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

Quarterly Report for the Period

April 1, 1995 - June 30, 1995

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Prepared for

THE UNITED STATES DEPARTMENT OF ENERGY

**James Hickerson
Project Officer
Pittsburgh Energy Technology Center
Pittsburgh, PA 15236**

Submitted by

Professor Reginald E. Mitchell

August 13, 1996

MASTER

**HIGH TEMPERATURE GASDYNAMICS LABORATORY
Mechanical Engineering Department
Stanford University**

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August 13, 1996

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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, 1995 - June 30, 1995
(work was actually performed over the extended period
April 1, 1995 - May 31, 1996)

REPORTED BY: Reginald E. Mitchell

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RESEARCH OBJECTIVES

This document is the eleventh quarterly status report of work on a project concerned with the fragmentation of char particles during pulverized coal combustion that was 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 allows 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 provides insight into causes of unburned carbon in the ash of coal-fired utility boilers and furnaces. Work was to be performed over the three-year period from September 1992 to September 1995. Because of student-related delays, the work period was extended about one year.

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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TECHNICAL PROGRESS DURING THIS QUARTER

SUMMARY

The information reported is for the period April 1 to June 30, 1995, although the actual work was performed over an extended period of time, from April 1, 1995 to May 1996. During this period, activities were undertaken in Tasks 3 and 4 of the research project. Parameters were determined to quantify attrition-type fragmentation that occurs in the sampling system, partially reacted chars were extracted from the flow reactor at selected residence times and analyzed to yield extents of mass loss and particle size distributions, and the particle population balance model was used to determine burning and fragmentation rate parameters that best describe the experimental results.

In Task 3 activities, the extent of fragmentation caused by the sampling process was characterized quantitatively. Particle size distributions were measured for char samples before and after passage through the sampling system and the particle population balance model was used to determine the rates of fragmentation events that occurred. In the calculations, particle residence time and gas temperature and composition were specified to match corresponding properties in the sampling system. The measured number size distributions of the feed chars were used as starting distributions and the fragmentation rate parameters were adjusted to provide calculated number distributions that agree with the number distributions measured for the chars that passed through the sampling system. The following attrition-type fragmentation parameters were determined for sampling-induced fragmentation:

$$k_{probe} = 2.2 \left(1 + (\phi - 0.16)e^{0.94(\phi - 0.16)} \right) \mu\text{m}^{-1}\cdot\text{s}^{-1}$$

$$\alpha_{probe} = 1.0$$

$$\beta_{probe} = 3.0$$

where ϕ is the char porosity on a fractional basis. In the fragmentation model, k controls the frequency of fragmentation events, α governs the tendency for particles of a given size to fragment, and β regulates the distribution of fragments. These results allow us to account accurately for the effects of sampling-induced fragmentation and hence, to characterize more accurately fragmentation associated with the char oxidation process.

In other Task 3 activities, partially reacted chars were extracted from the laminar flow reactor at selected residence times and characterized for extents of mass loss and number size distributions. In these combustion tests, the oxygen concentration in the reactor was 12 mole-% and the gas temperature was nominally 1500 K. Two synthetic chars were employed in the tests:

one having an initial porosity of 23% and the other, 36%. The measured number distributions show a large increase in the numbers of small particles during heat-up and devolatilization, the 36% porosity char exhibiting the larger increase. Results show that char burnoff increases with porosity at any given residence time, demonstrating an impact of fragmentation on char burnoff. The data indicate that both particle diameter and apparent density decrease during burnoff and support power-law relations between char particle mass, apparent density, and diameter.

In Task 4 activities, the particle population model was used to characterize the type of fragmentation exhibited by the 23% and 36% porosity chars during char oxidation and to quantify burning and fragmentation rates. Calculations indicate that fragmentation during burnoff is percolative in nature. Char fragmentation is necessary in order to generate the large number of small particles observed after the onset of char oxidation. Without fragmentation, small particles in the feed char would have been consumed before the longer residence times in the reactor are reached. The calculations also show that char burning rate parameters determined from mass loss, size, and temperature measurements are too high if account is not made for the effects of particle fragmentation.

Calculations also suggest that fragmentation during heat-up and devolatilization is percolative in nature and that during this period, the extent of fragmentation is influenced by the volatile matter content of the coal. The 36% porosity char, having a lower volatiles yield than the 23% porosity char, exhibited the greater extent of fragmentation during the first 28 ms after injection into the flow reactor. Fragmentation rates during heat-up and devolatilization are estimated to be as high as five times the fragmentation rates during char oxidation.

Details of activities performed during this reporting period are discussed in the sections that follow. A paper based on the results of tests performed was accepted for presentation at the Twenty-Sixth International Symposium on Combustion that was held July 28 - August 2, 1996 in Naples, Italy. The paper is entitled "The Impact of Fragmentation on Char Conversion during Pulverized Coal Combustion."

TASK 3: CHAR FRAGMENTATION STUDIES

Characterization of Sampling-Induced Fragmentation

In order to characterize accurately the rates of char fragmentation associated with char combustion in the laminar flow reactor, it is necessary to assure that accurate account can be made for fragmentation that occurs as a result of the particle sampling process. In our efforts to characterize sampling-induced fragmentation, the size distributions of feed chars and chars collected just after passage through the sampling system were measured and the particle population

model was used to quantify the consequences of fragmentation events. Synthetic chars having overall porosities ranging from 16% to 56% were employed in these probe-characterization tests. The chars were dry-sieved; particles in the 75 to 125 μm size range were used.

Figure 1 shows micrographs of chars having overall porosities of 16% and 56%. As discussed in previous progress reports (see for example, Diaz and Mitchell, 1993a), the chars are produced from the polymerization of furfuryl alcohol. Carbon black particles added during the synthesis procedure give the chars a microporous structure and spores of lycopodium plants added during the synthesis procedure give the chars a macroporous structure. Mercury porosimetry indicates that the largest intraparticle pores for the 16% char (which is made without the addition of lycopodium spores), are about 0.05 μm . The macropores associated with the 56% char are nominally 20 μm in diameter, and are produced when the lycopodium plant spores vaporize during the polymer curing process. The 16% porosity char, having no macropores, provides a means of assessing the propensity to fragment due to char microporosity. Comparative tests with chars having porosities greater than 16% provide a means for characterizing the propensity to fragment due to char macroporosity.

Fig. 1 Micrographs of synthetic chars having porosities of 16% (left) and 56% (right). Particles are in the 75 to 125 μm size range.

When using the population balance model to determine the rates of fragmentation events that occurred during sampling, the measured feed distributions were used as starting distributions and the differential equations describing the changes in the numbers of particles in selected size classes were integrated for 171 ms, the time it takes for particles to travel through the sampling system. [For a complete description of the fragmentation submodel used in the particle population model that is being developed, see Diaz and Mitchell (1994), Mitchell (1995), or Mitchell, Diaz, and Ramdeen (1995).] One-hundred logarithmically-spaced size classes were used in the range 0.55 to 160 μm and the set of 100 differential equations were solved using LSODE, a Runge-Kutta variable-step, ordinary differential equation solver developed by Radhakrishnan and Hindmarsh

(1983). In the calculations, the apparent chemical reaction rate coefficient was set to zero (no burning occurs in the sampling system) and the fragmentation rate parameters k , α , and β were adjusted to provide agreement between the calculated size distributions and the size distributions measured for particles that passed through the sampling system.

Figures 2, 3, and 4 show measured and calculated size distributions for chars having porosities of 16%, 28%, and 56%, respectively. Between 10,000 and 50,000 particles were monitored for each distribution using a Coulter Multisizer that classifies particles into 256 channels, depending upon size. The Coulter Multisizer was equipped with an orifice tube sufficient to measure particles having diameters in the range 6 to 170 μm . The top panels in each figure show the cumulative percentage number of particles that have diameters greater than 6 μm and the bottom panels show the percentage number of particles per micron.

The distributions for the feed chars reflect the sieved size range used in the experiments and indicate that with dry-sieving, up to 60% of the particles have diameters less than 20 μm . As indicated previously (Diaz and Mitchell, 1993b), wet-sieving is required to reduce significantly the number of particles in the population having diameters less than 20 μm . [Since less than 1% of the mass of a char sample is contained in particles having diameters this small, mass loss measurements are essentially the same for replicate tests with dry- and wet-sieved samples.]

The size distributions of the chars collected after passage through the sampling system are similar to those of the feed chars but have a higher percentage of particles with diameters less than 20 μm . Each distribution reflects few particles having diameters in the range 20 to 70 μm . The measurements suggest that the sampling process causes attrition-type fragmentation. Fragments as large as 20 μm are produced but there are relatively few of these in comparison with the large numbers of particles in the smaller size ranges.

The particle population model was used to quantify the rates of fragmentation events for each of the chars that passed through the sampling system. When modeling attrition-type fragmentation, we assume that no more than 0.1% of the mass of a particle can be lost from its periphery during a single attrition-type fragmentation event and that a fragment can be no larger than 10% of the radius of the attriting particle. Thus, a 100 μm diameter particle undergoing attrition-type fragmentation can produce an attrited particle as large as 5 μm .

In the fragmentation model, three parameters are used to characterize the fragmentation process: k , α , and β . The fragmentation rate coefficient k controls the frequency of fragmentation events, the size sensitivity parameter α governs the tendency for particles of a given size to

Figure 2. Measured and calculated cumulative (top) and differential (bottom) number distributions for the 16% porosity char. Distributions are shown for the feed and probe (the material collected just after passage through the sampling system) chars. In the calculation, the following attrition-type fragmentation parameters were used: $k = 2.2 \mu\text{m}^{-1}\cdot\text{s}^{-1}$, $\alpha = 1.0$, $\beta = 3.0$.

Figure 3. Measured and calculated cumulative (top) and differential (bottom) number distributions for the 28% porosity char. Distributions are shown for the feed and probe (the material collected just after passage through the sampling system) chars. In the calculation, the following attrition-type fragmentation parameters were used: $k = 2.5 \mu\text{m}^{-1}\cdot\text{s}^{-1}$, $\alpha = 1.0$, $\beta = 3.0$.

fragment, and the fragment distribution parameter β regulates the distribution of fragments. In determining values that yield distributions that agree with the measurements, these parameters were varied systematically until differences in the calculated and measured cumulative size distributions were minimized (in the least squares sense). Calculated distributions were noted to be most sensitive to the value of k , the parameter that gauges the frequency of fragmentation events, and were only marginally affected by the choices of α and β . Therefore, the size sensitivity parameter α was set to unity (in accord with the work of Austin *et al.*, 1984) and the fragment distribution parameter β was set to 3, a value that results in fragmented volumes being distributed equally among the size classes that can receive pieces of fragmenting particles. With these values, the fragmentation rate coefficient for attrition-type fragmentation in the sampling system was found to increase with increasing char macroporosity and was correlated as

$$k_{probe} = 2.2 \left(1 + (\phi - 0.16)e^{\{0.94 (\phi - 0.16)\}} \right) \mu\text{m}^{-1}\cdot\text{s}^{-1}.$$

As noted in the figures, the calculated number distributions are in excellent agreement with the measured ones on both a cumulative and a differential basis. Discrepancies are greatest in the 10 to 25 μm size range. Attrited fragments of this size would have to come from particles larger than 200 μm undergoing attrition-type fragmentation. Since the size measurements indicate that there are relatively few, if any, particles this large in the feed chars, it is likely that fragments in the 10 to 25 μm size range result from breakage as particles impact the filter paper during the char collection process. A comparison between measured and calculated cumulative size distributions suggest that the number of particles that break upon impacting the filter paper is relatively low, accounting for possibly 15% of the sampling-induced fragmentation events with the 16% porosity char. It is our contention that we have characterized sampling-induced fragmentation to the extent needed to permit accurate characterization of fragmentation events that occur prior to the sampling process.

Measured Changes in Particle Size Distributions during Combustion

In our efforts to characterize char fragmentation during combustion, a series of combustion tests were performed in the laminar flow reactor in gaseous environments containing 12 mole-% oxygen at nominally 1500 K. Chars having initial porosities of 23% and 36% were employed. In these tests, measured amounts of char particles in the 75 to 125 μm size range were fed to the flow reactor and partially reacted chars were extracted at residence times of 28, 72, and 117 ms. The amounts of char collected in each test were weighed and extents of conversion were calculated from the weight measurements. For the 23% porosity char, values for m/m_0 were determined to be 0.71, 0.21, and 0.19 at the respective residence times and for the 36% porosity char, 0.41,

0.20, and 0.21. Based on duplicate measurements, error bars as large as 20% are placed on the m/m_0 -measurements.

Figure 5 shows the measured cumulative number distributions, each based on about 20,000 particles. An orifice tube sufficient to measure particles having diameters in the range 6 to 170 μm was used in the Coulter Multisizer instrument. The distributions for the 23% porosity char show increases in the number of particles having diameters less than about 20 μm up to the 72 ms residence time. Thereafter, particles having diameters in the 6 to 20 μm size range are being consumed faster than they are being generated. For the 36% porosity char, the distribution at 28 ms shows a large increase in the number of particles having diameters less than about 40 μm . [A duplicate test at this residence time yielded an almost identical distribution.] Particles at this residence time were extracted just subsequent to devolatilization, as evidenced by the disappearance of luminous clouds that surround particles during volatiles release. Devolatilization tests performed in a thermogravimetric analyzer indicate that the higher the weight fraction of lycopodium used in the synthesis procedure, the lower the volatile matter content of the synthetic char. Thus, the 36% porosity char has a lower volatile matter content than the 23% porosity char. The data suggest that volatile matter content influences particle fragmentation during heat-up and devolatilization.

The distributions at 72 and 117 ms indicate a reduced level of fragmentation in comparison with that which occurred during the first 28 ms in the flow reactor. Factors that control fragmentation during heat-up and devolatilization differ from those that control fragmentation during char oxidation. It is not expected that the same fragmentation rate parameters apply in the two regimes.

Figures 6 and 7 show cumulative and differential weight distributions for the 23% and 36% porosity chars. The lines are curves drawn through the data to facilitate interpretation. The distributions show a monotonic reduction of particle size with time and hence, with mass loss. For the 23% porosity char, the weight-averaged diameters at the 0, 28, 72, and 117 ms residence times are respectively, 107, 88, 70, and 63 μm and for the 36% porosity char, 91, 68, 63, and 61 μm .

Values of D/D_0 determined using weight-averaged diameters for each size distribution are plotted against the measured m/m_0 values in Fig. 8. Values obtained with a 16% porosity char are also included in the plot. The lines in the figure are calculations in accord with the following correlation for the mode of particle burning:

$$\left(\frac{m}{m_0}\right)^\alpha = \frac{\rho}{\rho_0} \qquad \left(\frac{m}{m_0}\right)^\beta = \frac{D}{D_0}$$

Figure 5. Cumulative number distributions for the 23% (a) and 36% (b) porosity chars. Only particles having diameters greater than 6 μm are included in the particle populations.

Figure 6. Cumulative (a) and differential (b) weight distributions for the 23% porosity char. Weight-averaged diameters at the 0, 28, 72, and 117 ms residence times are 107, 88, 70, and 73 μm , respectively.

Figure 7. Cumulative (a) and differential (b) weight distributions for the 36% porosity char. Weight-averaged diameters at the 0, 28, 72, and 117 ms residence times are 91, 68, 63, and 61 μm , respectively.

Figure 8. Diameter and apparent density variations with burnoff. The lines are calculations using the relation $(m/m_0)^\beta = D/D_0$ and the indicated values for β .

For spherical particles, $\alpha + 3\beta = 1$. For $\beta = 1/3$, particles burn at constant density and for $\beta = 0$, particles burn at constant diameter. For $0 < \beta < 1/3$, particles burn with decreases in both size and apparent density. The data support a value of β near 0.25. The corresponding value for α is 0.25, a value consistent with those previously determined (Mitchell *et al.*, 1991 and Smith, 1971).

TASK 4: FRAGMENTATION MODELING

Characterization of Fragmentation during Char Oxidation

In order to quantify the rates of fragmentation events, the population balance model was used to calculate the number distributions at residence times of 72 and 117 ms using the distributions at 28 ms as starting distributions. One hundred logarithmically-spaced size bins in the range 0.55 to 170 μm were used in the calculations. The set of 100 differential equations were solved using LSODE (Radhakrishnan and Hindmarsh, 1983), an ordinary differential equation solver. Ambient conditions were specified ($T_{\text{gas}} = 1500 \text{ K}$, $P_g = 0.12 \text{ atm}$), and char combustion model parameters were taken from the literature (Mitchell *et al.*, 1991 and Hurt and Mitchell, 1992). The apparent activation energy was taken as 26 kcal/mol, consistent with results of

previous work (Hurt and Mitchell, 1992) for chars containing 90% carbon. Adjustable parameters included A_a (the pre-exponential factor for the apparent chemical reaction rate coefficient) and k (the fragmentation rate coefficient). Sampling-induced attrition-type fragmentation was accounted for by readjusting A_a to zero and k to k_{probe} at the end of the specified residence time in the reactor and integrating an additional 171 ms, the time it takes particles to pass through the sampling system.

Figure 9 shows calculated cumulative number distributions for the 23% porosity char assuming no fragmentation. In order to get good agreement between measured and calculated cumulative and differential weight distributions, diffusion-limited burning had to be assumed. The calculated number distributions, however, do not reflect the trends depicted in Fig. 5. With diffusion-limited burning, small particles in the feed char are completely burned before the 72 ms residence time in the reactor is reached. No increases in the number of small particles are predicted at the high particle burning rates needed to match the weight loss data.

Figure 9. Calculated number distributions (broken lines) assuming no fragmentation and diffusion-limited burning (zone III). Calculated m/m_0 values agree with the measurements at the various residence times. Solid lines through the data at 0 and 28 ms represent fits used as starting distributions in the calculations.

It was not possible to determine values of A_a and k that resulted in number size distributions that reflected the measured trends when either attrition-type or breakage-type

fragmentation was assumed. Figures 10 and 11 show representative cumulative number distributions calculated for the 23% porosity char assuming these types of fragmentation patterns. The apparent reaction rate coefficient was taken as $200 \text{ gC cm}^2\text{-s-atm}^{0.5}$ and the fragmentation rate coefficient was adjusted to provide agreement between calculated and measured weight loss at the 72 and 117 ms residence times. As evidenced, the calculated distributions do not reflect the trends experimentally observed. Unlike the measured distributions, the calculated number distributions at the 72 and 117 ms residence times do not show the large number of small particles having diameters less than $20 \mu\text{m}$.

Figure 10. Calculated number distributions (broken lines) assuming attrition-type fragmentation with $k = 13 \mu\text{m}^{-1}\text{-s}^{-1}$ and $A_a = 200 \text{ gC cm}^2\text{-s-atm}^{0.5}$. Calculated m/m_0 values agree with the measurements at the various residence times. Solid lines through the data at 0 and 28 ms represent fits used as starting distributions in the calculations.

Only percolation-type fragmentation yields calculated cumulative number distributions having the characteristic shapes of those observed experimentally. Figure 12 shows the distributions calculated for the 23% porosity char assuming percolation-type fragmentation with $A_a = 200 \text{ gC/cm}^2\text{-s-atm}^{0.5}$ and $k = 0.05 \mu\text{m}^{-1} \text{ s}^{-1}$. With these parameters, both the calculated weight and number distributions adequately reflect the trends exhibited by the data. Due to fragments of all sizes being generated with larger fragments fragmenting further as time progresses, the large number of small particles observed in the reactor at residence times of 72 and 117 ms are predicted.

Figure 11. Calculated number distributions (broken lines) assuming breakage-type fragmentation with $k = 0.4 \mu\text{m}^{-1}\cdot\text{s}^{-1}$ and $A_a = 200 \text{ gC cm}^2\cdot\text{s}\cdot\text{atm}^{0.5}$. Solid lines through the data at 0 and 28 ms represent fits used as starting distributions in the calculations.

With the value of A_a determined, char particles having diameters in the 30 to 80 μm size range burn at rates ranging from 78% to 94% of their diffusion-limited rates in 12 mole-% oxygen at 1500 K. This is to be compared with the need to use diffusion-limited burning rates in order to obtain agreement between calculated and measured weight distributions when no fragmentation is assumed. This suggests that apparent chemical reaction rate coefficients determined under conditions when overall particle burning rates are controlled by the combined effects of pore diffusion and the intrinsic chemical reactivity of the particle material (*i.e.*, under zone II burning conditions) are too high when account is not made for the effects of char particle fragmentation. Any intrinsic reactivities determined from these apparent chemical reaction rate coefficients would be too high also. This could contribute to the lack of agreement found between intrinsic reactivities determined under zone I (negligible mass transport effects) and zone II conditions.

Figure 13 shows the number distributions calculated for the 36% porosity char assuming burning in concert with percolation-type fragmentation with $A_a = 200 \text{ gC/cm}^2\cdot\text{s}\cdot\text{atm}^{0.5}$ and $k = 0.07 \mu\text{m}^{-1} \text{ s}^{-1}$. With these parameters, the cumulative and differential weight distributions adequately reflect the data and so do the number distributions. The value determined for k suggests that the fragmentation rate coefficient increases slightly with char macroporosity.

Figure 12. Calculated number distributions (broken lines) assuming percolation-type fragmentation with $k = 0.05 \mu\text{m}^{-1}\cdot\text{s}^{-1}$ and $A_a = 200 \text{ gC cm}^2\cdot\text{s}\cdot\text{atm}^{0.5}$. Solid lines through the data at 0 and 28 ms represent fits used as starting distributions in the calculations.

In order to obtain calculated number size distributions that better agree with those measured, it is necessary to model more accurately apparent density changes associated with burning and fragmentation. When a particle fragments, its fragments do not have the same apparent densities as those of the smaller classes of particles into which the fragments fall. As such, at any time after the onset of burning and fragmentation, a distribution of apparent densities exists for each size class of particles.

In the present particle population model, this consequence of burning and fragmentation is not followed. An average char apparent density at any time is calculated in accord with the equations given above for the mode of particle burning using weight-averaged particle diameters. In effect, the mass of char at any time is calculated using a time-dependent average apparent density of the char and the time-dependent number size distribution, as given by the population balance model. Such an approach assumes that all particles in a given size class have the same apparent density, a reasonable assumption when there is no fragmentation. This treatment may also be reasonable for attrition-type fragmentation but tends to breakdown as large fragments are

generated. Only by having density-classes associated with each size-class can apparent density effects be modeled accurately when account is made for percolation-type char fragmentation:

Figure 13. Calculated number distributions (broken lines) assuming percolation-type fragmentation with $k = 0.07 \mu\text{m}^{-1}\cdot\text{s}^{-1}$ and zone II burning with $A_a = 200 \text{ gC cm}^2\cdot\text{s}\cdot\text{atm}^{0.5}$. Solid lines through the data at 0 and 28 ms represent fits used as starting distributions in the calculations.

Fragmentation during Heat-up and Devolatilization.

The population balance model was used to assess fragmentation during heat-up and devolatilization relative to that during char oxidation. Using a fit to the measured size distribution at $t = 0$ ms for a starting distribution (see Fig. 9) and the value determined for A_a , calculations indicate that fragmentation rates of the 23% porosity char during the first 28 ms in the flow reactor (*i.e.*, during heat-up and devolatilization) are about five times the fragmentation rates during the later stages of char oxidation. This estimate assumes very rapid devolatilization rates and no swelling during devolatilization. Similar calculations using data for the 36% porosity char indicate that the frequency of fragmentation events during heat-up and devolatilization is about three times higher with the 36% porosity char than with the 23% porosity char.

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. Account for the effects of sampling-induced fragmentation can be made using the particle population balance model with the following parameters for attrition-type fragmentation:

$$k_{probe} = 2.2 \left(1 + (\phi - 0.16)e^{0.94(\phi - 0.16)} \right) \mu\text{m}^{-1}\cdot\text{s}^{-1}$$

$$\alpha_{probe} = 1.0$$

$$\beta_{probe} = 3.0$$

where ϕ is the char porosity on a fractional basis. The parameter k controls the frequency of fragmentation events, α governs the tendency for particles of a given size to fragment, and β regulates the distribution of fragments.

During pulverized coal combustion, particles fragment as they heat-up and devolatilize and as they undergo oxidation. The fragmentation behavior can be characterized as being percolative, where fragmenting particles produce fragments of all sizes. Char burnoff increases with porosity at any given residence time and number distributions exhibit greater numbers of small particles with increases in porosity.

Both particle diameter and apparent density decrease during char oxidation. Power-law relations exist between particle mass, diameter, and apparent density. At any time during burnoff, the mode of char particle burning satisfies

$$\left(\frac{m}{m_0}\right)^{0.25} = \frac{\rho}{\rho_0} \qquad \left(\frac{m}{m_0}\right)^{0.25} = \frac{D}{D_0}$$

where ρ is the average apparent density of all the particles and D is the weight-averaged particle diameter. The subscript denotes initial char conditions.

Since overall particle burning rates depend upon particle size, it is apparent that accurate determination of mass loss rates during the char oxidation phase of coal combustion requires that account be made for char particle fragmentation. The neglect of fragmentation can result in the determination of apparent chemical reaction rate coefficients that are too high.

The particle population model developed to account for the effects of fragmentation and oxidation during char combustion is able to predict qualitatively the evolution of the number size distribution during burnoff. Calculations indicate that the numerous small particles observed

during burnoff are consequences of char particle fragmentation. With the 23% and 36% porosity chars used in the combustion tests, fragments of all sizes were generated. The adjustment of model parameters to fit data indicate that char fragmentation is percolative in nature and that fragmentation rates increase with char porosity. The model also indicates that fragmentation events occur at greater rates during heat-up and devolatilization than during char oxidation. Before the effects of fragmentation on the extent of mass loss can be predicted with greater accuracy, the model must be modified to allow for variations in density for each size class of particles considered.

ACTIVITIES UNDERTAKEN DURING THE TWELFTH QUARTER OF THE PROJECT

During the twelfth quarter of this project, tests were continued to obtain combustion data on synthetic chars burning in selected flow reactor environments. In addition, the particle population balance model was modified to allow for density variations for each size class of particles considered.

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