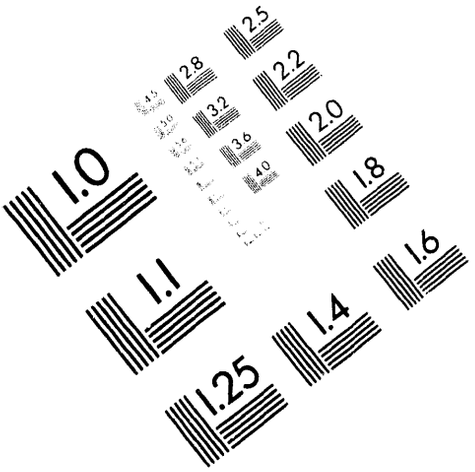

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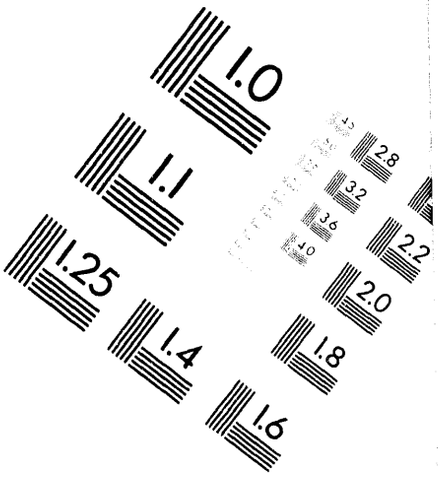

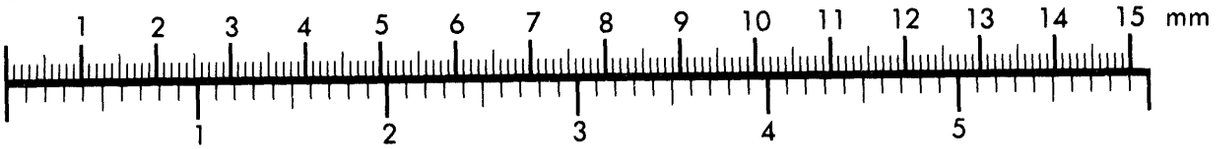

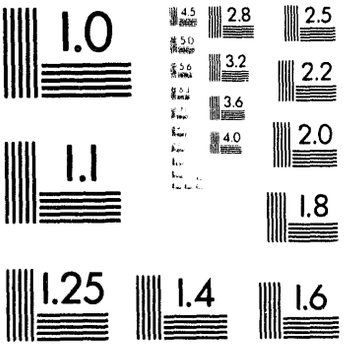

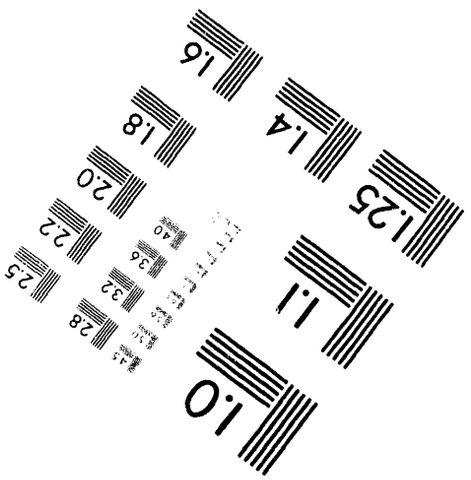

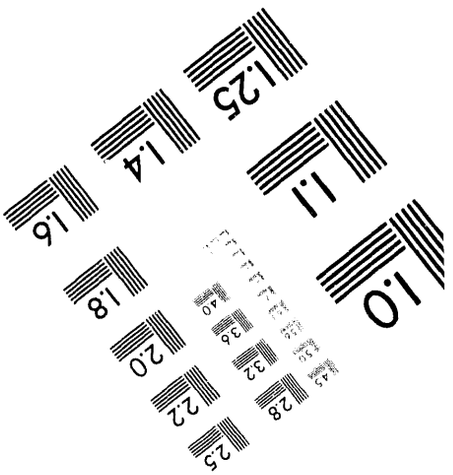

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Evolution of Char Chemistry, Crystallinity, and Ultrafine Structure during Pulverized-Coal Combustion

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The carbonaceous structure of partially reacted char samples, generated by direct injection of pulverized coal into a laboratory entrained flow reactor, was characterized by four techniques: elemental analysis, carbon dioxide vapor adsorption, X-ray diffraction, and fringe-imaging using high resolution transmission electron microscopy. It is observed that the early stages of heterogeneous oxidation proceed in parallel with the latter stages of carbonization, leading to preferential loss of hydrogen, a reduction in surface area, and the development of crystalline order. Typical combustion times and peak temperatures are insufficient to bring about true (three dimensional) graphitization for most coals, but rather, lead to the growth of regions of turbostratic order. This ordering is seen to occur over a time scale comparable to the combustion process itself—here, on the order of 100 msec at particle temperatures of 1800 K and oxygen concentrations of 12 mole-%. This work presents evidence that the reactivity of chars in the latter stages of burnout, which is critically important to the explanation and prediction of unburned carbon in flyash, is significantly impacted by the evolution of the carbonaceous matrix. Although internal surface area and hydrogen content evolve significantly during early char combustion, indicative of aromatic ring coalescence, they do not play a major role in the char deactivation noted in previous investigations. Among the four indicators of carbon structure evaluated herein (H/C ratio, carbon dioxide surface area, crystallite dimensions by X-ray diffraction, and HRTEM images), the volume fraction of ordered material as determined by HRTEM fringe-imaging correlates best with the observed reactivity loss for Illinois #6 coal chars.

Introduction

High levels of residual or unburned carbon in flyash have long been an important concern for the design and operation of pulverized-coal-fired boilers because of deleterious effects on the efficiency of combustion, heat transfer, and particulate removal processes. In addition, flyash containing more than 6% carbon cannot be sold to cement manufacturers, which necessitates

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disposal and payment of the resulting fees[1]. Combustion zone modifications for NO_x control and the increasing use of low-sulfur coals (in boilers designed for specific coals with very different properties) have made the task of maintaining low residual carbon levels in boiler flyash much more difficult. Residual carbon levels in boiler flyash are dependent on a number of factors including boiler design, operating conditions, and fuel properties. An improved understanding of the underlying physics and chemistry involved in the later stages of char combustion would improve our ability to optimize these parameters and to predict unburned carbon levels.

Recently, the process of carbon burnout has been reported to be a two-step process[2, 3]: a high-temperature rapid combustion phase consuming 50-80% of the char carbon, followed by deactivation and near extinction† to lower particle temperatures. The progressive loss of global reactivity and the asymptotic nature of the char combustion process is not predicted by widely used global models and has important implications for the modeling of carbon burnout in boilers[3]. New char combustion models are needed that account for the evolution of the char during the combustion process.

The underlying physical and chemical phenomena that may be responsible for the deactivation at high carbon conversion can be classified into three groups related to: 1) particle morphology and macroporosity, 2) carbon/mineral interactions, and 3) chemistry, crystallinity, and ultrafine structure of the organic material. The first two factors alone cannot explain the observed decrease in reactivity[3, 4] and the third is the topic of this paper.

Background

Much of the organic portion of coal char is composed of an imperfect arrangement of aromatic layers varying in size from less than 5 Å to greater than 100 Å. The size and ordering of

† Near extinction is defined as a large and abrupt, but mathematically continuous, decrease in particle temperature in the late stages of char combustion due to loss of global reactivity. The char combustion reaction continues after the near-extinction event, but at a lower temperature and slower rate.

these layers can be related to the reactivity of the carbon present in three fundamental ways. First, as the layers increase in size, the amount of hydrogen and the ratio of reactive edge sites to unreactive interior sites decrease. Second, as the individual layers approach a more perfectly graphitic arrangement of aromatic units, active sites associated with defects, heteroatoms, or non-sp^2-hybridized carbon are lost. Third, as the aromatic layers reach more compact stacking arrangements, the microscopically available surface area decreases. For fast oxidation reactions such as high temperature combustion, the ultrafine carbon structure can also affect reactivity through its effect on microporous diffusion coefficients[5, 6]. Although the relationship between reactivity and crystalline order is more complex than this simple scheme suggests, reactivity does, in general, decrease with increasing degree of order across the spectrum of carbon materials.

When pulverized-coal particles are rapidly heated by injection into a high-temperature environment, the processes of devolatilization, carbon structural ordering, and heterogeneous oxidation occur sequentially, but with significant overlap. Unlike experiments in which the char is stabilized by heat treatment prior to combustion, the experiments conducted in the present work subject chars to simultaneous oxidation and heat treatment (as do industrial applications). Many investigators have examined the effect of heat treatment on carbon structure and reactivity[7-10], but little information exists pertaining to carbon transformations on the millisecond time scale of relevance to pulverized-coal combustion[11]. Hecker and coworkers[12] have observed decreasing reactivities under combustion conditions as a function of residence time for a low-rank coal char whose oxidation rate was strongly influenced by inorganic catalysis. Many researchers have related high temperatures to ordered structures and low reactivities. Marsh[7] identified heat treatment temperature as the dominant factor in determining the uncatalyzed intrinsic reactivity of carbons. The oxidation process, independent of heat treatment, has also been shown to induce atomic rearrangements that lead to increased order in carbons[11, 13].

A variety of characterization techniques can be used to track the ordering of turbostratic† carbons. Elemental analysis is capable of following the decrease in H/C ratio, which is indicative of the loss of aliphatic material, the occurrence of dehydrogenation reactions and preferential oxidation, as well as the coalescence of aromatic units and loss of reactive edge sites. Hydrogen content has been shown to correlate with char oxidation reactivity as measured by thermogravimetry[16]. Measurements of total internal surface area by vapor adsorption methods also provide insight into the crystalline or ultrafine structure of chars, since most of the area lies in micropores and represents disorder in the carbon lattice. Carbon dioxide surface areas are believed to be an approximate measure of the total surface area available for heterogeneous oxidation reactions[17] and, under certain conditions, are proportional to oxidation rates[18].

Two additional techniques that have been widely used in non-combustion applications for the evaluation of pregraphitic crystallite formation are X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). XRD is a well developed approach that is useful for determining quantities such as turbostratic crystallite dimensions and interplanar spacing[18]. After proper "background" correction, XRD data can be used in conjunction with Scherrer-type equations and Bragg's Law to determine average crystallite diameters (L_a), aromatic layer stacking heights (L_c), and interlayer spacings (d_{002})[19]. The first comprehensive XRD work related specifically to coal was done in 1944[20] and since that time a number of investigators have evaluated the structure of raw coal as well as its graphitization under a variety of conditions.

In comparison with XRD, HRTEM is a recently developed tool for characterizing carbon structure. The lattice-fringe imaging mode of HRTEM, which is only practical for instruments with a low spherical aberration coefficient, is a very useful technique for the imaging of atomic planes in a carbon lattice. This technique has seen little use for the examination of raw coals, although a few studies have been done on heat-treated coals[21]. The potential of this technique

† This term, coined by Biscoe and Warren[14], is used to describe carbon materials which exhibit parallel stacking of aromatic layers (i.e., pregraphitization) but not the angular orientation with respect to neighboring layers, which leads to the formation of three dimensional crystalline structure (i.e. graphite). Among coals, only anthracite X-ray diffraction spectra indicate the presence of truly graphitic structure[15].

for obtaining quantitative information from amorphous or semi-amorphous phases is relatively unexplored.

Although XRD and HRTEM have been extensively used for the study of carbonaceous materials and the graphitization or pregraphitization process, no work has been reported that describes the structural evolution of carbon on time scales relevant to pulverized-coal combustion. In addition, few comparisons have been made of the results obtained from XRD and HRTEM lattice-fringe imaging for coal. This investigation extends the use of these techniques to partially reacted products of coal combustion and clarifies the phenomena of char deactivation during pulverized-coal combustion[3].

Samples and Characterization Techniques

This investigation employed Sandia's entrained flow reactor, which is equipped with a He-quenched, water-cooled, solids sampling probe for removal of partially reacted char particles at any residence time up to 117 msec. The reactor is discussed in detail elsewhere[2, 22]. The system was used to collect char samples at residence times of 47, 72, 95, and 117 msec. A residence time of 47 msec corresponds, approximately, to the completion of devolatilization, the disappearance of the visible volatile flame, and the onset of heterogeneous char combustion reactions. An additional sample (referred to herein as a residual carbon sample) was prepared by separating a carbon-rich extract from flyash produced by a utility boiler as discussed by Hurt and coworkers[25].

Several bituminous coals and one subbituminous coal were characterized using the techniques mentioned previously as shown in Table 1. Elemental hydrogen and carbon contents as well as total surface areas were determined for partially-reacted char samples by Coors Analytical Laboratories on duplicate 10 - 20 mg samples. Hydrogen-to-carbon ratios were determined for samples having an ash content less than 50% (high ash contents were found to interfere with the accurate determination of organic carbon, hydrogen and oxygen due to the presence of volatile

inorganic sources such as carbonates and hydroxides[4, 23]). Surface areas were determined by application of the Dubinin-Polanyi equation to carbon dioxide adsorption isotherms. The areas were then normalized by the weight of carbonaceous (organic) material in the samples (mineral matter has a negligible surface area relative to the carbonaceous matrix).

X-ray diffraction analyses were performed by a Rigaku diffractometer equipped with an 18 kW high-intensity rotating anode (Cu K_α radiation, λ = 1.5406 Å, 0.04 deg/step, 40 sec/step). These analyses were performed on thin powder samples of Illinois #6 coal chars mounted on low-background quartz. Samples were demineralized prior to the application of XRD using the procedure of Radovic and coworkers[9] in order to minimize mineral interferences. Precise determination of crystallite dimensions using XRD requires correcting the raw data for a number of "background" effects[19, 24]. This elaborate correction process is not justified for the accuracy desired in this investigation, particularly since the improvement is questionable for amorphous materials with significant amounts of non-carbon atoms (i.e. Illinois #6 chars)[15].

HRTEM was performed using a Phillips Model CM30 microscope (spherical aberration coefficient of 2.0 mm) operating at 300 kV. The axial images, produced in lattice-fringe mode, provide detailed information on the crystalline structure of carbon materials. The superior resolution of HRTEM allows one to distinguish individual graphitic layers oriented perpendicular to the image plane and, for a properly focused image, to extract information on interlayer spacings. Lattice-fringe images yield a wealth of information on the degree and nature of crystallinity in carbons, including the dimensions of the graphitic layers and the extent of parallel alignment of neighboring layers. Application of the technique to most carbon samples requires the preparation of thin sections, usually accomplished by ultramicrotoming. In the present work, optically thin regions of char particles are prepared by a simple and practical technique, in which the sample is hand-ground to a fine powder and then examined at moderate magnification to find wedge-shaped fragments that are optically thin at the edge. A number of such edge regions (typically ten or more)

are then photographed at high magnifications (2,000,000X), and representative fields of view are selected and reproduced for discussion.

Quantitative information on the size and amount of carbon crystallites was extracted from the lattice-fringe images using the commercial code Semper™ and a custom image analysis procedure developed in the course of this work[25]. In summary, these images are analyzed in the following three steps:

1. The raw image is filtered using Fourier transforms to eliminate structures that do not occur periodically with a distance characteristic of turbostratic carbons.
2. The filtered image is analyzed for fringe patterns, which are directly related to groups of turbostratic carbon layers, using an objective procedure designed to minimize noise and determine the most accurate fringe lengths.
3. Average fringe lengths (crystallite diameters) and relative amounts of crystalline structure (relative crystalline volume fractions) are determined.

Results and Discussion

The ratio of hydrogen to carbon for several coal chars is presented in Fig. 1. The H/C ratios of the raw coals vary from 5 to 7%. Hydrogen is evolved much more rapidly than carbon during devolatilization, leading to large decreases in H/C ratio between 0 and 47 msec (not shown in Fig. 1). The H/C ratio continues to decrease significantly during the early stages of char combustion, from 47 to 72 msec, but changes little thereafter. This decrease during char combustion reflects the coalescence of aromatic units and loss of reactive edge sites. However, the H/C ratio does not correlate with reactivity over the entire combustion process, reaching a nearly asymptotic value at 95 msec while the reactivity is decreasing sharply. This information illustrates that H/C ratio, although often an indicator of reactivity[16], does not correlate with observed reactivity at residence times greater than 72 msec for the combustion of these coals.

Surface area measurements for a number of coal chars are presented in Fig. 2. Surface areas generally decrease sharply in the early stages of char combustion and then much more gradually after 72 msec, with some curves displaying a minimum at 95 msec residence time. A similar downward trend has been observed by both Smith and Tyler[26] for semi-anthracite, and Anson *et al.*[27] for bituminous coals. Models that describe the widening and coalescence of pores by oxidation predict surface areas that increase monotonically with conversion when normalized per gram of remaining organic matter as in Fig. 2[13, 28]. The predominant downward trend in Fig. 2 cannot be predicted by considering the effect of oxidation on a rigid porous matrix, but instead, indicates the affects of thermally-induced lattice rearrangements or pregraphitization. This asymptotic decrease in surface area coincides with the observed decrease in H/C ratio and, again, does not correlate with reactivity.

XRD and HRTEM are capable of following ultrafine structural rearrangements more explicitly than measurements of hydrogen loss or micropore surface area, which are symptoms of these rearrangements. Figure 3 illustrates the changes in crystallite dimensions as a function of residence time as determined by XRD. The mean crystallite diameter, L_a, is seen to increase by a factor of 2 with time, while the mean stacking depth, L_c, increases by less than a factor of 1.2. A similar trend has been seen by Radovic and coworkers[9] for a demineralized lignite as a function of heat treatment temperature. For an Illinois #6 coal char, reactivity drops by a factor of two to three during the period from 72 to 117 msec and the reactivity of the residual carbon sample is similar to that of the 117 msec char[3]. In contrast, the crystallite dimensions show relatively little change during this period and the dimensions of the residual carbon (L_a = 42.6 Å, L_c = 17.1 Å) are significantly higher than those of the 117 msec char. As discussed earlier, as carbon atoms are incorporated into the aromatic layers, and to a lesser extent as the stacking of these layers increases, one would expect a corresponding decrease in reactivity. However, the average crystallite diameter is not a true measure of the relative amount of carbon in the aromatic layers nor does it express the barriers to oxidizer penetration that these layers may present on the time scale of

combustion processes. Although estimates of amorphous carbon fractions using XRD are possible[29-31], the results are laborious to obtain and only semi-quantitative.

Figure 4 contains lattice-fringe images for a series of three Illinois #6 chars and a residual carbon sample. By considering the thin regions near the sample edges, we can clearly see that the degree of turbostratic crystalline order increases between 47 and 117 msec residence time. Figure 4 shows that the 47 msec char is primarily amorphous, with only a few small regions of turbostratic order where parallel alignment of neighboring graphitic planes is visible. The char sample extracted after 72 msec of combustion contains amorphous regions comparable to those seen after 47 msec, as well as regions with easily discernible turbostratic structure with graphitic layers on the order of 30 - 100 Å long. A number of parallel arrangements, or turbostratic crystallites, are observed with stacking depths of up to five layers. The crystalline structure continues to develop from 72 to 117 msec, with stacking of up to 10 layers, and the residual carbon sample appears even more crystalline. The development of crystalline order under combustion conditions has also been noted by Levendis and Flagan[11] for polymer-derived carbons, and to a lesser extent for biomass-derived chars. The lack of crystalline order developed in biomass chars produced under conditions similar to those in the present work can be attributed to the high oxygen-content and structural rigidity in the nonfusible parent material[32].

These images provide strong qualitative evidence that the increase in crystallinity correlates with the observed decrease in reactivity. To complement this evidence, quantitative results from these images are presented in Fig. 5. Mean diameters are shown to increase only slightly with residence time, which is qualitatively similar to the XRD results. However, when the images are used to determine the total volume of material in a turbostratic structure normalized by the corresponding quantity present in the residual carbon sample, as shown in Fig. 5, the dependence on residence time changes This quantity, a function of both average diameter and number of layers, increases slightly from 47 to 72 msec before undergoing a rapid increase from 72 to 117 msec – this behavior is almost identical to that of the char reactivity. Also note that the crystalline

volume fraction of the residual carbon sample (by definition =1) and the 117 msec char are almost identical, as are their corresponding reactivities.

Values of the mean crystallite diameter, L_a, measured by HRTEM fringe-imaging (Fig. 3) and XRD (Fig. 5) differ by a factor of 3.7 ± 0.2 when the same averaging technique is used (evaluation of XRD spectra results in a mass average[18]). While both methods yield very similar trends, the inadequacies of sample preparation and image analysis for HRTEM lead to systematic underprediction of the fringe lengths due to contrast variations, twisting and overlapping of the aromatic layers, and amorphous interference. For these reasons the L_a values determined by fringe-imaging should be considered semi-quantitative.

Conclusions

When pulverized-coal particles are rapidly heated by injection into a combustion environment, the processes of devolitalization, carbon structural ordering, and heterogeneous oxidation occur sequentially, but with significant overlap. Unlike experiments in which the char is stabilized by heat treatment prior to combustion, entrained flow reactor experiments (and most practical devices) yield a young char that is highly amorphous, highly reactive, and possesses high surface area and residual hydrogen content during the early stages of combustion This young char is then subject to heat treatment and oxidation, simultaneously giving rise to large changes in char properties and reactivity with time. The early stages of heterogeneous oxidation proceed in parallel with the latter stages of carbonization, leading to preferential loss of hydrogen, a reduction in surface area, and the development of crystalline order. Typical combustion times and peak temperatures are insufficient to bring about true (three dimensional) graphitization for most coals, but rather lead to the growth of regions with turbostratic order. The development of turbostratic order is seen to occur gradually over a time scale comparable to the combustion process itself —

here, on the order of 100 msec at particle temperatures of 1800 K and oxygen concentrations of 12 mole-%.

This work presents evidence that the reactivity of chars in the latter stages of burnout, which is critically important to the explanation and prediction of unburned carbon in flyash, is significantly impacted by the evolution of the carbonaceous matrix. Although internal surface area and hydrogen content evolve significantly during early char combustion, indicative of aromatic ring coalescence, these changes do not play a major role in the noted char deactivation. Among the four indicators of carbon structure evaluated herein (H/C ratio, carbon dioxide surface area, crystallite dimensions by X-ray diffraction, and HRTEM images), the volume fraction of ordered material as determined by HRTEM fringe-imaging correlates best with the observed reactivity loss for Illinois #6 coal chars.

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TABLE 1

Coals investigated and the corresponding techniques employed.

coal	rank	elemental analysis	CO_2 surface area	X-ray diffraction	HRTEM
Illinois #6	hvC bituminous	✓	✓	✓	✓
Pocahontas	lv bituminous	✓			
Pittsburgh #8	hvA bituminous	✓			
Dietz	subbituminous B	✓			
Hiawatha	hvC bituminous		✓		
Eagle	hvB bituminous		✓		
Lower Freeport	mv bituminous		✓		
Lower Kittanning	lv bituminous		✓		

FIGURE CAPTIONS

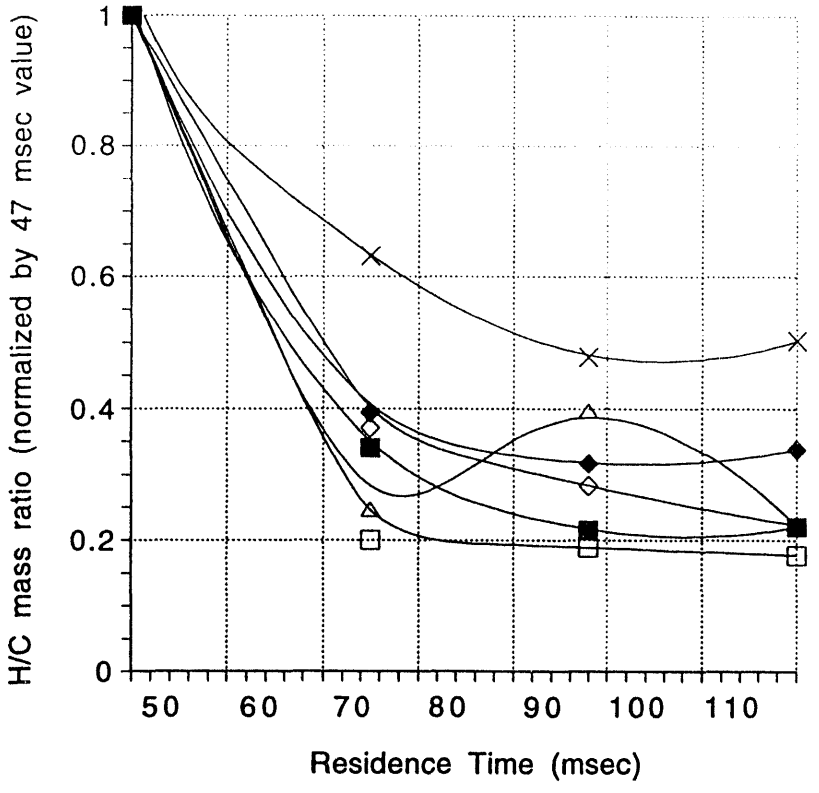
FIG. 1. Hydrogen to carbon ratios as a function of residence time in the Sandia entrained flow reactor (1600K, open symbols - 6% O_2, closed symbols - 12% O_2). × - Illinois #6 (hvcb), ◆ - Pocahontas (lvb), ■ - Pittsburgh #8 (hvab), ▲ - Dietz (subb).

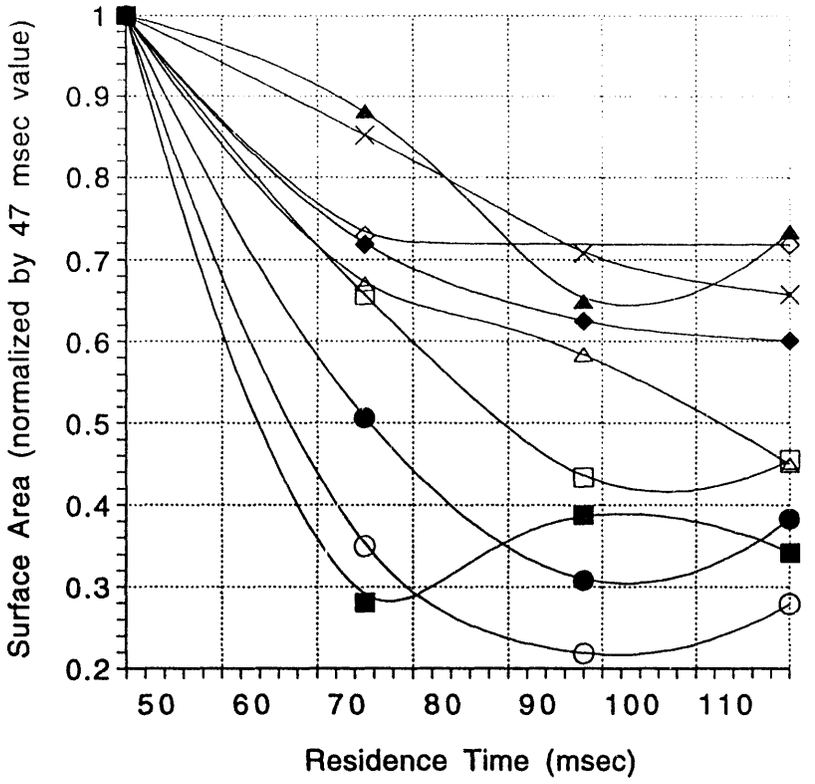
FIG. 2. Carbon dioxide surface area as a function of residence time in the Sandia entrained flow reactor (1600K, open symbols - 6% O_2, closed symbols - 12% O_2). × - Illinois #6 (hvcb), ◆ - Hiawatha (hvcb), ■ - Eagle(hvb), ▲ - Lower Freeport (mvb), ● - Lower Kittanning (lvb).

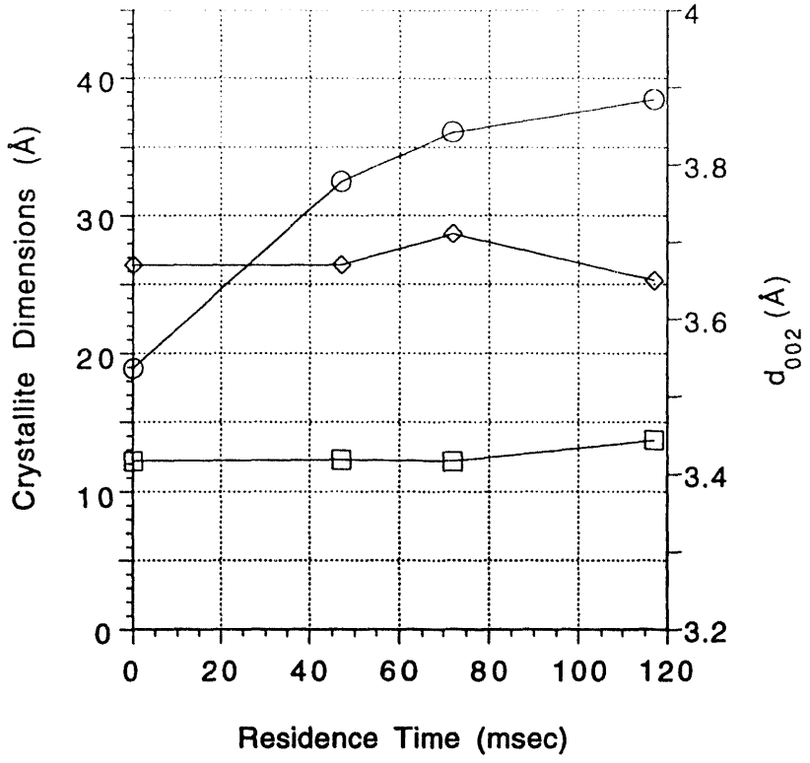
FIG. 3. Turbostratic carbon crystallite dimensions as a function of residence time for Illinois #6 coal in the Sandia entrained flow reactor (the results from the raw coal are listed at zero residence time). Stacking height, L_c (■), diameter, L_a (●), and interlayer spacing, d_{002} (Δ) as determined from XRD spectra using $L = K\lambda/\beta\cos\theta$ and $d = \lambda/\sin\theta$. K is the Scherrer constant for the reflection being considered ($K_a = 0.94$[14], $K_c = 1.84$[33]), λ is the wavelength of the incident radiation, β is the full width at half maximum of the reflection, and θ is the Bragg angle of the diffraction maximum[19].

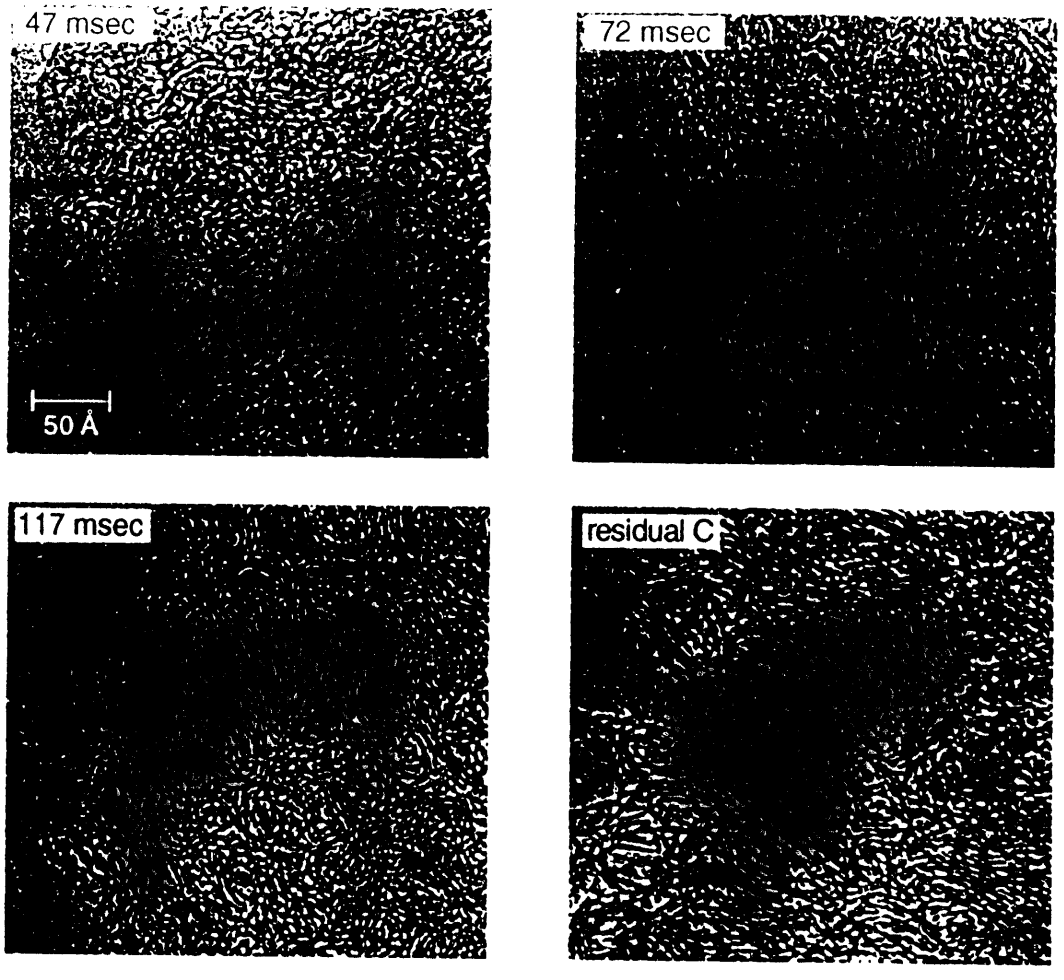
FIG. 4. HRTEM lattice-fringe images of three partially reacted Illinois #6 coal chars after various residence times in the Sandia entrained flow reactor and a residual carbon sample from the flyash of a boiler using the same coal (2,000,000X magnification).

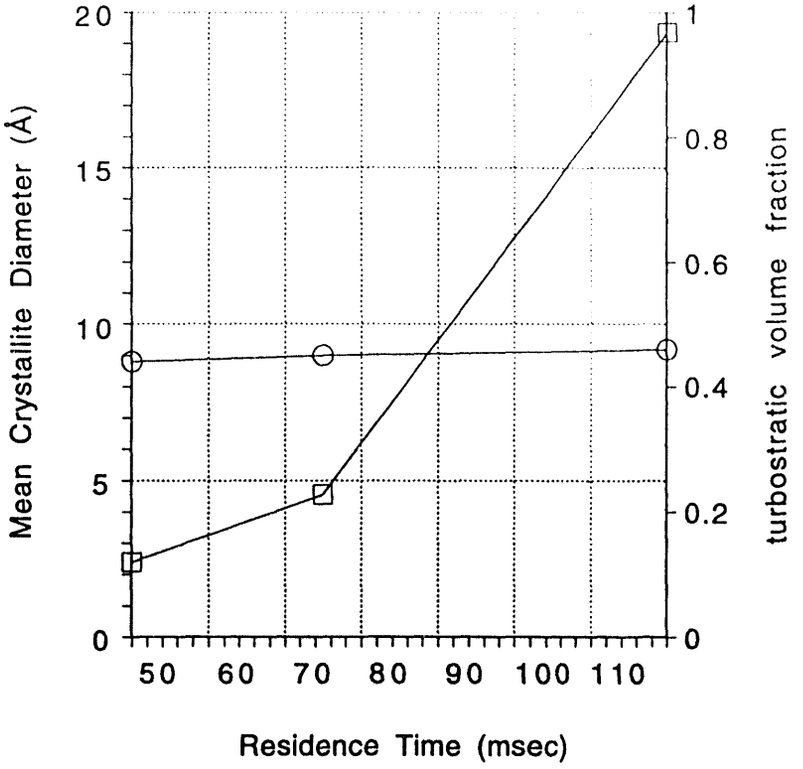
FIG. 5. Mean crystallite diameter (●) and turbostratic volume fraction (■) as a function of residence time for Illinois #6 coal in the Sandia entrained flow reactor. Determined by image analysis of HRTEM fringe images as described elsewhere[25].


H/C mass ratio (normalized by 47 msec value)
1
0.8
0.6
0.4
0.2
0
50
60
70
80
90
100
110
Residence Time (msec)


Surface Area (normalized by 47 msec value)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
50
60
70
80
90
100
110
Residence Time (msec)


Crystallite Dimensions (Å)
0
10
20
30
40
d_{002} (Å)
3.2
3.4
3.6
3.8
4
0
20
40
60
80
100
120
Residence Time (msec)


47 msec
50 Å
72 msec
117 msec
residual C


Mean Crystallite Diameter (Å)
20
15
10
5
0
1
0.8
0.6
0.4
0.2
0
turbostratic volume fraction
50
60
70
80
90
100
110
Residence Time (msec)

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6/17/94

END