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TECHNICAL PROGRESS REPORT

KINETICS OF COAL PYROLYSIS AND DEVOLATILIZATION

By

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Executive Summary

The effects of reaction process on the transient temperature history of a particle have been examined. The reaction process is found to significantly reduce the temperature gradient across a burning particle relative to a nonreactive particle. The pyrolysis process, on the other hand, does not severely affect the temperature history of a heating particle for the kinetic parameters employed. However, it is noted that the results are sensitive to variations in assumed kinetic parameters.

Devolatilization experiments have been performed on various size cuts of an HVA Bituminous coal in entrained flow and heated grid reactors. Final particle temperatures of 1073°K were achieved in a number of the experiments. Weight loss measurements were made in the entrained flow reactor (EFR) and tar yields and molecular weight distributions were measured for the heated grid reactor (HGR) experiments.

Ultimate weight loss yields in the EFR were observed to be relatively insensitive to particle size or heating conditions for final particle temperatures of 1073°K. The rate of weight loss varied significantly with heat transfer parameters--local gas composition around the particle and particle size. Low pressure tar yields and MWD's were also observed to be insensitive to particle size or heating rate in HGR devolatilization of the same coal. Similar to EFR weight loss, the rate of tar evolution varied significantly with particle size or rate of heating. The major fraction of tar formation is observed to occur at temperatures of 873°K or lower during the heating process.

The results imply the initial phase of the devolatilization of the HVA Bituminous coal is heat transfer controlled because the rate of tar formation and evolution is heat transfer controlled. The invariance in EFR ultimate weight loss and low pressure tar yields and characteristics with change in particle size can be explained by morphological considerations of the parent coal particles. The non-symmetric, irregular shapes of the coal particles result in an intraparticle mass distribution much nearer an interphase surface area than that of an equivalent sphere or cube.

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INTRODUCTION

The objective of these coordinated experimental and modeling studies is to develop an improved understanding of the kinetics of coal devolatilization which are relevant to suspension firing of powdered coal. These fundamental kinetic studies address several topics related to an improved understanding of pulverized coal combustion and includes both homogeneous and heterogeneous reactions. The principal topics include: (a) the pyrolysis and devolatilization of coal; and (b) the formation of char. Research activities include small-scale experimentation, interpretation of experimental results in terms of mechanistic understanding and the development and validation of kinetic models of fundamental processes.

SCOPE OF PROJECT

The experimental research is carried out in small, idealized reactor systems in which the effects of heat and mass transport are minimized or precisely known. Such experiments coupled with appropriate theoretical treatment allow reactor-independent kinetic rates to be extracted from observed behavior. It is generally accepted that to obtain useful kinetic data, the following experimental parameters must be known, estimated or be systemically varied:

- coal type including rank, geological province, and proximate and ultimate analyses
- amount and nature of mineral matter
- particle size and size distribution
- extent of particle dispersion
- reaction temperature
- heating rate
- ambient pressure
- ambient gas composition
- reaction time
- prior history of reactants

Because of the complexity of the phenomena involved in coal combustion, no single experimental technique can be expected to provide all of the required information. Therefore a broad range of experimental methods will be applied, each of which has its own strengths and weaknesses, but which taken together can provide the basis for comprehensive understanding of the overall processes. The qualitative and quantitative information derived from such careful experimentation can be used to develop hypotheses of behavior which can in turn be either validated or disproven. Inherent in this process is a methodology which closely couples experimentation with theoretical development and analytical modeling.

Because of the complexity of the fundamental chemical and physical processes involved in the pyrolysis and combustion of coal, identification of the dominant factors is difficult. However, quantification of these various factors is a principal objective of this research. Therefore careful and deliberate method of planning and executing the specific experiments and analyses employed is required and considered an integral part of the research effort.

The major tasks of this proposal can be summarized accordingly:

1. Improved engineering kinetics models will be developed at Ohio State for use in coal combustion calculations. The models will not be based solely on weight loss measurements but will include volatile product distribution and char properties and how these two are altered by temperature history.

2. An improved understanding of devolatilization and char formation will be obtained from a multi-reactor approach at three laboratories (i.e., United Technologies Research Center (UTRC), Penn State and Massachusetts Institute of Technology (MIT)). The data will be obtained by experienced workers in well-controlled experiments and special attention will be paid to the accuracy of temperature measurements, particle size determination and the interaction between these parameters.
3. Special efforts will be made to characterize the devolatilization products for a range of experimental conditions. The analysis will include not just the light gases but also the chemical composition of the tars and the reactivity of the chars. The chemical analysis of the tars will not attempt to measure every molecule but rather to determine molecular weight distribution, aromaticity, PAH size distribution, C/H, etc. The chars will be analyzed for elemental composition, particle size, BET surface area and pore size distribution, and intrinsic reactivity to air.
4. The results of the experimental work will be integrated into a fundamental model of devolatilization kinetics that will include heat and mass transport as well as chemical reactions. The model will also include consideration of secondary reactions of tars, and plastic behavior of coals.

TECHNICAL APPROACH

TASK 2.1: Engineering Kinetics of Coal Devolatilization (Ohio State U.)

Previous calculations demonstrated (DOE/PC/70768-4) the potential for significant differences in observable reaction rates which follow from large values in temperature within a particle during heating. Assuming a thermally neutral reaction process, the variations in rates observed would follow from variations in the conditions of heating and the magnitude of the rate constants for devolatilization relative to the characteristic rate of heating for a given environment. The calculations underlined the potential coupling among transport and chemical kinetic phenomena in determining observable rate parameters for the devolatilization process. The coupling would be quite close if the reaction time constants and thermodynamic properties are such that the reaction process affected the rate of particle heating. In this case, the temperature difference within a heating particle would, in part, be supported by the devolatilization process itself, rather than simply occurring with time constants comparable to the heating process. In short, the heat release or requirements of the reaction process provide an additional source or sink on the energy balance to the heating particle (see DOE/PC/70768-4, Equations 9-11, 14-16). Whereas the characteristic heating time constants were examined for non-reacting particles in a previous report (DOE/PC/70768-4), the effect of the reaction process is examined in more detail in what follows.

Effects of Combustion

The effects of combustion are illustrated in Figs. 1 to 4. In Fig. 1 the gas heating rate is almost instantaneous. The gas temperature has been set a little above the (minimum) ignition temperature. The T-t profile is then characteristic of a reactive particle under such conditions, with the temperature rising to a point of inflection a little above the gas temperature, and then jumping rapidly (the Thermal Explosion response.) This simulates, for example, the behavior believed to occur in the ignition experiments recently reported by Chen [1] and by Brooks [2].

In Fig. 1, the mean heating rate was about 10^4 deg/sec. Under these conditions, the values of ΔT were too small to show as separate lines on the T-t graph. The separation is seen in Fig. 2, however, at the higher heating rate produced by a higher gas (ambient temperature), although the gas temperature was also rising in a finite time instead of instantaneously. The final gas temperature was 1000°K (cf. Figs. 8,10,11 of DOE/PC/70768-4) with a characteristic time constant, T_g of 3 msec:

$$T_g - T_o = (T_m - T_o)(1 - \exp(-t/T_g))$$

There are some characteristic differences between Figs. 1 and 2. Because of the rising gas temperature, the particle temperature rise is almost linear up to the point of ignition. If ignition is defined as the point of inflection [1] this is impossible to detect by eye. The temperature jump is nevertheless clearly in evidence, and it shows that ignition occurs well below the gas temperature compared with the behavior illustrated in Fig. 1. Theoretically, the point of inflection (ignition temperature) is independent of heating rate.

Fig. 1 Temperature rise of a burning particle for maximum gas temperature of 800K and $r_0 = 500$ microns [$\tau_g = 3 \times 10^{-4}$ ms]

Fig. 2 Temperature rise of a burning particle for maximum gas temperature of 1500K and $r_0 = 50$ microns. [$\tau_g = 3$ ms]

Although the ΔT difference was too small to show on Fig. 1, there was a difference, and this is shown on Fig. 3. This can be compared with Fig. 5 of DOE/PC/70768-4 for the inert particle injected into gas at the same temperature (with the time scale running from right to left). Without reaction the maximum ΔT is 280 degrees compared with only about 10 degrees with reaction. The effect of the reaction process is clearly substantial. Figure 3 also shows the drop in ΔT to zero (which is just before the point of inflection), and then again a rapid jump (negative ΔT) after ignition as the center temperature rises rapidly above the surface temperature.

For the same particle conditions, Fig. 4 is the effective counterpart of Fig. 3 (DOE/PC/70768-4) for the variation of dT/dt with time, but using T as a stand-in for the time. The non-reacting case displays the heating rate falling to zero with increasing time; Fig. 4 shows it passing through a minimum, where the temperature at the minimum can be interpreted as the ignition temperature [1]. It should be emphasized that these results represent one set of combustion kinetic parameters.

Effect of Pyrolysis

The behavior of the pyrolysing particle is hardly distinguishable from that of the inert particle, except for the weight loss, for the kinetic parameters employed in these calculations. Figure 5 shows the variation of temperature with time (for a 100 micron particle; $T_g = 1000$). The separation of the surface and center temperatures is evident but the behavior is otherwise almost identical to the non-reacting particle. The heat of pyrolysis used was 100 kcal/kg.

The weight loss variation with time for the same conditions is illustrated in Fig. 6. There is no detectable weight loss for about 10 millisecond at which time the particle temperature is about 600°K. The weight loss then continues to rise, reaching about 10% at 800°K, taking 20 to 25 millisecond.

These calculations were made for the assumed "zero-order" pyrolysis reaction. It is anticipated that a first-order behavior will not significantly affect the onset of pyrolysis, but may strongly affect the last stages and thus the pyrolysis times.

Ignition

The pyrolysis behavior at or near the ignition point is of particular interest. Onset of significant pyrolysis at relatively low heating rates occurs at about 400°C for a bituminous coal. This temperature rises as heating rate increases. Recent measurements of ignition temperatures [1,2] yielded values in the range 300 to 450°C. This overlap of ignition and pyrolysis temperatures supports the possibility of heterogeneous ignition in some circumstances. This problem has not been explicitly addressed in this investigation, but some additional calculations to those described above were carried out to see how far it was possible to predict ignition temperatures from the combustion reactions, and to determine the sensitivity of the behavior to change in ambient conditions.

Fig. 3 ΔT as a function of time for a maximum gas temperature of 800K.

Fig. 4 dT/dt as a function of surface temperature for a maximum gas temperature of 800K and $r_0 = 50$ microns.

Fig. 5 Temperature response of a pyrolysing particle
for a maximum gas temperature of 1000K and
 $r_0 = 50$ microns.

Some of the curves obtained are illustrated in Figs. 1 to 4. These indicated some rapid changes in ΔT with time. Figure 3 showed that a high value of ΔT was initially established and this then fell monotonically to zero, and then became negative. At higher ambient temperatures (above ignition), the ΔT curve became double bumped, as shown in Fig. 7, so that the center initially lagged behind the surface, then caught up, and then the surface surged ahead again to a peak where the surface temperature exceeded ambient; the reaction in the center finally resulted in the rapid drop in ΔT which then rapidly became negative.

Figure 8 shows the corresponding T-t curves (on this scale the lines for the surface and center are indistinguishable; the maximum ΔT was about 20°). The ignition point (point of inflection) below the ambient gas temperature and subsequent temperature jump are clearly evident.

The ignition temperatures obtained in these calculations were 100 to 200 degrees higher than the measured values [1,2]. The adopted activation energy of 40 kcal was obtained and was close to that measured. The frequency factor used was obtained from studies of char combustion. If the material reacting is a solid hydrocarbon (unpyrolyzed coal) we could expect to have a higher frequency factor, as found experimentally. The calculated values using the higher frequency factor then bracket the experimental values. They would also then bracket the pyrolysis temperatures.

In the past, there has been some controversy regarding the ignition mechanism, whether it is homogeneous or heterogeneous. From the overlap in temperatures between heterogeneous ignition and pyrolysis it would seem very probable that the two processes are very strongly coupled. In particular, if ignition starts heterogeneously, the rapid jump in temperature at the center, at or following ignition could be responsible for onset of rapid pyrolysis, starting at the center; and the pyrolysis products would then flush the particles clear of oxygen to establish an "oil-drop" type of flame round the particle.

Discussion of Results

This analysis of a reacting coal particle on being heated by a gas in unsteady state conditions is intended to elucidate the pyrolysis behavior and mechanisms. The initial analysis of a non-reacting particle was done mainly to:

- (i) Test the numerical solution scheme.
- (ii) Estimate the heating rates, and the temperature differences between the center and the surface that can exist in the particle when it is heating up.
- (iii) Examine the variation of the maximum temperature difference with the heating rates and with the particle diameter.

Fig. 6 Weight loss (%) with time for $T_m = 1000K$ and $r_o = 50$ microns.

Fig. 7 ΔT as a function of time $r_0 = 50$ microns. [$T_m = 1500K$]

Fig. 8 Temperature response of a burning particle for $T_m = 1000\text{K}$ and $r_0 = 50$ microns.

(iv) Determine the variation of heating rates with the diameter of the particle.

(v) Calculate the heating times of the particles.

From the analysis of the non-reacting particle, it is concluded that the temperature differences between center and surface can be substantial. If these differences exist in a reacting particle, there may be an outer shell that is reacting much faster than the inner core. The temperature differences depend on the heating rates. For heating rates up to 10^{40} C/sec or more, the calculated temperature differences were as high as 700°C . At higher heating rates ($> 10^{50}$ C/sec) the non-uniform temperature distribution could have a significant effect on the overall reaction rates, provided the ΔT is maintained for a sufficient length of time.

The other point to be noted in this analysis is that the calculated heating rates varied over six orders of magnitude, from 10^0 C/sec to about 10^{70} C/sec, with the highest values at the start of the heat up. The question then is: How should we define the value of the average heating rate, and should it be based on the surface temperature or the center temperature? We have taken the "characteristic" heating rate to be the value when the maximum temperature difference exists; this value of heating rate was then found to be close to the average values determined by dividing the final temperature by the total heating time.

When the particle is burning, however, the above results are substantially modified. In general, the temperature differences (ΔT) were significantly reduced (see Fig. 3). In other results, when the surface was at a higher temperature, it ignited first. When the center reached the ignition temperature, the center temperature then rose faster than the surface and ΔT went to zero, and then went negative (Fig. 3).

For the burning particle, the temperature-time curve (Fig. 2) is sigmoid - the temperature rising steeply after a point of inflection. The classical Thermal Explosion Theory defines the temperature corresponding to the point of inflection as the ignition temperature. At these temperatures, the value of dT/dt is a minimum (see Fig. 4).

When the particle is pyrolyzing, its transient thermal behavior is similar to that of the non-reacting particle for the kinetic parameters employed in this examination and the conditions of heating examined. The T-t curve rises asymptotically to the gas temperature because the rate of heat absorption required to drive the reaction process described by the kinetic parameters is small compared to the rate of heat delivery in these heating conditions. Other investigators [3,4,5] have obtained different results depending on relative values of kinetic parameters and heating conditions. At the pyrolysis temperatures, the value of ΔT is about 10^0 C, which is not significant.

TASK 2.2 Fundamental Mechanisms and Kinetics of Volatile Formation and Evolution (M.I.T., U.T.R.C.)

and

TASK 2.3 Fundamental Mechanisms and Kinetics of Char Formation

Entrained Flow Reactor Investigation of PSOC 1451 (Pennsylvania State University)

Sample Characteristics

Devolatilization data has been obtained for PSOC 1451 samples size separated in this laboratory. Since ash tracer techniques are used in evaluating weight loss in this reactor, the ash content of the parent coal size fractions must be determined. Size segregated samples of PSOC 1451 produced at UTRC had shown that high temperature ash yields vary significantly with size fraction (DOE/PC/70768-3), generally decreasing with particle size determined by mesh separation. Similar results were observed in the Pennsylvania State U. size separated samples as noted in Tables I-IV.

Reactor Characterization

The reactor flow and temperature conditions are characterized by a computer model which is able to account for particle-gas velocity differences and estimated times required for a given particle size to reach terminal velocity in a given flow field. The computer code is written in modular form. Figures 9, 10 and 11 contain plots of dimensionless boundary layer thickness, average velocity and velocity at radial distance, respectively at reactor wall and gas temperatures matched at 1073°K. These plots are obtained from the gas velocity module of the computer transport model of the reactor.

TABLE I

PROXIMATE ANALYSIS FOR 60x70 MESH SIZE FRACTION
(230 Microns)

	<u>as det.</u>	<u>dry</u>	<u>d.a.f.</u>
moisture	1.73		
volatile	28.43	28.96	35.89
ash	18.99	19.32	
f. carbon	50.82	51.72	64.11

TABLE II

PROXIMATE ANALYSIS FOR 120x140 MESH SIZE FRACTION
(115 Micron)

	<u>as det.</u>	<u>dry</u>	<u>d.a.f.</u>
moisture	1.72		
volatile	30.11	30.64	34.82
ash	11.80	12.01	
f. carbon	56.37	57.35	65.18

TABLE III

PROXIMATE ANALYSIS FOR 170x200 MESH SIZE FRACTION
(81 Micron)

	<u>as det.</u>	<u>dry</u>	<u>d.a.f.</u>
moisture	1.59		
volatile	30.40	30.89	34.52
ash	10.34	10.51	
f. carbon	57.67	58.60	65.48

TABLE IV

PROXIMATE ANALYSIS FOR 200x230 MESH SIZE FRACTION
(69 Micron)

	<u>as det.</u>	<u>dry</u>	<u>d.a.f.</u>
moisture	1.67		
volatile	30.70	31.22	34.69
ash	9.83	9.99	
f. carbon	57.80	58.79	65.31

The particle velocity segment produces plots of particle residence time as a function of axial distance and particle size (Figure 12), and particle velocity/slip velocity as functions of residence time and particle size (Figure 13). The lines originating at the lower point in Figure 12 are particle velocity curves and those originating at the higher point are slip velocity curves.

The possible set of feeder and secondary gas combinations are: He/N₂, N₂/N₂, He/air, air/air and He/CO₂. In each combination, the first gas represents the particle entrainment gas and the second gas the main reactor flow. Thus, an He/N₂ combination would represent particle entrainment and feeding with He into a main flow of N₂.

DIMENSIONLESS BOUNDARY LAYER THICKNESS
FOR CARBON DIOXIDE AT 1073 K AS A FUNCTION
OF AXIAL DISTANCE

Figure 9

AVERAGE AXIAL GAS VELOCITY
FOR CARBON DIOXIDE AT 1073 K AS A FUNCTION
OF AXIAL DISTANCE

Figure 10

AXIAL GAS VELOCITY AS A FUNCTION OF RADIAL AND AXIAL DISTANCE FOR AIR AT 1073K

Radial Distance is dimensionless
R = 0.2, 0.4, 0.6, 0.7, 0.8, 0.9

Figure 11

PARTICLE RESIDENCE TIME IN AIR
AT 1073 K AS FUNCTION OF AXIAL DISTANCE
FOR 69,81,115, AND 230 MICRON DIAMETER
PSOC-1451 COAL

Figure 12

AXIAL PARTICLE VELOCITY AND SLIP VELOCITY
IN AIR AT 1073 K AS A FUNCTION OF RESIDENCE
TIME FOR 69,81,115, AND 230 MICRON DIAMETER
PSOC-1451 COAL

Figure 13

Weight Loss Data

Tables V, VI and VII contain particle weight loss data for 200x300 mesh, 170x200 mesh, and 120x140 mesh particles of PSOC 1451 devolatilized at reactor temperatures of 1073°K in the gas combinations listed.

TABLE V

PERCENT WEIGHT LOSS FOR 69 MICRON (200 x 230 mesh)
PARTICLES OF PSOC-1451 COAL AT 1073°K)

	<u>Axial Distance from Injector</u>			
Atmosphere	25 cm	40 cm	45 cm	55 cm
He/N ₂	59.6	72.6	69.8	59.8
N ₂ /N ₂	49.0	67.0	--	55.3
He/CO ₂	59.6	57.7	65.4	54.7
He/Air	72.2	64.3	--	66.7
Air/Air	78.8	60.4	--	74.5

TABLE VI

PERCENT WEIGHT LOSS FOR 81 MICRON (170 x 200 mesh)
PARTICLE OF PSOC-1451 COAL AT 1073°K

	<u>Axial Distance from Injector</u>		
Atmosphere	25 cm	40 cm	55 cm
He/N ₂	50.7	54.3	59.9
N ₂ /N ₂	39.7	46.5	50.0
He/CO ₂	47.5	52.6	52.4
He/Air	70.2	70.5	66.0
Air/Air	75.8	77.3	69.0

TABLE VII

PERCENT WEIGHT LOSS FOR 115 MICRON (120 x 140 mesh)
PARTICLES OF PSOC-1451 COAL AT 1073°K

	<u>Axial Distance from Injector</u>			
Atmosphere	25 cm	40 cm	45 cm	55 cm
He/N ₂	26.8	51.7	--	51.9
N ₂ /N ₂	19.7	46.6	--	48.8
He/CO ₂	47.8	54.1	--	53.0
He/Air	55.7	66.9	64.8	60.3
Air/Air	63.0	73.8	62.1	63.7

Plots of weight loss as a function of residence time are shown grouped by atmosphere in Figures 14-18 and grouped by particle size in Figures 19-21. Residence times as a function of axial distances are not included.

Tar samples, deposited on filter paper have been saved for most runs. These are to be analyzed - elemental composition, infrared absorption characteristics and molecular weight distributions. Char and ash samples are also being saved for subsequent elemental and infrared absorption analysis.

Figures 22-26 are photocopies of Polaroid micrographs of chars taken with a scanning electron microscope. Figure 22 shows a cenosphere produced in N₂/N₂ at a residence time of 202 msec. The cenosphere increased from a diameter of 80 μ m to one of about 140 μ m; or 1.75 times the original size. It is thought the ridges were produced during a fluid phase.

Figure 23 shows a cenosphere that was prepared in He/N₂ at a residence time of 266 msec. In this case, the particle experienced a 6.2 fold increase in diameter. A greater number of fluid ridges can be seen in this case when compared to the N₂/N₂ run (Figure 22). Large deposits, some up to 5.5 cm in height, sticking to the top of the collection probe provided further evidence that this coal passes through a fluid stage at a reactor temperature of 1073°K.

Figures 24 and 25 are photographs of coals run in He/Air. Figure 24 appears to be composed of two particles which were fused together. The char is 1.4 times the original size. The texture of the material at the edge of the holes is rougher than that for chars prepared in pyrolysis atmospheres. An "amorphous" piece of material is visible at the top of Figure 24; this is thought to be soot. Figure 25 is a photograph of a second particle; also believed to be soot, it is about 80 microns in diameter. Soot was formed in all runs where air was present. It was removed from the char by agitation in an air stream before proximate analysis of the char was performed.

WEIGHT LOSS IN He/N₂ AT 1073 K
FOR PSOC-1451 COAL

Figure 14

WEIGHT LOSS IN N₂/N₂ AT 1073 K
FOR PSOC-1451 COAL

Figure 15

Figure 16

WEIGHT LOSS IN He/AIR AT 1073 K
FOR PSOC-1451

Figure 17

WEIGHT LOSS IN AIR/AIR AT 1073 K
FOR PSOC-1451 COAL

Figure 18

Figure 19

WEIGHT LOSS FOR 81 MICRON PARTICLES OF
PSOC-1451 COAL AT 1073 K

Figure 20

WEIGHT LOSS FOR 115 MICRON PARTICLES OF
PSOC-1451 COAL AT 1073 K

Figure 21

Figure 22. Cenosphere Produced in N_2/N_2

Figure 23. Cenosphere Produced in He/N_2

Figure 24. Cenosphere Produced in He/Air

Figure 25. Soot Particle

Finally, Figure 26 shows a particle produced in He/CO₂. It can be seen that its diameter increased by 1.75 fold (from 115 μ m to 200 μ m). Interestingly, this potentially reactive atmosphere produced a texture quite similar to that in air.

Heated Grid Devolatilization (UTRC)

Heat Transfer Analysis of Heated Grid

Review of Previous Experimentation

Previous experiments and analysis (see DOE/PC/70768-4) determined the main mode of power dissipation from the heated grid in low ambient pressure and for grid temperature greater than 700°K is radiation loss. For temperatures less than 700°K, statistical analysis of the data indicates that electrode loss becomes a significant fraction of the total power dissipation. The pseudosteady state power dissipation is satisfactorily described by a fourth power dependence on absolute temperature of the grid over the entire range of hold temperatures, 500°K-1250°K. The self-consistency and accuracy of the measurements and analysis are checked by extracting from the data values for the specific heat, emissivity and resistivity of the type of stainless steel (304) and noting the variation in steady state power dissipation with number of grid layers for a given temperature.

To determine the effects of an ambient gas on power dissipation from the heated grid surface, a series of experiments and analyses are performed to quantify the heat loss through the solid-gas interface. Single and two-layer (one-fold) grid samples were investigated. The grids were "pre-fired" a number of times to the highest temperatures investigated to obtain constant emissivity properties before the pseudo-steady state runs were performed. Upon obtaining several repeatable temperature trajectories with the same programmed power input, a set of three conditions were chosen for each programmed power input: vacuum, 10⁻² torr; one atmosphere argon; one atmosphere helium.

Figures 27 and 28 display typical temperature-time trajectories obtained for single and double layer screens in the low pressure (a), one atmosphere argon (b), and one atmosphere of helium (c), respectively. Identical voltage programmed trajectories are imposed on the grids, the low pressure trajectory programs selected as the references. Figures 29a, b, and c display the temperature, voltage and current trajectories for a single layer grid heated to approximately a 780°C plateau temperature in low pressure. Figures 30a, b and c show analogous data for a double layer (one fold) grid heated to a plateau temperature of 810°C in low pressure. Figures 31a, b and c display temperature, voltage and current traces for a double layer screen heated to a plateau temperature of 400°C in low pressure. The current and voltage traces of Figures 30 and 31 are plotted to emphasize the current response characteristics of the grid as the presence of the ambient gas changes the temperature of the grid material during the hold portion of the programmed temperature trajectory.

Figure 26. Cenosphere Produced in He/CO₂

FIGURE 27

Temperature-Time Trajectories
Single Layer (N=1)

(a)
 $\sim 10^{-2}$ torr

(b)
760 torr Argon

(c)
760 torr Helium

FIGURE 28

Temperature-Time Trajectories
Double Layer (N=2)

(a)
 10^{-2} torr

(b)
760 torr Argon

(c)
760 torr Helium

SEC

FIGURE 29

Temperature, Voltage, Current Trajectories
 $N=1$, $T_{\text{plateau}} (10^{-2} \text{ torr}) = 780^\circ\text{C}$

(a)
Temperature

(b)
Programmed Voltage

(c)
Current

FIGURE 30

Temperature, Voltage, Current Trajectories

$N=2$, $T_{\text{plateau}} (10^{-2} \text{ torr}) = 810^{\circ}\text{C}$

(a)
Temperature

(b)
Programmed Voltage

(c)
Current

FIGURE 31
 Temperature, Voltage, Current Trajectories
 $N=2$, $T_{\text{plateau}} (10^{-2} \text{ torr}) = 410^{\circ}\text{C}$

The time-resolved data for both the single and double layer grids tested has the following characteristics:

- a) Relative to the low pressure conditions, the grids heated in helium and argon show a decrease in temperature with time. The temperature drop is more pronounced during times corresponding to vacuum hold temperatures but also is observed during the transient to plateau temperatures.
- b) The temperature drops are more pronounced in the presence of helium rather than argon. That is, there is a more rapid drop in temperature from the peak values observed and the magnitude of the drop is greater in helium than argon.
- c) The magnitude of the "fall-off" as a fraction of the peak temperature is inversely proportional to the peak temperature while the rate of "fall-off" is directly proportional to the magnitude of the peak temperatures.
- d) The temperature drop of the grid during a constant voltage cycle can be large enough to cause an observable increase in current through the grid (Figures 29c, 30c, 31c). Since the greater temperature drops are observed with helium, the greater current increases are observed for helium.

The effects of ambient gas on the power dissipation from grid systems can also be observed under pseudo-steady state conditions with respect to grid temperatures. As noted in the temperature plots above, the presence of an ambient gas introduces another mode of heat exchange of the grid with the reactor housing. The additional mode of power dissipation causes the grid surface temperature to decrease and asymptotically approach a lower pseudo-steady state temperature relative to the low pressure plateau temperature. By comparing the power requirements needed to maintain pseudo-steady temperatures in the presence of an ambient gas, relative to that required in low pressure conditions, the power dissipation due to the presence of an ambient gas can be estimated.

Figures 32a and b display the power loss/cm² of grid surface under pseudo-steady state conditions for the single layer (N=1) and double layer (N=2) cases. Figure 32c compares the surface area normalized power loss of the single layer and double layer cases. The following observations are appropriate relative to the time independent data displayed in Figures 32a, b and c.

- a) Power dissipation of either grid system (N=1 or N=2) is greater in the presence of helium than argon. Argon only slightly increases the power dissipation of the grid systems relative to a vacuum.
- b) The power dissipation curves are highly non-linear functions of the grid temperature over the range of temperatures from 700°K to 1200°K.

FIGURE 32
Pseudo-Steady State Power Losses

(a)
N = 1

(b)
N = 2

(c)
N = 1 vs. N = 2
760 torr Helium

- c) The functional form of the temperature dependence of the power dissipation is similar for the N=1 and N=2 cases, but the normalized magnitude of the power dissipation is greater for the N=1 case.

To estimate the helium component of the total power dissipation function, interpolated values from the low pressure power loss curves are subtracted from the high pressure data. For a given layer number, N, and at pseudo-steady conditions with respect to grid temperature:

$$\text{Total Loss} \Bigg|^{T_{HG}} = \text{Power Input} \Bigg|^{T_{HG}}_{I \times V} = \text{Power Loss} \Bigg|^{T_{HG}}_{\text{Radiation+ Electrode}} + \text{Power Loss} \Bigg|^{T_{HG}}_{\text{Solid-Gas Interface}} \dots (1)$$

$$\text{Vac Loss} \Bigg|^{T_{HG}} = \text{Power Input} \Bigg|^{T_{HG}}_{I \times V} = \text{Power Loss} \Bigg|^{T_{HG}}_{\text{Radiation+ Electrode}} \dots (2)$$

$$\text{He Component} \Bigg|^{T_{HG}} = \left(\text{Power Input Difference} \right) \Bigg|^{T_{HG}} = \text{Power Loss} \Bigg|^{T_{HG}}_{\text{Solid-Gas Interface}} \dots (3)$$

Figures 32a and b illustrate the results obtained for N=1 and N=2 grids. The "Total Loss" curves represent the total power dissipation at a given temperature, that is, the combined radiation, electrode and solid-gas power loss (Equation 1). The "Vac" curves represent the combined radiation and electrode losses (Equation 2). The "He (Diff)" plots represent the surface area normalized power loss attributed to the surface-to-gas transfer in the presence of helium (Equation 3). Similar plots are obtained for Argon, but the argon component of the total power dissipation is generally a factor of 5 to 8 lower than the corresponding helium effect, as is implied in Figures 32a and 32b.

Discussion of Heat Transfer Observations

The results indicate the close coupling among the heat transfer parameters associated with a particular grid environment, the programmed power input to the grid, and the intrinsic properties of the grid material itself. The observable temperature trajectory is the result of the interaction of these factors in determining the energy balance in time. The interaction is most readily apparent when the energy balance is presented in terms of power density normalized with respect to total strand surface area.

The magnitude of the components of power dissipation from a unit surface area of a heated grid depend on the nature of the ambient gas and the grid geometry. Multiple layers of grid material require less power input/surface area to maintain a given temperature than a single layer (see DOE/PC/70768-4 and Figures 32 and 33). In low pressure conditions, this has been interpreted as the result of a reduction in the average view factor of the screen material with fold number (DOE/PC/70768-4). In one atmosphere pressure of helium the reduction in power dissipation with folded screens is also primarily the result of a reduction in radiative loss per unit surface area. For temperatures below 700°K, the power dissipation due to screen-helium interface is a slightly greater fraction of the total power loss for N=2 than N=1, but for greater grid temperatures, the fractional contribution of the helium gas to total power loss is substantially the same for N=1 and N=2. For temperatures greater than 700°K, the helium contribution becomes a

decreasingly smaller component of the steady-state power dissipation. At 1000°K, the fractional power dissipation due to helium is ~0.40 of the total for N=1 and ~0.36 for N=2. Such a decrease in solid-gas contribution to the power dissipation with increasing grid temperature is to be expected since radiative loss has a T^4 dependence, whereas the solid-gas transfer has a T^1 dependence. The decreasing contribution of the solid-gas interface to the power dissipation with increase in T_{HG} is apparent in the diminishing fall-off in temperature as a fraction of peak value at the higher programmed temperatures (Fig. 30a and 31a).

The dependence of power dissipation on the nature of the ambient gas is apparent in both the time resolved data (Figures 26-30) and the pseudo-steady state observations (Figures 31 and 32). The gas motion between the ambient gas and grid is that established by natural convection. The convective currents established are low velocity and vectored away from the grid by the electrode bar under the length of the grid. The appropriate heat transfer analysis is essentially a flat plate analysis with natural convection. Such an analysis essentially leads to a solid-gas heat transfer rate which depends largely on the thermal conductivity of the surrounding gas and the first power difference in temperature between the solid and gas. Since the thermal conductivity of argon is ~10% that of helium, the power dissipation due to argon at a given grid temperature should be ~10 times less than helium. In short, argon is not expected to provide a substantial mode of power dissipation from the grid relative to radiative losses except at grid temperatures less than 600°K. This is in agreement with the time resolved and pseudo-steady state observations (see Figures 27-33).

A further check on this quantitative understanding of the mechanisms of power dissipation as a function of immediate grid environment can be made by selecting a gas having a thermal conductivity intermediate to that of helium and argon. N_2 has a thermal conductivity 40% greater than that of argon. For equivalent power input conditions in the grid, a N_2 environment should display a more rapid fall-off to a lower pseudo-steady state temperature than argon, but a much slower fall-off to a higher temperature than helium. Figure 34 displays time resolved data for a N=2 grid in low pressure, argon, nitrogen and helium environments. N_2 has the anticipated effect on the power dissipation properties of the grid relative to argon and helium.

The coupling among the heat transfer environment, power input and intrinsic properties of the screen in determining the observable temperature trajectories is most clearly illustrated by the time resolved data of Figures 30 and 31. The power dissipation properties of the various environments discussed above is apparent in the temperature trajectories of Figures 30a and 31a. The voltage programmable nature of the power input to the grid system is apparent in Figures 30b and 31b, which indicate the same voltage was impressed on the grids in each of the experiments. Figures 30c and 31c show the variation in delivered current as a function of time as the grid temperature changes due to the varying power dissipation properties of the gases present. The helium gas extracts more heat from the grid than argon, causing the grid to slightly cool. The grid cooling results in a lowering resistivity of the grid material (see DOE/PC/70768-4), which in turn causes an increase in current passage for a given voltage impression across the grid.

FIGURE 33
Power Dissipation Components

(a)
N = 1

(b)
N = 2

Summary and Implications with Respect to Coal Particle Heating

The modes of power dissipation from the grid material have been quantitatively characterized. A quantitative understanding of the heat transfer from the grid surface has been developed and the close coupling among heat transfer characteristics of the reactor system, power input mechanism into the grid and intrinsic properties of the stainless steel material in determining observable temperature trajectories has been established. The quantitative measurements and model developed have been checked for accuracy and consistency by extracting from the data accurate values for heat capacity, emissivity and resistivity ratios of the stainless steel material employed. Power dissipation observations made in the presence of various gases are qualitatively and quantitatively consistent with standard heat transfer analyses and reported thermal conductivity of the gases employed.

The measurement and semi-empirical model developed for the grid system permits a direct estimate of the heat transfer rate to coal particles placed between the folds of the grid. It appears possible that heats of reaction may be extracted from sample (coal) loaded data. Heat capacity information as a function of coal type may also be obtained. To obtain measurements of these two quantities: a) calibration runs must be performed with samples of appropriate particle size and known specific heat properties; b) close coupling between the grid temperature, as measured by the thermocouples, and the sample temperature should be established or a definitive method of relating the two must be demonstrated. Low pressure and ambient gas runs are now being performed with carbon fiber, anthracite, activated charcoal, silicon, alumina and quartz.

Heated Grid Devolatilization - Particle Size Effects: PSOC 1451

Char and Tar Yields

A series of experiments were performed in which particle size was varied while the programmed heating of the grid was kept constant. Low pressure conditions were established to minimize pronounced sample softening observed for this coal in pressure runs. (See also above discussion of softening in Pennsylvania State U. entrained flow reactor.) Such plastic behavior in the heated grid system tends to mask particle size effects by particle agglomeration and sample adhesion to screen strands. Low pressure minimizes softening behavior and was established since the purpose of these runs was to assess the importance of intraparticle heat and mass transport on tar yields and structure. Table VIII lists the yields obtained for the particle sizes and programmed heating conditions employed. Figure 35 displays typical temperature, voltage and current traces for the 2.5 sec hold time runs. Similar traces are obtained for the shorter hold time runs. All runs were performed with a helium gas jet quench of the screen-sample complex at the end of the programmed heating cycle.

FIGURE 34
Power Dissipation and Ambient Gas

Figure 35
Temperature, Voltage, Current Trajectories

TABLE VIII

Heated Grid Char and Tar Yields: Effect of Initial Particle Size Cuts

Coal: PSOC 1451

Ambient Pressure: $\sim 10^{-2}$ torr

Run I.D.	Particle Size Mesh Range	Heating Rate (C/sec)	Programmed Heating Conditions		% Sample		
			Plateau Temperature (C)	Hold Time (sec)	% Char	% Tar	
216	-270+325 (49 microns)	1000	800	2.5	52.6	24.4	
217	-270+325	1000	800	2.5	54.6	24.8	
218	-270+325	1000	800	2.5	55.3	30.3	
245	-100+140 (127 microns)	1000	800	2.5	54.0	28.4	
246	- 50+ 70 (250 microns)	1000	800	2.5	58.0	25.1	
247	- 20+ 25	1000	800	2.5	72.1	23.3	
248	- 20+ 25	1000	800	2.5	68.2	24.7	
255	-100+140	1000	800	0	81.4	13.2	
256	-100+140	1000	800	0.5	61.2	20.4	
257	-100+140	1000	800	1.0	63.1	31.8	
258	-100+140	1000	700	0	94.5	4.0	
259	-100+140	1000	700	0.5	77.7	18.8	
249	-20 + 25 (774 microns)	1000	800	0	98.6	--	
250	-20 + 25	1000	800	0.5	98.2	--	
252	-20 + 25	1000	800	1.0	97.5	0.4	
254	-20 + 25	1000	800	1.5	92.5	2.0	
253	-20 + 25	1000	800	2.0	71.4	24.3	
251	-20 + 25	1000	800	2.0	65.1	32.3	

The results indicate no measurable dependence of tar yield on particle size as determined by mesh range in these moderate heating rate conditions. There is a notable difference in response time of the tar evolution process as indicated by the results for varying hold times for the -100+140 and -20+25 mesh cuts. The variation in tar evolution response time with particle size is related to the variation in heating rate of the different size particles within the folded screen in low pressure conditions. As noted above and in previous reports (DOE/PC/70768-4), the main means of heat transfer from the screen in low pressure conditions is radiation, assuming screen-coal contact heating is small due to poor area contact. The screens are programmed to generate the same blank screen temperature rise and temperature hold. Screen to screen emissivity properties do not vary significantly since all screens were given the same pretreatment process. As a result, each sample was subjected to the same radiant flux heating conditions in time. Differences in sample response time result from differences in particle size characteristics of the samples. Given a time-dependent radiant flux density ($\dot{Q}(t)$), such as is generated by the heating grid, the instantaneous time rise in a particle of diameter D is:

$$(4) \quad \dot{T}(t) = \frac{\dot{Q}(t) \cdot \alpha_p F_{ps} \cdot S_D}{\rho c V_D}$$

where S_D and V_D are the particle surface area and volume respectively. $\dot{Q}(t)$ is the instantaneous radiant flux density (w/m^2) to the particle surface; α_p the particle absorptivity of the radiation; F_{ps} the particle screen view factor. Assuming spherical particles:

$$(5) \quad \dot{T}(t) = \frac{k \dot{Q}(t)}{D}, \text{ where } k = \frac{\alpha_p F_{ps}}{\rho c}$$

or

$$(6) \quad \dot{T}(t) = k \cdot \frac{\dot{Q}(t)}{D} = \frac{F(t)}{D}$$

For two different particle sizes in the same radiant heating conditions:

$$\frac{\dot{T}_2(t)}{\dot{T}_1(t)} = \frac{D_1}{D_2}, \text{ where the same radiant flux density is delivered in time to the particles}$$

In such a heating system, the time dependent particle temperature response is inversely related to particle diameter, given identical radiation density environments. Not enough data is available to do a complete diameter dependence analysis, but the data reveals the substantial variation in tar evolution response with particle size given the same heat transfer conditions. For example, the tar evolution of the -100+140 mesh sample is essentially complete in a little over 0.5 sec interval of the transient heating cycle, whereas the -20+25 mesh particles require 2.0+ sec of the heating cycle.

Assuming the particles had to achieve similar temperatures to evolve the same quantity of tar, the ratio of response times is ~ 4 . The particle mesh diameter ratio is ~ 6 . The tar evolution response and particle heating rate response show similar inverse particle size dependence. A more detailed study is to be performed upon reception of the D.O.E. size classified particles. It should be noted that a similar analysis would be appropriate for non-spherical particles in such a low pressure radiant heating system. However, absolute temperature response times of non-spherical particles would be different than equivalent spherical diameter particles, because of variations in the S/V ratio terms of Equation (4).

Molecular Weight Distribution (MWD's) of Tar Yields

Discussion of Results

The data indicate asymptotic tar yields and molecular weight distributions of the tar yield do not vary with particle size characteristics, as determined by mesh range. In conditions where interphase mass transfer is minimized, tar yields and molecular weight characteristics are independent of particle size. Tar evolution times vary appreciably with particle diameter, displaying an inverse dependence on particle size for equivalent power density inputs. Heat transfer investigations of the heated grid indicate the temperature response of particles in the grid would follow an inverse particle diameter dependence. The results indicate the rate of tar evolution is heat transfer limited, but that tar yields and characteristics, in conditions wherein interphase mass transfer is minimized, are not measurably affected by intraphase secondary reactions.

These results agree with those reported in the Report DOE/PC/70768-4, wherein it was observed that varying the average heating rate of -270+325 mesh particles between 100°C and 800°C did not appreciably affect asymptotic tar yields or molecular weight distributions. In those investigations, the heating rate was externally imposed on the sample by varying the temperature trajectory of the grid around the sample. In these investigations, the heating rate was determined by the particle size characteristics of the sample in relation to a constant grid heating pattern. In both cases, interphase mass transfer resistance was minimized by performing the experiments in low pressure conditions. Runs performed in which -270+325 mesh samples (DOE/PC/70768-4) were held at 600°C for 10 seconds under low pressure conditions indicate 90% of the asymptotic yield can be generated at particle temperatures of 600°C or lower. Again, the MWD of these tar yields does not vary appreciably from that generated by heating to 800°C and holding for shorter times.

The results imply that under these heating conditions and for this coal type the tar formation and evolution process follows a preferred reaction pathway to an asymptotic tar yield and molecular distribution. Variations in particle temperature trajectories created by changing the immediate external heat transfer environment or the particle size within a constant environment vary the rate of tar evolution but not the potential tar yield or molecular weight characteristics. For an HVA Bituminous coal, devolatilized in low pressure conditions, the tar evolution reaction pathway is invariant with

heating rate or particle size. The rate of tar evolution varies with rate of heating but the asymptotic yield and MWD properties do not. The major fraction of tar species is formed at particle temperatures of 600°C or lower. Intraphase mass transfer resistance has little effect on tar yields or composition.

MWD's of Tar Yields

Molecular weight distributions of tars obtained from the devolatilization of four particle size cuts of PSOC 1451 in the heated grid reactor were determined by SEC. The MWD's (Fig. 36 and Table IX) are observed to have little variation over a wide range of particle sizes. One might expect that the increasing resistance to mass transport with increasing particle size would lead to lower MWD's due to the longer time available for the conversion of tars to light gases and non-volatiles by cracking and condensation/polymerization reactions, respectively. Increasing particle diameter also results in lower surface heating rates and therefore lower particle heating rates. The time-temperature history during volatiles formation and transport through the particle and boundary layer is of longer duration and lower temperature for larger particle size. It is possible that the decrease in transport path with decrease in particle size compensates for the increase in average particle temperature environment experienced by the tars as they escape, relative to the longer transport path and lower temperature conditions in the larger particles. However, previous experiments (DOE/PC/70768-4) revealed substantial changes in heating rate for a given particle size revealed little change in tar yields or MWD's for this same coal PSOC 1451. The net result observed being similar tar yields with very similar MWD's.

TABLE IX

MOLECULAR WEIGHT DISTRIBUTIONS OF TARS

<u>Mesh</u>	<u>Nominal Diameter (m)</u>	<u>Mn</u>	<u>Mw</u>	<u>Mz</u>	<u>Exp.</u>	<u>% Tar</u>
-270/+325	48.5	664	1429	2619	221C	21.24
-100/+140	127.0	492	1152	1846	245A	28.4
- 50/+ 70	253.5	618	1217	1960	246A	25.1
- 20/+ 25	774.0	545	1226	2017	247A	23.3

Particle Shape Effects

The insensitivity of tar yields and composition to particle mesh size is, at first thought, surprising. Such results indicate that intraparticle secondary reactions of tars do not vary significantly with particle size as determined by mesh range. Since "primary" tars are known to rapidly undergo gas phase secondary reactions, the results imply intraparticle residence times

Fig.36 EFFECT OF PARTICLE SIZE ON TAR MWD - PSOC 1451

Heated Grid Conditions:

1000°C/s to 800°C, 2.5 sec. hold

Vacuum

He quench

of primary tars do not vary significantly with mesh determined particle size. One explanation lies in a consideration of the distribution of mass in particles which are not identically symmetric with respect to all three axes.

The fractional distribution of parent particle mass in particular have three identical axes of symmetry and as a function of penetration fraction, $f = (d_o - d_i) / d_o$ from the particle surface is:

$$d_o$$

$$\eta = 1 - (1-f)^3$$

where η is $\frac{M_o - M_i}{M_o}$ and $f = \frac{d_o - d_i}{d_o}$.

M_o is the mass of the parent particle of spherical diameter or cubic edge length, d_o .

M_i is the mass contained in an inner volume of diameter or edge length, d_i .

η then represents the mass fraction from d_i to the particle surface.

For a sphere or cube 90% of the parent particle mass resides in a penetration fraction of 0.5 and 50% in a penetration fraction of ~0.2. Coal particles are highly irregular in shape, having pronounced aspect ratios (see Figure 37). Such "irregularity", as described by aspect ratios, significantly changes the mass distribution as a function of penetration fraction.

A less regular particle geometry can serve to illustrate the distribution pattern. Consider a rectangular parallelepiped of length l_o , width w_o , and thickness h_o and where $l_o = \alpha w_o = \beta h_o$. α and β are thought of as aspect ratios

with respect to the major dimension l_o . The penetration fraction is defined relative to the major length l_o :

$$f = \frac{l_o - l_i}{l_o}$$

where l_i is the length of an inner rectangular parallelepiped arrived at by penetrating the surface a distance $l_o - l_i$. In terms of aspect ratios, the particle volume becomes:

$$V_o = \frac{l_o^3}{\alpha\beta}$$

The inner volume is:

$$V_i = \frac{l_o^3}{\alpha\beta} \cdot \left\{ (1-f)(1-\alpha f)(1-\beta f) \right\}$$

where it is assumed equal penetration in each of the three principal

X 100

Fig. 37 Coal Particles, -270+325 mesh.
Note: Translucent particles are mineral particles.

directions. The mass fraction contained in the penetration fraction f is:

$$\eta = \frac{V_o - V_i}{V_o} = 1 - \left\{ [(1-f)(1-\alpha f)(1-\beta f)] \right\}$$

Limiting values of f are established corresponding to $\eta = 1$:

$$f = 1$$

$$f = 1/\alpha = \frac{w_o}{l_o}$$

$$f = \frac{1}{\beta} = \frac{h_o}{l_o}$$

Assuming equal penetration steps from each direction, η will reach the value of 1 when f achieves the smallest of the three values. If $\alpha = 2$, and $\beta = 4$, a not unlikely set of aspect ratios for coal particles approximated as rectangular parallelepipeds, then 100% of the particle mass is within a penetration fraction of 0.25 from the surface. For a sphere or cube only 50% of the particle mass is at a penetration fraction of 0.25. Similar, but more complex, relationships can be derived for particles having greater degrees of irregularity. η for a solid trapezoid is:

$$\eta = 1 - \left\{ \frac{(\alpha(1-2f)+1)(1-\beta f)(1-\tau f)}{\alpha+1} \right\}$$

where $\alpha = b_o/b_1$, $\beta = b_o/c$, $\tau = b_o/h$ and $f = (b_o - b_1)/b_o$.

b_o , b_1 , c , and h are the trapezoidal bases, height and thickness, respectively. Again, the aspect ratios, irregularity aspects of the particle, relative to the sphere and cube, dramatically change the distribution of particle mass relative to a surface plane.

The observation that primary tar yields and characteristics do not change significantly with particle size as denoted by mesh range can be understood on the basis of the irregularity of coal particle shapes relative to spheres or cubes. The irregularity of the coal particles, relative to standard spheres or cubes, results in a greater fraction of particle mass near a surface site. For example, a penetration path of 100 μm in a set of rectangular parallelepiped particles with aspect ratios 2 and 4, relative to the longest length, would encompass 100% of the potential tar mass for particles 400 μm and below, 91% of 500 μm particles and 74% of 700 μm particles. Thus, although particle heating rates would vary in a given heat transfer field ($\dot{T} \propto \frac{S}{V}$) intraparticle diffusion paths of the greater fraction of particle mass would not change appreciably.

References

1. Ming-ru Chen, Liang-shih Fan, and Essenhigh, R.H., "Prediction and Measurement of Ignition Temperatures of Coal Particles," Twentieth Symposium (International) on Combustion, The Combustion Institute, 1984, pp. 1513-1521.
2. Brooks, P.J. and Essenhigh, R.H., "Variation of Ignition Temperatures of Fuel Particles in Vitiated Oxygen Atmospheres: Determination of Reaction Mechanism," submitted for: Joint Technical Meeting, Central/Western States Section, The Combustion Institute, San Antonio, Texas, April 1985.
3. Freihaut, J.D. and Vastola, F.J., "A Numerical and Experimental Investigation of Rapid Coal Pyrolysis," Coal Research Section, The Pennsylvania State University, University Park, Pennsylvania.
4. Guin, J.A., Tarrer, A.R. and Tagler, Z.L., "Solvent Refined Coal Studies," (NSF 38701), Chem. Eng. Dept., Auburn U. (1975).
5. Mills, A.F., James, R.K. and Antoniuk, D., Lett. Heat Mass Transport 3, No. 1, 1-12 (1976).

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