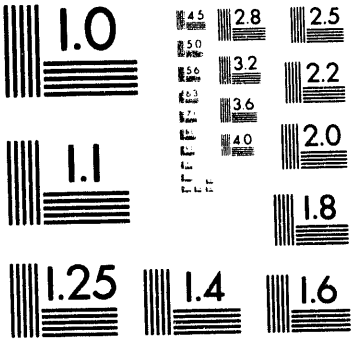
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CHAR PARTICLE FRAGMENTATION AND ITS EFFECT ON UNBURNED CARBON DURING PULVERIZED COAL COMBUSTION

Quarterly Report for the Period

April 1, 1993 - June 30, 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

July 1993

HIGH TEMPERATURE GASDYNAMICS LABORATORY
Mechanical Engineering Department
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US/DOE Patent Clearance is <u>not</u> required prior to the publication of this document.

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

ORGANIZATION: **High Temperature Gasdynamics Laboratory**
Stanford University

CONTRACT: **DOE DE-FG22-92PC92528**

REPORTING PERIOD: **April 1 - June 30, 1993**

REPORTED BY: **Reginald E. Mitchell and Ruben Diaz**

Phone: 415-725-2015

RESEARCH OBJECTIVES

This document is the third 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, contribute to unburned carbon in ash can be predicted.

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DISCLAIMER

TECHNICAL PROGRESS DURING THIS QUARTER

SUMMARY

The information reported is for the period April 1 to June 30, 1993. During this quarter, activities were undertaken primarily in Tasks 1 and 2: synthetic chars were produced and characterized, the solids-sampling probe was fabricated and tested, and chars were pyrolyzed in the pressurized thermogravimetric analyzer (PTGA). During the PTGA tests, problems associated with aligning the balance pan were resolved as well as were problems associated with overshooting the target temperature during the temperature ramping. The PTGA is now ready for use in pyrolysis and combustion tests.

Synthetic chars prepared with 50%, 60% and 67% weight percent lycopodium were produced and characterized. Apparent density measurements indicate that the porosities of the chars are 0.47, 0.57, and 0.60, respectively. Presently, synthetic chars having porosities in the range 17% to 60% are available for experiments.

Scanning electron micrographs of the high-porosity (> 50%) synthetic chars showed many particles having pores with diameters greater than 20 μm, the pore size typical of that left by an evaporated lycopodium spore in the low-porosity chars. This is a consequence of coalescence of pores during the synthesis procedure.

Also this quarter, the pressurized thermogravimetric analyzer (PTGA) was modified to allow gas blending and switching. With this modification, char particles can be heated in an inert environment to a temperature of interest before switching to an oxidizing environment. In several tests, particles of varying porosity were heated to 1000 °C in a nitrogen environment and then combusted in an atmospheric environment containing 10% oxygen in nitrogen. During the heating period, particles were observed to lose about 10% of their weight. This weight loss is associated with the release of volatiles, the hydrogen and oxygen remaining in the synthetic char after curing at 550 °C for one hour. The PTGA results indicate that heating the one-hour cured char in a nitrogen environment at a rate of 10 °C/min to 1000 °C is sufficient to remove the volatiles.

During combustion, the rates of weight loss were the same for particles differing in porosity indicating that mass transfer limitations were insignificant. This includes both external mass transfer from the ambient to the particles in the PTGA pan as well as mass transfer through

the pores of the carbonaceous particles in the pan. Thus, at the conditions employed in the PTGA, the mass loss rates were limited by the intrinsic chemical reactivity of the synthetic char material.

Other activities this quarter included constructing and leak-testing the solids-sampling probe that will be used to extract partially reacted char samples from the laminar flow reactor at selected residence times. Also, flow meters and regulators for the reactor gases, the sampling probe coolant, and particle quench gas were purchased. In addition, a particle feeder capable of feeding char to the reactor at a nominal rate of one gram per hour was designed.

TASK 1: PRODUCTION AND CHARACTERIZATION OF SYNTHETIC CHARS

Char Production

Synthetic chars were produced that have porosities greater than 40% by adding lycopodium to the furfuryl alcohol polymer in greater quantities than used previously (Diaz and Mitchell, 1993a). The same synthesis procedure outlined in the first quarterly status report was employed. The weight percents lycopodium used in the lycopodium/polymer mixtures were 50%, 60% and 67%. Thus, these chars are produced using more lycopodium than polymer. After the chars were cured at 550 °C for one hour, they were ground with a mortar and pestle to obtain pulverized particles in the desired 75-125 μm size range. As reported last quarter (Diaz and Mitchell, 1993b), with high-porosity particles, our mechanical grinding technique is too vigorous, yielding too few particles with diameters greater than 75 μm.

Char Characterization

The bulk densities of the synthetic chars produced with 50%, 60% and 67% lycopodium (by weight) were determined from the tap density data presented in Fig. 1, which shows a plot of the mass required to fill arbitrary volumes of a cylindrical tube. The slope of each line is the bulk density of the char. The plot shows that the bulk density of the char decreases as the relative amount of lycopodium increases. The bulk densities of the three chars are listed in Table 1. Also shown are the apparent densities and the porosities, calculated using 0.39 for the bed void fraction and 1.58 g/cc for the true density (as found in the previous work) (Diaz and Mitchell, 1993b).

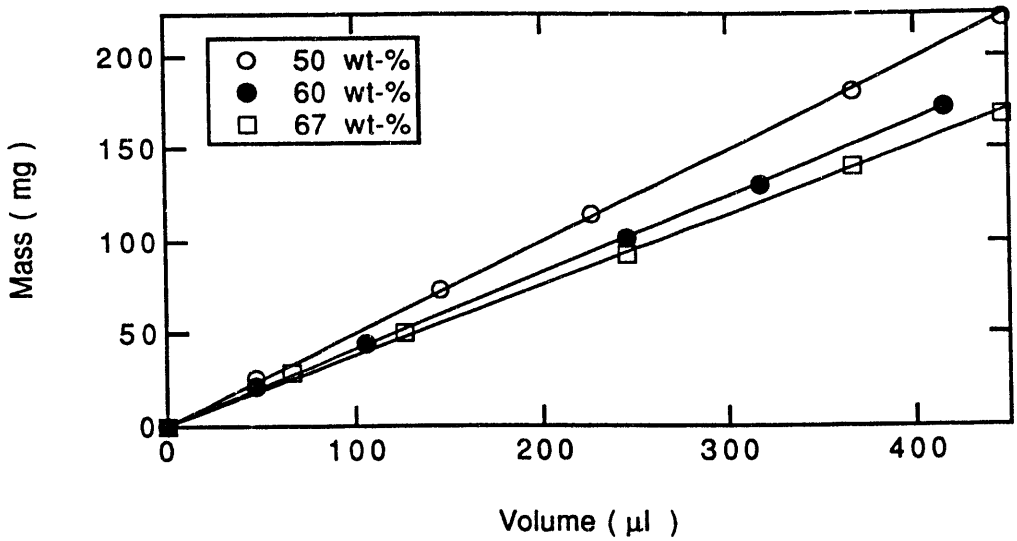

Figure 1. The mass of synthetic char that packs various tube volumes for three different char samples, having various wt-% lycopodium, in the particle size range 75-125 µm. Lines represent least-squares fits to the data.

Table 1. Bulk and apparent densities, determined from a tap density technique and calculated porosities for chars made with various wt-% lycopodium.

wt-% lycopodium	bulk density (from tap density technique) g/cc	apparent density (assuming $\theta_f = 0.39$) g/cc	porosity (assuming $\rho_t = 1.58$ g/cc) %
50	0.50	0.82	48
60	0.41	0.67	57
67	0.38	0.62	60

Figure 2 shows porosity as a function of lycopodium content; all measurements obtained to date are included in the plot along with a least squares fit to the data. The uncertainty in porosity is shown by error bars whose heights are equal to nine percent of each porosity value. The value of nine percent was determined to be the largest uncertainty in the porosity measurement using the tap density technique and the bed packing factor mentioned above. As seen by the plot, the full range of attainable porosities (so far) is 17% to 60%, which covers most of the desired char porosity range of 30% to 75%. The entire range will be completed next quarter when polymer mixtures containing about 90% lycopodium (by weight) will be processed.

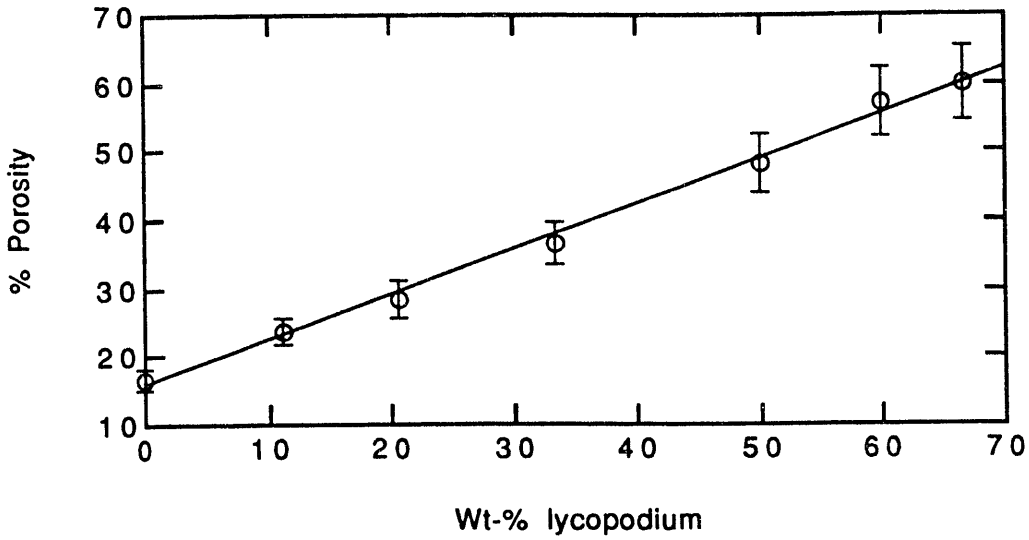

Figure 2. The measured porosity of the synthetic chars versus the weight percent of lycopodium added during synthesis. The solid line is the least squares fit to the data and the height of the error bars are equal to 9% of each porosity value. Carbon black was added to all chars at a mass ratio of carbon black-to-polymer of 1:3.

Scanning Electron Micrographs of Synthetic Chars

Figures 3-6 are scanning electron micrographs (SEM) taken of synthetic chars produced with two different levels of measured porosity, 37% and 57%. Each micrograph displays a bold, white, reference line whose length corresponds to either 100 or 10 μm. Figures 3 and 4 show a group of uniformly-sized particles of porosity 37% and 57%, respectively. Comparison of the two clearly indicates that the higher porosity char has more surface pores. It can be seen in the magnifications of the particles (Figs. 5 and 6) that the higher porosity char also has a larger number of pores of diameter greater than 20 μm, the nominal size of a pore produced by the evaporation of a lycopodium spore. These appear to be a consequence of the coalescence of pores formed from the evaporation of two or more adjacent lycopodium spores. As the amount of lycopodium is increased, the likelihood of such coalescence is increased.

Figure 7 is a micrograph of a 48%-porosity char that had been heated in a nitrogen environment at 550 °C for over 27 hours in an attempt to remove the nodules found within the pores of the synthetic char. Last quarter we hypothesized that these nodules might be residue from lycopodium remaining in the polymerized char after one hour of curing at 550 °C (Diaz and Mitchell, 1993b). Their size and spherical shape suggest that they may be a consequence of condensation. As shown in the figure, the nodules were not removed after prolonged heating at

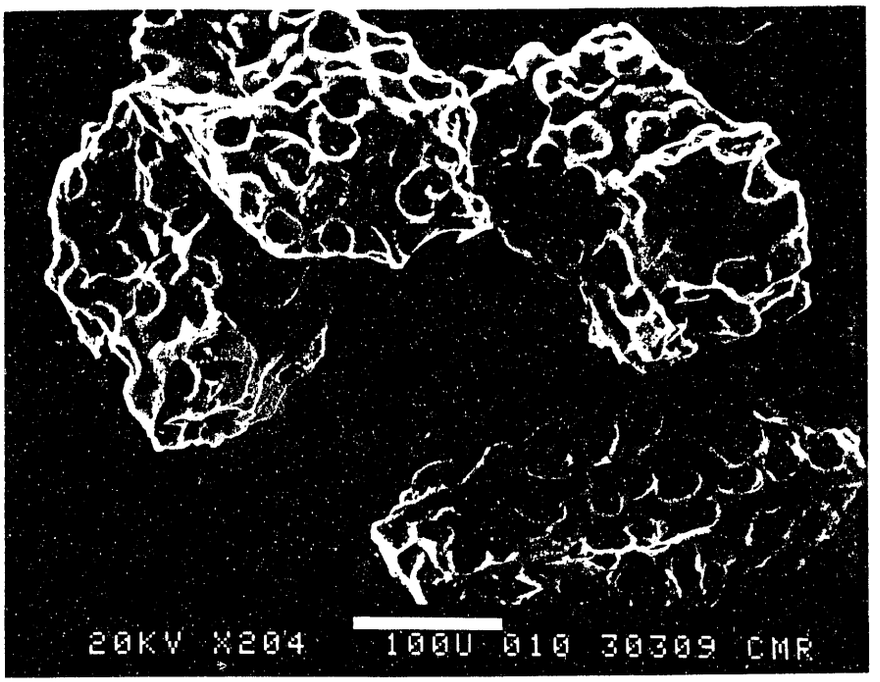

Figure 3. 204X magnification SEM photograph of synthetic char particles sized within a range of 75-125 μm and produced to have an average porosity of 37% . The bold white line represents 100 μm.

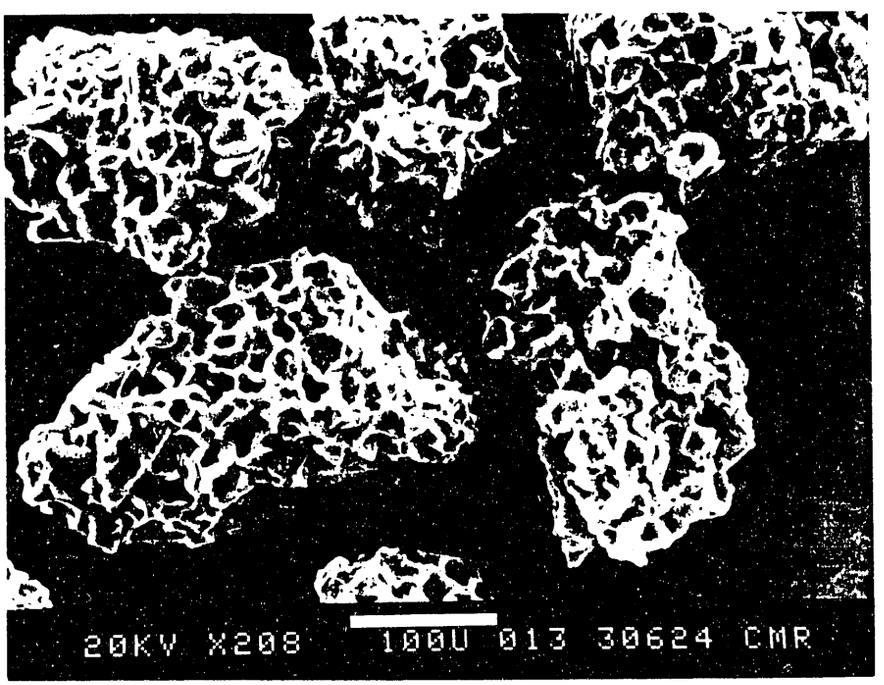

Figure 4. 208X magnification SEM photograph of a synthetic char particle produced to have an average porosity of 57%. The bold white line represents 100 μm.

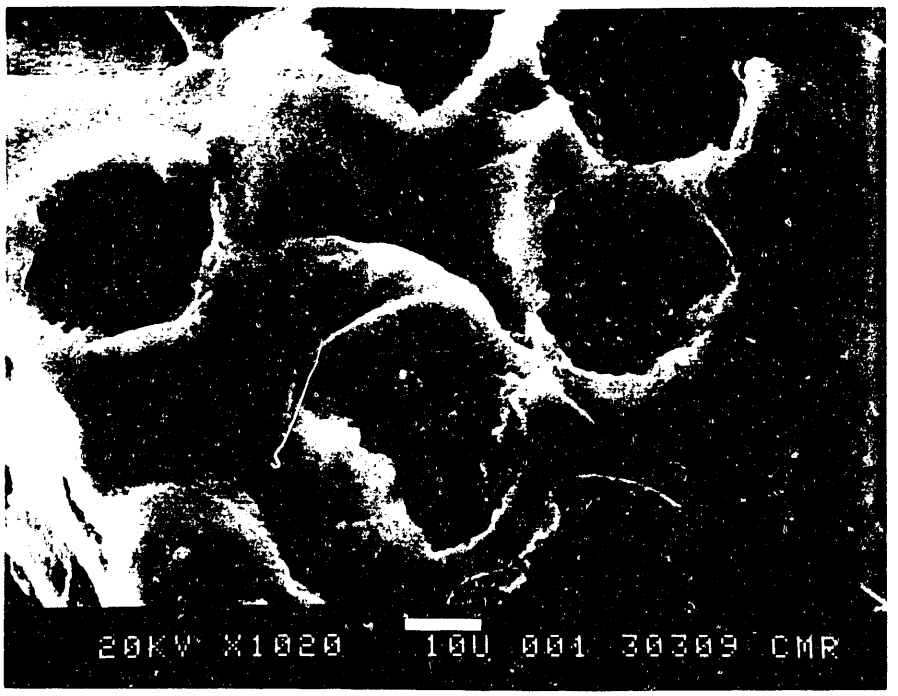

Figure 5. 1020X magnification SEM photograph of synthetic char particles sized within a range of 75-125 μm and produced to have an average porosity of 37%. The bold white line represents 10 μm.

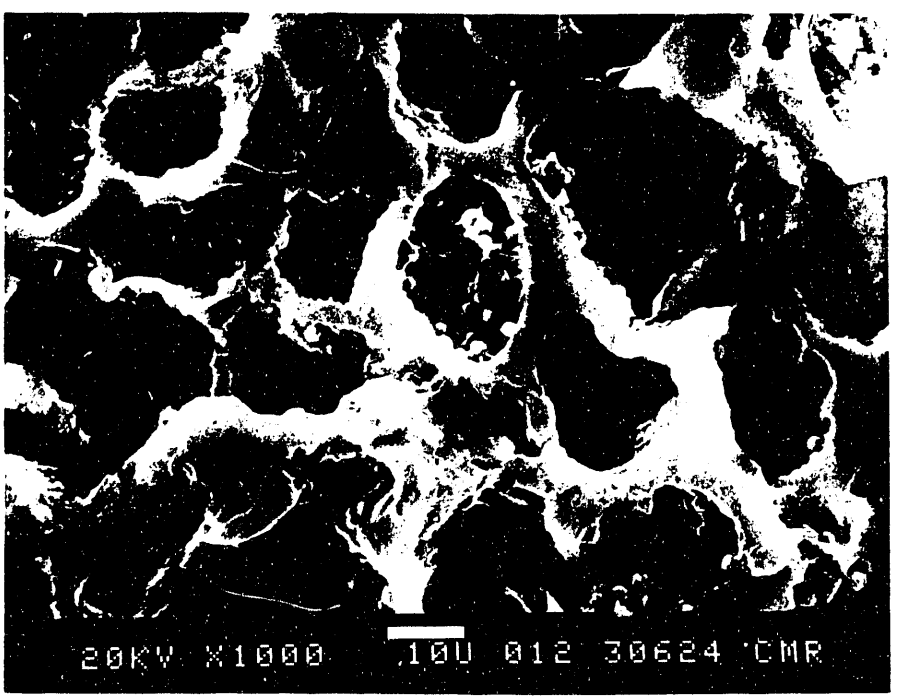

Figure 6. 1000X magnification SEM photograph of a synthetic char particle produced to have an average porosity of 57%. The bold white line represents 10 μm.

550 °C. If the nodules are made of a different material than the bulk synthetic char, they may have a different combustion rate thereby affecting our interpretation of weight loss measurements. We will cure the polymer mixture at higher temperatures to determine if the nodules are lycopodium tar that condensed within the particle pores. Higher curing temperatures may allow tars to escape the carbonaceous matrix before condensation. It is difficult to ascertain if these nodules will influenced adversely our fragmentation study.

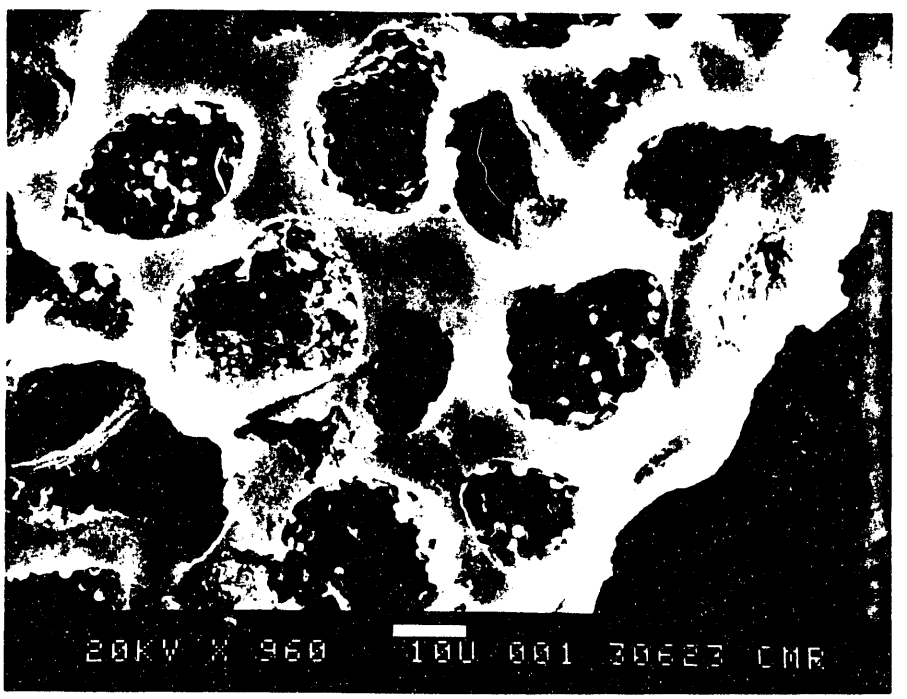

Figure 7. 960X magnification SEM photograph of a synthetic char particle with 48% porosity subjected to 27 hours of heating in nitrogen at 550 °C. The bold white line represents 10 μm.

TASK 2: BASELINE CHAR COMBUSTION EXPERIMENTS

Solids-Sampling Probe Assembly and Laminar Flow Reactor

The design and fabrication of the solids-sampling probe, which will permit extraction of partially reacted particles at selected residence times, was completed. The final design of the probe is shown in Fig. 8. The probe consists of four stainless-steel tubes that are welded to a probe tip that both positions the tubes concentrically and allows the helium quench gas to flow approximately perpendicularly to the incoming hot gas flow. The tubes are sealed on the opposite end with O-rings located in three end caps that are compressed together. Such a design permits easy access to the inner tubes (a necessary convenience when the probe was being tested for

leaks). The end caps allow the entry of helium quench gas and the entry and exit of the cooling water. The probe was tested for leaks with both liquid water and nitrogen gas. Leaks found during testing were eliminated. Flow metering devices for the probe cooling and quench systems and the particle collection system are currently being assembled.

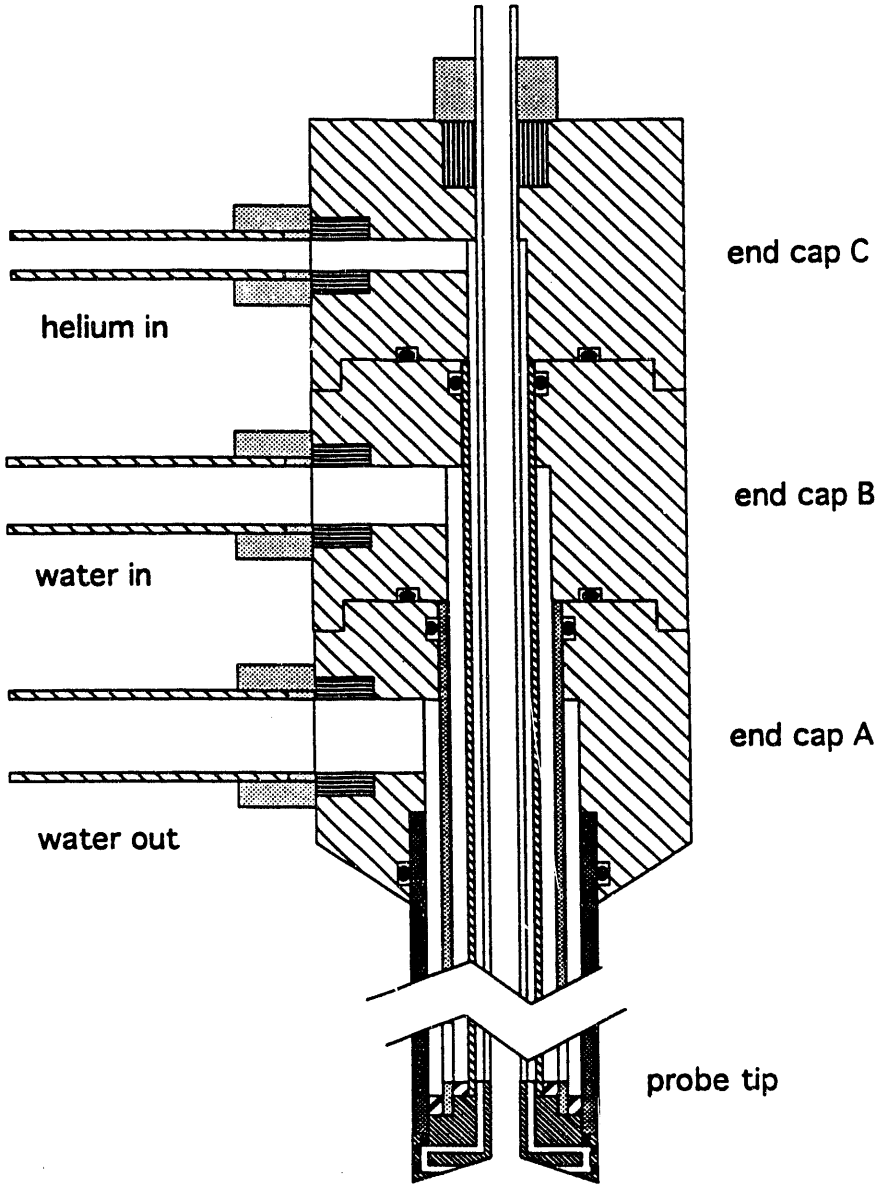

Figure 8. Drawing of the solids-sampling probe. It consists of four concentric stainless steel tubes of approximate length 51 cm held in place by three end caps containing ports for helium quench gas and cooling water. Helium quench gas is exhausted at the probe tip.

The components of the gas flow system for the laminar flow reactor, which include mass flow controllers and regulators, have arrived. The flow system will feed mixtures of methane, hydrogen, oxygen, and nitrogen to the burner that fuels the reactor at well-controlled rates. During the next quarter, flow rates of CH_4, H_2, O_2, and N_2 will be determined that yield post-flame gases having oxygen concentrations ranging from the parts-per-million level to about 30 mole-% and temperatures in the range 1300 to about 2000 K.

The design of the particle feeder was initiated; a drawing is shown in Fig. 9. The feeder is similar to that used in the Coal Char Combustion Laboratory at Sandia National Laboratories. The particle feeder consists of a glass syringe inserted into a sealed flask having a nozzle at the bottom for particle delivery to the reactor through a 0.16-cm diameter tube. The syringe plunger is advanced by a stepper motor translation mechanism. Nitrogen is fed into the top of the flask, and as particles fall from the syringe, the gas entrains the particles and carries them to the burner. Particle feeding rates of up to one gram per hour are possible. The feeder is being assembled and will be completed next quarter.

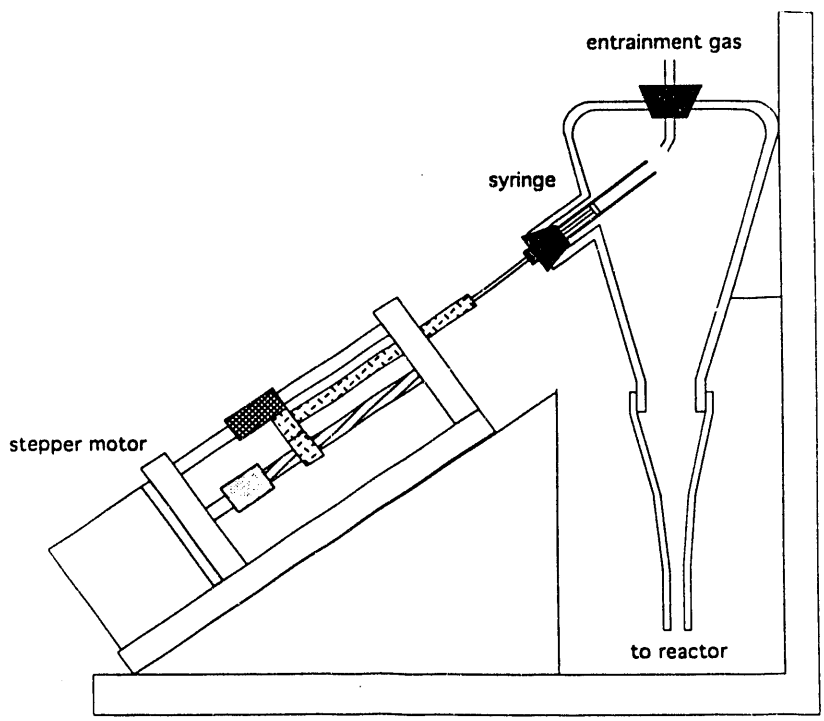

Figure 9. Drawing of the char particle feeder. Particles, loaded in a gas-tight syringe, are forced upward by the stepper motor translation mechanism and entrained by nitrogen gas as they fall.

PTGA: Modifications and Experiments

Modifications of PTGA

During the quarter, a gas blending and switching system was added to the pressurized thermogravimetric analyzer (PTGA) to allow particles to be heated at a specified rate to a desired temperature in an inert environment before switching to an oxidizing environment. The gas blending/switching system consists of a mass flow controller and two solenoid valves. The solenoid valves are on/off valves that can be programmed to switch their state at any time during an isotherm segment or at any temperature during a ramp segment. This new feature eliminates the need to quantify mass loss due to oxidation during the heating period - isothermal combustion experiments can be performed.

Testing of Modified System

Three identical experiments were performed to test the performance of the modified PTGA and to check the apparent weight change due to buoyancy against the calculated weight change for the conditions used. In the experiments, an inert quartz sample was subjected to a 10 °C/min temperature ramp to a 20-minute 200 °C isotherm, followed by another 10 °C/min ramp to a 30-minute 1000 °C isotherm. Five minutes into the 1000 °C isotherm, the reaction gas was switched from all nitrogen to 10% oxygen in nitrogen. Before the end of the 1000 °C isotherm, the reaction gas was switched back to all nitrogen. The results of the three experiments are plotted in Fig. 10, where both the weight loss curves and temperature profiles (numbered 1 through 3) are plotted versus time. The three temperature profiles fall on top of each other indicating that the temperature programming is repeatable. The three weight loss curves exhibit similar patterns of rises and falls except for the sudden (unexplained) weight loss exhibited during run 3, 10 minutes into the run. Note that the sudden weight loss is only 0.001 g, or about 0.1% of the sample weight, an inconsequential amount.

The effect of gas switching (from N_2 to the N_2/O_2 mixture at about the 125 minute mark, just subsequent to reaching the 1000 °C level) is evidenced by a sharp 0.0003 g spike with a rapid stabilization to a lower weight level (due to an increase in the density of N_2/O_2 mixture compared with the density of pure N_2). The small rise near the end of the isotherm is due to switching back to an all nitrogen environment.

The effect of buoyancy is evidenced by the apparent weight gain measured by the PTGA as the temperature is increased from 200 to 1000 °C. The weight gain of about 0.0003 g is in accord with the value of 0.0005 g calculated accounting for the effect of temperature on density.

These results suggest that buoyancy effects are insignificant and can be neglected in the planned combustion experiments at or near atmospheric pressures.

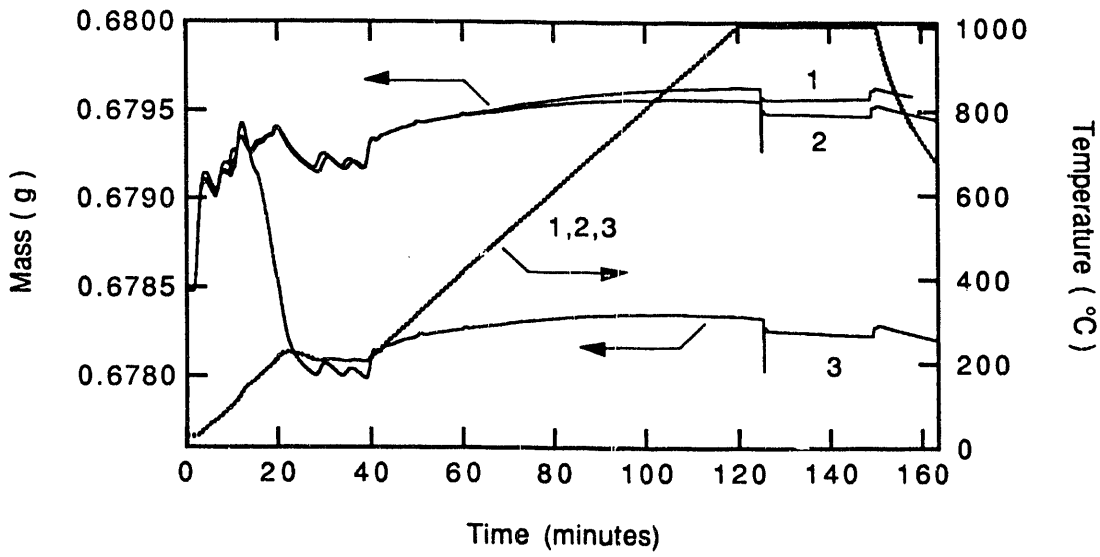

Figure 10. PTGA weight loss curves of three tests (numbered 1, 2, and 3) of an inert quartz sample subjected to the displayed temperature profiles. The plots show the reproducibility of the temperature profiles (dashed lines) and the negligible variation (< 0.001 g) of the weight loss curves (solid lines).

Devolatilization and Char Oxidation Experiments

Porous char (having 28% porosity) and non-porous char (made with no carbon black or lycopodium additives) were subjected to the same temperature and gas switching program used in the above performance tests. The temperature profile and mass loss curves are plotted in Fig. 11. Three regions are labeled: a region of heating in nitrogen to 200 °C during which water is lost; a region of devolatilization in nitrogen as temperature is ramped from 200 °C to 1000 °C; and a region of oxidation in a 10%/90% O_2/N_2 environment at 1000 °C. The water loss amounts to approximately 1% of the weight of the char. The mass loss that becomes appreciable near 550 °C is due to the release of volatiles from the char. The work of Senior (1984) indicates that the synthetic chars cured at 550 °C contain about 10% hydrogen and oxygen. These are probably released from the carbonaceous matrix as light gases, possibly CH_4, C_2H_2, H_2, CO_2, and CO. The difference in the volatile yields for the porous and non-porous chars is due to the fact that the carbon black and lycopodium added to the polymer mixture to produce a porous structure contain essentially no volatile matter. The difference in the volatile yields are consistent with the difference calculated using the carbon black-to-polymer (1:3) and lycopodium-to-polymer (1:4) ratios used in

preparing the char and assuming that the weight of any lycopodium residue after evaporation is negligible.

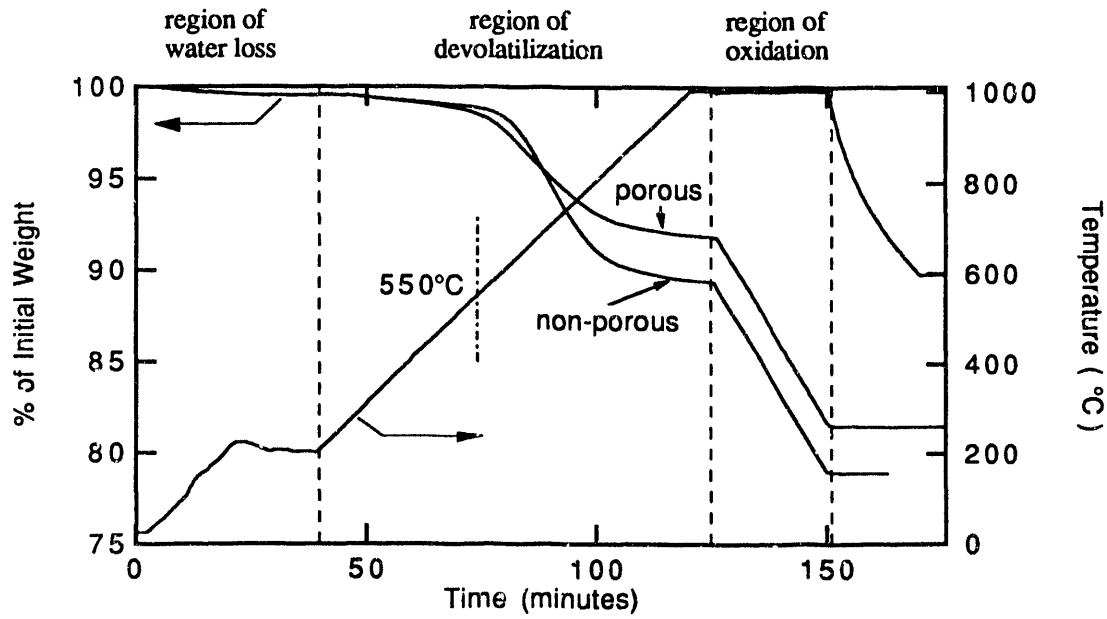

Figure 11. PTGA weight loss curves of porous and non-porous synthetic chars subjected to shown temperature profile. During heatup the environment was nitrogen. At five minutes into the 1000 °C isotherm, oxygen was added at about 10% of total reaction gas.

The mass loss during oxidation in a 10%/90% N_2/O_2 mixture at 1000 °C is observed to occur at the same rate for the two chars, as evidenced by the similar slopes of the two weight loss curves. This illustrates that for the conditions used, the overall particle burning rates were limited by the intrinsic chemical reactivity of the particle material and not by any mass transport effects. Since the non-porous char was produced without any lycopodium additive, it contains no lycopodium residue and hence, is free of the nodules discussed in reference to Fig. 7 (if these nodules are in deed due to evaporation of the lycopodium spore). The similarity in the mass loss rates suggests that either the nodules were eliminated during heat treatment at temperatures greater than 550 °C or the weight of the nodules is insignificant in comparison to the weight of the char.

PLANS FOR NEXT QUARTER

- Chars having porosities near 75% will be produced and characterized.

- Chars produced at a curing temperature of about 1000 °C will be examined to determine if their volatile matter content is lower than that of chars produced at 550 °C. The high-temperature chars will also be examined for the presence of nodules observed inside the pores.

- The particle feeder, reactant gas flow system, and the probe cooling and quench systems will be completed. Flow reactor environments will be characterized for temperature, composition, and velocity profiles for selected feed gas flow rates.

- Char combustion experiments in the flow reactor will be initiated to determine the conditions necessary for diffusion-limited combustion.

REFERENCES

Diaz, R. and Mitchell, R.E., "Char Particle Fragmentation and its Effect on Unburned Carbon During Pulverized Coal Combustion," DOE/PETC Quarterly Progress Report for September to December, 1992, DOE/PC/92528-1 (1993a)

Diaz, R. and Mitchell, R.E., "Char Particle Fragmentation and its Effect on Unburned Carbon During Pulverized Coal Combustion," DOE/PETC Quarterly Progress Report for January to March, 1993, DOE/PC/92528-1 (1993b)

Senior, C.L., Submicron Aerosol Formation During Combustion of Pulverized Coal, Ph.D. Thesis, California Institute of Technology (1984).

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