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

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Quarterly Report for the Period

July 1, 1995 - September 30, 1995

Grant DE-FG22-92PC92528

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Prepared for

THE UNITED STATES DEPARTMENT OF ENERGY

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Submitted by

Professor Reginald E. Mitchell

September 13, 1996

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September 13, 1996

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

ORGANIZATION: Thermosciences Division
Mechanical Engineering Department
Stanford University

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REPORTING PERIOD: July 1, 1995 - September 30, 1995
(work was actually performed over the extended period
July 1, 1995 - August 30, 1996)

REPORTED BY: Reginald E. Mitchell

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RESEARCH OBJECTIVES

This document is the twelfth 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 July 1 to September 30, 1995, although the actual work was performed over an extended period of time, from July 1, 1995 to August 1996. During this period, activities were undertaken in Tasks 3 and 4 of the research project. Partially reacted chars were extracted from the laminar flow reactor at selected residence times and analyzed to determine extents of mass loss and particle size distributions and the particle population balance model was modified to take into account density variations for each size class of particles considered in the model.

In Task 3 activities, a series of combustion tests were performed with a 16% porosity char, a char made without the addition of lycopodium plant spores. The char has no pores greater than about 0.05 μm and hence, is used to obtain information on the affect of char microporosity on fragmentation patterns during combustion. Char particles in the 75 to 125 μm size range were injected into a flow reactor environment containing 12 mole-% oxygen at nominally 1500 K. Partially reacted char samples were extracted from the reactor at selected residence times and characterized for extents of mass loss and number size distributions.

The measured size distributions show a large increase in the number of particles during heat-up and devolatilization, a consequence of fragmentation. The degree of fragmentation is much greater than that observed during the heat-up and devolatilization of the 23% and 36% porosity chars that were subjected to the same heating conditions in previous tests. The 23% and 36% porosity chars are quite macroporous with large openings at the outer surfaces of particles. The data suggest that the more open the porous structure of the char, the less the extent of fragmentation during heat-up and devolatilization induced by either thermal stresses or stresses due to the buildup of pressure of volatiles in the pore network. It appears that the greater the char macroporosity, the less steep the temperature and pressure gradients inside the particle.

The measured size distributions for the 16% porosity char suggest a reduced level of fragmentation during char oxidation than during heat-up and devolatilization. Fewer small particles are generated during the later stages of the combustion process. In comparison with the macroporous chars, the microporous (16% porosity) char exhibits a lower frequency of fragmentation events during char oxidation.

In Task 4 activities, the population balance model was modified to take into account density variations associated with each size class of particles. Size-bin i , consisting of particles having

diameters between its upper and lower cutoffs, x_i and x_{i+1} , respectively, is divided into K discrete density classes. Density-class k consists of particles having apparent densities ranging from its upper cutoff, ρ_{k-1} , to its lower cutoff, ρ_k . The modified model is given by a set of differential equations having the following form:

$$\frac{dN_{i,k}}{dt} = -S_{i,k} N_{i,k} + \sum_{j=1}^i \sum_{\lambda=1}^K (b'_{ij,k\lambda} S_{j,\lambda} N_{j,\lambda}) - C_{i,k} N_{i,k} + C_{i-1,k} N_{i-1,k} - D_{i,k} N_{i,k} + D_{i,k-1} N_{i,k-1}$$

The subscripts i and k refer, respectively, to size-class and density-class. Thus, $N_{i,k}$ is the number of particles in size-class i and density-class k , i.e., in class i,k . The first two terms on the right-hand side of the equation represent the rates at which particles leave and enter a particular class (class i,k) as a result of fragmentation, the third and fourth terms represent the rates at which particles leave and enter the class as a result of changes in size due to burning, and the last two terms represent the rates at which particles leave and enter the class as a result of changes in density due to burning.

For each size-class considered in the model, allowance is made for seven density-classes, spanning the range from 1.3 times the average apparent density of the unburned char ($1.3\rho_0$) to $0.1\rho_0$. For values of the burning mode parameters determined for most coal chars, particles having apparent densities less than $0.1\rho_0$ are at extents of burnoff greater than 99.99%, and are considered to have been completely consumed. The modified model was tested to assure that all aspects of fragmentation and burning are described accurately in the numerical code.

The modified population balance model allows us to take a more detailed look at the effect of apparent density on overall char burning rates. For specified reaction times, calculations show that the allowance for density variations within size-classes yields broader size distributions and faster overall mass loss rates, in comparison to the size distributions and mass loss rates calculated when all particles of the same size are assumed to have the same apparent density.

The modified model is more realistic than the previous model and will permit more accurate analysis of the experimental data and hence, lead to a more accurate determination of the rates of fragmentation events during burnoff. This, in turn, will yield a more accurate numerical code for predicting char combustion rates in pulverized coal combustor environments. Details of activities performed during this reporting period are discussed in the sections that follow.

TASK 3: CHAR FRAGMENTATION STUDIES

Measured Changes in Particle Size Distributions during Combustion

A series of combustion tests employing a synthetic char having an initial porosity of 16% were performed in the laminar flow reactor in gaseous environments containing 12 mole-% oxygen at nominally 1500 K. The char was made without the addition of lycopodium plant spores. The carbon black that was added during the synthesis procedure produced a char with a microporous structure, the largest pores being of the order 0.05 μm . Being void of large pores, we use this char to characterize the impact of char microporosity on fragmentation behavior during char oxidation. The apparent density of this microporous char was determined to be 1.33 g/cm³, using the tap density procedure described by Mitchell *et al.* (1991).

In the combustion 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 char collected at 28 ms was obtained just subsequent to devolatilization, as evidenced by the disappearance of volatile clouds surrounding particles. The amounts of char collected in each test were weighed and extents of conversion were calculated from the weight measurements. Values for m/m_0 were determined to be 0.86, 0.49, and 0.41 at the respective residence times. Duplicate tests at a residence time of 117 ms yielded m/m_0 values of 0.37 and 0.46, suggesting error bars of about 11% on the m/m_0 values.

The particle size distributions of the extracted chars were measured with the Coulter Multisizer instrument, employing an orifice tube sufficient to measure particles having diameters in the range 6 to 170 μm . Figures 1a and b show the measured cumulative and differential number distributions, respectively, for particles in the 6 to 170 μm size range. Each distribution is based on about 10,000 particles. For the unburned char (0 ms residence time), about 20% of the particles had diameters less than 17 μm . About 20% of the particles had diameters in the range 17 to 72 μm and about 51% had diameters between 72 and 100 μm . Less than 6% of the particles had diameters exceeding 100 μm . As noted in Fig. 1b, the number distribution of the unburned char is bimodal, with a large peak in the 0 to 10 μm size range and a modest peak at about 82 μm . The distribution reflects sieved particles in the 75 to 125 μm size range.

The distribution at 28 ms suggests significant fragmentation during heat-up and devolatilization. Whereas the unburned char consisted of about 20% of the particles having diameters in the 17 to 72 μm size range, the char at this stage of the combustion process had 51% of its particles in this size range. There are also significantly more particles in the 0 to 10 μm size range than in the feed char. The size distribution at this time is no longer bimodal, but instead, is quite broad over

Figure 1. Cumulative (a) and differential (b) number distributions for the 16% porosity char burning in 12 mole-% O_2 at 1500 K. Only particles having diameters greater than 6 μm are included in the particle populations.

the 20 to 80 μm size range with a large peak in the 0 to 10 μm size range. Such a large increase in the number of particles during heat-up and devolatilization was also observed with the 23% and 36% porosity chars that were subjected to the same heating conditions. Calculations indicated that the fragmentation behavior of these macroporous chars during their heating period is percolative in nature. The measurements support percolation-type fragmentation during heat-up and devolatilization of this microporous char as well.

In comparison to the size distribution at a residence time of 28 ms, the distribution at 72 ms shows a reduced number of particles in the 17 to 72 μm size range (38% of the particles monitored at 72 ms versus 51% of the particles at 28 ms). Like that of the unburned char, the size distribution at this stage of the combustion process is bimodal, the smaller peak being in the 40 to 80 μm size range.

The duplicate size distributions at 117 ms also indicate that about 38% of the particles have diameters in the 17 to 72 μm size range. The bimodal character of the number distribution still exists at this stage of burnoff with the smaller peak in the 60 to 80 μm size range. The distributions indicate a reduced number of particles having diameters less than 20 μm at the 117 ms residence time.

The data support a higher frequency of fragmentation events during heat-up and devolatilization than during char oxidation. This trend was also observed with the 23% and 36% porosity chars, the macroporous chars (see Mitchell, 1996). Whereas the frequency of fragmentation events during heat-up and devolatilization appears to be higher with the microporous char (the 16% porosity char) than with the macroporous chars, the frequency of fragmentation events during char oxidation appears to be lower with the microporous char. The particle population model will be used to determine if this is indeed the case.

Figures 2a and b show respectively, the cumulative and differential weight distributions obtained for the 16% porosity char. The distributions do not show a monotonic decrease in the weight-averaged diameters of particles with residence time (and hence, with mass loss). Weight-averaged diameters at the 0, 28, 72, and 117 ms residence times are 89, 69, 68, and 73 μm , respectively. With the broad size distribution resulting from heat-up and devolatilization, if there were no fragmentation during char oxidation, the weight-averaged particle size would increase with residence time, as smaller particles are consumed at faster rates than larger particles. The measurements reflect the impact of fragmentation (percolation-type fragmentation) on overall mass loss rates. We will use the population balance model to quantify burning and fragmentation rates of this microporous char in upcoming work.

Figure 2. Cumulative (a) and differential (b) weight distributions for the 16% porosity char burning in 12 mole-% O_2 at 1500 K. Values for m/m_0 at the 0, 28, 72, and 117 ms residence times are 1.0, 0.86, 0.49, and 0.41, respectively. Weight-averaged diameters at the respective residence times are 89, 69, 68, and 73 μm .

TASK 4: FRAGMENTATION MODELING

In order to have a more realistic char combustion model, it is necessary to describe more accurately apparent density changes associated with fragmentation. When a particle fragments, its fragments do not have, necessarily, 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 particle population model that has been discussed to date (see Diaz and Mitchell, 1994 and Mitchell, 1995), this consequence of burning and fragmentation is not taken into account. All particles in a given size-class are assumed to have the same apparent density, an average apparent density calculated using the weight-averaged diameter in the time-derivatives of the following equations, which characterize the mode of particle burning:

$$\left(\frac{m}{m_0}\right)^\alpha = \frac{\rho}{\rho_0} \qquad \left(\frac{m}{m_0}\right)^\beta = \frac{D}{D_0} \qquad (1)$$

This is 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.

The Modified Population Balance Model

In the modified population balance model, the size distribution of char particles at any time is described by n discrete size-classes (or size-bins) (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 total number of particles in bin i at any time, 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} .

There is a distribution of apparent densities in each size-class, which at any time is described by K discrete density classes. The upper cutoff of the k -th density-class is ρ_{k-1} and the lower cutoff is ρ_k . Thus, density-class k consists of particles having apparent densities as high as ρ_{k-1} and as low as ρ_k . The highest density-class (density-class I), consists of particles having apparent densities of ρ_I and higher. The apparent density distribution within a density-class is assumed to be uniform, consequently, of the number of particles in density-class k at any time, the fraction that have apparent densities between ρ and ρ_k is $(\rho - \rho_k)/(\rho_{k-1} - \rho_k)$, where ρ is between ρ_{k-1} and ρ_k .

The change in the number of particles in density-class k of size-bin i as a result of combustion and fragmentation is described by the following differential equation:

$$\frac{dN_{i,k}}{dt} = - S_{i,k} N_{i,k} + \sum_{j=1}^i \sum_{\lambda=1}^K (b'_{ij,k\lambda} S_{j,\lambda} N_{j,\lambda}) - C_{i,k} N_{i,k} + C_{i-1,k} N_{i-1,k} - D_{i,k} N_{i,k} + D_{i,k-1} N_{i,k-1} \quad (2)$$

$N_{i,k}$ is the number of particles in size-bin i within density-class k , i.e., in class i,k . The parameter $S_{i,k}$ is the fragmentation rate constant and the parameters $C_{i,k}$ and $D_{i,k}$ are burning rate constants associated with reductions in diameter and density, respectively. The $b'_{ij,k\lambda}$ are the elements of the fragmentation progeny matrix for fragmentation in class j,λ (fragments in class i,k). The first two terms in the equation represent the rates at which particles leave and enter class i,k as a result of fragmentation, the third and fourth terms represent the rates at which particles leave and enter the class as a result of changes in size due to burning, and the last two terms represent the rates at which particles leave and enter the class as a result of changes in density due to burning.

The distribution of the apparent densities of the fragments generated needs to be addressed. For irregularly shaped, macroporous char particles that have large internal voids, the apparent densities of fragments generated from particles in density-class k can range from considerably low values to the true density of the carbonaceous particle material. Some of the fragments will have apparent densities higher than that of the parent particle and others will have apparent densities lower. For attrition-type fragmentation, the apparent densities of attrited fragments can be quite variable while the apparent density of the large fragment (i.e., the remaining portion of the parent particle) remains essentially unchanged. For breakage-type fragmentation, the two to three relatively large fragments that are produced are likely to have apparent densities slightly different from that of the fragmenting particle. Percolation-type fragmentation is likely to yield fragments having apparent densities that span the range from a fraction of the apparent density of the parent particle to the density of the carbonaceous particle material.

In the present treatment, fragments in all density classes can be generated from a single fragmenting particle. Owing to the various unknown degrees of anisotropy and inhomogeneity of the pore structure of macroporous chars having large internal voids, it is assumed that the number of fragments falling into a particular size-bin are uniformly distributed amongst the density-classes. For mass conservation, this assumption requires that the number of fragments that fall into class i,k per particle fragmenting in class j,λ be given by

$$b'_{ij,k\lambda} = \frac{\rho_{\lambda}}{\sum_{m=1}^K \rho_m} b_{ij} \quad (3)$$

This expression applies to any density-class k receiving fragments. Here, b_{ij} are the elements of the fragmentation progeny matrix that were used in the previous model (see Diaz and Mitchell (1994)). They give the number of fragments of size x_i generated per particle of size x_j fragmenting, and are based on volume conservation, *i.e.*, the sum of the volumes of the "spherical" fragments generated equals the volume of the spherical, fragmenting particle.

Other scenarios for the distribution of fragments within a size-class would lead to different results for the relation between $b'_{ij,k\lambda}$ and b_{ij} . For instance, it could be assumed that the apparent densities of fragments within a size-class follow a Gaussian distribution centered about the average apparent density of the unburned char, ρ_0 . In this case, the density factor on the right-hand-side of Eq. (3) would be replaced by a factor proportional to a Gaussian function having $(\rho_\lambda - \rho_0)$ as the argument. Most fragments would have apparent densities near ρ_0 ; some would have higher apparent densities and some lower. Fewer fragments would have apparent densities that would place them in the highest or lowest density-classes.

The fragmentation rate constant for class i,k is expressed as:

$$S_{i,k} = k \left(\frac{\rho_0}{\rho_k} \right)^\omega x_i^\sigma \quad (4)$$

where the average apparent density of the unburned char is ρ_0 . As in the previous model, 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 size-sensitivity parameter σ . In this modification for apparent density variations with size, we also consider the relative tendency of a particle to fragment because of its density, and define a density-sensitivity parameter ω . For $\omega = 0$, the rate of fragmentation events is the same for all density classes. In an arbitrary sample of porous char particles, one might expect for the less dense (more open, higher porosity) particles to have relatively higher tendencies to fragment during oxidation than more dense particles of nominally the same size. For $\omega > 0$, the higher the particle's apparent density relative to the average apparent density of the unburned char, the less its frequency of fragmentation events.

An additional fragmentation parameter β , is associated with the b_{ij} and controls the size distribution of fragments. [See Diaz and Mitchell (1994) for a complete description of the fragmentation parameters used in the particle population balance model.] For $\beta = 3$, the fragmented volume 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 volume resides in larger particle sizes.

The parameter $C_{i,k}$ is the fraction of the particles in class i,k at time t that burns out of the class per unit time because of a decrease in diameter. These particles enter class $i+1,k$. As shown previously (Mitchell, 1995a), the rate of decrease in diameter of a particle initially having diameter D_0 and density ρ_0 can be expressed as follows:

$$\frac{dD}{dt} = - \frac{6\beta q}{\rho_0} \left(\frac{D}{D_0} \right)^{(3-1/\beta)} \quad (5)$$

Here, q is the overall particle burning rate per unit external surface area, which depends on the apparent chemical reaction rate coefficient $k_s (= A_a \exp(E_a/RT))$. It is applicable in the zone II burning regime, *i.e.*, when burning rates are controlled by the combined effects of pore diffusion and the intrinsic chemical reactivity of the particle material. Evaluating the rate of diameter decrease at the lower cutoff of the size-class leads to the following expression for $C_{i,k}$ (see Mitchell, 1995):

$$C_{i,k} \equiv \left(\frac{\text{fraction of particles in class } i,k \text{ at time } t \text{ that burn out of the size class per unit time}}{\text{fraction of particles in class } i,k \text{ at time } t} \right) = \frac{|dD/dt|_{x_i}}{x_i - x_{i+1}} = \frac{6\beta q}{\rho_{k,ave}(x_i - x_{i+1})} \left(\frac{x_{i+1}}{x_i} \right)^{(3-1/\beta)} \quad (6)$$

In this expression, $\rho_{k,ave}$ is the average apparent density of particles in class i,k (taken as $(\rho_{k-1} + \rho_k)/2$). This equation shows that for a given size-class of particles, lower apparent density particles leave the size-class at higher rates. In reality, this is true only as long as particles remain in the zone II burning regime. The assumptions underlying the development of Eq. (6) tend to become invalid when particles become so porous that they are readily penetrated by oxygen and hence, enter the zone I burning regime (in which overall burning rates are controlled solely by the material's intrinsic chemical reactivity) and burn almost at constant size.

The parameter $D_{i,k}$ is the fraction of the particles in class i,k at time t that burns out of the class per unit time because of a decrease in density. These particles enter class $i,k+1$. An expression for the rate of decrease in apparent density is derived from the mode of burning equations (Eq. (1)) and the equation for the rate of diameter decrease, Eq. (5). The burning mode equations can be combined to show that

$$\left(\frac{\rho}{\rho_0} \right) = \left(\frac{D}{D_0} \right)^{(\alpha/\beta)} \quad (7)$$

Differentiating with respect to time, and combining with Eq. (4) yields

$$\frac{d\rho}{dt} = \frac{\alpha}{\beta} \frac{\rho}{D} \frac{dD}{dt} = - \frac{6\alpha}{D_0} \frac{q}{\rho_0} \left(\frac{\rho}{\rho_0} \right)^{-(\beta/\alpha)} \quad (8)$$

Using an approach similar to that used in deriving Eq. (6) (see Mitchell, 1995), when the above result is applied to class i,k and the rate of density decrease is evaluated at the lower limit of the density-class, the following expression is obtained for $D_{i,k}$:

$$D_{i,k} \equiv \left(\frac{\text{fraction of particles in class } i,k \text{ at time } t \text{ that burn out of the density class per unit time}}{\rho_{k-1} - \rho_k} \right) = \frac{|d\rho/dt|_{\rho_k}}{\rho_{k-1} - \rho_k} = \frac{6 \alpha q}{x_{i,ave} (\rho_{k-1} - \rho_k)} \left(\frac{\rho_k}{\rho_{k-1}} \right)^{(\beta/\alpha)} \quad (9)$$

Here, $x_{i,ave}$ is the average diameter of particles in class i,k , (taken as the volume-mean diameter between x_i and x_{i+1}). This equation shows that for a particular density-class, small particles leave the density-class (entering a class of lower apparent density in the same size-bin) at higher rates than large particles. It also shows that for a given size-class of particles, the lower the apparent density, the faster particles burn out of the density-class.

Model Predictions

The modified particle population balance model was used to predict the size and apparent density distributions of char particles that had been burning in a gaseous environment containing 12 mole-% oxygen at nominally 1500 K for 1000 ms. One hundred logarithmically-spaced size-bins in the range 0.55 to 176 μm were used in the calculations. Each size-bin is sub-divided into seven density classes. The highest density-class consists of particles having apparent densities greater than 1.3 times the average apparent density of the unburned char ($\rho_0 = 1 \text{ g/cm}^3$). Other density classes consist of particles having apparent densities between $1.3\rho_0$ and $1.1\rho_0$, between $1.1\rho_0$ and $0.9\rho_0$, between $0.9\rho_0$ and $0.7\rho_0$, between $0.7\rho_0$ and $0.5\rho_0$, between $0.5\rho_0$ and $0.3\rho_0$, and between $0.3\rho_0$ and $0.1\rho_0$. For values of the burning mode parameter determined for most coal chars ($\alpha \sim 0.25$), char particles attaining apparent densities less than $0.1\rho_0$ are at extents of burnoff greater than 99.99%, and are considered to have been completely consumed.

For the initial distribution, 10,000 particles were assumed to be in the size-bin having lower and upper cutoffs of 83 and 97 μm , respectively, and density-class with lower and upper cutoffs of $0.9\rho_0$ and $1.1\rho_0$. The set of 700 differential equations were solved using LSODE (Radhakrishnan and Hindmarsh, 1983), an ordinary differential equation solver. Char combustion model parameters were taken from the literature (Mitchell *et al.*, 1991 and Hurt and Mitchell, 1992). Burning rate parameters for Pocahontas #3 coal, a low-volatile bituminous coal were selected: activation energy, $E_a = 30,000 \text{ cal/mole}$; pre-exponential factor, $A_a = 114 \text{ gC/cm}^2\cdot\text{s}\cdot\text{atm}^{0.5}$; burning mode parameter, $\alpha = 0.3$. In order to see more clearly the changes in size and density distribution as a result of char oxidation and to assess the impact of variations in

density with size on overall mass loss rates, in the initial calculations, fragmentation was not allowed.

Burning Only: Size and Apparent Density Distributions

The top and bottom panels of Figure 3 compare the cumulative and differential distributions, respectively, calculated using the previous and modified population balance models. For these calculations, only burning was taken into account; the fragmentation rate coefficient k in Eq. (4) was set to zero. The previous model, which assumes that all particles of a particular size have the same apparent density, predicts a narrower number distribution, with a higher weight-averaged size after 1000 ms of burning. Allowance for density variations within a size-class (the current, modified model) leads to the generation of more small particles (lower density particles have a higher rate of diameter reduction during burnoff), which broadens the size distribution and lowers the number-averaged size. Small particles burn at faster rates than large particles; hence, for the same burning rate parameters, variations in apparent density with size lead to faster overall mass loss rates. Using the previous model (in which it is assumed that all particles of a given size have the same apparent density), $m/m_0 = 0.090$ at 1000 ms and the weight-averaged diameter is 61 μm . With the modification for apparent density variations for each particle size, $m/m_0 = 0.045$ at 1000 ms and the weight-averaged diameter is 56 μm .

The four panels in Fig. 4 show the evolution of the size distribution when account is made for density variations within size classes. At short times (top left panel, 100 ms residence time), the number size distribution is quite narrow and most particles (76%) have apparent densities close to the average apparent density of the char (ρ_0), reflecting the initial condition. As burning progresses, both the size and density distributions broaden. After 250 ms, most particles still have apparent densities greater than $0.7\rho_0$. A few particles with apparent densities less than $0.3\rho_0$ have been produced. After 500 ms, only about one-fourth of the particles have apparent densities near ρ_0 . Most particles have apparent densities within the range $0.5\rho_0$ to $0.9\rho_0$; 15% of the particles have densities less than $0.5\rho_0$. After 1000 ms when burning is about 95% complete, relatively few high-density particles remain (about 6% of total number of particles), and most of these (60%) have diameters larger than the weight-averaged diameter at this time (56 μm).

The calculations show that the allowance for density variations within a size class yields a size distribution that is considerably broader than that calculated when it is assumed that all particles of the same size have the same apparent density. This is due to the fact that for particles of comparable sizes burning within the zone II burning regime, the ones having the lower apparent densities exhibit the faster reductions in both diameter and apparent density. Thus, with allowance

Figure 3. Cumulative (top) and differential (bottom) number distributions after 1000 ms of burning in 12% O₂ at 1500 K calculated with (current model) and without (previous model) density variations for each particle size. The initial distribution consisted of 10,000 nominally 90- μ m diameter char particles. For burning, $E_a = 30,000$ cal/mole and $A_a = 114$ gC/cm²·s·atm^{0.5}. Fragmentation is assumed not to occur.

Figure 4. Calculated number and density distributions at 100, 250, 500, and 1000 ms of burning in 12% O₂ at 1500 K. Initially, 10,000 nominally 90- μ m diameter char particles had apparent densities in the range $0.9\rho_0$ to $1.1\rho_0$. Burning rate parameters are given in the caption to Fig. 3. Fragmentation is assumed not to occur.

for density variations within size classes, particles having apparent densities lower than the average apparent density of the particles in the size-class generate fragments at higher rates than those having apparent densities higher than the average value. These low-density fragments generate an even greater number of small particles.

Burning and Fragmentation: Size and Apparent Density Distributions

Figure 5 shows the size distributions at 1000 ms residence time in a gaseous environment containing 12 mole-% oxygen at 1500 K, calculated using the previous and current models when both burning and percolation-type fragmentation are assumed to occur. As in the above calculations, 100 size bins were and seven density-classes were used. Initially, 10,000 char particles were assumed to be in the size-bin having lower and upper cutoffs of 83 and 97 μm , respectively, and all particles were assumed to have the same apparent density. The same burning rate parameters employed in the calculations discussed above were used. The fragmentation parameters were taken to be: $k = 0.05 \mu\text{m}^{-1}\text{s}^{-1}$, $\omega = 0$, $\sigma = 1$, and $\beta = 3$. The values for k , σ , and β were determined for the 23% porosity char using the previous model, which assumed that all particles of the same size had the same apparent density (see Mitchell, 1996). The value selected for ω assumes that the frequency of fragmentation events is independent of the apparent density of the fragmenting particle. The figure shows that at 1000 ms, there are fewer small particles when account is made for density variations within a size class (current model). This is due to the fact that the current model predicts a greater extent of mass loss after 1000 ms (owing to higher reduction rates of diameter and apparent density for low-density particles, as discussed above). With the previous model, at 1000 ms, $m/m_0 = 0.057$ and with the current model, $m/m_0 = 0.021$ at 1000 ms.

Figure 6 shows the evolution of the size and density distributions when allowance is made for density variations within size classes. At 100 ms, the size distribution has broaden considerably but there are still a large number of particles in the 80 to 90 μm size range. A somewhat bimodal character in the size distribution is evident, with a steep peak in the 80 to 90 μm size range and a broad peak centered at about 18 μm . Almost all the particles smaller than 70 μm are a consequence of fragmentation. The fragments have a broad apparent density distribution. A considerable number of fragments having diameters greater than $1.3\rho_0$ have been produced. A few high-density fragments are generated having diameters as large as 85 μm . Most of the smaller fragments have a low density, indicating that they are near burnout.

Figure 5. Cumulative and differential number distributions after 1000 ms of burning and fragmentation in 12% O₂ at 1500 K calculated using the previous and current models. The initial distribution consisted of 10,000 nominally 90- μ m diameter char particles. Calculation were made using the burning rate parameters given in the caption for Fig. 3 and employing the following fragmentation rate parameters: $k = 0.05 \mu\text{m}^{-1}\cdot\text{s}^{-1}$, $\omega = 0$, $\sigma = 1$, and $\beta = 3$.

Figure 6. Calculated number and density distributions at 100, 250, 500, and 1000 ms of burning and fragmentation in 12% O₂ at 1500 K. Initially, 10,000 nominally 90- μm diameter char particles had apparent densities in the range $0.9\rho_0$ to $1.1\rho_0$. Calculation were made using the burning rate parameters given in the caption for Fig. 3 and employing the following fragmentation rate parameters: $k = 0.05 \mu\text{m}^{-1}\cdot\text{s}^{-1}$, $\omega = 0$, $\sigma = 1$, and $\beta = 3$.

At 250 ms, the size distribution has developed a distinctive bimodal shape. One peak is at about 78 μm and the other peak is near 17 μm . The peak at 78 μm is representative of the regression in diameter due to burning and the peak in the small diameter range is representative of the combined effects of fragmentation and burning, primarily fragmentation. A broad density distribution develops as burnoff progresses. As fragments are generated, they are distributed uniformly among the density classes. But burning tends to deplete each density-class at a different rate, rendering a non-uniform density variation within a size-class.

By 500 ms, the bimodal character of the size distribution no longer exist. There are relatively few large particles, and these have high apparent densities. The 1000 ms distribution is at 97.9% burnoff. Few fragments remain compared to the large numbers generated during the course of combustion. About 50% of the particles have densities higher than $0.7\rho_0$, more than 25% higher than $0.7\rho_0$. This is in contrast to the situation when no fragmentation is assumed to occur, where relatively few particles were observed to have apparent densities greater than $0.9\rho_0$ (see the lower right panel of Fig. 4).

Fragmentation is noted to broaden both the size and apparent density distributions during char oxidation. Since all particles are assumed to be spherical, calculations made taking into account fragmentation show increased mass loss for comparable residence times. [Non-spherical fragments could possibly extinguish leading to decreased mass loss for comparable reaction times.] Since the rates of change in apparent density of particles increases with decreasing particle size, fragmentation also leads to increased apparent density variations with size.

Effect of the Fragmentation Density-Sensitivity Parameter, ω

It is expected that for particles of nominally the same size, the greater the char macroporosity, the higher the frequency of fragmentation events during oxidation. Accordingly, the fragmentation density-sensitivity parameter, ω , is expected to be greater than zero. A series of calculations were made to determine the impact of ω on the size and density distributions that evolve during burning and fragmentation. The same burning and fragmentation rate parameters employed above were used. Figure 7 shows the calculated cumulative and differential number distributions 250 ms after the onset of burning for selected values of ω . For $\omega > 0$, the frequency of fragmentation events increases inversely with apparent density. Thus, as particle densities decrease due to burning, fragmentation events occur at higher frequencies, generating smaller particles faster (than in the case for $\omega = 0$). Hence, as ω increases, the number of small particles increases. As shown in the lower panel of Fig. 7, the increase is for particles less than 10 μm .

Figure 7. Cumulative and differential number distributions (for diameters greater than 6 μm) after burning and fragmentation in 12% O_2 at 1500 K for 250 ms. Calculation were made using the burning and fragmentation rate parameters given in the captions for Figs. 3 and 5 and selected values of the fragmentation density-sensitivity parameter ω .

Little of the total mass is in particles this small. At 250 ms, values calculated for m/m_0 are 0.531, 0.533, 0.534, and 0.539, respectively, for $\omega = 0, 1/3, 1/2,$ and 1, indicating only a modest increase in overall mass loss rates with ω .

At all times during burnoff, values determined for m/m_0 are comparable for selected values of ω . These results show that with burning and fragmentation rate parameters typical of those expected for coal chars, the impact of ω on the overall mass loss rate is modest. Fragmentation rate coefficients and apparent densities determined in combustion studies using the 23% and 36% porosity chars (see Mitchell, 1996) support a value of ω near 1/3. For comparable sizes, with this value of ω , particles in the lowest density-class ($0.1 < \rho/\rho_0 < 0.3$) fragment at rates about twice as fast as those in the highest density-class ($\rho/\rho_0 > 1.3$). In upcoming efforts to determine burning and fragmentation parameters that are adequate for coal char oxidation, a value of 1/3 will be used for the fragmentation density-sensitivity parameter.

CONCLUSIONS OF THIS QUARTER'S WORK

The extent of mass loss and particle size distribution measurements obtained with the 16% porosity char, a microporous char, suggest higher rates of fragmentation during heat-up and devolatilization than during char oxidation. This was also observed with the macroporous chars that were tested similarly. The frequency of fragmentation events during heat-up and devolatilization appears to be higher with the microporous char. However, the frequency of fragmentation events during char oxidation is higher with the macroporous char.

The particle population model developed to account for the effects of fragmentation and oxidation during char combustion was modified to account for variations in apparent densities of particles nominally the same size. Such an allowance leads to broad distributions in size and apparent density, consequences of both burning and fragmentation. For particles of the same size, the lower density particles burn faster, broadening both the size and density distributions. When particles fragment, the fragments have a distribution of apparent densities and hence, fragmentation also broadens both the size and apparent density distributions. Compared with the previous model, the modified model should yield slightly lower fragmentation rate parameters for the 23% and 36% porosity chars that were discussed in the last quarterly report.

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