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RESIDUAL CARBON FROM PULVERIZED COAL FIRED BOILERS 1:
SIZE DISTRIBUTION AND COMBUSTION REACTIVITY

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ABSTRACT

The amount of residual, or unburned, carbon in fly ash is an important concern in the design and operation of pulverized coal-fired boilers. Char oxidation is the slowest step in the coal combustion process, and the rate at which this heterogeneous reaction proceeds has an important effect on the degree of carbon burnout. There is an extensive literature on char combustion kinetics based on data in the early and intermediate stages of carbon conversion. A critical fundamental question is whether the small fraction of the fuel carbon that passes unreacted through a boiler is representative of the char during the main portion of the combustion process. This article addresses that question through a detailed characterization of eight carbon-containing fly ash samples acquired from commercial-scale combustion systems.

The fly ash characterization included measurement of joint carbon/size distribution and determination of the combustion reactivity of the residual carbon. To minimize mineral matter interactions in the reactivity tests, the technique of incipient fluidization was developed for separation of carbon-rich extracts (≈ 75 wt-% carbon) from the inorganic portion of the fly ash. Reactivity measurements were made at 1400 - 1800 K to represent conditions in pulverized coal fired boilers. Measurements were also made at 700 - 1100 K to minimize transport effects and isolate the influence of char chemistry and microstructure. In both temperature regimes, the residual carbon extracts were significantly less reactive than chars extracted from a laboratory-scale laminar flow reactor in the early-to-intermediate stages of combustion. It is concluded that the boiler environment deactivates chars, making high carbon burnout more difficult to achieve than is predicted by existing char combustion kinetic models that were developed from data on the laboratory chars. Finally, the results are used to discuss potential char deactivation mechanisms, both thermal and oxidative, in coal-fired boilers.

INTRODUCTION

The amount of residual, or unburned, carbon in fly ash is an important concern in the design and operation of pulverized coal fired boilers. While most utilities are able to select a combination of equipment, fuels, and operating conditions to achieve acceptable carbon conversion, modern combustion zone modifications for NO_x control are leading to increasing problems with high residual carbon levels in ash. The delayed mixing that is an integral part of low-NO_x combustion systems makes complete fuel conversion inherently more difficult to achieve, especially in existing, retrofitted furnaces. Char oxidation is the slowest step in the coal combustion process, and the rate at which this heterogeneous reaction proceeds has an important effect on the degree of carbon burnout. There is an extensive literature on char combustion kinetics¹⁻⁴, primarily based on data in the early and intermediate stages of carbon conversion.

A critical fundamental question is whether the small fraction of the fuel carbon that passes unreacted through a boiler is representative of the char during the main portion of the combustion process. The answer to this question determines whether char reactivity can be treated as a constant, independent of environment and conversion, and whether existing oxidation kinetics, determined for laboratory-generated chars in the early-to-intermediate stages of combustion⁴, can be applied in the boiler environment and to the technologically important high burnout region.

A number of studies have directly addressed the problem of unburned carbon in pulverized coal combustion. These range from laboratory-scale combustion studies^{5,6} to pilot-scale combustion studies^{7,8} to studies focusing on the analysis of commercial-scale fly ash samples^{9,10}. Several studies have coupled the analysis of fly ash samples with modeling to gain insights into commercial-scale combustion processes^{11,12}. Predictive models used by industrial groups for boiler design and optimization have also been described in the open literature^{13,14}. None of these studies has attempted to measure the high-temperature combustion reactivity of residual carbon, nor to characterize its bulk physical and chemical properties. This is undoubtedly due in part to the difficulties associated with making meaningful measurements on samples of very high ash content.

The objective of the present work is to achieve a better understanding of the fuel-related factors determining unburned carbon levels through a detailed examination and characterization of fly ash samples from commercial boilers. A suite of fly ash samples

was obtained from commercial scale industrial and utility boilers and a new technique was developed to separate and extract residual carbon from the inorganic portion of the fly ash. The combustion reactivity of the residual carbon extracts was then determined by two independent techniques in two temperature ranges: 1400 - 1800 K (to simulate the boiler environment) and 700 - 1100 K (to minimize transport effects). In both temperature ranges, residual carbon samples are found to be much less reactive than laboratory chars in the early-to-intermediate stages of combustion, and the implications for carbon burnout in boilers is discussed.

MATERIALS AND EXPERIMENTAL PROCEDURES

Coal and fly ash samples

Eight fly ash samples were acquired from industrial and utility sources, representing various boiler types burning a range of U.S. coals. Table 1 provides some basic information on the samples and their sources. Eight samples were selected to determine if systematic trends could be observed—despite the complexity of the boiler environment and the wide variety of boiler operating conditions and fuels examined. The sample suite includes four high-volatile bituminous steam coals, a low-volatile coal, a western low rank/eastern high rank coal blend, and two fly ash samples from a utility boiler obtained during (a) low-NO_x and (b) conventional firing conditions. The fly ash samples were acquired from the hoppers of particulate collection systems, primarily electrostatic precipitators, or by high-volume entrained-particulate sampling at the economizer outlet. Overall residual carbon contents of the samples ranged from 5.5% to 10.8%. Most of the samples were generated as a part of commercial-scale testing programs, for which much additional information exists on the equipment and operating conditions (see for example Sorge et al.¹⁵).

For comparison, chars were also generated by partial combustion of raw coals in a laboratory-scale entrained flow reactor operating at oxygen levels of 12 mole-% and peak particle temperatures of 1800 - 2000 K, typical of pulverized coal-fired boilers. Residence times were 70 to 95 msec, yielding chars in the early-to-intermediate stages of combustion (char carbon conversion 20 - 60%).

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Sample characterization

Joint distributions of particle size and carbon content were determined for the as-received fly ash samples by dry sieving and a loss-on-ignition (LOI) measurement, using a modified technique for small sample sizes. The LOI measurement was carried out by exposing 100 - 500 mg of ash to air oxidation during heating at approximately 15 K/min to 1270 K followed by a 1 hour soak time at this peak temperature, after which the total weight loss was determined gravimetrically.

A primary focus of this study is to measure the high-temperature combustion reactivity of the residual carbon under conditions similar to those found in pulverized coal-fired boilers. Global reactivities of residual carbons and laboratory-generated chars were measured in a laminar flow reactor equipped with an optical diagnostic for *in-situ* measurement of the temperature, size, velocity, and spectral emissive factor of reacting particles. The reactor and optical diagnostic are described in detail elsewhere^{16,17}. A simple high-temperature reactivity test was devised to accommodate the special requirements of the residual carbon samples, chief among these being small sample size, low reactivity, and high ash content. To perform this test, optical measurements of size, temperature, and emissive factor were made on at least two hundred particles at 72 and/or 95 msec residence time in 12 mole-% oxygen at gas temperatures from 1500 - 1560 K. Burning rates were computed from the optical data using a model of gas-particle transport processes, described in the theory section.

Reactivities in the temperature range 700 - 1100 K were measured for Daltex and Illinois #6 samples by thermal gravimetric analysis (TGA). Prior to the TGA experiments, the laboratory chars were prepared by injection of raw coal (90-180 μm) in the laminar flow reactor and extraction of samples at 72 msec residence time, during the early-to-intermediate stages of char combustion. In the nonisothermal TGA technique used, the char or residual carbon samples were ground to a fine powder, and the weight loss in 7% oxygen recorded as the sample was heated from room temperature to approximately 1200 K at 15 K/min.

The large quantity of inorganic matter (90 - 95 wt%) makes meaningful and accurate measurements of high temperature combustion reactivity difficult on the raw samples. Two techniques were therefore used to minimize inorganic interferences. The first technique, incipient fluidization, was developed as part of this work, and uses an air-sparged, high-aspect-ratio fluidized bed to extract a carbon-rich sample from size-classified fly ash prior

to combustion studies. Incipient fluidization is described in detail in a separate section below. The second technique, described previously¹⁸, discriminates inorganic (fly-ash) particles from carbon-rich particles *during* combustion studies by *in-situ* measurement of their spectral emissive factors in the near-infrared. This second technique is reviewed briefly in the theory section.

Separation of residual carbon by incipient fluidization

Several techniques have previously been demonstrated for separation of residual carbon from fly ash, or for separation of coal from mineral grains (coal beneficiation), including flotation^{19,20} and density segregation in heavy media. Here we describe the simple, dry technique of incipient fluidization, which does not expose the carbon to potential contaminants that may alter its reactivity or properties.

The principle of carbon/fly ash separation by incipient fluidization is illustrated in Fig. 1. The technique utilizes a high-aspect-ratio air-fluidized bed, operating at incipient fluidization, to segregate carbon-rich particles from mineral-rich particles on the basis of density. Size-graded fly ash is introduced into a 1 cm diameter tube to form a bed with height-to-diameter ratio of approximately four. Nitrogen gas is introduced through a fritted disk at a flow rate less than that required to fully fluidize the bed. The flow rate is chosen to generate local particle motion, while avoiding the large-scale bed flows that lead to macro-mixing and homogenization. The result is an efficient segregation of low and high density particles. When an adequate separation is achieved, the fluidizing air is interrupted, and the individual fractions are removed from the segregated fixed bed by a capillary suction sampling system. The technique requires a rough preclassification to remove particles smaller than 50 - 90 μm and is thus capable of carbon recovery from the coarse fractions of fly ash only. Application of the technique to the fly ash samples in this study typically produced an extract of approximately 75 wt-% carbon from the 90 - 180 μm size fraction of the raw fly ash. In some cases, size classification alone produced sufficient carbon enrichment, and the samples were not upgraded by incipient fluidization prior to combustion experiments.

THEORY

This section describes the technique used to determine global combustion reactivities and also presents equations relating these global reactivities to fundamental char properties. Although incipient fluidization removes most of the inorganic material, a significant number of inorganic-rich particles remain in the residual carbon extracts. Prior to determining

reactivities from the optical measurements, therefore, data points for inorganic-rich particles were excluded by the technique described below.

Optical discrimination of carbon-rich and inorganic particles

A recent paper¹⁸ proposed an optical diagnostic to distinguish inorganic from carbon-rich particles by *in situ* measurement of their spectral emissive factors at a wavelength of 800 nm[†], ϵ_{800} . Carbon, being a strong absorber of visible and near-infrared radiation, is by Kirchoff's law also a strong emitter and exhibits a high emissive factor. Carbon-free fly ash particles, although they possess a wide range of optical properties, are generally transparent or reflective, and will, by Kirchoff's law, exhibit low emissive factors.

Application of this diagnostic is illustrated in Fig. 2 which presents optical data for three samples of Illinois #6 coal with very different combustion histories. Fig. 2a presents data for a predominantly carbon-rich laboratory-generated sample at 62% carbon conversion. Emissive factors for this sample lie almost exclusively above 0.3. The sample in Fig. 2b is a 100 - 190 μm size fraction of the high density extract from the Illinois #6 fly ash sample, containing numerous inorganic-rich fly ash particles and 6 wt-% residual carbon. The data fall into two groups: a dense collection of points in a curved band in the left portion of the diagram, and a scattering of points to the right over a wide temperature range, but at generally higher emissive factors. (Note that the high temperatures at low emissive factors have been shown to be an artifact of the optical diagnostic¹⁸). Fig. 2c shows optical data taken on the same sample after pretreatment of the high density extract by slow heating in air to 1000 K followed by a 2 hour hold time. This procedure removes the residual carbon and results in the disappearance of the second group of particles at high emissive factor. We can clearly associate the ash particles with the points clustered in the curved band in the left portion of the figure, and the carbon-containing particles with the scattered points at higher emissive factors. Based on data for fly ash samples from various origins, it was established¹⁸ that a threshold value of 0.3 for the emissive factor can be used to statistically classify particles as carbon-rich ($\epsilon_{800} > 0.3$) or inorganic ($\epsilon_{800} < 0.3$) with an error rate,

[†] The spectral emissive factor for an irregularly-shaped, emitting particle, with a diameter along the flow axis of d_p , is defined as the average spectral radiance ($\text{W}/\text{cm}^2\text{-st-}\mu\text{m}$) of the particle at a given wavelength (here 800 nm) divided by the spectral radiance of a spherical black body of diameter d_p . The spectral emissive factor is, in essence, the particle spectral emissivity, multiplied by a shape factor, $A/(\pi d_p^2/4)$, where A is the projected area of the particle as viewed from the optical axis.

or frequency of incorrect assignment, of 4% or less. Thus by sorting and selecting the raw optical data, kinetic data can be obtained on the subset of carbon-rich particles in a highly reacted, mineral-rich sample.

Determination of global reactivities

Burning rates were calculated from the measured particle temperatures using a numerical model of gas-particle transport processes, described in detail elsewhere²¹. The model treats unsteady convective and radiative heat exchange and multicomponent mass transport between the particle and the surrounding gas and has been validated by comparison to burning rates measured by extractive sampling and inorganic- tracer analysis²². Prior to the calculation of burning rates, particles with emissive factors less than 0.3 are excluded because of the high probability that they are inorganic rich. The combination of sample upgrading by incipient fluidization and statistical sorting of particles by the ϵ_{800} criterion essentially eliminates interferences due to inorganic material in these samples.

The remaining optical data are statistically sorted to determine the particles of median size and temperature²¹. The transport model is then used to calculate burning rates for the particles of median reactivity. For direct comparison, burning rates are reported in a standard environment (6% O₂, gas temperature 1500 K), which is typical of environments in the upper regions of pulverized coal fired furnaces in which the late stages of char combustion occur. The burning rates are corrected to these conditions assuming a common global activation energy of 20 kcal/mol⁴ and a common global reaction order²³ of 1/2. Because the standard conditions are close to those used in the flow reactor experiments, the results are not very sensitive to the values used in the correction for the reaction order and activation energy. A range of reaction rates is determined for a range of possible CO/CO₂ product ratios. An upper reactivity limit is calculated by assuming CO to be the only heterogeneous reaction product. A lower reactivity limit is calculated by assuming a product ratio given by:

$$CO/CO_2 = 3 \cdot 10^8 \cdot e^{(-60/RT_p)} \quad (1)$$

with RT_p in kcal/mol⁴. Both the mean reactivity and the limits of the reactivity range are reported. In addition, for direct comparison, the set of burning rates is converted to a set of global rate coefficients at a common particle temperature of 1500 K, k_{1500} , where

$$q_{1500} = k_{1500} P_s^{0.5} \quad (2)$$

where P_s is the calculated oxygen partial pressure at the particle surface.

The fundamental components of global reactivity

This section presents a brief treatment of the fundamental reaction and diffusion processes that determine global reactivity, based on the classical theory of Thiele²⁴ and previously applied to char combustion by numerous researchers²⁵. The particular form of the derivation presented below is for ash (inert)-containing porous particles. The global reactivity, r_g , of porous char particles is defined here as a burning rate per unit external surface at a specified particle temperature and surface oxygen concentration. The global reactivity, r_g , with units g-carbon/s-cm²-external surface, can be expressed as:

$$r_g = q_i S m_c \eta / (4\pi R_p^2) = q_i S (m_c / V_p) \eta (R_p/3) \quad (3)$$

where q_i is the intrinsic reaction rate per unit internal surface area, S is the internal surface area with units m²/g-carbon, (m_c / V_p) is the mass of carbonaceous solid per unit particle volume, η is the effectiveness factor accounting for pore diffusion effects, and R_p is the char particle radius. We assume for sake of this particular analysis that the intrinsic surface kinetics are described by simple, first-order kinetics, according to: $q_i = k_i P_s$ where k_i is the intrinsic reaction rate coefficient and P_s is the oxygen partial pressure at the external surface of the particle. For large internal diffusional resistances (zone II combustion) the effectiveness factor can be written in terms of the Thiele modulus (ϕ) as follows²⁶:

$$\eta = 3/\phi ; \quad \text{where } \phi = R_p \sqrt{\frac{k_v}{D_{eff}}} \quad (4)$$

In Eq. 4, D_{eff} is the effective diffusivity in porous media, and k_v is the volumetric rate constant, given by:

$$k_v = k_i S (m_c / V_p) \nu \quad (5)$$

where ν is a stoichiometric factor and . Combining Eqs. 3 through 5 yields for the global reactivity:

$$r_g = (P_s) (S)^{1/2} (k_i/\nu)^{1/2} (m_c / V_p)^{1/2} (D_{eff})^{1/2} \quad (6)$$

For a particle of radius R_p , burning in zone II under conditions that produce a surface oxygen partial pressure P_s , the global reactivity, r_g , is determined by the following set of char properties:

$$r_g \sim (S)^{1/2} (k_i)^{1/2} (m_c / V_p)^{1/2} (D_{eff})^{1/2} \quad (7)$$

Note that the parameter grouping (m_c / V_p) describes the availability of carbon mass in an ash-containing particle matrix and is referred to as carbon availability. The four parameter groupings in Eq. 7 represent the four fundamental components of the global reactivities measured at high temperature.

In the TGA experiments, in contrast, the combination of small particle size (samples are preground to a fine powder) and low temperatures (700 - 1100 °C) gives rise to oxidation in zone I, where reaction rates are determined only by the amount of internal surface and the intrinsic surface reactivity of the surface[†]. These zone I reactivities, R_I with units of g/s-g, scale with char properties as:

$$R_I \sim (S) \cdot (k_i) \quad (8)$$

Equations 7 and 8 will be useful in the interpretation of the measured combustion reactivities.

Results

Size distribution

Figure 3 summarizes the measurements of joint carbon/size distribution for the sample suite. For each coal, it can be seen that most of the sample mass is found in the smallest size fraction (< 38 µm), while the carbon content increases greatly with increasing size. The carbon content of the > 106 µm size fraction is quite high, varying from about 30 to 60 wt-% across the set of samples. Figure 4 illustrates the manner in which the residual carbon is partitioned among the various size fractions for each of the samples. (The residual carbon partitioning is obtained from Fig. 3 by multiplying the amount of sample mass in each of the size fractions and the carbon content of that size fraction.) The manner in which unburned carbon is partitioned is seen to vary greatly from sample to

[†] It is acknowledged that Eq. 8 may be incomplete, in that microporous diffusion rates can influence the rates, even under TGA conditions. Restricted diffusion is known to occur in carbon micropores and can be orders of magnitude slower than molecular or Knudsen diffusion.

sample. For the Indiana #4 and Illinois #6 samples, over 50% of the carbon mass is found in particles greater than 106 μm in diameter, while for the Alpine and Daltex ash samples, only 10 - 15% of the carbon mass is in this size range. During the course of the experiments, it was observed that the residual carbon particles are quite friable and subject to fragmentation upon handling. It is therefore possible that the sieving technique used to determine size and carbon distributions caused fragmentation of some of the residual carbon particles and a shift in the distributions toward smaller particle sizes.

Separation/recovery of residual carbon

Separation efficiencies were measured for six of the eight fly ash samples and are given in Table 2. The carbon-rich fractions are quite suitable for quantitative reactivity measurements in the laminar flow reactor; their ash contents (22 - 40%) are typically no higher than those of the laboratory chars in the early-to-intermediate stages of combustion.

Combustion reactivity at 1400 - 1800 K

The results of the reactivity tests are summarized in Fig. 5. To facilitate comparisons, reactivities are presented as burning rates in a selected environment and are plotted vs. rank of the parent coal, represented by its dry, ash-free carbon content. For comparison to the residual carbon materials, Fig. 5 also plots the reactivities of 12 different laboratory-generated chars at low-to-intermediate conversion⁴. The bars around the residual carbon data points represent the range of reactivities determined using different assumptions regarding the CO/CO₂ ratio at the particle surface, as discussed in the experimental section.

Char reactivity is seen in Fig. 5 to be a strong function of rank, with the reactivities of the laboratory chars falling in a well-defined band as a function of parent coal carbon content. At any given rank the residual carbon samples are less reactive than the laboratory chars by factors of 2 to 7. Also, in each case where chars were available from the same parent coal, the residual carbon samples are seen to be much less reactive. It is also found that thermally pretreating the samples at 1000 °C for 15 min to remove surface oxides has little

affect on reactivity[†].

The reactivity comparisons in Fig. 5 are relevant when char reactivity is compared at a fixed gas temperature, with the mean particle temperature varying from sample to sample as a function of reactivity. Table 3 presents an alternative representation of reactivity in the form of global rate coefficients at a common particle temperature of 1500 K. Rate coefficients for the residual carbon materials are lower than the laboratory-generated chars by factors of 2.2 - 5.

It is remarkable, that, despite the complexity of the boiler environment and the wide variety of boiler operating conditions and fuels examined here, the residual carbon samples, as a class of materials, exhibit consistently low combustion reactivities relative to laboratory-generated chars in the early-to-intermediate stages of combustion.

Combustion reactivity at 700 - 1100 K

Figure 6 presents nonisothermal TGA profiles for Daltex and Illinois #6 chars and residual carbon samples. Compared to the laboratory char data, the peak rate of weight loss for both residual carbon samples is shifted toward higher temperatures, indicative of lower reactivity. For both parent materials, the onset of weight loss, the completion of weight loss, and the maximum rate are all shifted to higher temperatures.

Figure 7 replots the four rate curves from Fig. 6 vs. $1/T$ to allow convenient comparisons of weight loss rates at a common temperature^{††}. The Illinois #6 residual carbon is less reactive than the corresponding laboratory char by an average factor of 15, while the Daltex residual carbon is less reactive by a factor of 2.6.

[†] A alternative explanation for the low particle temperatures could be related to the high oxygen contents of these highly reacted samples. This could lead to a lower heat of combustion and reduced particle temperatures for the same reaction rate. These tests rule out this explanation and instead indicate low reactivity as the cause of the low particle temperatures.

^{††} Note that in this Arrhenius-form plot, the carbon conversion varies along each curve, and also differs for different samples when they are compared at a common temperature. If the reaction rate is a function of conversion (which it typically is), then the influences of both conversion and temperature are imbedded in each curve, and these data must be interpreted with care. It has been shown for example²⁷ that heterogeneity in the char sample leads to curves with slopes that are significantly less than E/R , where E is the true activation energy of the oxidation reaction.

Discussion

Despite the complexity of the boiler environment and the wide variety of boiler operating conditions and fuels examined here, the residual carbon samples, as a class of materials, exhibit consistent and unique properties. Specifically, a consistent pattern is apparent in the data on particle size distributions of residual carbon, with the carbon greatly shifted toward larger sizes in relation to the distribution of total mass. The residual carbon distribution is also distinctly coarser than typical pulverized coal size distributions. The observed effect of combustion on the fuel particle size distribution is the net result of three competing effects: (1) a decrease in the size of each individual particle (2) the preferential consumption of carbon in smaller particles due to their higher specific surface area, and (3) fragmentation during combustion or sampling. For narrow size distributions in the parent coal, effects 1 and 3 prevail and combustion reduces mean particle size, while for broad size distributions characteristic of industrial practice, effect 2 prevails and combustion shifts the mass distribution to larger sizes. The shift toward larger sizes is thus an inherent feature of the combustion process for pulverized fuels and can be predicted by simple reaction engineering models of boilers¹¹ or by a simple Lagrangian model of a reacting char particle population for the limiting case of uniform one-dimensional combustion²⁸.

The most significant finding of this study is the consistently low global reactivity, under boiler-relevant conditions, of the residual carbon materials relative to the laboratory-generated chars at low-to-intermediate conversion[†]. It will be useful to speculate on the origin of this low global reactivity by examining Equation 7, which identifies the four underlying factors: the carbon availability, m_c / V_p (g-carbon/cm³-particle), the total surface area, S (m²/g-carbon), the intrinsic surface reactivity, k_i , and the effective diffusivity within the porous char D_{eff} (cm²/s).

Comparing the residual carbons and laboratory chars, we find that carbon availabilities, which are functions of particle density and ash content, are similar after inorganic elimination by incipient fluidization. The observed differences in global zone II reactivities

[†] This conclusion is based on data for a specific size fraction, from 90 - 180 μm in diameter, representing from 20 to 60 wt% of the total residual carbon. Gibbins and Williamson²⁹ have measured similar TGA reactivities for various particle size fractions of residual carbon samples for particles greater than 38 μm in diameter, and somewhat higher reactivities for the particles smaller than 38 μm in diameter. Based on this data and on the magnitude of the reactivity differences observed in the present study, we expect the above conclusion to hold for most or perhaps all of the residual carbon size fractions.

must therefore be proportional to the factor $(S \cdot k_i \cdot D_{eff})^{1/2}$ by Eq 7. The TGA reactivities provide different information on the samples, as they are proportional to $(S \cdot k_i)$ by Eq. 8. The ratio of the zone I reactivity of the residual carbon to that of the laboratory char to the one-half power, $(R_{Irc}/R_{Ilc})^{1/2} = (S \cdot k_i)_{rc}^{1/2} / (S \cdot k_i)_{lc}^{1/2}$ is a measure of the contribution of surface area and intrinsic reactivity differences to the global reactivity differences at high temperature. For the Illinois #6 samples, $R_{Irc}/R_{Ilc} = 15$ and $(R_{Irc}/R_{Ilc})^{1/2} = 3.8$ which is of the same order as the ratio of global reactivities, $r_{grc}/r_{glc} = 2.6$. This suggests that the lower global reactivity of the residual carbon is primarily due to lower value of $(S \cdot k_i)$, i.e. some combination of low intrinsic reactivity and low surface area. For the Daltex samples, $R_{Irc}/R_{Ilc} = 2.6$ and $(R_{Irc}/R_{Ilc})^{1/2} = 1.6$, accounting for some but not all of the lower global reactivity. $r_{grc}/r_{glc} = 5$.

In general, it appears that low values of $(S \cdot k_i)$ are important contributing factors to the low global reactivity of residual carbon under boiler relevant conditions. The product $(S \cdot k_i)$ is related to total (microporous) surface area and intrinsic reactivity, both properties of the carbonaceous char matrix. Conversely, it can also be said that the low reactivity of residual carbon is not primarily due to the persistence of certain particles types with macromorphologies that inhibit accessibility to internal surfaces. If this were the case, significant reactivity differences would not be observed under TGA conditions. Additional insight is being obtained through measurement of the physicochemical properties of the residual carbon samples³⁰.

The process of carbon burnout in boilers

Finally, we should consider what the residual carbon size distributions and reactivities may tell us about the combustion process in pulverized coal fired boilers. First, the coarse size distribution is indicative of an advanced degree of oxidation—the bulk of the residual carbon is not simply a fraction of the parent fuel that has bypassed regions of high temperature and oxygen concentration due to poor mixing. Secondly, the low reactivities indicate that it is considerably more difficult to reach high conversions in boilers than would be predicted by existing char oxidation models developed from data on the laboratory chars. These models are based on laboratory kinetic data taken during the early-to-intermediate stages of the char combustion process, when reactivities are high. At some point in the burnout process in commercial-scale boilers, chars undergo a deactivation that renders these laboratory kinetics inapplicable. The deactivation may occur quickly, at the peak flame temperature, or more gradually due to the integrated temperature history or the

effect of oxidation, depending on the mechanism. Various mechanisms that can lead to char deactivation in boilers are illustrated in Fig. 8.

Figure 8 shows a population of young char particles, newly formed upon rapid heating and devolatilization of coal within a single burner flame. This young char particle population undergoes a variety of transformations simultaneously. First, the oxidative consumption of carbon shifts the size distribution of the population to larger particles as discussed earlier. Secondly, the high temperatures prevailing at this point (1800 - 2400 K) cause a rapid annealing of the young amorphous char, causing an increase in crystallinity and decreases in hydrogen content, oxygen content, surface area, active sites concentration, and reactivity. The influence of heat treatment on char reactivity has been considered by a number of other researchers³¹⁻³⁴. Tsai and Scaroni³⁵ observed char reactivity to pass through a maximum during devolatilization with peak char reactivity coinciding with peak devolatilization rate. The loss of reactivity in the final stages of devolatilization correlated well with the loss of residual volatile matter, but poorly with microporous surface area or degree of optical anisotropy. The reactivity losses documented by Tsai and Scaroni occur at an earlier stage in the overall combustion process than those documented in the present study, where fully-devolatilized, partially-oxidized chars are compared to chars (residual carbons) in the late stages of combustion.

There is also evidence that the oxidation process itself (independent of its effect on particle temperature) can catalyze this annealing process³⁶. There have been few studies of reactivity changes or carbon transformations under time/temperature/oxygen conditions of direct relevance to pulverized-coal fired boilers, exceptions being Hecker et al.³⁷, Levendis and Flagan³⁶, Wornat et al.³⁸, and Davis, et al.³⁹. These studies suggest that high flame zone temperatures have the potential to deactivate chars, thus inhibiting their complete burnout at later times, downstream, in the lower temperature regions of the upper furnace. Thirdly, because the particles exhibit a range of reactivities and densities¹⁸, the more reactive and less dense components can be removed preferentially, leaving behind a carbon residue that is less reactive. Finally, in the latter stages of the process, fragmentation can alter the size distribution of the ash and residual carbon^{40,41}.

The data obtained in this study establish the importance of char deactivation in boilers, but do not identify the detailed mechanism from among the various possibilities depicted in Fig. 8. The boiler and laboratory combustor environments differ in peak temperature (1800 - 2400 K⁴² vs. 1700 - 2000 K, respectively), and in residence time (approximately 1 sec vs. 70 msec), which leads both to more severe heat treatment and to much higher

extents of oxidation (> 99% vs. 20-60%) in the boiler. The reactivity differences could also be influenced by differences in particle heating rates, but these are believed to be similar in the two environments. Fundamental bench-scale studies under controlled conditions, possibly augmented with time-resolved sampling in boilers, are now needed to understand the detailed mechanism of deactivation and to develop new carbon burnout models.

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NOMENCLATURE

A	projected area of particle, cm^2
D_{eff}	effective diffusion coefficient in porous media, cm^2/s
d_p	particle diameter, μm
E	global activation energy, $kcal/mol$
k_i	intrinsic rate coefficient, $g\text{-carbon}/s\text{-atm}\text{-}cm^2\text{-total surface area}$
k_v	volumetric rate coefficient, $mol\ O_2/s\text{-atm}\text{-}cm^3\text{-particle-volume}$
m_c	carbon mass, g
m_c / V_p	carbon availability, $g\text{-carbon}/cm^3\text{-particle-volume}$
n	global reaction order
P_s	partial pressure of oxygen at the particle surface, atm
q_i	intrinsic reaction rate, $g\text{-carbon}/s\text{-}cm^2\text{-total-surface}$
r_g	global char reactivity or burning rate, $g\text{-carbon}/s\text{-}cm^2\text{-external-surface}$
R	gas constant, $kcal/mol\text{-}K$
R_I	zone I reactivities measured by thermal gravimetric analysis, $g/g\text{-s}$
	$R_{I_{rc}}$ for residual carbon samples; $R_{I_{lc}}$ for laboratory char sample
R_p	char particle radius, μm
S	surface area, $m^2/g\text{-carbon}$
T_s, T_p	gas temperature, particle temperature, K
V_p	particle volume, cm^3

Greek symbols

ϵ_{800}	spectral emissive factor at 800 nm
η	effectiveness factor
ϕ	Thiele modulus
ν	stoichiometric factor, $mol\text{-}O_2/g\text{-carbon}$

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FIGURE CAPTIONS

- Figure 1. Principle of carbon and fly ash separation by incipient fluidization. Shown are the high aspect-ratio air-fluidized bed, the capillary solids sampling system, and examples of low (carbon-rich) and high (inorganic-rich) density extracts.
- Figure 2. Optical measurements for three Illinois #6 char samples of varying combustion histories. Gas environment: 12 mole-% oxygen, $T_g = 1555$ K. Samples are: (a) laboratory-generated char at 62% conversion made from raw coal injection into the laminar flow reactor; (b) high density extract from fluid-bed separation of the Illinois #6 fly ash sample; (c) same sample as in b, but after pretreatment by ashing in air at 970 K for 2 hours to remove residual carbon. Note that the range of true ash particle temperatures is shown in (c). The high temperatures at low emissive factors have been shown to be an artifact of the optical device¹⁸ and are not interpreted here as particle temperatures.
- Figure 3. Joint distributions of particle size and carbon content for various fly ash samples from commercial-scale pulverized coal-fired boilers. Top: size distribution of total mass; Bottom: carbon content of various size fractions.
- Figure 4. Partitioning of total residual carbon among four particle size fractions for various fly ash samples.
- Figure 5. Reactivities of various chars and residual carbon samples. Rates are for 100 μm particles in a selected standard combustion environment with a gas temperature of 1500 K, containing 6 mole-% oxygen. Triangles represent laboratory-generated char samples from a variety of parent coals of various rank⁴.
- Figure 6. Comparison of nonisothermal TGA profiles for laboratory char samples (solid lines) and residual carbon samples (dashed lines). Top: Illinois #6 samples; Bottom: Daltex samples.

Figure 7. Nonisothermal TGA profiles in pseudo-Arrhenius form for Illinois and Daltex char and residual carbon samples. Curves are derived from the portions of the profiles in Fig. 6 corresponding to carbon conversions between 2 and 90%.

Figure 8. Illustration of fuel-related mechanisms determining carbon loss in pulverized coal fired boilers.

Table 1
Properties of Coal and Fly Ash Samples

<i>Shorthand Sample Designation</i>	<i>Parent Coal</i>	<i>Samples Received</i>	----- parent coal properties -----						-- ash properties --	
			<i>%VM (dry)</i>	<i>%Fixed Carbon (dry)</i>	<i>%ash (dry)</i>	<i>%C (daf)</i>	<i>%LOI (dry)</i>	<i>%C[†] (dry)</i>		
Alpine	Alpine Seam lv-bit., WVa	coal, ash	22	67.8	10.2	88.6	9.7	7.8		
Indiana #7	Indiana #7 hv-bit.	coal, ash	38.5	50.7	10.8	81.8	9.2	--		
Indiana #4	Indiana #4 hv-bit.	ash	39.4	51.3	9.3	81.4	5.5	5.6		
Illinois #6	Illinois #6 hv-bit.	ash	35.3	53.5	11.2	82.5	6.7	6.2		
Blend	70/30 blend western (PRB) and eastern hvb	coal, ash	--	--	6.5	78	8.2	7.03		
Daltex	Daltex hv-bit.	coal, ash	34.6	52.7	12.7	84.1	10.8	9.1		
low-NO _x	eastern hv-bit.	coal, ash from low-NO _x firing	33	53	14	86.5	5.6	5.0		
Conv. Firing	eastern hv-bit (parent coal same as in 7)	coal, ash from conventional firing	33	53	14	86.5	5.4	5.0		

† Weight percent carbon in the fly ash sample, determined by a LECO elemental analyzer.

Table 2
Weight Percent of Combustible Organic Material
in Various Fly Ash Fractions Extracted by Incipient Fluidization

<i>Parent coal:</i>	Alpine	Indiana #4	Illinois #6	Blend	Daltex
<u><i>Extract type</i></u>					
low density (carbon-rich)	60.2	77.6	77.3	69.9	73.4
transitional	57.7	72.	71.8	62.1	71.0
high density (inorganic-rich)	32.8	8.6	6.1	9.7	30.9

Table 3
Reactivity of Various Char and Residual Carbon Samples

<i>Sample</i>	<i>Global rate coefficient at 1500 K</i> <i>(10³·g-carbon/cm²·s·atm^{0.5})</i>	
	Residual carbon	Laboratory char
Alpine	5.8	14.0
Indiana #7	4.5	--
Indiana #4	3.8	--
Illinois #6	4.6	--
Daltex	2.7	13.6
Blend	12.4	27.4
Low-NO _x	4.6	22.5
Conventional firing	5.2	22.5
<i>Other chars[†]</i>		
Pocahontas #3, PSOC-1508D		4.8
Lower Kittanning, PSOC-1516D		10.8
Pittsburgh #8, PSOC-1451D		9.2
Illinois #6, PSOC-1493D		11.8
Blue #1, PSOC-1445D		22.4
Hiawatha, PSOC-1502D		> 30 ^{††}
Dietz, PSOC-1488D		> 30 ^{††}
Smith-Roland, PSOC-1520D		> 30 ^{††}
Lower Wilcox, PSOC-1443D		> 30 ^{††}
Beulah lignite, PSOC-1507D		> 30 ^{††}

[†] taken from Hurt and Mitchell⁴.

^{††} reaction limited by boundary layer diffusion under experimental conditions employed.

Low-Density Extract
74 wt-% Carbon

High-Density Extract
6 wt-% Carbon

(d)

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(7)

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