THERMAL PROPERTY DATA FOR COAL PARTICLES FOR USE IN RAPID DEVOLATILIZATION MODELS

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ABSTRACT
Recently devolatilization temperature histories were measured for single bituminous coal particles irradiated in an electrodynamic balance with well characterized Nd:YAG laser pulses at combustion level heat fluxes (heating rates on the order of 10^4-10^5 K/s). These temperature profiles were modeled successfully with a detailed heat transfer analysis that accounted for coupled chemical, mass, and thermal transport processes occurring during devolatilization. Simulations using temperature dependent heat capacity and thermal conductivity correlations routinely applied to coal severely under predicted the particle temperature rise during the early stages of heating. Simulations using constant room temperature values for heat capacity and thermal conductivity showed excellent agreement with measurements prior to devolatilization during rapid heating. Increases in heat capacity and thermal conductivity observed under slow heating conditions result from bond breaking and structural changes which lead to an increase in vibrational modes of freedom in the coal structure. This suggests that under rapid heating conditions the coal structure is frozen and that these vibrational modes only become accessible at higher temperatures or longer soak times. These considerations are important if one desires to accurately model the devolatilization behavior of coals and were discussed in a paper published in the journal of *Combustion and Flame* (in press).

Two heat capacity curves were used independently in the analysis to model temperature histories during devolatilization: one for the parent coal with the room temperature value and a second for the excited lost volatile molecules with the temperature-dependent values. Mass loss was considered employing Badzioch's kinetics, a first order Arrhenius type devolatilization kinetic model, in the analysis. Model predictions agreed well with data available in our previous studies. A paper in this subject will be presented at the *27th International Symposium on Combustion,* April 2-7, 1998, Boulder, CO.

Measurement of temperature histories for coal particles subjected to a range of heating rates employing the electrodynamic balance measurement system discussed above and a heated grid reactor developed by United Technologies Research Center, our industrial collaborator in a related project, is in progress. Following the measurement, transport parameters tested above will be applied to predict the data. Results presented in this paper shed some light onto the devolatilization characteristics of single bituminous coal particles under rapid heating conditions. This is important from a combustion modeling standpoint because devolatilization sets the location of the flame front.

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 devolatilization temperature history of the coal (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.

Characterization of the temperature history of pulverized fuel particles under rapid heating rates, representative of coal combustors, is critical to the understanding of devolatilization. A reliable prediction of devolatilization temperature histories for pulverized coal particles requires knowledge of particle shape, thermal properties for high heating rates, devolatilization kinetics, and heat of devolatilization.

Recently Maloney et al. [1], 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 slow heating rate thermal property correlations and spherical shape assumptions that are routinely applied to coals. Their predicted temperature transients agreed well with the measurements for carbon spheres during the early stages of heating. However, for coal particles their predicted temperature transients differed significantly from measurements, with the measured temperatures being higher (by a factor of 2). Significant underprediction of heating rates for coal particles have also been noted in the work of Fletcher [2] and Solomon et al. [3]. The experiments of Maloney et al. were conducted in a radiative heating/convective cooling environment, whereas the studies of Fletcher [2] were conducted in a convective heating/radiative cooling environment. This fact coupled with additional analysis led Maloney et al. [1] to conclude that the difference between measured and predicted temperatures were mainly due to uncertainties in the relevant coal thermal properties and failure to account for particle shape factors.

Coal thermal properties and particle shape factors involved in the coal particle heat transfer analysis can be conveniently separated. During rapid heating, prior to devolatilization, the size and mass of coal particles remain unchanged for the first several milliseconds [1,4]. Therefore, the prediction of the temperature history prior to devolatilization requires knowledge of initial particle shape and mass, and thermal properties. More recently, in addition to devolatilization temperatures, Maloney et al. [5] measured 3D shape, mass, and density for single coal particles prior to rapid heating. Measured shape and density information was then used to perform sensitivity analyses of the heat transfer model for variations of the heat capacity and thermal conductivity of coal prior to devolatilization. An excellent fit of the model to the rapid heating and cooling temperature measurements prior to devolatilization was found when the room temperature values for the coal thermal properties were incorporated into the analysis.

During and after devolatilization, a plateau was observed in the measured temperature histories for coal particles [1,4]. Sampath et al. [6] found that the application of the room temperature thermal properties in the heat transfer analysis overpredicted the temperature measurements for coal particles during the latter stages of heating. High-speed films showed heavy volatile evolution from the surface of the coal particles during the latter stages of heating. The volatile evolution continued several milliseconds into the cooling even after the laser was turned off. So, one approach to model the devolatilization stages might be an addition of a mass loss term in the heat transfer analysis. This would bring the calculated instantaneous mass of the remaining coal particle down during devolatilization. Consequently, for the same heat input, less mass would overpredict the temperature measurements still more. This lead Sampath et al. [6] to conclude that the endothermicity (heat capacity changes) for coal during devolatilization should also be accounted for in the calculations if one attempts to simulate the temperature histories during devolatilization.

Subsequently, Sampath et al. [6] extended the heat transfer model presented by Maloney et al. [5] (that predicted the early heat up well prior to devolatilization) by accounting for the heat capacity changes for coal during devolatilization in the analysis. While the heat capacity for the parent coal was assumed to remain at the room temperature value, it was shown that a temperature-dependent heat capacity correlation for the coal volatiles predicts well the plateau region seen in the measured temperature histories for coal particles during devolatilization. A first order Arrhenius type kinetic model [7] that predicted the measured heat-up time and devolatilization time scales was also incorporated in the analysis to account for the transient mass loss during devolatilization. While the liberation of volatiles predicted by the kinetic model was assumed to carry away the heat at the particle surface, the extended model presented here predicts well the measured temperature histories for coal particles prior to as well as during devolatilization.

In this paper, experimental methods and numerical analysis employed in our previous studies [5-6] and results obtained are briefly described below. Details of our current activities and future research direction in the subject matter are also presented.

EXPERIMENTAL METHODS AND NUMERICAL ANALYSIS

Single coal particles were isolated in an electrodynamic balance and their three-dimensional (external) surface areas (S_p), volumes (V_p), laser incidental areas (A_L), mass (m) and densities (D) were measured using rapid optical methods. The same particles were irradiated with a pulsed Nd:YAG laser beam from opposite sides. Delivered energy fluxes were selected to give heating rates on the order of 10^5 K/s. Temperature transients during heating and cooling (after the laser pulse has ended) were measured using a single-color pyrometer. Temporal intensity variations (I(t)) 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. Details of the experimental system are presented elsewhere [1,4-6]. Experiments were performed on individual particles of PSOC 1451D hvA Pittsburgh seam bituminous coal in the aerodynamic size range of 106 - 125 µm.

The approach taken in the present analysis to predict temperatures for irregular particles of arbitrary shape was the equivalent volume sphere approximation. Here the temperature was calculated for a sphere with volume and mass (Dv) equal to that of the irregular particle. During devolatilization, the volatiles evolve from within the particle, convect energy as they travel to the surface, and begin to decompose from there.

With further heating, more volatiles are brought to the surface and as they decompose at the surface, mass loss is experienced. While the liberation of volatile mass from within the particle to the surface is consuming most of the heat input, the heat capacity of the parent coal (C_{pc}) in the present analysis is assumed to remain at the room temperature value during devolatilization.

Since the intra-particle residence time of coal volatiles in small particles under high heat flux conditions will be negligible, it is assumed in the present analysis that the volatiles generated from within the particle reach the surface instantaneously and are lost at the surface. It is further assumed in the analysis that the liberating volatile mass consumes most of the heat input at the surface temperature to the extent of its instantaneous heat capacity, thus carrying away most of the thermal energy from the surface. Hence, temperature-dependent heat capacity values were assumed for the lost volatiles (C_{vol}) as they move to the surface.

With the above restrictions, the energy conservation equation including the rate of loss of thermal energy carried away by the lost volatiles at the surface temperature, T_s, is described for a volume equivalent sphere undergoing devolatilization as follows:

$$\rho_p(t) C_{pc} \frac{\partial T}{\partial t} = K_{pc} \left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) + \frac{\partial \rho_p(t)}{\partial t} \Delta H_e(T) \tag{1}$$

Where the effective heat of devolatilization,

$$\Delta H_e(T) = \Delta H_d + [C_{vol}(T_s - T_\infty) - C_{pc}(T - T_\infty)] \tag{2}$$

and

$$\frac{\partial \rho_p(t)}{\partial t} = \frac{\partial (\frac{m(t)}{v})}{\partial t} \tag{3}$$

$$i.e., \quad \frac{1}{v} \frac{\partial m(t)}{\partial t} = - \frac{1}{v} k_0 \, e^{-E/\breve{R}T} \, [m(t) - m(t_\infty)] \tag{4}$$

where m(t) is the instantaneous mass of the coal particle, and $m(t_4)$ is mass of the coal particle on complete devolatilization. A maximum volatility of 50% was assumed in this study for bituminous particles at rapid heating rates [8]. Thus $m(t_4)=0.5\ m_0$ where m_0 is the initial mass of the coal particle. k_0 and E are the first-order devolatilization kinetic parameters, the collision factor and activation energy respectively. Ì is the ideal gas constant. Equation (1) represents the nonisothermal, transient process of volatile evolution of a single coal particle by accounting for the actual differences in reaction rates between the center and the surface. This approach is relevant for most practical conditions but it is generally ignored and kinetics are limited to mostly isothermal conditions.

The following boundary conditions are applied:

(i) The initial condition at t = 0:

$$T(r,0) = T_o \qquad 0 \le r \le R \tag{5}$$

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

$$\frac{\partial T(0,t)}{\partial r} = 0 \qquad t \ge 0 \tag{6}$$

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

$$K_{pc}\,\frac{\partial T}{\partial r} = \left(\frac{2A_L \alpha I(t)}{S_p}\right) - [h\,\{T_s - T_\infty\} + \sigma\,\epsilon\,\{T_s^4 - T_\infty^4\}] \tag{7}$$

The left hand-side of Equation (7) 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 convection-conduction and radiation cooling terms were considered across the entire initial external surface area, S_p, of the particle measured prior to heating. The quantity F is Stefan-Boltzman constant (known). The fraction of energy absorbed by the particle, ", is assumed to be equal to the fraction of energy emitted by the particle [1]. The measured transient intensity, I(t), has been used as the transient laser input flux in the source term. This input flux has been 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 $2A_L$.

Method of Solution

A numerical solution of Equation (1)was obtained using an implicit Crank-Nicholson scheme since it is a nonlinear unsteady state heat conduction problem involving the temperature to the fourth power in the third boundary condition (Equation (7)). The particle was divided into separate concentric spherical nodes and each node was assumed to be isothermal. The transient mass loss at each node was determined by employing the Badzioch kinetic equations [7]. Finally, the integrated mass loss for all the nodes is calculated at each time during devolatilization. The number of nodes was determined by trial and error. The particle was divided into more and more nodes until no difference in the computed results could be determined. Generally, 20 nodal points are used.

<u>Model Input Parameters</u>

Measured initial values of d_v, $d_{sa,}$ and $S_p/2A_L$ ratio were input to the model and were assumed constant throughout the simulation. The measured density of the particle, D, was also input to the model. The density kept decreasing as the model calculated mass loss at each time during devolatilization. " was taken from the literature and assumed to be 0.85 for bituminous particles [1]. The size effect of particle swelling during heating on the predicted temperature histories was found to be small [4]. The room temperature heat capacity, C_{pc}, and the room temperature thermal conductivity, K_{pc}, for solid coal were input to the model. Their values are as follows: C_{pc} = 0.25 cal/g K [9], K_{pc} = 0.0005 cal/cm s K [10]. Reliable heat capacity data for coal volatiles at elevated temperatures (> 1500 K) are not available. The Merrick [9] model for the temperature-dependent heat capacity for coal was used to calculate the heat capacity of the lost volatiles. This assumption is also in line with Hertzberg et al. [11] who used Merrick's model heat capacity values in their prediction of the mass flux of volatiles emanating from the coal particles exposed to a laser beam. An apparent heat of devolatilization (ÎH_d) of -250 cal/g was assumed to best predict the devolatilization temperature measurements. This value is in good agreement with the endothermic heats of carbonization reported by Kasperczyk et al. [12] and Agroskin [13] of -272 and -250 cal/g respectively.

PRIOR RESULTS AND DISCUSSIONS

Measurements were made on more than 40 coal particles. These particles were characterized as discussed above and then heated rapidly using a pulsed heating beam. Heating intensities were varied in the range from 200 to 1400 W/cm^2. In addition to changing intensities, heat pulse duration was varied from 2 to 10 ms. Property data and heating pulse information from selected particles are presented in Table 1. In the figures that follow temperature profiles from these particles are presented. These data are representative of the entire data set, which can be found in reference [4] and the discussion that follows generally applies to all of the particles in this study.

A systematic analysis was undertaken in this study in order to predict the devolatilization characteristics of single bituminous coal particles. Various model assumptions and their effect on the predicted temperature histories were critically considered. Finally, Equation 1 was arrived at as one way of modeling the temperature history of coal particles prior to and during devolatilization.

The model with the appropriate thermal properties, kinetics, and apparent heat of devolatilization was then applied and found to predict the temperature histories for a large number of coal particles prior to and during devolatilization over a range of laser intensities. The average agreement of the measured and calculated temperatures for all the coal particles tested in this study during the entire sequence of heating, devolatilization, and cooling was found to be within ± 66BK. This value was determined by statistical analysis for the worst case differences between the predicted temperatures and data.

TABLE 1. Particle Property and Heat Flux Measurements for Selected Experiments

Particle #	d_{sa} µm	d_v µm	d_L µm	$S_p/2A_L$	D g/cm^3	m µg	I_{ta} W/cm^2	heating time ms
12	88	81	85	2.1	1.29	0.36	577	10
16	103	98	106	1.9	1.16	0.57	941	10
30	109	102	111	1.9	1.08	0.60	1104	2
31	123	107	125	1.9	1.20	0.77	1092	3
32	130	124	132	1.9	1.03	1.03	1017	5
36	124	116	120	2.1	1.14	0.93	1340	10

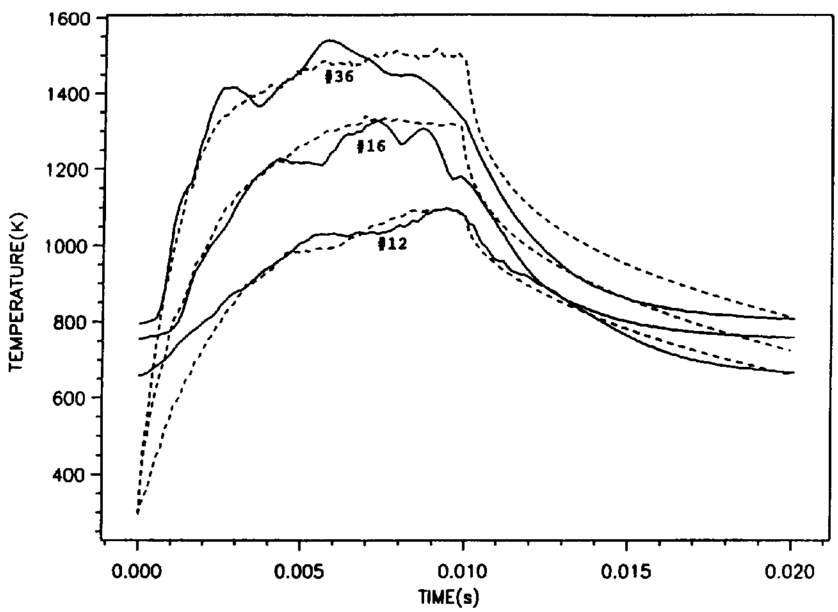

Figure 1. Comparison of Measured Temperature Histories with Model Projections for Several Coal Particles at Varying Heating Pulse Intensity: Solid line represents measurement; Dashed line represents model projection.

Figure 1 illustrates several comparisons between particle temperature measurements and model calculations. The temperature traces in this figure were selected to represent the range of heat flux conditions employed in this study. As illustrated, over the range of heat fluxes employed, temperature history calculations were in excellent agreement with the measured temperature profiles. Figure 2 illustrates some additional temperature history calculation and measurement comparisons. In this case, the three particles chosen were heated at similar flux levels but the heating pulse times were varied from 2 to 5 ms. These heating conditions were selected to provide test cases for the calculation approach. In these cases, the particles were heated rapidly and then the heating pulses were truncated at various stages of volatile evolution. As illustrated, in all three cases agreement between measurement and calculation was excellent. In the cases of particle 31 and 32 significant volatile evolution occurred during the cooling period after truncation of the heating pulse with excellent agreement between measurement and model.

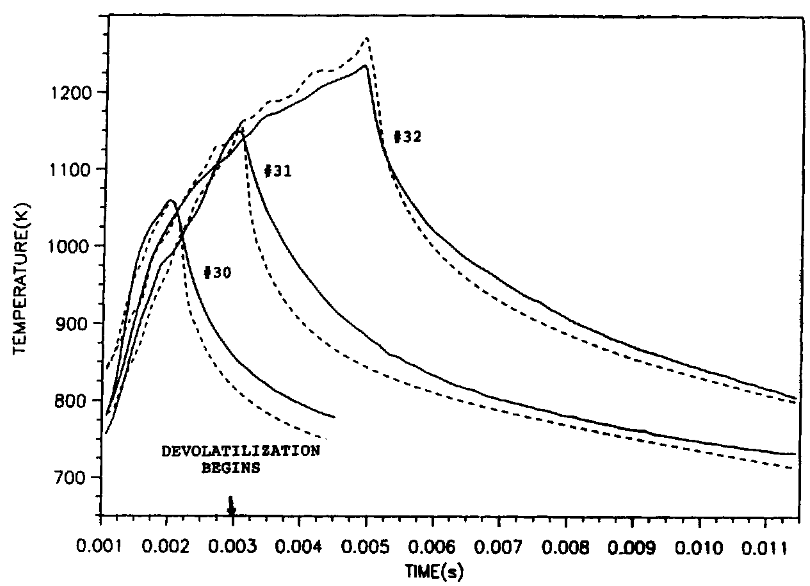

Figure 2. Comparison of Measured Temperature Histories with Projections for Several Coal Particles at Varying Heating Pulse Duration: Solid line represents measurement; Dashed line represents model projection.

WORK IN PROGRESS

Measurement of temperature histories for coal particles subjected to a range of heating rates employing the electrodynamic balance measurement system discussed above and a heated grid reactor [14-15] developed by United Technologies Research Center, our industrial collaborator in a related project, is in progress. Following the measurement, transport parameters tested above will be applied to predict the data. In the future, the numerical analysis presented here will be extended to predict species concentrations of the volatiles emanating from coal particles. This will provide reliable estimation of the evolution of NO_x precursors from coal particles subjected to rapid heating during combustion process and will lead to improved designs for low emissions of nitrogen oxides.

SUMMARY AND CONCLUSIONS

In most combustion models, either coal heat capacity is assumed constant or a temperature dependent heat capacity correlation such as the Merrick model is employed. In almost all cases devolatilization is considered to have no significant heat requirement. In the present study those approaches were found to yield significant errors when compared with actual temperature measurements.

The "stripping off" mechanism of volatiles from the parent coal was employed in this study as one physical mechanism to explain the coal devoalatilization process. While the liberating volatile mass from within the particle to the surface is allowed to consume most of the heat input by accounting for the enthalpy of the volatiles leaving the coal, the heat capacity of the parent coal in the analysis was assumed to remain at the room temperature value as long as raw material (volatile matter) for devolatilization was available. In addition to heating, this approach predicted well the cooling.

The significance of this work is the development of a detailed but simple model for bituminous coal particles which accounts for particle shape, high heating rate thermal properties, kinetics, and the heat of devolatilization. The model describes the nonisothermal, transient process of volatile evolution of a single coal particle. The model predicts well the fast temperature transients characteristic of a coal particle during the entire sequence of heating, devolatilization, and cooling. The predictions of the model reproduce the main trends of the coal devolatilization process noted in previous studies. Such a model would be useful for the more efficient design of advanced coal gasifiers, combustors, and liquefaction reactors.

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NOMENCLATURE

A	particle cross-sectional area (cm^2)
C	particle heat capacity (cal g^{-1} K^{-1})
E	activation energy (cal/gmol)
h	heat transfer coefficient at particle surface (cal s^{-1} cm^{-1} K^{-1})
I	intensity of the laser (W cm^{-2})
K	thermal conductivity of particle (cal s^{-1} cm^{-1} K^{-1})
m	particle mass (g)
R	particle radius (cm)
Ì	Ideal gas constant (1.987 cal/gmol BK)
r	radial position (cm)
S	surface area (cm^2)
T	particle temperature (K)
t	Time (s)

Greek Symbols

"	particle absorptivity at 1.06 µm wavelength
,	particle emissivity over the entire blackbody spectrum
F	Stefan-Boltzman constant (cal s^{-1} cm^{-2} K^{-4})
D	particle density (g cm^{-3})

Subscripts:

0	at time = 0
p	of the particle
pc	constant
r	to denote rate constant
S	at particle surface

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