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TECHNICAL PROGRESS REPORT

KINETICS OF COAL PYROLYSIS AND DEVOLATILIZATION

By

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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.)

Introduction

The objective of this project is to develop engineering equations for coal pyrolysis kinetics. Three problems have been identified, in attempting to synthesize literature results into a tractable scheme:

1. There are wide differences in reported values of pyrolysis rate constants and activation energies.
2. There are differences in the proposed pyrolysis models.
3. The models lack a mechanistic basis.

A contributing factor to reported variations in kinetic parameters of devolatilization could be non-uniform temperature distributions within particles during devolatilization. When reactions have activation energies in the region of 40 kcal/mole and reactant temperatures are about 500K, the reaction rate nearly doubles for a 10°C rise in temperature. A temperature difference between the center and surface of a particle would produce correspondingly varying pyrolysis rates across the particle.

Rough estimations of surface-to-center temperatures have not generally shown significant differences, leading to a lack of detailed considerations. The temperature difference across a heating particle is strongly influenced by the rate of heating of the particle surface. For a given thermal conductivity of the particle material, there will always be a (low) rate of heating at which the temperature difference is negligible for any given particle. Conversely, high surface heating rates may result in significant temperature differences. As noted below, it would appear that the transition between such low and high heating rate effects occurs at surface heating rates of approximately 10^{40}C/sec . Since a large number of investigations have been carried out at heating rates less than this, estimates generally showed negligible intra-particle temperature differences, although few distributed, variable transient calculations have been performed. A closer heat transport analysis is now appropriate because: 1) the heating rates are being increased in many experiments; and, 2) an average surface heating rate of 10^{40}C/sec implies initial surface heating rates near the pyrolysis temperatures can be two or three orders of magnitude greater. The intraparticle temperature differences can thus be substantial--in the region of 100°C --at such high surface heating rates, resulting in non-uniform intraparticle pyrolysis rates.

Physical Model

To assess the sensitivity of a particle response to heating conditions, a simple model is considered.

In the simplest case, a particle is dropped into a heated gas and the subsequent temperature history of the particle is calculated under a condition of transient heat transfer. Both the particle interior and the thermal boundary layer in the gas are considered. Of concern is the temperature differences (ΔT) between the particle surface and its center.

This is not a new problem. However, even in the classic analysis in Carslaw and Jaeger [1] it was assumed that the thermal boundary layer was established (quasi-steady approximation) and the unsteady state behavior was confined to the particle. This is a partial unsteady state situation.

In later work, the full unsteady state problem has been solved (numerically); for example, by Freihaut [2]. Details of the computations are not, however, generally available. This lack is part of the incentive for providing some degree of detail here.

In other analyses, a common assumption has been that the ambient gas temperature was constant, equivalent to dropping the coal particle into the center of a flame. In actuality, coal particles in a jet are mainly heated by conduction from entrained hot gases with the temperature profile of the ambient gas governed by turbulent exchange between the cold incoming jet and the hot entrained gases. The temperature rise of the edge of the jet will be faster than that of the core. Detailed calculation of the profiles is highly complex, but for the purpose of establishing the pattern of influence on the coal particles, such behavior is approximated in these calculations by writing

$$(T_g - T_o) = (T_m - T_o)[1 - \exp(-t/\tau_g)] \quad (1)$$

where τ_g is a characteristic time for the gas temperature (T_g) to heat from ambient^g at T_o to a maximum at T_m . Such a characteristic time^g reflects local mixing^o conditions and assumes the particle trajectory follows the local gas volume in which it is entrained. T_m can, if necessary, be interpreted as the "flame" temperature. For the extreme condition where τ_g is very small (0.1 msec) the rise time to T_m is less than 1 msec, and it is equivalent to the gas temperature being constant.

For different maximum gas temperatures and heating curves (different τ_g in Eq. 1) the behavior of a particle was examined for three different cases:

- (a) a non-reacting particle
- (b) a particle with combustion
- (c) a particle with pyrolysis

Mathematical Model

The heat transfer to a particle dropped into a hot gas is mainly across a gaseous boundary layer through conduction. The analysis takes into account the unsteady state heating of the particle, that is, intraparticle heat transfer, and the growth of the thermal boundary layer around it.

Non-reacting particle

For a non-reacting particle which just heats up when dropped into a hot gas, the equations in the two regions -- inside the particle and in the gas -- are identical in form, and differing only in the constant coefficients. The equations in the two regions are written as

$$(1/\alpha_g)(\partial T_g/\partial t) = [\partial(r^2 \partial T_g/\partial r)/\partial r]/r^2 \quad (2)$$

where: the subscript $g = p$ inside the particle (for $r < r_0$); and $g = a$ in the gas phase ($r > r_0$).

The two equations are coupled at the particle surface by the conditions

$$\lambda_p \partial T_p/\partial r = \lambda_a \partial T_a/\partial r \quad (3)$$

and

$$T_p = T_a$$

the other boundary conditions being

$$\partial T_p/\partial r = 0 \quad \text{at } r = 0 \quad (4)$$

and

$$T_a = T_{\text{gas}} \quad \text{at } r = \infty$$

In practice, calculation showed that $r = \infty$ was well approximated by taking the limit at $r = 100r_0$.

Defining the dimensionless groups

$$\theta = (T - T_g)/(T_0 - T_g) \quad (5.1)$$

$$\tau = (\alpha_p/r_0^2)t \quad (5.2)$$

$$\eta = r/r_0 \quad (5.3)$$

the non-dimensional forms of the equations can be written as

$$R_c \partial \theta/\partial \tau = (1/\eta^2) \partial[\eta^2 \partial \theta/\partial \eta]/\partial \eta \quad (6)$$

where: $R_c = 1$ for $r < r_0$; and $R_c = \alpha_p/\alpha_a$ for $r > r_0$.

The initial conditions become:

for $0 < \eta < 1$, $\theta = 1$ at $\tau = 0$

for $1 < \eta < \infty$, $\theta = 0$ at $\tau = 0$

and the boundary conditions are

at $\eta = 0$, $\partial\theta/\partial\eta = 0$

at $\eta = \infty$, $\theta = 0$

For the transformation into finite difference forms we use

$$\partial\theta/\partial\tau = (\theta_1^{n+1} - \theta_1^n)/\Delta\tau \quad (7)$$

and

$$\partial(\eta^2 \partial\theta/\partial\eta)/\partial\eta = [\eta_{1+1/2}^2 \theta_{i+1} - (\eta_{i-1/2}^2 + \eta_{i+1/2}^2) \theta_i + \eta_{i-1/2}^2 \theta_{i-1}]/\Delta\eta^2 \quad (8)$$

where subscripts $i-1$, i , $i+1$ denote the three consecutive grid points on the radial coordinate and superscripts n , $n+1$ denote the two consecutive time intervals.

The equations are formulated in an implicit scheme as described in the Appendix.

Reacting particle: Combustion Reaction

For simplicity in these initial comparisons to a non-reacting case, the combustion reaction is assumed to be a one-step, zero-order reaction. As such, it implies that the oxygen is present uniformly throughout the particle. The reaction rate per unit surface area is written as

$$R_s = k_{od} e^{-E_d/RT}$$

so that, for an internal surface of area S_v /unit volume, the heat released per unit volume would be

$$H_v = S_v k_{od} e^{-E_d/RT} (\Delta H) \quad (9)$$

where (ΔH) is the heat of reaction for unit mass of fuel. The heat transfer equations are then written as

$$(1/\alpha_s) \partial T_s / \partial t = (1/r^2) \partial [r^2 \partial T_s / \partial r] / \partial r + (H_v / \lambda_p) \delta \quad (10)$$

where, as before (see Eq. 2) $s = p$ for $r < r_0$ and $s = a$ for $r > r_0$; and in addition $\delta = 1$ for $r < r_0$ and $\delta = 0$ for $r > r_0$.

The boundary conditions and the coupling conditions on the particle surface remain the same as for the non-reacting particle (Eqs. 3 and 4). Defining

$$\theta_c = RT/Ed \quad (11)$$

and

$$C_c = [(s_v k_{od} \Delta H r_0^2)/\lambda p](R/Ed)$$

In non-dimensional form, the equations become,

$$R_c \partial \theta_c / \partial \tau = (1/\eta^2) \partial [\eta^2 \partial \theta_c / \partial \eta] / \partial \eta - C_c \exp(-1/\theta_c) \delta \quad (12)$$

where R_c and δ are defined as before.

For numerical solution, the difference equations are

$$-\eta_{i-1/2}^2 \theta_{i-1}^{n+1} / \Delta \eta^2 + [R_c \eta_i^2 / \Delta \tau + (\eta_{i+1/2}^2 + \eta_{i-1/2}^2) / \Delta \eta^2] \theta_i^{n+1} \quad (13)$$

$$-\eta_{i+1/2}^2 \theta_{i+1}^{n+1} / \Delta \eta^2 = \delta C_c \eta_i^2 \exp(-1/\theta_i^n) + \eta_i^2 R_c \theta_i^n / \Delta \tau$$

The difference equations are modified at the boundaries ($r = 0$ and $r = \infty$), and at the surface of the particle ($r = r_0$), to take into account the conditions existing there.

Pyrolyzing Particle

Pyrolysis is assumed to be a one-step, first-order volumetric reaction. For initial computations where we are interested in the temperature at which significant pyrolysis sets in, the rate is introduced as an n th order reaction so that we can take $n = 0$ in the preliminary calculations, and $n = 1$ for later calculations.

The rate is then expressed as

$$R_v = k_{op} (1 - VM/VM_0)^n \exp(-E_p/RT) \quad (14)$$

If (ΔH) is the heat of the pyrolysis reaction, then the heat released/consumed per unit volume is

$$H_p = R_v \cdot \Delta H_p \quad (15)$$

The sign of (ΔH) is in agreement with the convention that it is negative for an exothermic reaction and positive for an endothermic reaction.

The heat transfer equations are then identical to Eqs. 12 and 13 in the dimensionless and finite difference forms respectively, with only a change of definition for the constant C_c which now must be written as

$$C_c = C_d = [k_{op} \Delta H_p r_o^2 / \lambda_p] (R/E_p) \quad (16)$$

Weight Loss

In a thin spherical shell, dr , of radius r , the mass reduction due to pyrolysis is

$$dm_t = 4\pi r^2 R_v dr$$

and the mass reduction in the whole particle at any instant of time is

$$m_t = \int_0^{r_o} 4\pi r^2 R_v dr$$

The cumulative mass loss in a time period, t , is

$$M_t = \int_0^t m_t dt$$

For numerical evaluation, this is written

$$M_t = \sum_{i=0}^n m_{ti} \Delta t$$

Results

Characteristic Particle Responses. Figure 1 is a typical temperature profile as T varies with radius from the center of the particle out through the gas phase to infinity. This is for a 100 micron particle, without reaction, plunged into gas at 1500K. It illustrates what is to be expected, which is that the center of the particle is at a lower temperature than the surface. As will be shown below, this order is inverted with combustion reaction.

As the particle heats up, the surface temperature initially rises very rapidly in comparison with the center. This is clearly illustrated in Fig. 2. There is a time delay before the heat flows to the particle center and, in that time, the value of T is increasing rapidly with a maximum value in this example of nearly 700°C in 0.1 msec after the start of heating.

In this example, the particle temperature rose 1200° in about 6 msec for an average heating rate of 2×10^{50} /sec. The instantaneous rates, however, were initially substantially faster. This is shown in Fig. 3, which gives the variation of instantaneous heating rate with time for the surface. As can be seen, the initial rates are nearly 10^{80} /sec, and falling to 10^{30} /sec as the temperature levels off. The heating rates at the center are initially near zero, but they are then comparable to the surface as the center heats up.

FIGURE 1

Temperature distribution in the particle and in the air at any instant of time.

FIGURE 2

ΔT as a function of dT/dt for $T_g = 1500\text{K}$ and $r_o = 25$ microns.

FIGURE 3

ΔT as a function of dT/dt for $T_g = 1500\text{K}$ and $r_0 = 5$ microns.

Such drastic differences in temperature are not necessarily reflected by similar differences in local rates of mass loss as the duration of the period of high ΔT is often so short that there is no time for significant reaction. This is not always the case, however, and it is the conditions when the duration is long enough that we are concerned about in this study.

Variation of ΔT with Heating Rate for the Non-Reacting Particle

Because of the evident importance of heating rate, that is, heat transfer conditions, the effect this has on the temperature difference between surface and center has been given particular attention. A set of results is illustrated in Figs. 4 to 11. These graphs are plots of ΔT against heating rate. Since heating rate falls with increasing time (see Fig. 3), the time scale runs in the "-x" direction (i.e. $t = 0$ at the highest value of dT/dt).

All the graphs have the same form; they differ substantially in the numerical values of ΔT obtained for the different ambient conditions. In all cases, ΔT rises from zero at $t = 0$, through a maximum, and then declines to zero again as $dT/dt \approx 0$ (and $t \rightarrow \infty$).

Figures 4 to 9 are for the same particle size (100 microns) at gas temperatures of: 500K, 800K, 1000K, 1200K, 1500K, and 2000K. Figures 10 and 11 are for 10 microns and 50 microns at gas temperatures of 1500K. For the first set (Figs. 4 to 9) the evident characteristic is the increase in T , from a lowest value of about 100 degrees to a highest value of nearly 1000 degrees. The rate of heating at the maximum also increases, from about 10^{50} /sec at the lowest gas temperature, to about 10^{80} /sec at the highest.

The effect of particle size at the same gas temperature (Figs. 8, 10, and 11) is to increase the heating rate at the maximum ΔT (up to nearly 10^{80} /sec in Fig. 10), while the maximum ΔT remains unchanged.

These results show the potential for drastic differences in reaction rate because of large values of ΔT . Whether the potential is realized then depends on the values of the rate constants, since the duration of the large ΔT is typically quite short (millisec to 10's of millisec). In addition, the ΔT values can be drastically affected by the reaction process itself. Subsequent analyses will deal with the reacting particle cases.

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

Heat Transfer Analysis of Heated Grid Reactor

It is well established that observable coal devolatilization/pyrolysis behavior varies significantly with conditions of heating (3). One of the primary objectives of this program is to determine the relative effects of heat transfer, mass transfer and varying chemical characteristics of coal on the devolatilization process. By "effects" is meant product yields, product compositions and rate-determining regimes. In order for this objective to be accomplished, the heat transfer conditions established within the devolatilization reactors need to be quantified as precisely as possible.

FIGURE 4

Variation of ΔT with dT/dt for $T_g = 1500$ and $r_0 = 50$ microns.

FIGURE 5

Variation of ΔT with dT/dt for $T_g = 2000\text{K}$ and $r_o = 50$ microns.

FIGURE 6

Variation of ΔT with dT/dt for $T_g = 1000\text{K}$ and $r_o = 50$ microns.

FIGURE 7

Variation of ΔT with dT/dt for $T_g = 1200\text{K}$ and $r_o = 50$ microns.

FIGURE 8

Variation of temperature difference between the surface and the center of the particle with heating rate (dT/dt) [$T_g = 500\text{K}$; $r_o = 50$ microns].

FIGURE 9

Variation of ΔT with dT/dt for $T_g = 800\text{K}$ and $r_o = 50$ microns.

FIGURE 10

Variation of heating (dT/dt) with time [$T_g = 1500K$ and $r_0 = 50$ microns]

FIGURE 11

Temperature rise at the center and the surface of the particle with time [$T_g = 1500K$ and $r_0 = 50$ microns].

MML# 08959
SAMPLE Grid
Section 3

FIGURE 12

FIGURE 13
(A)
GRID MESH DIAGRAM

(See Figure 12
for Weave Pattern)

$$\eta_L = \frac{\# \text{ strands in L direction}}{\text{cm}}$$

$$\eta_W = \frac{\# \text{ strands in W direction}}{\text{cm}}$$

$$\eta_W = \eta_L = 118 \text{ strands/cm}$$

(see Table I)

FIGURE 13
(B)
GRID FOLDING TECHNIQUES AND DIMENSIONS

Zero Load Conditions - Physical Properties, Geometric Considerations,
Configuration in the Reactor:

325 mesh stainless steel (type 304) mesh is used as the heating substrate in the heated grid reactor. The manufacturer's specifications on the screen indicate a wire diameter of 0.0014" (35.6 μm), an opening between wires of 0.0017" (43.2 μm), and a mass/superficial area of 21.5 mg/cm^2 . Figure 2 displays a scanning electron microscope (SEM) view of a section of the grid at approximately 425X. Since the physical and geometric characteristics of the grid determine its heating rate and heat transfer characteristics, and, thereby, the immediate environment heating the coal sample, a systematic SEM study of the wire mesh was performed. The wire diameters and wire spacings were measured at several hundred locations within five different samples of the screen. Table I indicates the results.

Table I

Stainless Steel Grid Characteristics

	<u>Wire Diameter (μm)</u>	<u>Wire Spacing (μm)</u>	<u>Strands/cm (Calculated)</u>
Average:	36.5	48.2	118
Range:	33.3 - 39.4	42.3 - 54.2	
Standard Deviation:	1.6	3.1	

Figure 13a shows a grid mesh pattern with the symbols used to calculate grid properties. Figure 13b shows the folding technique employed to create a captive sample environment for the coal and to clamp the grid between the electrodes. Appropriate dimensions are also shown. Table II lists property values employed in subsequent calculations, while Table III defines the symbols.

Assuming reasonable accuracy in measured characteristics of the grid and reported property values of the stainless steel material, a number of grid properties can be calculated and compared to experimentally determined values.

Table IV lists some zero-load intensive and extensive properties of the grid system, the expressions used to calculate values, and the measurements needed to experimentally determine the calculated property. These properties are experimentally determined and then compared to literature values to insure the geometry used to model the grid and real time measurements are accurate and consistent. Properties 4) and 5) are necessary to determine the mechanism of particle heating in load conditions and the components of radiative versus conductive heat loss. These characteristics are necessary to determine the heat transfer conditions to particles under load conditions and to estimate heat of devolatilization values. Table Va-c compares experimentally

determined values of grid properties with those extracted from the literature or calculated from a combination of measurements and literature values. In Table Vb, the ratio of the grid electrical resistances at various temperatures during a temperature-time ramp are shown. These values represent averages taken from various runs using a single layer ($n = 1$) screen cut. Since current, voltage and temperature (Figure 14) are measured during a run, the overall resistance of the screen as a function of temperature can be determined. The overall resistance of the screen is related to its intrinsic resistivity as shown in Equation 21:

$$R_{HG}(T) = \alpha \cdot \left(\frac{L_{EE}}{mNW\sigma_s} \right) \cdot R_{304}(T) \quad (21)$$

where σ_s represents a single strand cross section area and α is a parameter incorporating electrode contact resistance and the coefficient of expansion of the screen. Assuming changes in α are small with temperatures less than 600°C:

$$R_{HG}(T)/R_{HG}(100) = R_{304}(T)/R_{304}(100) \quad (22)$$

Table II

Stainless Steel Type 304 Properties

<u>Property*</u>	<u>Value</u>	<u>Temperature Dependence</u>
Specific Heat Capacity (cal/g-°C), C_{304}	0.12 (4) at 20°C	Increases to 0.15 at 650°C
Emissivity, ϵ	0.40-0.70 (4,5)	Increase with Temperature
Thermal Conductivity (cal- m/cm ² -sec), k_{304}	0.038 at 20°C (4,6)	$(3 \times 10^{-5})T^1 + 0.033$
Resistivity (ohm-cm), R_{304}	72×10^{-6} -cm at 22°C (4)	$(72 \times 10^{-6})[1 + 0.00095(T-22)]$
Density (g/cm ³), ρ_{304}	7.817 (4)	

*Subscript 304 refers to type 304 stainless steel.

Table III

Symbol Definitions

Symbols

n	number of grid layers
C_{304}	specific heat capacity of stainless steel (type 304) in cal/g-°C
$\bar{d}_s$	average strand diameter in cm (see Table I)
T	grid temperature in °C
W	fold width in cm
L	length of grid sample in cm
N	number of wire strands/cm
ρ_{304}	density of type 304 stainless steel in g/cm ³

Subscript

EE.	electrode to electrode length (see Figure 13)
TG.	total grid sample (see Figure 13)
HG.	heated portion of grid sample (see Figure 13)

Table IV

Zero-Load Extensive Properties of Heated Grid System

<u>Property</u>	<u>Calculated by:</u>	<u>Measurements</u>
1) Mass (M), g	$(\pi/2)n(NWL)P_{304}\bar{ds}^2*$	Weight
2) Strand Surface Area (S), cm ²	$2\pi n(NWL)ds$	Length, Width N, ds from SEM
3) Resistivity Change with Temperature	$R(T_2)/R(T_1)*$	Current and voltage at various temperatures during heating ramp
4) Steady State Heat Loss ($\dot{Q}_L$), watts	$(IV)_{@T=\text{constant}} - \dot{Q}_{\text{Loss}}$	Current, voltage, temperature at steady state
5) Average Specific Heat (C), cal/g-°C	$\frac{IV - \dot{Q}_{\text{Loss}}(T)}{M_{\text{HG}} \cdot T}$	Current, voltage, temperature during initial heating ramp

*R - Resistance of grid; **HG - heated portion of grid

L - L_{EE} for heated portion of grid

Table Va

Grid Properties - Mass and Surface Area

<u>Property</u>	<u>n</u>	<u>Measured</u>	<u>Determined from Literature</u>
			<u>Values and/or System Geometry</u>
Mass _{TG}	1.00	186 mg	189 mg
	2.27	428 mg	420 mg
	3.00	558 mg	567 mg
M _{HG}	1.00		144 mg
	2.27		332 mg
	3.00		432 mg
S _{HG}	1.00		20.2 cm ²
	2.27		45.9 cm ²
	3.00		60.7 cm ²

Table Vb

Resistivity Change with Temperature

<u>Temperature (C)</u>	<u>Measured</u>		<u>Literature (4)</u>
	<u>Resistance (Ω)</u>	<u>R(T)/R(100)</u>	<u>R₃₀₄(T)/R₃₀₄(100)</u>
100	0.63	---	
200	0.69	1.10	1.10
300	0.75	1.19	1.17
400	0.80	1.26	1.20
500	0.83	1.32	1.31
600	0.86	1.38	1.38

If reasonably accurate measurements of I, V and T are being made, then the resistance ratios determined from these values should follow resistivity ratios as a function of temperature. As noted in Table Vb, the agreement is consistent.

Another check on internal consistency of the measurements can be obtained by considering an energy balance on the heated portion of the grid:

$$\text{Energy In} = \text{Energy Stored} + \text{Energy Loss} \quad (23)$$

$$I(t) \cdot V(t) = \dot{M}_{\text{HG}} \cdot C_{304}(T) \cdot \dot{T}_{\text{HG}}(t) + \dot{Q}_{\text{Loss}}(t) \quad (24)$$

or,

$$C_{304}(T) = \frac{I(t) \cdot V(t) - \dot{Q}_{\text{Loss}}(t)}{\dot{M}_{\text{HG}} \cdot \dot{T}_{\text{HG}}(t)} \quad (25)$$

• The specific heat of the grid material can be estimated provided the $\dot{Q}_{\text{Loss}}$ is small or can be determined empirically.

Figure 14 shows the power input/screen surface area required to maintain steady state temperatures for various screen samples, that is, different layer values, n. These measurements were taken under low pressure (~0.01 torr) conditions. Figure 14 is discussed in more detail below. Figure 15 gives an example of real time data acquired.

Using the empirical expressions for the heat loss as a function of temperature, Equation (25) can be used to estimate the specific heat of the grid material. Again, if the measurements are consistent and reasonably accurate, then the determined values should be reasonably close to literature values. Table Vc lists experimentally determined and literature values of C_{304} . For T_{HG} below 250°C, $\dot{Q}_{\text{Loss}}$ was assumed ≈ 0 .

Table Vc

C_{304} , Specific Heat Values of Grid Material (cal/g-°C)

<u>$T_{\text{HG}}(\text{C})$</u>	<u>Determined from Equation 5</u>	<u>Literature Values (1)</u>
240	0.13	0.123
320	0.15	0.125
400	0.14	0.135
475	0.13	0.142
600	0.13	0.155

The derived magnitudes for the specific heat are correct, but the expected temperature dependence is not apparent. The current, voltage and temperature measurements which are input to Equation 25 either directly or via the T and $\dot{Q}_{\text{Loss}}$ expression all have ~10% uncertainty associated with their values.

FIGURE 14

FIGURE 15 VOLTAGE, CURRENT, TEMPERATURE DATA ACQUISITION

The derived values $\dot{T}$ and $\dot{Q}_{\text{Loss}}$ have a greater uncertainty. Over the temperature range considered, 100-600°C, the specific heat has a 26% change in value, according to the literature. The resistivity undergoes approximately a 38% change in value over the same range and its temperature dependence was reflected in the measured values. However, the resistance ratios involve no derived expressions, being determined directly from the current and voltage measurements for a given temperature. In short, one would expect to determine the average magnitude for C_{304} in this manner, but not necessarily the correct temperature dependence, due to the manner of determination.

The self-consistency of the measurements and the consistency with reported literature values for the material properties of the stainless steel indicate the transient measurements are reasonably accurate and sensitive. There remains the central question--what is the mode of heat loss, power dissipation, from the zero load grid?

Steady State Power Dissipation -- Low Ambient Pressure

Figure 14 shows the steady state power requirements to maintain center thermocouple temperatures for grids containing n layers. Two aspects of these plots of relevance to the heat loss question are: 1) the temperature dependence of the power balance; and 2) the variation in power requirements as a function of number of grid layers to maintain a given temperature.

In all cases, the power loss was fit with a fourth power dependence on absolute temperature. A fourth power dependence gave the best set of statistical parameters -- coefficient of determination, coefficient of correlation, standard error of estimate. Figure 16 shows the power loss for the single layer grid as a function of T_{HG}^4 . With T_{HG}^4 as the independent variable, a linear fit was obtained. The linear fit has a coefficient of determination of 0.9992, coefficient of correlation of 0.996 and a standard error of estimate of 0.193. Similar fourth power fits were obtained for two-layer and three-layer grid samples. The fourth power dependence of power dissipation with respect to absolute temperature of the grid indicates the main mode of heat transfer of the grid to its surrounding environment is via radiation, irrespective of the number of layers.

The double and triple layer cases show lower heat loss per unit surface area of screen than that observed for the single layer (Fig. 14). That is, a lower steady state power input is needed to maintain a given temperature for the folded cases relative to the single layer screen. The reduction in heat loss per unit surface area of grid with folding is expected due to the change in radiation interchange view factor. Upon folding, the wire strands that are now facing each other exchange radiation with surfaces at the same temperature, establishing a radiation exchange equilibrium condition between these surfaces. The result is a reduction in net power dissipation/surface area for a given temperature relative to the unfolded single layer case ($n = 1$). A triple layer case should show similar reduction relative to the double layer case, since the central layer is effectively surrounded by layers in thermal equilibrium with itself. The reduction in power dissipation with

FIGURE 16

POWER DISSIPATION vs. T_{HG}^4

increase in fold layers is consistent with the radiation dissipation being the main mode of heat loss to the environment.

A further check on self-consistency of the steady-state measurements can be made by considering a power balance at steady state for these conditions:

Power In = Power Dissipated

$$I \cdot V = \dot{Q}_{\text{Loss}} = \dot{Q}_{\text{Radiation}} + \dot{Q}_{\text{Conduction to Electrodes}}$$

$$IV = P = \sigma_{\text{SB}} \epsilon_{304} F_{\text{HG-e}} S_{\text{HG}} (T_{\text{HG}}^4 - T_e^4) + k_{304} (NW \sigma_s) (T_{\text{HG}} - T_{\text{EE}}) / \Delta L_{\text{EE}}$$

$$S_{\text{HG}} = 2\pi(NWL)d_s$$

where $F_{\text{HG-e}}$ is the heated grid strands view factor to the surrounding environment at temperature T_e , $(\Delta L)_{\text{EE}}$ is the length of strand from electrode clamp to the strand location where the temperature is T_{HG} , σ_{SB} is the Stefan-Boltzmann constant. The T_{HG}^4 dependence of power dissipation indicates that the heat loss by conduction to the electrodes is much less than the radiation loss to the environment. Consequently, as a first order approximation:

$$P_n = \sigma_{\text{SB}} \epsilon_{304} F_{\text{nHG-e}} [2\pi(NWL)d_s] (T_{\text{HG}}^4 - T_e^4)$$

$F_{\text{HG-e}} \neq 1$ for the case of a single layer ($n = 1$) since (see Figure 13) the weave pattern of the strands places a significant fraction of each strand surface area in touch with another strand, which is in thermal equilibrium with it. An examination of the SEM photographs indicates the fraction of "unexposed" surface area of a strand due to the wave pattern is ~0.27. As a first approximation, then, $F_{\text{HG-e}} = (1 - 0.27) = 0.73$ for $n = 1$.

$$P = \sigma_{\text{SB}} \epsilon_{304} (0.73) [2\pi(1)(NL)d_s] (T_{\text{HG}}^4 - T_e^4)$$

Using the measured values of I , V , T_{HG} , T_e , N , W , L and d_s , one can estimate ϵ_{304} from Equation 31. Table Vd indicates the estimated emissivities of the type 304 stainless. The results compare favorably with reported literature values (4, 5, 6), although reported results vary considerably with polishing, heat treatment and oxidation histories of the sample. The increase in emissivity with temperature is in agreement with literature values for various types of stainless steel.

Table Vd

Estimated Emissivities of Grid Material

<u>T_{HG}(K)</u>	<u>ε₃₀₄</u>
593	0.45
673	0.38
788	0.47
858	0.46
953	0.50
1009	0.47
1093	0.53
1193	0.55
1253	0.60

Using Equation 30 for the multiple layer cases, one can estimate the change in overall view factor from the change in power requirement, P_n , relative to the $n = 1$ case, required to maintain a given T_{HG} for a given n :

$$\frac{P_n}{P_1} = \frac{F_{nHG-e}}{F_{HG-e}} \quad (32)$$

Power ratios associated with a given temperature for each of the multiple layer cases relative to $n = 1$, should decrease in a manner consistent with the change in view factor.

Table Ve
Power Ratio Changes With n

$T_{HG}(K)$	P_3/P_1	$P_{2.27}/P_1$
600	0.87	1.05
700	0.72	1.00
800	0.70	0.78
900	0.56	0.72
1000	0.55	0.75
1100	0.54	0.78
1200	0.53	0.71

The results indicate the effective view factor decrease for an approximately double layer system decreases by ~25% relative to the single layer case whereas the three layer case shows a ~50% relative reduction in effective view factor. The absolute reduction depends, of course, on the manner in which the strands align themselves upon folding. The low temperature ($\leq 800K$) ratios reflect the scatter in the I, V and I measurements and the increasing contributions of $Q_{Conduction}$ to overall power dissipation.

Summary of Steady State Power Dissipation -- Low Pressure Conditions

The T_{HG}^4 dependence of power dissipation indicates the main mode of heat transfer of the grid is radiation interchange with its environment. Taking into account the weave structure for a single layer grid, reasonable values of emissivity can be extracted from the measured parameters. The values show an expected increase with temperature. Increasing the number of grid layers decreases the power input required to maintain a given T_{HG} in a manner expected by considering changes in view factor for the strands of the grid.

Summary of Zero Load Calibration of Heated Grid System -- Low Pressure

Real time, current, voltage and temperature measurements lead to type 304 stainless steel materials property values -- resistivity, specific heat, emissivity -- in agreement with those reported in the literature. Such measurements are indicative of the accuracy of the measurements and reflect a consistent understanding of the energy transfer dynamics in the heated grid apparatus. Measurements indicate the main mode of energy dissipation in the grid is via radiative interchange with its environment for temperatures of $800^{\circ}K$ and above. Power dissipation data as low as $550^{\circ}K$ have been fit by a T^4 expression, but conduction loss to the electrodes becomes competitive in this regime.

Heated Grid Devolatilization -- Char and Tar Yields

A series of runs were performed using the heated grid apparatus with a high volatile bituminous Pittsburgh seam coal (PSOC 1451). Run conditions and char and tar yields are indicated in Table VI. Figures 17a and 17b indicate the programmed, zero-load, and sample-loaded voltage, current and temperature trajectories for a particular run (Run 227). The voltage traces are identical, aside from the high frequency noise on the programmed voltage system. However, relative to the zero-load case, the sample loaded temperature and current traces vary substantially from the zero-load case. The voltage trajectory is fixed for both the zero and sample loaded cases. The temperature trajectories vary because of the sample loading of the screen and the current trace varies, relative to the zero-load case, because of the temperature dependence of the resistivity of the grid material (see above). The sample presence obviously perturbs the power input process. The resultant change in temperature trajectory is apparent. It is thought that quantitative comparisons of the two cases will allow estimation of the heat of devolatilization process.

The various temperature trajectories to 800°C were chosen to investigate the effect of average heating rate on char and tar yields. Using the non-plateau 10³°/sec to 800°C as a reference, the low pressure data appears to indicate that higher tar yields and lower char are associated with the runs having the higher average programmed temperatures. The effect of changes in temperature trajectory on tar and char yields in low pressure conditions is not as pronounced on tar yields as a change in ambient pressure (Runs 235, 236, 238). The pronounced effect of ambient pressure is observed again in low temperature runs wherein the grid is rapidly heated to 600°C and held there for 10 seconds. Again, the ambient pressure (Runs 242, 243) has a pronounced effect on tar and char yields at prolonged times at relatively low pressure.

MWD's of Heated Grid Tars

Molecular weight distributions (MWD's) of coal tars resulting from the devolatilization of -270+325 mesh PSOC 997 and PSOC 1451 in the UTRC heated grid reactor have been obtained using the SEC technique described previously (see quarterly report DOE/PC/70768-3). The devolatilization conditions used in the experiments and the resulting number average and weight average molecular weights of the tars are summarized in Table VII.

PSOC 997 and PSOC 1451, both HVA Bituminous coals from Pittsburgh seam #8, were devolatilized under vacuum by heating at 1000°C/sec to 800°C and holding for 2.5 sec, and then quenched with room temperature helium to 350°C or less within 0.3 sec. Figure 18 shows that the molecular weight distributions of the two coals are very similar. In fact, differences of this magnitude are approximately equivalent to the limits of the SEC experimental precision.

The effect of varying the grid heating program on tar molecular weight distributions is shown in Fig. 19 for PSOC 1451 devolatilized under vacuum

TABLE VI

Heated Grid Char and Tar Yields for Given Programmed Heating Conditions

Coal: PSOC 1451		Gas	Level 1		Temperature (C)	Level 2		% Sample	
Run I.D.	Particle Size: -270+325 Mesh Pressure (Atm)		Temperature (C)	Hold (sec)		Temperature (C)	Hold (sec)	%Char	%Tar
237	0	---	---	---	800	800	2.5	52.4	24.4
222	0	---	---	---	800	800	2.5	59.0	27.3
223	0	---	---	---	800	800	2.5	53.2	28.7
224	0	---	350	1.0	800	800	1.5	56.1	20.0
225	0	---	350	1.5	800	800	1.0	55.0	26.0
226	0	---	350	2.0	800	800	0.5	68.6	20.9
227	0	---	450	1.0	800	800	1.5	50.2	33.8
228	0	---	450	1.5	800	800	1.0	61.3	26.4
229	0	---	450	2.0	800	800	0.5	75.2	14.2
230	0	---	550	1.0	800	800	1.5	52.7	27.1
231	0	---	550	1.5	800	800	1.0	56.7	29.0
232	0	---	550	2.0	800	800	0.5	53.6	35.3
233	1	AR	---	---	800	800	2.5	69.5	19.7
235	1	AR	---	---	800	800	2.5	61.7	17.5
236	1	AR	---	---	800	800	2.5	58.8	17.2
238	1	AR	550	2.0	800	800	0.5	68.8	14.9
239	0	---	---	---	600	600	10.0	61.2	25.1
240	0	---	---	---	600	600	10.0	63.1	22.2
242	1	He	---	---	600	600	10.0	75.1	12.7
243	1	He	---	---	600	600	10.0	81.8	13.3

FIGURE 17a PROGRAMMED VOLTAGE, CURRENT, TEMPERATURE TRAJECTORIES - Run 227: Zero-Load

FIGURE 17b VOLTAGE, CURRENT, TEMPERATURE TRAJECTORIES - Run 227: Coal-Loaded

Table VII
Heated Grid Tar Characteristics

<u>Coal</u>	<u>Ambient Environment</u>	<u>Heating Program*</u>		<u>T**</u>	<u>Mn</u>	<u>Mw</u>	<u>Mz</u>
		<u>Level 1</u>	<u>Level 2</u>				
997	VAC	840°C/2.5 sec	---	703	566	1328	4439
1451	VAC	800°C/2.5 sec	---	703	600	1195	1936
1451	1 atm Ar	350°C/1.0 sec	800°C/1.5 sec	703	514	1031	2864
1451	VAC	350°C/1.0 sec	800°C/1.5 sec	567	610	1230	2004
1451	VAC	450°C/2.0 sec	800°C/0.5 sec	491	609	1243	3001
1451	VAC	550°C/2.0 sec	800°C/0.5 sec	552	605	1555	6779
1451	1 atm Ar	550°C/2.0 sec	800°C/0.5 sec	552	507	1013	4046
1451	VAC	600°C/10.0sec	---	583	605	1039	1535
1451	1 atm He	600°C/10.0sec	---	583	529	1175	7703

* 1000°C/sec temperature ramp to given plateau temperatures

**Avg. temp. calculated from nominal heating program

$$\bar{T} = \int T dt / \int dt$$

FIGURE 18

TAR MWD'S OF 2 COALS
HEATED GRID
VACUUM
1000°C/S to 800°C, 2.5 sec
hold at 800°C

FIGURE 19

TAR MWD'S OF PSOC 1451 FOR DIFFERENT GRID HEATING PROGRAMS

HEATED GRID, VACUUM

- A. 800°C/2.5 sec
- B. 350°C/1.0 sec, 800°C/1.5 sec
- C. 450°C/2.0 sec, 800°C/0.5 sec
- D. 550°C/2.0 sec, 800°C/0.5 sec
- E. 600°C/10.0 sec

FIGURE 20
TAR MWD'S OF PSOC 1451 FOR DIFFERENT AMBIENT PRESSURE HEATED GRID EXPERIMENTS

conditions. The heating conditions, when ordered by molecular weight of the tars produced, result in the following: $D > B > A > C > E$. Conditions A, B, and D result in tars with nearly equivalent MWD's. PSOC 1451 appears to be insensitive to the heating program, at least within this range of conditions. Condition C results in the lowest average temperature over the experiment (see Table VI) and yields somewhat lower molecular weight tars than any of the other heating programs with a final plateau temperature of 800°C . The lowest molecular weight tars, however, are formed from Condition E, a 10 sec hold at 600°C .

The effect of the ambient gas environment on tar MWD's is shown in Fig. 20 for three different heating programs. In all cases, the tars devolatilized under vacuum conditions contain more high molecular weight compounds than do the tars produced under 1 atmosphere pressure.

Summary

Task 2.1 - Engineering Kinetics of Coal Devolatilization

Unsteady state heat transfer analysis of particles entrained in a transient heating gas stream indicate the possibility of significant intraparticle temperature gradients during rapid coal devolatilization. Such behavior implies that observable devolatilization is due to a mass-weighted average temperature during the volatiles release phase. The mass-average transient temperature history of a particle varies significantly with heating conditions -- particle size, gas temperature, volatiles content of the initial coal particle. The sensitivity of the particle heating curve to heating conditions implies varying observable devolatilization behavior with heating conditions. Activation energy values extracted from weight loss measurements become reactor dependent via reactor determination of heating conditions. These initial calculations were performed using a simplified devolatilization scheme. Subsequent calculations will employ various kinetic schemes to assess conditions in which significant heat transport and chemical kinetic coupling occurs for each pyrolysis model.

Task 2.2 Fundamental Mechanisms of Tar Evolution and Char Formation

The calculations performed in Task 2.1 reiterate the importance of characterizing the heat transfer conditions in a reactor if fundamental information concerning coal devolatilization is to be extracted. An extensive zero-load, experimental and semi-empirical heat transfer analysis of the heated grid reactor was performed. The analysis included self-consistency checks to determine if real time power and temperature measurements lead to screen properties in agreement with literature values for specific heat, resistivity changes with temperature and emissivity values for type 304 stainless steel. The temperature dependence of the power dissipation of the heated grid was best correlated by a fourth power dependence on absolute temperature, for temperatures greater than 700°K . The fourth power dependence implies the major mode of power dissipation is radiative in this temperature range. The radiation loss hypothesis was checked by changing the average view factor of a unit surface area of screen by systematically increasing the layers of screen clamped between the electrodes. In addition,

using the fourth degree power dissipation model led to the emissivity values and changes in emissivity with temperature reported in the literature for similarly heat treated stainless steel.

The heated grid apparatus was used in the plateau temperature voltage programming mode to devolatilize a HVA Bituminous coal by heating the coal to 800 °C in a variety of manners. The char and tar yields in low pressure conditions varied slightly with temperature trajectories and total heating time in the range of conditions examined. Molecular weight distributions of the low pressure tars did not vary significantly with temperature trajectory. Runs performed at one atmosphere pressure showed significant changes in char yields, tar yields and molecular weight distributions of tars relative to the corresponding low pressure conditions. In all cases, the sample load and properties were observed to effect the programmed, zero-load temperature trajectory of the screen. For this coal, ambient pressure appears to have a greater effect on char and tar yields and composition than temperature path to a given final temperature under low pressure conditions. The results also imply that pressure induced secondary reactions of tars occurring during the tar evolution process have a significant impact on resultant yields and the nature of the tar volatiles released.

Next Quarter Activity

Further calculations will be performed to ascertain the particle temperature trajectories during rapid devolatilization as a function of heating conditions and proposed pyrolysis models.

The zero-load calibration of the grid system will be extended to include the effects of ambient gas on power dissipation from the grid. In addition, sample-load effects will be considered in relationship to observed temperature trajectories during devolatilization in low pressure and in the presence of an ambient gas.

Elemental compositions of chars produced during flash lamp and heated grid devolatilization experiments of the same coal will be compared.

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APPENDIX

1. Formulation of difference equations:

The non-dimensional differential equations are

$$R_c \partial \theta / \partial \tau = (1/\eta^2) \partial [\eta^2 \partial \theta / \partial \eta] \partial \eta \quad (1)$$

$$R_c = 1 \quad \text{for } r < r_0 \text{ and}$$

$$R_c = \alpha P / \alpha_s \quad \text{for } r > r_0.$$

Using the Forward difference approximation in time and central difference approximation in spatial coordinate, the derivatives for a grid point i can be written as

$$(\partial \theta / \partial \tau)_i = (\theta_i^{n+1} - \theta_i^n) / \Delta \tau$$

$$[\partial (\eta^2 \partial \theta / \partial \eta) / \partial \eta]_i = [\eta_{i+1/2}^2 (\partial \theta / \partial \eta)_{i+1/2} - \eta_{i-1/2}^2 (\partial \theta / \partial \eta)_{i-1/2}] / \Delta \eta$$

$$= [\eta_{i+1/2}^2 (\theta_{i+1} - \theta_i) - \eta_{i-1/2}^2 (\theta_i - \theta_{i-1})] / \Delta \eta^2$$

$$= [\eta_{i+1/2}^2 \theta_{i+1} - (\eta_{i+1/2}^2 + \eta_{i-1/2}^2) \theta_i + \eta_{i-1/2}^2 \theta_{i-1}] / \Delta \eta^2$$

and then the complete difference equation is written as

$$-\eta_{i-1/2}^2 \theta_{i-1}^{n+1} / \Delta \eta^2 + [R_c \eta_i^2 / \Delta \tau + (\eta_{i-1/2}^2 + \eta_{i+1/2}^2) / \Delta \eta^2] \theta_i^{n+1} - \eta_{i+1/2}^2 \theta_{i+1}^{n+1} / \Delta \eta^2 = R_c \eta_i^2 \theta_i^n / \Delta \tau \quad (2)$$

2. Coupling of differential equations on particle surface:

The grid points in the neighborhood of surface are reported as:

Multiplying both sides of Eq. (1) by $4\pi\eta^2$ and integrating over the small region (a,b) across the surface (s), we obtain

$$\int_a^b R_c(\partial\theta/\partial\tau)4\pi\eta^2 d\eta = \int_a^b 4\pi[\partial(\eta^2\partial\theta/\partial\eta)/\partial\eta]d\eta \quad (3)$$

LHS of Eq. (3) can be evaluated as follows:

$$\begin{aligned} \int_a^b R_c(\partial\theta/\partial\tau)4\pi\eta^2 d\eta &= 4\pi(\partial\theta/\partial\tau) \left[\int_a^s R_c\eta^2 d\eta + \int_s^b R_c\eta^2 d\eta \right] \\ &= 4\pi(\partial\theta/\partial\tau) \left[(\eta_s^3 - \eta_a^3)/3 + (\alpha_p/\alpha_a)(\eta_b^3 - \eta_s^3)/3 \right] \end{aligned}$$

Then the difference form of Eq. (3) is written as

$$\begin{aligned} (\theta_s^{n+1} - \theta_s^n) \left[(\eta_s^3 - \eta_{s-1/2}^3) + (\alpha_p/\alpha_a)(\eta_{s+1/2}^3 - \eta_s^3) \right] / 3\Delta\tau \\ = [\eta_{s+1/2}^2(\theta_{s+1} - \theta_s) - \eta_{s-1/2}^2(\theta_s - \theta_{s-1})] / \Delta\eta \end{aligned}$$

where $s + 1/2 = b$ and
 $s - 1/2 = a$

END

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