EFFECT OF HEATING RATE ON THE THERMODYNAMIC PROPERTIES OF
PULVERIZED COAL

Final Technical Report

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ABSTRACT

This final technical report describes work performed under DOE Grant No. DE-FG22-96PC96224 during the period September 24, 1996 to September 23, 1999 which covers the entire performance period of the project. During this period, modification, alignment, and calibration of the measurement system, measurement of devolatilization time-scales for single coal particles subjected to a range of heating rates and temperature data at these time-scales, and analysis of the temperature data to understand the effect of heating rates on coal thermal properties were carried out. A new thermodynamic model was developed to predict the heat transfer behavior for single coal particles using one approach based on the analogy for thermal property of polymers. Results of this model suggest that bituminous coal particles behave like polymers during rapid heating on the order of 10^4 - 10^5 K/s. At these heating rates during the early stages of heating, the vibrational part of the heat capacity of the coal molecules appears to be still frozen but during the transition from heat-up to devolatilization, the heat capacity appears to attain a sudden jump in its value as in the case of polymers. There are a few data available in the coal literature for low heating rate experiments (10^2 - 10^3 K/s) conducted by UTRC, our industrial partner, in this project. These data were obtained for a longer heating duration on the order of several seconds as opposed to the 10 milliseconds heating time of the single particle experiments discussed above. The polymer analogy model was modified to include longer heating time on the order of several seconds to test these data. However, the model failed to predict these low heating rate data. It should be noted that UTRC's work showed reasonably good agreement with Merrick model heat capacity predictions at these low heating rates, but at higher heating rates UTRC observed that coal thermal response was heat flux dependent. It is concluded that at combustion level heating rates (10^4 - 10^5 K/s) coal structural changes are delayed and attendant increases in heat capacity and thermal conductivity are pushed to higher temperatures or require significant hold times to become manifest.

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EXECUTIVE SUMMARY

In this final technical report, the work performed under DOE Grant No. DE-FG22-96PC96224 during the period September 24, 1996 to September 23, 1999 is described and the accomplishments are highlighted summarizing the work for the entire period, including implications of results.

In all major coal conversion processes, coal undergoes a devolatilization stage while it is heated to the reaction temperature. The recent experimental studies of devolatilization of pulverized coal at rapid heating rates representative of coal combustors have greatly improved our general understanding of this process. But the heat transfer analysis with commonly-applied thermal properties developed from slow heating rate experiments did not predict either the early heating or the latter stages of heating. Knowledge of the role of heating rate on coal thermal properties is essential for progress towards advanced coal utilization technology.

The objectives of this project were to understand the effect of heating rate on thermal properties of pulverized coal particles. The specific objectives were to subject coal particles into a broad range of heating rates, measure temperature histories, and develop thermal property (heat capacity and thermal conductivity) data that predict the measured temperature histories. Experiments and modeling were carried out to meet the project objectives. The successful accomplishment of the above goals enhances our understanding of coal thermal properties and hence progress towards advanced combustion modeling.

Collection and reduction of experimental data for a total of 28 single coal particles using the Single Particle Laboratory, NETL's Morgantown facility was completed during this period. Also a new thermodynamic model was developed to predict the heat transfer behavior for coal particles subjected to a range of heating rates using one approach based on the analogy of polymers. The model prediction was first verified with data available in our previous studies, and then subjected to comparison with the data obtained in the present study. Results of this model suggest that bituminous coal particles behave like polymers during rapid heating on the order of 10^4 - 10^5 K/s. At these heating rates during the early stages within the first few milliseconds of heating time, the vibrational part of the heat capacity of the coal molecules appears to be still frozen but during the transition from heat-up to devolatilization, the heat capacity appears to attain a sudden jump in its value as in the case of polymers. There are a few data available in the coal literature for 10^2 - 10^3 K/s obtained by our industrial partner in this project, UTRC, in their previous studies. These data were obtained for a longer heating duration on the order of several seconds as opposed to the 10 milliseconds heating time in the single particle experiments discussed above. The polymer analogy model was modified to include longer heating time on the order of several seconds to test these data. However, the model failed to predict these low heating rate data. It should be noted that UTRC's work showed reasonably good agreement with Merrick model predictions at 1000K/s, but at higher heating rates they observed similar trends in coal behavior as evidenced and predicted in the present study. It is concluded that at combustion level heating rates (10^4 - 10^5 K/s) coal structural changes are delayed and attendant increases in heat capacity and thermal conductivity are pushed to higher temperatures or require significant hold times to become manifest.

INTRODUCTION

Devolatilization is an important initial step in virtually all commercial coal applications such as combustion, gasification, and liquefaction. The quality and yield of liquid fuels and the nature of the byproduct char derived from coal liquefaction depend on the coals' devolatilization temperature history (heating rate), and other process variables. In coal combustion and gasification, devolatilization sets the flame front location; it also has a strong influence on product distribution (gas, liquid, tar, and char formation), soot production, and fuel-bound nitrogen and sulfur evolution. It is clear that accurate knowledge of devolatilization kinetics is essential for more efficient design of coal combustors, gasifiers, and liquefaction reactors. This in turn requires accurate knowledge of the temperature-time histories of the coal particle during devolatilization.

Over the past thirty years much emphasis has been placed on the measurement of devolatilization kinetics for pulverized coal particles at heating rates typical of combustion applications. Despite the many years of research, the mechanism and kinetics of devolatilization for pulverized coal particles have not yet been thoroughly understood [1-2]. Even the most recent investigations of coal devolatilization disagree by many orders of magnitude in rate constants at a given reported temperature [1-2]. For heating rates typical of gasifiers and combustors, $10^4 - 10^5$ K/s, most volatiles appear before the coal particles reach the reactor temperature [3]. For coal particles in an entrained flow reactor whose source temperature was 1300BC, coal particles with sizes between 45 and 75 μm were completely devolatilized by the time they reached particle temperatures of 700 and 800BC [4]. In the absence of a direct measurement of those temperatures, previous investigators generally inferred the coal particle devolatilization temperatures from measured gas or heated grid temperatures [5-6]. Thus, these variations in rate constants can be attributed primarily to a poor understanding of the temperature history prior to and during devolatilization. In order to avoid this ambiguity in devolatilization temperatures, recent attempts have concentrated on in-situ temperature measurement and careful characterization of heat transfer fields [5,7-8]. In cases where such temperature measurements were made, however, large empirical corrections were required in order to match the predictions with the measurements [7-8].

Recently Maloney et al. [9] reported results of an investigation to determine temperature histories for coal particles during the early stages of heating and devolatilization. In addition to making in-situ temperature measurements with sufficient accuracy, they modeled the early stages of the heating process using thermal property correlations that are routinely applied to coals. Like a number of other researchers [2-3,7-8,10-14], they also assumed a spherical particle for coal with a density taken from the literature. Their predicted temperature transients agreed well with the measurements for carbon spheres during the early stages of heating. These carbon spheres were used to evaluate the capabilities of the temperature measurement system and to test the validity of the heat-transfer analysis. However, for coal particles their predicted temperature transients differed significantly from the data (by a factor of 2), with the measured temperatures being higher. Similar discrepancies have been noted for coal particle devolatilization temperatures in the work of Solomon et al. [7] and Fletcher [8].

One of the following could be the reason for the observed differences in the coal particle temperature histories. Either the measured temperatures may be higher than the actual ones or the predicted temperatures are lower than the actual ones. The former can occur if there is a problem in the temperature measurement techniques employed in the above referred studies [7-9], if the temperature measured is the temperature of the volatile cloud or if oxidation is occurring.

Maloney et al. [9] used a single-color pyrometer whereas Fletcher [8] used a two-color pyrometer to measure the particle temperatures. Solomon et al. [7] measured temperatures using FTIR (Fourier Transform infrared spectroscopy) emission and transmission spectroscopy. Single or multiple-color pyrometry involves measuring the intensity of light at a given wavelength and obtaining the temperature through manipulation of Planck's law. In single color pyrometry, emissivity is obtained from published data whereas in two color or multi-color pyrometries emissivities are solved for known temperature and wavelengths using Planck's law. The errors due to single and multiple color pyrometries have been studied rigorously by Spjut [15] who noted that the errors in two-color pyrometry are greater than that of a single-color pyrometry. This is due to a slower response time in two-color pyrometers and also due to the addition of errors from the two measurements. However, he states that if the pyrometers (single or two colors) were well aligned and corrected for noises and stray radiation, then the errors can be minimized as low as $\pm 2\text{K}$. Extensive measures were taken in the systems of Maloney et al. [9] and Fletcher [8] to reduce these errors. Moreover, a comparison of the temperatures measured for carbon spheres by these systems with predictions from a heat transfer model assessed the measurement uncertainty to within $\pm 50\text{K}$. It was concluded that the higher temperatures measured for coal particles in these studies cannot be due to the use of pyrometers. Solomon et al. [7] validated the FTIR measurements with independent thermocouple measurements made at the same point. They [7] studied three different ranks of coal (North Dakota lignite, Rosebud subbituminous coal and Illinois No. 6 bituminous coal) and observed a similar trend of rapid rise in their measured temperatures during heating for all the three coals studied.

Grosshandler [16] studied theoretically the effect of soot on pyrometric measurements of coal particle temperatures and presented measurement errors associated with different wavelength regions. Near-infrared wavelengths were chosen for the pyrometers in the studies of Maloney et al. [9] and Fletcher [8] in order to penetrate the tar cloud. Fletcher [8] confirmed that the tar cloud did not influence the pyrometry measurements as he found emission intensities for coal particles similar to those obtained for pure carbon spheres in his studies and got smaller particle diameters than would be expected from a tar cloud. Hence, the higher measurement temperatures in these studies [8-9] cannot be due to that of tar cloud.

Phouc et al. [17] calculated the relative contribution to the energy balance due to particle oxidation and found it to be insignificant below 1500K. It can be inferred in the work of Maloney et al. [9] that if the higher measured temperatures were originating from the oxidation of the particle, then the associated heat release would surely have ignited the particles, but, no evidence of particle ignition has been observed in the high-speed photographs obtained in their experiments.

The above qualitative and experimental analyses suggest that the higher temperatures measured in the above discussed studies [7-9] are close to the actual and the problem lies in the estimation of the model temperatures.

The predicted temperatures can be lower than the actual ones due to the following three assumptions in these models [7-9]: 1) use of the value of Nusselt number, $Nu = 2$ in the heat transfer analysis and assuming no free convection, 2) assumption of coal particle shape as spherical, and 3) use of temperature-dependent thermal property correlations that are developed based on measurements obtained from slow heating rate experiments. Fletcher [8] used a Nusselt number of greater than two to get a good agreement with measured temperature histories. The reason he suggested is that the faster heating rate is due to non-steady boundary effects. He conducted his experiments in a hot gas laminar flow reactor where the primary mechanism of heating the coal particle is by convection. However, convection is the predominant cooling mechanism in the experiments of Maloney et al [9] where the particles were heated by a laser. So, it is not possible that the discrepancy in particle temperatures is due to unsteady boundary layer effects.

Coal particles are irregular in shape and have unique external surface area, volume, and mass. While energy absorption and emission mechanisms depend on particle surface area (S), temperature response strongly depends on particle mass (Dv). So, the irregularity of the shape of the coal particles needs to be dealt with carefully in the analysis [9,13-14]. Assumption of spherical shape might underestimate the particle surface area because, for example, if the shape of the particle is assumed to be a parallelepiped, cylinder, cube, or ellipsoid, then it has a surface area larger than that of a sphere. Also, the spherical assumption might overestimate the particle volume and hence the mass, which in turn will underestimate the predicted temperature histories. Thus a reliable temperature prediction requires the knowledge of the particle shape. In an effort to quantify the magnitude of errors in estimating surface area (S) and volume (v) by assuming a spherical particle, Maloney et al. [18] recently developed a 3-D shape characterization technique to obtain particle external surface area and volume. To quantify the magnitude of errors in estimating the particle mass (m) by assuming a published density (D), Maloney et al. [19] developed a drag coefficient-to-mass ratio (C_d/m) measurement methodology. When combined with the application of an analysis for the prediction of C_d for deformed spheres by Brenner [20], this approach yielded an experimental particle mass and density. For the coal particles tested, the equivalent diameters for surface area and that for volume differed significantly [21]. Also, between coal particles, the density was found to be non-uniform [21-22]. From a devolatilization and combustion perspective, these results indicated that the spherical particle assumption employed in most single particle models can lead to significant errors (20 to 25 percent on average) in the calculated particle volume and associated thermal mass [21]. In a previous work, Maloney et al. [13-14] assessed the errors associated with the prediction of temperature histories resulting from particle shape assumption. It can be inferred from this assessment that a variation in the particle mass of 20 to 25 percent into the temperature history calculations would improve the fit between model and data. But this alone could not account for all of the observed differences.

Specific heat strongly influences the rate of heating of pulverized fuel particles and this in turn affects the rate of devolatilization and the ease of ignition of coal. Accurate knowledge of the specific heat of coal as a function of temperature under rapid heating conditions is important to progress in coal utilization technology. The specific heat of coal is closely related to the amount of heat required per unit mass of coal to raise its temperature to a given value and this is an important factor during rapid heating in the utilization of coal. Merrick [23] constructed his temperature-dependent heat capacity equation for coal during carbonization with the available specific heat data from room temperature to about 600K. In the absence of a better alternative, the Merrick model of specific heat during carbonization is commonly employed in rapid devolatilization studies. Under high heating rates when insufficient time is available for the coal particle to heat-soak at a given surface temperature, part of the degrees of freedom may be initially frozen in, which would result in a lower value of the molar heat capacity at the early stages of heating [24-25]. The specific heat would then increase as the heating continues. The increase of the heat capacity with temperature depends on an increase of the vibrational degrees of freedom. On the basis of the energy content of a molecule over the degrees of freedom, the maximum value of the molar heat would correspond to $3R$ per atom. Solomon et al. [7] concluded that a much higher heat capacity value than the room temperature value is required at the latter stages of heating during volatile evolution. Under high heating rates typical of gasifiers and combustors ($10^4 - 10^5$ K/s), no independent data on specific heats of coal are available either during the early heating prior to volatile evolution or during volatile evolution. At these heating rates, the coal particle remained stationary for the first several milliseconds known as the early heating time or the surface heat-up time or more specifically known as the mass loss induction time [17,26-27], then underwent continuous physical and chemical transformations associated with volatile evolution [17]. It can be inferred from the work of Phouc et al. [17] that at any heating rate, there exists a mass loss induction time (surface heat-up time) for coal particles and this induction time decreases with increase in the heating rate. It can also be inferred from the work of Phouc et al. that for rapid heating rates typical of combustors, that this induction time is on the order of 2 to 5 msec and the devolatilization would be complete in less than ~20 milliseconds. The non-availability of an instrument with a very short response time to measure the specific heat of coal under these conditions virtually forced the investigators [7-9] to extrapolate Merrick's model to their conditions.

To evaluate the potential errors arising from the use of the Merrick model in the analysis, Maloney et al. [13] conducted an extensive survey on published heat capacity data for high volatile bituminous coals. Heat capacity data from Badzioch et al. [28], Singer et al. [29] and MacDonald et al. [30] over a temperature range of 300 - 600K were compared with the predictions from the Merrick model. These comparisons indicated that in all cases the Merrick model overpredicts the measured heat capacity values. In the best case, the measurements of MacDonald et al. [30] were 10 percent lower than the Merrick predictions, while in the worst case the data of Singer et al. [29] were 40 percent below the Merrick predictions. When corrections of this magnitude were introduced to the model, Maloney et al. [13] found significant improvements in the agreement between their model temperatures and data during the early stages of heating.

Thermal conductivity influences the conduction of heat through pulverized fuel particles and this in turn affects the rate of heating of coal. Knowledge of the thermal conductivity of coal as a function of temperature under rapid heating conditions is also important to progress in coal utilization

technology. The thermal conductivity of coal is related to the amount of heat that flows through it by virtue of a temperature gradient and this is an important factor during rapid heating in the utilization of coal. The thermal conductivity data of Badzioch et al. [28] indicate a constant thermal conductivity of $-0.0005 \text{ cal s}^{-1} \text{ cm}^{-1} \text{ K}^{-1}$ from room temperature up to about 700K. Then the thermal conductivity of coal increases sharply to a value of $-0.004 \text{ cal s}^{-1} \text{ cm}^{-1} \text{ K}^{-1}$ at 1200K. Considerable structural changes with the coal were observed by Badzioch's et al. [28] during this temperature interval (700 to 1200K) and those changes were found to accompany by a considerable temperature variation of the thermal conductivity.

Solomon et al. [7] and Fletcher [8] modeled the devolatilization by a lumped analysis assuming an infinite thermal conductivity for a small coal particle. Coal belongs to the class of poor conductors of heat. Since significant internal temperature gradients are likely during rapid heating even for small particles, Maloney et al. [9] used a temperature-dependent thermal conductivity based on Badzioch's data in their analysis. Maloney et al. [13] assessed the temperature calculations using the room temperature thermal conductivity value since no significant swelling was observed in their previous work [9] during the early stages of heating (up to $\sim 1200\text{K}$) and found better agreement between model and data. The implication from the above discussion is that modeling the early stages of rapid devolatilization process of a coal particle by a lumped approach assuming infinite thermal conductivity or by a distributive analysis extrapolating temperature-thermal conductivity data obtained from slow heating rate experiments may lead to significant error.

Thus based on a number of experiments and comparisons with other published studies, Maloney et al. [9, 13-14] concluded that the particle density and spherical assumption alone cannot be the source of errors for all of the observed differences between model and experiment during the early stages of heating. Thermal property assumptions applied in the temperature history calculations must also be a source of significant errors.

Maloney and coworkers [9] observed a steady rise in particle temperature until volatile evolution commenced. At that point the rate of temperature rise dropped quickly followed by a pronounced temperature plateau over which heavy volatile evolution proceeded. These observations suggest a substantial thermophysical and thermochemical heat requirement associated with volatile evolution. In a more recent work, Sampath et al. [31] examined this issue and developed a heat transfer analysis to evaluate the magnitude of this heat requirement. The analysis included a first order rate expression with rate constants selected to match observed devolatilization times scales to account for volatile evolution (mass loss). Devolatilization heat requirements were treated using a lumped approach that considered the enthalpy of the volatiles leaving the particle. Excellent agreement was obtained between model projections and measurements for a range of heat fluxes.

It is accepted that there are uncertainties in the heat capacity of coal especially for the high heating rate studies [7-9]. It is also accepted that the large thermal gradients within the particle (due to thermal conductivity of coal) make prediction of the temperature difficult during the early heating in these studies [7-9]. However, there has been no independent study conducted to investigate the effect of heating rate on the thermal properties of coal particles. Knowledge of the role of heating rate on coal thermal properties is essential for progress towards advanced coal utilization technology.

To this end, the effect of heating rate on the heat capacity and thermal conductivity of pulverized coal particles was investigated in this project. Experiments involving high heating rates on the order of 10^4 to 10^5 K/s were performed using the electrodynamic balance measurement system at the single particle laboratory, National Energy Technology Laboratory (NETL), Morgantown. Data for the experiments involving low to intermediate heating rates on the order of 10^2 to 10^3 K/s obtained by our industrial partner in this project, United Technologies Research Center (UTRC), in their previous studies employing the heated grid differential thermal analyzer were used to assess the effect of low heating rates on the thermal properties of coal particles. Modeling the effect of heating rate on the thermal properties of coal was also carried out for a large range of heating rates (10^2 to 10^5 K/s).

EXPERIMENTAL METHODS

This study is unique in that detailed measurements on coal particle volume, external surface area, mass, density, changes in size, temperature, and laser power in addition to high-speed filming of particle behavior during rapid heating were performed in single particle level for a broad range of heating rates ($\sim 10^4$ - 10^5 K/s). The 3-D rotational technique of Maloney et al. [18] was applied in this study to obtain the external surface area and volume for individual coal particles. C_d/m ratios [19] were also found for individual particles. Following Monazam et al. [21], surface area and volume measurements were used to predict particle drag coefficient applying the analysis for the prediction of C_d by Brenner for deformed spheres [20] which was then used to predict the initial mass for individual coal particles. Following the shape and mass characterization, the same particle was subjected to radiative heating and the particle surface temperatures were measured prior to and during devolatilization. Dynamics of particle swelling and volatile evolution were recorded using time-resolved high-speed cinematography. A broad range of laser intensities were employed in heating the particles and temporal laser power variations were followed for each heating pulses for use in the heat transfer analysis.

Measurement of Particle C_d/m , External Surface Area, Volume, Mass, and Density:

Individual coal particles were levitated in an electrodynamic balance (EDB) and characterized using high-speed optical and electronic instruments. Single particles were backlit with a red He:Ne laser at the side and with a light emitting diode (LED) from the bottom of the balance. The magnified shadow image of the side view was split and projected onto the detector of a CCD video camera imaging system and a high-speed diode array imaging system. The magnified shadow image of the bottom view was projected onto the detector of a second CCD video camera imaging system positioned above the balance. The diode array imaging system was used to characterize particle drag coefficient/mass (C_d/m) ratios. The video-based imaging systems (side and top) were used for routine particle observation and shape characterization. The details of the diode array and the video based imaging systems can be obtained elsewhere [18-19]; only brief discussion is given below.

Particle C_d/m ratios were determined based on measurements of particle trajectory in the EDB. Particles were balanced in the EDB and a step change was applied to the EDB endcap voltage, stimulating a dynamic response of the particle from its balance position. The resulting transient

motion of the particle was measured using the high-speed diode array imaging system which provided an analog output indicating particle position along the EDB center axis. A force balance model referred to as the Particle Dynamic Model (PDM) was used to simulate the particle trajectory in the EDB. The only unknown in the force balance was particle C_d/m which was determined by matching the model output with the measurements. The details of the C_d/m measurement can be obtained elsewhere [19].

Following the approach of Maloney et al. [18], volumes and external surface areas were obtained by rotating particles and recording image data for successive video fields as a function of rotation angle using side view video imaging system. Particles were rotated about the EDB center axis using six directed gas jets equally spaced about the EDB centerplane. Rotation rates were established in the range of 10 to 15 revolutions per minute and were determined with the aid of the top view video camera. Surface areas and volumes were calculated by summing the surface and volume elements swept out during rotation from one video field to the next. The observed surface area and volume were used to estimate particle drag coefficient by applying Brenner's approach [20] for deformed spheres. The particle mass was then separated from the C_d/m ratio. From the mass and volume, the particle density was determined. Complete details of the video imaging system and the experimental determination of particle 3-D surface area, volume, mass, and density are discussed elsewhere [21].

Measurement of Laser Incidental Area, Particle Surface Temperatures, Temporal Intensity Variations in the Heating Pulse, and Size Changes During Heating and Cooling:

Single particles were heated bidirectionally and the cross-sectional area of the particle that the laser beam was incident upon called laser incidental area in this study (A_L) was also obtained. This area was needed to calculate the energy absorption response of the particle for use in the heat transfer analysis. The two opposite access ports for the heating beam were located at 60° anti-clockwise or 120° clockwise to the access port of the side view video-based imaging system. Stable side view cross-section of the particle prior to heating was measured and was used as a reference area. The laser incidental area was extracted from the measured rotational frame data. This was done by locating the reference area in the rotational data and extracting the laser incidental area by going backward 60°. Also, the same area was confirmed by going forward 120° from the reference area.

Following the measurements of the particle shape, mass, stable reference area, and laser incidental area, the same particle was heated with the pulsed Nd:YAG laser beam of equal intensity from opposite sides. Temporal power variations in the laser pulse was measured by an ultra-fast fiber optic uv light transmitter coupled with a silicon photodiode laser monitor included in the beam path. Details of the transient laser power measurement can be seen elsewhere [31].

Measurements of changes in particle size and temperature that accompany rapid heating were made respectively using the high-speed diode array imaging system and a single-wavelength radiation pyrometer. The diode-array imaging system was made of 16 x 62 elements of silicon photodiodes spaced 100 Fm apart. The magnified image of the particle projected onto the array blocks a certain number of photodiode elements yielding an analog output (at 6200 Hz) that is proportional to the cross-sectional area of the particle. The array was calibrated using polystyrene spheres of known

diameter following the procedure described by Maloney et al. [32]. Uncertainty in the size (diameter) measurement was on the order of ± 5 Fm.

Measurements of the radiant emissive power from the heated particles were made using a single wavelength pyrometer on the same optical access as the particle size measurements were made with the diode array. The pyrometer incorporated a thermoelectrically cooled InGaAs detector. The detector was filtered to provide a 100-nm bandpass centered at 1.5 Fm with high blocking levels at the HeNe ($> 10^{-5}$) and Nd:YAG ($> 10^{-9}$) wavelengths. The pyrometer was calibrated against a standard General Electric tungsten strip lamp to a temperature greater than 1500K. The lamp filament was imaged 1:1 with a lens system onto a pinhole of known size at the balance center. The radiant energy from the pinhole was then collected and re-imaged onto the pyrometer detector with the use of a second similar lens system. Effective wavelength of 1.5 Fm was found to reproduce lamp temperature data within 7K at 1040K and within 20K at 1600K. Particle temperatures were calculated using the measurements of particle size and radiant emissive power applying the Wein approximation to Plank's law. Emissivity (0.85) used in these calculations were taken from the literature [8-9].

Data Acquisition Timing and High-Speed Motion Pictures During Heating and Cooling:

Photographic records of the particle behavior during heating were obtained. Individual particles were backlit with a yellow He:Ne laser and a magnified shadow image of the particle was projected onto the film plane of a high-speed 16 mm movie camera that was operated at 5000 frames per second. Timing marks were recorded on the film to accurately determine the film speed and to mark the initiation of the heating pulse. As reported elsewhere [9,17], the high-speed movies provided excellent time resolution of the particle response, including rotation, swelling, volatile evolution and the time the particle began to move off the imaging system array.

Analog outputs from the diode array imaging system, the pyrometer, and the laser monitor were acquired using a Data Translation DT2828 interface card in a desktop computer. Data acquisition was triggered from the movie camera, when the desired framing rate was achieved, and continued at a rate of 15 KHz per channel for a period of 50 msec. The heating pulse was initiated -7 msec after initiation of data acquisition. A nominal 5-V TTL synchronization pulse was initiated at the radiation source coincident with the heating pulse and was used to activate a timing light for the high-speed movies.

Measurements were made on individual particles of PSOC 1451D HVA bituminous coal in the aerodynamic size range of 106 - 125 Fm. Various heat fluxes ranging from -700 to -1600 W/cm² were employed to heat the particles. The coal was collected by the Coal Research Section of the Pennsylvania State University and aerodynamically size classified by Vortec Products Co. The D designation indicates that the sample was part of a DOE effort to generate and distribute a common suite of coal samples to a number of independent research laboratories. Ultimate and proximate analyses of the coal sample are presented in Table 1.

TABLE 1
Ultimate and Proximate Analysis for PSOC 1451D:
(As reported by the Penn State Office of Coal Research)

ULTIMATE ANALYSIS	DRY ASH FREE BASIS
% Carbon	83.3
% Hydrogen	5.4
% Nitrogen	1.6
% S + O (diff)	9.7
PROXIMATE ANALYSIS	AS RECEIVED BASIS
% Moisture	2.5
% Ash	13.3
% Volatile Matter	33.6
% Fixed Carbon	50.6

ANALYSIS

Incorporation of Particle Volume, Surface Area, Laser Incidental Area, and Density into the Heat Transfer Model:

Measured temperature histories of the particle surface were compared with theoretical estimates of the temperature response of radiatively heated coal particles. The model described here has been influenced by the previous model of spherical coordinate system discussed before [9] , but it incorporates many of the recent findings on particle volume, density, surface area, and laser incidental area. The particle was heated with laser beams of equal intensity, $I(t)$, from two sides. It was assumed that the particle absorbs a fraction of the energy proportional to its absorptivity ($\alpha=0.85$), distributes this energy uniformly throughout its entire surface and exchanges heat with the surrounding air. While heating, initially, it was assumed that the particle retains its irregular shape with no swelling, no rotation and no mass loss. Commonly applied Merrick heat capacity correlation developed for coal [23] was assigned to predict temperature-dependent particle heat capacities. Temperature-dependent thermal conductivities were assigned using the measured average conductivity data for various coals of Badzioch and coworkers [28]. Mass loss, heat of devolatilization, thermal property characterizations, and size changes during heating were also considered during the latter stages of heating.

One approach to predict temperatures for irregular particles of arbitrary shapes is the equivalent volume sphere approximation, in which the temperature is calculated for a sphere with volume and mass (D_v) equal to that of the irregular particle. In addition, the energy absorption response was calculated using the cross-sectional area, A_L , incident to the laser beam. The emission response was calculated using the measured particle surface area, S_p . Heat was assumed to only flow in the radial direction of the volume equivalent sphere. With the above restrictions, the heating of the particle was described by the Fourier equation for a sphere as,

$$\rho_p C_p (T) \frac{\partial T}{\partial t} = K_p (T) \left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) \quad (1)$$

The following boundary conditions were applied:

(i) The initial condition at $t = 0$:

$$T(r, 0) = T_o \quad 0 \leq r \leq R \quad (2)$$

(ii) The symmetry condition at the center $r = 0$:

$$\frac{\partial T(0, t)}{\partial r} = 0 \quad t \geq 0 \quad (3)$$

(iii) The energy delivered at the surface $r = R$:

$$K_p (T) \frac{\partial T}{\partial r} = \left(\frac{2A_L \alpha I(t)}{S_p} \right) - [h(t) \{T_s - T_\infty\} + \sigma \epsilon \{T_s^4 - T_\infty^4\}] \quad (4)$$

The left hand-side of equation (4) represents heat transfer to the particle interior by conduction while the first term on the right-hand side accounts for heat input by radiation, the second and third for cooling by convection and radiation respectively. The measured transient intensity, $I(t)$, was used as the transient laser input flux in the source term. This input flux was divided by a factor, $S_p/2A_L$, to account for the two-sided heating employed in the experimental system which gives a heating cross-section of $2A_L$, while the convection-conduction and radiation cooling terms were considered across the entire external particle surface area. The transient heat transfer coefficient, $h(t)$, has been determined from the transient Nusselt number, $Nu(t)$, solving the partial differential equation describing the unsteady temperature in the surrounding fluid and is given below. The effect of using this $Nu(t)$ as compared to the use of steady state value $Nu=2$ on the predicted temperature histories is negligible since the predominant heating is not convection in this study. However, it does keep the theory more consistent with the transient nature of the experiment.

$$Nu(t) \big|_{r=R} = 2R \left(\frac{1}{R} + \frac{1}{[\pi k(T) t]^{\frac{1}{2}}} \right) \quad (5)$$

where, $k(T)$, is temperature dependent thermal conductivity of the surrounding gas (air) calculated for the mixture of N_2 and O_2 .

RESULTS AND DISCUSSIONS

The temperature measurement and analysis procedures employed here were validated using carbon spheres [9,31]. Experiments were conducted on single coal particles to understand the effect of heating rates on the thermal properties of coal particles prior to and during devolatilization.

Various heat fluxes covering a broad range of heating conditions were employed to heat the coal particles in this study. The time-averaged energy fluxes were varied from -700 to -1600 W/cm². Knowing the time-averaged intensity and the analog output of the laser monitor, the transient laser intensity for each heating pulse was calculated. Details of this calculation can be obtained elsewhere [31]. The temperature calculations presented in this study were obtained using this transient intensity as the source in the heat transfer model.

The dynamic features of the devolatilization process, such as, particle softening, bubbling, swelling, evolution of volatiles, and contracting during heating were clearly resolved on the high-speed film records for the bituminous coal particles tested in this study. In general during the first few milliseconds of heating, the particles were stationary with no indication of mass loss (no evolution of volatiles) or noticeable swelling. After this heat-up time, the particles began to rotate slowly. This slow rotation is considered to be an indication of light volatile evolution [17]. Particle softening, bubbling, and swelling were noticed subsequently. Within a fraction of millisecond, a light tar cloud was seen surrounding the particle. Particles swelled significantly and intense bubbling occurred at the surface for a period of time. Particle continued to rotate with occasional jetting of volatiles. A dense cloud of heavy volatiles continued to evolve during the last half and for several milliseconds beyond the completion of the 10 millisecond heating pulse.

During devolatilization as the evolution of volatiles continued, the coal particles lost charges rapidly, and began to move off the imaging system array, producing a rapid drop in the analog output (size measurement) of the diode-array imaging system. These transitions were further substantiated by analysis of the high-speed film. These films showed slow rotation and motion of the particles off the balance center with volatile evolution. At the magnification factors used for the imaging system (3.8 x) and the pyrometer (1 x), particle images moved off the imaging system array (effective width = 400 Fm) before leaving the pyrometer detector (effective width = 1000 Fm). Because both size and radiant emission data were required to determine particle temperature measurements, following Maloney et al. [9], the pyrometer temperatures and the model predictions in this study were conducted only up to the time the particles were in the detector array of the imaging system.

Presentation of Detailed Shape, Mass, Temperature, and Transient Laser Power Measurements Under Various Heat Flux Conditions:

Experiments were conducted on single bituminous coal particles for a broad range of heating rates (10^4 - 10^5 K/s) up to a surface temperature of about 1600K to evaluate the effect of heating rates on the thermal properties of coal particles. Each particle was rotated in the EDB, 3-D external surface area, volume obtained, C_d/m , mass and density found, the temporal intensity variations of the heating pulse followed, and the surface temperatures measured. The shape information (equivalent

TABLE 2
Shape, Mass, Density, and Heat Flux Information for Coal Particles

Particle #	Surface Area Diameter, d_{sa} (Fm)	Volume dia, d_v (Fm)	C_d/m (1/s)	mass, m (Fg)	density, D (g/cm ³)	T i m e - Averaged Intensity, I(ta) (W/cm ²)
1	93	85	49	0.37	1.12	N/A
2	104	97	33.5	0.58	1.2	717
3	105	99	36	0.54	1.06	727
4	129	117	30	0.86	1.04	745
5	113	108	29	0.71	1.08	763
6	102	96	28	0.68	1.45	764
7	141	123	27	1.15	1.18	894
8	103	96	34	0.58	1.24	906
9	87	83	40	0.39	1.29	1092
10	126	116	25	0.98	1.19	1105
11	125	118	26	0.9	1.05	1138
12	117	111	26	0.82	1.14	1209
13	124	118	24	0.94	1.09	1302
14	134	125	23	1.1	1.09	1319
15	108	102	30	0.66	1.18	1328
16	109	106	28	0.7	1.13	1402
17	99	92	35	0.54	1.33	1453
18	105	101	31	0.61	1.14	1469
19	104	100	32	0.59	1.14	1475
20	115	110	28	0.74	1.08	1482
21	112	106	27.5	0.75	1.21	1488
22	101	94	33	0.57	1.3	1494
23	123	115	22.5	1.03	1.28	1500
24	108	101	32	0.63	1.15	1506
25	107	100	28	0.71	1.36	1507
26	103	95	52	0.38	0.84	1507
27	126	115	27	0.91	1.14	1511
28	155	143	80	0.38	0.25	1542

diameters for particle surface area, volume), particle C_d/m , mass and density, and the time-averaged intensity (I_{ta}) of the various heating pulses employed for the 28 particles examined in this study are presented in Table 2. The large variability seen in the surface area diameter, volume diameter, and density between coal particles suggest that this variability between particles must be accounted for in the single particle modeling in order to reliably predict the temperature measurements for individual particles.

Treatment of Thermal Properties for Coal Particles Prior to Devolatilization During rapid Heating:

The sensitivity analysis performed on coal particle thermal properties suggests that the effect of coal particle heat capacity, C_p , on temperature profile is dramatic. For example, a 50% increase in C_p from 0.3 to 0.45 cal/g K depress the surface temperature as much as -300K at 1400K and a 100% by -500K.

The effect of the coal particle thermal conductivity, K_p , on temperature profile was found smaller even when the thermal conductivity is about 3 times of the room temperature value. For example, a -330% increase in K_p from 0.0003 to about 0.001 cal/cm s K depress the surface temperature by only -300K at 1400K at 2 msec heating time, by -125K at -1800K at 5 msec heating time, and by -50K at 1900K at 7 msec heating time. When K_p is greater than 0.001 cal/cm s K, there is no further significant depression in the predicted surface temperatures at least after 5 msec heating time.

Coal particles have a rapid rise in temperatures during rapid heating. Maloney, Sampath and Zondlo [33] critically evaluated the thermal property assumptions employed in coal combustion modeling and found that thermal property values in the neighborhood of room temperature value best replicated the rapid rise in temperatures during rapid heating. Whereas the Merrick's heat capacity equation predicted very slow heating profiles. They hypothesized that at combustion level heating rates the vibrational part of the heat capacity of the coal molecules appears to be still frozen. Following the approach of Maloney et al. [33], a combination of the average room temperature heat capacity and thermal conductivity values were used in the present analysis to predict the early heat-up for single coal particles prior to devolatilization during rapid heating.

Heavy volatiles were seen to evolve from the coal particles during the latter stages of heating. One approach to model this process is that mass loss must be accounted for in the calculations during devolatilization. Addition of mass loss together with the assumption of the room temperature thermal properties for coal particles in the calculations would overpredict the temperature measurements still more. Consequently, endothermicity of coal must also be accounted for in the temperature calculations during devolatilization.

Addition of Devolatilization Kinetics to Predict Mass Loss; Distributive Analysis - Latter Stages:

The conservation of energy equation for a single coal particle undergoing devolatilization process assuming mass loss can be written as follows [34-35]:

Rate of change of sensible energy content of the particle	=	Rate of energy in by conduction	-	Rate of energy utilized for devolatilization	-	Rate of energy leaving the solid because of solid to gas transformation at temperature, T.
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$$\frac{\partial \rho_p C_p (T - T_\infty)}{\partial t} = \nabla (K_p \nabla T) - \left(-\frac{\partial \rho_p}{\partial t}\right) \Delta H_d - \left(-\frac{\partial \rho_p}{\partial t}\right) C_p (T - T_\infty) \quad (6)$$

where $\hat{H}_d$ is the heat of devolatilization for coal. Since C_p and K_p are constants or function of temperature only, taking them out of the differentials will yield,

$$C_p \frac{\partial \rho_p (T - T_\infty)}{\partial t} = K_p \nabla^2 T - \left(-\frac{\partial \rho_p}{\partial t}\right) \Delta H_d - \left(-\frac{\partial \rho_p}{\partial t}\right) C_p (T - T_\infty) \quad (7)$$

$$\text{i.e., } \rho_p(t) C_p \frac{\partial T}{\partial t} + C_p (T - T_\infty) \frac{\partial \rho_p}{\partial t} = RHS \quad (8)$$

On simplification,

$$\rho_p(t) C_p \frac{\partial T}{\partial t} = K_p \left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) - \left(-\frac{\partial \rho_p(t)}{\partial t}\right) \Delta H_d \quad (9)$$

where,

$$\frac{\partial \rho_p(t)}{\partial t} = \frac{\partial \left(\frac{m(t)}{v} \right)}{\partial t} \quad (10)$$

taking v as constant,

$$\frac{1}{v} \frac{\partial m(t)}{\partial t} = -\frac{1}{v} A e^{-E/RT} [m(t) - m(t_\infty)] \quad (11)$$

where $m(t)$ is instantaneous mass of the coal particle at any instant of time and $m(t_4)$ is mass of the coal particle on complete devolatilization. A maximum volatility of 50% is assumed in this study for bituminous particles at rapid heating rates [1] and thus $m(t_4) = 0.5 m_0$ in this study where m_0 is the initial mass of the coal particle.

Selection of Devolatilization Kinetics for Coal Particles Subjected to Rapid Heating:

During heating, heavy volatiles were seen to evolve from the coal particles. As reported elsewhere [9,17,31], time-resolved high speed films provided excellent time resolution for the onset of particle rotation or the commencement of volatile evolution. Maloney and coworkers [9,31] observed a steady rise in particle temperature until volatile evolution commenced. At that point the rate of temperature rise dropped quickly followed by a pronounced temperature plateau over which heavy volatile evolution proceeded. These observations suggest a substantial thermophysical and thermochemical heat requirement associated with volatile evolution. In a more recent work, Sampath, Maloney and Zondlo [31] examined this issue and developed a heat transfer analysis to evaluate the magnitude of this heat requirement. The analysis included a first order rate Arrhenius expression developed by Badzioch et al. [36] with rate constants selected to match observed devolatilization times scales to account for volatile evolution (mass loss). Excellent agreement was obtained between model projections and measurements for the onset or the commencement time of devolatilization over a range of heating rates (10^4 - 10^5 K/s). Following the approach of Sampath et al. [31], Badzioch's kinetics was used in the present analysis to predict the devolatilization of coal particles subjected to high heating rates.

Consequences on the Addition of Devolatilization Kinetics:

It was shown [33] that application of room temperature thermal properties best predicts the coal particle temperature measurements prior to devolatilization. Also, it was shown that it overestimates the measurements during devolatilization. Addition of devolatilization kinetics brought the instantaneous mass of the coal particle down. Consequently, less mass would overpredict the instantaneous temperature measurements still more during devolatilization.

Freihaut et al. [6] observed a plateau in the actual time-temperature path of a coal particle during devolatilization and concluded that such a trajectory is the result of the thermal flux to the particle coupled to the heat requirement of the devolatilization process. Andrei et al. [37] inferred constant temperature for coal particles during devolatilization and suggested that an endothermic process could be the reason. Therefore, one approach to predict the latter stages in the present study would be accounting for the endothermicity of the coal particle in the calculations during devolatilization. This endothermicity is a combination of 1) the heat capacity changes for coal during devolatilization, and 2) the heat of devolatilization of coal, $\hat{H}_d$. Such a combined effect to account for the coal endothermicity during devolatilization has been previously followed by Hertzberg et al. [26-27] in the heat transfer calculations.

Treatment of Heat Capacity Changes For Coal During Devolatilization to Predict Devolatilization Temperatures:

The present hypothesis assumed a 'sudden jump' in the heat capacity of coal from its room temperature value to Merrick's model [23] temperature-dependent values once devolatilization (mass loss) begins. This approach is analogous to the heat capacity data of polymers that undergo phase changes [25]. If one looks at temperature-specific heat data of polymers, it is apparent that there is nearly a discontinuous change in their specific heat as they undergo phase change from solid to glass transition [25]. The glass transition temperature of a polymer is defined as the temperature below which an amorphous polymer (or an amorphous region of a crystalline polymer) is rigid and brittle

(glassy) and above which it is rubbery or fluid like [38]. The sudden change in specific heat of a polymer with phase change is attributed to an increase in the degrees of freedom available to the functional groups of the polymeric material [39]. The specific volume of the polymers increases linearly with temperature up to the glass transition temperature after which the specific volume continues to increase linearly but at a steeper gradient [40]. The glass transition phenomena with increase in specific volume observed in polymers can be viewed as similar to the metaplast phenomena with swelling seen in plastic coals during devolatilization. High-speed films showed that swelling is accompanied with onset of particle rotation or commencement of light volatile evolution in coal particles. In other words, commencement of light volatile evolution in coal particles can be viewed as an indication of phase change in coal particles from solid to plastic. Thus the phase change from glassy (solid) to rubbery in polymers is analogous to the phase change from solid state to plastic state (swelling with volatile evolution) in bituminous coals. The polymers go through a sudden jump in their heat capacity during the phase change from glassy to rubbery. Similarly, the bituminous coal particle in the present heat transfer analysis is assumed to display analogous behavior in its heat capacity from the average room temperature value to temperature-dependent value once mass loss begins (when $t = t_{0.1\%}$ where $t_{0.1\%}$ is the time to take 0.1% of volatile matter loss (a conservative value assumed in the present analysis to predict the start-up-time for volatile release or to let the model know that devolatilization has begun). Thermal conductivity of the polymers go through rather a flat maximum at glass transition temperature and remain fairly constant in the rubbery region [25]. Since, there is not much change in the thermal conductivity data for polymers from glassy to rubbery, thus, analogous to polymers, the thermal conductivity of the coal particles in the present model is assumed to remain constant at the average room temperature value from the solid state to plastic during devolatilization. With this assumption, the energy conservation equation 9 becomes as follows:

$$\rho_p(t) C_p \frac{\partial T}{\partial t} = K_p \left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) - \left(-\frac{\partial \rho_p(t)}{\partial t} \right) \Delta H_d \quad (12)$$

For $t < t_{0.1\%}$, $C_p = C_{pc} = 0.25 \text{ cal/gm K}$

For $t > t_{0.1\%}$, $C_p = f(T) = C_p(T)$ Merrick

For all t , $K_p = K_{pc} = 0.0005 \text{ cal/cm s K}$.

ΔH_d is generally a constant value for coal and thus is an user input to the model in this study.

Treatment of Thermal Conductivity For Coal During Devolatilization to Predict Devolatilization Temperatures:

Thermal conductivity for coal during rapid heating and devolatilization might be different from the data obtained using slow heating techniques. For example, Maloney et al. [33] suggested that the thermal conductivity for coal particles (106 - 125 Fm size cut) during rapid heating at about 1200K would be still about the room temperature value whereas Badzioch's conductivity data give a value ten times higher. This suggests that in rapid heating conditions, there might be a slow increase in the thermal conductivity for coal from the room temperature value to a flat maximum value during devolatilization as in the case of polymers discussed above[25]. A possible thermal insulation during heating by the plastic coal shell of the bituminous coal particle due to rapid swelling [41], a possible hindrance in the transmission of heat during the latter stages of heating by the intense volatile transport

from within the particle to the surface in the opposite direction [42], and/or the possible shielding of the inner region by the presence of an ever-thickening char layer from transmitting the heat to the colder region during the latter stages of heating and cooling [26-27] could be some of the reasons for the possible slow increase in the thermal conductivity for coal in rapid heating studies. However, even if there is a large change in the thermal conductivity value for coal during rapid devolatilization, its effect on the particle temperatures is not severe. For example, it was seen in the sensitivity analysis on coal thermal conductivity that the assumption of the room temperature K_p value overpredicted the surface temperature by only about 50K at about 7 msec of the 10 msec heating time when compared to the prediction by a 10 times larger thermal conductivity. It should be important to note that most of the temperature depression during the latter stages of heating is attributed to the changes in the heat capacity of coal as discussed earlier in this study.

Since coal thermal conductivity data at rapid heating conditions are not available and since the effect of the changes in thermal conductivity from the average room temperature value (K_{pc}) to about 10 times of K_{pc} on the predicted surface temperatures during the latter stages of heating is small, the thermal conductivity of coal in the present heat transfer analysis was assumed to remain at the average room temperature value during the latter stages of heating.

Treatment of Heat of Devolatilization for Coal, $\hat{H}_d$, During Rapid Heating:

While the assumption of coal heat capacity changes during devolatilization in the model improved the model agreement with the measurements to about 80%, it was found that a heat of devolatilization term was still needed in the model to improve the fit somewhat, accounting for about 20% of the endothermic heat requirement. A $\hat{H}_d$ value in the range of -150 to -350 cal/g was seen to bound the particles tested in this study. In general, a value of -250 cal/gm was selected based on optimization of model projections over all for the entire particles examined. The -250 cal/g value is in good agreement with the endothermic heats of carbonization reported respectively by Kasperczyk et al. [43] and Agroskin [44] of 272 and 250 cal/g. The upper bound is close to the range of -315 to -340 cal/g values suggested recently by Hertzberg et al. [26-27] on Pittsburgh seam bituminous coal particles. It should also be noted that similar to the present work, Hertzberg et al. [26-27] also used a room temperature thermal conductivity value for coal in their analysis and obtained -300 cal/gm for $\hat{H}_d$ in their calculations.

Validation of the Model:

The model prediction was first verified with data available in our previous studies, and then subjected to comparison with the present data. One such validation carried out in the present study is shown in Figure 1. The solid line in the figure is the experimental temperatures and the dashed line is the output of the present model. The experimental temperatures correspond to particle number 6 of Table 1 in the work of Maloney et al. [33]. The particle was heated with a 10ms heating-pulse with a time-averaged intensity, $I(ta)$, of 1340 W/cm². The physical properties of the particle were $d_v=116$ Fm, $d_{sa}=124$ Fm, $D=1.14$ g/cm³, and $m=0.93$ Fgm. The emissivity and absorptivity in the model were assumed to be equal to 0.85 [9]. The total energy absorbed by the particle was calculated from the

Figure 1. Validation of the Model: Comparison of temperature measurements for a coal particle obtained in our previous study [33] with simulations of the present model. Solid line: measured temperatures; dashed lines: simulation results.

measured laser incidental initial cross-sectional area (A_L) and the surface area (S_p). As can be seen, the agreement between model and measurement is excellent throughout the entire heating period. The fluctuation in the temperature measurements during the latter stages of heating is mainly due to the compounded effect of particle rotation and two-sided heating (non-uniform heating) employed in this study. While two sides of the particle are heated, the other sides keep cooling until they face the laser as the particle rotates. No provisions were made in the present analysis to predict the fluctuations in the temperature measurements due to this small non-uniform heating of the particle as it rotates during two-sided heating. The mass variation was considered in two different ways: (1) constant volume diameter, changing density, and (2) input measured initial mass, input measured initial size during heating as initial volume equivalent diameter, calculate initial density, input size changes during heating as changing volume equivalent diameters, calculate mass loss and changing densities. There was very little difference in the predicted temperatures for the two cases. The former case was used in the simulations to compare the data obtained in this study.

Performance of the Model:

A combined effort of carefully designed experiments and systematic analysis is imparted in this study in order to understand the effect of heating rates on the thermal properties of coal particles. Various model assumptions and their effect on the predicted temperature histories were carefully considered. Finally, equation 12 was chosen as one approach to model the coal devolatilization process in this study. As discussed before, the model was first validated with the data available in our previous studies. Following the validation, the model with the same thermal properties, kinetics, and apparent heat of devolatilization (-250 cal/g) was then applied and found to predict the temperature measurements prior to and during devolatilization for the coal particles tested in this study. One such comparison is shown in Figure 2. The solid line in the figure is the experimental temperatures and the dashed line is the output of the present model. The experimental temperatures correspond to particle number 16 of Table 2 in the present study. The particle was heated with a 10ms heating-pulse with a time-averaged intensity, $I(ta)$ of 1402 W/cm². The physical properties of the particle were $d_v=106$ Fm, $d_{sa}=109$ Fm, $D=1.13$ g/cm³, and $m=0.7$ Fgm.. As can be seen, the agreement between model and measurement is excellent throughout the entire heating period. The average agreement of the measured and calculated temperatures for all the coal particles tested in this study throughout their residence time during heating and devolatilization was found to be within ± 70 K.

Low Heating Rate (10^2 - 10^3 K/s) Work:

United Technologies Research Center (UTRC), CT, was our industrial partner in this project. Approvals from NETL/Pittsburgh, CAU, and UTRC for performing the heated grid work at Clark Atlanta University (CAU), GA, that was originally planned at UTRC, CT, were obtained during the second year of the project. UTRC finally donated a number of components of its heated grid reactor to CAU after a long negotiation between CAU and UTRC on to loan or donate. The grid was put together at CAU and started testing the system in the last several months. It was noticed the temperature of the heated grid did not correlate with the rate of heating power input. Several attempts to correct this problem including the rearrangement of power supply circuit input did not help. A

Figure 2. Performance of the Model: Comparison of temperature measurements for particle 16 with simulations of the present model. Solid line: measured temperatures; dashed lines: simulation results.

crack in the reactor in which the heated grid is housed was noticed and this crack could be a problem for the poor heat load. Attempts to fix this crack would be expensive (no money was budgeted for this kind of problem and no money available) and time consuming and since the project completion date was already near, it was decided to use the heated grid data available in the literature. This approach was discussed with the Technical Monitor, NETL, Pittsburgh. It was originally proposed to collect low heating rate (on the order of 10^2 - 10^3 K/s) data using the heated grid reactor. There are few data available in the coal literature for 10^2 - 10^3 K/s obtained by UTRC in their previous studies. UTRC has no problem with our approach of using their data as these data are already available in the public domain/literature. While still the scope of the entire proposal remains the same covering the effect of both the high and low heating rates (10^2 - 10^5 K/s) on the thermal properties of coal particles, the polymer analogy model discussed above was applied to predict the heated grid data. These data were obtained for a longer heating duration on the order of several seconds as opposed to the 10 milliseconds heating time in the single particle experiments discussed above. So, the polymer analogy model was modified to include longer heating time on the order of several seconds to test these data. Intensity term of the model was modified to accommodate a constant heat flux as in the case of the heated grid. However, it was found the present model did not predict the heated grid data for the low heating rates tested.

Table 3 summarizes the heated grid data such as t_{asy} - time from initiation of the heating flux until an asymptotic temperature was reached in the experiment, and T_{asy} - Asymptotic temperature at $t = t_{asy}$ were retrieved from the literature [45] for various heating rates (150, 300, and 1000 K/s). Also shown in the table were t_{asy} and T_{asy} predicted by the present model for the heating rates examined. It should be noted that the rate of mass loss kept increasing with the temperature from $t_{0.1\%}$ and was found to be constant at t_{asy} in the model. Particle parameters used in the model were as follows: $d_p=110$ Fm, $D=1.15$ g/cm³, $\bar{H}_d=-250$ cal/g, $\gamma=.85$, and Badzioch's kinetic coefficients. The $t_{0.1\%}$ not provided in Table 3 for the three heating rates examined were 0.1s, 0.04s, and 0.02s respectively. The $T_{0.1\%}$ not provided in Table 3 for the three heating rates examined were 589K, 706K, and 810K respectively. While the asymptotic temperature between the model and heated grid data were somewhat in close agreement, however, the model failed to predict the time to reach the asymptotic mass loss. The model predicted the asymptotic temperatures somewhat in close agreement but in a much earlier time frame in each of the three heating rates assessed. It should be noted that UTRC's work showed reasonably good agreement with Merrick model predictions at 1000K/s, but at higher heating rates they observed similar trends in coal behavior as evidenced and predicted by the present model. Merrick model predicts increase in heat capacity with the increase in temperature. In the case of high heating rate experiments it seems the heat capacity does not increase with the rise in temperature at the early stages suggesting the vibrational part of the heat capacity of the coal molecules still remains to be frozen but during the transition from heat-up to devolatilization, the heat capacity appears to attain a sudden jump in its value as in the case of polymers. It is concluded that at combustion level heating rates (10^4 - 10^5 K/s) coal structural changes are delayed and attendant increases in thermal property are pushed to higher temperatures or require significant hold times to become manifest.

TABLE 3
Comparison of the Model Predictions with the Heated Grid Data

Heating Rate (K/s)	Present Model t_{asy} , T_{asy} (s), (K)	Heated Grid Data t_{asy} , T_{asy} (s), (K)
150	1, 600	4, 673
300	0.5, 800	2, 850
1000	0.2, 1102	1, 1173

t_{asy} - time from initiation of the heating flux until an asymptotic temperature is reached.

T_{asy} - Asymptotic temperature at $t = t_{asy}$.

OUTCOMES OF THE PROJECT

Joie C. Taylor, an undergraduate student in the Department of Engineering, was partially supported and trained in the subject matter. Several theoretical analyses were conducted to improve the model performance of the present work and the results were compared with data available from our previous studies. These activities resulted in one journal publication [33], several conference presentations, and one symposium presentation [31] to date.

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3. Taylor, J. C., Sampath, R., Maloney, D. J., Zondlo, J. W., and Monazam, E. R., Transport Phenomena of Irregularly-Shaped Solid Particles in an Electrodynamic Balance, Poster Paper, Fifth Annual DOE/HBCU conference, Southern University and A&M College, LA, March 1997.
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7. Sampath, R., Maloney, D. J., and Proscia, W., Thermal Property Data for Coal Particles for Use in Rapid Devolatilization Models, Technology Transfer Session, Historically Black Colleges/Universities and Other Minority Institutions Sixth Annual Symposium, April 28-29, 1998, Ocean City, MD.
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SUMMARY, CONCLUSIONS, AND SIGNIFICANCE

An accurate prediction of the devolatilization temperature histories of coal particles is essential in the successful design of coal combustors, gasifiers, and liquefaction reactors. This in turn requires knowledge of the effect of heating rates on the thermal properties of coal particles..

In this study, the measurement and prediction of the devolatilization temperature histories of single HVA bituminous coal particles (of size cut 106 - 125 Fm) were carried out for a broad range of heating rates (10^4 - 10^5 K/s) by a combined effort of carefully designed experiments and analysis. Single coal particles were isolated in an electrodynamic balance and their three-dimensional (external) surface areas, volumes, and densities were measured using rapid optical methods. The same particles were then irradiated with a pulsed Nd:YAG laser beam of equal intensity from opposite sides. Devolatilization temperature transients during heating were measured using a single color pyrometer. Temporal power variations of individual laser pulses were followed using an ultra- fast uv light transmitter coupled to a laser monitor. Size changes were measured using a high-speed diode array imaging system. Dynamics of volatile evolution and particle swelling were recorded using high-speed cinematography.

The on-line high-speed motion pictures provided excellent time resolution for commencement of volatile evolution and/or the onset of particle rotation. This information was used to incorporate a first-order Arrhenius type devolatilization kinetic model so that the mass loss is included in the heat transfer analysis.

One more term was added into the heat transfer analysis to account for the endothermicity of the coal particles during devolatilization. This term is a combination of 1) heat capacity changes for the bituminous (plastic) coal during devolatilization following the analogy of polymers, and 2) the apparent heat of devolatilization, $\hat{I} H_d$, for coal.

The conclusion from this study is as follows: Bituminous coal particles subjected to combustion level heat fluxes heat faster than is predicted using commonly employed approaches to model heat transfer with assumptions for thermal properties routinely applied to coal. The significance of this work is the development of a detailed model for bituminous coal particles subjected to combustion level heat fluxes which accounts for the effect of heating rates on the thermal properties of coal particles. The model can predict accurately the temperature history of a single coal particle during rapid heating, and devolatilization. Such a model would be useful for the more efficient design of advanced coal gasifiers, combustors, and liquefaction reactors.

There are a few data available in the coal literature for low heating rate (10^2 - 10^3 K/s) experiments conducted by our industrial partner, UTRC, in their previous studies. These data were obtained for a longer heating duration on the order of several seconds as opposed to the 10 milliseconds heating time in the single particle experiments discussed above. The polymer analogy model was modified to include longer heating time on the order of several seconds to test these data. However, the present model failed to predict these low heating rate data. It should be noted that UTRC's work showed reasonably good agreement with Merrick model predictions at 1000K/s, but at higher heating rates they observed similar trends in coal behavior as evidenced and predicted by the present model. It is concluded that at combustion level heating rates (10^4 - 10^5 K/s) coal structural changes are delayed and attendant increases in heat capacity and thermal conductivity are pushed to higher temperatures or require significant hold times to become manifest.

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NOMENCLATURE

C	Heat capacity ($\text{cal g}^{-1} \text{K}^{-1}$).
I	Incident energy flux ($\text{cal cm}^{-2} \text{s}^{-1}$).
K	Thermal conductivity of particle ($\text{cal s}^{-1} \text{cm}^{-1} \text{K}^{-1}$).
r	Radial position (cm).
R	Particle radius (cm).
t	Time (s).
T	Temperature (K).
"	Particle absorptivity at $1.06 \mu\text{m}$ wavelength.
,	Particle emissivity over the entire blackbody spectrum.
F	Stefan-Boltzman constant ($\text{cal s}^{-1}, \text{cm}^{-2}, \text{K}^{-4}$).
D	Particle density (g cm^{-3}).

Subscripts:

0	At time = 0.
s	At particle surface.
4	Ambient condition.
P	Of the particle.

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