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THE THERMAL DECOMPOSITION OF PULVERIZED COAL PARTICLES

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The physical, thermal, and chemical behavior of pulverized coal particles during thermal decomposition are examined for five coal types and two particle sizes for one of the bituminous coals. Particles were injected axially into a lean (35% excess air) methane/air flat flame with a nominal peak temperature of 1750°K. The significant events observed are classified by three time scales. Particles heat to the gas temperature in less than 10 msec, devolatilization occurs between 10 and 75 msec and, under the appropriate conditions, large soot particles are formed WRS and grow for times exceeding 75 msec.

The events that accompany devolatilization are dependent upon coal type and particle size. For large bituminous particles (ca., 80 μm) a significant volatile fraction is ejected from the particle as a jet. This volatile jet reacts close to the particle producing a trail of small solid particles. The local heat released during the reaction of the volatiles, in combination with heterogeneous oxidation, increases the particle temperature and raises it above that of the bulk gas stream. At later times, large soot structures are formed which are attributed to the agglomeration of small, homogeneously formed soot on the volatile trail structures.

Small bituminous particles (ca., 40 μm) burn with a higher intensity (i.e., higher temperature and more rapidly) with few trails and do not produce soot structures probably because of the more diffuse nature of the devolatilization process.

Other ranks of coal exhibit different physical, thermal, and chemical behavior. For example, neither the lignites nor the anthracite produce volatile trails. Further, the particle temperature for the lignites is only slightly shifted above the bulk gas temperature in the devolatilization region while anthracite takes 50 msec to reach the bulk gas temperature level. This is attributable to the relatively low heat content of the volatiles in the former case and the low volatile content in the latter.

The impact of the above observations on the formation of fuel NO is discussed.

Introduction

The design of pulverized coal combustors requires that the various phenomena occurring during thermal decomposition are understood in order to minimize pollutant emissions while providing optimum operating conditions. For example, fuel NO constitutes the major fraction of NO_x emitted from pulverized coal-fired boilers. The partition of fuel nitrogen between the volatile and the char will impact the production of fuel NO. Since the fate

of fuel nitrogen species in the volatiles is dictated by the environment in which they react, their conversion to NO or N_2 will depend both on the degree to which they mix with the bulk flow before reacting and the temperature at which they react. Thus, an understanding of the thermal decomposition processes is desirable in order to formulate control strategies.

The results described in this paper were obtained in a study designed to examine the physical, thermal, and chemical behavior that accompany the thermal decomposition of pulverized coal particles. Such information is required to develop mechanistic models of thermal decomposition, and to provide data for numerical model development. Several

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questions require resolution if these models are to be based upon representative physical behavior. For example, 1) how are the volatile gases released from the particles, 2) what is the effect of fuel type and particle size on volatile release, and 3) how do these physical phenomenon influence fuel nitrogen conversion to NO_x ?

The approach taken in the present study was to observe coal particles under well-controlled conditions which simulate those encountered in real systems. This was accomplished by the construction of a reactor which allowed coal particles to be injected into high temperature post-flame gases. The data presented focus on the temporal description of the behavior associated with the thermal decomposition of coal particles, and the impact of coal particle size and coal type on these events.

Experimental

Reactor

The reactor (Fig. 1) was designed to satisfy two general criteria: (1) allow adequate control of the gaseous environment surrounding the coal particles, and (2) provide ready access for several physical and optical diagnostic systems. These criteria were satisfied by injecting the coal particles into the combustion products of a methane-air fired flat flame, stabilized on a 7.62 cm (3-inch) square sintered bronze burner with an embedded cooling coil. The flat flame was downfired within a 10.16 cm (4-inch) square stainless steel chimney in order to

minimize heat loss and external influences. A small amount of nitrogen was introduced between the burner housing and the chimney walls to prevent carbon deposition. Schlieren quality fused silica windows (7.62 cm diameter) were mounted on two opposing sides of the 91 cm long chimney for optical access. Two 7.62 cm \times 30.50 cm (3-inch \times 12-inch) flat Vycor plates were mounted on the third side to provide access for those optical measurements not requiring high quality viewing ports.

Particle Injection

The coal was introduced into the reactor from a 1 mm (0.043-inch) bore transport tube centered within a 6.35 mm (1/4-inch) copper tube which was sintered into the center of the burner perpendicular to the face. The coal feed rate was controlled through the use of a fluidized bed feeder similar to the design of Hamor and Smith.^{1,2} The coal particles were transported with air through the transport tube (see Fig. 3) and then diluted in the center tube with the same fuel/air mixture as that used in the flat flame burner to reduce uncertainties in mixing time between the coal carrier gas and the bulk gas.

Visualization

Two techniques were used to provide a visual record of the physical events occurring during thermal decomposition. Particles were extracted from the reacting stream and viewed with a scanning electron microscope (SEM), and holography was used as a means of providing *in situ* observations of the particle field.

The particle extraction probe consisted of a water-cooled tube positioned from the side of the burner and a small removable stainless steel plate held on an extension rod. The cold plate was pushed into the coal stream and rapidly retracted before the plate temperature could change significantly. The plate was then removed from the probe and coated with copper before SEM analysis.

The utility of holography for visualizing reacting coal particles was demonstrated in an early study.³ The interaction on a hologram plate of a reference laser beam with an information beam directed through the combustor produces an instantaneous three-dimensional record of the physical events occurring within the viewing volume. In the present experiment, the viewing volume was 2.54 cm (1-inch) in diameter and 5.08 cm (2-inches) in depth. The Ruby laser used in the holocamera had a pulse width of approximately 20 nsec, thus freezing any motion of the particles. The laser could also be fired in rapid succession (with time separation variable between 50 and 500 μsec) to provide dynamic information and confirmation of particle injection velocity.

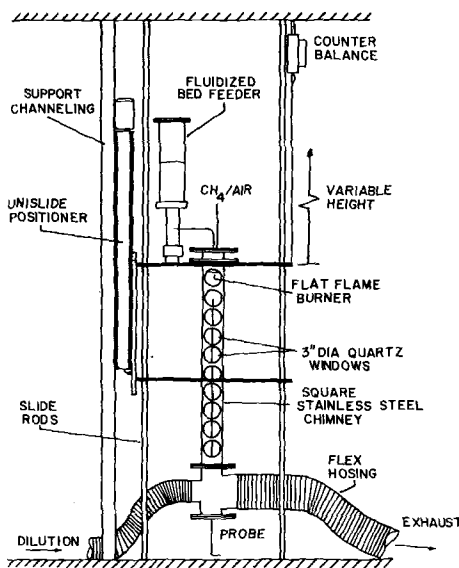


FIG. 1. Reactor system.

A detailed description of the holocamera used in the present study is presented elsewhere.⁴

Gas and Particle Temperature

Gas temperatures were measured by calibrated coated thermocouples and sodium line reversal. A two-color pyrometer based upon the technique described by Ayling and Smith⁵ was used to determine particle temperatures. The technique is founded upon a ratio of emissions at two wavelengths which eliminates the need to know the emissivity of the solid body or particle cloud, or the number density of the particles. However, it is assumed that the body whose temperature is being measured has an emissivity which is relatively independent of wavelength. For clouds containing both pulverized coal particles and soot, this assumption may not be valid.

Figure 2 shows a schematic arrangement of the two-color particle temperature measurement system used in this study. A water-cooled probe containing a fiber optics light guide was mounted on the side of the burner. The probe acted as a collimator for the fiber optics controlling the field of view. A quartz window on the opposite side of the burner acted as a background to prevent the pickup of radiation from warm walls. Thermal emission from particles passing through the sensing volume was received by the light guide. The fibers were bifurcated within the light guide, and the light signal was thus divided and directed to two lens/filter head assemblies which isolated the wavelengths and directed the light onto independent silicon photodiodes. After amplification, the signals were stored in digital form.

The two wavelengths were selected to (1) provide a reasonable signal intensity, and (2) be removed from any spectral lines associated with the combustion products. In this study, the near infrared lines used were 750 nm and 950 nm. This separation allowed sufficient sensitivity without sacrificing accuracy due to any nongray behavior of the source.

The pyrometer was calibrated against a tungsten strip lamp which, in turn, was calibrated against a disappearing filament pyrometer. The accuracy of the particular temperature measurement system was assessed by injecting inert 1 μm diameter alumina particles and comparing their temperature with that of the combustion products. The data presented in Fig. 2 indicate that the two-color optical pyrometry system gave temperatures which were in good agreement with the gas temperatures measured with sodium line reversal in the absence of particles.

Gas and Solid Chemical Composition

Gas and solid samples were extracted with a double-walled water-cooled isokinetic sampling probe with small tubes between the walls that served as pressure taps, water inlets, quench lines, and gas

sample extraction lines. Two of the 1/8-inch diameter internal lines penetrated the inner wall of the probe and could be used either for a quench stream such as water or nitrogen, or for aerodynamically separating and removing gaseous products from the sample. Gaseous and solid chemical analyses were conducted using conventional instruments and methods.

Test Conditions

The test conditions are listed in Table I, and the coal types and associated properties are presented in Table II. The methane/air fired flat flame burner was operated at 35% excess air in order to simulate the vitiated air environment experienced by particles in a turbulent diffusion flame operated under excess air conditions. The mixture ratio and velocity of the methane/air dilution flow matched those of the burner. Coal was injected through the center tube at 0.7 gm/min. The location of the coal transport tube was selected to approximately match the coal particle velocity with the "hot" burner velocity (200 cm/sec) calculated by multiplying the cold flow velocity by the ratio of the adiabatic flame temperature to ambient temperature.

The coal types selected span in rank from lignites (Savage, Montana; Beulah, North Dakota) to anthracite (Pennsylvania) and included two high volatile bituminous coals (Utah; Four Corners, New Mexico), and one medium volatile bituminous (Black Creek, Alabama). The samples were pulverized and repeatedly sieved through 400 mesh (38 μm) and 150 mesh (104 μm) screens until microscopic analysis indicated that a small fraction of fine particulate remained. One coal type (Four Corners, New Mexico) was selected to examine the influence of particle size. Aerodynamic classification was employed to reduce the base size distribution into two narrow size classes with particle diameters of $40 \pm 4 \mu\text{m}$ and $80 \pm 8 \mu\text{m}$.

Results

Experiments were conducted with the seven coal samples to examine the physical, temperature, and chemical characteristics associated with thermal decomposition of pulverized coal particles. The results presented here address three main topics: (1) temporal behavior, (2) the impact of particle size, and (3) the effect of coal type.

1. Temporal Behavior

A composite picture of the decomposition process for the Utah high volatile bituminous coal is presented in Fig. 3 along with a schematic of the flame radiation profile. The changes that occurred over

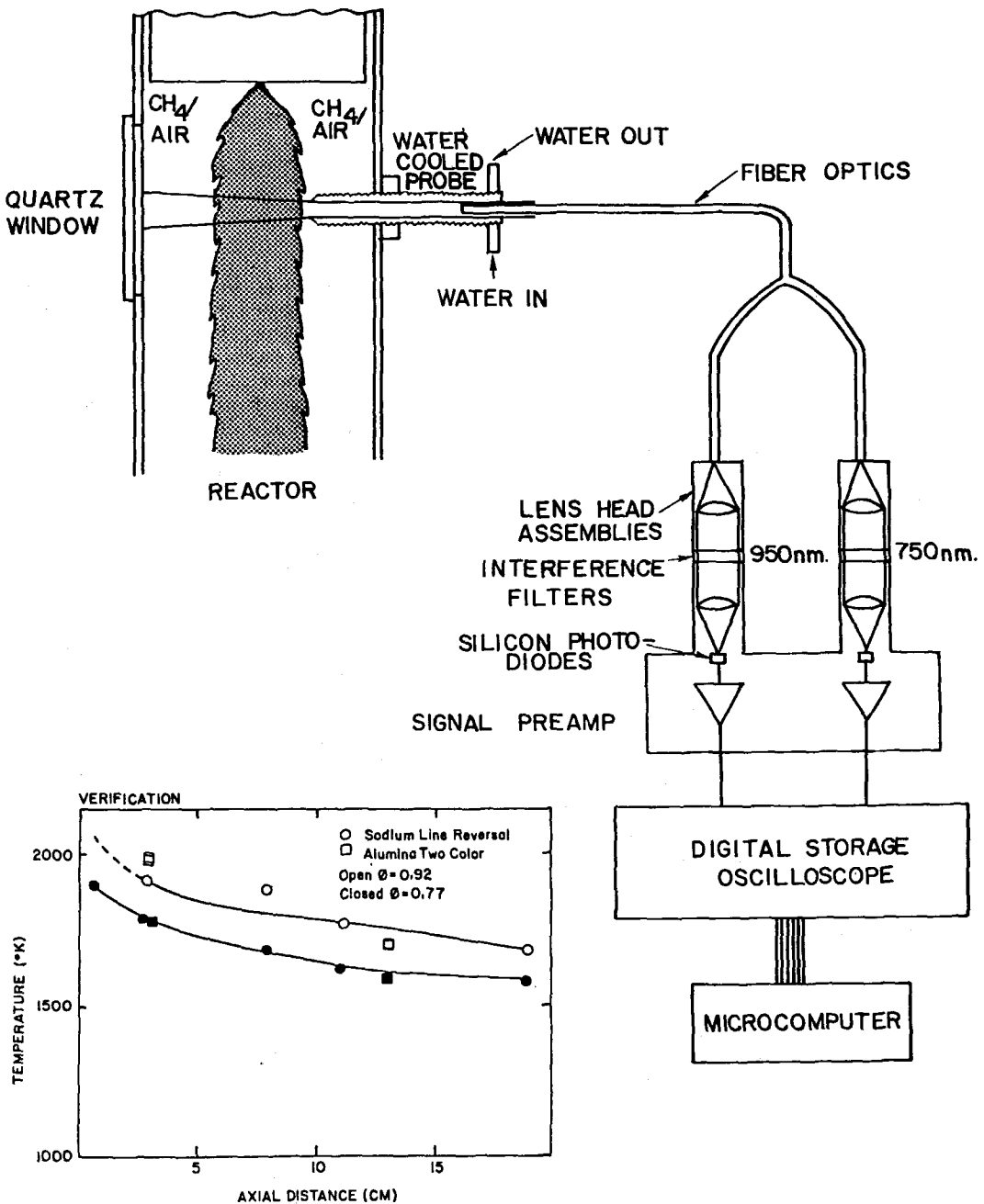


FIG. 2. Two-color pyrometer.

the 250 msec shown in this figure are illustrated by micrographs of samples withdrawn from the flame, and by representative photographs of reconstructed holograms.

Visual observation of the coal flame indicated that near the burner there was a 1 cm long region with

almost no luminosity. Thereafter, the luminosity rapidly increased, peaked 5 to 10 cm from the burner and then slowly declined. These observations, in conjunction with the study of a large number of holograms, temperature measurements, and chemical data taken at select axial locations, suggest that

TABLE I
Test conditions

Flat Flame Burner	
Reactants: Methane-Air	
Mixture Ratio: 35% Excess Air ($\phi = 0.77$)	
Methane Flow: 8.6 l/min	
Cold Flow Velocity: 31 cm/sec	
N ₂ Screen Flow: 10 l/min	
Dilution Flow	
Reactants: Methane-Air	
Mixture Ratio: 35% Excess Air ($\phi = 0.77$)	
Methane Flow: 37 cc/min	
Air Flow: 463 cc/min	
Coal Transport Flow	
Coal Flow Rate: 0.7 gm/min	
Transport Air Flow: 0.6 l/min	

the phenomena occurring can be described by considering three major regions:

- Zone 1, particle heatup region
- Zone 2, devolatilization region
- Zone 3, soot growth region

The delineation of these zones is conveniently presented in terms of the temporal variation in physical, temperature, and chemical characteristics.

1.1 Physical Characteristics

Particle Heatup Region. Initial particle heating is rapid, approximately 4×10^5 °K/sec, which is typical of conditions within pulverized coal flames. Hologram 1 in Fig. 3 (which shows the burner image on the upper edge) indicates that the coal particles are relatively inactive in this early region. Solid samples extracted from this location (illustrated in micrograph A) are different from the unreacted coal in two ways: large holes have formed in the particle surface, and swelling has occurred. The mean size of the bituminous coal particles was found to increase by almost 65% in the heatup region before leveling off midway through the devolatilization region.

Devolatilization Region. After this very short heatup zone, the particles begin to decompose and their volatile content is reduced. The devolatilization region extends to approximately 13 cm or 75 msec from the injection point. Holograms 2 through 5 are typical of the events that occur in this region. Many coal particles are associated with trails which

TABLE II
Coal analysis

Location	Rank	Proximate analysis, dry (wt %)				Ultimate Analysis, dry (wt %)		
		Volatile Matter	Fixed Carbon	Moisture (as Recv'd)	Ash	Carbon	Hydrogen	Nitrogen
Savage, Montana	Lignite	44.76	47.99	36.36	7.25	64.99	4.04	1.14
Beulah, North Dakota	Lignite	42.82	46.54	33.10	10.64	65.29	3.96	0.99
Black Creek, Alabama	Med. Volatile Bituminous	28.92	66.52	2.25	4.56	82.12	5.21	1.79
Four Corners, New Mexico	High Vol. B Bituminous	40.87	40.50	4.02	18.62	63.49	5.31	1.54
Utah	High Vol. B Bituminous	41.94	48.52	7.41	9.54	72.24	5.75	1.55
Hazleton, Pennsylvania	Anthracite	3.84	87.54	5.46	8.62	84.23	1.78	0.77

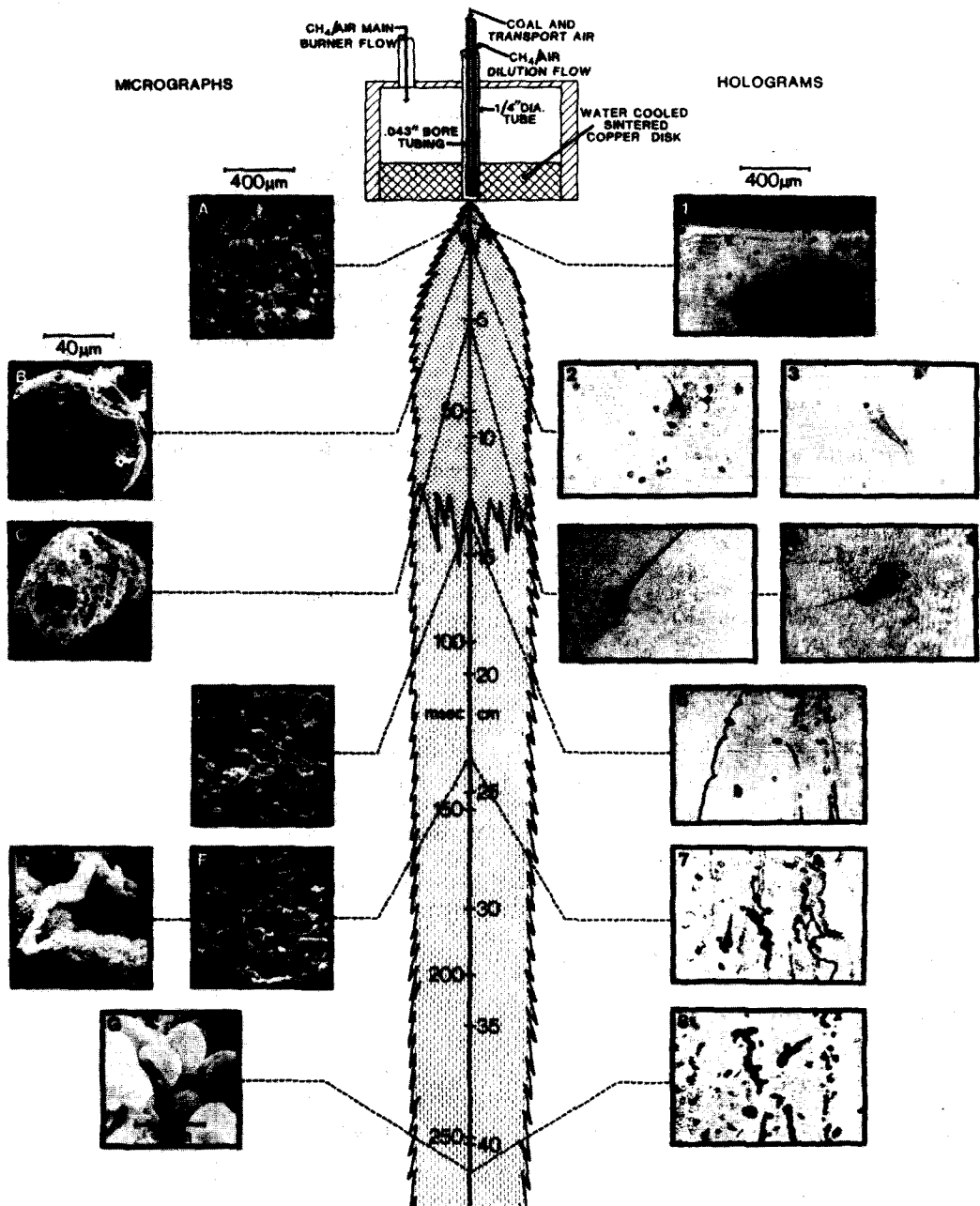


FIG. 3. Physical profile - Utah coal.

appear to be composed of very small particles. It is believed that these trails are produced from the volatile products ejected from the particle during the decomposition process. Current speculation is that they represent high molecular weight gases

which pyrolyze or burn rapidly in the region close to the parent particle producing solids. Alternatively, because of the high particle temperatures and large tar fraction of bituminous coals, the tar fraction may exit the coal matrix as a gas and rapidly condense

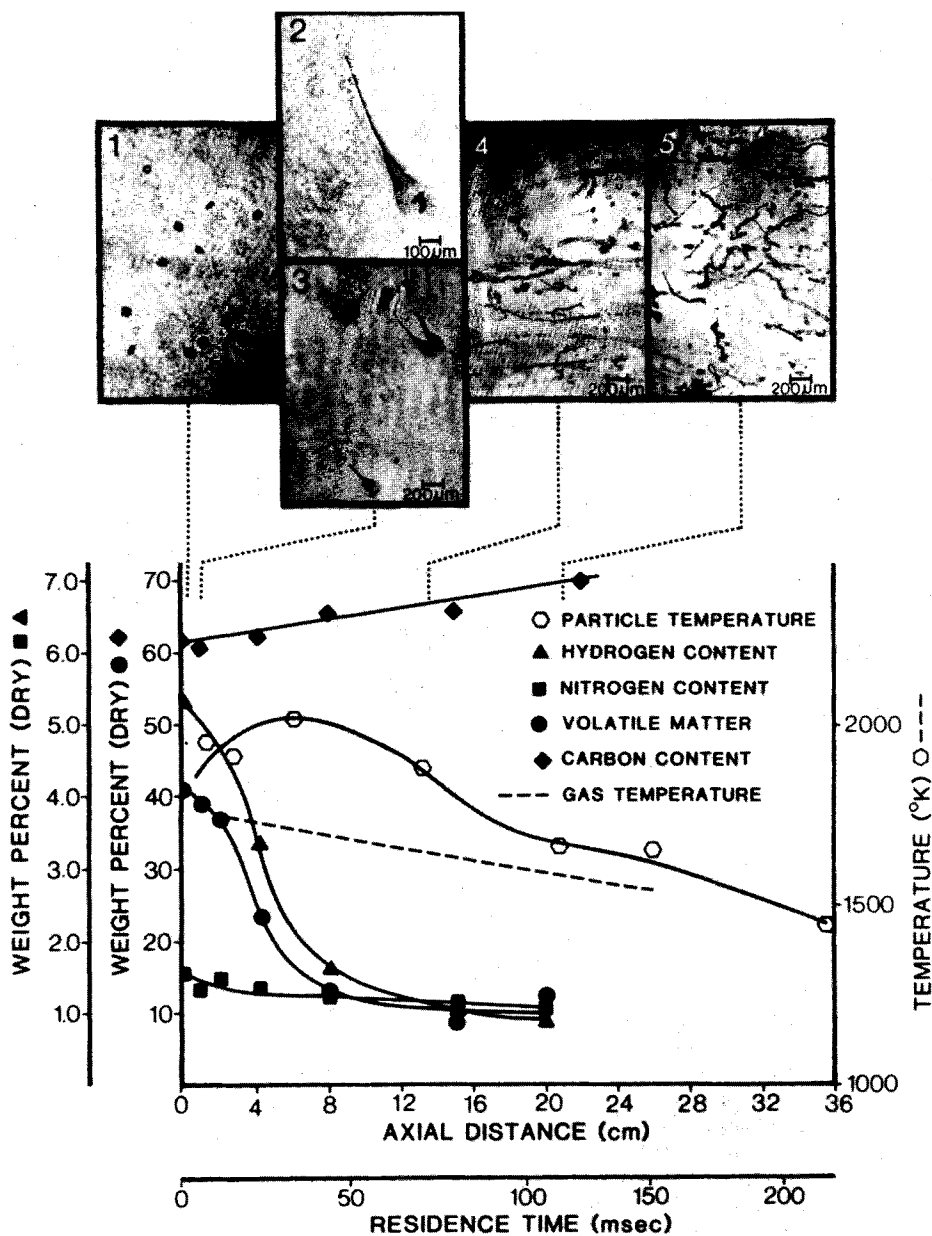


FIG. 4. Physical, temperature, and chemical (solids composition) profiles—Four Corners coal.

when it meets the cooler bulk gas.

The trails are associated only with the devolatilization region, and their shape is a result of volatile jetting action and the relative velocity between the bulk gas and the particle. In a more quiescent atmosphere, more spherical clouds have been observed. The length of trails are large in comparison to the parent coal particles ranging from about 300 μm to 1 mm. There are several observations which

indicate that the trails result in part from the evolution of volatiles as jets. Their directions are oriented randomly with the mean flow, although a significant fraction of the trails are upstream of the particle. Also, many particle/trail pairs are observed outside the main particle field suggesting that they are propelled away from the main stream as the volatiles are ejected from the particle.

Micrograph B shows a particle typical of those

found in the early regions of the decomposition zone. It is relatively spherical with one large blowhole which was likely formed when the volatiles were ejected. Solid samples taken later in the devolatilization zone (e.g., Micrograph C) show a lacy structure surrounding a large primary blowhole which is indicative of a more uniform evolution of the residual volatiles after the initial release from the primary jet.

Soot Growth Region. The third zone starts approximately 13 cm from the injection point (75 msec) and is characterized by the growth of particles whose lengths (several thousand microns) are large compared to their diameter (5 to 10 microns). These particles, which are not associated with char particles, are believed to be produced by the agglomeration of relatively small (<500 Å) soot particles formed from the bulk gases, on the volatile trail structures. Similar large soot strands have been observed in a large-scale turbulent diffusion flame for bituminous coal.⁷ These structures continue to grow, both in length and width. They are aligned with the gas flow and completely mask any remaining char. Micrographs from this region (D, E and F) confirm the presence of long particles. The surface structure appears to be formed from a multitude of fine particles less than 0.1 μm in diameter. Holograms 6, 7 and 8 give an indication of the size, and micrographs D and F illustrate the heavy concentration of these long soot particles.

1.2 Temperature Characteristics

Figure 4 shows the background gas temperature measured by sodium line reversal in the absence of any particles. The two-color particle temperature measurements for the 80 μm New Mexico bituminous coal are also presented for comparison. It can be seen that the particle temperature is far in excess of the background gas temperature.

This initial particle temperature overshoot is attributed to a combination of heterogeneous surface oxidation and heat feedback to the individual particles from gas phase reaction in the vicinity of the particle. Heat balance calculations indicate that there is not sufficient heat release from the coal to significantly alter the bulk gas temperature. This fact was confirmed experimentally by placing an uncoated thermocouple in the reacting coal stream. The measured temperature remained unchanged when the coal flow was terminated. Particle heat balance calculations based on literature values for the surface oxidation rate suggest that equilibrium surface temperatures could be attained which were similar to those measured by two-color pyrometry. Consequently, it appears that the measured temperature overshoot is attributable to microscale particle behavior and not to bulk heating.

1.3 Chemical Characteristics

Figure 4 also shows the relationship between particulate composition and the events occurring in the particle-laden stream as observed by holography. These results were obtained with a Four Corners, New Mexico high-ash bituminous coal. The volatile content of the particulate catch decreases dramatically from 0 to 40 msec. Hologram 1 shows details of the initial coal particles prior to activity of any kind in the particle heatup region. Very rapidly, the particles begin to exhibit the characteristic trailing phenomena described above. The particle shown in Hologram 2 shows evidence of either swelling or breaking up and it is closely associated with the vapor cloud. It is unusual to find more than one particle in focus at the same time. However, Hologram 3 shows evidence of several particles in the same focal plane suggesting that they were formed when one particle broke up.

The region of soot growth is illustrated in Holograms 4 and 5 which represent a time of 75 and 125 msec, respectively. During this time there is no further loss of volatiles from the particulate catch. Hydrogen loss from the particles parallels the volatile loss.

Parallel gas phase measurements for this large bituminous coal (Fig. 5b) indicate a rapid fall in

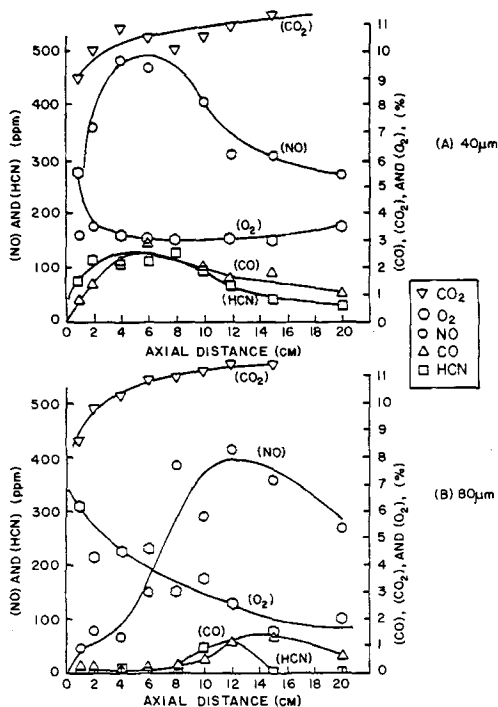


FIG. 5. Chemical (gaseous composition) profiles—Four Corners coal.

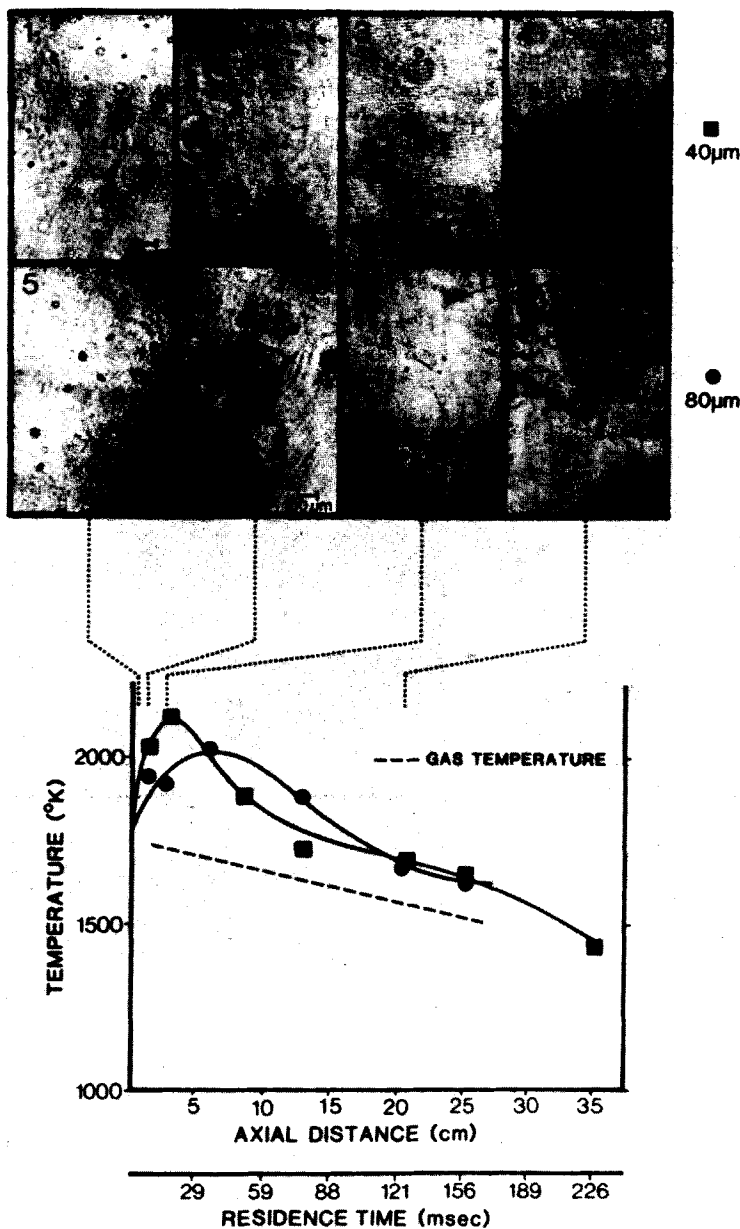


FIG. 6. Size effects: Physical and temperature profiles—Four Corners coal.

oxygen and increase in CO₂ early in the devolatilization region. Other measured concentrations, HCN, CO and NO, were found to peak late in the devolatilization zone after the appearance of the volatile trails. Only negligible amounts of NH₃ were measured. The concentration of NO declines after the peak, even in the presence of at least 2% oxygen. The decline in NO may be associated with entrain-

ment of the bulk gases together with homogeneous or heterogeneous reactions which yield molecular nitrogen.

2. Particle Size

The data presented in Fig. 4 indicate that the measured particle temperature exceeds the gas tem-

perature measured in the absence of particles. These data were observed for a large coal particle size having a mean diameter of about 80 μm . To assess the effect of size, the Four Corners bituminous coal was classified aerodynamically into two fractions of nominal diameters 40 to 80 microns. Results

obtained with these two size fractions are shown together in Fig. 6.

Decreasing the particle size has several major effects on the particle thermal decomposition behavior. First, the initial particle temperature peak is higher than for the large-size cut, and the peak

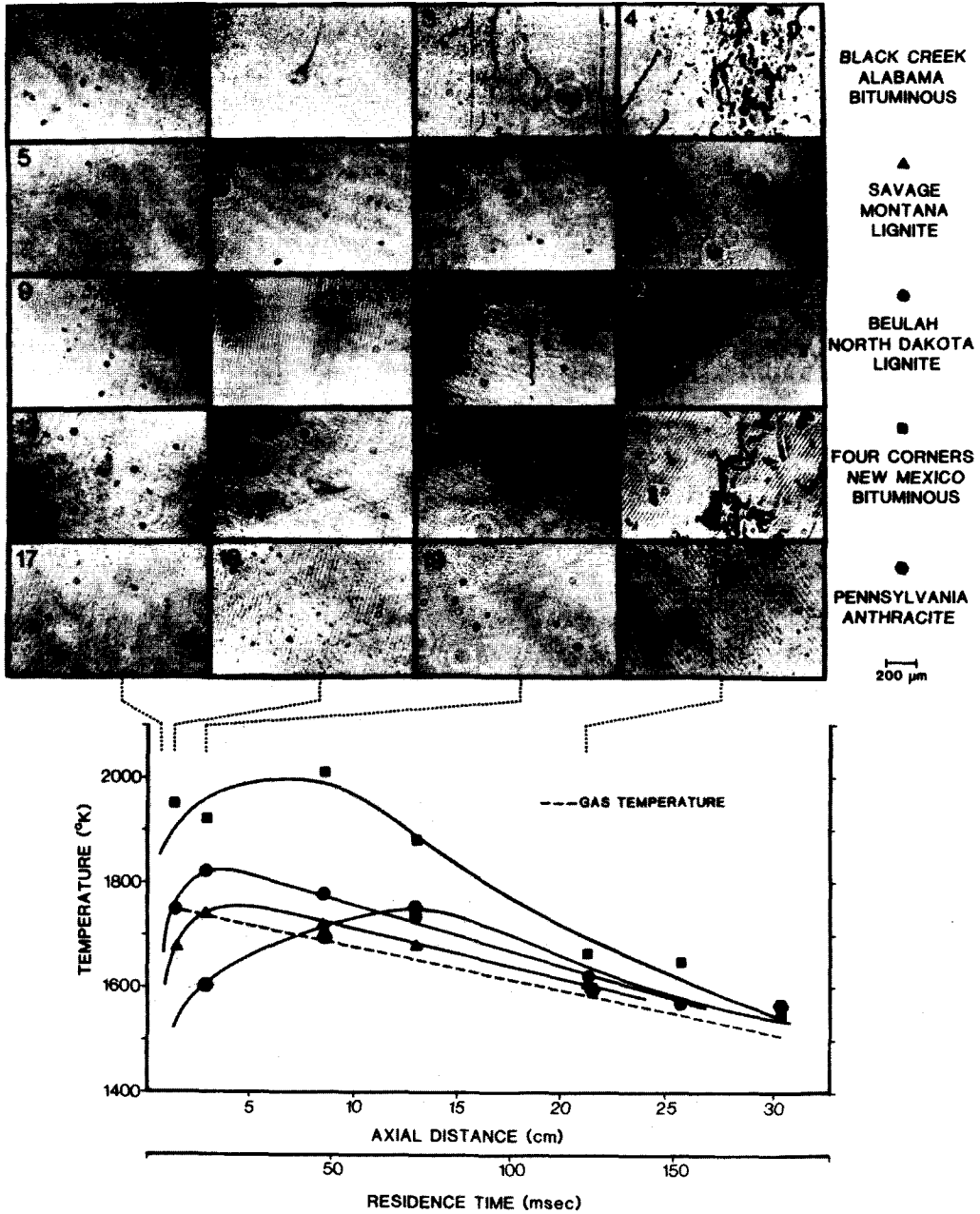


FIG. 7. Coal type effects: Physical and temperature profiles.

temperature occurs at shorter times for the smaller particles. Also, the characteristic trails and large soot structure are almost completely absent for small particles. Finally, the gas phase chemistry associated with the particle decomposition is altered by changing to smaller particles.

The absence of trails suggests that the volatile release mechanism for small particles results in more rapid mixing of the volatiles with oxygen. The larger jets associated with larger particles have longer diffusion and mixing times and, hence, longer time for pyrolysis reaction to occur. For the smaller size cut the lack of large soot structures might well be associated with a reduced local concentration of hydrocarbon species in the gas phase, resulting from either a more effective early mixing or oxidation of the volatiles near the particle surface.

The gas phase chemical behavior of the small particles is also dramatically different from the larger size cut (Fig. 5a). The concentration of CO, NO and HCN peak in half the distance as the larger size cut. Further, the peak heights are larger than the corresponding data from the 80 μm coal. This behavior appears to be consistent with the hypothesis made for soot formation of more effective early mixing of the volatiles with air for the smaller particles. The resulting more effective oxidation of the volatiles gives rise to higher conversion of released fuel nitrogen to NO_x .

3. Fuel Type

Figure 7 compares holograms taken with five different coals (Table II) at the same feed rate and background stoichiometry. There appears to be no difference in the phenomena occurring with any of the bituminous coals. The bituminous coals produce copious amounts of large soot structures and exhibit evidence of volatile jet evolution. These phenomena are not observed with either lignite or anthracite. Other workers⁶ have shown that the major decomposition products of lignites are H_2 and CO. Bituminous coal volatiles are rich in hydrocarbons and tars which probably accounts for the formation of soot with these high rank coals.

Particle temperature measurements also show a large effect of coal type. The increase over the bulk temperature is largest for bituminous coals, and smaller for lignites, but it is dependent upon the lignite source. This effect has also been observed in bench scale flames.⁶ Anthracite particle temperatures increase slower and then stay near the bulk gas temperature.

The initial particle temperature is associated with the devolatilization region. It is concluded that the volatiles react rapidly after leaving the surface causing an increase in the local gas temperature. This results in less heat loss from the oxidizing surface, and in turn, further volatile evolution and increased

surface oxidation. The temperature peak will depend upon the volatile evolution rate and speciation. Since anthracite is low in volatile content, it is reasonable, therefore, that particle heat-up would be less rapid. The heating value of the volatiles produced from lignite is lower than those produced from bituminous coals which is consistent with the data presented in Fig. 7.

Discussion

Data have been presented on the events that occur when coal particles are injected into a high-temperature gas stream. The most significant observations are concerned with the impact of devolatilization on particle temperature, the evolution of volatiles in the form of trails from large coal particles, and the formation of soot.

Models of NO production in pulverized coal flames have been proposed which assume that the volatile fractions mix with the bulk gases immediately upon release from the particle. This assumption leads to an overprediction of NO because, in the devolatilization region, the volatile would react under oxidizing conditions. Data presented in this paper indicate that the model should consider the detailed microstructure of volatile evolution because large volatile jets behave as diffusion flames.

It has been shown experimentally in a bench-scale tunnel furnace that fuel NO formation is dependent upon particle size.⁶ Small particles produce more fuel NO than large particles. This is consistent with the mechanistic model presented here and the observed influence of size. Volatile gases evolved from small particles mix rapidly and react with their surroundings. With large particles, the volatiles do not mix as rapidly and oxygen is not as readily available to form fuel NO from the volatile fuel nitrogen fractions.

Acknowledgments

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COMMENTS

R. F. Chaiken, U.S. Bureau of Mines, USA. The higher than gas temperatures measured for the particle is extremely interesting. If one assumes that devolatilization is endothermic, the particle temperature must be less than the gas temperature. What I suggest is that you may be measuring the temperature of an exothermic reaction involving volatiles emanating from the coal and surrounding the particle. This may involve a tar oxidation reaction or perhaps be simply tar condensation reaction to form solid (e.g., soot). Such condensation reactions are believed to be highly exothermic (1000 to 2000 cal/gm) from laser pyrolysis experiments carried out at the Bureau of Mines. In either case, the relationship between measured excess "particle" temperature and volatile content of the coal would be as you depicted.

Author's Reply. There are at least two plausible mechanisms that can be put forth which can account for the difference between the bulk gas temperature and the solid temperature. The first involves a combination of surface oxidation and devolatilization in which exothermic surface oxidation reactions compete with the endothermic devolatilization reactions. If the exothermic oxidation reactions dominate the heat balance, the coal matrix will heat above the gas temperature.

The second mechanism which can be envisioned is similar to that suggested by the commentators. As the volatiles evolve, they can be rapidly consumed near the particle surface in a diffusion-controlled zone around the particle. The local heat release associated with gas-phase oxidation can increase the temperature of gases in the vicinity of the particle and, in turn, can increase the particle temperature. The temperature of the microsystem, including the particle and the gases evolved in a zone near the particle, may be above the bulk stream temperature. The solid temperature measured was found to exceed the bulk gas temperature by several hundred degrees; but no information has been supplied on the local

gas temperature surrounding the particle. Plausibility calculations based on spherical diffusion of volatiles from a particle utilizing a reasonable devolatilization time (10 msec) and volatile speciation based on pyrolysis experiments, support the concept of a high local temperature.

P. J. Smith, Brigham Young University, USA. I was impressed with the quality and quantity of information coming from this study. Would you indicate how you obtained our gas temperature profile and its accuracy?

Author's Reply. The gas temperature measurements were performed by sodium line reversal in the absence of coal particles. The sodium was injected into the burner in the form of either salts or vapor with the transport air so that the measured temperature would be that experienced by the coal particles. A tungsten strip lamp was used as the background source and was calibrated with a reversing filament pyrometer through the optical system to account for reflection losses at windows and lenses. The accuracy of the technique is dependent upon the accuracy of the calibration, the accuracy of the knowledge of the emissivity of tungsten and the sensitivity of the instrument to changes in light intensity. An estimate of the accuracy for the particular system used in these early measurements would be about $\pm 30^\circ\text{K}$.

C. W. Kauffman, University of Michigan, USA. Could you indicate the valve used for the emissivity of the coal particles and how it was obtained?

Author's Reply. The pyrometry technique employed was a two color technique which measures the ratio of the continuum intensities at two separate

wavelengths. A basic premise of this technique is to assume that the emissivity is relatively independent of wavelength and hence the ratio is directly related to the solid temperature. An independent measurement of the emissivity was not required and was therefore not attempted.

I. W. Smith, CSIRO Minerals Research, Australia. The work described by the authors is valuable and shows the useful data that can be obtained with modern diagnostic techniques. It would be of even greater value if the apparatus could be used in experiments where devolatilization were separated from char burn-out, experiments where devolatilization were separated from char burn-out, in order to provide time-resolved data on char combustion. Do the authors plan such work?

Author's Reply. The present study addressed the sequence of pulverized coal combustion from heatup to char burnout. Certainly, the regimes must be uncoupled if detailed kinetic information is to be obtained. Future work will be directed to the individual regimes with emphasis on char oxidation and the fate of char nitrogen.

T. A. Brzustowski, University of Waterloo, Canada. In your model, you have associated the formation of soot strands with the char burnout regime. I would suggest that it should be associated with the volatile combustion phase. The reason for my suggestion is our observation (Ref. 1) that soot strands of the same kind form in the burning of pure liquid hydrocarbons at elevated pressures. In those studies, we observed the formation of such strands in the laminar wakes of burning droplets. The wakes were initially brightly luminous, then become darker and eventually showed the appearance of "solid" strands which were occasionally broken in the flow. I think that the process you have observed is essentially similar.

REFERENCES

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Author's Reply. The mechanistic model put forth purports only that soot strands persist into the char burnout zone. The formation of solid or condensed material within the volatile cloud is incorporated in the model as a result of the observation of such

processes by the visualization techniques, in general, and high-speed photography in particular. The resemblance between the physical behavior of evaporating droplets and large bituminous coal particles in terms of wake cloud development and soot formation is striking.

T. Singh, Wayne State University, USA. From the analysis of your data, have you developed any correlation for the swelling factor (mean size after devolatilization initial size) as a function of coal type and other factors?

Author's Reply. No effort has been made as of yet to quantify the swelling data; only general trends with coal type have been identified, e.g., bituminous coals can swell by 65% during devolatilization while lignites are characterized by slight size changes. Detailed size distribution measurements as a function of residence time have been recently obtained and demonstrate the difficulties of developing a simple swelling factor correlation. Early in the devolatilization zone 80 μm bituminous coal particles were found to swell and to broaden the distribution to larger sizes while a significant number remain at the original size. The fragile structures then appear to fracture and broaden the distribution to smaller sizes. High-speed photography has revealed that particles may actually swell and then contract slightly during the devolatilization sequence. These observations tend to discourage a simple one-size to one-size correlation.

E. T. McHale, Atlantic Research Corporation, USA. The two-color temperature measurements yield values several hundred degrees above those of the gas temperature very early in the combustion. Inasmuch as the particle process occurring at that point is endothermic devolatilization, the two-color temperature cannot refer to the particle surface, which must be cooler than the gas. Perhaps an explanation lies in the results of McLean (this symposium) wherein observations of particles burning above a flat flame show initial intense brightness which they attributed to emission from secondary soot particles formed from the pyrolysis of products formed in the coal devolatilization. This explanation is consistent with your results for anthracite particles where temperatures below those of the gas were observed.

Author's Reply. See reply to question by Chaiken.

W. Blazowski, Exxon Research & Engineering Co., USA. The observation of soot in the trails of devolatilizing coal particles is a very interesting finding. Two questions arise which address the practical importance of the early presence of soot. First, does the soot play a significant role in radiative heat transfer beyond that, or different from that, of the coal/clear particles themselves? Secondly, can the presence of the soot influence the consumption of volatiles, the fate of fuel nitrogen, or the subsequent char oxidation process? These are complex questions, but the author's present views on these issues would be valuable.

Author's Reply. Given the license to speculate on the impact of some of the observations, the areas mentioned qualify as those of primary importance. The present results indicate that the staging of pulverized coal flames (i.e., enriching the primary zone) to reduce fuel NO_x production will enhance the tendency of bituminous coal particles to form large soot structures. This conclusion is reinforced by the observations of such structures in large-scale turbulent diffusion flames.⁷ The subsequent oxidation of this residual carbon will undoubtedly result in more radiation sources than if the char particles were alone and hence could impact heat transfer in the radiant zone of the boiler. An estimate of the impact has not yet been attempted.

The influence of soot on volatile and char oxidation as well as on the fate of fuel nitrogen is indeed complex. Experimental results by others on the

reduction of NO by carbonaceous materials suggest that the intimate contacting of the volatile NO with the soot in the volatile cloud could result in significant reductions. The relative magnitude of heterogeneous reduction as compared to homogeneous reduction by other fixed-nitrogen species is difficult to assess but likely is of second order. Finally, the presence of soot could indeed impact both volatile and char oxidation by virtue of local oxygen consumption in the vicinity of the particle.

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T. Houser, Western Michigan University, USA. In our work at Western Michigan University, we have found during the fuel-rich oxidation of pyridine that under some conditions the nitrogen would concentrate in the tarry-solid product. Have you any data to indicate if the nitrogen tends to preferentially distribute itself in the solid or volatile products at incomplete extents of combustion!

Author's Reply. Nitrogen loss data are beyond the scope of the present paper. However, measurements of nitrogen loss have been made and indicate that the nitrogen retention in the char is strongly dependent on the time-temperature history experienced by the coal particles. The breakdown of nitrogen into the various components is also dependent upon coal type and size. However, under the present experimental conditions, the volatile nitrogen fraction is larger than the fraction retained in the char.