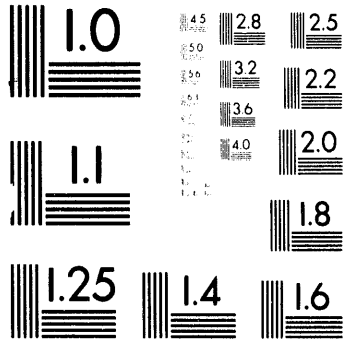
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CHAR PARTICLE FRAGMENTATION AND ITS EFFECT ON UNBURNED CARBON DURING PULVERIZED COAL COMBUSTION

Quarterly Report for the Period

July 1, 1993 - September 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

October 1993

HIGH TEMPERATURE GASDYNAMICS LABORATORY
Mechanical Engineering Department
Stanford University

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US/DOE Patent Clearance is not 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:	**July 1, 1993 - September 30, 1993**
REPORTED BY:	**Reginald E. Mitchell and Ruben Diaz**
	Phone: 415-725-2015

RESEARCH OBJECTIVES

This document is the fourth 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 July 1 to September 30, 1993. During this quarter, activities were undertaken in Tasks 1 and 2: additional synthetic chars in the porosity range 17% to 60% were produced and characterized, and chars were pyrolyzed in nitrogen in the thermogravimetric analyzer. The pyrolysis studies were aimed at determining the origin (and identity) of the nodules observed on the inside surfaces of the synthetic chars produced.

Highly magnified scanning electron micrographs of porous char revealed that the nodules seen in the macropores had a polygonal shape resembling the surface cells of lycopodium plant spores. These polygonal nodules are believed to be bits of cured polymer that were forced into the surface cells of the lycopodium spores during mixing and which remained after the lycopodium evaporated. Also seen on char with porosity greater than 50% were surface cellular structures that are believed to be indentations of the spore cell walls into the cured polymer. Based on these observations and the fact that chars with nodules exhibited the same mass loss rates as chars produced without the addition of lycopodium when burned under similar conditions (Diaz and Mitchell, 1993c), we conclude that the nodules are cured polymer having the same composition as the overall particle material.

Heat treatment of the raw materials used in producing synthetic chars showed that devolatilization of the lycopodium spores and of the furfuryl alcohol polymer was not complete until 1000 °C at the heating rates employed in the synthesis process. Thus, the chars that were cured at 550°C still contain a fair amount of volatile matter. Since our method of determining char reactivity via thermogravimetric analysis would be adversely affected if volatile material were present in our samples, we have modified our synthesis procedure to allow for two-hour curing times at 1000 °C. A tube furnace capable of temperatures up to 1200 °C was obtained for use in high temperature curing of the synthetic chars.

Other activities this quarter included the fabrication of a gas flow panel that combines the gas flow system for the laminar flow reactor and the quench and coolant systems for the solids sampling probe. A particle feeder capable of feeding char to the reactor at a nominal rate of one gram per hour was completed.

TASK 1: PRODUCTION AND CHARACTERIZATION OF SYNTHETIC CHARS

Char Production

In the previous quarterly (Diaz and Mitchell, 1993c), a range of 17% to 60% was achieved in attainable particle porosities for synthetic chars produced from mixtures of furfuryl alcohol polymer, carbon black, and lycopodium plant spores. Production of synthetic chars having porosities within this range for use in fragmentation experiments was continued this quarter. In addition, higher porosity levels were attempted by increasing the amount of lycopodium beyond the 67 wt-% lycopodium level used to produce the 60% porosity chars. The weight percents lycopodium used in the synthesis mixtures were 25%, 30% and 75%. To obtain pulverized particles in the desired 75-125 μm size range, chars produced with wt-% lycopodium levels below 50% were mechanically ground, while those chars produced with higher lycopodium contents, were ground with a mortar and pestle. As reported earlier (Diaz and Mitchell, 1993b), our mechanical grinding technique is too vigorous for the high-porosity char, producing many fragments with diameters less than 75 μm and few particles in the desired size range.

All synthetic char particles produced to date, underwent a prescribed curing program that ended with heating at 550 °C for one hour (Diaz and Mitchell, 1993a). During experiments with a thermogravimetric analyzer (TGA), it was found that the synthetic char produced still had up to 10% (by weight) of volatiles remaining after the 550 °C curing (Diaz and Mitchell, 1993c). TGA experiments at 1000°C (discussed below) indicate that curing at this temperature should yield a volatile-free material. Our char synthesis procedure will now include an additional curing step -- heating at 1000 °C. To perform the additional stage of high-temperature curing, a tube furnace capable of achieving temperatures of 1200 °C was obtained.

Char Characterization

Using the procedures outlined in an earlier quarterly report (Diaz and Mitchell, 1993b), the bulk and apparent densities and the porosities of the chars produced this quarter were determined; values are displayed in Table 1. Based on our experimentally-derived curve relating lycopodium content to char particle porosity (Diaz and Mitchell, 1993c), measured porosity values for the chars made with 25% and 33% lycopodium fall within 7% of the values predicted using the curve. The char produced with 75 wt-% lycopodium was expected to have a porosity of 65%, rather than the measured value of 56%. We believe that the measured value is too low and that particles are likely

to have a porosity near 65% for the following reason: the high-porosity particles are so fragile that they readily fragment during our determination of apparent density, impacting the value we use for a bed void fraction. In addition, we find that with these high-porosity fragile chars, it is difficult to obtain a narrow size distribution because of attrition during the sieving process. Figure 1 shows the size distributions for particles of the 25 wt-% and 75 wt-% lycopodium chars. Most of the particles for the 25 wt-% char fall within about 70 μm and 130 μm (as expected from sieving with 75 and 125 μm sieves), while the particles for the 75 wt-% char have a large number of particles less than 75 μm in diameter.

The generation of fragments impacts the value of the bed void fraction, which in turn affects the values calculated for apparent density and porosity. Experiments with particles in the 75 to 125 μm size range yield a bed void fraction of 0.39 (which we use in our calculations). Significantly smaller particles would decrease this value. A bed void fraction of 0.22 would yield an apparent density of 0.55 g/cc and a porosity of 65% for the 75 wt-% lycopodium char.

These findings indicate that with the high-porosity chars, assessing the consequences of fragmentation during combustion may prove to be difficult. A significant amount of fragmentation will occur when the material is fed to the reactor. Attributing the extent of fragmentation observed in samples extracted from the flow reactor to combustion phenomena may lead to erroneous conclusions concerning the impact of combustion on particle fragmentation.

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) %
25	0.67	1.10	30
33	0.62	1.02	35
75	0.43	0.70	56

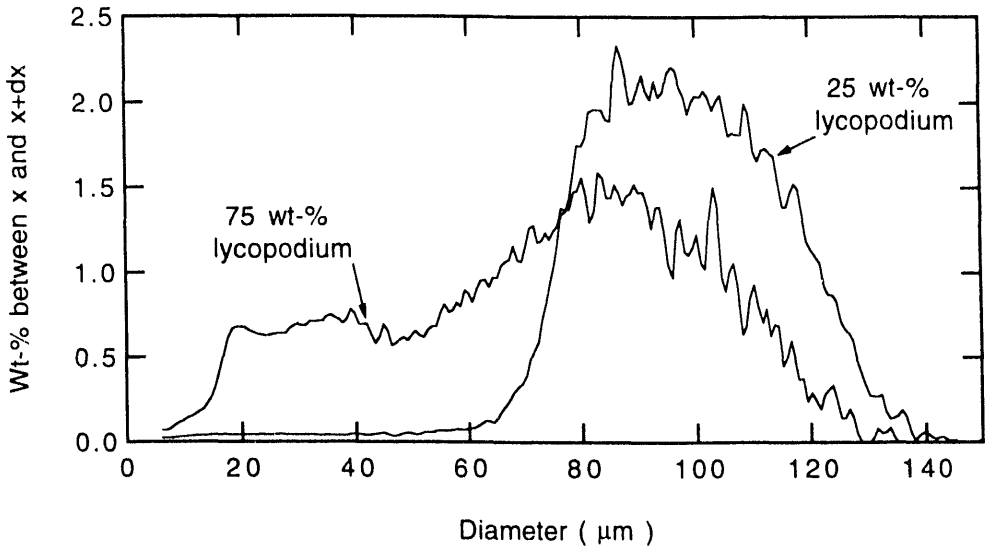

Figure 1. Weight Percent of particles having diameters between x and x+dx versus diameter for two batches of char made with different lycopodium contents and size classified for a nominal size range of 75 - 125 μm.

Scanning Electron Micrographs of Synthetic Chars and Lycopodium Spores

In our investigation of the nodules observed in the pores of the synthetic char produced, char particles were subjected to a higher curing temperature than used previously (the original procedure was to cure at 550 °C for one hour). If the nodules were residue from lycopodium evaporation, higher temperature curing would drive off the residue. A sample of porous char was heated in a nitrogen environment at 1000 °C for two hours. Figure 2 is a magnified scanning electron micrograph of a typical pore of a 30%-porosity char particle that had undergone the additional curing. The highly magnified image of the particle shows that the high-temperature heat treatment did not remove the nodules. It also shows that the particles are not completely spherical and have a finite number of sides. These polygonal shapes resemble the cells found on the surface of reticulate-type lycopodium plant spores (Thomas, *et al.*, 1991). Figure 3 shows a micrograph of several lycopodium spores having the surface polygonal cell structure. Because the nodules were not removed after the high-temperature heat treatment and because the nodules are shaped like the spore surface cells, it is believed that the nodules are cured polymer that had been forced into the cells during mixing. During the 550 °C, the lycopodium spores evaporated leaving behind the polygonal-shaped cured polymer nodules.

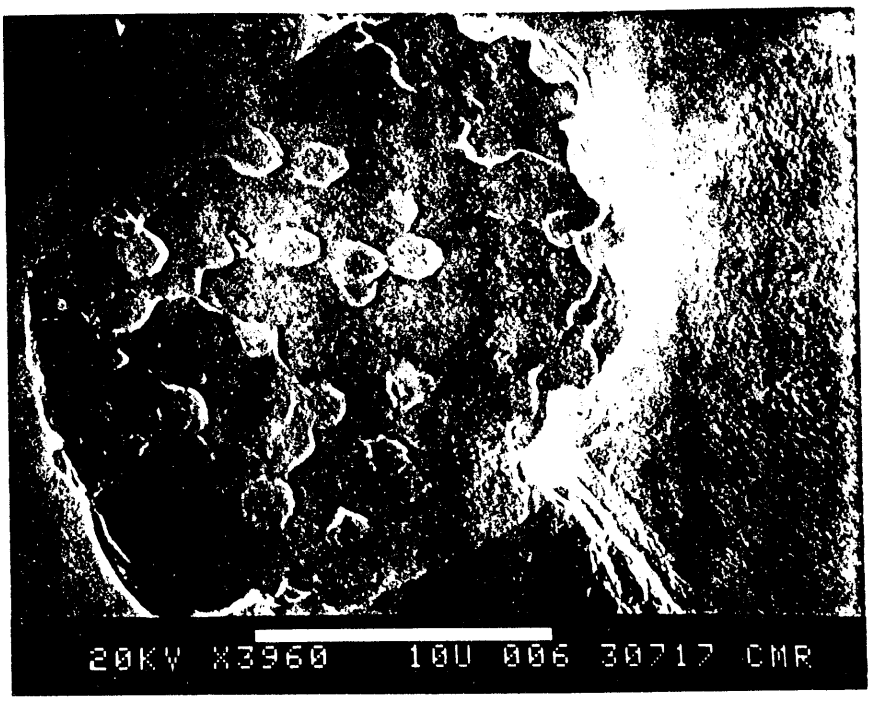

Figure 2. 3960X magnification SEM photograph of a synthetic char particle with 30% porosity subjected to 2 hours of heating in nitrogen at 1000 °C. The bold white line represents 10 µm.

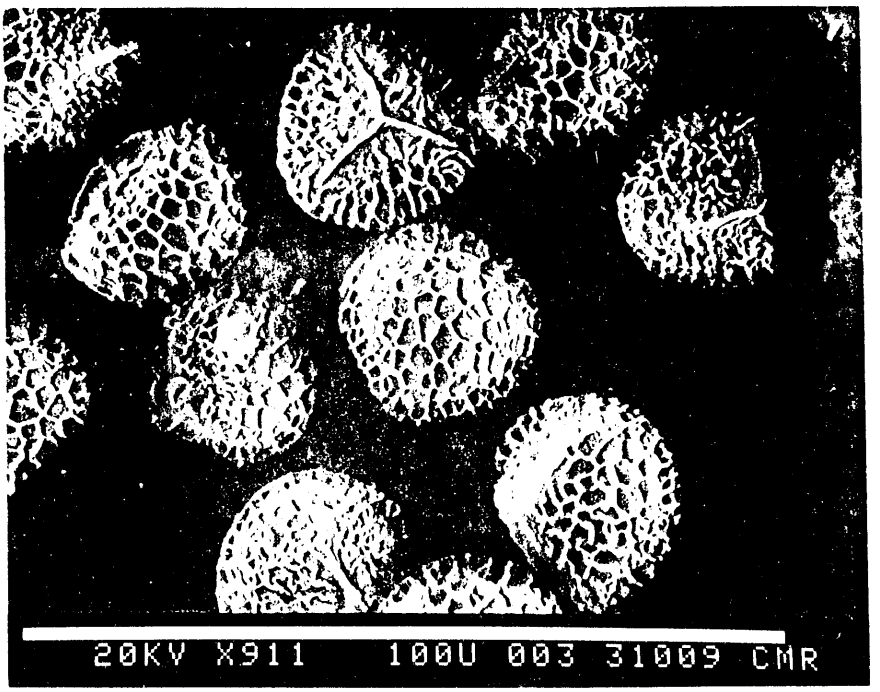

Figure 3. 911X magnification SEM photograph of lycopodium spores. The bold white line represents 100 µm.

Close examination of particles with porosities greater than 50% revealed that these particles exhibited the cellular structure of the lycopodium spore. Figure 4 shows a single pore of a 55% porosity char particle that has the cellular features on its surface. The cellular structure is believed to be indentations into the cured polymer caused by the walls of the spore cells. Because both the nodules and the cellular features are associated with the bulk synthetic char and not another material, such structures should not affect our interpretation of weight loss results.

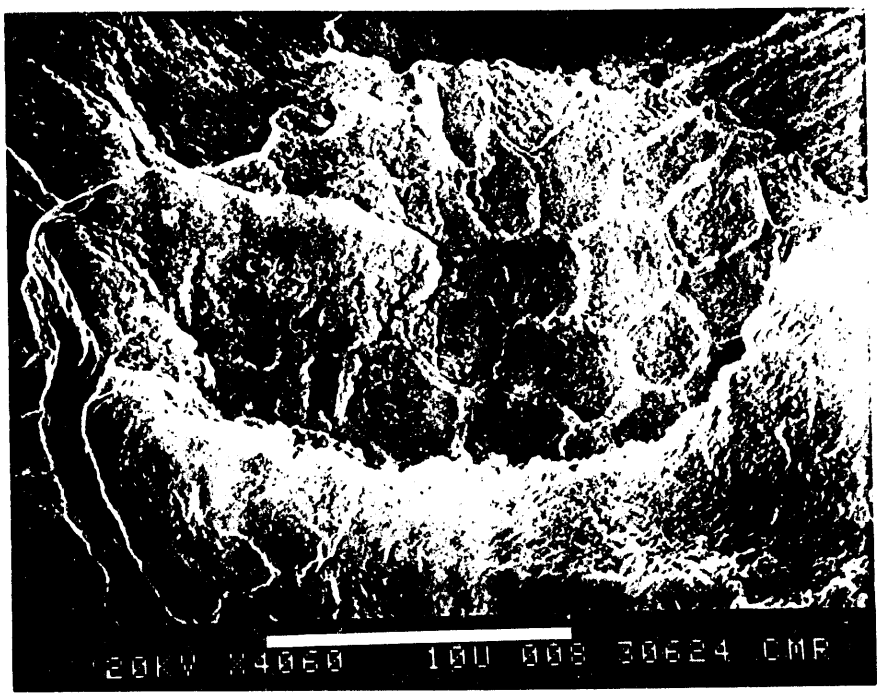

Figure 4. 4060X magnification SEM photograph of a synthetic char particle with 55% porosity. The bold white line represents 10 μm.

TASK 2: BASELINE CHAR COMBUSTION EXPERIMENTS

Laminar Flow Reactor

A flow panel that integrates all components of the gas flow system for the laminar flow reactor as well as the quench and coolant systems for the solids sampling probe has been completed. All gas flow lines have been connected and leak checked. The particle feeder, sketched in the previous quarterly report, has been assembled and will soon be tested. It consists

of a glass syringe inserted into a specially made flask whose outer rim had been reduced to 5 mm to allow easier delivery of particles through the central 2 mm particle feeder tube within the laminar burner. As the syringe plunger is advanced by a stepper motor translation mechanism, particles fall from the syringe and are entrained toward the burner by nitrogen gas. The laminar burner has been positioned onto a traverse mechanism. Testing of the entire system will be initiated next quarter.

TGA Experiments

Devolatilization and Oxidation of Synthetic Char and the Raw Materials used to Produce Char

The objectives of these TGA experiments were to verify that additional curing at 1000 °C removes most of the volatiles from the synthetic char and to confirm our hypothesis as to what happens during the curing procedure to the individual raw materials (polymer, lycopodium, and carbon black) used to produce the chars. We believe that all lycopodium material is removed during the 550 °C curing while most of the carbon black remains. Thus, we believe that the polymer is the origin of the volatiles that are released during char particle heatup beyond 550 °C.

To verify that additional curing at 1000 °C removes all the volatiles, a 35% porosity char that underwent curing at 1000 °C for two hours was subjected to the TGA temperature program (heatup in nitrogen from room temperature to 1000 °C, followed by oxidation in 10% O_2 in N_2) indicated in Fig. 5. Weight loss curves of this char and of a char that only underwent curing at 550 °C are also shown. The data indicate that during heatup, the char cured at 1000 °C lost less weight than the char cured at 550 °C. The percentage volatile content is determined to be about 0.7% for the 1000 °C char and 5.5% for the 550 °C char when the initial weight loss of 0.6% is attributed to moisture. The identical weight loss rates of the cured materials is evidenced by the identical slopes in the weight loss curves during the oxidation phase of the experiments.

In order to confirm our hypothesis on the outcome of the individual raw materials during the curing procedure, the individual materials were subjected to the curing program used in the char synthesis procedure (Diaz and Mitchell, 1993a). The curing program includes heating in an inert environment at 125 °C for six hours, 200 °C for ten hours, and 550 °C for one hour. An additional curing step, heating at 1000 °C for two hours, was included in these experiments. The first two curing stages were conducted within a vacuum oven while the final two stages were performed within the thermogravimetric analyzer.

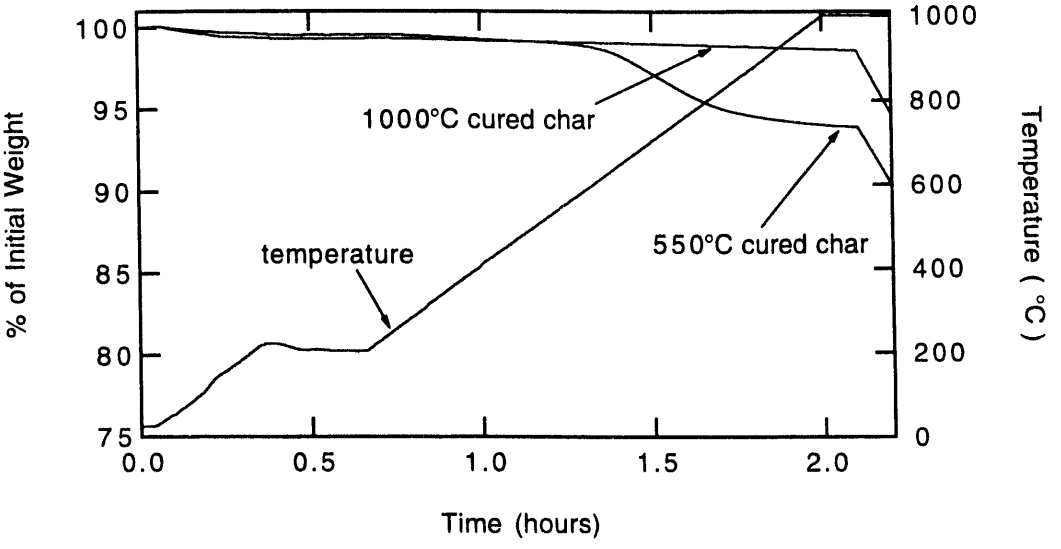

Figure 5. TGA weight loss curves of two 35% porosity chars subjected to shown temperature profile. One of the chars underwent additional curing at 1000 °C before the experiment. During heatup the environment was nitrogen. At five minutes into the 1000 °C isotherm, oxygen was added at about 10% of total reaction gas.

The experiments were performed with two samples of each of the raw materials. Since the differences in the measured weight losses for the two samples at each stage of heating were negligible, it can be concluded that the composition of both samples of each raw material was similar and that experiments were repeatable. The temperature profile and mass loss curves for the raw materials are plotted in Fig. 6. It is observed that the weight of the carbon black is essentially constant throughout the program while the weight of the cured polymer drops approximately 35% during the heatup to 550 °C. The cured polymer experiences an additional 5% weight loss during heatup to 1000 °C, which is due to volatiles remaining within the polymer. These observations were expected; however, the behavior of the lycopodium was not. We expected the lycopodium to be completely evaporated when heated to these high temperatures. Instead, we find that about 17% of lycopodium residue remains after heating to 1000 °C.

The final percentage weight loss levels attained, taking into account weight loss observed during the curing at 125 °C and 200 °C within the vacuum oven, were: 2.7% for the carbon black, 49.1% for the cured polymer, and 84.9% for the lycopodium spores. The lycopodium results show that up to 15% of the initial lycopodium mass added to the polymer/carbon black

mixture before curing remains within the synthetic char after the three stages of curing. Using the weight loss values of the three materials, it is calculated that the synthetic char produced with 67 wt-% lycopodium contains about 26% (by weight) lycopodium residue after the curing process. Because of this, we expect for the mass loss rate of the synthetic char during oxidation to depend on the rates of oxidation of the polymer and the lycopodium.

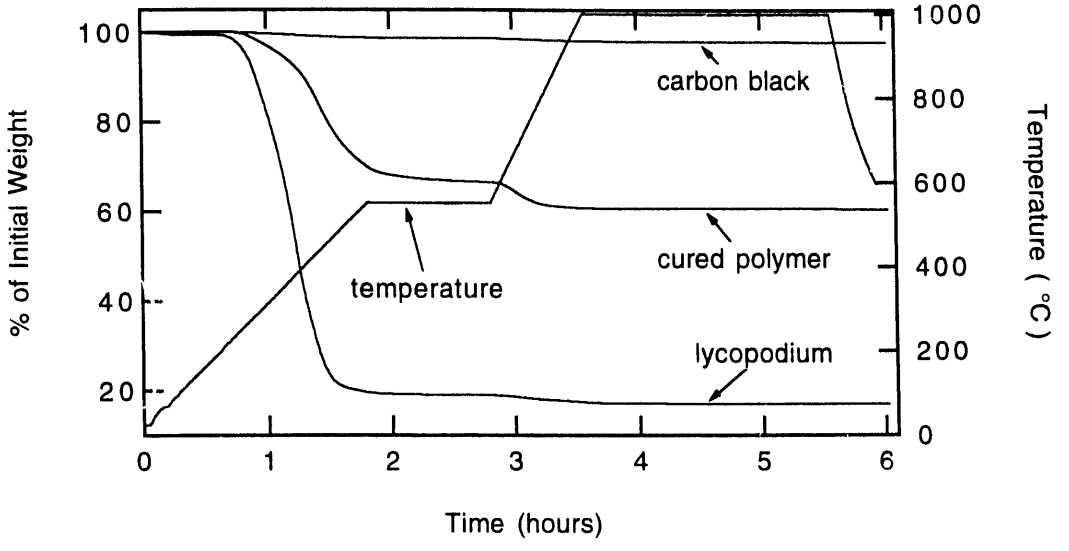

Figure 6. TGA weight loss curves of the raw materials used to produce synthetic chars subjected to the shown temperature profile. The environment in all cases was nitrogen.

As a first step in assessing the effects of the residual lycopodium, the lycopodium material remaining after the three heat treatments was again heated to 1000 °C in nitrogen and then oxidized for one hour in 10% O_2 in N_2. The weight loss curve and the temperature profile are shown in Fig. 7, where the dotted lines mark the regions where oxygen is present. During heatup there is about a 5 wt-% drop due to moisture. Within an oxidizing environment, the residual lycopodium material loses over 80% of its weight before achieving a steady state weight of about 8 wt-%. This clearly shows that the remaining material is ash. This ash accounts for 1.2% of the initial untreated lycopodium mass, a level that is in agreement with Thomas *et al.* (1991) value of 1.1%.

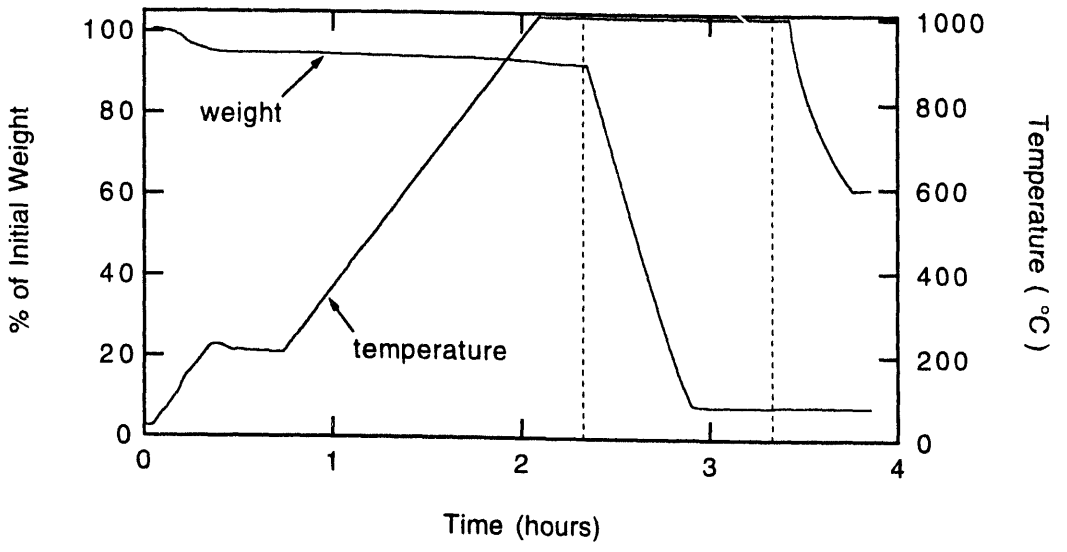

Figure 7. TGA weight loss curve of the 15% (by weight) lycopodium material remaining from above mentioned heat treatments subjected to shown temperature profile. During heatup the environment was nitrogen. At five minutes into the 1000 °C isotherm, oxygen was added at about 10% of total reaction gas.

PLANS FOR NEXT QUARTER

- Flow reactor environments will be characterized for temperature, composition, and velocity profiles for selected feed gas flow rates.

- 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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