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**THERMODYNAMIC PROPERTIES OF PULVERIZED COAL DURING
RAPID HEATING DEVOLATILIZATION PROCESSES**

QUARTERLY PROGRESS REPORT

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1.0 Executive Summary

Knowledge of the thermodynamic and morphological properties of coal associated with rapid heating decomposition pathways is essential to progress in coal utilization technology. Specifically, knowledge of the heat of devolatilization, surface area and density of coal as a function of rank characteristics, temperature and extent of devolatilization in the context of rapid heating conditions is required both, for the fundamental determination of kinetic parameters of coal devolatilization, and to refine existing devolatilization sub-models used in comprehensive coal combustion codes.

The objective of this research is to obtain data on the thermodynamic properties and morphology of coal under conditions of rapid heating. Specifically, the total heat of devolatilization, external surface area, BET surface area and true density will be measured for representative coal samples. In addition, for one coal, the contribution of each of the following components to the overall heat of devolatilization will be measured: the specific heat of coal/char during devolatilization, the heat of thermal decomposition of the coal, the specific heat capacity of tars, and the heat of vaporization of tars.

Work was initiated on this contract during this quarterly period. A Project Plan has been completed and approved. The technical elements of the plan have been included in this report to communicate to other investigators the specific data being generated in this experimental investigation. The thermodynamic properties of coal will be determined using a combination of UTRC facilities including a proprietary rapid heating rate heated grid calorimeter, a microbomb calorimeter (MBC), an entrained flow reactor (EFR), an elemental analyzer (EA), and a FT-IR. Morphological characterization of coal/char will be performed at the University of Pittsburgh using a Leitz TAS PLUS image analyzer, BET apparatus, helium pycnometer, and mercury porosimeter. The methods and technical approach to be used to achieve each of these objectives is described in this report.

Calibration of the heated grid calorimeter (Task 2) was initiated this reporting period. The heated grid apparatus has been modified to improve the optical access to the grid. The heat loss characteristics of the new device have been correlated as a function of temperature. Standard reference materials (SRM's) for temperature, heat of fusion and heat capacity have been obtained from NIST. Initial heat capacity runs using synthetic sapphire standards have been conducted. An error propagation analysis has been performed to estimate the magnitude of the sources of error in the heat capacity determination. The preliminary experiments and error analysis have identified several areas for improvement of the experimental technique.

Planned activities will focus on continuing the efforts to establish the sensitivity of the FHG apparatus for obtaining heat capacity measurements. Several refinements to the apparatus have been identified and will be implemented. A 2-D, transient analysis code previously developed at UTRC will be improved and used to perform grid energy balance calculations. Work on Task 5 will be initiated next month in order to provide char samples for the Task 10 effort in a timely manner.

2.0 Project Objectives

The objective of this research is to obtain data on the thermodynamic properties and morphology of coal under conditions of rapid heating. Specifically, the total heat of devolatilization, external surface area, BET surface area and true density will be measured for representative coal samples. The coal ranks to be investigated will include, at a minimum, a high volatile A bituminous (such as PSOC 1451D) and a low volatile bituminous (such as PSOC 1516D). An anthracite (such as PSOC 1468) will be used as a non-volatile coal reference. In addition, for a minimum of one coal sample, the contribution of each of the following components to the overall heat of devolatilization will be measured: the specific heat of coal/char during devolatilization, the heat of thermal decomposition of the coal, the specific heat capacity of tars, and the heat of vaporization of tars.

3.0 Introduction

Motivation

Knowledge of the thermodynamic and morphological properties of coal associated with rapid heating decomposition pathways is essential to progress in coal utilization technology. Specifically, knowledge of the heat of devolatilization, surface area and density of coal as a function of rank characteristics, temperature and extent of devolatilization in the context of rapid heating conditions is essential to the fundamental determination of kinetic parameters of coal devolatilization. These same properties are also needed to refine existing devolatilization sub-models utilized in large-scale modeling of coal combustion systems.

In many instances the kinetic analysis of rapid coal devolatilization data acquired in laboratory reactors depends on an assumed set of heat capacity, heat of devolatilization and particle morphology parameters. In other cases, attempts to measure particle temperatures during devolatilization (Refs. 1,2,3) lead to results that are not in agreement either with a priori determinations obtained with energy balance expressions using estimations of thermodynamic properties of coal found in the open literature or inert, carbon-based calibration standards used to calibrate the reactor system. Although it is not always clear if the discrepancies are due to inadequate thermodynamic properties of the particle during devolatilization, particle shape factors, inadequate emittance values or some combination of these factors, it is now apparent that independent determinations of these properties in heating conditions characteristic of disperse phase coal utilization technology is necessary. Moreover, since it is now well-established that the energy transfer rate between an environment and injected coal particles, significantly influences the observable devolatilization response time of the particles (Ref. 4), the independent determination of the specific heat and devolatilization heat of reaction of coal is necessary.

Background

The specific heat of coal has been examined in a number of previous investigations, but never in rapid heating, dynamic conditions. Many of the investigations have used large, packed bed samples in an attempt to simulate coking oven conditions (Refs. 5,6). Some investigations utilized small sample quantities, but still employed low heating rates (Refs. 7,8). Due to difficulties involved in making dynamic energy flow measurements for a decomposing sample, some measurements were restricted to sample temperatures below 300° C, the initiation temperature for the thermal decomposition of coal in low heating rate conditions. Others thermally "precondition" the coal sample by heating to a given carbonization temperature before any attempt to measure the specific heat of the sample (Refs. 5,6,9,10). The partially carbonized sample is then cooled and reheated to the same pretreatment temperature while specific heat measurements are made. Differences in devolatilization pathway with heating rate is not accounted for in any of these low heating rate investigations. The applicability of these determinations for rapid heating devolatilization is questionable. An examination of representative approaches follows.

Perhaps the most extensive set of heat capacity measurements have been made by Agroskin and co-workers (Refs. 5,6,11,12). They made two sets of measurements on each sample, the initial measurements, called "effective specific heat," and a reheating of the thermally pretreated samples termed the "true specific heat" (Figs. 1,2). Presumably, the temperature dependent difference between the two measurements represents some sort of heat of carbonization. Agroskin and other Soviet scientists (Refs. 6,11,13-17) report values of total heat of carbonization, temperature ranges of endothermic and exothermic heats of carbonization, and various forms of "effective" and "true" specific heats. Unfortunately, they never present the final, dynamic, temperature or extent of carbonization functions of these variously defined quantities.

Agroskin's effective specific heat measurements indicate two local maxima and one local minimum as a function of sample temperature. The initial shoulder occurs between 600 and 700 K while the primary maximum occurs between 750 and 850 K. The low temperature maximum could be interpreted as indicating disruption of intermolecular bonding within the coal matrix, increasing the degrees of freedom. The primary maximum is presumably associated with the thermal decomposition of the coal matrix components and reflects the endothermic phase of the carbonization process. The high temperature minimum might be associated with the growth of aromatic lamella in the devolatilized coal. Since this represents an ordering, ring condensation process, it is an exothermic process. The problem with interpreting Agroskin's results on a fundamental basis lies in the nature of the experiment. The large sample size results in a gradient in sample temperature during the experiments and the slow heating rates employed are not useful in modeling rapid heating of pulverized coal.

Singer and Tye (Refs. 9) approached the determination of the specific heat of coal during devolatilization in a manner similar to Agroskin et al. They measured the specific heat of dry and wet coal samples to temperatures of 300° C. They then partially carbonized the coal and measured the heat capacities of the partially carbonized samples up to the temperature of partial carbonization (Fig. 3). A global, "dynamic" specific heat can be constructed from their data by using the specific heat data of the samples applicable to the transition temperature data from one char to another (Fig. 4). The shape of this effective specific heat curve is similar to that of Agroskin's data for bituminous coals. The local maximum between 575 and 875 K is similar to the local maximum in the Agroskin data. The data clearly shows the effects of water vaporization on the apparent specific heat of the coal sample. The Singer and Tye data also shows that the local maximum that Agroskin associates with the heat of carbonization corresponds to the maximum differential mass loss during low temperature carbonization. However, this occurs at approximately 200° C lower temperature than in Agroskin's data. The differences in results probably reflect differences in devolatilization pathway with apparatus-dependent heating rates and/or the method of measuring sample temperature during pyrolysis.

Callanan, Sullivan and MacDonald (Ref. 8) used a commercially available DSC apparatus to investigate the specific heat of a Colorado bituminous coal in the 315 to 525 K temperature range at a heating rate of 5 K/min. They studied small samples in sealed capsules using different ambient gases. The apparent, effective specific heats of a "virgin" sample differed significantly from those determined on the same sample in replicate runs (Fig. 5). The "true" specific heat of the coal was that observed in the repeat runs in ambient gases other than air. The initial enthalpy determinations represent the superimposed, irreversible reactions within the coal matrix and the underlying true specific heat observed in subsequent determinations with the same sample. Contrary to the observations of both Agroskin, et al. and Singer and Tye, the concurrent reaction energies in the 315 to 525 K regime appear to be both endothermic and exothermic, depending on the temperature regime of interest.

Callanan et al.'s results vary with the ambient gas used. It is interesting to note that both the initial and true specific heat data obviously reflect differences in the thermal conductivity of the ambient gas. The magnitudes of the apparent endo- and exotherms also mirror the thermal conductivity of the ambient gas. The data may merely reflect apparatus dependent conditions such as difficulties in establishing thermal equilibrium within the system with gases of different thermal conductivity.

All the reported specific heat measurements for coal were obtained in low heating rate conditions. Despite the common heating conditions, there is not good agreement among the measured "effective" or "true" heat capacities of coal, as indicated in Fig. 6. Furthermore, pulverized coal research and application engineers have been forced to extrapolate the available, low heating rate, heat capacity data to their conditions because of the unavailability of appropriate data and corresponding models. Merrick developed a theoretical model of the specific heat and heats of reaction during coal carbonization at

coking oven conditions (Ref. 18). This model is commonly employed in rapid devolatilization/pyrolysis studies. Such extrapolations have been made despite the known variance in rapid devolatilization product yields and characteristics (Ref. 19,20), relative to low heating rate yields and characteristics, and despite clear indications that a different thermal process is occurring in the different heating conditions. The limitations of the Merrick model and previous experimental investigations of the thermal properties of coal with respect to rapid devolatilization conditions are the primary motivation for this work.

FIGURE 1
Effective and True Specific Heats
Flame Coal (Agroskin)

FIGURE 2
Effective and True Specific Heats
Grade K Coal (Agroskin)

FIGURE 3
Specific Heats of Partially Carbonized Coals
(Singer and Tye)

FIGURE 4
Global Heat Capacity and Mass Loss
(Singer and Tye)

FIGURE 5
"Initial" and "Subsequent" Cp's
N2 Ambient Gas (Callanan et al.)

FIGURE 6
Specific Heat Comparisons
Bituminous Coals

4.0 Work Breakdown Structure

The work required to complete the objectives of the contract has been divided into eleven tasks. Each of these tasks is described briefly here and will be discussed in more detail in the Technical Approach section.

Task 1 - Project Work Plan

UTRC shall provide the DOE with a detailed Project Plan within 30 days of contract initiation. Work on no other tasks shall proceed until written approval of this plan is obtained by UTRC from the DOE Project Manager. The Project Plan shall include a Management Plan, Milestone Schedule, Status Report, and Cost Plan.

Task 2 - Calibration of the Heated Grid Calorimeter

UTRC shall measure the specific heat of the non-volatile reference coal (such as anthracite, PSOC 1468) from 25° C to 800° C at heating rates of 1000° C/sec and lower in the heated grid (HG) device. The values will be established relative to NBS calorimeter standards for differential scanning calorimeter (DSC) and differential thermal analysis (DTA) samples. The sensitivity of the heated grid device for determining thermodynamic properties at high heating rates will be established before proceeding with Tasks 3-9.

Task 3 - Low Temperature Specific Heat Capacity of Volatile Coal Samples

UTRC shall measure the specific heat capacity for a minimum of one coal sample over the temperature range of 25° C to 300° C. The measurements will be conducted at heating rates of 1000° C/sec and lower in the UTRC HG.

Task 4 - Heat of Devolatilization of Volatile Coal Samples

UTRC shall measure the heat of devolatilization for a minimum of one coal sample over the temperature range of 25° C to 800° C using heating rates of 1000° C/sec in the calibrated HG. Devolatilization product characteristics will be determined to ensure the devolatilization pathway is that followed in the entrained flow reactor (EFR).

Task 5 - Heat of Thermal Decomposition of Volatile Coal Samples

UTRC shall measure, using the EFR and microbomb calorimeter (MBC), the heat of decomposition for a minimum of one coal sample by: (1) devolatilizing the coal in the EFR, (2) determining the char, tar and gas yields, (3) measuring the tar and char elemental compositions, (4) determining the heat of combustion of the char and tar products using the MBC, (5) estimating the heat of combustion of the gaseous products, and (6) using Hess's and Kirchoff's laws to derive the heat of decomposition.

Task 6 - Specific Heat and Heat of Fusion of Tars from Rapid Heating

UTRC shall measure the specific heat and heat of fusion of tar samples for a minimum of one coal sample over the temperature range from 25° C to 300° C using the HG and tar samples generated in the EFR.

Task 7 - Heat of Vaporization of Tars from Rapid Heating

UTRC shall measure the heat of vaporization of tar samples for a minimum of one coal sample over the temperature range from 300° C to 700° C using the HG and tar samples generated in the EFR.

Task 8 - Specific Heat of Char Samples

UTRC shall measure the specific heat of the coal/char as a function of extent of devolatilization and temperature for a minimum of one coal sample using partially devolatilized samples from the EFR and the HG.

Task 9 - Comparison of Directly Measured Heat of Devolatilization and Thermodynamic Function Determined Value

UTRC shall determine the heat of devolatilization for a minimum of one coal sample based on independent measurements of heat of decomposition (Task 5), specific heat and heat of fusion of tars (Task 6), heat of vaporization of tars (Task 7), and specific heat of coal/chars (Task 3 and Task 8). This value shall be compared and contrasted to the directly measured heat of devolatilization values from 25° C to 800° C obtained in Task 4.

Task 10 - Morphological Characterization of Coal/Char Samples as a Function of Extent of Devolatilization

UTRC shall characterize statistically representative samples of coal/char particles as a function of extent of devolatilization for a minimum of one coal sample. The characterization shall be with respect to combustion related reactivity parameters such as swelling and cenosphere development, CO₂ or O₂ surface areas, and helium (true) density.

Task 11 - Reporting

UTRC shall comply with all required reporting over the 18 month period of an awarded contract.

5.0 Technical Approach

5.1 Overview

As described above the general objectives of this investigation are to:

- 1) determine the thermodynamic properties, and
- 2) morphology

of pulverized coal during rapid heating devolatilization processes. The thermodynamic properties will be determined using a combination of facilities available only at UTRC, including a proprietary rapid heating rate heated grid calorimeter, a microbomb calorimeter (MBC), an entrained flow reactor (EFR), an elemental analyzer (EA), and a FT-IR. Morphological characterization of coal/char will be performed at the University of Pittsburgh using a Leitz TAS PLUS image analyzer, BET apparatus, helium pycnometer, and mercury porosimeter. The methods and technical approach to be used to achieve each of these objectives will be described in separate sections below.

Figure 7a,b,c displays the interrelationship of the various program tasks to be performed in this investigation. The calibration of the heated grid for calorific measurements will be conducted first (Task 2) to establish the sensitivity of the device. Task 5 will be initiated about one month after DOE approval of the project plan. Matched char and tar samples at varying extents of devolatilization will be generated in the UTRC-EFR under this Task. The char and tar samples are needed for the performance of Tasks 5, 6, 7, 8, and 10.

FIGURE 7a

PROGRAM FLOW CHART

FIGURE 7b

PROGRAM FLOW CHART (cont.)

FIGURE 7c

PROGRAM FLOW CHART (cont.)

5.2 Thermodynamic Properties Characterization

The quantities that are to be measured are displayed in terms of the thermodynamic path followed during devolatilization in Fig. 8. The elemental compositions of the specific char and tar yields are indicated as $\text{CH}_{xc}\text{O}_{yc}\text{N}_{uc}\text{S}_{vc}$ and $\text{CH}_{xt}\text{O}_{yt}\text{N}_{ut}\text{S}_{vt}$ respectively, while the yields are designated as $f_{\text{coal}}^{\text{char}}$ and $f_{\text{coal}}^{\text{tar}}$, respectively. As can be seen in the Figure, the heat of devolatilization represents the intrinsic heat of decomposition required to formulate a particular set of products and the enthalpy requirements associated with raising the products to the final temperature. In the actual reaction process the coal follows a thermodynamic path along the diagonal vector from the reactant state to the product state. The path taken is a function of the particle temperature-time history. It is possible to estimate any one of the thermodynamic properties of the system of reactants and products by measuring all but one of the values and then determining the other by energy balance considerations, that is, by utilizing Kirchoff's law.

An objective of this investigation is to measure each of the values along the orthogonal legs of the reaction process - heat of decomposition, char enthalpy, and tar enthalpy (including enthalpy of vaporization of tar). The enthalpy of the volatiles - vapor-phase tars and light gases - will be estimated using available data for hydrocarbons (Ref. 21). These values will then be combined to provide an estimate for the total heat of devolatilization for the process. An independent, direct measurement of the total heat of devolatilization will also be made and compared to the estimated value. In summary, the thermodynamic properties to be measured are:

- 1) the total heat of devolatilization of coal,
- 2) the heat of thermal decomposition of coal,
- 3) the low temperature specific heat capacity of coal,
- 4) the specific heat of chars as a function of extent of devolatilization,
- 5) the specific heat capacity and heat of fusion of tars, and
- 6) the heat of vaporization of tars.

Thermodynamic Path: Devolatilization

FIGURE 8

$$\Delta H_{\text{dev}} = \Delta H_{\text{dec}} + \int_{298\text{K}}^{1073\text{K}} C_p^{\text{char(s)}} dT + \int_{298\text{K}}^{\langle T \rangle} C_p^{\text{tar(s)}} dT + h_{\text{fusion}}^{\text{tar}} + \int_{\langle T \rangle}^{\langle T \rangle} C_p^{\text{tar(l)}} dT + h_{\text{vap}}^{\text{tar}} + \int_{\langle T \rangle}^{1073\text{K}} C_p^{\text{tar(g)}} dT + \sum_i \int_{298\text{K}}^{1073\text{K}} C_p^{\text{gas}_i} dT$$

$$\int_{298\text{K}}^{1073\text{K}} C_p^{\text{char(s)}} dT = \int_{298\text{K}}^{1073\text{K}} C_p^{\text{organic char}} dT + \int_{298\text{K}}^{1073\text{K}} C_p^{\text{ash}} dT$$

Directly measurable thermodynamic quantities

The means by which each of these thermodynamic quantities will be measured is indicated in Fig. 9. The tar and char samples needed to perform the heated grid calorimetric experiments will be generated in the UTRC-EFR, which is described in a later section. The total heat of devolatilization, specific heat capacity of coal, specific heat capacity of char, and the combined specific heat capacity and heat of fusion of tar will be measured directly using the UTRC-HG as a calorimeter. Details on the use of the heated grid as a calorimeter will be discussed below.

Heat of vaporization of tar

The heat of vaporization of tar will be determined indirectly as the difference between two directly measured quantities,

$$h_{\text{vap}}^{\text{tar}} = \Delta H_{\text{dev}}^{\text{tar}} - \Sigma [C_p^{\text{tar}} + h_{\text{fusion}}^{\text{tar}}].$$

Each of these quantities - the total heat of devolatilization of the tars, and the combined specific heat capacity and heat of fusion of the tars - will be measured in separate experiments utilizing tar samples in the heated grid. The combined specific heat capacity and heat of fusion of the tars will be determined in an experiment with a final temperature equal to the end point melting temperature of the tars. A series of exploratory experiments with increasing final temperature will be used to determine the melting point. Imaging of the sample during the experiment will also be used to aid in defining the phase transition point. The total heat of devolatilization of the tars will be determined by re-vaporizing tars in the heated grid.

Heat of thermal decomposition

The heat of decomposition will be determined by application of Hess's Law to measurements or estimates of the heat of combustion of the parent coals and each of the products of devolatilization. The complete sequence of steps required to determine the heat of decomposition is as follows:

- (1) devolatilize the coal in the EFR,
- (2) determine the char, tar and gas yields,
- (3) measure the tar and char elemental compositions,
- (4) determine the heat of combustion of the parent coal, char and tar products using the MBC,
- (5) estimate the heat of combustion of the gaseous products, and
- (6) using Hess's and Kirchoff's laws to derive the heat of decomposition.

FIGURE 9

The UTRC-EFR will be used to generate matched tar and char samples in sufficient quantities to allow elemental analysis and microbomb calorimetric determinations to be performed. Product yield data and elemental composition results will be examined to ensure that the devolatilization pathway followed in the EFR is the same as that in the heated grid. The heat of combustion of the parent coal, partially devolatilized chars, and corresponding matched tars will be measured directly using a modified Parr microbomb calorimeter (MBC). The UTRC-MBC is capable of determining the heat of combustion of small samples (15-25 mg) of char and tar samples.

Hess's Law states that the enthalpy change for a reaction is equal to the sum of enthalpy changes for individual reactions that can be added together to give the desired reaction. Thus adding,

results in the equivalent reaction:

Therefore, the heat of decomposition is given by:

$$\Delta H_{\text{dec}} = \Delta H_{\text{comb}}^{\text{coal}} - \sum f_{\text{coal}}^i \Delta H_{\text{comb}}^{\text{product}_i}$$

where f_{coal}^i is the mass fraction yield of the i^{th} product.

Use of the UTRC-HG as a Calorimeter

Direct measurement of thermodynamic properties will be accomplished by using the heated grid as a calorimeter, that is, as a device to measure flow of heat to the sample. Currently available differential scanning calorimeters

(DSC's) are capable of making these measurements at low heating rates only. Even at low heating rates, it is difficult to obtain meaningful results using a DSC for volatile samples (Ref. 8). However, it is instructive to consider the data analysis techniques used for a standard DSC determination as a starting point in understanding the methodology that will be employed with the heated grid.

The standard DSC procedure is to measure, for a constant heating rate experiment, the rate of heat flow to the sample holder, or power (P), as a function of time for four separate runs:

- 1) empty sample pan 1 (P_{blank1}),
- 2) NBS reference material in sample pan 1 (P_{std}),
- 3) empty sample pan 2 (P_{blank2}), and
- 4) unknown sample in sample pan 2 (P_{samp}).

The *measured* specific heat of the NBS standard is:

$$C_{p\text{std}}^{\text{meas}} = \frac{(P_{\text{std}} - P_{\text{blank1}})}{\dot{T} m_{\text{std}}}$$

and the *measured* specific heat of the unknown sample is:

$$C_{p\text{samp}}^{\text{meas}} = \frac{(P_{\text{samp}} - P_{\text{blank2}})}{\dot{T} m_{\text{samp}}}$$

The actual specific heat of the sample can then be determined through calculation of a calibration factor using the known specific heat of the NBS standard:

$$C_{p\text{samp}}^{\text{act}} = \left[\frac{C_{p\text{std}}^{\text{NBS}}}{C_{p\text{std}}^{\text{meas}}} \right] \cdot C_{p\text{samp}}^{\text{meas}}$$

This simplified analysis assumes a constant heating rate and does not account for mass loss or constant temperature phase changes during a run.

The use of a heated grid as a calorimeter under high heating rate conditions is significantly more complicated. To use the heated grid for volatile samples, in addition to power, the time rate of change of temperature and sample mass must also be determined as a function of time (temperature) for each run. The calculation of the temperature derivative from the raw temperature data is straightforward, requiring filtering or smoothing to remove the noise from the signal. The sample mass loss can be accounted for by either conducting a series of experiments at increasing extents of reaction or by using a previously determined correlation for mass loss.

As a result of the nature of operation of the heated grid and due to the high heating rates to be employed, several additional refinements are necessary.

The power dissipated by the grid during a blank run is the sum of the grid material energy storage term ($mC_p\dot{T}$) and the heat loss term. Implicit in the DSC analysis above is the assumption that these two terms are identical in both the blank and sample-loaded run. This is not the case in the heated grid due to the fact that the additional thermal load of the sample on the grid results in a lowering of the temperature of the combined grid/sample mass relative to the same point in time during a blank run. The local reduction of temperature results in lower electrical resistivity in the sample loaded area. As the grid is run in a voltage controlled mode, the voltage potential across the full length of the grid is known and invariant from run-to-run. However, the ΔV 's in the sample-loaded and non-loaded areas of the grid are free to adjust subject only to the imposed overall potential drop across the grid. The effect of the sample loading is to change the overall resistance of the grid and therefore the current and power will adjust accordingly. The power dissipated in a blank run cannot be subtracted from the power during a sample loaded run to arrive at the sample energy storage rate ($mC_p\dot{T}$).

This difficulty can be resolved by considering the energy balance for the sample-loaded area of the screen only. Both the sample-loaded area of a "loaded" run and the non-loaded region of a "blank" run in the proximity of the measurement thermocouple are similar isolated areas on the grid. As a first approximation, the power dissipation per unit area as a function of time of both the loaded and blank runs *within* these isolated areas are assumed equal,

$$P^L(t) / A_s = P^B(t) / A_s$$

$$m_s C_s(T^L) \dot{T}^L + m_g C_g(T^L) \dot{T}^L + \dot{Q}^L(T^L) = m_g C_g(T^B) \dot{T}^B + \dot{Q}^B(T^B)$$

where m_s and m_g are the sample and grid mass per unit area, respectively; $C_s(T^L)$ and $C_g(T^L)$ are the sample and grid specific heat at the loaded grid temperature; $C_g(T^B)$ is the grid specific heat at the blank grid temperature; and $\dot{Q}^L(T^L)$ and $\dot{Q}^B(T^B)$ are the loaded and blank grid heat loss rate per unit area, respectively. Note the implicit assumption that the sample and grid temperature in the loaded region of the grid are equal. Solving for sample specific heat:

$$C_s(T^L) = \frac{m_g}{m_s} \left(C_g(T^B) \frac{\dot{T}^B}{\dot{T}^L} - C_g(T^L) \right) + \frac{\Delta \dot{Q}^{B-L}}{m_s \dot{T}^L}$$

where $\Delta \dot{Q}^{B-L} = \dot{Q}^B(T^B) - \dot{Q}^L(T^L)$ is a heat loss correction due to the difference in temperature between a blank and loaded run at a given time. The heat loss is correlated as a function of grid temperature by using the $P(t)$ data obtained from the blank run for that particular grid and calculated values for the grid energy storage term ($mC_p\dot{T}$). Note that the area of the grid covered by the sample enters into the equation through m_s in the heat loss correction term. Therefore, the sample mass and area must be measured as a function of time.

If the assumption that the blank and loaded grid power dissipation are equal is relaxed, then the following equation for sample specific heat results:

$$C_s(T^L) = \frac{m_g}{m_s} \left(C_g(T^B) \frac{\dot{T}^B}{\dot{T}^L} - C_g(T^L) \right) + \frac{\Delta \dot{Q}^{B-L}}{m_s \dot{T}^L} - \frac{\Delta \dot{P}^{B-L} / A_s}{m_s \dot{T}^L}$$

where a term for the difference in *local* power dissipation in the sample-loaded area now appears. There are two approaches for quantifying this term, direct measurement and calculation. The difference in power dissipation ($\Delta \dot{P}^{B-L} = P_{local}^B - P_{local}^L$) can be determined directly by measuring the voltage drop across the sample-loaded area of the grid. This would be accomplished by spot welding voltage taps at the edges of the sample area (Fig. 10a). The validity of this approach is dependent on maintaining a true one-dimensional voltage distribution across the grid. Two-dimensional effects arise from sample distributions which do not span the full width of the grid (Fig. 10b).

The second approach is to perform a transient 2-D calculation of the entire grid area between the electrodes. The grid is discretized into a 2-D mesh and an energy balance is applied to each element accounting for resistive heating, heat loss, and conduction in two dimensions. The influence of the sample heat capacity on the local response of the grid is included by adding the sample thermal inertia to the appropriate mesh elements in the model. Given the grid current as a function of time and correlations for heat loss as a function of grid temperature, the energy balance model calculates the temperature and electrical resistance of each element. The resistance across the sample-loaded region of the grid, and therefore local voltage drop and power dissipation, can then be determined. Thus, the 2-D model allows an estimate for $\Delta \dot{P}^{B-L}$ to be calculated given an assumed sample specific heat. The overall procedure for determining the sample specific heat is, therefore, an iterative process.

FIGURE 10

Fig. 10a: 1-D SAMPLE LOADING

**VOLTAGE DROP IN SAMPLE-LOADED REGION OF GRID
IS CONSTANT ACROSS ENTIRE WIDTH OF GRID**

Fig. 10b: 2-D SAMPLE LOADING

**VOLTAGE DROP ACROSS SAMPLE-LOADED REGION
OF GRID VARIES ACROSS THE WIDTH OF THE GRID**

Calibration of the UTRC-HG Calorimeter

The theory presented above accounts for all the relevant terms which contribute to measuring sample specific heat in a heated grid used at high heating rate. If each of the terms can be accurately determined, the method allows *estimation* of sample specific heats *without* the use of a calibration protocol. Ultimately, accurate determination of sample specific heat requires calibration of the technique with NBS certified calibration standards. This will be accomplished in a manner analogous to that used in conventional DSC analysis, where

$$C_{p \text{ act samp}} = \left[\frac{C_{p \text{ std}}^{\text{NBS}}}{C_{p \text{ std}}^{\text{meas}}} \right] \cdot C_{p \text{ samp}}^{\text{meas}}$$

and $C_{p \text{ std}}^{\text{meas}}$ and $C_{p \text{ samp}}^{\text{meas}}$ are simply the measured specific heats for the NBS standard and sample, respectively, as determined by the method described above.

Measurement of Enthalpy Changes

In addition to heat capacity measurements, several enthalpy changes will also be measured using the heated grid calorimeter. These are: the total heat of devolatilization of coal, the heat of fusion of tars, and the heat of vaporization of tars. Such measurements require that the heat flow to the sample be integrated over the temperature range of interest. A term for the heat flow due to change of state, $m_s \dot{q}_{\text{phase change}}$, is added to the grid power balance equation given previously, yielding:

$$\begin{aligned} m_s \dot{q}_{\text{phase change}} + m_s C_s(T_L) \dot{T}^L + m_g C_g(T_L) \dot{T}^L + \dot{Q}^L(T_L) \\ = m_g C_g(T_B) \dot{T}^B + \dot{Q}^B(T_B) - \Delta \dot{P}^{B-L} / A_s . \end{aligned}$$

Re-arranging and integrating to obtain the total enthalpy change over a given temperature range:

$$\begin{aligned} \Delta h &= \int (\dot{q}_{\text{enthalpy change}} + C_s(T_L) \dot{T}^L) dT \\ &= \int_{T_1}^{T_2} \frac{1}{m_s} \left\{ m_g (C_g(T_B) \dot{T}^B - C_g(T_L) \dot{T}^L) + \Delta \dot{Q}^{B-L} - \Delta \dot{P}^{B-L} / A_s \right\} dT \end{aligned}$$

During the phase change of a pure compound the temperature is constant and therefore the T^L terms vanish and the measured enthalpy change is that associated with the phase change alone. However, coal tars are a complex mixture of hydrocarbons which do not all melt or vaporize at the same temperature. Over any given temperature interval, the measured enthalpy change reflects the heat capacity of that fraction of the sample which is not currently undergoing change of state as well as the phase change enthalpy of the fraction which is. It is not possible to deconvolute these two contributions to the enthalpy of the tar. As a result, for solid-phase tar, the heat capacity and heat of fusion will be measured as a lumped parameter.

UTRC HG Calorimeter Hardware Description

UTRC's proprietary rapid heating rate heated grid calorimeter, which was developed and reduced to practice with corporate IR&D funds, will be used to obtain the thermodynamic properties of coal. The device will be employed to measure the overall heat of devolatilization as well as the enthalpy requirements for heating coal to 300° C, tars through the solid-liquid phase transition and vaporization process, and chars at various extents of reaction. The apparatus will employ parent coal particles as well as tar and char samples partially devolatilized in a well-characterized entrained flow reactor.

The HG calorimeter apparatus (Fig. 11) is basically a resistively heated wire mesh, or heated grid device, with several important refinements. The utilization of a heated grid as a calorimeter exploits the known coupling of the local thermal response of the grid to the local sample mass loading and heat capacity. The importance of this coupling was discovered at UTRC and has been thoroughly documented in previous reports and publications (Refs. 4,22,23). Using the heated grid as a calorimeter requires quantitative knowledge of the sample distribution relative to measuring thermocouples in the wire mesh. Since mechanical displacement of the grid induced by rapid heating and phase changes of the samples can result in changes from their initial distributions, it is necessary to image the sample and reference materials during the heating process. UTRC has implemented a rapid response imaging system in which the sample and reference distributions are recorded before, during and after the heating process (Fig. 12). An image of the sample is formed by backlighting the grid and using appropriate magnification optics and a CCD video camera. A 632 nm narrow bandpass interference filter is used to eliminate large changes in image brightness as emission from the grid increases above temperatures of 600-700° C. In order to minimize obscuration of the sample image during tar evolution, a laminar flow of nitrogen gas is used to sweep the tars away.

A Macintosh II computer is used to both control the heated grid and acquire all experimental data (Fig. 13). The heated grid control, data acquisition and 2D thermal analysis software was all written at UTRC using LabVIEW2, Image

Concept Vi and FORTRAN development environments. The desired grid temperature profile is converted to a control voltage waveform using heat loss correlations for the grid. The voltage waveform is then sent to a voltage-controlled power supply to initiate an experiment. Data is acquired from two thermocouples spot-welded to the grid, as well as grid voltage, grid current and reactor pressure sensors. A frame grabber acquires as many as 5-10 sample images for each experiment. The thermocouple, current, voltage and sample mass distribution data is entered into a proprietary UTRC thermal analysis program in which the two-dimensional transient thermal response of the sample-loaded grid is modeled.

HEATED GRID IN DIFFERENTIAL MODE

FIGURE 11

POLYETHYLENE SAMPLE PLACED BETWEEN GRID FOLDS

a) BEFORE HEATING - Sample area = 0.400 sq cm

FIGURE 12

b) AFTER HEATING - Sample area = 1.73 sq cm

HEATED GRID DATA ACQUISITION SYSTEM

FIGURE 13

UTRC-EFR

The essential components of the UTRC entrained flow reactor (EFR) are shown in Figures 14-16. The reactor consists of a coal feeder, a drop tube furnace using argon as the entrainment gas, and a product collection and separation system. The EFR is operated without preheating the entrainment gas so that gas temperatures remain below wall temperatures throughout the reactor. Extra-particle gas-phase reactions of tars are minimized by operating in this mode. This is in contrast to the operation of most entrained flow reactors, where the entrainment gas temperature is matched to the reactor wall temperature. The heat transfer environment of the reactor has been characterized and documented in previous investigations (Refs. 4,19,23).

The coal feed system consists of a jet-stirred, fluidized-bed supply reservoir connected to the reactor primary stream injector via a narrow bore transfer tube. The feed system is capable of sustained delivery of optically thin streams of constant mass delivery rate, provided the feeder is loaded with a narrow particle size range initially. Particle sizes from 10 to 300 microns have been used in the feeder.

The product separation system collects the entire flow stream from the reactor into a water cooled probe. An aerosol phase separation system is employed to obtain char-free tar samples (Figs. 15,16). The separator is designed to "pull off," in quantities proportional to the gas split, all particles or aerosols that are less than 2 microns in diameter. Inertia carries larger particles into the char separation (cyclone train) system. The smaller particles are able to follow the curved flow streamlines and enter the aerosol separation (impactor) system. Both separation trains contain porous metal filters as final stages. Tars are primarily deposited on these filters. Detailed mass fraction analysis of the tars deposited throughout the separation system showed that only about 15% of the total tar mass is deposited in the pre-filter stages (4). Furthermore, chemical characterization of the samples collected within the product separation system indicate that the tars collected on the final filters are representative of the collective, captured tar mass. After particulate and aerosol separation, the gas stream is analyzed on line for IR-active gases by use of a Fourier transform infrared spectrometer (FT-IR) coupled to a multipass cell having an equivalent path length of 43.5 m.

FIGURE 14

FIGURE 15

FIGURE 16

5.3 Morphological Characterization

The morphology of coal and char will be determined at the University of Pittsburgh under the direction of Prof. George E. Klinzing. Image analysis, BET surface area, helium pycnometry and mercury intrusion porosimetry will be used to characterize the structural parameters of the samples.

Characteristics such as external surface area, swelling and cenosphere development will be determined using image analysis techniques in conjunction with an optical microscope. The samples will be prepared for analysis in two ways: 1) by dispersion on a microscope slide and 2) by embedding in epoxy binders. The later technique requires polishing of the sample for analysis by reflectance techniques instead of the transmission technique used on the dispersed sample.

A Leitz TAS PLUS unit will be used to characterize particle morphology using image analysis techniques. The initial data reduction processes are shown in Fig. 17, starting with the image of the particle from the microscope. Much of the data reduction process is automated by the image analysis software. The morphological parameters which can be extracted from the data are shown in Fig. 18. Various particle shape factor definitions are shown in Fig. 19. Investigators such as Beddow et al. (Refs. 24,25) and Meloy and coworkers (Ref. 26) have used Fourier coefficients in order to reconstruct the true particle shapes. A number of coefficients have been identified and some physical meanings have been attached to these coefficients.

Another descriptor of particle shape is the fractal dimension as put forth by Mandelbrot (Ref. 27) and practiced by Kaye and coworkers (Ref. 28). Simply stated this dimension measures the space filling capacity of the particle. The fractal dimension of a two-dimensional view as seen under an optical microscope can be determined by a series of particle dilations carried out by the image analysis software. This process measures the perimeter of the particle by altering the basic stepping size that is used to march around the particle. The fractal dimension is determined by the slope of the plot of the logarithm of the step size versus the logarithm of the perimeter of the particle (Richardson plot). The process often yields data that can be represented by two straight lines of different slopes and thus different fractal dimensions. One slope gives the structural fractal or the overall shape of the particle while the second gives the textural fractal or the intricacy of the particle shape. In addition to this classic perimeter analysis, the fractal dust technique will also be used to determine the fractal dimension of the particles. A large number of particles will be analyzed by these techniques in order to establish the proper statistics of the fractal dimension variations.

In addition to image-based particle characterization techniques, independent measurements of particle morphology will be made using carbon dioxide adsorption, helium pycnometry and mercury intrusion porosimetry. A BET apparatus will be employed to determine the surface area of the particles by

using carbon dioxide gas adsorption properties. The relationship between surface area and extent of reaction will be determined. The true (or solid) density of the coal and char will be determined using helium pycnometry. A mercury intrusion porosimeter will be employed at low pressures to have a minimum of penetration of the mercury into the internal structure of the particles. These measurements will provide, in addition to particle density, an estimate of the external surface area of the particles. Particle size and shape factors determined by image analysis will be used to calculate external surface area from the sample volume data.

DATA REDUCTION OF PARTICLE PROFILE

PIXEL IMAGE OF PARTICLE

DIGITAL IMAGE OF
PARTICLE PROFILE
IN SCREEN
COORDINATES
WITH REFERENCE
MEASUREMENT

CENTROID COORDINATE SYSTEM OF PARTICLE

TRANSLATE ORIGIN OF CARTESIAN
SYSTEM TO CENTROID
ESTABLISH (r, θ) COORDINATE SYSTEM

$$r = (y^2 + x^2)^{1/2}$$

$$\theta = \tan^{-1} (y/x)$$

CARTESIAN IMAGE OF PARTICLE

ESTABLISH CARTESIAN
COORDINATES SYSTEM
USING TANGENTS TO
PARTICLE PROFILE

POLAR DESCRIPTION OF PARTICLE PROFILE

SAVE (θ, r(θ)) PARTICLE DESCRIPTORS
WITH REAL LENGTH
MEASUREMENT REFERENCE

CARTESIAN CENTROID OF PARTICLE

DETERMINE CENTROID
COORDINATE OF
PARTICLE:

$$x_{cm} = \frac{x_1 \int_0^{x_1} [f_1(x) - f_2(x)] dx}{\int_0^{x_1} [f_1(x) - f_2(x)] dx}$$

ROTATE COORDINATE SYSTEM AND
REPEAT PROCESS TO DETERMINE y_cm

GENERATE 3-DIMENSIONAL PARTICLE
BY STEPPING THROUGH ϕ WHILE RANDOMLY
SELECTING A SET OF PROFILE PARAMETERS
FROM SHAPE SET (SEE FIGURE 10)
WHILE REDUCING r(θ, d) TO FIT
ϕ ± 1/2 AT d = ± π/2

FIGURE 17

FIGURE 18

FIGURE 19

PARTICLE SHAPE PARAMETER DEFINITIONS

THE FOURIER COEFFICIENT PARAMETERS ARE DEFINED BY: $(a_0, a_1, \dots, a_n, b_1, \dots, b_n)$

$$r(\theta) = \left(\frac{a_0}{2}\right) + \sum_{i=1}^{\infty} a_i \cos(i\theta) + b_i \sin(i\theta)$$

$$a_i = \left(\frac{1}{\pi}\right) \int_{-\pi}^{\pi} r(\theta) \cos(i\theta) d\theta$$

$$b_i = \left(\frac{1}{\pi}\right) \int_{-\pi}^{\pi} r(\theta) \sin(i\theta) d\theta$$

$$a_0 = \left(\frac{1}{\pi}\right) \int_{-\pi}^{\pi} r(\theta) d\theta$$

IN PRACTICE $\{a_0, a_i, \dots, a_n, b_i, \dots, b_n\}$ ARE CALCULATED FROM:

$$r(\theta_i) = \left(\frac{a_0}{2}\right) + \sum_{k=1}^N a_k \cos(k\theta_i) + b_k \sin(k\theta_i)$$

where $i \in \{1, \dots, N\}$ = Steps around particle

FRACTAL PARAMETER:

$$f_p = \text{slope}(\log p_i \text{ vs. } \log(\Delta x))$$

where $(\Delta x)_i$ is measuring step

and p_i is measured perimeter log using $(\Delta x)_i$

6.0 Summary of Technical Progress

The start date for this contract was July 21, 1992. A poster presentation was prepared and delivered at the 8th Annual Coal Preparation, Utilization, and Environmental Control Contractors Conference, on July 27-30, 1992 in Pittsburgh, PA. The Project Plan was prepared under the Task 1 effort and submitted to the DOE's Contracting Officer's Representative on August 19, 1992. Approval of the Project Plan by the DOE Contracting Officer's Representative was received on Sept. 10, 1992. Work was initiated on Task 2 at that time. Task 10 will be performed under subcontract to the University of Pittsburgh under the direction of Prof. George Klinzing. Negotiations are continuing for this subcontract.

The Project Plan includes: 1) an overview of the project objectives and their relationship to the work of previous investigators, 2) a Work Breakdown Structure detailing the tasks required to meet the objectives of the contract, 3) the technical approach to be followed for each of the project tasks, including description of the samples, the experimental equipment, and the data analysis techniques which will be used, 4) the Milestone Schedule Plan, Cost Plan, and Key Personnel for the project, and 5) the Hazardous Substance Plan. The first three elements of the plan have been included in this quarterly report to communicate to other investigators the specific data being generated in this experimental investigation.

Task 2. Calibration of the Heated Grid Calorimeter

Calibration of the heated grid calorimeter was initiated this reporting period. The heat loss characteristics of the FHG as a function of temperature are required as a part of the data reduction process for heat capacity determinations. The apparatus that will be used to perform heat capacity measurements differs in two respects from the previous heated grid used at UTRC (Ref. 22). The current version provides for a laminar flow of nitrogen sweep gas across the grid to transport evolving tars away from the imaged sample-loaded area of the grid. Heat loss correlations for the original grid were obtained in a stagnant helium environment at 1 atm. pressure. In addition, the flowing heated grid (FHG) uses a stainless steel mesh with a smaller grid area (6.06 cm^2) between the electrodes than the original apparatus (7.52 cm^2). Heat loss data for the FHG has been obtained (Table I) and is compared with the original correlation in Table II. The heat loss data is correlated as a function of temperature ($^{\circ}\text{C}$) quite well ($R^2 = 0.999$) with a 4th order polynomial (Figure 20a). An expanded plot of the low temperature region is given in Figure 20b.

FIGURE 20

a.) FHG HEAT LOSS CORRELATION: 50 - 1000 °C

b.) FHG HEAT LOSS CORRELATION: 50 - 400 °C

TABLE I
FLOWING HEATED GRID (FHG) HEAT LOSS DATA

TEMP (C)	50.7	74.2	97.4	152	175	205	249	294	348
FHG Q _{loss}	0.42	0.92	1.58	2.81	3.52	5.03	6.04	7.81	10.12

TEMP (C)	402	453	505	554	606	710	818	899	990
FHG Q _{loss}	12.64	15.56	19.98	25.14	32.53	50.04	73.40	88.33	122.1

TABLE II
COMPARISON OF HEAT LOSS CORRELATIONS FOR TWO HG CONFIGURATIONS

TEMP (C)	OLD HG Q _{loss} (W)	FHG Q _{loss} (W)	OLD Q _{loss} /A (W/cm ²)	FHG Q _{loss} /A (W/cm ²)
50	2.46	0.37	0.327	0.061
75	2.88	1.07	0.383	0.177
100	3.82	1.73	0.500	0.286
125	5.21	2.37	0.692	0.392
150	6.96	3.01	0.925	0.496
175	9.02	3.65	1.199	0.603
200	11.33	4.33	1.507	0.714
250	16.54	5.83	2.200	0.962
300	22.31	7.64	2.967	1.261
350	28.50	9.88	3.790	1.630
400	35.09	12.67	4.666	2.090
450	42.19	16.11	5.611	2.659
500	50.06	20.32	6.657	3.353
550	59.07	25.39	7.854	4.190
600	69.71	31.42	9.271	5.185
700	98.61	46.73	13.11	7.711
800	143.4	66.90	19.07	11.04
900	212.8	92.51	28.30	15.27
1000	317.6	124.1	42.23	20.47

The heat loss correlation coefficients are:

	a ₀	a ₁	a ₂	a ₃	a ₄
OLD	3.5374E+00	-5.0965E-02	6.4413E-04	-1.1453E-06	8.6616E-10
FHG	-1.2216E+00	3.5157E-02	-7.5757E-05	2.0052E-07	-3.4632E-11

$$\text{with } Q_{\text{loss}} = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4$$

Several NIST standard reference materials (SRM's) have been obtained: sapphire, biphenyl, tin and zinc. Several others are no longer available, including: graphite (SRM 729), and differential thermal analysis (DTA) standards SRM 759 and 760. SRM 720, synthetic sapphire ($\alpha\text{-Al}_2\text{O}_3$), is an enthalpy or heat capacity standard certified over the temperature range 10 - 2250 K. The heat capacity values have an accuracy of $\pm 0.3\%$ or better at temperatures up to 1200 K. The heat capacity of sapphire is plotted in Fig. 21. Tin (SRM 2220), zinc (SRM 2221) and biphenyl (SRM 2222) are DSC enthalpy standards. The fusion temperature and enthalpy of fusion of these materials are certified by NIST to high accuracy.

Several experiments with sapphire have been performed in an effort to establish the sensitivity of the heated grid device for determining heat capacity at high heating rates. Approximately, 15 mg of sapphire is distributed over a 0.5 - 1.0 cm^2 area around the center T/C of the grid. The grid and sample are heated at 1000 $^\circ\text{C/s}$ to 1000 $^\circ\text{C}$. Data for the sample loaded "center" T/C, the blank screen (unloaded) "edge" T/C, grid voltage, grid current and reactor pressure are acquired at 200 Hz.

A video camera with zoom optics images a 2 cm x 2 cm field of view centered on the sample (Fig. 22a). The grid and sample image are recorded on VHS tape for later frame-by-frame analysis. The sample load area is found by backlighting the grid and observing the silhouetted area of the sample. Image enhancement techniques are used to threshold and convert the sample area to a binary "high" state while the unloaded area is set to binary "low" (Fig. 22b). This is considerably more difficult to do with the nearly transparent synthetic sapphire than with coal. Repeated runs with sapphire have shown little movement of the sample load to during a run as the grid expands thermally, thus the sample area can be obtained at any time before, during or after the run for this inert material. A more distinct demarcation between the unloaded and loaded regions of the grid can be seen when the blank screen begins to radiate significantly in the visible as the temperature reaches about 700 $^\circ\text{C}$ while the loaded screen has not yet reached such a temperature (Fig 23). Note that the "loaded" sample temperature, T_s , given in the Figure is the temperature of the T/C spot welded to the upper grid surface while the images are of the lower grid surface. This will be discussed further below.

FIGURE 21

**HEAT CAPACITY OF SYNTHETIC SAPPHIRE AND
304 STAINLESS STEEL**

FIGURE 22

DETERMINATION OF SAMPLE-LOADED AREA

a.) GRID LOADED WITH 15 mg SAPPHIRE

b.) ESTIMATE OF SAMPLE-LOADED AREA: 1.04 cm²

FIGURE 23

IMAGES OF SAMPLE LOADED REGION OF GRID DURING HEATING

a.) $t = 0.90 \text{ sec}$ $T_s = 802^\circ\text{C}$ $T_b = 918^\circ\text{C}$

b.) $t = 1.06 \text{ sec}$ $T_s = 898^\circ\text{C}$ $T_b = 1014^\circ\text{C}$

c.) $t = 1.50 \text{ sec}$ $T_s = 936^\circ\text{C}$ $T_b = 980^\circ\text{C}$

The extraction of heat capacity measurements from the raw data involves evaluating each variable in the following expression:

$$C_s(T^L) = \frac{m_g}{m_s} \left(C_g(T^B) \frac{\dot{T}^B}{\dot{T}^L} - C_g(T^L) \right) + \frac{\Delta Q^{B-L}}{m_s \dot{T}^L}$$

The mass per unit area of blank grid material, m_g , is typically 43-45 mg/cm² for the 325-mesh screen used. Grid-to-grid variability is accounted for by weighing each screen. The sample mass loading per unit area, m_s , is determined by weighing the sample mass and by measuring the sample area as recorded by the video imaging system. The heat capacity (cal/g-K) of the stainless steel (304) grid material is given by the correlation (Fig. 21):

$$C_g(T^L) = 0.12438 - 6.400 \times 10^{-5} T + 1.918 \times 10^{-7} T^2 - 9.830 \times 10^{-11} T^3$$

where T is given in degrees K. The blank and loaded temperature derivatives are determined by first smoothing the raw temperature data to eliminate noise (Fig. 24) and then fitting the smoothed data with 5th order polynomials. The difference in heat loss, ΔQ^{B-L} , between the loaded and unloaded grid areas as a result of their differing temperatures is calculated from the correlation for the FHG described previously.

The first term in the expression given above for sample heat capacity dominates, with the second term, the heat loss correction, contributing about 2.5% of the total. The data obtained to-date results in heat capacity values for sapphire about a factor of five too low. An error propagation analysis has been conducted to establish the most likely sources for this discrepancy. Estimates of the error in each of the measured and derived quantities in the experiment are tabulated below (Table III). Cumulative errors for derived quantities are estimated by the root-sum-squares (RSS) method.

FIGURE 24

a.) RAW TEMPERATURE DATA FOR SAPPHIRE RUN 6.9

b.) SMOOTHED TEMPERATURE DATA FOR SAPPHIRE RUN 6.9

TABLE III
ERROR ANALYSIS

QUANTITY	ABSOLUTE ERROR	% ERROR
Temperature	10 °C	1 - 10
time	0.5 μ sec	0.01
dT/dt		1 - 10
grid mass	0.1 mg	0.02
grid area	0.05 cm ²	4
grid mass/area		4
sample mass	0.1 mg	0.1 - 0.7
sample area	0.05 cm ²	5 - 10
sample mass/area		5 - 10
grid heat capacity	0.01 cal/g-K	1
Term 1		18

None of these errors can explain the five times lower than actual values for sapphire calculated by the analysis technique. However, the error analysis does point out two areas where further refinement of measurement accuracy would be advantageous: temperature measurement, particularly at low temperatures where the relative error is larger, and sample area measurement. The 10 °C temperature error is actually quite a conservative estimate based on the amplitude of the noise in the signal. After smoothing, the error is likely to be substantially lower. A better estimate for the accuracy of the temperature measurements will be obtained by using melting point temperature standards. It may be possible to reduce the sample area measurement error by improving the sample backlighting. Each of these improvements is currently under investigation.

The probable cause for the low sapphire heat capacity values obtained to-date are poor coupling of the sample to the grid/thermocouple. There is some evidence for this in the recorded images as the sample loaded region of the grid remains non-luminous while the "loaded" center T/C reads temperatures well above 800 °C. The most likely explanation for this is that the T/C, which is located on the top side of the grid, is *not* in intimate contact with the sample. This is a result of buckling of the upper grid away from the lower grid and sample. In the original heated grid apparatus the T/C was located on the underside of the grid, which was always in direct contact with coal as a result of gravity. The FHG apparatus is currently being modified to locate the T/C beads on the lower grid surface.

There are several reasons for choosing a heat capacity reference other than sapphire for day-to-day operation of the FHG device: the difficulty in defining the sample area of a near transparent material, the low absorptivity of sapphire in the near IR, and cost. For these reasons, anthracite will be used as a non-

volatile reference standard. The particle size of the anthracite must be the same as that of the study coals to be effective as a heat capacity reference. Several hundred milligrams of 75-106 mm particle size PSOC 1468 anthracite coal have been prepared using dry-sieving followed by aerodynamic separation using the UTRC coal feeder and cyclone separation system. The aerodynamic separation processes reduced, but did not eliminate, the amount of fines present in the sample. The heat capacity of the anthracite will be determined using a commercial differential scanning calorimeter (DSC) apparatus and referenced to the sapphire standard. The DSC runs will be conducted under nitrogen at low heating rates. The anthracite will then be used as an internal UTRC standard throughout this investigation.

7.0 Planned Activities

Efforts to establish the sensitivity of the FHG apparatus for obtaining heat capacity measurements will continue. Several refinements to the apparatus have been identified and will be implemented. The thermocouples will be relocated to the lower grid surface to ensure that the sample is in direct contact with the T/C. Grid temperature measurements will be calibrated with melting point standards. The grid backlighting will be improved by modifying the equipment to allow a more direct illumination path. The heat capacity of the anthracite reference coal will be measured using a commercial DSC.

The 2-D, transient grid energy balance code developed at UTRC several years ago will be used to perform calculations as described in Section 5.2 above. Improvements will be made to the code to allow time varying sample load area boundary conditions to be derived from the experimental imaging data and imposed on the governing equations.

Work on Task 5, Heat of Thermal Decomposition of Volatile Coal Samples, will be initiated next month. The matched tar and char samples which are to be used throughout this investigation are to be generated in the UTRC EFR as a part of the Task 5 effort. Part of the rationale for initiating this task now is to provide char samples for the Task 10 effort in a timely manner.

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