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

Quarterly Report for the Period

January 1, 1995 - March 31, 1995

Grant DE-FG22-92PC92528

Prepared for

THE UNITED STATES DEPARTMENT OF ENERGY

**James Hickerson
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Pittsburgh, PA 15236**

Submitted by

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August 1995

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August 1995

High Temperature Gasdynamics Laboratory
Department of Mechanical Engineering
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COMBUSTION

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Stanford University

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RESEARCH OBJECTIVES

This document is the tenth quarterly status report of work on a project concerned with the fragmentation of char particles during pulverized coal combustion 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 loss rates during pulverized coal combustion. 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. Results with the synthetic chars are used to define parameters that appear in the char oxidation-fragmentation model being developed. The model is validated by comparing predicted mass loss and fragmentation rates with those measured during combustion tests with real coal chars.

The overall objectives of the project are: (i) to characterize fragmentation events as a function of combustion environment, (ii) to characterize fragmentation with respect to particle porosity and mineral loadings, (iii) to assess overall mass loss rates with respect to particle fragmentation, and (iv) to quantify the impact of fragmentation on 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 ranging from about 16% to 60% 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 sampling 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. Partially reacted chars will be extracted from the flow reactor at specified residence times and extents of mass loss and particle size distributions will be determined.

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 oxidation-fragmentation model that describes the results of Task 3 experiments. The model will be capable of accurately predicting overall char mass loss and significant fragmentation events in gaseous environments typical of pulverized coal combustors. With the model, the extent to which fragments might extinguish and hence, contributes to unburned carbon in ash can be predicted.

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TABLE OF CONTENTS

RESEARCH OBJECTIVES	i
TECHNICAL PROGRESS DURING THIS QUARTER	1
Summary	1
Task 3. Char Fragmentation Studies.....	2
Experimental Reproducibility	2
Sampling-Induced Fragmentation	4
Task 4. Fragmentation Modelling	7
Modification of the Particle Population Model.....	7
Determination of Fragmentation and Burning Rate Parameters.....	15
CONCLUSIONS OF THIS QUARTER'S WORK.....	18
PLANS FOR NEXT QUARTER	20
REFERENCES.....	20
COMMENT FROM THE PI.....	21
APPENDIX.....	22

TECHNICAL PROGRESS DURING THIS QUARTER

SUMMARY

The information reported is for the period January 1 to March 31, 1995. During this period, activities were undertaken in Tasks 3 and 4 of the research project. Char samples were extracted from the flow reactor at selected residence times and analyzed to determine particle size distributions and the particle population model was modified to allow for the effects of both CO and CO₂ as reaction products and for Stefan flow in the boundary layers surrounding particles. The model was further modified to include variations in particle temperature with size. Also during this period, a procedure for analyzing experimental data was formalized.

In Tasks 3 activities, the degree of experimental reproducibility was assessed by comparing data obtained in different runs. Duplicate tests indicate good experimental repeatability. The cumulative number size distributions of char samples extracted 117 ms after injection into a 12 mole-% reactor environment at nominally 1500 K were essentially the same. The number of particles per micron for particle diameters greater than about 10 μm were also similar. These results indicate that meaningful and reliable rate parameters can be determined from analysis of the experimental data.

In other Task 3 activities, the extent of fragmentation caused by the sampling process was assessed, this time using a char whose initial porosity was about 60%. Results support the conclusions reached previously when a 16% porosity char was tested (see Diaz and Mitchell, 1994a). It was observed that the particle collection system causes attrition-type fragmentation, producing a few fragments as large as 10 μm in size but most fragments less than about 5 μm in size. These results further support our contention that we can distinguish clearly between sampling-induced fragmentation and the percolation-type fragmentation that occurs during the char oxidation process.

In Task 4 activities, the particle population model was modified to allow for Zone II type burning, *i. e.*, burning at rates controlled by the combined effects of pore diffusion and the intrinsic chemical reactivity of the carbonaceous particle material. Modifications were also made to allow for both CO and CO₂ as products of the heterogeneous char oxidation reaction and for Stefan flow in the boundary layers surrounding particles, a necessary condition when CO is a reaction product. In addition, the model was modified to allow for variations in particle temperature with size. The particle energy balance is used to calculate particle temperature, assuming gas and particle to be in thermal equilibrium. Heat generated within the particle due to exothermic char oxidation reactions is balanced by heat loss from the particle's outer surface via conduction, convection, and radiation.

In other Task 4 activities, we formalized our data reduction process. A procedure for using measured particle size distributions and weight loss data to determine parameters in the particle population model was developed. Details of activities performed during this reporting period are discussed in the sections that follow.

TASK 3: CHAR FRAGMENTATION STUDIES

Experimental Reproducibility

Tests were run to determine the extent to which various experiments could be duplicated so that confidence limits could be placed on our results. Particles in the 75 to 90 μm size range of a synthetic char having an initial porosity of 60% and an apparent density of 0.62 g/cc were injected into a flow reactor environment having 12 mole-% oxygen. Temperatures along the reactor centerline ranged from 1550 K near the reactor inlet to 1450 K at the 25.4 cm height in the reactor where particles were extracted. The mean particle residence time to this height was about 117 ms. The size distributions of the partially reacted chars were measured using a Coulter Multisizer with an orifice tube diameter of 280 μm , sufficient to measure particle diameters in the range 6 to 170 μm . The lower limit of size measurement is consistent with the "2% of orifice diameter limit" set by the manufacturer. Tests have indicated that a lower limit of 4% of orifice diameter may be more accurate (Ghosal, 1993). We employ the 2% lower limit, realizing increased error in the numbers of particles distributed in the 6 to 10 μm size range.

Figures 1 and 2 show the size distributions obtained for two runs taken about a week apart. Figure 1 shows the cumulative number percentage of particles having diameters greater than 10 μm and less than the specified diameter x and Fig. 2 shows the percentage number of particles per micron (the number of particles in each of the 0.71 μm Coulter Multisizer bin-widths divided by the total number of particles having diameters greater than 10 μm). Agreement is quite good, suggesting that burning-induced fragmentation and the fragmentation that occurred as particles were being extracted from the flow reactor are nearly the same for the two runs. The degree of reproducibility illustrated indicates that the data can be used to derive meaningful rate parameters.

Figure 2 shows that the partially reacted char has a bimodal particle size distribution with a large peak in the range 0 to 10 μm and a smaller peak at about 65 μm . The feed char had a similar bimodal size distribution but the small peak was near 90 μm , in accord with the sieve trays used for size classification. The data indicate that the mean size of char particles greater than 10 μm shifted from about 90 μm to 65 μm during the 117 ms residence time in the flow reactor as a result of burning and fragmentation. An objective of this project is to develop a char combustion model

capable of predicting the particle size distribution at any particular residence time in the reactor given the gaseous conditions in the reactor and the size distribution of particles that entered it.

Figure 1. Cumulative number of particles having diameters greater than 10 μm . Distributions are for the char extracted at a residence time of ~ 117 ms in the flow reactor. The feed char had a porosity of 60%. The different curves denote results of experiments run one week apart.

Figure 2. Percentage number of particles per micron. Distributions are for the feed char and the char extracted at a residence time of ~ 117 ms in the flow reactor. The feed char had a porosity of 60%. The different curves for the partially reacted char denote results of experiments run about a week apart.

Sampling-Induced Fragmentation

In order to meet the objectives of this project, it is necessary to assure that fragmentation that occurs as a result of extracting char particles from the reactor can be distinguished from fragmentation that occurs as a result of char combustion. Earlier tests with a 16% porosity char (see Diaz and Mitchell, 1994a) indicated that the sampling process causes attrition-type fragmentation. The tests indicated that these low-porosity char particles are rather robust, tending not to break as they travel through the sampling probe and tube that connects the probe to the filter housing assembly (the connecting tube), and then impact the filter paper in the filter paper housing assembly. Relatively few (if any) fragments were produced in the 30 to 70 μm size range. Fragments as large as 10 μm were produced but there were relatively few of these in comparison to the large numbers of particles in the smaller size ranges.

The 16% porosity chars were produced without adding any spores of the lycopodium plant. The porous structure of this char is due to carbon black that was added during the curing process. The largest pores within the 16% porosity char are of the order 0.05 μm , and there are no large openings at the external surfaces of particles. These characteristics are likely reasons why the particles of this particular char did not break or shatter into large pieces as they collided with the walls of the probe and connecting tube or impacted the filter paper on which particles are collected.

Particle porosity increases during burning, and particles become more fragile as a result. It is expected that high-porosity chars may produce large attrited fragments during the sampling process since large pores exist at the outer surfaces of particles. Some particles may even break, especially when they impact the filter paper. The extent to which high-porosity chars might fragment during the sampling process was assessed by comparing the size distribution of a 60% porosity char that had passed through the sampling system with that of the feed char. Scanning electron micrographs reveal pore-openings as large as 16 μm on the outer surfaces of the 60% porosity char particles. A 12 mole-% O_2 , 1500 K gaseous environment was established in the flow reactor and particles in the 90 - 106 μm size range were injected along the reactor centerline. Particles were extracted as they emerged from the reactor's burner surface, *i.e.*, at a residence time of 0 ms in the flow reactor. Particle temperatures never exceeded about 450 K, the maximum temperature of the sampling probe quench gas (helium). No burning occurred in the sampling system.

Figures 3 and 4 show the numbers of particles counted in each of the 0.71 μm bin-widths associated with the 256 channels of the Coulter Multisizer. As noted, there are a large number of small particles in both the feed char (Fig. 3) and the probe char (Fig. 4). The feed char was not wet-sieved to remove the smaller particles.

Figure 3. Size distribution for the feed char. Presented are the numbers of particles counted in each of the $0.71 \mu\text{m}$ bin-widths associated with the 256 channels of the Coulter Multisizer. A total of 41,834 particles were monitored having diameters in the range 6 to $170 \mu\text{m}$.

Figure 4. Size distribution for the probe char. Presented are the numbers of particles counted in each of the $0.71 \mu\text{m}$ bin-widths associated with the 256 channels of the Coulter Multisizer. A total of 46,943 particles were monitored having diameters in the range 6 to $170 \mu\text{m}$.

Figure 5 shows the cumulative number distributions of the feed and extracted chars (labeled feed char and probe char, respectively), presented as the percent of particles having diameters greater than $6\text{ }\mu\text{m}$. The distributions are quite similar, the probe char having a larger number of particles with diameters less than about $10\text{ }\mu\text{m}$. For particles having diameters greater than $10\text{ }\mu\text{m}$, the percentage number of particles per micron (the number of particles in each of the $0.71\text{ }\mu\text{m}$ Coulter Multisizer bin-widths divided by the total number of particles in the $6\text{ to }170\text{ }\mu\text{m}$ size range) are about the same for both char samples, as noted in Fig. 6. Significant differences in the number of particles per micron begin to emerge only for particle diameters less than $8\text{ }\mu\text{m}$. The measurements clearly indicate that the sampling process causes particles to fragment and that fragments as large as $8\text{ to }10\text{ }\mu\text{m}$ are produced. The data support attrition-type fragmentation during the sampling process. This was verified with calculations using the particle population model, as illustrated below in the discussion of Task 4 activities.

Figure 5. Cumulative percent of the number of particles having diameters greater than $6\text{ }\mu\text{m}$. Distributions are for the feed char and the char extracted as particles first entered the flow reactor (labeled probe char).

As indicated in the previous quarterly report (Mitchell, 1995), burning-induced fragmentation is characterized as being percolative, where fragmenting particles produce fragments of all sizes smaller than the size of the fragmenting particle. Our results show that burning-induced fragmentation can be distinguished clearly from the attrition-type fragmentation that occurs during the sampling process. Our goal is to combine the measurements with the theoretical relations

derived below to determine how burning-induced fragmentation depends on char porosity and on the gaseous environments in which the char particles burn.

Figure 6. Percentage number of particles per micron. Distributions are for the feed char and the char extracted as particles first entered the flow reactor (labeled probe char). The feed char had a porosity of 60%.

TASK 4: FRAGMENTATION MODELLING

Modification of the Particle Population Model

In our description of the particle size distribution of particles at any time in the flow reactor, a number of discrete size classes (or size bins) are used (see Diaz and Mitchell, 1994). The upper cutoff of the i -th size bin is x_i and the lower cutoff is x_{i+1} . Thus, size bin i consists of particles as large as x_i and as small as x_{i+1} . The size distribution within a bin is assumed to be uniform, consequently, of the N_i particles in bin i at any time t , the fraction that have diameters between x and x_{i+1} is $(x - x_{i+1})/(x_i - x_{i+1})$, where x is between x_i and x_{i+1} .

In the particle population model, changes in the numbers of particles in each size bin as a result of combustion and fragmentation are described by the following set of differential equations:

$$\frac{dN_i}{dt} = -S_i N_i + \sum_{j=1}^i (b_{ij} S_j N_j) - C_i N_i + C_{i-1} N_{i-1} \quad i = 1, n \quad (C_0 = N_0 = 0) \quad (1)$$

The parameters S_i and C_i are the fragmentation and burning rate constants, respectively, and b_{ij} are the elements of the fragmentation progeny matrix, which depend upon the type of fragmentation (attrition, breakage, or percolation) assumed. The fragmentation rate constant is expressed as:

$$S_i = k x_i^\alpha \quad k > 0, \alpha > 0 \quad (2)$$

where the frequency of fragmentation events is given by the fragmentation rate coefficient k , and the relative tendency for a particle of size x_i to fragment is given by the fragmentation sensitivity parameter α . An additional fragmentation parameter β , is associated with the b_{ij} and controls the size distribution of fragments. If all fragments have the same apparent density, for $\beta = 3$, the fragmented mass is distributed equally in each of the size bins that can receive pieces of the fragmenting particle. As β is decreased, a larger fraction of the fragmented mass resides in larger particle sizes. [See Diaz and Mitchell (1994a), Mitchell (1995), or Mitchell, Diaz, and Ramdeen (1995) for a complete description of the fragmentation parameters used in the particle population model.] An expression for the burning rate constant is derived in the sections below.

Let $(dD/dt)_{x_{i+1}}$ denote the rate of change in diameter of a particle of size x_{i+1} as a result of burning. Consider the time increment δt during which the diameters of particles will be reduced. Assume that δt is so small that only particles with diameters near x_{i+1} (the lower cutoff of bin i) are reduced in size enough to leave bin i and enter bin $i+1$. The diameter of the largest particle in bin i that will burn enough during the time δt to reach the lower bin cutoff is given approximately by:

$$\left(\begin{array}{l} \text{largest size particle in} \\ \text{bin } i \text{ that will burn out} \\ \text{of the bin in time } \delta t \end{array} \right) \equiv x_{\max,i} \equiv x_{i+1} + \delta t \left| \frac{dD}{dt} \right|_{x_{i+1}} \quad (3)$$

This expression assumes that dD/dt is the same for all particles with diameters in the range $x_{\max,i}$ to x_{i+1} , a valid assumption since for such small δt , $x_{\max,i}$ is close to x_{i+1} . The fraction of particles that leave size bin i in the time increment is given by:

$$\left(\begin{array}{l} \text{fraction of particles} \\ \text{in bin } i \text{ at time } t \text{ that} \\ \text{burn out of the size bin} \\ \text{during the time } t + \delta t \end{array} \right) = \frac{x_{\max,i} - x_{i+1}}{x_i - x_{i+1}} \quad (4)$$

Employing the expression for $x_{\max,i}$ yields:

$$\left(\begin{array}{l} \text{fraction of particles} \\ \text{in bin } i \text{ at time } t \text{ that} \\ \text{burn out of the size bin} \\ \text{during the time } t + \delta t \end{array} \right) = \frac{(x_{i+1} + \delta t \left| \frac{dD}{dt} \right|_{x_{i+1}}) - x_{i+1}}{x_i - x_{i+1}} = \frac{\delta t \left| \frac{dD}{dt} \right|_{x_{i+1}}}{x_i - x_{i+1}} \quad (5)$$

The combustion rate constant in the particle population model is the above fraction per unit time; hence:

$$C_i \equiv \left(\frac{\text{fraction of particles in bin } i \text{ at time } t \text{ that burn out of the size bin per unit time}}{\text{fraction of particles in bin } i \text{ at time } t \text{ that burn out of the size bin during the time } t + \delta t} \right) = \frac{1}{\delta t} \left(\frac{\text{fraction of particles in bin } i \text{ at time } t \text{ that burn out of the size bin during the time } t + \delta t}{x_i - x_{i+1}} \right) = \frac{|dD/dt|_{x_{i+1}}}{x_i - x_{i+1}} \quad (6)$$

An expression for dD/dt in terms of the overall particle burning rate and initial particle size and apparent density is derived below.

Rate of Change of Particle Diameter due to Burning

The particle mass loss rate is expressed as follows:

$$\frac{dm}{dt} = - q \pi D^2 \quad (7)$$

where m is the mass of a particle of diameter D and q is the overall particle burning rate per unit external surface area. As the particle burns, both its diameter and apparent density change, depending upon the extent that oxygen penetrates the outer surface of the particle. We refer to such burning as mixed mode burning. For mixed mode burning, the particle mass, diameter, and apparent density are assumed to be related via the following two relations:

$$\left(\frac{m}{m_0} \right)^\alpha = \frac{\rho}{\rho_0} \quad \left(\frac{m}{m_0} \right)^\beta = \frac{D}{D_0} \quad (8a, b)$$

where the burning mode parameters α and β are determined from experiment and where the subscript 0 indicates properties of a char particle at some initial time. Theoretical justification for such power-law relations for porous carbon particles has been given by Essenhigh (1988). For spherical particles, α and β satisfy the relation $\alpha + 3\beta = 1$.

The derivative of Eq. 8b with respect to time yields the following:

$$\beta \left(\frac{m}{m_0} \right)^{\beta-1} \frac{d(m)}{dt(m_0)} = \frac{d(D)}{dt(D_0)} \quad (9)$$

Employing the relation $m_0 = \pi/6 (D_0)^3 \rho_0$ and combining Eqs. (7), (8b) and (9) yields the following expression for the rate of change of diameter due to burning.

$$\frac{dD}{dt} = - \frac{6\beta q}{\rho_0} \left(\frac{D}{D_0} \right)^{(3-1/\beta)} \quad (10)$$

This relation can be applied to particles in the i -th size bin and combined with Eq. (6) to yield the following expression for the combustion rate constant for bin i :

$$C_i = \frac{6\beta q}{\rho_0 (x_i - x_{i+1})} \left(\frac{x_{i+1}}{x_i} \right)^{(3-1/\beta)} \quad (11)$$

The initial apparent density of the char is assumed to be the same for all size classes of particles in the population.

The Char Combustion Model

The single-film model (Field, 1967) of a burning carbon sphere is used to describe a burning char particle. The primary assumption of the model is that there is no reaction in the boundary layer surrounding the particle. Hence, any CO formed at the particle surface is oxidized to CO₂ sufficiently far from the particle's surface that heat release associated with the homogeneous oxidation has no effect on particle temperatures. Mitchell *et al.* (1990b) used a computational model to examine the extent of conversion of CO to CO₂ in the boundary layers of char particles as large as 150 μm burning in gaseous environments containing 6 and 12 mole-% oxygen in the temperature range 1500 to 1700 K. Their detailed, finite-rate gas-phase chemistry calculations indicate that for a 100 μm diameter particle, the affect of gas-phase reaction in the boundary layer on the overall particle burning rate is relatively small for gas temperatures less than 1700 K. In 6 mole-% oxygen, essentially no CO oxidation occurs in the boundary layer surrounding the particle. At 1700 K in 12 mole-% oxygen, CO oxidation in the boundary layer increases the particle temperature by less than 25 K and decreases its burning rates by about 5% as a consequence of the formation of CO₂ via heat-releasing, oxygen-consuming reactions. The results of Mitchell *et al.* (1990b) support the use of the single-film model for particles as large as 150 μm burning in gaseous environments containing up to 12 mole-% oxygen at temperatures less than 1700 K.

In our analysis, the porous coal char particles are assumed to be spherical in shape and isothermal. Previous studies on the combustion of the chars of bituminous coals have shown that the isothermal particle assumption is valid when burning is under typical pulverized-coal combustor conditions.

Oxygen is transported to the outer surface of the particle by diffusion. Allowance is made for a fraction ψ of the carbon content of the particle (by weight) to be converted to CO₂ at the particle surface and a fraction $(1-\psi)$ to CO. Account is made for Stefan flow, the convective flow

emanating from the particle surface when there is a change in the number of moles upon reaction, as is the case when CO is formed.

The overall particle burning rate

The overall char-particle burning rate per unit external surface area is expressed as:

$$q = \left(\frac{k_d}{\gamma} \right) \ln \left[\frac{1 - \gamma P_s/P}{1 - \gamma P_g/P} \right] \quad (12)$$

where P_s and P_g denote the oxygen partial pressure at the particle surface and in the ambient gas, respectively, and P denotes the total pressure. The change in volume upon reaction per unit of oxygen present at the surface is γ and the mass transfer coefficient, k_d , is given by:

$$k_d = \frac{P M_C D_{ox} Sh}{D R' T_m v_o} \quad (13)$$

In this expression, M_C is the molecular weight of carbon, D_{ox} is the effective diffusion coefficient of oxygen through the other gases in the particle's boundary layer, Sh is the Sherwood number (taken as 2), R' is the gas constant, T_m is the mean temperature in the boundary layer, and v_o is the stoichiometric oxygen coefficient for reaction at the particle surface (mole O_2 consumed per mole carbon converted to CO or CO_2). When CO_2 is the sole heterogeneous reaction product (or when account is not made for Stefan flow), $\gamma = 0$ and the limiting form of Eq. (12) must be used. It can be shown that as $\gamma \rightarrow 0$, $q \rightarrow k_d (P_g - P_s)$.

The value of γ depends upon the moles of CO and CO_2 formed per mole of carbon consumed at the particle surface. Following the lead of others (Arthur, 1951; Rossberg, 1956; Field, 1967), the CO to CO_2 molar product ratio (MR) is assumed to depend upon temperature and is expressed as:

$$\frac{\text{moles CO}}{\text{moles CO}_2} \equiv MR = A_{CO} \exp(-E_{CO}/R T_p) \quad (14)$$

Values for A_{CO} and E_{CO} for selected coal chars examined are given by Hurt and Mitchell (1992). The fraction ψ of the carbon content of the particle converted to CO_2 is determined from the relation $\psi = 1/(1 + MR)$.

In terms of an apparent chemical reaction rate coefficient, k_s , the overall particle burning rate is expressed as:

$$q = k_s P_s^{1/2} \quad (15)$$

The apparent chemical reaction rate coefficient includes the combined effects of pore diffusion and the intrinsic chemical reactivity of the particle material. It is expressed in Arrhenius form as:

$$k_s = A_a \exp(-E_a/R T_p) \quad (16)$$

Equations (12) and (15) can be combined to yield the following expression that the overall particle burning rate must satisfy:

$$q = k_s \left\{ \frac{P}{\gamma} \left[1 - (1 - \gamma P_g / P) \exp\left(\frac{\gamma q}{k_d}\right) \right] \right\}^{1/2} \quad (17)$$

This is an implicit expression for q , which can be solved iteratively once the other parameters in the expression are specified.

Particle energy balance

Particles are assumed to attain a state of thermal equilibrium with the surrounding gas as they burn. As such, gas and particle temperatures satisfy the following particle energy balance equation:

$$q \Delta H = - \frac{Nu \lambda}{D} \frac{\kappa}{(1 - e^{\kappa})} (T_p - T_g) + \varepsilon \sigma (T_p^4 - T_w^4) \quad (18)$$

where

$$\kappa = \frac{\gamma c_{p,g} D v_o q}{M_C \lambda Nu} \quad (19)$$

The energy balance equation takes into account the energy generated at the particle surface as a consequence of chemical reaction, for conductive and convective energy losses from the particle to the surrounding gas, and for radiative energy losses from the particle's outer surface to any surrounding walls. In these equations, ΔH is the effective heat of reaction, Nu is the Nusselt number (taken as 2), λ and $c_{p,g}$ are the thermal conductivity and heat capacity, respectively, of the gas in the particle's boundary layer, ε is the emissivity of the particle (taken as 0.8), and σ is the Stefan-Boltzmann constant. T_p , T_g , and T_w represent the temperatures of the particle, the gas, and the reactor wall (taken as 500 K). Temperature-dependent properties in the particle's boundary layer are evaluated at the mean of the gas and particle temperatures. The only species deemed to be important in determining gas properties in the boundary layer are oxygen and nitrogen. Heat capacities of these species as a function of temperature are obtained by fitting data taken from the JANAF Thermochemical Tables (1970).

The values of v_o , γ , and ΔH depend upon the products of the heterogeneous carbon oxidation reaction. In terms of ψ , the fraction of carbon converted to CO_2 at the particle surface, the relations are:

$$v_o = 0.5(1 + \psi) \quad (20)$$

$$\gamma = \frac{\psi - 1}{\psi + 1} \quad (21)$$

$$\Delta H = \frac{1}{M_C} [(1 - \psi) \Delta H_1 + \psi \Delta H_2] \quad (22)$$

where ΔH_1 and ΔH_2 are the heats of reaction per mole carbon for the reactions $C + 1/2 O_2 \Rightarrow CO$ and $C + O_2 \Rightarrow CO_2$, respectively. The heats of reaction are evaluated at the particle temperature.

For specified gas temperature and oxygen partial pressure, Eqs. (12) to (22) constitute a set of equations that can be used to calculate the overall particle burning rate and temperature given the size of the particle, the parameters A_a and E_a for the apparent chemical reaction rate coefficient, and the parameters A_{CO} and E_{CO} for the CO to CO_2 product ratio. With these parameters, the following iterative procedure is used to determine q and T_p for specified T_g , P_g , and D :

- Step 1. Assume a particle temperature, T_p . The ambient temperature is a reasonable initial guess.
- Step 2. Evaluate all properties and parameters.
- Step 3. Solve Eq. (17) for the overall particle burning rate, q . Iteration is necessary. Use a fraction, say 50%, of the diffusion-limited rate with no Stefan flow ($q = k_d P_g$) as an initial guess.
- Step 4. Using the q determined, solve Eq. (18) for the particle temperature, T_p . Iteration is necessary. Neglect the convective/conductive term in the equation for an initial guess.
- Step 5. Compare the calculated particle temperature with the temperature assumed in Step 1. If they agree, (say, within 1 K of each other), the values of q and T_p satisfy the system of equations - the problem is solved. If they do not agree, assume a new value for T_p and repeat from Step 2. The temperature calculated in Step 4 is a good next guess.

Variations of particle temperature with size

Calculated temperatures of particles having diameters in the range 6 to 160 μm are shown in Fig. 7 when burning is in 6 and 12 mole-% oxygen (the balance, N_2) at ambient gas temperatures of 1500 and 1800 K. Calculations were made using rate parameters reported by Hurt

and Mitchell (1992) for the char of Pocahontas #3 coal, a low-volatile bituminous coal from West Virginia. Parameters for the chemical reaction rate coefficient are $A_a = 114 \text{ g}/(\text{cm}^2 \cdot \text{s} \cdot \text{atm}^{0.5})$ and $E_a = 30 \text{ kcal/mole}$ and parameters for the heterogeneous product ratio are $A_{CO} = 3 \cdot 10^8 \text{ mole-CO/mole-CO}_2$ and $E_{CO} = 60 \text{ kcal/mole}$. Pocahontas #3 coal char burns relatively slowly, at about one-third the burning rate of the char of a typical sub-bituminous coal. For example, in 6 mole-% oxygen at 1500 K, Pocahontas #3 coal char particles lose about 50% of their mass in 0.63 s whereas Pittsburgh #8 coal char particles lose 50% of their mass in about 0.19 s.

Figure 7. Variations in particle temperature with size for char particles burning in 6 and 12 mole-% oxygen (the balance, N_2) at 1500 and 1800 K. Burning rate parameters: $A_a = 114 \text{ g}/(\text{cm}^2 \cdot \text{s} \cdot \text{atm}^{0.5})$, $E_a = 30.0 \text{ kcal/mole}$, $A_{CO} = 3 \cdot 10^8 \text{ mole-CO/mole-CO}_2$, $E_{CO} = 60 \text{ kcal/mole}$. Surrounding walls are at 500 K.

The figure shows that variations in particle temperatures with size are more pronounced the higher the gas temperature and the higher the oxygen content of the ambient gas. In 6 mole-% oxygen (dashed lines in the figure), overall particle burning rates are relatively low at gas temperatures of 1500 and 1800 K and consequently, gas and particle temperatures are about the same for all particle sizes. When burning rates are sufficiently low, large particles can have temperatures slightly lower than the local gas temperature because of radiative energy losses to the surrounding walls (which were maintained at 500 K in the calculations). In 12 mole-% oxygen, particle burning rates are relatively high, yielding particle temperatures that exceed the local gas temperature. With the burning rate parameters for Pocahontas #3 coal char, the temperature of a

100 μm diameter particle exceeds that of the gas by 70 K when the gas temperature is 1500 K and by 155 K when the gas temperature is 1800 K. With the burning rate parameters for Pittsburgh #8 coal char (a faster burning char), a 100 μm diameter particle attains a temperature that exceeds that of the gas by about 215 K when the gas temperature is 1500 K and when it is 1800 K.

Determination of Fragmentation and Burning Rate Parameters

Particles extracted from the flow reactor include the combined effects of burning-induced fragmentation and probe-induced fragmentation. Our goal is to characterize burning-induced fragmentation by evaluating parameters in the particle population model that govern the frequency of fragmentation events (the parameter k), the tendency for particles of a given size to fragment (the parameter α), and the distribution of fragments (the parameter β). Burning-induced fragmentation parameters need to be adjusted to yield calculations that agree with "probe-free" size distributions. Our approach is to use the particle population model to characterize probe-induced attrition by determining probe fragmentation rate parameters: k_{probe} , α_{probe} , and β_{probe} . We will use these parameters to predict the impact of the sampling process on the "probe-free" size distributions.

In data analysis, the measured feed particle size distributions will be used as initial conditions when predicting the size distributions at specified residence times in the flow reactor, at say, 117 ms, the residence time at which the data presented in Figs. 1 and 2 were obtained. For these calculations, model parameters will correspond to those associated with burning-induced fragmentation, and are subject to adjustment. These calculated distributions will then be used as initial conditions when predicting the size distributions of particles that passed through the particle sampling system. For these calculations, model parameters will correspond to those associated with probe-induced fragmentation, and accordingly, specified as k_{probe} , α_{probe} , and β_{probe} . This approach is tantamount to using the particle population model to predict the sequential effects of burning-induced fragmentation followed by sampling-induced fragmentation. The size distribution calculated including probe-induced fragmentation will be compared with the measured size distribution on a percent number cumulative basis and on a number per micron basis for particles having diameters greater than 6 μm . Adjustments will be made to the burning-induced parameters until the best agreement is found between measured and calculated distributions.

Comparison of Particle Size Distributions

Burning-induced fragmentation parameters are determined by focusing only on particles in the measured size range, from about 6 to 160 μm . Although the particle population model is capable of predicting the numbers of particles having diameters smaller than 6 μm (presently, we employ a lower size limit of 0.55 μm in the model), we normalize the calculations by the total

number of particles having diameters in the range 6 to 160 μm and compare these normalized distributions with the measured ones. In actuality, the measured distributions are such normalized distributions. This approach differs from that we used previously in analyzing the 16% porosity char data (see Mitchell and Diaz, 1994a). In the earlier work, we determined the number of particles per micron as a function of size from the measurements and extrapolated the results to determine the numbers of particles per micron for sizes in the range 0.5 to 6 μm . Results were used to determine the numbers of particles in logarithmically-spaced size bins within the 0.5 to 6 μm size range. Next, modified cumulative distributions for particles having diameters greater than 0.5 μm for the "feed" and "probe" chars were calculated. Rate parameters in the model were adjusted to provide calculated distributions that agreed with these modified distributions. Our new approach is more direct and perhaps more accurate since only the measured size range of particles is considered when determining rate parameters.

Determination of k_{probe} , α_{probe} , and β_{probe}

The particle population model (see Diaz and Mitchell, 1994b) was used to characterize the fragmentation behavior of the 60% porosity char as it passed through the particle sampling system. The gas temperature was taken as 400 K, the average temperature of the gas inside the sampling probe, which consisted of about 67% helium (the quench gas) and 33% nitrogen (the carrier gas used in the particle feeder). The feed char size distribution represented in Figs. 3, 5, and 6 was used as the initial particle size distribution. The residence time in the sampling system (sampling probe, connecting tube, and filter paper housing assembly) was taken to be 171 ms, as discussed in the appendix. One hundred logarithmically-spaced size classes were used in the calculation with $x_i/x_{i+1} = 1.06$ and $x_n = 0.55 \mu\text{m}$, where x_n is the smallest particle size considered. The set of 100 differential equations describing the changes in the numbers of particles in each size class (Eq. 1) were solved using LSODE, a Runge-Kutta variable-step, ordinary differential equation solver developed by Radhakrishnan and Hindmarsh (1983).

The fragmentation parameters in the population balance model (k , α , and β) were adjusted to get agreement between the calculated size distribution and the size distribution measured for the probe char for particles in the 6 to 160 μm size range. The largest attrited particle sizes were taken to be 10% of the radii of the attriting particles. Thus, a 100 μm particle could produce fragments as large as 5 μm . This is consistent with the measurements presented in Figs. 5 and 6. As observed previously when analyzing the data of the 16% porosity probe char, adequate agreement between measurement and calculation could not be obtained when either breakage-type or percolation-type fragmentation was assumed (see Diaz and Mitchell, 1994a). The solid line in Fig. 8 shows the calculated cumulative number distribution when attrition-type fragmentation is assumed with $k_{probe} = 0.2 \mu\text{m}^{-1}\text{s}^{-1}$, $\alpha_{probe} = 1$, and $\beta_{probe} = 1$. Agreement between the

measured and calculated particle size distributions is quite good. Even the number of particles per micron is well predicted despite the fact that optimum parameters (those that minimize the differences between calculated and measured distributions) have not yet been determined.

These results indicate that sampling-induced fragmentation can be described to the extent needed to characterize accurately the fragmentation that occurs prior to the sampling process. The 16% and 60% porosity feed and probe char data discussed above will be augmented with data using a 30% porosity char to assess the extent to which these parameters vary with porosity and to provide a means for accurate interpolations and extrapolations, if necessary.

Figure 8. Measured and calculated cumulative number distributions of the char that passed through the sampling system.

Illustration of the impact of sampling-induced fragmentation

Figure 9 shows particle size distributions calculated using burning rate parameters for Pocahontas #3 coal char with constant-density burning in a 12 mole-% O_2 environment at 1500 K. Percolation-type fragmentation is assumed during combustion with $k = 0.01 \mu m^{-1} \cdot s^{-1}$, $\alpha = 1$, and $\beta = 3$. Three distributions are shown: the measured size distribution of the feed particles (open boxes), the calculated size distribution of particles at a residence time of 117 ms in the gaseous environment (solid line), and the calculated size distribution of particles after an additional 171 ms with all $C_i = 0$ (*i.e.*, no burning) and $k_{probe} = 0.2 \mu m^{-1} \cdot s^{-1}$, $\alpha_{probe} = 1$, and $\beta_{probe} = 1$ (dashed line). The distributions are for particles having diameters greater than 6 μm .

Figure 9. Cumulative number distributions for particles greater than $6\text{ }\mu\text{m}$ for the feed char and the char after burning in 12 mole-% oxygen at 1500 K for 117 ms. Calculations employ the burning rate parameters for Pocahontas #3 coal char and the following burning-induced fragmentation parameters for percolation: $k = 0.01\text{ }\mu\text{m}^{-1}\cdot\text{s}^{-1}$, $\alpha = 1$, and $\beta = 3$. The dashed line includes "sampling-induced" fragmentation.

Note that the sampling process barely changed the cumulative size distribution of particles having diameters greater than $6\text{ }\mu\text{m}$ at the 117 ms residence time. There were a large number of fragments less than $5\text{ }\mu\text{m}$ in size generated while sampling however. At this late time in the flow reactor, there are few particles with diameters large enough to produce attrited fragments as big as 8 to $10\text{ }\mu\text{m}$ (particles as large as $160\text{ }\mu\text{m}$ are required). This is evident in Fig. 10, which shows that there are hardly any particles with diameters greater than about $110\text{ }\mu\text{m}$ after 117 ms of burning and fragmenting.

CONCLUSIONS OF THIS QUARTER'S WORK

The sampling system causes particles to undergo attrition-type fragmentation with fragments as large as 10% of the radius of the attriting particle being formed. Since we are able to predict accurately the sampling-induced changes in the size distribution of particles having

diameters in the 6 to 170 μm size range, we will be able to characterize fragmentation that occurs as a result of char oxidation in the flow reactor.

The modified particle population balance model accounts more accurately for overall particle burning rates. Allowances for simultaneous CO and CO₂ formation at the surfaces of particles, Stefan flow in the boundary layers surrounding particles, and variations in particle temperature with size permit accurate characterization of the rates that particles burn out of selected size ranges.

The data reduction procedures outlined above will permit the determination of parameters in the particle population balance model that describe char fragmentation behavior in environments typical of practical pulverized coal combustors. Tests using chars differing in porosity and mineral matter content and composition will provide information needed to describe these parameters for the chars of real coals.

Figure 10. Number of particles per micron for particles greater than 6 μm for the feed char and the char after burning in 12 mole-% oxygen at 1500 K for 117 ms. Calculations employ the burning rate parameters for Pocahontas #3 coal char and the following burning-induced fragmentation parameters for percolation: $k = 0.01 \mu\text{m}^{-1}\cdot\text{s}^{-1}$, $\alpha = 1$, and $\beta = 3$. The dashed line includes "sampling-induced" fragmentation.

PLANS FOR NEXT QUARTER

During the next quarter, we will continue to obtain combustion data on synthetic chars burning in selected flow reactor environments. The data will be used to evaluate parameters that characterize the oxidation and fragmentation rates. Experiments will be aimed at determining how the fragmentation rate parameters vary with char porosity. Specific plans for next quarter include the following:

- Evaluate probe-induced fragmentation parameters using chars differing in porosity.
- Obtain additional mass loss and size distribution data on partially reacted chars. Use the data to evaluate burning and fragmentation parameters.
- Test chars differing in mineral content and composition and determine fragmentation parameters for each.

REFERENCES

- Arthur, J. (1951). *Trans. Faraday Soc.* **47**, 164.
- Diaz, R. and Mitchell, R. E. (1994a) "Char Particle Fragmentation and its Effect on Unburned Carbon During Pulverized Coal Combustion," DOE/PETC Quarterly Progress Report for April 1 to June 30, 1994, DOE/PC/92528-7.
- Diaz, R. and Mitchell, R. E. (1994b). "Char Particle Fragmentation and its Effect on Unburned Carbon During Pulverized Coal Combustion," DOE/PETC Quarterly Progress Report for January 1 to March 31, 1994, DOE/PC/92528-6.
- Essenhigh, R. H. (1988). *Twenty-Second Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh p. 89.
- Field, M. A., Gill, D. W., Morgan, B. B., and Hawksley, P. G. W. (1967). Combustion of Pulverized Coal, BCURA, Leatherhead, p. 186.
- Ghosal, Sarbjit (1993). "Optical Characterization of Coal Fly Ashes and Infrared Extinction Measurements on Ash Suspensions," Ph.D. Thesis, Mechanical Engineering Department, Stanford University.
- Hurt, Robert H. and Mitchell, Reginald E. (1992). *Twenty-Fourth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh p. 1243.
- JANAF (Joint Army, Navy, Air Force) Thermochemical Tables: Second Edition. (1970). (D. R. Stull and H. Prophet, Project Directors), National Standard Reference Data System (NSRDS) - NBS 37; also, JANAF Thermochemical Tables, (Prepared by the Dow Chemical Company, Midland Michigan), Distributed by the Clearing House for Federal, Scientific and Technical Information, PB 168-370 and addenda 1, 2, and 3.

Mitchell, R. E. (1990a). *Twenty-Third Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, p. 1297.

Mitchell, R. E. (1990b). *Twenty-Third Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, p. 1169.

Mitchell, Reginald E., Diaz, Ruben, and Ramdeen, Gayle. (1995). "The Effect of Porosity on Char Particle Fragmentation during Pulverized Coal Combustion." Paper No. 95S-116, Central and Western States Sections and The Mexican National Section of The International Combustion Institute and American Flame Research Committee Joint Technical Meeting, San Antonio, April 23-26.

Mitchell, R. E. (1995). "Char Particle Fragmentation and its Effect on Unburned Carbon During Pulverized Coal Combustion," DOE/PETC Quarterly Progress Report for October 1 to December 31, 1994, DOE/PC/92528-9.

Radhakrishnan, K. and Hindmarsh, A.C. (1983). "Description and Use of LSODE, the Livermore Solver for Ordinary Differential Equations", Lawrence Livermore National Laboratories, UCRL-ID-113855.

Rossberg, M. Z. (1956). *Electrochem.* **60**, 952.

COMMENTS FROM THE PI

The High Temperature Gasdynamics Laboratory is being brought into compliance with state and federal laws governing the use of toxic and flammable gases. In the process, the building is being structurally strengthened to prevent potential damage caused by earthquakes. Periodically, experiments in the laboratory are stopped as construction crews replace exhaust gas ventilation systems and perform other mechanical and electrical work throughout the building. The renovation is to take two years. No long-term delays are forecast, but one- to two-day delays are possible as water and electricity in the building are temporarily shutdown. Such delays have contributed to the lateness of this quarterly report.

Tests that were run during the months from January to March had to be repeated due to the fact that the pump used to extract gases from the flow reactor was found to be undersized. The char samples being extracted were not being quenched properly. This was realized only after the PI had students run replicate tests that had initially been run by the PI while at Sandia National Laboratories. It was not possible to obtain agreement with mass loss measurements that had been made in an identical flow reactor at Sandia. Essentially all tests that were run in January, February, and March were rerun in April and May. This is the primary reason for the lateness of this quarterly report.

Appendix

Determination of the Mean Particle Residence Time in the Solids Sampling System

In order to determine values of k_{probe} , α_{probe} , and β_{probe} that accurately describe fragmentation during sampling, it is necessary to specify the particle residence time in the sampling system. However, there is uncertainty in the value determined for the time it takes particles to travel through the system because of the unknown flow patterns in the filter paper housing assembly. Residence times in the sampling probe (12 ms) and the tube that connects the sampling probe to the filter housing assembly, the "connecting tube," (28 ms) are considered to be somewhat accurate, because the paths that particles take through these parts of the sampling system occupy essentially all the available volume. The paths that particles actually take in the hemispherically-shaped filter paper housing assembly are unknown, however. If the housing is assumed to be well-stirred, the mean gas residence time in the housing assembly is 232 ms, based on the total hemispherical volume and the measured volumetric flow rate through the sampling system. This is also a good estimate of the mean particle residence time in the housing if particles more or less follow the gas streamlines, thereby yielding a uniform dispersion of particles within the filter housing assembly. If particles take the more direct route discussed in the next paragraph from the end of the connecting tube (located at the center of the hemispherical dome) to the center portion of the filter paper (located at the base of the hemispherical housing), the mean particle residence time in the housing is about 31 ms.

Examination of the filter paper after several tests revealed that particles are almost uniformly distributed on the paper. The center portion of the paper is slightly less covered than the outer portion. We hypothesize that upon entering the filter paper housing assembly, most particles occupy the frustum-like volume between the top of the hemispherical dome (where they enter, emerging from the end of the connecting tube) and the less-covered center portion of the filter paper. When they hit the center portion of the paper, they bounce to the outer portion. It is expected that large particles may take this more direct route and small particles and fragments may follow gas streamlines and hence be uniform within the volume. Based on the volume of a frustum having a top surface defined by the cross-sectional area of the connecting tube and a bottom surface defined by the less-covered, center portion of the filter paper, the mean residence time in the housing filter is 31 ms.

Thus, residence times within the filter paper housing assembly could be as short as 31 ms for large particles and as long as 232 ms for small particles and fragments. Using an average value of ~132 ms for the residence time in the filter paper housing assembly, the total sampling system

residence time is taken as 171 ms. We will use this value in evaluating k_{probe} , α_{probe} , and β_{probe} and when simulating sampling effects when analyzing the data. The impact of the uncertainty in sampling system residence time on quantifying probe-induced fragmentation needs to be assessed.

[In our previous analysis of probe-induced fragmentation (Diaz and Mitchell, 1994a), the sampling system residence time was taken as 140 ms. Consequently, the "probe" fragmentation parameters reported for the 16% porosity char apply for that length of time in the sampling system. We intend to reanalyze the 16% porosity probe data in order to determine fragmentation rate parameters consistent with a sampling system residence time of 171 ms.]

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