon. This remains to be investigated in future work.

3. Oxidation of Single Char Particles in the Electrodynamic Balance

Single particle oxidation experiments were initiated using an electrodynamic balance constructed under an earlier DOE contract. The electrodynamic balance (or "electrodynamic thermogravimetric analyzer": EDTGA) system shown schematically in Figure 7 consists of the balance proper (top, bottom and ring electrodes), a system for position detection (HeNe laser and associated optics), the heating laser (CO₂) and associated optics and a two-color infrared pyrometer (not shown in Figure 1) for continuous measurement of particle temperature. A microscope and Video Camera is used for direct optical measurement of the particle. Figure 8 shows schematically a top view of the overall system. Figure 9 is a schematic of the two-color pyrometer optics.

A typical experiment is carried out by charging and inserting a char particle in the center of the balance. Direct optical observation of the particle provides shape/size information. The CO₂ laser is turned on and stabilized at some suitable power level. The laser beam is prevented to reach the particle by a shutter. At the chosen time the shutter is opened electronically for a duration of a few hundred milliseconds. Upon exposure to the laser beam, the particle heats up within a few milliseconds from ambient temperature to a new temperature in the range 600-800°C and then can remain at that unignited state or can undergo ignition. Upon ignition, the temperature exceeds 900°C at which rapid charge and the particle cannot be held electrostatically at the center of the balance any longer. The signal from the optical pyrometer then declines down to the noise level.

Experiments were carried out with particles from the Pittsburgh No. 8 char and a "spherocarb" synthetic char obtained from a vendor. The spherocarb char was used because the particles are nearly spherical thus avoiding the complications of irregular particle shape. Figure 10 shows the temperature trace of a spherocarb particle suspended in nitrogen. At the commencement of the laser pulse, the particle's temperature increases from ambient (the 300°C level before the pulse is apparent, due to detector noise) to a new steady state of about 850°C. Fluctuations are small, within $\pm 10^\circ\text{C}$. Figure 11 shows another temperature trace from a spherocarb particle, this time in 25 kPa oxygen. The temperature trace is very similar to that of Figure 10. A steady temperature is attained and there is no ignition. Oxidation under these conditions is quite slow and does not produce any significant change in the shape of the temperature trace. The steady temperature level is of course slightly higher than that in N₂ at the same level of laser intensity.

Figures 12 and 13 show temperature traces of coal char particles pulsed in N₂ and 25 kPa oxygen respectively. A steady state temperature is achieved in both cases. The traces are similar to those of the spherocarb particles with the notable difference of much larger temperature fluctuations, $\pm 50^\circ\text{C}$. The nonspherical coal char particles undergo tumbling or rotation exposing a fluctuating optical cross section to the laser beam which, in turn, changes the amount of radiant energy absorbed and causes the large temperature fluctuations.

Figure 14 shows a spherocarb particle suspended in 55 kPa oxygen. Following the beginning of exposure to the laser the particle heats up rapidly from ambient to about 800°C, by radiation, then more slowly to about 1000°C by the heat of oxidation, and finally more rapidly again as reaction accelerates signifying ignition. The rapid drop of the trace is due to particle loss from the focus of the pyrometer. The period of about 200 ms of slowly rising temperature is an induction period of accelerating rate preceding ignition. Figure 15 is a trace of a coal char particle. The trace is similar to the one of Figure 14 with the difference of the temperature fluctuations discussed previously, and a somewhat longer induction period. It must be noted that the length of the induction period is variable. It increases as conditions move towards the unignited state. At the threshold of ignition the induction period is theoretically infinite.

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Table 1. Chars produced by devolatilization of a hvBituminous Coal
(Pittsburgh No. 8 - PSOC 1451) at 1600 K.

Char	Carrier Gas	Residence Time
A	N ₂	100 ms
B	N ₂	200 ms
C	1% O ₂ -N ₂	200 ms

Figure 1. Replicate weight loss curves of char A subjected to 20 minutes flow of N₂ followed by flow of 5% O₂-N₂ mixture at 500°C in the TGA.

Figure 2. Replicate weight loss curves of char B subjected to 20 minutes flow of N₂ followed by flow of 5% O₂-N₂ mixture at 500°C in the TGA.

Figure 3. Duplicate conversion vs. time curves for char A oxidized in 5% O₂-N₂ at 500°C.

Figure 4. Duplicate conversion vs. time curves for char B oxidized in 5% O₂-N₂ at 500°C.

Figure 5. Duplicate conversion vs. time curves for char C oxidized in 5% O₂-N₂ at 500°C.

Figure 6. Conversion vs. time during oxidation of the three Pittsburgh No. 8 chars.

Figure 7. Schematic of the EDTGA

Figure 8. Top view of EDTGA system.

Figure 9. Pyrometer schematic.

CarboSphere, in Nitrogen
CS5325.DAT

Figure 10. Temperature trace of a carbosphere particle suspended in the electrodynamic balance in N₂ and pulsed by the CO₂ laser.

CarboSphere, in 25 KPa Oxygen
CS5338.DAT

Figure 11. Temperature trace of a carbosphere particle suspended in the electrodynamic balance in 25 kPa O_2 and pulsed by the CO_2 laser.

Coal Char, Pulsed, in Nitrogen
C5256.DAT

Figure 12. The temperature trace of a char particle suspended in the electrodynamic balance in pure nitrogen and pulsed at $t = 300$ ms with the CO_2 laser.

Coal Char, Pulsed, in 25 kPa Oxygen
C5307.DAT

Figure 13. The temperature trace of a char particle suspended in the electrodynamic balance in 25 kPa O₂ and pulsed at $t = 300$ ms with the CO₂ laser.

Carbosphere, in 55 kPa Oxygen
CS5351.DAT

Figure 14. Temperature trace of a carbosphere particle suspended in 55 kPa oxygen.
Particle underwent ignition.

Char, in Oxygen, Pulsed
Approx. 330 um dia.
C2124.DAT

Figure 15. Temperature trace of a char particle suspended in 55 kPa oxygen. Particle underwent ignition.

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