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Char Particle Fragmentation and Its Effect on Unburned Carbon During Pulverized Coal Combustion

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By
Reginald E. Mitchell

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U.S. Department of Energy
Office of Fossil Energy
Federal Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
Stanford University
High Temperature Gasdynamics Laboratory
Mechanical Engineering Department
Stanford, California 94305

MASTER
[Signature]

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EXECUTIVE SUMMARY

During pulverized coal combustion, a significant number of char particles are formed during devolatilization that have large voids within them. These macrovoids allow oxygen to penetrate the particle during char oxidation and consume the inner particle material. As a consequence, particles may fragment as interior surfaces are consumed. Char fragments burn at rates governed by their individual sizes and not at rates controlled by the sizes of their parent particles. Consequently, overall mass loss rates depend upon the extent of fragmentation. This project was aimed at characterizing the impact of fragmentation on carbon conversion during pulverized coal combustion.

Three types of fragmentation behavior are considered: attrition, breakage, and percolation. During attrition fragmentation, numerous small fragments are produced while the overall sizes of parent particles diminish only slightly. During breakage fragmentation, only a few fragments are produced and these are relatively large, having sizes not much smaller than their parent particles. Percolation fragmentation refers to the transition from a connected solid network to a completely fragmented state. Whereas attrition produces fine fragments and breakage produces relatively large fragments, percolation fragmentation produces fragments ranging in size from the diameters of the parent particles to those of the small fragments.

In the experimental effort, synthetic chars with controlled pore structures were used to avoid complications associated with the heterogeneity of real coal chars are eliminated. The chars were produced from the polymerization of furfuryl alcohol with p-toluenesulfonic acid. Carbon black particles added during the synthesis procedure form micropores by causing the carbonized furfuryl alcohol matrix to crack around the locations of the carbon black inclusions. The addition of lycopodium plant spores produce macropores of a uniform size ($\sim 20\text{ }\mu\text{m}$ in diameter) when they vaporize during the thermal curing step of the synthesis procedure. Synthetic char particles representing a range of porosities from 16% to 55% were produced. Mercury porosimetry indicated that the largest intraparticle pores for the 16% porosity chars are $\sim 0.05\text{ }\mu\text{m}$.

The chars produced were ground and size-classified. True densities of the chars were determined using helium pycnometry and apparent densities were determined using mercury intrusion porosimetry combined with a tap density procedure for bulk density.

Chars were burned in an atmospheric, laminar flow reactor that permits the control of gas temperature and oxygen content. Particles were injected along the reactor centerline and extracted from the reactor at selected residence times using a helium-quench solids sampling probe. The

reacted chars were characterized for extents of burnoff (determined from the measured weights of char fed and char extracted) and particle size distributions. Size distributions were measured with a Coulter Multisizer, using 256 channels to classify approximately 20,000 particles per measurement in the 6 to 168 μm size range.

The extent of fragmentation associated with the particle feeding and collection systems was assessed in cold-flow experiments. Results indicated that the feed system causes insignificant fragmentation and that the collection system causes attrition-type fragmentation with fragments as large as 10% of the radius of the attriting particles. Calculations using the population balance model that was developed during the course of the project were used to determine that for chars with porosities in the range 16% to 60% passing through the sampling system, the fragmentation rate coefficient, k , was equal to $2.5 \mu\text{m}^{-1} \text{s}^{-1}$. This value was designated as k_{probe} .

Chars of 16%, 23% and 36% porosity were injected into flow reactor environments containing 12 mole-% O_2 at nominally 1500 K. Partially reacted chars were extracted from the reactor at residence times of 28, 72, and 117 ms. 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 with the 16% porosity char was 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.

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.

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.

A particle population balance model was developed and used to characterize the type of fragmentation that occurs during coal devolatilization and char oxidation and to quantify the rates of

fragmentation events. The model allows for attrition-type behavior (in which only fines are produced), breakage-type behavior (in which particles break into two or three smaller particles), and percolation-type behavior (in which particles fragment into a distribution of smaller size particles).

In the model, a number of size bins are used to describe the particle size distribution. Bin i is characterized by its upper and lower size cutoffs, x_i and x_{i+1} , respectively. Bin 1 contains the largest size particles in the distribution (diameters in the range x_1 to x_2) and bin n , the smallest size particles (diameters in the range x_n to 0). Each size bin 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 particle population balance model is represented 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 . $S_{i,k}$ is the fragmentation rate constant and $C_{i,k}$ and $D_{i,k}$ are the burning rate constants. The b_{ij} are elements of the fragmentation progeny matrix, which specify the number of fragments that enter bin i per particle that fragments in bin j . Particles fragmenting in bin j can produce fragments only in bin i where $i \geq j$, therefore, $b_{ij} = 0$ for $i < j$. The progeny elements were determined for each type of fragmentation considered.

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 fragmentation rate constant S_i represents the fraction per unit time of particles of size x_i that fragment, and is expressed in terms of a fragmentation rate coefficient k , which gives the frequency of fragmentation events, a fragmentation sensitivity parameter σ , which gives the relative

tendency for a particle to fragment because of its size, and a density-sensitivity parameter ω , which gives relative tendency of a particle to fragment because of its density. 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 and 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. Both $C_{i,k}$ and $D_{i,k}$ depend on the overall particle burning rate q , which is expressed in terms of an apparent chemical reaction rate coefficient $k_s (= A_a \exp(E_a/RT))$.

The single-film model of a burning carbon sphere is used to describe a burning particle. Allowance is made for CO and CO₂ formation at the particle surface and account is made for Stefan flow in the boundary layer surrounding the particle. Particle temperatures during burnoff are determined from an energy balance, wherein the rates of energy generation due to char oxidation are balanced by the rates of energy loss by conduction, convection, and radiation.

The key adjustable parameters in the particle population balance model are the Arrhenius parameters for the apparent chemical reaction rate coefficient (A_a and E_a) and the fragmentation rate coefficient (k). These are adjusted to provide time-resolved agreement between measured and calculated extents of mass loss and particle number distributions.

Calculations using the model indicate that fragmentation during heat-up and devolatilization is percolative in nature and that the extent of fragmentation increases with coal volatile yield. Calculations 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. Calculations also indicate that fragmentation during burnoff is percolative in nature. The adjustment of model parameters to fit data indicate that char fragmentation rates increase with char porosity.

Fragmentation rates during devolatilization are estimated to be as high as five times the fragmentation rates during char oxidation. Factors that govern fragmentation during heat-up and devolatilization differ from those that control fragmentation during char oxidation, and hence, it is not expected that the same fragmentation rate parameters apply in the two regimes.

Calculations suggest 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. Since all char fragments are not spherical, the possibility exists that fragments having large surface to volume ratios extinguish before complete burnout, leading to unburned carbon in ash. The extent of non-sphericity on unburned carbon in ash needs to be investigated, and is the focus of continued work.

Activities associated with each of the tasks into which the project was divided are to be discussed in detail in the various sections of the final report. This draft version of the final report does not contain the completed sections. They are still under preparation and will appear in the final form of the report.

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

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REPORTED BY: Reginald E. Mitchell

Phone: 415-725-2015

RESEARCH OBJECTIVES

This document is the final 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 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 were performed using synthetic chars having particle morphologies similar to those of the char particles formed during coal devolatilization. Results with synthetic chars differing in porosity were used to define parameters that appear in the char oxidation-fragmentation model that was developed.

The overall objectives of the project were: (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 can be used to predict accurately the overall mass loss rates of coals based on both the physical and chemical characteristics of their chars. The work provides a means of assessing reasons for unburned carbon in the ash of coal fired boilers and furnaces.

The overall research project was divided into four tasks. Specific objectives associated with each task were as follows:

Task 1: Production and Characterization of Synthetic Chars

Objective: The objective of this task was to produce and characterize synthetic chars with controlled macroporosity and known mineral content. Particle diameters, true and apparent densities, porosities, pore size distributions, and total surface areas were measured.

Deliverables: Results of this task yielded 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% were produced.

Task 2: Baseline Char Combustion Experiments

Objectives: The objectives of this task were 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.

Deliverables: The following was accomplished 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 were available for use.
- The extent to which particles fragment during the sampling process was characterized.
- Oxygen concentrations and gas temperatures that yield diffusion-limited burning of the synthetic chars produced were identified.

Task 3: Char Fragmentation Studies

Objective: The overall objective of this task was to obtain the data necessary to understand how the porosity of char particles affects their fragmentation behavior. Partially reacted chars were extracted from the flow reactor at specified residence times and extents of mass loss and particle size distributions were determined.

Deliverables: The following information was available after completion of this task:

- A measure of fragmentation events that result as a consequence of devolatilization as a function of particle porosity.
- A measure of fragmentation events that result as a consequence of burning in various gaseous environments as a function of particle porosity.

Task 4: Fragmentation Modeling

Objective: The objective of this task was to develop and validate a fragmentation model that can be incorporated into a char oxidation model.

Deliverable: The completion of this task yielded a char oxidation-fragmentation model that describes the results of Task 3 experiments. The model is capable of accurately predicting overall char mass loss in gaseous environments typical of pulverized coal combustors when account is made for particle fragmentation. With the model, the extent to which fragments might extinguish and hence, contribute to unburned carbon in ash can be assessed.

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