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VOLATILE PRODUCTION DURING PREIGNITION HEATING

Final Technical Report for the Period September 15, 1980—
September 30, 1982

By
A. Ballantyne
H. P. Chou
A. Flusberg
K. Neoh
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D. Stickler

October 1983

Work Performed Under Contract No. AC22-80PC30291

Avco Everett Research Laboratory, Inc.
Everett, Massachusetts

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October 1983

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Pittsburgh, Pennsylvania

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ABSTRACT

Pulverized coal particles, in a flowing inert nitrogen stream, have been heated by high power Carbon Dioxide Laser. The consequence of such an irradiation have proved to be both novel and surprising as a result of the rapid quenching of primary coal products. It has been found that the gas phase yield from such heating (typically, temperatures in excess of 1400 K at rates $\sim 2 \times 10^5$ K/s) is very small (< 0.2 percent of coal carbon and hydrogen). Analysis of the solid residue has shown the presence of fine lacy particulate chains of material of $0.1 \mu\text{m}$ diameter, which appears to be soluble in tetrahydrofuran. The yields of solute were significantly much higher than for raw coals. Molecular weight of the solute material was high, being in the range of 600-3000.

The above and substantiating evidence point to a new mechanism of high heating rate pyrolysis in which only tar-like materials are produced as primary products from the coal. It is hypothesized that gas phase products are primarily the result of secondary reactions of these primary products in the hot gas environments usually employed by other heating techniques.

1.0 INTRODUCTION

1.1 STATEMENT OF PROBLEM

In this report, we address the experimental determination of volatile yield, rate and mechanisms from pulverized coal particles under conditions comparable to those associated with boiler firing applications. Pulverized coal combustion in a typical industrial swirl burner environment involves heating rate on the order of 3×10^4 K/s, as a lower bound, determined from a bulk temperature rise of about 1500 K over a time scale about 50 ms, associated with recirculation zone flow in such a swirl burner. Actual particle heating rates may be appreciably higher than that. Volatile matter production from this heated coal has a major influence on flame stabilization, due to the combustion of that gaseous volatile matter with the oxygen content of the primary air stream, and that of the secondary air and combustion products, which mix with the primary stream. The rate of production of heating value of gaseous volatiles basically determines the flame location relative to the burner and its flow field, and combustion stability, as well as influencing the overall flame structure.

The principal thrust of the work is to investigate experimentally the behavior of pulverized coal under preignition heating condition in the vicinity of particles of several coal types. The experimental results will be correlated with a detailed kinetic and transport model. The overall purpose of carrying out this work is definition of combustible matter production from pulverized coal as it relates to flame stabilization in a boiler environment.

Particular reference is made to such currently used combustor types as swirl stabilized burners. While extensive measurements of pyrolysis have been made in the past, none has combined high heating rate to high temperature with precise diagnostic measurements.

The principal objective of the experimental effort is establishment of a well controlled heating rate environment for pulverized coal in a flowing system. Within this controlled heating rate environment, measurement of particle temperature, pyrolysis yield and observations of ignition within the flow will be made. In carrying out these measurements, detailed analysis of the lower molecular weight volatile species produced during devolatilization should be performed together with observation of tar and other higher molecular weight species. This information has direct bearing on the combustion stability and ignition behavior of pulverized coal flames. In order to obtain data on actual volatile composition as it emerges from the coal particle without significant further decomposition by interaction with hot gas, it is desirable to establish a condition with a cold background gas rather than a hot gas driving heat transfer to the particle. It is also preferable to have the pulverized coal particles dispersed in this gaseous environment rather than being in contact with physical structures such as heating elements. The observations should be correlated using a detailed predictive model of pulverized coal combustion. The resulting predictive capability will be of direct applicability to design of improved industrial boiler combustors in the context of optimizing flame stability in a recirculating field and with respect to minimizing soot and NO_x production by control of the mixing behavior in the primary flame zone. The principal areas of difficulty associated with this class of

measurement are associated with establishment of controlled heating rate to high particle temperature and application of unequivocal diagnostics. It is important to achieve heating rate and peak temperature comparable to those projected and measured in real combustor environments and to do so with a well controlled flow and gaseous environment condition so that well defined measurements can be made. In such a system, it is not in any way easy to obtain high quality composition data from a two-phase flow that may, typically, include at a given point a background atmosphere, gaseous pyrolysis product species, soot, high molecular weight pyrolysis species such as tars, and partially reacted coal that may, in some cases, be capable of caking. Consequently, great attention must be paid both to establishing a well-defined heating environment in which measurements can be readily carried out to the measurement of gas composition itself. Use of captured particle properties as a diagnostic by particle quenching and subsequent analysis is also difficult in this class of flow, and will be further discussed in subsequent sections.

1.2. TECHNICAL APPROACH

1.2.1 Literature Overview

There is a very extensive literature in the art of monitoring pyrolysis of pulverized coal. This has evolved most notably over the last ten to twelve years.

An overview of particle heating techniques and the associated heating rate and volatile yield is shown in Figure 1-1. The overall trend, from top to bottom, is toward increased temperature, heating rate, and volatile production. A comprehensive review of work in the moderate heating rate and temperature regime is given by Anthony and Howard, 1976. Results at higher heating

VOLATILE YIELD DEPENDS ON T, dT/dt , & MIXING

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Figure 1-1 Regimes of Heating Rates for Coal Devolatilization Studies

rates and higher peak temperature were reported by Kimber and Gray, 1967, and further investigated by Kobayashi, 1976a,b. Much of the data base on mass yield dependence on heating conditions was reviewed and organized in a series of papers: Kobayashi, 1972; Stickler, 1974; Ubayakar, 1976a,b; Stickler, 1979. The primary emphasis in much of this work was on net mass loss, with relatively small attention paid to evolution of particular species. More recently, this has been investigated, notably by Solomon, 1978, who used a large sample on a heated wire grid apparatus. They describe kinetic inferences for various species yields, but with considerable limitation in heating rate, peak temperature, and heating rate definition. Total volatile yield found in their vacuum apparatus is typically lower than observed for high-rate pyrolysis in entrained flow. Some information on element yield distribution under entrained flow particle heating in a hot argon atmosphere was reported by Kobayashi, 1976a. However, as discussed below, there are some important uncertainties introduced by the experimental procedure. Although not called out specifically on Figure 1-1, extensive efforts have also been made using laser heating of stationary samples. Selected efforts that bear directly on definition of an optimum experimental and diagnostic approach to high precision monitoring of volatile yield under high heating rate, high final temperature conditions, are discussed below.

1.2.2. High Heating Rate Techniques

Experimental approaches that have been used in the past to obtain high rate pyrolysis yield data break down into three major groups. These are entrained flow of pulverized coal in hot gas; heated grid experiments in which the coal is heated by conduction from a solid object; and optical radiation

heating using, for example, a pulsed laser source. Extensive work has been done on coal particle heating by entrainment in a flowing hot gas, with the gas either heated prior to coal introduction or heated, for example, by RF discharge or arc, with the coal entrained in it. The principal uncertainties associated with this class of experiment are caused by inadequate knowledge of particle temperature versus time in the flow typically inferred by transport modeling, and volatile decomposition upon mixing with the hot gas surroundings. However, this approach does have the advantage of allowing particle heating to high temperature. Associated with that is a coupling between the heating rate that one can achieve and final particle temperature. It is most difficult to establish a very high particle heating rate to limited final temperature. Consequently, measurements carried out in this class of system, such as those by Kimber and Gray and Kobayashi, do leave an uncertainty in the effect of heating rate as distinct from final system temperature.

A second class of measurements that avoids some of those problems utilizes a wire grid structure that contains or supports a pulverized coal sample. This is established in a cold gaseous atmosphere and heated electrically. A very rapid current discharge through the wire grid can drive bulk temperature to moderate levels at controlled rate. Typical numbers are a peak temperature on the order of 1200 K and a maximum heating rate on the order of 10^4 K/sec. Uncertainties associated with this class of measurement include thermal contacting between the wire grid and the particles, affecting heat transfer to them and, consequently, particle heating rate relative to wire grid heating rate. Pyrolysate decomposition may also occur in the vicinity of the particle-grid structure, which is physically large compared to an

individual dispersed coal particle. The peak temperature and heating rates achievable are lower than those commonly projected in boiler environments. Consequently, the limited volatile yield observed under inert atmosphere conditions in this class of measurements is not obviously representative of that achieved by pulverized coal under realistic firing conditions.

1.2.3. Laser Heating of Coal

With the advent of the laser, coal researchers realized its potential as a source of intense heating. The earliest investigation of laser pyrolysis of coal was performed by Sharkey, Shultz and Friedel, 1964, at the Pittsburgh Coal Research Center (presently PETC), where a ruby laser was used to irradiate samples of particulate coal inside evacuated glass tubes. The results indicated that the rapid heating produced a high concentration of acetylene in the product gases, in addition to ethylene and higher hydrocarbons, as compared to low heating rate carbonization. This work was extended further by PCRC personnel, using both pulsed and CW lasers (Karn, et al., 1967).

The work of Karn, et al., 1967, is of special interest because they investigated pulsed laser heating of several different coals, ranging from low volatile anthracite through high volatile bituminous to lignites. The gaseous products of the irradiation were notably richer in hydrogen than the parent coals, although the difference becomes small for the high volatile lignites. The total gaseous product was found to increase with decreasing coal rank. The production of methane, acetylene and hydrogen was highest for the lowest-rank coals.

The effect of background gas upon gaseous product was first studied by Shultz and Sharkey, 1967, using helium, nitrogen, argon, hydrogen and water

vapor. As pointed out by Hanson, 1978, these results were somewhat compromised by the multiple-pulse irradiation of the samples, whereby secondary reaction of products from previous pulses could lead to inaccuracies. Hanson found large increases in the yield of acetylene and lower hydrocarbons in consequence of reaction of hydrogen with carbonaceous species. In another study, Hansen, et al., 1977, found that the use of a pulsed ruby laser led to a product gas composition correlated with a gas temperature of 3300 K, prior to quenching by carrier gas.

Joy, et al., 1970, found significant differences in pyrolysis of coals, aromatic compounds and polymers on pulsed laser heating. They used a time of flight mass spectrometer in this study. The coals produced lower hydrocarbons (with molecular weights < 100), whereas the aromatic compounds showed a strong peak corresponding to evaporation of the compounds and peaks associated with their decomposition products. Polymers decomposed into sub-units attributed to breaking of the polymer chain. Thus polyethylene decomposed into units of general formula $(CH_2)_n$, arising from breakdown of the aliphatic chain.

Using a CO_2 cw laser, Karn, et al., 1972, were able to heat coal samples at 140 W/cm^2 . The difference between these results and those with the pulsed laser were quite marked, and pulsed laser giving a higher yield of volatiles. The yield of high molecular weight hydrocarbons is greater in the case of cw heating, which may in part be explained by differences in estimated temperatures (1500 K for pulsed and 1300 K for cw irradiation) and in part by differences in heating rates ($\alpha = 55000 \text{ W/cm}^2$ for pulsed and 140 W/cm^2 for cw).

Although giving significant insight into the coal pyrolysis composition, the basic limitation of experiments to date has been the lack of time resolution of the pyrolysis process. All the above experiments gave statements of final product composition, as opposed to transient development. Even though Joy, et al., 1970, looked at the time history of the mass spectra of their pyrolysis experiment, it was essentially during post-irradiation cool down of the sample.

The value of the preignition pulverized coal pyrolysis data base presently available is consequently limited by several factors. These are, first, control and knowledge of heating rate and particle temperature versus time during the pyrolysis period, and coupled with that achievement of realistic heating rate and final temperature conditions. A second area of difficulty is pyrolysis secondary reaction in a hot atmosphere, used in all entrained flow experiments to date, as a means of transporting heat to the particles. Finally, much of the work done using heated grid and pulsed laser experiments, do not give time resolved information on volatile production but instead give only "endstate" results.

1.2.4 Conceptual Approach

One area of experimental difficulty is diagnosis of real time test conditions as established experimentally. Simultaneous measurement of the pyrolysis yield composition and particle temperature as a function of time during the particle heating history is badly needed. In order to obtain welldefined data, avoiding the limitations of existing techniques, measurements are carried out in a flow of pulverized coal entrained in a gas carrier stream, with heating by absorption of 10.6 μm radiation from a high power CW laser. This

method is chosen to eliminate uncertainties associated with mixing of particles with a hot gas, and to decouple heating rate from particle size, gas temperature, and gas composition. As a free jet experiment is feasible in this heating mode, extensive optical and probe diagnostics are feasible, with excellent position resolution at high heating rate. Flow time is correlated using LDV measurement, with particle temperature tracked with Schmidt and two-color systems. Local sampling is performed using suction probes.

Pyrolysis data can then be correlated using a comprehensive kinetic transport model of entrained flow pulverized coal processing developed at AERL, with transport and kinetic descriptions modified as required. Using this model, the implications of the results can be explored in terms of recirculation stabilized pulverized coal combustion. The thrust of the experimental program is the use of the AERL HPL[®] 15 KW CO₂ laser. The use of such a high power laser is found necessary in order to obtain adequate spatial and temporal resolution for establishing the kinetics of the pyrolysis reactions. A schematic of the experimental arrangement is shown in Figure 1-2. An underlying problem of high heating rate irradiation is that of sampling probe survivability; to this end, the probe is shielded from the laser flux by means of a mirror congruent with the axial location of the probe. A controlled atmosphere around the particle is maintained by use of a coflowing shield flow, which presents air entrainment into the test region. The test region itself is confined to the potential core of the jet in order to maintain one dimensional flow.

Energy absorption by particles has been extensively investigated at AERL (Reilly, et al., 1977a,b; Singh and Knight, 1978; Singh, 1978, 1979), using a

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Figure 1-2 Schematic of Experimental Arrangement

pulsed CO₂ laser with inorganic particles and water mists. For particle size greater than the laser wavelength, very high energy deposition was observed. No direct data exists for coal particle energy absorption depth of 4 μm for 10.6 μm radiation, and simple polymers are found to have e-fold absorption depth in the neighborhood of 30 μm . Consequently, it appears that adequate energy absorption will, in fact, occur in pulverized coal. Finite absorption depth results in essentially volumetric particle heating, which considerably simplifies kinetic treatment.

In a continuous flow-free jet system, particle temperature measurements can be obtained by using various forms of optical devices such as a Schmidt system or a two-color pyrometer working in the appropriate wavelength band for the temperatures of interest. Chemical composition measurements can, in principle, be made by in situ optical methods or by probing to extract samples for external analysis. The latter approach is chosen for the purposes of this effort. A number of probe types have been developed and used in sampling such reacting streams. They generally display one or more significant disadvantages. The entrained flow work carried out by Kobayashi used a sintered bronze particle capture device with cold gas quenching of the sample stream as it entered the capture region. The system was sized and designed so that the bulk of the particulate matter present in the system entered and was captured in this sintered structure. Subsequently, following completion of a flow test, this capture element was removed and its contents analyzed. This methodology has limitations associated with completeness of sample capture and quenching of reaction during the sampling period, which introduces uncertainties in time scale. It also raises questions regarding the condensation of

high molecular weight volatiles that may be present in the hot stream and which, following quench and capture, become associated with the solid contained by the capture stream. A more appropriate probe approach that has been employed is a water-cooled, water-quenching probe, employed by Prado, et al., 1976, based on a design by Lahaye and Lasagne at CNRS Mulhouse, France. While this probe has the potential for very good spatial resolution and rapid quench of the captured sample, it also introduces an uncertainty regarding the flow and sampling of high molecular weight compounds, which being condensable may coat the inner probe wall structure and become lost subsequently in the flow system. This can introduce considerable uncertainty in the overall element balance. Definition of volatile matter composition under conditions of very high heating rate, high volatile yield in which molecular weight condensable species are probably present, as shown by previous pulsed laser pyrolysis experiments for example, requires a different class of probe design. Rather than attempt to obtain a detailed chemical analysis of these volatile species, it appears most attractive from the viewpoint of overall combustor design to obtain information about the relative elemental composition of the volatiles produced compared to the elemental composition of the coal as fed, and an overall heating value. An adiabatic sampling probe incorporating catalytic oxidation of the sample stream was designed and is described in Section 2.0. It was intended that its output could be explicitly resolved in terms of volatile concentration and element distribution. However, it proved to have a severe limitation. In consequence, another probe was designed, based on the realization of the extremely rapid quenching provided by the particular environment of the laser heating experiment. Use of the two

probes described gives extensive and partially redundant data on volatile behavior. The probes used both for optical and gas sampling are chosen to spatially resolve flow stream properties. However, in order to correlate the observation with kinetic descriptions of the coal behavior, it is necessary to establish a time-space correlation for the flow stream. While flow conditions can exist in which the stream velocity is essentially constant, it appears preferable to avoid this constraint. Use of an LDV system for stream velocity determination is, in consequence, desirable.

2.0 EXPERIMENTAL APPROACH

2.1 DESIGN CONCEPT

The program proposed here is to use the Avco HPL[®] CO₂ laser as a source of well-characterized heating, which is capable, by virtue of its 15 kW peak power, of giving good temporal resolution of the pyrolysis process. This section describes the laser, its operation, heating rates of interest, and experimental diagnostics

2.1.1 HPL[®] Laser

The HPL[®] laser is a commercially available CO₂ cw metal-working laser (Figure 2-1). It has been developed as a cost-effective energy source for welding, cutting or surface-treating of metals. Utilization of its high output power (15 kW) can shorten processing cycles, reduce material costs and eliminate time consuming setup procedures. HPL[®] laser systems are provided with time-sharing capabilities (up to four separate work stations), and custom designed external focussing optics allowing precise spot size selection. Further details of this laser system are given in Section 2.3.

This program was carried out on the Avco Everett Metal-working Laser Applications Research and Development device at Somerville, Massachusetts.

2.1.2 Experimental Requirements

The use of an HPL[®] laser for coal pyrolysis studies is of great interest when one considers the relevant scaling laws for rapid heating. We consider a flowing stream of coal and carrier gas passing perpendicularly through a beam of laser radiation of flux ϕ W/cm² (Figure 2-2). Assuming an absorption cross section of each particle equal to its cross section (πa^2), and

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Figure 2-1 Avco HPL[®] Metalworking Laser

FLOW GEOMETRY

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Figure 2-2 Schematic of Experimental Concept

heating from two diametrically opposed directions, its initial heating rate on entering the laser beam is given by

$$\left. \frac{dT}{dt} \right|_{t=0} = \frac{3}{2} \frac{(1-r)}{\rho_s c_s a} \phi \quad (2-1)$$

where

r is the reflectivity at the laser wavelength

ρ_s is the particle density

c_s is the specific heater, and

a is the particle radius

This leads to a requirement for laser flux at a given heating rate. Thus, for the range of interest, 10^4 - 10^6 K/s, the required laser fluxes range from the order of 10^2 to 10^4 W/cm² for representative particle sizes (Figure 2-3).

Over this range of heating rates, the required time for irradiation, τ_{REQ} , may vary substantially. Figure 2-4 illustrates this point using the kinetic scheme of Stickler, et al. The two reaction time scales are defined by

$$\frac{m_o - m_{pyro}}{m_o} = \exp(-t/\tau_n) \quad (2-2)$$

where

$$\tau_n = \frac{1}{k_n \exp \left(\frac{-E_n}{RT} \right)} \quad (2-3)$$

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Figure 2-3 Heating Rates as Function of Laser Flux Density

Figure 2-4 Timescales for Devolatilization (after Ubhayakar 1976)

k_n and E_n being the rate factors and activation energies of the two reactions. As can be seen in Figure 2-4, heating at 10^4 K/s results in pyrolysis by the slow heating route, whereas at 10^6 K/s, the rapid heating route dominates. In order for the reaction to go to completion, $((m_0 - m_{\text{pyro}})/m_0 \sim 0.01)$ we require $\tau_{\text{REQ}} \sim 4 \tau_n$. This gives a range of required time scale of order 70 ms at 10^4 K/s to only 1 ms at 10^6 K/s.

The above analysis is, of course, an oversimplification. Conduction and radiative heat transfer play an important role in the thermal history of the particle. The heat transfer from the particle is modified by the pyrolysis behavior, both in terms of an endothermic heat sink and a mass loss induced change in particle density. The effect of these loss mechanisms can be seen in Figures 2-5 and 2-6. The existing AERL coal combustion code was adapted to use radiative heating and inert gas carrier. The flux was uniform during the entire irradiation. The particle temperature history shows a reduced dT/dt during peak volatile production, followed by a rapid rise in temperature on termination of volatile production. In the case of the lower heating rates, significant differences in yield of volatiles can be seen (Figure 2-7). This is, of course, using the competing reaction scheme of Kobayashi and Stickler. The particle temperatures at termination of pyrolysis can be seen to increase with flux, being 700 K for 520 W/cm^2 , 1400 K for 930 W/cm^2 and 1900 K for 5600 W/cm^2 .

The effect of conductive and radiative cooling to the gas surrounding the particle may be very significant at lower heating rates. Using a conductive loss corresponding to a Nusselt Number equal to 2.0, we obtain a temperature rate of change of the particle as given by

Figure 2-5 Simulation of Laser Induced Pyrolysis, $\Phi=500-1000 \text{ W/cm}^2$

Figure 2-6 Simulation of Laser Induced Pyrolysis, $\Phi=5600 \text{ W/cm}^2$

Figure 2-7 Steady State Temperatures of Particles Under Laser Heating

$$\frac{dT_p}{dt} = \frac{3}{\rho_s C_s a} \left[\frac{q_\epsilon}{2} - \sigma \epsilon T_p^4 - k \left(\frac{T_p - T_g}{a} \right) \right] \quad (2-4)$$

where ϵ is the emissivity of the coal (assumed grey body behavior), k is the thermal conductivity of the gas, and σ is the Stefan Boltzmann constant.

This gives a final steady-state temperature, as given by $dT/dt = 0$, for a given incident flux. This is illustrated in Figure 2-7. As can be seen, a difficulty arises if a matching of temperature and heating rate is required. At low fluxes, although the initial heating rate may be sufficiently high, the final temperature is below that required for pyrolysis. This implied the use of a contoured flux-time history for the particle heating. The simplest approach, neglecting pyrolysis energy losses, is to require the flux to correspond to a fixed temperature gradient; thus

$$q(T_p) = \frac{2T_p \rho_p C_p}{3} + 2\sigma T_p^4 + \frac{2k(T_p - T_g)}{a\epsilon} \quad (2-5)$$

Thus, as shown in Figure 2-8, the flux must increase across the spot if a current heating rate is to be obtained. At low heating rates (10^4 K/s) the flux must increase by an order of magnitude between start and finish, whereas at higher heating rate the flux change becomes much smaller. Although there is no inherent difficulty in obtaining such beam flux profiles, in practice it imposes great constraint upon flexibility and simplicity of the design. The total time required for the particle to pyrolysis completely is assumed to be equivalent to heating up to a particle temperature of 1500 K. This would appear to be a reasonable number to assume, even based on existing, lowheating-rate data. Thus,

Figure 2-8 Laser Flux Density for Constant Heating Rate

$$\tau_{REQ} = \frac{1200}{T} \quad (2-6)$$

Now the laser has a mean flux across the beam (π), which is related to spot size by

$$P = \overline{\sigma} d L \quad (2-7)$$

P being the total laser power. Thus, taking a given beam depth, d, commensurate with realistic one-dimensionality at the sample probe (~ 1-2 cm), we can obtain a resolution criterion for the experiment. The irradiated zone has a length in the flow direction

$$L = \frac{P}{\overline{\sigma} d} \quad (2-8)$$

This is shown in Figure 2-9, for a 10 kW laser. Realistically, the resolution (L_{RES}) possible with a sampling probe is ~ 5 mm. Thus we have a figure of merit for time resolved investigation of the pyrolysis process, given by

$$n = L/L_{RES} \quad (2-9)$$

This parameter is plotted against heating rate (T) and laser power in Figure 2-9. It would appear that it is necessary to have a 10-kW laser if

Figure 2-9 Experimental Resolution Parameter as a Function of Laser Power and Heating Rate

some time resolution of a 10^6 K/s heating is to be possible. This indicates that a laser similar to HPL[®] makes an adequate tool for such a controlled heating experiment.

2.2 FLOW SYSTEM DESIGN

2.2.1 Coal Mass Loading Considerations

It would appear necessary that both sides of each particle be heated uniformly. This requires that the laser beam pass through the test section twice before going to a beam dump. Under such conditions the mass loading of solids is given by

$$\frac{m_s}{m_g} = \frac{2}{3} \propto \frac{\rho_s}{\rho_g} \cdot \frac{\alpha}{l} \quad (2-10)$$

where

α is the total beam attenuation

ρ_s, ρ_g the solid and gaseous mass densities

l is the test section dimension in the laser direction.

For uniform irradiation of the test section, α must be small and, thus, by implication, m_s/m_g . For the flux to be essentially uniform, the attenuation per pass could be < 10 percent. For example, using an argon carrier gas and a 5-cm path length, this translates to a 2.8-5.6 percent mass loading for 50-100 μ m diameter particles.

The mass loading is further influenced by heat transfer to the gas and by any reaction exothermicity resulting from addition of a low concentration of oxygen to the carrier system. Approximating the heat transfer by pure conduction, under conditions of constant temperature gradient, the heat flux to the gas (assuming the gas temperature does not rise significantly) is given by

$$q = \frac{3k(T_p - T_g) m_s}{\rho_p a^2} \quad (2-11)$$

and as $T_p = T_t + T_g$, we have

$$\int q dt = m_s (3T_t / 2\rho_p a)$$

which gives a temperature rise in the gas phase at the end of the irradiation zone, assuming uniformity throughout the gas, of

$$\Delta T_{gas} = \left(\frac{m_s}{m_g} \right) \cdot \frac{3kT_t \tau_{REQ}^2}{2\rho_p c_{pg} a^2} \quad (2-12)$$

or

$$\Delta T_{gas} = \left(\frac{m_s}{m_g} \right) \cdot \frac{3k\Delta T_t \tau_{REQ}^2}{2\rho_p c_{pg} a^2}$$

As can be seen from Figure 2-10, the temperature rise is only significant for the low heating rate, 10^4 K/s, the higher heating rates giving an almost negligible increase in gas temperature.

2.2.2 Gas Velocities

From the consideration of laser power and resolution, the gas velocity is defined by the reaction time and beam dimension

Figure 2-10 Conduction Heat Transfer to Carrier Gas

$$u = L/\tau_{REQ}$$

For 10^4 K/s, this gives ~ 1 m/s, whereas, for 10^6 K/s, a high value of 19 m/s is required.

2.2.3 Experimental Configuration

The experiment envisaged comprises a coal-gaseous carrier test stream surrounded by an inert shield flow (Figure 2-11), which would protect the test stream from reaction with ambient air. The reason for the use of such an open-jet flow is two-fold. First, it enables more flexibility for access to diagnostics, and eliminates the attendant constraints imposed by a walled test section. Second, the high flux levels of the irradiation ($> 5 \text{ kW/cm}^2$) make it nearly impossible to have solid windows for the test section.

The co-axial shield flow can be velocity-matched to the coal/gas jet to minimize the rate of mixing (as the mass loading of the coal is low, they are essentially momentum-matched as well). As far as possible, the test region will be within the potential core of the jet.

Nitrogen primary carrier flow is passed through the coal-metering device and the uniformly particle laden stream fed to the jet. A fluidized bed feeder is used.

The test section requires a shield mirror (Figure 2-12) to protect the probing devices from the incident laser flux. The reflected laser energy is taken to the beam dump, as is unused laser energy from the irradiated zone. The complete system assembly is illustrated in Figure 2-12, showing the required subsystems for flow, laser, optics, and diagnostics.

J4696

Figure 2-11 Experimental Configuration

J4693

Figure 2-12 Experimental Systems Assembly

2.3 LASER FACILITY

The present laser facility consists of a 15 kW CO₂ laser slaved to three test cells (Figure 2-13). These test cells are normally used for laser metal-working development and are operated on a time-sharing basis. The test cells are supplied with laser power via a beam channel above the cells. By suitable changes being made in optical configuration, the beam can be directed selectively to a given work station. The laser pyrolysis experiment was installed in the end cell, as shown in Figure 2-14. During laser operation, the test cell is off limits to personnel, for reasons of safety. Operation of laser, flow system and diagnostics was performed from a remote station outside of the cell. The gas supply lines and diagnostics cables are passed through an access panel into the cell. The gas supply system was fed by a bottle bank, which is to be placed in an adjoining area. The laser is operated from remote terminals, typically located outside of the cell door.

The experimental test equipment inside of the cell consists of the laser mirror assemblies, the flow nozzles and all of the necessary diagnostics. The nozzle assembly and mirror assemblies are fixed. The diagnostics are to be mounted on a traversing mechanism. The traversing mechanism is a one-degree-of-freedom system, which is motorized and has remote-control capability.

Operation of the present experimental program required that a new gas extraction system be installed in the test cell as opposed to using the existing exhaust system. This is primarily as a consequence of the necessity of preventing contamination of the other work stations by coal and char particles. The test cell is equipped with an exhaust duct coupled to a filter unit and an air blower (360 cfm capacity).

Figure2-13 Test Facility Layout

J8574

Figure 2-14 Experimental Layout in Facility

2.4 FLOW SYSTEM

2.4.1 Test Section and Flow System Scaling

The test flow delivery assembly, shown in Figure 2-15, uses a core flow of carrier gas plus pulverized coal, surrounded by a velocity-matched shield flow of inert gas. The constraints upon flow system parameters are imposed by various experimental requirements. First, the required residence time (τ_{req}) of the coal particles in the laser beam defines the flow velocity of the carrier gas. This is related to the heating rate, as

$$\tau_{\text{req}} = \Delta T / \dot{T}_p$$

where ΔT is the required temperature rise of the particles, and $\dot{T}_p$ is the heating rate. The second system requirement is that the whole test region lies within the potential core of the coal/carrier jet. This precludes dilution of reaction products by the shield gas. From Figure 2-15, the depth of the test region (ℓ) is given by

$$\ell = S - L/4 \quad (2-13)$$

where L is the length of the test region (and, hence, the laser irradiation zone) and s is the nozzle assembly dimension. This is derived on the basis of a typical turbulent jet core being approximately $4s$ in length. For flow rates to be minimized, the nozzle is taken to be square.

The flow velocity through the test region is given by

J8221

Figure 2-15 Test Flow Assembly

$$\bar{u} = L / \tau_{\text{req}} \quad (2-14)$$

and, hence, the mass flow rate of carrier gas through the nozzle is given by

$$\dot{m}_g = \rho_g S^2 \bar{u} \quad (2-15)$$

Now, the achievable power of the laser is given by

$$P = \phi L \ell \quad (2-16)$$

where ϕ is the mean flux density in the test region. Thus

$$\dot{m}_g = \rho_g \frac{P \dot{T}_p}{\phi \Delta l} \quad (2-17)$$

Now ϕ is related to heating rate as given by Eq. (2-5), assuming that we have approximately constant heating rate (i.e., $\dot{T}_p = \text{constant}$) and the particles do not change size during heating, and the background gas temperature remains constant.

Thus it can be seen that, for a given final particle temperature,

$$\phi = A \dot{T}_p + B \quad (2-18)$$

where A and B are constants. Using Eqs. (2-14 to 2-18), the required flow rates can be calculated for given required heating rates and realistic values of laser beam depth. Typical design conditions are shown in Figure 2-16. For gas sampling purposes, λ should not be less than 1.0 cm. For efficient use of the carrier gas, the nozzle depth should be as small as is feasible. In addition to the carrier gas, a shield gas flow is required. To minimize residence time errors, the flow velocity of the shield flow is matched to that of the carrier gas. This defines the shield gas flow requirements for a given geometry. The width of the shield flow nozzle is more arbitrary than for the coal/carrier nozzle. However, a reasonable value of 2.0 cm gap between inner and outer walls has been chosen. As can be seen, the carrier flow requirements are small, being of order 10 scfm. However, the shield gas flow rates are much greater than the carrier flow rates, and dominate the design of the flow system. The nominal design conditions of a carrier gas nozzle dimension of 3.0 cm appears adequate for most of the range of conditions considered. At the low heating rate conditions, this test section is sufficiently large that no significant loss of experimental resolution is lost by using a smaller test section than the analysis would indicate.

2.4.2 Coal Feed System

The selection of the type of coal feed device is predicted by total coal mass flow rate requirements. For the scale of experiment that is feasible, the flow rates are of order 10 gm/min. Under these conditions, rotating feeders are not acceptable. In consequence, a fluidized bed feeder was designed. This is illustrated schematically in Figure 2-17. The feeder sits upon a precision-weight scale. The fluidizing gas flows through the bed, and

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HEATING RATE T_p (K/sec)	BEAM LENGTH L (cm)	NOZZLE WIDTH S (cm)	BEAM DEPTH 1 (cm)	CARRIER FLOW RATE SCFM	SHIELD FLOW RATE SCFM
10^4	12.0	4.0	4	3.4	13.7
3×10^4	11.4	3.9	3	8.9	37.2
5×10^4	8.8	3.2	3	7.9	40.4
10^5	8.5	3.1	2	14.5	75.4
2×10^5	4.9	2.2	2	8.6	67.7
5×10^5	4.3	2.0	1	16.7	142.0
10^6	2.3	1.6	1	9.7	123.0

BASED ON 10 KW LASER POWER

K9205

Figure 2-16 Design Conditions

J 8222

Figure 2-17 Fluidized Coal Feeder

Figure 2-18 Coal Feeder

coal plus gas is asperated into the main part of the carrier stream. An additional gas exhaust post was installed in the roof of the bed in order to provide additional control of flow rate, but it was found that this was not necessary.

The feeder was constructed from plexiglass and is illustrated in Figure 2-18. The control of mass loading/flow rate was performed by altering the position of the exhaust tube relative to the collapsed bed surface.

2.4.3 Flow System Calibration

The coal feed device was tested and appeared to work very satisfactorily. However, the dynamic response of the weight scale digital readout was not fast enough for our requirements. This has necessitated use of the analogue readout capability of the device. Unfortunately, this device originally did not have the capability to tare out the initial value as does the scale's own digital readout, limiting our capability to measure very low flow rates as accurately as we would wish. The manufacturer modified the scale to our specifications, in order to counteract this problem. Typical calibration results are shown in Figure 2-19. There is some scatter about a linear rate of change in scale reading, especially so at early times when the change is small. This is most likely an artifact of the previously described scale-reading problem. However, the flow rates do appear to be reasonably stable and constant. Further calibrations were carried out when the scale had been modified, using the analogue readout to drive a chart recorder, to check that flow stability is at its required level for the experiment. This is illustrated in Figure 2-20, and it shows that the flow is very stable.

Figure 2-19 Typical Feeder Calibration

K9208

Figure 2-20 Typical Flow Rate as Function of Time

Spatial and temporal stability of the nozzle coal flow has also been investigated. Figure 2-21 illustrates the spatial uniformity of the coal particle number density across the jet. This was obtained by utilizing attenuation of a He-Ne laser beam across the jet. The central region of the jet is remarkably uniform, with roughly 10% fluctuations being observed. At the edges of the orifice, the density does drop off. There also appears to be a slight shift in density to the lower side of the nozzle, which would appear due to gravitational settling. However, the nozzle flow appears adequately uniform for use in the experimental program.

2.4.4 Laser Optics

During the early design phase, it was believed that the use of the available laser power could be maximized by reflecting the beam back through the test section and, in effect, doubling the effective power of the system. This also had the effect of making a more uniform irradiation of the particles. This, as well as some other optical design concepts, was found to be severely limited by geometrical and accessibility issues. In fact, these two issues were the driving forces behind the eventual optical system.

These problems of accessibility are described in detail in Section 2.4.9 where we describe the integration of all the subsystems into the experimental facility. The cause of the problem is that there are a number of diagnostic devices that have to be placed in the vicinity of the laser heating zone. As mentioned earlier, the probe requires the use of shield mirrors to prevent its damage by the laser radiation. In addition, LDV and two-color pyrometer optics require access to the heating zone. The geometry issue is a function of the test cell dimensions and optical component focal lengths. The latter is also impacted by the accessibility of the diagnostics to the measuring volume.

Figure 2-21 Spatial Uniformity of the Coal Particles in the Nozzle

The fundamental issue, when designing a suitable mirror assembly to deliver the required flux to the test section, is that of obtaining a useful beam profile from the laser. The HPL[®] laser has an unstable resonator construction, leading to an annular output beam shape. In addition, flux non-uniformity occurs across the cavity. The technique of obtaining a uniform flux density over a well defined spot is that of beam integration. By overlapping segments of the original output beam, a uniform flux can be obtained at the focal plane of the integrating mirror. For our purposes, a uniform flux profile is advantageous. The original conceptual framework for flux density profiles was that of beam tailoring, with nonuniform distribution, to achieve well-defined and specified thermal histories. However, this was found to be subject to severe limitations. Particle shattering, swelling and mass loss rate are unknown prior to actual experimentation and have significant impact upon thermal history of the particles. Preselection of flux contours thus appeared less attractive than had been originally thought. In addition, it became apparent that the particular constraints imposed by the laser itself make it cost-effective to use a uniform flux density distribution.

The implementation of the basic optical system is shown schematically in Figure 2-22. The laser output beam is directed to the beam integrator, which focuses and overlaps segments of the annular beam. This integrated beam is directed to a concave mirror, which re-images the uniform flux distribution upon a prismatic mirror assembly. This splits the beam into two parts and changes the beam shape from square to the required rectangular one. The beams are then re-imaged at the test section by means of concave mirrors. This is the basic optical system.

J9920

Figure 2-22 Optical System Design

The initial optical system designed for the delivery of laser power to the test section was found to possess a severe astigmatic aberration problem. Although the system should in principle work adequately, the constraints, imposed by a degree of inflexibility in mounting the mirrors, rendered it impossible to use without some modification.

The solution to the problem, although relatively straightforward, did require redesign of one optical component and produced an attendant delay arising out of fabrication. The component in question was the beam-dividing roof prism. By suitably increasing the pitch angle of the mirror, the previous problems could be eliminated completely. Unfortunately, no such mirror has been available from stock. Because such mirrors require to be cooled during operation, their fabrication requires an internal coolant flow system. A schematic of the mirror is shown in Figure 2-23. The new mirror was constructed from OHFC copper.

The integration of the new mirror into the optical train proved very successful. Beam delivery was found to be straightforward, albeit timeconsuming for alignment purposes, with up to eleven elements having to be brought into alignment consecutively.

2.4.5 Beam Dump

Use of the high power laser implies use of a final energy-absorbing surface, or beam dump. The operation of the two-color pyrometer imposes a constraint upon the operation of the beam dumps. Beam dumps normally have high surface temperatures ($\sim 1000^{\circ}\text{C}$) and this usually presents no problem. However, for our specific application, the surface temperature of the dump has to be as low as possible, in order to prevent excessive noise levels for the

Figure 2-23 Roof Prism Mirror Design

pyrometer. The beam dumps developed for this program consist of a water-cooled copper plate coated with a thin layer of zirconium dioxide (Figure 2-24). These were fabricated using a castable refractory powder, as has been used in our high-temperature combustor development programs. This design has been found to work well. The nature of the optical system, with its beam integration technique, allows for a divergence of the beam elements at the face of the beam dump. This condition provides a low average radiant flux density ($\sim 50 \text{ W/cm}^2$). However, there are usually one or two "hot spots" in the laser beam which replicate on the beam dump. The dumps have proved to be reliable and durable.

2.4.6 Laser Doppler Velocimeter

The LDV used in this program was a TSI one-component optical system using photomultiplier detection. The laser used was a Spectra Physics 15 mW He-Ne operating at 6328 Å. This was used because of constraints imposed by geometric difficulties in placement of the optical components, which indicated the need for the high power of this laser. The details of implementation of this are to be found in Section 2.4.8. The data processing was performed by a TSI Counter system with analog output. For the problem in question, a simple output is sufficient since the flow is essentially within the potential core of the jet. Both time average and rms velocity data were obtained.

2.4.7 Two-Color Pyrometer

2.4.7.1 Design Approach

Our existing capability for temperature measurement was found to be not directly applicable to the range of interest in this experiment. The small optical path and low temperatures (700K - 1500 K) necessitated a significant upgrading of both equipment and approach.

K2445

Figure 2-24 Laser Beam Dump Design

The low signal levels expected from the dilute coal stream necessitate the use of cooled high gain photomultiplier tubes operating in the near IR ($\sim 0.7 - 0.9 \mu\text{m}$). The pyrometer system is shown schematically in Figure 2-25. It consists of two photomultipliers in thermoelectrically cooled housings. The thermal radiation from the particles is passed through a series of neutral density filters, mounted on a wheel driven by a stepping motor in order to maintain signal levels below saturation throughout the temperature range of interest.

The radiation is split and directed through interference filters to the photomultipliers. The signal-to-noise characteristics of the system are augmented by means of lock-in amplifiers and a signal chopping device. The output of the two amplifiers is then ratioed by an analog circuit, from which the temperature can be analytically determined.

The low signal levels inherent in the system imply that the test cell be protected from stray ambient light. This fact necessitates the enclosure of the test region and the diagnostics inside a light-shielded box. Obviously, the requirement for laser power injection renders it extremely difficult to completely exclude all ambient light, but suitable baffling and shielding in the test cell eliminates this as a problem.

The particular photomultiplier type chosen for this application is an RCA C310345 tube with S-20 cathodes. This has excellent noise characteristics and good spectral performance. The analysis of the pyrometer requirements and operating characteristics are described in the following section.

2.4.7.2 Pyrometer Design Analysis

In the low wavelength limit ($h\nu/kT \gg 1$), the average particle emits photons at the rate of

J9926

Figure 2-25 Two Color Pyrometer Schematic

$$\frac{n_p}{4\pi a^2} = f(\nu)\Delta\Omega$$

where $4\pi a^2$ is the surface area of the particle, $\Delta\nu$ the bandwidth of the emission and $\Delta\Omega$ the solid angle of radiation collection. The function $f(\nu)$ is given by

$$f(\nu) = 2e\nu^2 \exp(-h\nu/kT) \langle \cos\theta \rangle / c$$

where

$$\langle \cos\theta \rangle = \frac{1}{\Delta\Omega} \int_{\Omega\Delta} \cos\theta \, d\theta$$

which is approximately unity for conditions of interest.

The total signal delivered to the detector is thus given by

$$n_L = NAhn_p$$

where h is the smaller of the depth of field or width of particle stream, a is the area in the object plane, and N is the number density of particles. The number of photoelectrons then generated by a photodetector is given by

$$n_e = \eta n_L$$

where η is the quantum efficiency, α is the duty cycle loading (i.e., fraction of time that the detector receives signal from the particles) and t is the optics transmission. It should be noted that the effective field of view of the system $A\Delta\Omega$ is directly equivalent to that at the image plane, $A'\Delta\Omega'$.

For representative conditions, of $N \sim 400/\text{cm}^3$ (i.e., approximately 3-percent mass loading and 50 μm particle diameter), $f/8$ optics of 5 cm diameter, and a flow depth, h , of 1 cm, we can obtain the signal strength of a photodetector. Using a 6-percent transmission through the optics, a 10-percent quantum efficiency and 50 percent duty cycle, we obtain

$$n_e \sim 10^6 \left(\frac{v}{c}\right)^2 \exp(-h\nu/kT)$$

(v/c) being in inverse centimeters.

This is plotted in Figure 2-26 as a function of temperature. The limits imposed by the device upon temperature are given by the maximum anode current of the device and the dark current. The anode current is given by

$$I_A = n_e g e$$

where g is the gain of the device and e is the charge per electron. For RCA C31034 low noise, high gain photomultiplier (with extended infrared capability using an S-20 cathode), the maximum current is $\sim 0.1 \mu\text{A}$, giving $n_e \sim 10^6/\text{s}$. The dark current is typically $5 \times 10^{-6} \mu\text{A}$ at -70°C . This gives an operating

Figure 2-26 Two Color Pyrometer Operating Map

regime as plotted in Figure 2-26. It can be seen that temperatures in excess of 700 K are accessible. At 22°C, the dark current is 10 nA. This would, as can be seen in Figure 2-26, increase significantly the minimum observable temperature as well as providing significant problems with lack of dynamic range. At high temperatures, neutral density filters are necessary if damage to the device is to be avoided.

The wavelength selection for the devices in the two-color system is governed by the acceptable ratio between the two signals. This is given by

$$r_{1,2} = \frac{v_1^2}{v_2^2} \exp(-h(v_2 - v_1)/kT)$$

The acceptability of the signal ratio is governed by the required resolution of the temperature; i.e.,

$$\Delta r = \left(\frac{dr}{dT}\right) \Delta T$$

giving

$$\frac{\Delta r}{r} = \frac{h(v_2 - v_1)}{kT} \cdot \frac{\Delta T}{T}$$

Thus, for a reading error of

$$\frac{\Delta r}{r} = 1.0 \times \frac{\Delta T}{T}$$

we require $\lambda_2 - \lambda_1 \sim 400\text{\AA}$. Thus, a 1 percent reading error corresponds to a 1 percent error in temperature. Likewise, an 800 Å wavelength difference yields a 1/2 percent error in temperature for a 1 percent reading error.

2.4.7.3 Instrument Construction and Calibration

A photograph of the device is shown in Figure 2-27 and a schematic of the entire system is shown in Figure 2-28. The entire detection element of the system is enclosed in an optically shielded box, which is mounted upon an optical table. The entrance slit is shielded by a remotely controlled shutter. The incoming radiation passes through a filter wheel, giving a dynamic range of 10^8 in attenuation. The filter wheel is controlled by a stepping motor and filter position displayed on a light board. The beam, after splitting and focusing, is directed through the narrow band filters onto the photomultiplier faces. The photomultiplier tubes are cooled to -20°C by thermoelectric cooling elements with a convective water flow heat sink. As a consequence, the photomultiplier housing windows have to be heated in order to prevent condensation interfacing with operation of the device. This improves dark current performance by factors greater than two orders of magnitude as compared to ambient. In fact, use of both cooled tubes and the neutral density filter wheel are the means by which the whole technique becomes viable; without either of these devices, the dynamic range of the phototube is not wide enough for the system to be workable. For run-to-run reproducibility, the photomultipliers are driven by one power supply using a voltage divider, in order that no gain errors creep into the system.

Figure 2-27 Photograph of Two Color Pyrometer

Figure 2-28 Schematic of Two Color Pyrometer

With the use of the lock-in amplifiers, referenced to the chopping wheel, the system has successfully been operated at 600 K, using a reference black-body source. With more fine tuning, a slightly lower temperature could be accessible. This translates to a lower bound on operation, for the actual coal flow experiment, of ~ 800 K. Using a blackbody source, calibration curve have been obtained. As can be seen in Figure 2-29, the signal ratio measured has a slope in precise agreement with the theoretical value ($=h\Delta\nu/k$). The actual value of the ratio is different from the theoretical value as a consequence of the different transmission behavior of the optical component at the two wavelengths (7600°A and 8400°A with 100 A bandwidths).

2.4.8 Sampling Probes

The original concept of sample capture was centered upon the use of an adiabatic catalytic sampling probe (Figure 2-30). This use of this probe was believed to offer potential in providing an overall mass conversion by pyrolysis. The use of a sintered metal side wall suction ring, along with a rounded tip was believed to avoid accumulation of partially reacted coal on the sampling surface. The sinter material was chosen to have a $5\text{ }\mu\text{m}$ pore size that was large enough to allow access of product, but block the coal particles.

The catalytic part of the probe required the use of electrical power to provide a modest ($\sim 100^\circ\text{C}$) temperature rise. It was this fact that was found to be the cause of the problems with the probe. Bench-testing of the probe was carried out with a representative mixture of light hydrocarbon gases diluted by nitrogen. The probe, when being heated to catalyze the gases with the oxygen stream, became blocked rapidly. The cause of this block was eventually found to be the sintered element of the probe. The electrical heating of the

Figure 2-29 Typical Pyrometer Calibration Curve

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Figure 2-30 Catalytic Sampling Probe

probe was sufficient to cause cracking of hydrocarbon gases inside the sintered elements, which led to rapid blockage. It was decided that this approach was realistically unworkable, and further efforts were abandoned.

It had been recognized early in the program that the heating process by laser is very different from conventional heating. The coal particles are the only part of the flow that is heated. Some conduction from the particles to the carrier gas occurs, but the overall temperature rise is small, at the heating rates of interest (Figure 2-10). The realization that the quench times for both products and coal particles, upon leaving the irradiation zone, are very short offered the potential for a very simple probe design. Conventional quench probes require small diameters in order to promote rapid diffusion of heat from the gas to the walls. The water-spray-cooled probe of Howard and associates was felt to be an unnecessary complication for this experiment in view of the rapid quench rates inherent in the carrier gas temperature deficit relative to the particles. The probe design was therefore a simple large bore tube (~ 5 mm) of stainless steel, enclosed in a two-mirror protective jacket to prevent heating of the probe by the laser (Figure 2-31). The mirrors are water-cooled copper plates, the cooling tubes being soldered to the back of the plate. The plates were kept sufficiently far from the probe to minimize flow perturbation (typically, ~ 5 cm, which puts them at the edge of the shield gas flow).

The probe was found to perform excellently, giving little deposition internally and few problems. The major problem was that of char buildup at the tip, which, as described in Section 4.0, was solved by moving the probe downstream relative to the mirrors by a distance of 0.5-1.0 cm.

Figure 2-31 Sampling Probe and Shield Mirrors

2.4.9 Facility Integration

As has been pointed out earlier, the integration of each of the subsystems provided some significant difficulties at the design stage as a consequence of geometric and access constraints. The immediate vicinity of the heating zone must allow access by two high power CO_2 laser beams, the LDV probe beams and scattered signal, the thermal radiation signal to the pyrometer, as well as the sampling probe and its pair of shield mirrors. The requirement for spatial scanning of the laser heating region necessitates all the diagnostics being movable relative to the CO_2 beams.

The above issues were solved using the following approach. The two-color pyrometer is too heavy and too bulky to be moved without any problem of alignment and stability becoming excessive. The diagnostics were thus mounted upon a rigid frame that keeps the pyrometer in a fixed location (Figure 2-32). The table has a one-degree-of-freedom traverse attached to it, which allows the focal volume of the pyrometer to be moved along the flow direction. This is illustrated in Figure 2-33. It can be seen that the optical system is constructed as a collimating telescope, whereby the horizontal motion of the transverse, as driven by a stepping motor, allows the location of the focal volume to be moved along the flow axis. In addition, the use of the collimation system allows the pyrometer to be calibrated by means of a blackbody source without change of alignment.

The LDV system is also mounted upon the traverse. This proved to be the most troublesome part of the diagnostics integration. The presence of two incoming and two outgoing CO_2 laser beams precluded the horizontal mounting of the LDV optical axis, as would be conventionally used. The large particle

Figure 2-32 Experimental Diagnostics Configuration

A) PYROMETER FOCUSING SYSTEM

B) PYROMETER CALIBRATION SYSTEM

K2440

Figure 2-33 Schematic of Diagnostics Optical System

sizes made it somewhat limiting to operate in a backscatter mode and the vertical orientation is affected by presence of the pyrometer optics as well as CO₂ laser optics above the test section. The chosen solution is illustrated in Figure 2-34. Both receiving and transmitting optics for the LDV were mounted on the traverse bed. The light scattered from the probe volume is redirected by means of a small front surface mirror into the detection system. This proved to be the only effective placement of the LDV system and, after some initial mounting problems proved to be a very stable system. Figure 2-35 shows a photograph of the diagnostics system.

The system was found to operate well and optical stability was eventually achieved (see Section 4.0). All the subsystems were found to operate together with minimal interference. Alignment of probe, LDV and pyrometer could be performed in a straightforward manner. The only major problem was the precise and careful alignment required by the laser optical system. This proved to be a rate-limiting step in setting up the experiment. A photograph of the rig in operation is shown in Figure 2-36. The LDV beams are clearly discernable, as is the thermal re-radiation from the hot coal particles passing through the high power beams.

K2439

Figure 2-34 Schematic of LDV-CO₂ Laser Integration

Figure 2-35 Photograph of Diagnostics System

Figure 2-36 Photograph of Experiment in Operation

3.0 MODELLING OF THE PYROLYSIS PROCESS

3.1 INTRODUCTION

The reduction of data is made most effective if a full mathematical description of the processes can be matched to the experimental observations. The complexity of the mathematical description requires implementation of a numerical analysis. The existing AERL coal pyrolysis/combustion code, which is described in detail in Appendix A, was found not to be optimal for the particular case of laser heating. It was then necessary to build a new code that could provide an effective tool in data analysis. In addition, it served a further purpose in that it enabled the potential sensitivities of the experiment to operating parameters to be scoped, and therefore, to provide a better basis for choice of operating conditions.

3.2 ANALYTIC FORMULATION OF LASER INDUCED PYROLYSIS

3.2.1 Code Formulations

The underlying requirements of the code are that it is capable of handling the following conditions:

- Laser flux density as an arbitrary function of time or temperature
- Swelling of coal, which is essentially a diameter change with temperature
- Multiple competing or parallel reactions
- Condensation of volatile species in cooler gas phase

The governing equations are based upon the following assumptions:

- Uniform surface heating, particle temperature and volatile release.

The heating and temperature uniformity are acceptable at all but the highest heating rates. The uniform volatile release is suspect in view of the Sandia Laboratory observations of "jet" effects. However, such behavior is far from tractable at this time and the assumption of uniform surface behavior is a reasonable approximation.

- Gas and particles of all sizes travel with same velocity. The gas is transparent to the laser radiation. Scattering of radiation by the particles is assumed negligible.
- Specific heat of volatiles is equal to specific heat of gas.
- Power to swell coal is negligible.
- Constant pressure in gas phase.

The following sections describe the conservation equations used in the analysis.

3.2.2 Energy Balance - Solid Phase

The rate of change of temperature of a given particle size is given by

$$m_{s,i} c_{p,s} \frac{dT_{s,i}}{dt} = q_R'' \frac{\pi d_{s,i}^2}{4} n_p - q_{conv,i} i - \sum (m_{v,n})_i h_{p,n} \quad (3-1)$$

$$- \epsilon \pi d_{s,i}^2 (T_{s,i}^4 - T_R^4)$$

where

$m_{s,i}$, mass of solid particle at any time t for n th particle

c_{ps} , specific heat of solid

T_s , temperature of solid.

q_R'' , laser flux per pass, generally imposed as a function of time or temperature to control temperature

n_p , number of passes

$d_{s,i}$, ith particle diameter at any time t

$$d_{s,i} = (d_{s,i})_0 \left\{ 1 + (SW-1) \cdot X_v \right\} \quad (3-2)$$

$(d_{s,i})_0$, particle diameter at $t = 0$

SW, swelling index (based upon ratio of final to initial particle diameter)

X_v , fraction of mass volatized

$q_{conv,i}$, heat transferred from solid gas

$$= \pi k \sum F_{Knud,i} F_{B,i} (T_{s,i} - T_g) Nu_i d_{s,i}$$

where

k = thermal

T_g , gas temperature

$F_{Knud,i}$, correction due to Knudsen

$$= 1 - 1/(1 + 0.17 \frac{d_{s,i}}{\lambda_m})$$

$$Nu_i = (2 + 0.6 Re_i^{1/2})$$

- λ_m , mean free path
 Re_i , Reynolds number
 $F_{B,i}$, Correction due to blowing

$$F_{B,i} = \frac{C_{p,v} m_{v,i} / \pi \lambda \mu_i d_{s,i}}{[\exp (C_{p,v} m_{v,i} / \pi \lambda \mu_i d_{s,i}) - 1]}$$

- σ , Stefan-Boltzmann constant, $5.67 \times 10^{-12} \text{ w/cm}^2 \text{K}^4$
 ϵ , emissivity of the particle
 T_R , temperature of radiation background

3.2.3 Energy Balance - Gas Phase

Consider energy change in a small length in the flow direction, ΔX ,

$$\dot{m}_g \Delta (C_{pg} T_g) = q'' A \Delta X \quad (3-3)$$

where q'' is the heat generated per unit volume.

Multiplying both sides by ρ

$$\frac{\dot{m}_g}{A} \frac{\Delta}{\Delta X} (C_{pg} T_g) = q_{\text{conv},i} n_i + \sum F_{c,i} m_{v,i} n_i H_c \quad (3-4)$$

where

- C_{pg} specific heat of gas
 $F_{c,i}$ fraction of volatiles condensed in gas phase
 H_c heat of condensation
 n_i number of particles per g mixture

$q_{\text{conv},i}$, heat transferred by each particle to gas phase.

if we assume that all particles travel with same velocity. If such an assumption is not made, then large particles contribute heat in different locations to smaller particles. Under the conditions of the experiment, it is expected that such an assumption is valid.

$$f_g \frac{d}{dt} (C_{pg} T_g) = \sum_i q_{\text{conv},i} n_i + \sum F_{c,i} H_c m_{v,i} n_i \quad (3-5)$$

where

$\Delta X_s = V \Delta t$

V , velocity of the mixture

f_g , mass fraction of gas in mixture of gas and particles, m_g/m

T_g , gas temperature

n_i , number of particles of size $d_{s,i}$ per unit mass

$m_s = A_p V$

3.2.4 Mass Balance - Solid Phase

Consider a particle of size $d_{s,i}$. Mass loss rate due to each competing reaction is

$$\begin{aligned} -\dot{m}_{n,i} &= m_{cu,i} \alpha_n B_n \exp(-E_n/RT_{s,i}) \\ m_{cu,i} &= -m_{s,0} \sum B_n \exp(-E_n/RT_{s,i}) \end{aligned} \quad (3-6)$$

where

$\dot{m}_n$ mass loss rate from coal due to nth competing reaction

α_n stoichiometric coefficients (or stoichiometric volatile yield by route n)

m_{cu} mass which remains undecomposed

B_n frequency factor for n th competing reaction

E_n activation energy for pyrolysis

Total mass loss rate for each particle of size $d_{s,i}$ is then given by

$$\dot{m}_{v,i} = \frac{dm_i}{dt} = \sum_n \dot{m}_{n,i} \quad (3-7)$$

3.2.5 Overall Mass Balance

The total volatile mass liberated by particles of all sizes given by

$$\dot{m}_v = \sum_i \frac{dm_i}{dt} (1 - F_{c,i}) \quad (3-8)$$

where $F_{c,i}$ fraction condensed as liquid or solid. Hence net rate of mass gain by gas phase within a distance of ΔX is given by

$$\Delta \dot{m}_g = \dot{m}_v'' A \Delta X$$

where $\dot{m}_v''$, net volatiles liberated per unit volume in space.

$$\frac{\Delta \dot{m}_g}{A \rho \Delta X} = \sum \dot{m}_{v,i} n_i \quad (3-9)$$

$m_{v,i}$, net volatiles liberated per unit time per particle

n_i number of particles per unit mas of mixture

Again, if I assume that all particles travel with same velocity, then

$$\frac{\Delta f_g}{\Delta t} = \sum m_{v,i} n_i (1 - F_{c,i}) \quad (3-10)$$

3.3 CONSERVATION EQUATIONS IN NONDIMENSIONAL FORM

Reference Quantities

The equation from (1) to (10) are normalized with the following reference quantities.

Temperature:

$$T_r = \frac{\epsilon q_{R,IN}^M}{4Nu_n k} \quad (3-11)$$

where

$q_{R,in}$ Initial radiation flux per pass

ϵ_L absorbtivity of particles in the wave length of range of

M median size of a given distribution; for monosized stream $M =$

$(d_{s,i})_0$, initial particle size

Nu_n reference Musselt Number = 2

Size: $d_r = M$

Time $t_r = C_{p,s} m_M / \pi Nu_n k M \quad (3-12)$

where

m_M , mass of median size

$$\text{Heat: } Q_r = C_{p,s} T_r \quad (3-13)$$

Activation Energy

$$E_r = RT_r \quad (3-14)$$

Define the following:

$$m_i^* = m_i / m_M \quad (3-15)$$

$$m^* = m t_r / m_M \quad (3-15a)$$

$$d_i^* = d_{s,i} / M \quad (3-16)$$

$$n_i^* = n_i m_M \quad (3-16a)$$

$$F_{\text{Knud},i} = 1 - \frac{\lambda_m^*}{\lambda_m^* + .17 d_i^*} \quad (3-17)$$

$$\lambda_m = \lambda / M$$

$$H^* = H / C_{ps} T_r$$

$$f_{B,i} = e^{n_i} - 1$$

$$\sigma = q_R / q_R^{\text{ref}}, m$$

$$n_i = \frac{dm_i}{d} \frac{C_{p,v}}{C_{p,s}} [d_i^* (2 + 0.6 \text{Re}_i^{1/2})] / \text{Nu}_n \quad (3-18)$$

$$\tau = t / t_r \quad (3-19)$$

$$\theta = T / T_r \quad (3-20)$$

$D_R = \epsilon \sigma M T_n^3 / \lambda \mu_n$, radiation Damkohler number

$D_n = B_n t_r$, Damkohler number for pyrolysis (ratio of heating time of particle to pyrolysis time)

$$E^* = E/RT_r \quad (3-21)$$

We can then rewrite the conservation equations in the following form:

Energy-Solid

$$\begin{aligned} m_i^* \frac{d\theta_i}{d\tau} = & d_i^{*2} (n_p \phi - F_{Knud,i} f_{B,i} (\theta_i - \theta_g) \frac{\mu_i}{d_i \mu_r} - Q_{v,i} / d_i^{*2} \\ & - D_R (\theta_i^4 - \theta_R^4) , i = 1 \dots N \end{aligned} \quad (3-22)$$

where

$$Q_{v,i} = \sum_n \frac{m_{vm} t_r}{m_M} \frac{R_{p,n}}{C_{p,s} T_r} \quad (3-23)$$

Energy - Gas

$$\begin{aligned} \frac{d\theta_g}{d\tau} = & \frac{1}{f_g} \left[+ \frac{C_{p,s}}{C_{p,v}} F_{Knud,i} f_{B,i} (\theta_i - \theta_g) \frac{\mu_i d_i^* n_i}{\mu_r} \right. \\ & \left. + \frac{C_{p,s}}{C_{p,v}} F_{c,i} H_c^* m_{v,i}^* n_i^* \right] \end{aligned} \quad (3-24)$$

Mass - Solid

Volatile Mass liberation rate due to competing route n:

$$(m_{v,n})_i = + f_{cu,i} m_i^* D_n \alpha_n e^{-E_n / \theta_i} \quad (3-25)$$

Net volatiles liberation rate due to all competing reactions

$$-\frac{dm_i}{d\tau} = m_{v,i}^* = + \sum_n (m_{v,n})_i \quad (3-26)$$
$$\sum_n f_{cu,i} m_i^* D_n \alpha_n e^{-E_n / \theta_i}$$

$$\frac{df_{cu,i}}{d\tau} = - f_{cu,i} \sum_n D_n e^{-E_n / \theta_i} \quad (3-27)$$

Mass - Gas

$$\frac{df_g}{d\tau} = \sum_i m_{v,i}^* n_i^* (1 - F_{c,i}) \quad (3-28)$$

3.4 NUMERICAL APPROACH

For each particle size we have three differential equations (Eqs. (22), (26) and (27)). Further we have two additional differential equations (Eqs. (24) and (28)) for gas phase. Thus, if there are N sizes in a given distribution, then total number of differential equations is $(3N + 2)$. These differential equations are presented in subroutine DIFF (Figure 1). The DIFF subroutine demands the output for all competing reactions (see Eq. (26)),

which is separately computed in subroutine COMPR. The energy balance equation for solid phase (Eq. (A.22)) needs the distribution profile for laser flux ϕ as a function of time or temperature. The distribution profile is given in the function subroutine F(x).

The integration is by 4th order Runge-Kutta method in the first four time steps. Four derivatives are computed for each time interval. After the 4th time step, the Adams' Predictor-Corrector method is used for integration, if the step size remains constant. When the step size has to be reduced (i.e., when volatile liberation rate curve is very steep) during integration, the integration switches back to the 4th order Runge-Kutta method. If step size remains constant beyond four consecutive time steps, further integration precedes according to Predictor-Corrector method. The time step is adjusted according to allowable decomposition mass (Δf_{cu}) within the time step ($\Delta \tau$).

The two reasons for using the Predictor-Corrector method are: first, it is quite fast compared to Runge-Kutta method (fewer number of calculations for derivatives), which is an important consideration when one has 23 differential equations; and second, accuracy is comparable to the Runge-Kutta method since it corrects for local truncation effects as the integration proceeds.

The results in nondimensional form are then converted back to real variables and printed out.

3.5 CODE TESTING

As pointed out earlier, the realistic dispersion of particle sizes will lead to dispersion of particle temperatures. The code has been exercised to obtain estimates of this, both upon pyrolysis yields and upon the measured temperatures (Figure 3-1).

Figure 3-1 Effect of Coal Size Dispersion Upon Measured Temperature

The original concept of nonuniform flux density distribution in the test series was found to be unviable (cf Section 2.0). The laser heating scenarios subsequently envisaged are illustrated in Figure 3-2. In the first case, the flux is to be made uniform; in the second, the use of a second uniform flux or lower level is envisaged. In the first case, particle temperatures will increase until termination of the flux; changes in particle injection velocity will result in changing final temperature. The second case will allow, in principle, for a maintenance of the maximum temperatures. This is illustrated more fully in Figure 3-3. The particles are initially heated by a flux of 1000 W/cm^2 and, upon reaching a specified temperature, the flux is reduced to 500 W/cm^2 . The subsequent particle temperatures show an eventual increase, consequent of both continuing pyrolysis mass loss and background heating. The 1400 K case has an initial drop in temperature as it has almost completely pyrolysed by this point (see Figure 3-4). The yields can be seen to be strongly influenced by the maximum temperatures achieved. The result of turning off the flux upon reaching the specified temperatures can be seen in Figure 3-5. The final yields can be seen to be dramatically affected by the thermal history after reaching the specified maximum temperature. This appeared to be a useful means of promoting sensitivity of the data to kinetic rates, and use of these two schemes together was thought to be capable of enhancing our data interpretation.

As would be expected, the detailed behavior of the pyrolysis is strongly influenced by the detailed kinetic mechanism. The above results were obtained with competing reaction scheme, at nominal kinetic rates based upon existing AERL data for high-volatile bituminous coal. Changes in kinetic constants can

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Figure 3-2 Laser-Heating Scenarios

Figure 3-3 Coal Thermal History

Figure 3-4 Coal Devolatilization History

Figure 3-5 Effect of Flux Turndown.

dramatically alter out a sensitivity analysis of the thermal and pyrolysis response to changes in kinetic constants.

The actual flux profile was a slightly smoothed saw tooth - as opposed to uniform-flux. A representative particle size distributoin was used (see Chapter IV) and the thermal history of such a laser heating computed for a variety of conditions. It is important to note that the particle absorption cross section, as given by its normalized form with respect to geometric cross section, is essentially uniform about 10 μm diameter (Figure 3-6). This curve was computed using Mie Theory by H.P. Chou.

The one that has an impact upon code use is that of the gaseous thermal conductivity. The modeling requires a constant value to be used; indeed, the model precludes the computation of the complex non-uniform and transient environment around the coal particles. The gas is asymptotically at room temperature far away from the surface of the particle. Thus, the effective value used to describe the conduction heat loss from the particle can dramatically influence the predicted thermal histories using room temperature or, approximately, the median particle temperature (100 K) values of 3×10^4 and 6×10^4 W/cm K leads to significant differences (Figures 3-7 and 3-8). What is clear from both of these computations is that gas temperature is very nearly constant through the heating. The highly logarithmic temperature profile outside of the particle, coupled with the low gas temperature, leads us to infer that the lower temperature value is probably more reasonable in this particular experimental scenario.

The flux density used in these experiments is, realistically, known only to 20 percent accuracy. Figures 3-9 and 3-7 show the impact of such a flux

Figure 3-6 Particle Absorption Cross Section

Figure 3-7 Thermal History $\bar{\Phi} = 800 \text{ W/cm}^2$, $k = 3 \times 10^{-4} \text{ W/cmK}$

Figure 3-8. Thermal History $\bar{\phi} = 800 \text{ W/cm}^2$, $k = 6 \times 10^{-4} \text{ W/cmK}$

K9196

Figure 3-9 Thermal History $\bar{\Phi} = 800$ W/cm², $k = 6 \times 10^{-4}$ W/cmK

density difference. The "experimental" size distribution averaged radiation temperature that would be seen by the two-color pyrometer can be seen to drop from a 2700°K peak, at 800 W/cm² coverage flux, to 1750°K at 600 W/cm². Similarly, for the low conductivity value, the variation between 500-600 W/cm² can be seen in Figures 3-10 and 3-11.

All the above curves show the marked impact of flux reduction upon "experimental" temperature, with it falling much more rapidly than that of the larger particle sizes. The curves also clearly show that the smaller size particles do not heat up to temperatures that are likely to play a role in the pyrolysis under the short timescales. This is, of course, the inverse of hot gas heating. Here it is the larger particles that will play a significant role in the devolatilization process.

Figure 3-10 Thermal History $\bar{\Phi} = 550 \text{ W/cm}^2$, $k = 3 \times 10^{-4} \text{ W/cm K}$

K9198

Figure 3-11 Thermal History $\bar{\Phi} = 600 \text{ W/cm}^2$, $k = 3 \times 10^{-4} \text{ W/cmK}$

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4.0 EXPERIMENTAL RESULT

4.1 INTRODUCTION

The scope of the experimental testing was curtailed by problems associated with the laser facility but nevertheless, the data obtained were of a very surprising and valuable nature. The following sections will describe the problems associated with the laser test facility and their impact upon the testing, and a detailed evaluation of the experimental data and their interpretation.

4.2 FACILITY ISSUES

The progress of the experimental program was curtailed by a series of sequential problems with the laser test facility. The first problem to arise was that of a beam locational hypothesis; on a test-to-test basis, the location of the test region, as defined by the crossing of the two high-power laser beams, was found to change and, in addition, the beams were found to move relative to one another. At first sight, this appeared to be only a simple matter of mirror stability within the test cell with, perhaps, a mirror incorrectly mounted. However, on performing a series of careful checks of the optical system, no such problem could be found and the entire system was performing perfectly. It was, therefore, concluded that the problem had to lie in the laser beam delivery system that directs the beam from the laser cavity to the the test cells. Because of the necessary safety requirements for dealing with such an intense laser beam, the system is equipped with a number of interlocks and beam control devices that prevent accidental irradiation of the

test cells. The particular element of the system that was found to be the cause of the problems was the test cell director mirror (Figure 4-1), which, by means of its pneumatic actuation system, enables or prevents laser energy access to the cell. The mirror is mounted upon a slide whereby, upon request and under control of the safety interlock system, it can be pneumatically moved to intercept the beam and directed into the cell. It was found that the control and actuation system was undergoing a degradation of performance, allowing a slight rotation of the mirror each time the system was operated, thereby causing the beam alignment to change.

This problem was obviously a facility issue and did not come within the scope of this program, and it was agreed that it would be solved at no cost to the program. This was done and the system subsequently performed adequately.

After the aforementioned issues had been resolved, a scheduled shutdown of the experiment was due to occur, as a consequence of commitment of the laser facility to other programs. During this period, however, problems arose with respect to the laser itself. For the previous five months, apart from routine maintenance and short duration repairs the laser had performed very well. At this time, the laser developed both contamination and arcing problems. This meant that a complete overhaul and examination were necessary. These problems were overcome, but their effect proved to be long-lasting in their effect upon scheduling of this and other programs. The system downtime caused a significant backlog of scheduled work of which this program comprises but a part, and a delay of several months resulted.

K3750

Figure 4-1 Test Facility Optical System

4.3 EXPERIMENTAL TESTING

4.3.1 Introduction

These problems severely reduced the progress of the experimental program. In addition, the remaining funding enabled only two further short duration test periods to be possible. The first of these provided limited data when some experimental difficulties were encountered. The second provided a limited but very significant and unexpected data set.

In view of the surprising and significant nature of the results, AERL provided additional funding to obtain further data with additional coal types. However, only a partial analysis of these data has been possible at this time.

4.3.2 Experimental Testing

Initial testing was carried out using a Pittsburgh No. 8 coal type. The flowing coal stream, on passing through the laser, was found to stick to the probe and build up a layer that would eventually protrude into the laser beam. This then caused heating and damage to the probe. This problem was solved by moving the probe back with respect to the shield mirrors. The distance between the end of the heating zone and the probe was typically ~ 5 mm. (It was found that the distance was required to be larger for bituminous coals than for sub-bituminous coals.) This distance corresponds to approximately an e-folding of particle temperature.

Only a few test samples were obtained during this test period. These results were surprising in that gas chromatographic analysis indicated the presence of no detectable hydrocarbon product. This was interpreted initially as a possible problem with laser/flow alignment and the data discarded as

being suspect. However, in the light of subsequent data it becomes significant. For subsequent testing the alignment of the probe with respect to the coal stream and laser heating zone, was very carefully checked.

The conditions for this second test series were as follows:

- Nominal laser power: ~ 5 kW
- Beam dimensions: 1.2 cm x 3.0 cm
- Nominal average flux density: 700 W/cm²
- Residence time in beam: 11-16 msec
- Coal: Wyoming Sub-bituminous, d ≈ 35 μm.

The laser focal region was approximately triangular in flux density profile, as determined from plexiglass burn patterns, giving a maximum flux density of ~ 1200-1600 W/cm² at peak. It is difficult to be any more precise than this owing to the uncertainties in total power delivered to the test section, the total beam losses at the mirrors and the resolution of the burn pattern. For example, total delivered power, owing to variations in mirror reflectivity arising from the cleanliness problems of the mirrors in the test cell may be as large as ±10 percent.

Two sets of data were obtained: one with nitrogen carrier gas; the other with a 91/9 mix of N₂ and CO₂. This latter was an attempt to evaluate possible volatile stabilization effects. Gas and particle samples were obtained.

4.3.3 Temperature Data

The mean temperature data for the two runs are shown in Figure 2-2. The nominal residence time is plotted as x-coordinate. The error in this time scale is 2-4 msec's owing to low power leading edge effects of the laser beam.

Figure 4-2 Temperature Data for Wyoming Subbituminous Coal

The nominal leading edge was taken with respect to the central high flux sawtooth profile. However, there is a spillover of flux at the upstream edge which will cause significant preheating. The observed mean temperatures as computed from plots of the pyrometer signal ratio can be seen to be as high as 1800 K, with the temperature peak occurring in the middle of the irradiation zone, as would be expected from modeling of the sawtooth flux distribution and a representative particle size distribution (see Figure 4-3). The mean temperature is subject to a ± 50 K error, but more important is the significant fluctuation in temperatures with time (Figure 4-4). The rms levels are typically ~ 100 K, but at early times appear to be significantly larger. The reasons for this behavior are not clear, but several explanations are possible. The measured rms turbulence levels in the jet are higher than expected, being ~ 10 percent, if this is due to large scale structure in the jet, the residence times likewise has an inherent ± 10 percent error, with a consequent variation in temperature of order 100 K being possible. The pyrometer, which images a thin slice of the laser region of width ~ 1 mm (giving a ± 0.3 msec resolution) is not subject to error in arising from particle size density or signal intensity. However, changes in the local particle size distribution can lead to a significant variation in observed mean temperature. As the signal intensity ratio is given by an integrated, surface area averaged value, changes in mean particle size will alter the thermal history of the particles. A ± 10 percent change in particle size will give up to ± 100 K variation in observed mean temperature during the laser heating. In addition, laser power fluctuation of a few percent were noted during the experiments, which would lead to a corresponding level of ~ 50 K fluctuations in temperature.

Figure 4-3 . Computed Temperature Profiles for Size-Averaged Radiation Temperature and Individual Particle Sizes

Figure 4-4 Temperature Fluctuations

Using existing kinetic rate data, the combination of the above temperatures and residence times should lead to significant devolatilization.

4.3.4 Gas Chromatography

The sampled gases were collected in one-liter flasks at pressures up to 400 torr. These were then analyzed by gas chromatography. Calibration, using previously mixed samples of dilute hydrocarbons in a nitrogen carrier, as would be representative of the expected pyrolysis product, was carried out and detection limits for each species obtained. This was typically 0.01 percent by volume. For the coal mass loadings used in the experiments, this would result in a minimum detectable devolatilization between 2 and 4 percent.

The results were uniformly surprising, as shown in Figure 4-5. No detectable devolatilization was observed. The only species detected, other than nitrogen or the added carbon dioxide carrier gas, was water vapor, at levels commensurate with the coal moisture levels. Under the conditions of heating and residence time, this is a very unexpected and surprising result, and was viewed with dismay initially, as had been the earlier tests. However, it was felt that there was an underlying physical explanation rather than a source of experimental error, and solids analysis was carried out.

4.3.5 Solids Analysis

Both proximate and ultimate analyses were carried out on all samples. Each sample was typically ~ 1-2 gms in mass and a small fraction of this used in both of these tests. The proximate analysis, using a PE T95-2 Thermogravimetric system, yielded more surprising data. The residual matter, within the limits of experimental error and repeatability of the tests, did not show any change in proximate yield of volatiles. With raw coal, the yield of volatiles

H₂O — COMMENSURATE WITH COAL MOISTURE

H₂
CO₂
CO
CH₄
C₂H₂
C₂H₄
C₃H₄
C₃H₆
C₃H₈
C₄H₁₀ ETC.
H₂S
COS

— NOT DETECTABLE

— THIS WOULD IMPLY LESS THAN
2-4% OF COAL IS CONVERTED
TO LIGHT VOLATILES

K7606

Figure 4-5 Chromatography Results

was 37.9 ± 0.5 percent. All other samples had values between 36.4 and 38.9 percent (see Figures 4-6 and 4-7). With regard to the possible mass loss during pyrolysis, it was found that the ash content of the samples was essentially constant. The ultimate analysis showed a correspondingly similar behavior (Figure 4-8).

At this point, it was felt that the analysis of the samples was incomplete and that further types of analysis were necessary. A cursory evaluation could have been that experimental error had lead to these "erroneous" results. However, the laser heated samples themselves were visually different from the raw coal (Figure 4-9). The fine particulate structure of the raw coal was not present in the heated samples. These had a clumped and sticky quality with a distinct color change from black to a dark brown. It was strongly felt that these had been significantly changed in the structure of the coal.

An examination of the residue particle size distribution showed no major changes through the heating process. The observed distributions are shown in Figures 4-10 and 4-11. The difference between the two test runs is a consequence of a loading of the feed hopper between runs and subsequent change in the size distribution. Several of the samples indicated that there were large numbers of very small particles present, but as they were smaller than the $0.5 \mu\text{m}$ resolution limit of the optical counter, they could not be counted. This would be indicative of soot or condensate from the pyrolysis process or perhaps fragments of shattered particle.

At this point it was decided that FTIR spectroscopy, as suggested by Dr. Peter Solomon of Advanced Fuels Research, Inc. may indicate if structural

WYOMING SUBBITUMINOUS COAL WITH LASER HEATING

BACKGROUND GAS 91% N₂, 9% CO₂

MASS LOADING ≈ 0.026

TIME (msec)	PARTICLE TEMPERATURE (K)	SOLUBILITY % WGT, DAF	MOISTURE*%	VOLATILE* YIELD %	FIXED* CARBON %	ASH* %
0 (RAW COAL)	300K	3 - 7	2.8	37.9	48.8	10.6
2.5	1680 ± 60	8 - 12	3.3	37.3	48.1	11.3
10	1780 ± 50	45 - 51	2.0	38.8	48.9	10.3
12	1440 ± 35	19 - 36	2.7	37.8	48.1	11.5
16	1264 ± 40	10 - 22	1.6	38.9	48.9	10.6

*REPEATABILITY ± 0.5%

K7607

Figure 4-6 Solid Analysis of Wyoming Samples

BACKGROUND GAS N_2
 MASS LOADING ≈ 0.037

TIME (MSEC)	PARTICLE TEMPERATURE	SOLUBILITY % WGT DAF	MOISTURE* %	VOLATILE YIFID* %	FIXED CARBON* %	ASH* %
0 (RAW COAL)	300 K	3 - 7	2.8	37.9	48.8	10.6
3.5	1665 $\pm$ 100	8 - 14	2.3	38.3	48.1	11.4
6	1450 $\pm$ 36	10	3.1	36.4	47.8	12.7
8.5	—	14 - 16	2.2	37.3	48.8	12.2
11	1340 $\pm$ 40	27	2.0	38.2	47.7	12.2

*REPEATABILITY $\pm 0.5\%$

K8364

Figure 4-7 Solids Analysis of Wyoming Samples

BACKGROUND GAS 91% N₂ 9% CO₂

MASS LOADING $\approx$ 0.026

RESIDENCE TIME (MSEC)	CARBON %	HYDROGEN %	NITROGEN %
0 (RAW COAL)	64.9 $\pm$ 0.3	4.34 $\pm$ 0.03	1.14 $\pm$ 0.04
2.5	64.2 $\pm$ 0.2	4.02 $\pm$ 0.05	1.22 $\pm$ 0.06
10	66.0 $\pm$ 0.8	4.05 $\pm$ 0.09	1.20 $\pm$ 0.03
12	64.5 $\pm$ 0.1	4.18 $\pm$ 0.09	1.43 $\pm$ 0.27
16	66.5 $\pm$ 0.3	3.95 $\pm$ 0.02	1.19 $\pm$ 0.04

SAMPLES WERE DRIED AT 110°C FOR TWO HOURS PRIOR TO ANALYSIS.

K8363

Figure 4-8 Ultimate Analysis of Wyoming Samples

Figure 4-9 Photographs of Raw and Laser-Heated Samples

Figure 4-10 Particle Size Distribution

Figure 4-11 Particle Size Distribution

changes had occurred in the coal. Accordingly, Dr. Solomon provided an analysis of three samples; viz., a raw coal sample, the 11 msec/ N_2 sample and the 16 msec/ $N_2 + CO_2$ sample. No significant changes could be observed between the heat-treated coals and the raw coals.

In the light of all the above negative evidence, indicating the surprising and the unexpected result that no change had occurred, it was suggested that an organic solubility test be carried out on the samples. Therefore, a series of solvent extractions was carried out, predominantly with Tetrahydrofuran ($CH_2(CH_2)_2CH_2.O$) but also with methyl ethyl ketone. These were carried out using a Soxhlet extractor, refluxing for two hours at 1 atm. The coal samples partially dissolved in the organic solvent, giving a brown clear liquid, which was subsequently dried in an oven for an excess of 12 hours at $70^\circ C$. The viscous black tarry residue was then weighed, then replaced in the oven and reweighed until the residue weight asymptoted. The results of this test were very surprising (Figure 4-12) and showed that the heat-treated coal was substantially different from the raw coal. The solubility of the raw coal was typically 5 to 7 percent. The laser heated samples showed very much higher levels of solubility, reaching as high as 50 percent on a dry-ash-free basis. This would indicate that the coal has undergone significant physical reorganization, as the raw coal did not show substantial yield and would indicate that the source of the solute is a devolatilization mechanism. The few MEK solvent extractions performed showed very similar yields to that of the THF extractions.

A further test was performed, albeit a qualitative one, upon the 10 msec/ $N_2 + CO_2$ sample. A 100 mg quantity of the coal was placed in

Figure 4-12 Solubility of Laser-Heated Coals in THF

100 ml of 0.1 normal sodium hydroxide and gently heated for a period of two hours. At the end of this time, the alkaline solution had become dark brown in color. The alkali was neutralized with dilute nitric acid, after first filtering out solid coal residue with 0.5 μm filters. Within a short time, the solution precipitated out a very finely dispersed brown particulate material, within the colorless fluid. These particles were very fine, being significantly below the limit of resolution of optical microscopes (i.e., $\ll 1 \mu\text{m}$). This is very interesting in the light of further AERL funded tests whereby a very small sample of laser heated material was captured. In this case, the load of solid-per-unit area of filter was low, such that the occurrence of typical coal particle, (~ 30 to $40 \mu\text{m}$ diameter) was less than one at any filter location, as opposed to the rather densely packed samples typically obtained). In this case, the filter was covered with very fine dispersed light brown particles. This strongly suggests the existence of condensed devolatilization products.

4.3.6 Data Interpretation

The data and analysis provide several very surprising features as follows:

- No light hydrocarbon, hydrogen, carbon oxides or sulphurs gases were detected. In the light of many investigations [See, for example, Kimber and Gray, Solomon, Solomon and Colket, Suuberg, et al., (1978)], this appears, at first sight, contradictory.
- The FTIR analysis indicates no detectable change in the bonding structure of the laser-heated coal residue as compared to the raw coal. Again, this is different from observations using conventional heating techniques (Solomon) whereby significant differences are seen between the unreacted and reacted coals.

- The proximate and ultimate analyses reinforce the observation of no gas yield, in that they indicate no significant loss of hydrocarbon material from the coal samples collected.
- Visual inspection of the heated coals clearly indicates that physical changes have occurred, including This strongly suggests the existence of condensed devolatilization products. the generation of a very fine particulate phase.
- The solubility of the heated coals was very much greater than that of the raw coal.

Under the constraints imposed by these results and many other observations using conventional heating techniques and high heating rate experiments, it is possible to construct a consistent hypothesis of the physical mechanisms of the observed behavior. This hypothesis is illustrated schematically in Figure 4-13. A similar hypothesis has been suggested by Suuberg et al.

There is one major difference in the experimental environment imposed by the laser-heating experiment as compared to all other devolatilization experiments. This is the nature of the gaseous background. Conventional heating imposes a hot background gas environment upon the devolatilization experiments. In this experiment, the gas is heated by conductive loss from the particles, the temperature rise is very small at the experimental heating rates ($\sim 0(10)$ K at $\sim 0(10^5)$ K/s). Thus, any product species leaving the particles becomes very rapidly quenched to near-ambient temperatures. The characteristic timescale for quenching is given by

$$\tau_{\text{quench}} = \frac{(\rho c) a^2}{3k}$$

K7605

Figure 4-13 Hypothesis of Devolatilization Mechanisms

where (ρc) is the volumetric specific heat of the product, a is the size of the fragment of product material, and k is the thermal conductivity of the gaseous medium. For an assumed liquid/tar product of the same density and specific heat as the coal, the characteristic quench timescales are of order 10^{-5} sec for a $1\text{ }\mu\text{m}$ diameter particle and 1 msec for a $10\text{ }\mu\text{m}$ diameter particle. For gas phase products, the timescales would drop by approximately three orders of magnitude for equivalent sizes of product cloud. Therefore, it becomes clear that what we have observed in these experiments is what might be termed primary high heating rate devolatilization products. It would appear clear that these primary products are being stabilized by rapid quenching and condense and are therefore collected along with the char, giving a material that essentially contains all the carbonaceous matter of the raw coal. Samuelson et al., have observed holographically that clouds of small particles were produced using combustion, which they suggested were soot. In the light of these investigations, their data are very suggestive of the above behavior.

This material, which apparently has the same bond structural framework as the raw coal, as implied by the FTIR analysis, coats the outside of the char particles or turns its own particles through condensation. It is, therefore, far more easily soluble than would be the parent coal. There is evidence that shows that tar does have a similar physical structure and composition to that of the parent coal (Solomon and Colket), and are what may be termed representative "monomers" of the coal "polymer". The above evidence, in addition to the fact that the proximate yield of volatiles is unchanged, strongly suggests that under these high heating rate and high temperature conditions, the devolatilization process is not one of pyrolysis but of evaporation of the

characteristic high molecular weight building blocks of the parent coal. At low reaction temperatures and heating rates, the more classic pyrolysis behavior is dominant with polymeric cross linking, leading to relatively low gas yields and high char yields. Under the high heating rate, high temperature conditions, the classic observations of Kimber and Gray and Kobayashi, et al., where high gas phase yields are observed, are consistent with the hypothesis of these high molecular weight building blocks being reacted in the hot gaseous background and stabilized as low molecular weight products. Indeed, it is plausible that at slightly low temperatures such primary volatile products crack in a manner akin to the low heating rate, low temperature kinetics, leaving a soot and char solid residue, and reducing the gaseous yield.

4.4 AERL-FUNDED EXPERIMENTS

4.4.1 Introduction

Owing to lack of funds, it was not possible to collect any further data or perform any further analysis. The implications of the data, albeit being of limited quantity, were so novel and potentially important that it was felt that additional data collection was necessary. To this end, AERL funded a further set of data collection and analysis. Because of its consistency and collaboration with the data of this program it is included in this report, and it reinforces the postulated model of high heating rate devolatilization described in the previous section.

4.4.2 Experimental Conditions

The limited residence times of the prior testing directed us to choose a larger value for these tests. Typically, this was 30 msec. A small quantity of Wyoming Subituminous were used for a limited data set. However, most of

the data was obtained with Montana Rosebud Subbituminous and Pittsburgh No. 8 bituminous coals.

Coal loadings were chosen to be higher than in the previous runs, as the potential gas phase yields would be larger and hence easier to detect. Typically, these mass loadings were in the range of 5 to 7 percent. It was difficult to operate the fluidized bed repeatably at these conditions and, although stable operation was achieved during each run, sequential runs were subject to variations. This should not, however, have any impact on the validity of the data.

The laser operating conditions were, for the most part, similar to that of the previous tests, with the same nominal beam area at the test section being used. However, the residence times were increased by reduction in both shield and carrier flow rates.

4.4.3 Experimental Data

4.4.3.1 Gas Analysis

The collection of gas samples provided a very similar result to the previous data set. Both Pittsburgh No. 8 and Montana Rosebud samples showed no trace of small hydrocarbons using the same gas chromatographic approach as before. Owing to the higher coal loadings, this indicated that no more than 1 to 2 percent of the coal material entered the gas phase. However, it was felt that additional gas phase data should be obtained if possible, using flame ionization detectors. This was performed for two samples: a Wyoming sample, with peak temperature of ≈ 1700 K and ~ 30 msec residence time; and a Pittsburgh No. 8 sample at ≈ 1560 K and ~ 30 msec. Not surprisingly, the content of small hydrocarbon was small (Figure 4-14). In both cases, the most

abundant species was methane. The total carbon conversion equivalent of the detected gases can be seen to be < 0.2 percent for the Wyoming and 0.01 percent for the Pittsburgh No. 8. This reinforces the prior data and the conclusion that little primary gas phase species are formed.

4.4.3.2 Solids Analysis

Both proximate and ultimate analyses were carried out on a representative selection of the solids samples obtained. These data are shown in Figures 4-15 and 4-16 for Pittsburgh No. 8 and Figures 4-17 and 4-18 for the Rosebud. There appears to be no great change in the proximate analyses as compared with the raw coal, with differences being comparable to repeatability and variability in the samples. There is a possible trend of some hydrogen loss in the case of the Pittsburgh coal, but in view of the repeatability issues, this cannot be substantiated.

Again, these data strongly support the previous Wyoming data and, in view of the maximum observed mean temperatures and ~30 msec residence times, classical heating techniques would have shown significant gas phase yields and changes in char composition.

The Wyoming data taken during this test-series further substantiate the postulated model of primary product evolution. Several samples were obtained with temperatures in excess of 1700 K and between 20-30 msec residence time. Unlike the other samples, where the necessity for analysis required large samples to be obtained, these samples were very small (~ 100 mg). Consequently, the density of the sample on the filter surface was very low. The samples have the appearance of a very fine light brown powder. One of these samples was used for an ultimate analysis and gave results very similar to that of raw Wyoming (see Figure 4-8).

	CONCENTRATION (PPM)						
	CH ₄	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄
SAMPLE # 1 WYOMING (1700K, 30 ms)	49.7	2	16.4	7.6	5.0	2.0	ND
SAMPLE # 11 PITT # 8 (1560K, 30 ms)	8.9	ND	2	ND	ND	ND	ND

ND = < 1 PPM RESOLUTION LIMIT OF INSTRUMENT

SAMPLE # 1: AT 2.5% MASS LOADING $\Rightarrow$ LESS THAN 0.2% CARBON CONVERSION
TO GAS PHASE

SAMPLE # 11: AT 7.5% MASS LOADING $\Rightarrow$ LESS THAN 0.01% CARBON CONVERSION
TO GAS PHASE

K9200

Figure 4-14 Gas Chromatographic Data for Pittsburgh No. 8 and Wyoming Coals

PITTSBURGH # 8
NITROGEN CARRIER

SAMPLE #	RESIDENCE TIME (MSECS)	MASS LOADING %	TEMPERATURE (K)	SOLUBILITY % WGT DAF	PROXIMATE ANALYSIS WGT %			
					MOISTURE*	VOLATILE YIELD*	FIXED CARBON*	ASH*
RAW COAL	-	-	-	4 - 9	1.4	39.0	53.4	6.2
15	4.6	42	1930 ± 300	7	1.4	39.0	53.0	6.6
16	21.8	3.3	1570 ± 75	14 - 18	1.6	39.0	53.5	6.0
17	14.8	5.1	1330 ± 40	15 - 17	1.4	38.6	54.0	6.1
18	6.9	5.9	1585 ± 20	11 - 17	0.8	39.2	53.5	6.5
19	27.6	5.8	2090 ± 120	24 - 27	0.6	38.8	55.8	6.7

*REPEATABILITY ± 0.5%

K9202

Figure 4-15 Proximate Analysis of Pittsburgh No. 8 Samples

PITTSBURGH # 8: ULTIMATE ANALYSIS (DRIED SAMPLES)

SAMPLE #	WGT %					
	RESIDENCE TIME (MSECS)	CARBON	HYDROGEN	NITROGEN	SULFER	ASH
RAW COAL	0	75.2 ± 0.1	5.03 ± 0.01	1.58 ± 0.04	0.25 ± 0.1	6.14 ± 0.02
15	4.8	74.9 ± 0.1	5.23 ± 0.8	1.79 ± 0.50	0.28 ± 0.1	6.72 ± 0.15
18	6.9	74.9 ± 0.2	4.71 ± 0.03	1.72 ± 0.02	0.20 ± 0.02	6.62 ± 0.14
17	14.8	76.0 ± 0.1	4.76 ± 0.04	1.86 ± 0.40	0.18 ± 0.05	6.74 ± 0.01
16	21.8	75.3 ± 0.3	4.72 ± 0.05	1.84 ± 0.05	0.08 ± 0.01	6.06 ± 0.20
19	27.6	76.4 ± 0.2	4.38 ± 0.30	1.62 ± 0.30	0.15 ± 0.05	5.85 ± 0.05

K9203

Figure 4-16 Ultimate Analysis of Pittsburgh No. 8 Samples

**MONTANA ROSEBUD
NITROGEN CARRIER**

SAMPLE #	RESIDENCE TIME (MSECS)	MASS LOADING %	TEMPERATURE (K)	SOLUBILITY % WGT DAF	PROXIMATE ANALYSIS WGT %			
					MOISTURE*	VOLATILE YIELD*	FIXED CARBON*	ASH*
RAW COAL	0	—	—	3	9.7	34.6	42.0	13.7
22	13.8	7.1	1660 ± 130	11 - 12	4.8	31.9	46.2	17.1
24	13.8	5.9	1390 ± 40	8 - 10	5.5	35.0	43.0	16.9

* REPEATABILITY ± 0.5%

K9201

Figure 4-17 Proximate Analysis of Montana Rosebud Samples

MONTANA ROSEBUD ULTIMATE ANALYSIS (DRIED SAMPLES)

SAMPLE #	WGT %				
	CARBON	HYDROGEN	NITROGEN	SULFER	ASH
RAW COAL	59.3 ± 0.1	2.94 ± 0.01	0.82 ± 0.14	0.29 ± 0.12	16.4 ± 0.3
22	57.0 ± 0.7	3.34 ± 0.10	0.61 ± 0.12	0.17 ± 0.06	14.8 ± 1.6
24	57.6 ± 0.3	3.62 ± 0.10	0.85 ± 0.01	0.12 ± 0.03	12.5 ± 0.3

K9204

Figure 4-18 Ultimate Analysis of Montana Rosebud Samples

Sample (20 msec, 1700 K)	Carbon	68.0 percent
	Hydrogen	5.31 percent
	Nitrogen	1.15 percent
	Ash	10.0 percent

It should be noted that both the carbon and hydrogen contents are slightly higher than the raw coal. The H/C ratio is higher than for the raw coal. However, this is possibly due to the small sample size available for analysis.

A series of solvent extractions was performed, using the previously described procedure and tetrahydrofuran. The resulting solute yields are illustrated in Figures 4-19 and 4-20. Again, we see a pattern similar to the previous results, with substantially higher yields being obtained than for the raw coals. The yields for the Pittsburgh No. 8 were similar to the previously obtained Wyoming data. However, the Rosebud yields were substantially lower (~ 15 percent). This may be explained in part by the lower particle temperatures measured for the Rosebud tests as compared to some of the Pittsburgh. There was a slight variation in particle size distribution for the two coals ($d \approx 32 \mu\text{m}$ for Pittsburgh No. 8, and $\sim 38 \mu\text{m}$ for Rosebud).

The data in Figure 4-19 indicate that no clear-cut temperature dependence is apparent. In view of the difficulties associated with the experiment and the uncertainties arising out of particle size effects, this is not too surprising.

The composition of the extract from the THF tests was found to be significantly different from the parent coal. This is illustrated in Figure 4-21 for Pittsburgh No. 8. The H/C and N/C ratios are given for the raw coal and

K9209

Figure 4-19 Pittsburgh No. 8 THF Extraction

Figure 4-20 Montana Rosebud THF Extraction

SAMPLE	ATOMIC RATIOS	
	H/C	N/C
RAW COAL	0.803	0.0089
RAW COAL THF EXTRACT (6.8%)	1.288	0.0048
RAW COAL THF RESIDUE (93.2%)	0.806	0.0173
SAMPLE # 19	0.729	0.0176
SAMPLE # 19 THF EXTRACT (24.3%)	0.954	0.0127
SAMPLE # 19 THF RESIDUE (75.7%)	0.697	0.0172
SAMPLE # 17	0.752	0.0210
SAMPLE # 17 THF EXTRACT (15.8%)	0.945	0.0139
SAMPLE # 17 THF RESIDUE (84.2%)	0.764	0.0222

K9206

Figure 4-21 H/C and N/C Ratios in Pittsburgh No. 8

two heated samples (No. 17, 14.8 msec, 1330 K and ~ 19, 27.6 msec, 2090 K). The extract from the raw coal, although small in quantity (~ 6.8 percent) is rich in hydrogen. The heated samples show a lower hydrogen content in the extract as compared to the raw coal extract but, nonetheless, show a marked increase as compared to the untreated coal sample. There is also an indication that the extract is low in nitrogen. However, the variability between samples prevents further conclusions being drawn from the data.

A further test was performed upon these two Pitt. No. 8 samples. The extract was examined for molecular weight distribution using gel permeation chromatography. These tests were carried out with reference to a polystyrene standard. The size distributions are shown in Figure 4-22 for sample No. 17. The upper trace is for an extraction as generally performed, using hot condensate of THF with prolonged drying at 100°C. The distribution is bimodal, with peaks at ~ 1000 and 30,000; the number mean is 1120 and the mass mean is 32,800. This is similar to that obtained with the raw coal extract (650 and 38,300 respectively). However, the prolonged heating at 100°C for the drying of the samples was an issue with respect to possible repolymerization of the solute material. Consequently, a separate extraction and drying was done, using a room-temperature drying of the THF/solute mix. This was carried out with a nitrogen purge over the sample to enhance evaporation of the THF. It was found that the high molecular weight peak did not occur in this case, yielding a significantly lower number and mass mean size of 223 and 394, respectively. This would substantiate the hypothesis that the high molecular peak was caused by repolymerization. The cold extraction indicates that molecular weights of 600 to 3,000 are present. This is very similar to the data of

K9207

Figure 4-22 Molecular Weight Distributions

Unger and Suuberg. Their data have higher values of molecular weight, but this can be explained in terms of their different reference standards, which were actual coal tar species as opposed to polystyrene. Using the comparison of tar and polystyrene references obtained by Unger and Sullberg, it is possible to produce a qualitative comparison of the two data sets. This is shown in Figure 4-23. The inferred distribution shows no low molecular weight molecules, (< 700), but this is possibly a result of THF peroxide effects. This may result in changes in the relative scales of the two curves. However, the data do suggest the presence of significantly large molecules in the laser-irradiated samples, and may give higher mean molecular weight than the grid-generated tars of Unger and Suuberg.

4.4.3.3 Electron Microscopy

Several of the samples were subjected to high magnification electron microscopy. A fairly consistent pattern emerged. The fine brown powder generated in the Wyoming tests was dispersed in water ultrasonically and deposited upon graphite and dried at 100°C . Figure 4-24 shows the typical result, where clusters of small spherical particles ($\sim 0.1 \mu\text{m}$) form macroparticles of order $1 \mu\text{m}$ in size. Examination of Pittsburgh No. 8 under three physical states provided some interesting data. Raw coal can be seen in Figure 4-25 as compared to a laser-heated sample. It is apparent that the heated particles are covered with a fine dispersion of very fine particles that do not occur on the raw coal. There is also some evidence of blow holes in the particles. The structure of the heated particles can be seen more clearly in Figure 4-26, where the blow holes are clearly evident. The multiple blow hole structure in some of the particles is also clearly seen. These photographs are representative of the solvent extracted coal residue. It can be seen that the fine powder, previously seen in Figure 4-25, is no longer in evidence.

Figure 4-23 Comparison with Data of Unger and Suuberg

1 μ m

WYOMING (SAMPLE #3,1632 K, 20msec)

K9378

Figure 4-24 Fine Particulate Condensate

5 μ m
RAW COAL

5 μ m
SAMPLE #19(2090K,28msec)

K9377

PITTSBURGH #8 COAL

Figure 4-25 Pittsburgh No. 8 Microphotographs

20μm

5μm

**PITTSBURGH #8 THF RESIDUE
(SAMPLE #19)**

K9379

Figure 4-26 Heated Pittsburgh No. 8 Coal Samples

Figure 4-27 illustrates the same behavior for one of the earlier data set samples of Wyoming subbituminous coal. Again, the fine dispersion of particles can be seen on the coal particles, forming lacy networks of submicron material. Multiple blowholes are again in evidence.

The above photographs point towards the same hypothesis as described earlier, in that the particles yield a primary product of high molecular weight for material that escapes from the parent coal and condenses in small particles. The observation of cleanup of the residue surface, as compared to the original sample, would appear to reinforce the concept that it is this "tarrie" primary product that dissolves in the THF.

4.5 KINETIC RATES

The original thrust of this experimental effort was the collection of data that would allow new kinetic rates to be calculated for high heating rate coal devolatilization. The original experimental design was based on this postulation. However, the quite unexpected nature of the experimental data, in that the product of devolatilization was not gaseous, but high molecular weight tars or polymeric material rendered it impossible to obtain kinetic rates. What is important to realize is that the experiment has provided a completely new and unexpected insight into the mechanics of high heating rate coal processing. The presence of a cold background gas, which acts as a quenchant for the products, has provided a unique opportunity to establish that the primary mechanism of high heating rate coal devolatilization is one of high molecular weight evaporation or large fragment separation from the parent coal and not, as has been previously believed, small hydrocarbon gases.

5 μm

10 μm

1 μm

**WYOMING SUBBITUMINOUS
(SAMPLE 6-15, 1780 K, 10 msec)**

Figure 4-27 Wyoming Microphotographs

4.6 CONCLUSIONS

The aforementioned analysis of the laser-heated coals leads us to a novel and important conclusion. Although several authors have been directing their thoughts in the directions indicated by the data, there has, heretofore, been no evidence to substantiate the proposed model of coal devolatilization under high heating rate conditions.

The laser-heated coal samples have provided the following experimental observations:

- Very little gas phase yield was detected from Wyoming and Montana Rosebud Subituminous, and Pittsburgh No. 8 Bituminous coals under conditions of 10-30 msec heating at temperatures in excess of 1400 K. Flame ionization detector chromatography indicates that < 1 percent of the coal carbon is converted to gas phase hydrocarbons.
- Proximate and ultimate analyses are consistent in that they clearly indicate little compositional change from the raw unheated coals, with the exception of moisture content.
- Visual inspection, as well as electron microscopy, clearly show the effects of heating, with a fine particulate phase being generated from the heating. Multiple blowholes are seen in the heated particles.
- FTIR analysis indicates no detectable change in chemical bond structure between heated and raw coals.

- Solubility of the heated samples is markedly enhanced as compared to raw coals. The extract consists of high molecular weight structures (up to 3000) as determined by gel permeation chromatographic analysis. The hydrogen content of the extract is significantly higher than that of the raw coals.

The conclusion of these observations is clearly that the primary product of devolatilization at high heating rates are tars. It is hypothesized that previous observations of gas phase products are purely the consequence of secondary gas phase reactions or secondary decomposition of tar molecules in the hot gas background. This experiment by its very nature provides a very rapid quench of the primary product stream, preventing such reactions to occur.

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APPENDIX A

ENTRAINED PULVERIZED COAL CODE

A.1 NUMERICAL MODEL STRUCTURE

This model was developed to describe the behavior of pulverized coal in simple entrained flow environments. It has evolved from an initial conceptual chemical model and kinetic description of high yield coal devolatilization^(1,2) based upon observations of entrained flow coal pyrolysis behavior in hot inert atmospheres.^(3,4,5) The overall result of this work was a simple and effective kinetic description of coal devolatilization mass yield, capable of treating effects of particle thermal history on instantaneous and integrated mass loss. It is represented by two decomposition reactions of an assumed homogeneous coal "polymer", with both competing for that material. As indicated in Eqs. (A-1) and (A-2), each reaction route proceeds at its temperature-dependent intrinsic rate, to yield a route-specific mix of residual solid material (char) and volatiles. Also, the elemental composition of these products is typically route specific. Based on the experimental results reported here, it appears reasonable to treat the primary volatiles as averaged composition organic structures.

The two competing reactions are taken to be of first order, each degrading coal to residual chars (R_1 and R_2) and volatiles (V_1 and V_2) according to:

where $k_n = B_n \exp [-E_n/RT_c(r_i, t)]$ are the two Arrhenius rate constants, and α_n are the mass stoichiometry coefficients, $n = 1$, and 2 .

Here $T_c(r, t)$ is the temperature of particles of radii r_i , B_n and E_n are pseudo-frequency factors and activation energies, respectively, and R is the gas constant. As discussed below, the particle size dependence of heating rate results in a range of particle decomposition rates and yields, for a typical-size distributed coal grind. There is also, of course, a strong coupling to the thermal environment, as imposed by fluid dynamic, thermochemical, and radiative processes, as well as devolatilization endothermicity.

Heterogeneous reaction of condensed phase material is, of course, the other major mass loss route for a particle. It is discussed in more detail below, but in this numerical model it is based on interactive mixed rate control. This uses species diffusion rate to the particle surface, and single step first order forward reaction kinetics on an assumed rough sphere surface. Because of model applications in very high temperature systems,^(8,9) reactions of char with O_2 , O , OH , H_2O , and CO_2 were formally included, with CO as the product. For most conventional applications, of course, only O_2 appears to be significant, but appropriate rate parameters are still poorly defined.⁽¹⁰⁾ The instantaneous particle energy balance includes the surface reaction exoand endothermicity, which, in

turn, affects rate of particle temperature change, and hence kinetic rates. Effects of mass transfer (blowing), gas phase oxidation reactions, and velocity slip (instantaneous particle Reynolds' number) are also significant, particularly in the mixed reaction regime of transition from devolatilization to heterogeneous CO production.

This description of particle centered reactions could be incorporated in gas phase chemistry and fluid dynamic models covering a wide range of complexity. In this numerical treatment, relatively simple approaches were taken to both. This was done for computational convenience and speed, and because the primary concern is with modeling or correlating overall reaction rate, rather than, for example, kinetically controlled pollutant emissions. Also, the model is oriented about systems for which particle phenomenology provides the basic rate control step.

Gas phase chemistry is assumed to be instantaneous and in thermochemical equilibrium at local gas phase element concentration and specific enthalpy. Species such as NO_x , SO_x , and soot are included at their equilibrium levels. This is consistent with overall rate control by particle reactions. No flame envelope is specifically modeled for the particles. Instead, they are assumed to interact thermally and chemically with the local homogeneous equilibrium gas derived from fluid mixing and reaction of the particle size distribution.

Macroscale fluid dynamics are treated on a Lagrangian basis, using externally imposed fluid mixing rates. The evolution of the coal input stream is tracked, with enthalpy and species input to it from one or two other streams, such as oxidant and recirculated combustion products. Conse-

quently, the reacting stream is instantaneously uniform, without transverse gradient effects. This allows relatively simple time domain modeling of a very complex process for exploration of relative rate control and time scale effects. For many practical systems, in which the general flow and mixing structures are empirically characterized or independently modeled on a multi-dimensional viscous flow basis, the essential fluid dynamic quantities can be usefully approximated as inputs. The specific case discussed below is an example of this approach in swirl stabilized burner stability modeling.

The equation set treated is given below, and discussed in detail elsewhere. (8,11,12)

Devolatilization

Dry, ash-free (daf) coal is represented as $CH_xN_yO_z$, with the organic sulfur content lumped with the oxygen for simplicity. The composition of the volatiles produced is represented by elemental formulae of the form $CH_hN_nO_o$. It is assumed that the residual char consists of a specified C, H, N, O elemental distribution. A mass balance is then used with the α_n values to determine the overall elemental compositions of the two volatiles. This appears consistent with observed residual char composition under high temperature conditions.

The instantaneous mass rates of production of volatiles at time t by reactions represented by Eqs (A-1) and (A-2) are:

$$m_{V,n}(r_i, t) = \alpha_n m_{cu}(r_i, t) k_n, \quad n = 1, 2 \quad (A-3)$$

where the dot represents time rate and m_{cu} is the undegraded daf part of a coal particle of radius r_i , and the symbols used are defined in Table A-1. Integrating Eq. (A-3), we have

$$m_{cu}(r_i, t) = m_{co}(r_i) - \int_0^t \left[\sum_n \dot{m}_{V,n}(r_i, t) / \alpha_n \right] dt \quad (A-4)$$

where $m_{co}(r_i)$ is the initial daf mass of the coal particle. The total daf mass of coal and char is given by:

$$m_c(r_i, t) = m_{co}(r_i) - \int_0^t \left[\sum_n \dot{m}_{V,n}(r_i, t) \right] dt \quad (A-5)$$

In Eqs. (A-4) and (A-5), the initial particle mass is computed from the equation $m_{co}(r_i) = (4/3) \pi r_i^3 \rho_{co} F_V$, where ρ_{co} is the particle density and F_V is a volume factor that accounts for the non-spherical nature of the coal particles.

This same relationship is used subsequently to define $\rho_{ci}(t)$, for a particle radius $r_i(t)$ which is held invariant with respect to pyrolysis mass loss. That is, pyrolysis reactions are assumed to be volumetric at constant particle radius, as a balance between particle swelling and shattering.

The mass fractions of the volatiles produced by the two reactions given by Eqs. (A-1) and (A-2), relative to the total mass of the two phase system are:

$$f_n(t) = f_{co} \sum_i [g_i / m_{co}(r_i)] \int_0^t \dot{m}_{V,n}(r_i, t) dt, \quad (A-6)$$

$n = 1, 2$

Char Oxidation

In general, heterogeneous oxidation of a particle may occur at any time during its reaction history. The instantaneous rate is controlled by a combination of kinetics and diffusive transport. For the particular case of high temperature combustion, it is assumed that reaction occurs on a rough surface equivalent sphere, without significant pore diffusion. In general, heterogeneous reactions may occur not only with O_2 , but also with other major species such as O , OH , H_2O , and CO_2 . As such, the reactions can be either exothermic or endothermic, depending on which of these species diffuses toward and react at the surface of the particle. Heterogeneous kinetic rates are described in terms of single-step Arrhenius kinetics, first order in each reactive species concentration as calculated at the particle surface.

The heterogeneous reaction rate is taken as

$$\dot{m}_{j,i} = k_j Y_{ji} \frac{4\pi r_i^2}{v_j} \quad (A-7)$$

where $\dot{m}_{j,i}$ is the mass consumption rate of species j at the surface of a particle of radius r_i , and $Y_{j,i}$ the mass concentration of j at the surface of that particle. The reaction rate k_j is described as having the temperature dependence

$$k_j = B_j e^{-E_j/RT}$$

where the B_j represent the mass of carbon reacted per unit density of reactant j at the surface per unit surface area-time. The mass concentration of j , relative to its concentration in the local bulk equilibrium gas, is obtained from a balance among surface reaction, diffusion, and mass blowing blockage, which gives

$$\frac{Y_{j,i}}{Y_j} = \frac{e^{-(M_{Hi} + M_{Pi})}}{1 + \frac{k_{ji}}{M_{Hi} + M_{Pi}} \frac{1 - e^{-(M_{Hi} + M_{Pi})}}{1 - e^{-(M_{Hi} + M_{Pi})}}} \quad (A-8)$$

where the M_{Hi} and M_{Pi} are heterogeneous and pyrolysis mass removal rates, respectively, nondimensionalized as

$$M_{(H,P)i} = \frac{\dot{m}_{(H,P)i}}{4\pi\rho D r_i (1+0.3R_e(r_i))^{1/2}} \quad (A-9)$$

$$\dot{m}_{Pi} = \sum_n \dot{m}_{v,n}(r_i, t) \quad (A-10a)$$

$$\dot{m}_{Hi} = \sum_j \dot{m}_{ji} (t) v_j \quad (A-10b)$$

and the v_j are stoichiometric mass coefficients for carbon conversion by the reaction of the j gaseous species with carbon to form CO and H_2 as products. Convection is represented by the term including particle Reynolds number. The kinetic and diffusive rates are described by the K_{ji} as

$$K_{ji} = \frac{r_i k_j}{D(1+0.3R_e (r_i)^{1/2}) v_j} \quad (A-11)$$

While a particle is pyrolyzing, it also may be possible for a diffusion flame to exist around it. Since the minimum local temperature in the absence of a flame is about 1300 K at the surface of a rapidly pyrolyzing particle, it is assumed that such a flame exists. Transport of the oxidizing species to the particle surface can be blocked by this chemical reaction.

The formulation of the chemical blockage is simplified by assuming that the volatiles react completely, but preferentially first with O, then with OH, O_2 , H_2O and finally with CO_2 , with CO and H_2 as products.

The gas phase species that are in excess of the stoichiometry defined by each of these reactions are then assumed to diffuse toward the surface and react heterogeneously to form CO as the end product. This constraint is applied to Eq. (A-7), to eliminate the surface reaction contribution of those diffusing species reduced in the gas phase by pyrolysis products.

Spherical flow symmetry, as assumed both for mass blowing and chemical blockage, may be a gross oversimplification for a pyrolyzing coal particle. A degree of asymmetry of volatile matter distribution around a pyrolyzing particle is observed in holographic particle studies.⁽¹³⁾ This could be argued to imply a relatively limited overall blockage effect. Consequently, this model treats an extreme case of high transport blockage. Equations (A-7) through (A-11) clearly form an implicit set, which must be solved iteratively at each particle and gas environment condition.

Consistent with the assumption of heterogeneous surface reaction, the mass loss $m_{Hi}(t)$ is used to define a new radius for the reacting particle of size group i , as

$$r_i(t) = \left[r_{i0}^3 - \frac{3}{4\pi} \int_0^t \frac{\dot{m}_{Hi}(t)}{\rho_{ci}(t)} dt \right]^{1/3} \quad (A-12)$$

where the instantaneous particle density is determined as described above from pyrolysis mass loss. The mass fraction of carbon reacted heterogeneously is given by

$$f_H(t) = f_{co} \sum_i [g_i/m_{co}(r_i)] \int_0^t \dot{m}_{Hi} dt \quad (A-13)$$

The instantaneous fraction of the mass present as gas consists of contributions from the carrier and oxidizer flow, together with that portion of the coal reacted. It is given by

$$f_g(t) = f_o + f_k + \sum_n f_n(t) + f_H(t) \quad (A-14)$$

The heterogeneous rate control mechanism given above allows continuous transition between pyrolysis and heterogeneous reaction, with both capable of occurring simultaneously on a given particle. Further, the heterogeneous reaction of each oxidizing species is treated with combined rate control, smoothly varying between kinetic and diffusion, as particle temperature increases. Particle temperature is coupled to the overall conductive and reaction enthalpy transport rates for each particle size, as described below.

Heat and Momentum Transfer

The instantaneous particle temperature controls the specific reaction rates through Eqs. (A-3) and (A-7). It is determined from an energy balance for each particle size group. The phenomena included in this balance are: conduction, convection, blowing, pyrolysis endothermicity, heterogeneous reaction, and radiation. The local bulk gas temperature is taken as the source for heat transfer, with no explicit correction for local pyrolysis or oxidation. The resulting relation is

$$q(r_i, t) = 4\pi\lambda r_i (1 + 0.3 R_e (r_i)^{1/2}) \left[\frac{M_{Pi}/L_e}{\exp^{M_{Pi}/L_e} - 1} \right].$$

$$\begin{aligned}
& \left[1 - \left(1 + \frac{0.17}{K_{ni}} \right)^{-1} \right] F_s \left[T_g(t) - T_c(r_i, t) \right] \\
& + \sum_n m_{V,n}(r_i, t) h_n + \sum_j m_{ji} \Delta h_j \\
& + 4\pi r_i^2 \sigma (\epsilon_w T_w^4 - \epsilon_c T_c^4(r_i, t))
\end{aligned} \tag{A-15}$$

where the $m_{V,n}(r_i, t)$ are given by Eq. (A-3), and the m_{ji} are defined by solution of Eqs. (A-7) through (A-11). The heterogeneous contribution to heat transfer blockage has been ignored, relative to the pyrolysis term. The instantaneous heat capacity of the particle is used to define the rate of temperature change as

$$\frac{dT_c(r_i, t)}{dt} = \frac{\dot{q}(r_i, t)}{c_c m_c(r_i, t) + m_{co}(r_i) c_A \frac{\sigma_A}{1 - \sigma_A}} \tag{A-16}$$

Generalized radiative heat transfer is not included in this description. A valid model for it would radically complicate the solution of the combustion problem. A simple limiting case is easily treated, however. Equation (A-15) as written can be interpreted as representing a highly dilute flow, with radiation mean path large relative to the combustor dimensions. Alternatively, the term $\epsilon_w T_w^4$ can be replaced by a sum of

terms representing solid angle contributions from wall and recirculation zone. This allows exploration, for example, of the effect of radiative heat transfer on flame stabilization.

The convective contribution to particle heat transfer is of significance both in rate and extent of pyrolysis, due to the heating rate dependence implicit in Eqs. (A-1) through (A-4). To estimate it, particle velocity relative to the gas flow is determined as the time integral of the instantaneous acceleration. A drag coefficient is chosen to match smooth sphere data in the range $10 \leq Re \leq 10^3$, in the form $C_D = 14.2 Re^{1/2}$, and $Re = 2\rho r_i(u_0 - v)/\mu$. The result is

$$\frac{\Delta V}{u_0} = \left[3.75 \frac{\rho}{\rho_{co}} \left(\frac{\mu}{\rho r_i u_0} \right)^{1/2} \frac{u_0}{r_i} t + 1 \right]^2 \quad (A-17)$$

where it has been assumed that the time scale for particle acceleration is small relative to that for mass loss, to allow explicit integration.

Gas Phase Conservation Relations

The properties of the gas phase in the far field of the reacting particles are described in terms of elemental composition and specific enthalpy. It is assumed that the gas is locally homogeneous, and that gas phase reaction rates are rapid, relative to particle mass loss processes. Based on this, local thermochemical equilibrium is determined for the assigned combustion pressure, to give gas phase temperature and composition.

The flow field is described in terms of one or more gas streams that diffusively mix with the pulverized coal and carrier gas stream. The mixing of these gas streams with the coal-carrier gas stream is approximated by a

cosine function, having a characteristic mixing time. The numerical value of this mixing time is determined by injection conditions such as the type of injectors and flow velocities. This description of mixing results in a temporally varying enthalpy (or temperature) and composition of the gaseous field in the vicinity of each coal particle. In the framework of the mixing field, local plug flow is assumed, with progressive hot gas and oxidizer entrainment up to a limit imposed by overall stoichiometry. Consequently, the environment around each particle evolves during the mixing process, approaching global conditions as mixing approaches completion. Based on this mixing scheme,* a single component is used as an example, rather than two as defined in the code. Following the approach of Ref. 12, the elemental composition of the local gas phase in terms of mass fractions at any instant of time t can be written as:

$$X_k = [X_{k,mix} + X_{k,V} + X_{k,H}]/f_g(t) \quad (A-18)$$

where the contribution by mixing is:

$$X_{k,mix} = (F_o + f_k) X_{kk} (1-g(t)) + (f_o X_{ok} + f_k X_{kk}) g(t)$$

the volatile contribution is

$$X_{k,V} = \sum_n f_n(t) X_{nk}$$

* The implicit assumption of mixing plug flow used here is not consistent with particle slip relative to gas implied in Eq. (A-17). However, the magnitude of this is small, in terms of its effect on the properties of the gas environment of the particle.

and the heterogeneous contribution is:

$$X_{k,H} = f_H(t) \delta_{kc}$$

where $\delta_{kc} = 0$ for $k \neq c$, and $\delta_{kc} = 1$ for carbon, in the case where char is assumed to be carbon. Alternatively, assuming a C, H, O, N composition for char, Eq. (A-13) is modified to describe the instantaneous composition

of each size group i . The time variation of gas injection into the coal/primary stream is given by

$$g(t) = \frac{1}{2} (1 + \cos \frac{\pi t}{2})$$

$$0 \leq t/ \leq 2$$

$$g(t) = 1; t/ > 2$$
(A-19)

The local gas phase specific enthalpy is similarly expressed as:

$$H_g(t) = [H_{mix} + H_{sens} + H_{chem}]/f_g(t)$$
(A-20)

where the contribution by mixing is

$$H_{mix} = (f_o + f_k) H_k (1 - g(t)) + (f_o H_o + f_k H_k) g(t)$$

The sensible enthalpy term is

$$H_{sens} = -f_{co} \sum_i g_i \left[\left(\frac{m_c(r_i, t)}{m_{co}(r_i)} c_c + \frac{\sigma_A}{1 - \sigma_A} c_A \right) T_C(r_i, t) \right. \\ \left. - \left(c_c + \frac{\sigma_A}{1 - \sigma_A} c_A \right) T_{co} \right]$$

and the chemical enthalpy contribution is

$$H_{chem} = \sum_n f_n(t) (\Delta h_n + \Delta H_{Vn})$$

Solution Procedure

Because of the range of particle thermal inertia time scales and steep rate dependence on particle temperature, this is a very "stiff" equation set. Solution is by a fourth order Range-Kutta approximation, with time step size determined at each iteration. This is done by limiting the allowed fractional change in temperature and mass of each particle size group, and calculating the corresponding allowable time step. Upper and lower absolute step size bounds are also imposed. Also, to improve computational efficiency, the instantaneous gas thermochemical equilibrium composition and temperature are calculated in two different ways. The baseline program is a standard complete multi-phase equilibrium code, called as a subroutine (P2161B). It is similar to the commonly used NASA equilibrium code.⁽¹⁴⁾ Because of its relatively long convergence time and the large number of time steps used in a typical Lagrangian calculation (about 2500), a much simpler code has been incorporated as well. It treats only the major products, a water-gas equilibrium, and a first order approximation to their dissociation radicals (subroutine EQU LIB). It is called until gas temperature reaches 1000 K, and subsequently used for N-1 time steps, and the complete code for the Nth time step. Results of the simple code are ratioed to the comprehensive code at the Nth step, which provides updated bias multipliers for the simple code output of the following N-1 steps.

A complete code listing is given below as Table A-4. It includes definitions of terms and internal comments delineating local section and subroutine functions.

A sample case of coal combustion is outlined in Table A-2. It describes input of a primary coal-air stream, and a secondary air stream, to a swirl stabilized burner with recirculation of hot products.

For this example, it is assumed that the primary stream of pulverized coal conveyed in air initially begins mixing with hot combustion products from the recirculation zone, with the mixed fraction of products given by a cosine law, using a $\pi/2$ time scale of 50 ms. After a 20 ms delay, this partially mixed fluid begins to ingest secondary air as well, again on a 50 ms ($\pi/2$), or 100 ms (total) time scale. Subsequently, entrainment of both combustion product and secondary air continues, together with particle and gas phase chemistry. The reaction parameters for the coal devolatilization model, and the size distribution breakdown, are given in Table A-3. It is interesting to note that the volatile yield dependence on thermal history could potentially give two stable operating conditions for a recirculation stabilized burner: high yield, high temperature; and low yield, "smoky flame."

A.2 RESULTS

Output from the code is shown graphically in Figures A-1, A-2, and A-3. The code output is given as Table A-5, with output time results selected for purposes of illustration. Figure A-1 shows the thermal history of the gas in which the coal particles are dispersed, and of three size groups ($d = 30, 60, 130\mu\text{m}$) of the input coal particles. Initial gas heating is driven by mixing hot combustion products with the coal-primary air stream. During this time (0 to ~ 15 ms), particle heating occurs with limited chemical reaction, and local gas stoichiometry (Figure A-3) changes only because

Figure A-1 : Temperature History of Combustion Gas and Reacting Particles Predicted for Recirculation Stabilized Combustor Simulation.

Figure A-2 Fuel Utilization History Predicted for Discrete Particle Size Groups and for Total Coal Input.

Figure A-3 Combustion Gas Stoichiometry and Temperature History Predicted for Recirculation Stabilized Combustor Simulation.

of combustion product mixing with the primary air-coal stream. At longer time ($15 < t < 27$ ms) the finer coal particles are predicted to pyrolyze and combust with the primary air. This drives both local stoichiometry through unity, and forces a transient peak in gas temperature. Secondary air mixing, initiated at 20 ms, is proceeding too slowly to maintain a locally oxidizing environment. Continued devolatilization of large particles dominates in the time period $30 < t < 60$ ms, as shown on Figure A-2, providing a fuel-rich gas ($\phi > 1$) and driving a transient temperature dip in the local gas mixture. Starting at $t > 30$ ms, oxygen supply by secondary air mixing is faster than gas phase fuel evolution, resulting in a decrease in stoichiometry toward unity and an increase in local gas temperature. During this period, with $\phi > 1$, combustion product gas mixing continues as well (to $t = 100$ ms), and heterogeneous char reaction is predicted to be negligible. Figure A-3 shows the gas stoichiometry to shift to oxidizing at about 60 ms, with a continuing weak temperature decrease. Figure A-2 shows the finer particles ($d = 30, 60 \mu\text{m}$) that had completed devolatilization, and were not losing significant mass heterogeneously, to begin rapid mass loss via the carbon-oxygen reaction at about 60 ms. Continuing secondary air injection results in a minimum in stoichiometry and temperature at about 120 ms, when air injection is complete. Subsequent temperature and stoichiometry increase are driven by heterogeneous oxidation of the residual char distribution. Product temperature in the period $t > 200$ ms approximates the initially assumed value of 1700 K, suggesting that it is a stable flame temperature.

TABLE A-1
NOMENCLATURE

B	=	Kinetic rate factor (m/s)
C	=	Specific heat (J/K/kg K)
D	=	Molecular diffusivity (m ² /s)
E	=	Activation energy (kJ/mol)
f	=	Component mass fraction (-)
F	=	Shape factor (-)
g	=	Mixing time dependence function
g _i	=	Mass fraction of coal of radius with g _i =1 (-)
h	=	Enthalpy w.r.t. 0 K (kJ)
H	=	Specific enthalpy w.r.t. 0 K (kJ/kg)
k _j	=	Heterogeneous rate constant (m/s)
k _n	=	Devolatilization rate constant (s ⁻¹)
K _{ji}	=	Damkohlers group (-)
K _n	=	Knudsen number (L/2r)
L	=	Mean free path of gas (m)
L _e	=	Lewis number of gas (-)
m	=	Mass component of a coal or char particle (kg)
m	=	Particle mass loss rate

TABLE A-1

NOMENCLATURE (Continued)

M	=	Dimensionless particle mass loss rate (-)
q	=	Heat transfer rate to particle (kJ/s)
r	=	Particle radius (m)
R	=	Gas constant (8.314×10^{-3} kJ/mol $^{\circ}$ K)
R	=	Residual char (kg)
Re	=	Reynolds number (-)
t	=	Time (s)
T	=	Temperature (K)
u	=	Velocity (m/s)
V	=	Volatiles (kg)
X	=	Gas-phase mass fraction (-)
Y	=	Gas-phase mass concentration (kg/m ³)
α	=	Mass stoichiometry coefficients (-)
δ	=	Kronecker delta (-)
Δh	=	Heat of reaction (kJ/kg)
ΔH	=	Heat of formation at 0 K (kJ/kg)
ϵ	=	Emissivity (-)
λ	=	Thermal conductivity (kJ/mKs)
ν	=	Mass stoichiometry coefficients (-)

TABLE A-1

NOMENCLATURE (Concluded)

μ	= Gas viscosity (kg/ms)
ρ	= Density (kg/m^3)
σ	= Stefan-Boltzmann constant ($5.671 \times 10^{-11} \text{ kJ/m}^2 \text{ K}^4 \text{ s}$)
	= Characteristic mixing time scale (s)
ϕ	= Fraction in daf coal or char (-)

SUBSCRIPTS

A	= Ash
c	= Coal + Char
g	= Gas, far from particle surface
H	= Heterogeneous reaction
i	= Particle size fraction
j	= Gas phase chemical species
k	= Carrier gas, or elemental species
n	= Devolatilization route (1,2)
o	= Initial conditions, Initial hot gases
P	= Pyrolysis reaction
R	= Residual char
s	= Surface
u	= Unreacted
v	= Volume
V	= Volatiles
w	= Wall

TABLE A-2

BASE CONDITIONS USED IN COMPUTER CODE

Equivalence Ratio	0.90
Coal: Primary Air Loading	1:1
$\frac{\text{Primary Air}}{\text{Total Air}}$	9.6
Primary Air Temperature	300 K
Secondary Air Temperature	500 K
Swirl Number	1
RZ Gas Flow/Total Air Flow	0.96
Characteristic Mixing Time for RZ Gas	50 ms
Mixing Delay for Secondary Air	20 ms
Characteristic Mixing Time for Secondary Air	50 ms
Boiler Wall (Water Wall) Temperature	600 K

TABLE A-3
COAL PROPERTIES AND CHARACTERISTICS

ANALYSIS

Type: Illinois No. 6

Properties:

Hydrogen	5.6	Percent (Mass)
Carbon	81.9	Percent
Nitrogen	1.12	Percent
Oxygen	11.3	Percent
Ash	14	Percent
Volatile Matter	40	Percent Proximate
Heating Value	7177	cal/g

DEVOLATILIZATION PARAMETERS

	<u>Constant</u>	<u>Reaction Rate</u>	
	<u>1</u>	<u>2</u>	
α	0.40	0.80	(0)
E	17.6	60	(K cal/gm mole)
B	$3.7 \cdot 10^5$	$1.46 \cdot 10^{13}$	(sec ⁻¹)

PARTICLE SIZE DISTRIBUTION

<u>Diameter</u>	<u>Mass Fraction</u>
10 μ m	0.01
20	0.09
30	0.20
40	0.20
60	0.20
80	0.20
130	0.10

TABLE A-4
PROGRAM LISTING

DEFINITIONS AND OUTLINE

LINES 1-193

MAIN SEGMENT

LINES 194-1364

*** ISO FOREGROUND HARD COPY ***
 DSNAME=B09X888.STCM.FORT

C	CODE FOR KINETICS OF COAL PYROLYSIS AND HETEROGENEOUS REACTIONS	00000100
C	D. STICKLER, S. UBAYAKAR, L. YOUNG AND K. ANNAMALAI	00000200
C	FOR COAL GASIFICATION AND COMBUSTION	00000300
C	INCLUDES SECONDARY AIR COMBUSTION/PRODUCT GAS RECIRCULATION	00000400
C	PROGRAM INPUT DESCRIPTION LIST	00000500
C	RUNNO EXAMPLE 072177.02 (JULY 21, 1977 RUN NO. 2)	00000600
C	FGAS MASS FRACTION HOT GAS	00000700
C	FKAR MASS FRACTION CARRIER GAS	00000800
C	...ASH INCLUDED IN TOTAL	00000900
C	FCRAC1, FCRAC2 FRACTION OF VOLATILES BY REACTIONS 1 AND 2 WHICH CRAC	00001000
C	TO EXHAUST GAS TEMP (DEG K)	00001100
C	TCO INITIAL COAL CARRIER TEMP	00001200
C	CC SPECIFIC HEAT OF COAL (CAL/G-K)	00001300
C	CA SPECIFIC HEAT OF ASH (CAL/G-K)	00001400
C	XL MEAN FREE PATH OF GAS (CM)	00001500
C	SPGRC DENSITY OF COAL INCLUDING ASH (G/CM3)	00001600
C	PHIA ASH MASS FRACTION OF DRY COAL	00001700
C	XLAMDA GAS THERMAL CONDUCTIVITY (CAL/(CM-SEC-K))	00001800
C	DVISC DYNAMIC VISCOSITY	00001900
C	TCH CHARACTERISTIC CARRIER AND COMBUSTION GAS MIXING TIME	00002000
C	ALPHA1, ALPHA2 STOICHIOMETRIC COEFFICIENTS FOR VOLATILE REACTIONS 1	00002100
C	B1, B2 FREQUENCY FACTORS (SEC**-1)	00002200
C	E1, E2 ACTIVATION ENERGIES FOR VOLATILE REACTIONS (CAL/(G-MO	00002300
C	ROD DENSITY TIMES DIFFUSION CONSTANT (ASSUMED VALUE)	00002400
C	DELHV1, DELHV2 HEATS OF FORMATION OF VOLATILES (CAL/G)	00002500
C	DELH1, DELH2 HEATS OF VOLATILIZATION (CAL/G)	00002600
C	ZC(J) MASS OF ATOMIC SPECIES IN DAF COAL RELATIVE TO C=1	00002700
C	XJC(J) MASS FRACTION OF ATOMIC SPECIES IN DAF COAL	00002800
C	XJO(J) MASS FRACTION OF ATOMIC SPECIES IN HOT EXHAUST GAS	00002900
C	ALL FOUR MUST BE NONZERO	00003000
C	XJI(J) MASS FRACTION OF ATOMIC SPECIES IN CARRIER GAS	00003100
C	IRDIUS NUMBER OF COAL SIZE GROUPS	00003200
C	R(I) RADIUS OF ITH SIZE GROUP (CM)	00003300
C	G(I) MASS FRACTION OF ITH SIZE GROUP	00003400
C	SHAPEV, SHAPES VOLUME AND CONDUCTIVE HEAT TRANSFER SHAPE FACTORS	00003500
C	TPRINT TIME STEP SIZE FOR PRINTOUT	00003600
C	TFINAL FINAL TIME	00003700
C	DTMAX MAXIMUM STEP SIZE	00003800
C	DTMIN MINIMUM STEP SIZE	00003900
C	XAT ALLOWED FRACTIONAL CHANGE IN COAL MASS/TIME INCR/DEG K DIFF	00004000
C	XAM ALLOWED FRACTIONAL CHANGE IN COAL MASS/TIME INCR AND PARTIC	00004100
C	UO INITIAL RELATIVE VELOCITY BETWEEN PARTICLES AND GAS	00004200
C	UO U-ZERO = PARTICLE VELOCITY (INPUT)	00004300
C	TWALL WALL TEMP (DEGREES KELVIN)	00004400
C		00004500
C		00004600
C		00004700
C		00004800
C		00004900
C		00005000
C		00005100
C		00005200
C		00005300
C		00005400
C		00005500
C		00005600

C	EMIS	GAS EMISSIVITY	00005700
C	DTR	CHANGE IN WALL TEMP WITH RESPECT TO DISTANCE (DEG K/C	00005800
C	VEL	PLUG FLOW VELOCITY	00005900
C	PRES	REACTION VOLUME PRESSURE (ATM)	00006000
C			00006100
C	TTRANS	TEMP AT WHICH P2161B KICKS IN	00006200
C	IPR21	PRINT P2161B OUTPUT IF NOT = 0	00006300
C	NCCMPR	IF=10, THEN P21B USED EVERY TENTH ITERATION	00006400
C	NPRINT	PRINTOUT FREQUENCY	00006500
C	STOKES	=1 USES CD _{RAG} =24/R. =0 USES CD _{RAG} =14.2/SQRT(R)	00006600
C	INTERNAL PROGRAM	VARIABLE DESCRIPTIONS	00006700
C	AJ(J)	ATOMIC WEIGHT OF ELEMENT I	00006800
C	ABC(I)	(NEW RADIUS)**3 AFTER EA CHAR OXIDATION STEP	00006900
C	ALFA1, ALFA2	STOICHIOMETRIC COEFFICIENTS FOR VOLATILES VIA REACTIO	00007000
C	CAPHK	CARRIER GAS ENTHALPY RELATIVE TO ZERO DEGREES KELVIN	00007100
C	CAPR	GAS CONSTANT	00007200
C	CORR(I)	CORRECTION TO PREVIOUS GUESS IN N-R PROCEDURE	00007300
C	DTCDT(I)	COAL PARTICLE TEMP DERIV. WRT TIME	00007400
C		IMIX = 3 HOT REC PROD. IS ONE STREAM, P.AIR AND S.AIR IS IND STR	00007500
C		IMIX = 1 HOT REC. PRODUCTS + S.AIR IS ONE STREAM	00007600
C		IMIX = 4 HOT REC. PROD IS 2ND STR., P.AIR IS 1ST TR., S.AIR IS 3RD.	00007700
C	EM(I)	TOTAL MASS FLUX FROM PARTICLE (VOLATILES + CHAR REMOV	00007800
C	EMC(I)	TRIAL VALUE FOR XCGAS(I)	00007900
C	EMP(I)	SUM OF VOLATILIZATION MASS FLOW RATES (G/SEC)	00008000
C	F	MASS FR OF MIXED HOT + CARRIER GAS + UNCRACKED VOLATI	00008100
C		OXIDIZED CHAR	00008200
C	FC	REMAINING MASS FRACTION OF DAF COAL	00008300
C	FCO	INITIAL DAF COAL MASS FR	00008400
C	FC1, FC2	MASS FR OF CARBON WHICH CRACKS TO SOOT FROM VOLATILES	00008500
C	F1, F2	MASS FR OF UNCRACKED VOLATILES FROM REACTIONS 1 AND 2	00008600
C	FMC(I)	FUNCTIONAL USED IN NEWTON-RAPHSON PROCEDURE (EVALUATE	00008700
C	FPMC(I)	DERIVATIVE OF FUNCTIONAL IN N-R PROCEDURE	00008800
C	FCKMF(I)	SURFACE CONCENTRATION FORM FACTOR	00008900
C	FO	MASS FR OF CARRIER + EXHAUST GAS	00009000
C	FVOL1, FVOL2	MASS FR OF VOLATILES FROM REACTIONS 1 AND 2	00009100
C	HCHEM	CHEMICAL ENTHALPY OF EQUILIBRATED LOCAL GAS SPECIES	00009200
C	HSENS	SENSIBLE ENTHALPY OF EQUILIBRATED LOCAL GAS SPECIES	00009300
C			00009400
C		MGM+MC+MK=MP+MCH	00009500
C	MGG	MASS OF EXHAUST GAS	00009600
C	MGM	MASS OF EXHAUST GAS MIXED WITH COAL AND CARRIER	00009700
C	MC	MASS OF DAF COAL	00009800
C	MK	MASS OF CARRIER GAS	00009900
C	MP	MASS OF PRODUCT GAS	00010000
C	MCH	MASS OF CHAR	00010100
C		...ALL RELATIVE TO C=1 IN DAF COAL	00010200
C			00010300
C	QDOT(I)	HEAT FLUX TO ITH PARTICLE SIZE GROUP	00010400
C	RHOC(I)	DENSITY OF DAF COAL PARTICLE (GM/CC)	00010500
C	SCOT1, Soot2	(MASS FR OF SCOT)/(ORIGINAL MASS FR OF DAF COAL)	00010600
C	SUM1, SUM2	MASS FR OF VOLATILIZED MATERIAL FROM REACTIONS 1 AND	00010700
C	SUMX1	SENSIBLE ENTHALPY TERM OF DAF COAL IN PARTICLE	00010800
C	SUMX2	SENSIBLE ENTHALPY TERM OF ASH IN PARTICLE	00010900
C	TEMP(I)	TEMP OF ITH SIZE COAL PARTICLE	00011000
C	VOLYLD	(MASS OF CR + UNCR VOLATILES)/(ORIGINAL MASS FR OF DA	00011100
C	XJ1(J), XJ2(J)	MASS FR OF ELEMENT J FOR VOLATILE REACTIONS 1 AND 2	00011200
C	XCGAS(I)	CARBON MASS FLOW RATE FROM PARTICLE DUE TO CHAR OXIDA	00011300
C			00011400
C	XM(I)	(MASS REMAINING DAF COAL + CHAR)/(ORIGINAL MASS)	00011500
C		FOR ITH SIZE COAL GROUP	00011600


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      *
      *
      *****
      * CALCULATE NEW HEAT FLUX TO 00017800
      * (AND TEMP) PARTICLE FROM 00017900
      * 1) CONDUCTIVE, RADIATIVE, AND 00018000
      * DRAG CONTRIBUTIONS 00018100
      * 2) ENDOTHERMIC VOLATILIZATION 00018200
      * AND ENDOTHERMIC HETEROC 00018300
      * GENEGUS CHAR OXIDATION 00018400
      ***** 00018500
      ***** 00018600
      *
      *
      *
      *
      ***** 00018700
      *
      *
      *
      ***** 00018800
      *
      *
      ***** 00018900
      * CALCULATE NEW PARTICLE TEMP 00019000
      ***** WITH RUNGE-KUTTA TECHNIQUE 00019100
      ***** 00019200
      ***** 00019300
      ***** 00019400
      ***** 00019500
      ***** 00019600
      ***** 00019700
      ***** 00019800
      ***** 00019900
      ***** 00020000
      ***** 00020100
      ***** 00020200
      ***** 00020300
      ***** 00020400
      ***** 00020500
      ***** 00020600
      ***** 00020700
      ***** 00020800
      ***** 00020900
      ***** 00021000
      ***** 00021100
      ***** 00021200
      ***** 00021300
      ***** 00021400
      ***** 00021500
      ***** 00021600
      ***** 00021700
      ***** 00021800
      ***** 00021900
      ***** 00022000
      ***** 00022100
      ***** 00022200
      ***** 00022300
      ***** 00022400
      ***** 00022500
      ***** 00022600
      ***** 00022700
      ***** 00022800
      ***** 00022900
      ***** 00023000
      ***** 00023100
      ***** 00023200
      ***** 00023300
      ***** 00023400
      ***** 00023500
      ***** 00023600

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	5 (PM,PERT(61)),(SM,PERT(62)),(EU,PERT(63)),(GD,PERT(64)),	00023700
	6 (TB,PERT(65)),(DY,PERT(66)),(ER,PERT(68)),	00023800
	7 (TM,PERT(69)),(YB,PERT(70)),(LU,PERT(71)),(HF,PERT(72)),	00023900
	8 (TA,PERT(73)),(W,PERT(74)),(KE,PERT(75)),(OS,PERT(76)),	00024000
	9 (IR,PERT(77)),(PT,PERT(78)),(AU,PERT(79)),(HG,PERT(80))	00024100
	EQUIVALENCE (TL,PERT(81)),(PB,PERT(82)),(BI,PERT(83)),	00024200
	1 (PO,PERT(84)),(AT,PERT(85)),(KN,PERT(86)),(FR,PERT(87)),	00024300
	2 (RA,PERT(88)),(AC,PERT(89)),(TH,PERT(90)),(PA,PERT(91)),	00024400
	3 (U,PERT(92)),(NP,PERT(93)),(PU,PERT(94)),(AM,PERT(95)),	00024500
	4 (CM,PERT(96)),(BK,PERT(97)),(CF,PERT(98)),(E,PERT(99))	00024600
	EQUIVALENCE (NUMBER(1),SPNUM(1))	00024700
	COMMON/A/XJ(4),AJ(4),YJ(4)	00024800
	COMMON/B/YFH2,YFH20,YFCO,YFCO2,YFN2,YFC,YFO2	00024900
	COMMON/C/YFC,YFH,YFOH	00025000
	COMMON/D/D1	00025100
	COMMON/E/C SUBP	00025200
	COMMON/F/BJJ(6),EJJ(6),XNUJJ(6),ROD,PIE,RHOG,CAPR,SHAPES,EXPNT	00025300
	COMMON/G/WV1,WV2	00025400
	COMMON/H/DELHV1,DELHV2	00025500
	COMMON/P/CC,PRESS,TOXR	00025600
C	SPECIES CODE NUMBERS FOR C, CH4, CO, CO2, C2H2, H, OH, H2, H2O, NO,	00025700
C	N2, N2O, O, O2, CC	00025800
C	DATA NUMBER/10.09600,10.12900,10.13500,10.13700,10.14600,	00025900
	*10.25300,10.26300,10.26700,10.27200,10.30300,10.31000,	00026000
	*10.31100,10.32500,10.33200,30.09500, 5*0.000/	00026100
	DATA PERT/99*0.000/XMU/ 4*0.000/	00026200
	DATA YFNO/0.00/YFN20/0.00/	00026300
	DATA MEMO,CASE,DATE,EPSI,MIF,HANDP/0,0.00,0.00,.00100,50,1.00/	00026400
	DATA PANDI,NOPAIR,IPINPT,NSAME,NGTH,TOL5/0.00,1.0,0,0,1.0-5/	00026500
	DATA OP,IPRINT,L6,IDAM,CPSCAL/0.00,0.6,0,1.00/	00026600
C	INITIALIZE MOLES OF ELEMENTS GREATER THAN ZERO SO THAT SPECIES LIST	00026700
C	BE READ FROM CHEMTAPE, OTHERWISE WILL NOT	00026800
C	DATA H/1.000/,C/1.000/,N/1.000/,O/1.000/	00026900
C	INITIAL PARAMETERS FOR P2161B EQUILIBRIUM PACKAGE	00027000
C	CALL ERRSET(208,256,-1,1)	00027100
	GASCON=82.05700	00027200
C	CM**3-ATM/(MOLE-DEG K)	00027300
	XNUJJ(1)=1.00	00027400
	XNUJJ(2)=16.00/17.00	00027500
	XNUJJ(3)=1.00	00027600
	XNUJJ(4)=16.00/18.00	00027700
	XNUJJ(5)=16.00/44.00	00027800
	PIE=3.14159265300	00027900
	CAPR=1.98700	00028000
	AJ(1)=1.000	00028100
	AJ(2)=12.00	00028200
	AJ(3)=14.00	00028300
	AJ(4)=16.00	00028400
C	READ SPECIES INFORMATION FROM CHEMTAPE	00028500
C	IPRDX=IPRINT	00028600
C	IDUU=-100.000	00028700
	CALL PTCHEM(IDUU,PRS,PERT,SPNUM,NSAME,IPROX,HOMWX,SOMWX,ROGGX,	00028800
		00028900
		00029000
		00029100
		00029200
		00029300
		00029400
		00029500
		00029600

	1 ACPSX,SUMMWX,SUMNIX,ZX,OHOTX,OHOPX,OSDTX,OSDPX,OROTX,OROPX,XMU,	00029700
	2 RTP,PPP,NELEX,IGASEX,ICONEX,ISENT,D,XNAM1,XNAM2,NGTH,TOLS,0,0)	00029800
C	EDG VOLATILIZATION PROGRAM INPUTS	00029900
C	BEGIN NEW CASE	00030000
C	1 READ(5,29,END=610) DESCR	00030100
	READ 10,FGAS,FKAR,FCRAC1,FCRAC2,YPF8,FLPOS,HPART,OXYC	00030200
	READ 10,FGAS3,T3DEL,TCH3,QEXT,EMISGE	00030300
	READ 10,TO,TCO,CC,CA,XL,SPGRC,PHIA,PHIM	00030400
	READ 10,XLAMDA,DVISC,FCH,TTRANS,DTR	00030500
	READ 10,ALFA1,ALFA2,B1,B2,E1,E2,RGD	00030600
	READ 10,DELHV1,DELH1,DELHV2,DELH2,HCHAR,DELT	00030700
	READ 10,(ZC(J),J=1,4)	00030800
	READ 10,(CHMB(J),J=1,4)	00030900
	READ 10,(XJO(J),J=1,4)	00031000
	READ 10,(XJO3(J),J=1,4)	00031100
	READ 10,(XJI(J),J=1,4)	00031200
	READ 10,(BJJ(I),I=1,5)	00031300
	READ 10,(EJJ(I),I=1,5)	00031400
	READ 11,IRDIUS	00031500
	READ 10,(R(I),I=1,IRDIUS)	00031600
	READ 10,(G(I),I=1,IRDIUS)	00031700
	READ 6,SHAPEV,SHAPES,DSQDV,EXPNT,HCOAL,PSI,TSAIR,IREC	00031800
	READ 10,TPRINT,TFINAL,DTMAX,DTMIN,XAT,XAM,TPAIR,YTR	00031900
	READ 6,UO,TWALL,EMIS,FRACL,VEL,PRESS,FREC,ICT	00032000
611	READ 611,IMIX,ISTAGE	00032100
C	FORMAT(219)	00032200
	READ 11,IPR21,NPRINT,NCOMPR,STOKES,IPREQ	00032300
	READ 10,(XMU1(J),J=1,4)	00032400
	READ 10,(XMU3(J),J=1,4)	00032500
	READ 10,(XMU2(J),J=1,4)	00032600
29	FORMAT(36A2)	00032700
6	FORMAT(7D9.0,19)	00032800
10	FORMAT(8D9.2)	00032900
11	FORMAT(519)	00033000
	TUXR=1./OXYC-1.	00033100
	TPAIRS=TPAIR	00033200
	TSAIRS=TSAIR	00033300
	ALF(1)=ALFA1	00033400
	ALF(2)=ALFA2	00033500
	HPYR(1)=DELH1	00033600
	HPYR(2)=DELH2	00033700
	CALL VLCOMP(ALF,HPYR,ZC,XJ1,XJ2,2,HCOAL,CAB,CHMB,HCHAR)	00033800
	IF(IREC.EQ.1)CALL GINLET(FKAR,FGAS,TSAIR,TO,CAB,PSI,PHIM,HCOAL,	00033900
	1 XJO,XJI,TCO,TPAIR,FREC,ICT,YTR,IMIX,YPF8,HPART,FLPOS,FGAS3,	00034000
	2 CAPHO3,XJO3)	00034100
	UO=UO*TSAIR/TSAIRS	00034200
	VEL=VEL*TPAIR/TPAIRS	00034300
	UO=DABS(UO-VEL)	00034400
	SIGN=(UO-VEL)/DABS(UO-VEL)	00034500
	MC=ZC(1)+ZC(2)+ZC(3)+ZC(4)	00034600
	MGG=FGAS*MC/(1.D0-PHIA)/(1.D0-FGAS-FGAS3-FKAR)	00034700
	MGG3=FGAS3*MC/(1.D0-PHIA)/(1.D0-FGAS-FGAS3-FKAR)	00034800
	MK=FKAR*MC/(1.D0-PHIA)/(1.D0-FGAS-FKAR-FGAS3)	00034900
	SUM=0.D0	00035000
	DO 201 J=1,4	00035100
	ZK(J)=MK*XJI(J)	00035200
		00035300
		00035400
		00035500
		00035600

201	SUM=SUM+ZC(J)	00035700
	DO 202 J=1,4	00035800
	XJC(J)=ZC(J)/SUM	00035900
202	XJCH(J)=XJC(J)	00036000
	YYC(1)=ZC(1)/AJ(1)	00036100
	YYC(2)=ZC(2)/AJ(2)	00036200
	YYC(3)=ZC(4)/AJ(4)	00036300
	YYO3(1) = XJO3(1)/AJ(1)	00036400
	YYO3(2) = XJO3(2)/AJ(2)	00036500
	YYO3(3) = XJO3(4)/AJ(4)	00036600
	SUM=0.00	00036700
	SUM3 = 0.00	00036800
	DO 220 M=1,3	00036900
	SUM3 = SUM3 + YYO3(M)	00037000
220	SUM=SUM+YYC(M)	00037100
	DO 221 M=1,3	00037200
	YYO3(M) = YYO3(M)/SUM3	00037300
221	YYC(M)=YYC(M)/SUM	00037400
C		00037500
	YYO(1)=XJO(1)/AJ(1)	00037600
	YYO(2)=XJO(2)/AJ(2)	00037700
	YYC(3)=XJO(4)/AJ(4)	00037800
	SUM=0.00	00037900
	DO 228 M=1,3	00038000
228	SUM=SUM+YYO(M)	00038100
	DO 229 M=1,3	00038200
229	YYO(M)=YYO(M)/SUM	00038300
C		00038400
	YYK(1)=XJI(1)/AJ(1)	00038500
	YYK(2)=XJI(2)/AJ(2)	00038600
	YYK(3)=XJI(4)/AJ(4)	00038700
	SUM=0.00	00038800
	DO 222 M=1,3	00038900
222	SUM=SUM+YYK(M)	00039000
	IF(SUM.LE.1.0-10) GO TO 219	00039100
	DO 223 M=1,3	00039200
223	YYK(M)=YYK(M)/SUM	00039300
219	CONTINUE	00039400
C		00039500
	YY1(1)=XJ1(1)/AJ(1)	00039600
	YY1(2)=XJ1(2)/AJ(2)	00039700
	YY1(3)=XJ1(4)/AJ(4)	00039800
	SUM=0.00	00039900
	DO 224 M=1,3	00040000
224	SUM=SUM+YY1(M)	00040100
	DO 225 M=1,3	00040200
225	YY1(M)=YY1(M)/SUM	00040300
C		00040400
	YY2(1)=XJ2(1)/AJ(1)	00040500
	YY2(2)=XJ2(2)/AJ(2)	00040600
	YY2(3)=XJ2(4)/AJ(4)	00040700
	SUM=0.00	00040800
	DO 226 M=1,3	00040900
226	SUM=SUM+YY2(M)	00041000
	DO 227 M=1,3	00041100
227	YY2(M)=YY2(M)/SUM	00041200
C		00041300
	DO 230 J=1,4	00041400
	ZGG(J)=MGG*XJO(J)	00041500
	ZGG3(J) = MGG3*XJO3(J)	00041600

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230 ZTOT(J)=ZC(J)+ZGG(J)+ZK(J) + ZGG3(J)
YYTOT(1)=ZTOT(1)/AJ(1)
YYTOT(2)=ZTOT(2)/AJ(2)
YYTOT(3)=ZTOT(4)/AJ(4)
SUM=0.00
DO 231 M=1,3
231 SUM=SUM+YYTOT(M)
DO 232 M=1,3
232 YYTOT(M)=YYTOT(M)/SUM
XATSAV=XAT
XAT1=XAT/5.000
TGUSS=TTRANS
ITITER=1
TEQLB=TCO
INCREM=0
CHEC=TPRINT
KK=0
EBG + CHAR BURN PROGRAM
INITIALIZE
FO=FGAS+FKAR+ FGAS3
FCO=(1.00-FO)*(1.00-PHIA)
ASH INCLUDED IN TOTAL
TGAS=TCO
FASH=PHIA*(1.00-FO)
SUMPRT=0.00
SUMDP2=0.00
SUMDP3=0.00
DO 2121 I=1,IRDIUS
XMCQ(I)=(4.00*PIE/3.00)* R(I)**3*SPGRC*(1.00-PHIA)*SHAPEV
PART(I)=FCO*G(I)/XMCQ(I)
SUMPRT=SUMPRT+PART(I)
SUMDP2=SUMDP2+R(I)**2*PART(I)
SUMDP3=SUMDP3+R(I)**3*PART(I)
2121 CONTINUE
DSURM=(SUMDP2/SUMPRT)**.500
DVOLM=(SUMDP3/SUMPRT)**.33300
DVSM=DVOLM**3/DSURM**2
PRINT 12,DESCR
12 FORMAT(1H1,///10X,36A2///20X,
1'COAL DEVOLATILIZATION INPUTS')
PRINT 20,FGAS,FKAR,FCRAC1,FCRAC2,DTR,PHIM,DSODV,EXPNT,HCOAL,IREC,
1PSI,TSAIR,YTR,HCHAR,OXYC
PRINT 21,FGAS3,T3DEL,TCH3,ISTAGE
21 FORMAT(5X,'FGAS3 = ',E11.4,2X,'MIX DELAY = ',E11.4,/,5X,
1'TCH3 = ',E11.4,2X,'ISTAGE = ',I3)
20 FORMAT(//,2X,'FGAS=',1PE11.4,2X,'FKAR=',E11.4,2X,'FCRAC1=',E11.4,
12X,'FCRAC2=',E11.4,2X,'DTR=',E11.4,/,2X,'PHI-MOIST = ',OPF5.3,2X,
2'DS/DVAG = ',F6.3,2X,'CD/EXPNT = ',F6.3,2X,'H-COAL = ',1PE11.4,
32X,'IREC = ',I1,2X,'EQUIV. RATIO = ',OPF5.2,/,2X,'SEC. AIR TEMP =
4',F6.1,2X,'TR.AIR FR. = ',F5.3,2X,'HCHAR=',1PE11.4,/,3X,'OXY. ',
5'MOLE CONC = ',E11.4,/)
PRINT 13,FO,TCO,CC,CA,XL,SPGRC,PHIA,XLAMD4,DVISM,TCH,CAPHK,ALFA1,A
1LFA2,B1,B2,E1,E2,ROD,DELHV1,DELH1,DELHV2,DELH2
13 FORMAT( 2X,'FO=',1PE11.4,2X,'TCO=',E11.4,2X,'CC=',E11.4,2X,'CA='
1,E11.4,2X,'XL=',E11.4,2X,'SPGRC=',E11.4,2X,'PHIA=',E11.4,/,2X,
2'XLAMD4=',E11.4,2X,'DVISM=',E11.4,2X,'TCH=',E11.4,2X,'CAPHK=',E11.
34,2X,'ALFA1=',E11.4,2X,'ALFA2=',E11.4,/,2X,'B1=',E11.4,2X,'B2=',E1

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41.4,2X,'E1=',E11.4,2X,'E2=',E11.4,2X,'RCD=',E11.4,2X,'DEL 00047700
5/,2X,'DELHV1=',E11.4,2X,'DELH1=',E11.4,2X,'DELHV2=',E11.4,2X,'DEL 00047800
6H2=',E11.4) 00047900
PRINT 1919, (BJJ(I), I=1,5), (EJJ(I), I=1,5) 00048000
1919 FORMAT(5X,'REACTION VEL (CM/S) =',5(1PE11.4,3X),/,5X, 00048100
1'ACT.ENER (CAL/MOL) =',5(1PE11.4,3X)) 00048200
PRINT 250, (ZC(I), I=1,4) 00048300
250 FORMAT(5X,'ZC(H) =',1PE11.4,2X,'ZC(C) =',E11.4,2X,'ZC(N) =',E11.4, 00048400
12X,'ZC(O) =',E11.4) 00048500
PRINT 61, (YYC(M), M=1,3) 00048600
61 FORMAT(5X,'YYC(H) =',1PE11.4,2X,'YYC(C) =',E11.4,2X,'YYC(O) =', 00048700
'E11.4) 00048800
PRINT 14, (XJO(I), I=1,4) 00048900
14 FORMAT(5X,'XJO(H) =',1PE11.4,2X,'XJO(C) =',E11.4,2X,'XJO(N) =',E11.4, 00049000
12X,'XJO(O) =',E11.4) 00049100
PRINT 68, (XJO3(J), J=1,4) 00049200
68 FORMAT(4X,'XJO3(H) =',1PE11.4,' XJO3(C) =',E11.4,' XJO3(N) =',E11.4, 00049300
*' XJO3(O) =',E11.4) 00049400
PRINT 62, (YYO(M), M=1,3) 00049500
62 FORMAT(5X,'YYO(H) =',1PE11.4,2X,'YYO(C) =',E11.4,2X,'YYO(O) =', 00049600
'E11.4) 00049700
PRINT 15, (XJI(I), I=1,4) 00049800
15 FORMAT(5X,'XJI(H) =',1PE11.4,2X,'XJI(C) =',E11.4,2X,'XJI(N) =',E11.4, 00049900
12X,'XJI(O) =',E11.4) 00050000
PRINT 63, (YYK(M), M=1,3) 00050100
63 FORMAT(5X,'YYK(H) =',1PE11.4,2X,'YYK(C) =',E11.4,2X,'YYK(O) =', 00050200
'E11.4) 00050300
PRINT 16, (XJ1(I), I=1,4) 00050400
16 FORMAT(5X,'XJ1(H) =',1PE11.4,2X,'XJ1(C) =',E11.4,2X,'XJ1(N) =',E11.4, 00050500
12X,'XJ1(O) =',E11.4) 00050600
PRINT 64, (YY1(M), M=1,3) 00050700
64 FORMAT(5X,'YY1(H) =',1PE11.4,2X,'YY1(C) =',E11.4,2X,'YY1(O) =', 00050800
'E11.4) 00050900
PRINT 17, (XJ2(I), I=1,4) 00051000
17 FORMAT(5X,'XJ2(H) =',1PE11.4,2X,'XJ2(C) =',E11.4,2X,'XJ2(N) =',E11.4, 00051100
12X,'XJ2(O) =',E11.4) 00051200
PRINT 65, (YY2(M), M=1,3) 00051300
65 FORMAT(5X,'YY2(H) =',1PE11.4,2X,'YY2(C) =',E11.4,2X,'YY2(O) =', 00051400
'E11.4) 00051500
PRINT 67, (YYTOT(M), M=1,3) 00051600
67 FORMAT(5X,'YYT(H) =',1PE11.4,2X,'YYT(C) =',E11.4,2X,'YYT(O) =', 00051700
'E11.4) 00051800
PRINT 66, (XMU1(I), I=1,4) 00051900
PRINT 66, (XMU3(I), I=1,4) 00052000
PRINT 66, (XMU2(I), I=1,4) 00052100
66 FORMAT(5X,'XMU(1) =',1PE11.4,2X,'XMU(2) =',E11.4,2X,'XMU(3) =', 00052200
*1E11.4,2X,'XMU(4) =',E11.4) 00052300
PRINT 251, MC, MGG, MK 00052400
251 FORMAT(2X,'MC=',1PE11.4,' MGG=',E11.4,' MK=',E11.4) 00052500
PRINT 18, (K(I), I=1, IRDIUS) 00052600
18 FORMAT(5X,'R=',1P10E11.4) 00052700
PRINT 19, (G(I), I=1, IRDIUS) 00052800
19 FORMAT(5X,'G=',1P10E11.4) 00052900
PRINT 193, (PART(I), I=1, IRDIUS) 00053000
193 FORMAT(5X,'N=',1P10E11.4) 00053100
PRINT 9, FO, SHAPEV, SHAPES, TPRINT, TFINAL, FCO 00053200
1,DTMAX,DTMIN,XAT,XAM 00053300
9 FORMAT(2X,'FU=',1PE11.4,2X,'SHAPEV=',E11.4,2X, 00053400
1'SHAPES=',E11.4,2X,'TPRINT=',E11.4,2X,'TFINAL=',E11.4,2X,'FCO=', 00053500
'E11.4/2X, 00053600

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* 'DTMAX=' ,E11.4,' DININ=' ,E11.4,' XAT=' ,E11.4,' XAM=' ,E11.4) 00053700
PRINT 33,UO,TWALL,EMIS,FRACL,VEL,PRESS,UO,DSURM,DVCLM,DVSM 00053800
33 FORMAT(2X,'REL.VEL=' ,1PE11.4,2X,'TWALL=' ,E11.4,2X,'EMIS=' ,E11.4,2X,00053900
1'FRACL=' ,E11.4,2X,'GAS VEL=' ,E11.4,2X,'PRLSS=' ,E11.4,7,5X,'PART VE00054000
2L' ,E11.4,2X,'SURF.MN.RAD =' ,E11.4,2X,'VCL.MN.RAD =' ,E11.4,2X,00054100
3'VOL/SURF.RAD =' ,E11.4) 00054200
PRINT 973, NCOMPR 00054300
973 FORMAT(2X,'NCOMPR=' ,I4) 00054400
PRINT 974, TTRANS 00054500
974 FORMAT(2X,'TTRANS=' ,E8.2) 00054600
PRINT 975, STOKES 00054700
975 FORMAT(2X,'STOKES=' ,I4) 00054800
C 00054900
XJOTOT=0.00 00055000
XJITOT=0.00 00055100
XJ1TOT=0.00 00055200
XJ2TOT=0.00 00055300
XJ03TC = 0.00 00055400
GTOTAL=0.00 00055500
DO 100 I=1,IRDIUS 00055600
GTOTAL=GTOTAL+G(I) 00055700
XMC0(I)=(4.00*PIE/3.00)*(R(I)**3)*SPGRC*(1.00-PHIA)*SHAPEV 00055800
XMCU(I)=XMC0(I) 00055900
XMC(I)=XMC0(I) 00056000
MCHO(I) = G(I)*MC 00056100
QDCT(I)=0.000 00056200
TEMP(I)=TCO 00056300
TEMPO(I)=TEMP(I) 00056400
H. EMC(I)=0.00 00056500
XCGAS(I)=0.00 00056600
PART(I)=FCO*G(I)/XMCU(I) 00056700
RHOC(I)=XMCU(I)/((4.00/3.00)*PIE*(R(I)**3)) 00056800
100 CONTINUE 00056900
DO 55 J=1,4 00057000
XJCTOT=XJOTOT+XJO(J) 00057100
XJ03TC = XJ03TO + XJ03(J) 00057200
XJITOT=XJITOT+XJI(J) 00057300
XJ1TOT=XJ1TOT+XJ1(J) 00057400
XJ2TOT=XJ2TOT+XJ2(J) 00057500
C 00057600
55 CONTINUE 00057700
IF(ZC(2).NE.1.000)GO TO 9992 00057800
C EVALUATION OF CARRIER GAS AND COMBUSTION GAS PROPERTIES 00057900
IF(DABS(GTOTAL-1.00).GT.1.00-04)GO TO 9996 00058000
IF(DABS(XJ03TO -1.00).GT. 1.00-04) GO TO 9996 00058100
IF(DABS(XJOTOT-1.00).GT.1.00-04)GO TO 9996 00058200
IF(DABS(XJITOT-1.00).GT.1.00-04)GO TO 9996 00058300
IF(DABS(XJ1TOT-1.00).GT.1.00-04)GO TO 9996 00058400
IF(DABS(XJ2TOT-1.00).GT.1.00-04)GO TO 9996 00058500
C 00058600
C CAPHK, CAPHO AND MULE FRACTIONS 00058700
DO 50 J=1,4 00058800
XMU(J)=XMU1(J) 00058900
XJ(J)=XJO(J) 00059000
50 CONTINUE 00059100
TGAS = TO 00059200
NCOMB = 1 00059300
IPROX = 1 00059400
GO TO 1105 00059500
51 CONTINUE 00059600

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EMWT=2.D0*YFH2+18.D0*YFH20+28.D0*YFCO+44.D0*YFCO2+32.D0*YFU2+
128.D0*YFN2+12.D0*YFC+16.D0*YFO+YFH+17.D0*YFOH+16.D0*YFCH4+26.D0*
2YFC2H2+30.D0*YFNO+44.D0*YFN20
DENS=EMWT*PRESS/GASCON/T0
CAPHO = HOMWX
TSCALE=1.D0
CPSCAL=1.D0
PRINT 8
8 FORMAT(//////,20X,'COMBUSTION GAS PROPERTIES')
PRINT 7,CAPHO,YFH2,YFH20,YFCO,YFCO2,YFN2,YFC,YFU2,YFG,YFH,YFOH,
1YFCC,EMWT,DENS
7 FORMAT(//,2X,'CAPHO=',1PE11.4,2X,'YFH2=',E11.4,2X,'YFH20=',E11.4,
12X,'YFCO=',E11.4,2X,'YFCO2=',E11.4,2X,'YFN2=',E11.4,2X,'YFC=',E11.
24,/,2X,'YFO2=',E11.4,2X,'YFC=',E11.4,2X,'YFH=',E11.4,2X,'YFOH=',E
*11.4,2X,'YFCC=',E11.4/2X,'MOLWT=',E11.4,'GM/MOLE',2X,'DENS=',
*E11.4,'GM/CC')
DO 52 J=1,4
XMU(J)=XMU3(J)
XJ(J)=XJO3(J)
52 CONTINUE
IGAS = TSAIR
NCOMB = 3
IPROX = 1
GO TO 1105
53 CONTINUE
EMWT=2.D0*YFH2+18.D0*YFH20+28.D0*YFCO+44.D0*YFCO2+32.D0*YFU2+
128.D0*YFN2+12.D0*YFC+16.D0*YFO+YFH+17.D0*YFOH+16.D0*YFCH4+26.D0*
2YFC2H2+30.D0*YFNO+44.D0*YFN20
IPROX = 1
DENS=EMWT*PRESS/GASCON/TSAIR
CAPHO3 = HOMWX
NCOMB = 0
TSCALE=1.D0
CPSCAL=1.D0
PRINT 2
2 FORMAT(//////,20X,'SECONDARY GAS PROPERTIES')
PRINT 4,CAPHO3,YFH2,YFH20,YFCO,YFCO2,YFN2,YFC,YFO2,YFO,YFH,YFOH,
1YFCC,EMWT,DENS
4 FORMAT(//,2X,'CAPHO3=',1PE11.4,2X,'YFH2=',E11.4,2X,'YFH20=',E11.4,
12X,'YFCO=',E11.4,2X,'YFCO2=',E11.4,2X,'YFN2=',E11.4,2X,'YFC=',E11.
24,/,2X,'YFO2=',E11.4,2X,'YFC=',E11.4,2X,'YFH=',E11.4,2X,'YFOH=',E
*11.4,2X,'YFCC=',E11.4/2X,'MOLWT=',E11.4,'GM/MOLE',2X,'DENS=',
*E11.4,'GM/CC')
DO 489 J=1,4
XJ(J)=XJI(J)
489 CONTINUE
CALL EQUILIB(TCO,HSENS,HCHEM)
EMWT=2.D0*YFH2+18.D0*YFH20+28.D0*YFCO+44.D0*YFCO2+32.D0*YFU2
1+28.D0*YFN2+12.D0*YFC+16.D0*YFO+YFH+17.D0*YFOH
CAPHK=HSENS+HCHEM
PRINT 743
743 FORMAT(//////,20X,'CARRIER GAS PROPERTIES')
PRINT 3,CAPHK,YFH2,YFH20,YFCO,YFCO2,YFN2,YFC,YFO2,YFC,YFH,YFOH
*,EMWT
3 FORMAT(//,2X,'CAPHK=',1PE11.4,2X,'YFH2=',E11.4,2X,'YFH20=',E11.4,
12X,'YFCO=',E11.4,2X,'YFCO2=',E11.4,2X,'YFN2=',E11.4,2X,'YFC=',E11.
24,/,2X,'YFO2=',E11.4,2X,'YFC=',E11.4,2X,'YFH=',E11.4,2X,'YFOH=',E
*11.4,2X,'MOLWT=',E11.4,'GM/MOLE')
PRINT 26
26 FORMAT(1H1)

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	HV=0.00	00071700
	SENSEN=0.00	00071800
	SUMMQR = 0.00	00071900
	SUMMQE = 0.00	00072000
	SUMX2=0.00	00072100
C		00072200
C	NEW TIME STEP	00072300
C	150 IF (TIME.GE.TFINAL) GO TO 99	00072400
	TIME=TIME+DELT	00072500
		00072600
C	HEAT LOSS FROM REACTOR	00072700
C		00072800
	CAPHO=CAPHO-VEL*DELT*HSENS*FRACL	00072900
	TW=TWALL-VEL*DELT*DTR	00073000
C		00073100
	INCREM=INCREM+1	00073200
	TSAVE=TGAS	00073300
	SUM1=0.00	00073400
	SUM2=0.00	00073500
	SUMQR = 0.00	00073600
	SUMXX = 0.00	00073700
	SUMQE = 0.00	00073800
	SUMC=0.00	00073900
	DO 151 J=1,4	00074000
151	SUMCC(J)= 0.00	00074100
	DO 200 I=1,IRDIUS	00074200
	TEMPO(I)=TEMP(I)	00074300
	IF(R(I).LE.1.E-20) XM1(I)=0.00	00074400
	IF(R(I).LE.1.E-20) XM2(I)=0.00	00074500
	IF(R(I).LE.1.E-20) XCGAS(I)=0.00	00074600
	IF(R(I).LE.1.E-20) XCC(I)=0.00	00074700
	IF(R(I).LE.1.E-20) GO TO 180	00074800
	XMCUS(I)=XMCU(I)	00074900
	XMCS(I)=XMC(I)	00075000
	XCGASS(I)=XCGAS(I)	00075100
	XM1DOT(I)=ALFA1*B1*XMCUS(I)*DEXP(-E1/(CAPR*TEMP(I)))	00075200
	IF(XM1DOT(I).LE.1.D-69) XM1DOT(I)=0.000	00075300
	XM1(I)=XM1DOT(I)/XMCU(I)	00075400
	XM2DOT(I)=ALFA2*B2*XMCUS(I)*DEXP(-E2/(CAPR*TEMP(I)))	00075500
	IF(XM2DOT(I).LE.1.D-69) XM2DOT(I)=0.000	00075600
	XM2(I)=XM2DOT(I)/XMCU(I)	00075700
	XMCU(I)=XMCUS(I)-(XM1DOT(I)/ALFA1+XM2DOT(I)/ALFA2)*DELT	00075800
	IF(XMCU(I).LE.0.000) XMCU(I)=0.00	00075900
C		00076000
C	EVALUATE COAL/CHAR BURNOUT AND	00076100
C	REDUCTION OF PARTICLE RADIUS	00076200
		00076300
	EMP(I)=XM1DOT(I)+XM2DOT(I)	00076400
	XMC(I)=XMCS(I)-EMP(I)*DELT	00076500
	ZZ(I)=4.00*PIE*R(I)*ROD	00076600
	IF(XMC(I).LT.0.00) GO TO 387	00076700
	XCGAS(I)=EMC(I)	00076800
	RHOC(I)=RHOC(I)-(XM1DOT(I)+XM2DOT(I))*DELT/(4.00/3.00*PIE*R(I)**3)	00076900
	IF(RHOC(I).GT.0.000) GO TO 737	00077000
	RHOC(I)=0.000	00077100
387	R(I)=0.00	00077200
	XM1(I) = XM1(I)*XMCS(I)/(XMCS(I) -XMC(I))	00077300
	XM2(I) = XM2(I)*XMCS(I)/(XMCS(I) -XMC(I))	00077400
	XCGAS(I)=0.	00077500
		00077600

	XMC(I)=0.00	00077700
	GO TO 2500	00077800
737	XMC(I)=XMC(I)-XCGAS(I)*DELT	00077900
	XXXX= R(I)*K(I)*K(I)-EAC(I)*DELT/(4.00/3.00*PIE*RHOC(I))	00078000
	IF(XXXX.GT.0.000)R(I)=XXXX*(1.00/3.00)	00078100
	IF(XXXX.LE.0.000)R(I)=0.000	00078200
2500	XM(I)=XMC(I)/XMC0(I)	00078300
	IF(XM(I).LE.1.0-6)XM(I)=0.000	00078400
	IF(XM(I).LE.1.0-6)TEMP(I)=0.000	00078500
	IF(XM(I).LE.1.0-6)R(I)=0.000	00078600
	IF(XMC(I).LT.0.)XCGAS(I) = XCGAS(I) + XMC(I)/DELT	00078700
	XCC(I)=XCGAS(I)/XMC0(I)	00078800
	MCHH(I) = 0.00	00078900
	DO 160 J = 1,4	00079000
160	MCHH(I) = MCHH(I) + ZCHH(J,I)	00079100
	DO 165 J = 1,4	00079200
165	XJCHH(J,I) = ZCHH(J,I)/MCHH(I)	00079300
	IF(TEMP(I).GE.TCO) SUMXX = SUMXX + FCO*G(I)*(CC*(XM(I)*TEMP(I)	00079400
	1 -TCO) + CA*(PHIA/(1.00-PHIA))*(TEMP(I)-TCO))	00079500
	SUM1=SUM1+FCO*G(I)*XM1(I)*DELT	00079600
	SUM2=SUM2+FCO*G(I)*XM2(I)*DELT	00079700
	SUMC=SUMC+FCO*G(I)*XCC(I)*DELT	00079800
	DO 170 J = 1,4	00079900
170	SUMCC(J) = SUMCC(J) + FCO*G(I)*XCC(I)*XJCHH(J,I)*DELT	00080000
	DO 180 J = 1,4	00080100
	ZCHH(J,I) = ZCHH(J,I) - (XM1(I)*XJ1(J)+XM2(I)*XJ2(J)	00080200
	1+ XCC(I))*XJCHH(J,I))*DELT *MCHO(I)	00080300
180	CONTINUE	00080400
C		00080500
C	ADJUST DELT ACCORDING TO ALLOWED	00080600
C	FRACTIONAL CHANGE IN MASS	00080700
		00080800
	XDOT(I)=DABS(XM1(I))+DABS(XM2(I))+DABS(XCC(I))	00080900
	IF(XDOT(I).LE.1.0-20) XDOT(I)=1.0-20	00081000
	DELT(I)=XAM/XDOT(I)	00081100
	DELT(I)=DELT(I)	00081200
	IF(I.EQ.1) GO TO 152	00081300
	IF(DELT(I-1).LT.DELT(I)) DELT(I)=DELT(I-1)	00081400
152	DELT(I)=DELT(I)	00081500
	SUMQR = SUMQR+4.00*PIE*R(I)**2*PART(I)*EMIS*1.35450-12*(TW**4-	00081600
	1 TEMP(I)**4)*SHAPES	00081700
	SUMQE = SUMQE+4.00*PIE*R(I)**2*SHAPES*QEXT*PART(I)*EMISQE	00081800
	RHOCOR(I) = RHOC(I)/SHAPEV	00081900
200	CONTINUE	00082000
C	END IRDIUS LOOP	00082100
	SUMQR = SUMQR + SUMQR*DELT	00082200
	SUMQE = SUMQE + SUMQE*DELT	00082300
	SUMX1=SUMX1+SENSEN*DELT	00082400
	FVOL1=FMOL1+SUM1	00082500
	FVOL2=FMOL2+SUM2	00082600
	FC1=FMOL1*FCRAC1*XJ1(2)	00082700
	FC2=FMOL2*FCRAC2*XJ2(2)	00082800
	FCGAS=FCGAS+SUMC	00082900
	DO 3353 J=1,4	00083000
3353	FCGASS(J)=FCGASS(J) + SUMCC(J)	00083100
	A161=-TIME/TCH	00083200
C	FGM=FGAS*(1.00-DEXP(A161))	00083300
	A161=-A161	00083400
	IF(A161.LE.2.00) FGM=FGAS*(1.-DCOS(PIE*A161/2.00))/2.00	00083500
	IF(A161.GT.2.00) FGM=FGAS	00083600

	F=FKAR+FGM+FVOL1+FVOL2-FC1-FC2+FCGAS	00083700
	FC=FCO-FVOL1-FVOL2-FCGAS	00083800
	VOLYLD=(FVOL1+FVOL2)/FCO	00083900
	CGAS=FCGAS/FCO	00084000
	SOOT1=FC1/FCO	00084100
	SOOT2=FC2/FCO	00084200
C	HGM=FGAS*(1.00-DEXP(A161))*CAPHU	00084300
	HGM=FGM*CAPHU	00084400
	HV=(DELH1+DELHV1)*FVOL1+(DELH2+DELHV2)*FVOL2-(FC1+FC2)*CC*TGAS	00084500
	FGM3 = 0.00	00084600
	HGM3 = 0.00	00084700
	HHH=(HGM+HK+HV-SUMXX + SUMMQR + SUMMQE)/F	00084800
	IF(ISTAGE.EQ.0) GO TO 399	00084900
	IF(TIME.LT.T3DEL) GO TO 399	00085000
	A162 =-(TIME- T3DEL)/TCH3	00085100
C	FGM3 = FGAS3*(1.00-DEXP(A162))	00085200
	A1622=-A162	00085300
	IF(A1622.LE.2.00) FGM3=FGAS3*(1.00-DCOS(PIE*A1622/2.00))/2.00	00085400
	IF(A1622.GT.2.00) FGM3=FGAS3	00085500
C	HGM3=FGAS3*(1.00-DEXP(A162))*CAPHO3	00085600
	HGM3=FGM3*CAPHO3	00085700
	F=FKAR+FGM+FVOL1+FVOL2-FC1-FC2+FCGAS+FGM3	00085800
	HHH=(HGM+HK+HV-SUMXX + SUMMQR + SUMMQE+HGM3)/F	00085900
399	CONTINUE	00086000
C	PRINT 210,HHH,HGM,HK,HV,SUMXX,SUMMQR,SUMMQE,HGM3	00086100
C210	FORMAT(/' HHH,HGM,HK,HV,SUMXX,SUMMQR,SUMMQE,HGM3 = ',1P8E10.3/)	00086200
	DO 300 J=1,4	00086300
	XJ(J)=(FKAR*XJ1(J)+FGM*XJO(J)+XJ1(J)*FVOL1+XJ2(J)*FVOL2+FCGASS(J)	00086400
	+ FGM3 * XJO3(J))/F	00086500
300	CONTINUE	00086600
	XJ(2)=XJ(2)-(FC1+FC2)/F	00086700
C	CALCULATION DOESN'T FOLLOW SOUT IN MASS BALANCE	00086800
	DO 2020 I=1,IRDIUS	00086900
2020	CONTINUE	00087000
C	COMPUTE NEW LOCAL GAS ENTHALPY FROM HHH USING EBG EQUIL. SUBROUTINE	00087100
C	TGUESZ=TGAS*TSSCALE	00087200
	IF(TIME.LE.DELT) TGUESZ=TCO	00087300
C	IF(TGAS.GT.350.00) GO TO 303	00087400
C	HSENS=HHH-HCHEM	00087500
C	CPAV=HSENS/TGUESZ	00087600
C	TGAS=HSENS/CPAV	00087700
C	GO TO 404	00087800
303	CONTINUE	00087900
	LL=0	00088000
	NSHIFT=0	00088100
350	CONTINUE	00088200
	IF(IPREQ.GT.0)	00088300
	*PRINT 9898,TGUESZ,HSENS,HCHEM,TTRIAL,LL,NN,NSTEPS	00088400
9898	FORMAT(' BEFORE',4(2X,1PE14.4),3(2X,15))	00088500
	CALL EQUILB(TGUESZ,HSENS,HCHEM)	00088600
	YFCC=0.00	00088700
	CPAV=HSENS/TGUESZ	00088800
	TTRIAL=(HHH-HCHEM)/CPAV	00088900
	IF(IPREQ.GT.0)	00089000
	*PRINT 9899,TGUESZ,HSENS,HCHEM,TTRIAL	00089100
9899	FORMAT(' AFTER',4(2X,1PE14.4),/)	00089200
	DO 601 I=1,4	00089300
	IF(XJ(I).GT.100.DC)GO TO 5555	00089400
		00089500
		00089600

601	CONTINUE	00089700
	IF(DABS((TGUESZ-TTRIAL)/TGUESZ).LE.0.01D0) GO TO 400	00089800
	IF(LL.EQ.0)GO TO 360	00089900
C	NN IDENTIFIES REGIME IN EQUILIB	00090000
	NDUM=NNN-NN	00090100
	IF(NDUM.NE.0)GO TO 353	00090200
	DTEMP=IG-TGUESZ+TTRIAL-TT	00090300
	IF(DTEMP.EQ.0.0D0)GO TO 360	00090400
	TGG=TGUESZ	00090500
	TGUESZ=(TG*TTRIAL-TGUESZ*TT)/DTEMP	00090600
C	THIS RESULT IS EXACT IF TTRIAL IS A LINEAR FUNCTION OF TGUESZ	00090700
	TG=TGG	00090800
	GO TO 362	00090900
358	NSHIFT=NSHIFT+1	00091000
	IF(NSHIFT.GE.4) TGAS=(TGUESZ+TTRIAL)/2.D0	00091100
	IF(NSHIFT.GE.4) PRINT 361,NSHIFT	00091200
361	FORMAT(2X,'NSHIFT = ',I3,' EQUILIB IS HUNTING - USE P2161B')	00091300
	IF(NSHIFT.GE.4) GO TO 1105	00091400
C	IF(NSHIFT.GE.2) EQUILIB IS HUNTING-USE P2161B	00091500
360	TG=TGUESZ	00091600
	TGUESZ=(TTRIAL+TGUESZ)/2.D0	00091700
362	NN=NN	00091800
	TT=TTRIAL	00091900
	LL=LL+1	00092000
	IF(LL.GE.35)GO TO 365	00092100
	GO TO 350	00092200
C		00092300
365	PRINT 366,TTRIAL,TGUESZ,CPAV,HHH,HSENS,HCHEM,LL	00092400
366	FORMAT(/,' TTRIAL,TGUESZ,CPAV,H,HSENS,HCHEM,LL',/,', YJ(1),YJ(2)	00092500
	1,YJ(3),YJ(4),/,', YFH2,YFH2O,YFCO,YFCO2,YFN2,YFC,YFC2,YFO,YFH,YFCO	00092600
	2H,YFCC',/,6E11.4,I2)	00092700
	PRINT 1234,YJ(1),YJ(2),YJ(3),YJ(4)	00092800
1234	FORMAT(' ',4E11.4)	00092900
	PRINT 4321,YFH2,YFH2O,YFCO,YFCO2,YFN2,YFC,YFO2,YFO,YFH,YFCH,YFCC	00093000
4321	FORMAT(' ',11E11.4)	00093100
	GO TO 99	00093200
C		00093300
400	TGAS=(TGUESZ+TTRIAL)/2.D0	00093400
	TMIN=DMIN1(TO,TCO)-10.D0	00093500
	IF(TGAS.LT.TMIN) GO TO 402	00093600
	GO TO 404	00093700
402	CONTINUE	00093800
	PRINT 403,TGAS	00093900
403	FORMAT(' TGAS = ',1PE14.4,' - TOO COLD. USE P2161B')	00094000
	TGAS=TMIN	00094100
C	GAS TOO COLD - - USE P2161B	00094200
	GO TO 1105	00094300
404	TEQLB=TGAS	00094400
	CPEQLB=CPAV	00094500
	TGAS=TGAS/TSCALE	00094600
	PRINT 872,TGAS,TSCALE,CPSCAL,DELT,TEMP(1),INCREM	00094700
872	FORMAT(' TGAS, TSCALE, CPSCALE, DELT, TEMP(1), NSTEPS...',	00094800
	*1P5E14.4,I4)	00094900
C	PRINT 873,HGM,HK,HV,SUMX1,SUMX2,F	00095000
C	873 FORMAT (2X,'HGM, HK, HV, SUMX1, SUMX2, F...',1P6E14.4)	00095100
	CPAV=CPAV/CPSCAL	00095200
	IF(TGAS.LT.TTRANS)GO TO 420	00095300
	IF(ITTTK-NCMPK)405,1105,1105	00095400
405	ITTTK=ITTTK+1	00095500
	INDEX=0	00095600

	YFCH4=0.00	00095700
	YFC2H2=0.00	00095800
	YFNO=0.00	00095900
	YFN2O=0.00	00096000
C	420 CONTINUE	00096100
C	NUMERICAL QUADRATURE USING RUNGE-KUTTA SCHEME	00096200
C	SENSEN=0.000	00096300
	DO 500 I=1,IRDIUS	00096400
	IF(R(I).LE.1.0-20) DELTT(I)=DTMAX	00096500
	IF(R(I).LE.1.0-20) GO TO 453	00096600
	IF(KK.EQ.0) GO TO 425	00096700
	TGDI F=DABS(TSAVE-TEMP(I))	00096800
425	CONTINUE	00096900
	IF(TEMP(I).LT.0.00) PRINT 415,TEMP(I)	00097000
415	FORMAT(2X,'415',1PE12.4)	00097100
	TIMP=TIME-DELT	00097200
	TEMPS(I)=TEMP(I)	00097300
	J=0	00097400
	TC(I)=TEMP(I)	00097500
	TCS=TC(I)	00097600
	RHOG=(01*PRESS)/(82.0600*TGAS)	00097700
	TAUD=2.00*(R(I)**2)*SPGRC/(9.00*DVISG)	00097800
	IF(DABS(TIMP/TAUD).GE.1.04)V=0.000	00097900
	IF(DABS(TIMP/TAUD).LT.1.04.AND.STUKES.EQ.1)V=UO*DEXP(-TIMP/TAUD)	00098000
	IF(STUKES.EQ.1)GO TO 4515	00098100
	VALUE=DSQRT(DVISG*RHOG)*SHAPES**EXPNT	00098200
	VALUE=VALUE/(.266*(R(I)**1.5)*SPGRC)	00098300
	DENOM2=(TIMP*VALUE*DSQRT(UO)/2.00)+1.00	00098400
	DENOM2=DENOM2*DENOM2	00098500
	V=UO/DENOM2	00098600
	VELP(I)=UO-SIGN*V	00098700
4515	CONTINUE	00098800
	KEY=2.00*(R(I)*V*RHOG/DVISG)	00098900
450	A444=(DABS(FLOAT(J)-1.500)-.500)*((-1)**J)	00099000
	IF(A444)4507,4506,4505	00099100
4505	TGASS=TSAVE	00099200
	XMCUT(I)=XMCUS(I)	00099300
	XMCT(I)=XMCS(I)	00099400
	XCGAST(I)=XCGASS(I)	00099500
	GO TO 4508	00099600
4506	TGASS=(TSAVE+TGAS)/2.00	00099700
	XMCUT(I)=(XMCUS(I)+XMCU(I))/2.00	00099800
	XMCT(I)=(XMCS(I)+XMC(I))/2.00	00099900
	XCGAST(I)=(XCGASS(I)+XCGAS(I))/2.00	00100000
	GO TO 4508	00100100
4507	TGASS=TGAS	00100200
	XMCUT(I)=XMCU(I)	00100300
	XMCT(I)=XMC(I)	00100400
	XCGAST(I)=XCGAS(I)	00100500
4508	CONTINUE	00100600
	QDT1(I)=4.00*PIE*XLAMDA*R(I)*(TGASS-TC(I))*(1.00-(1.00+0.3400*	00100700
	1*(R(I)/XL)**(-1))*SHAPES	00100800
	X1DT=XMCUT(I)*ALFA1*81*DEXP(-E1/(CAPR*TC(I)))	00100900
	X2DT=XMCUT(I)*ALFA2*82*DEXP(-E2/(CAPR*TC(I)))	00101000
	FLUX=4.00*PIE*R(I)*XLAMDA*(1.00+0.300*REY**0.500*SHAPES**EXPNT)	00101100
	1*SHAPES	00101200
	BLOW=(X1DT+X2DT+XCGAST(I))*CPAV/FLUX	00101300
		00101400
		00101500
		00101600

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IF (BLGW.LE.0.00100) GO TO 451
IF (BLGW.GT.300.00) FLUX=0.000
IF (BLOW.LE.300.00) FLUX=(X10T+X2DT+XCGAST(I))*CPAV/(DEXP(BLOW)
*-1.00)
451 CONTINUE
C
C CONVECTIVE AND RADIATIVE TRANSFER
C
CONST=FLUX/(4.00*PIE*R(I)*XLAMDA*SHAPES)
IF (TEMP(I).EQ.TGAS) QDT1(I)=0.00
SENSE=QDOT(I)*CONST*PART(I)
QDT2(I)=CONST*QDT1(I)+4.00*PIE*(R(I)**2)*EMIS*1.3545D-12*
1(TW**4-TC(I)**4)*SHAPES
C
C HEAT RELEASE (ABSORPTION) AT SURFACE
C
IF (ZZ(I).LE.1.0-20) GO TO 457
C
C CALCULATE NEW VALUE OF EMC-CALL FUNCTION EMQI
C
HETHT=EMQI(EMC(I),R(I),XM1DOT,XM2DOT,TEMP(I),REY)
QDOT(I)=QDT2(I)+HETHT
457 CONTINUE
XNUM=QDOT(I)+XMCUT(I)*(ALFA1*DELH1*B1*DEXP(-E1/(CAPR*TC(I)))+
1ALFA2*DELH2*B2*DEXP(-E2/(CAPR*TC(I))))
DENOM=CC*XMCUT(I)+(PHIA/(1.00-PHIA))*CA*XMCO(I)
DTCOT(I)=XNUM/DENOM
GO TO 475
470 PRINT 471,XNUM,DENOM,QDT1(I),QDT2(I),QDOT(I),CONST,TC(I)
471 FORMAT(7(2X,1PE12.4))
475 CONTINUE
IF (TC(I).LT.0.00) GO TO 461
IF (DABS(TC(I)-TCS).GE.100.00) GO TO 461
IF (DABS(DTCOT(I)).GE.1.0+08) GO TO 461
GO TO 462
461 PRINT 454,I,J,TIMP,TC(I),DTCOT(I)
454 FORMAT(2X,'IN',2(2X,12),3(2X,E12.4))
462 TCS=TC(I)
CALL RUNGE(TIMP,DELT,I,J,TC,DTCOT)
IF (TC(I).LT.0.00) GO TO 463
IF (DABS(TC(I)-TCS).GE.100.00) GO TO 463
IF (DABS(DTCOT(I)).GE.1.0+08) GO TO 463
GO TO 464
463 PRINT 456,I,J,TIMP,TC(I),DTCOT(I)
456 FORMAT(2X,'OUT',2(2X,12),3(2X,E12.4))
464 TCS=TC(I)
IF (J.NE.0) GO TO 450
TEMP(I)=TC(I)
IF (DABS(TEMPO(I)-TEMP(I)).GE.100.00) PRINT 2004,I,TEMPO(I),TEMP(I)
2004 FORMAT(2X,'2004',2X,'I=',2X,12,2X,'TEMPO=',2X,1PE12.4,'TEMP=',2X,
*E12.4)
TEMPO(I)=TEMP(I)
C
C ADJUST DELT ACCORDING TO ALLOWED
C FRACTIONAL CHANGE IN TEMPERATURE
C
XAT=XAT1
C
IF (TEMP(I).LT.2000.00) XAT=XATSAV
DELT(I)=TGAS*XAT/DABS(DTCOT(I))
DELTTP(I)=DELT(I)

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453	IF(I.EQ.1) GO TO 455	00107700
	IF(DELT(I-1).LE.DELET(I)) DELT(I)=DELT(I-1)	00107800
455	DELTTE=DELT(I)	00107900
	SENSEN=SENSEN+SENSE+HETHT*PART(I)	00108000
500	CONTINUE	00108100
	NSTEPS=INCREM	00108200
	IF(TGAS.GT.6000.00) GO TO 5555	00108300
	DO 550 I=1,IRDIUS	00108400
	IF(TEMP(I).LT.250.DC.OR.TEMP(I).GT.6000.00) GO TO 5555	00108500
C	IF(TEMP(I).GT.6000.00) GO TO 5555	00108600
550	CONTINUE	00108700
	DELT=DELT	00108800
	IF(DELTTE.LE.DELTMA) DELT=DELTTE	00108900
	IF(DELTTE.GT.DELTMA) DELT=DELTMA	00109000
	IF(DELT.GT.TIME) DELT=TIME	00109100
	IF(DELT.GT.DTMAX) DELT=DTMAX	00109200
	IF(DELT.LT.DTMIN) DELT=DTMIN	00109300
	IF((DELT/DELT).GE.1.500) DELT=1.500*DELT	00109400
	IF(DELT.GE.1.0-06) GO TO 862	00109500
	PRINT 860, (DELT(I), I=1,7)	00109600
860	FORMAT(2X, 'DELT(I)...', 1P7E12.4)	00109700
	PRINT 861, (DELT(I), I=1,7)	00109800
861	FORMAT(2X, 'DELT(I)...', 1P7E12.4)	00109900
862	CONTINUE	00110000
C		00110100
	PSUM1=0.00	00110200
	PSUM2=0.00	00110300
	PSUM3=0.00	00110400
	DO 1984 I=1,IRDIUS	00110500
	PSUM1=PART(I)*(R(I)**2)*TEMP(I)+PSUM1	00110600
	PSUM2=PART(I)*(R(I)**2)*PSUM2	00110700
	PSUM3=G(I)*XM(I)+PSUM3	00110800
1984	CONTINUE	00110900
	TBB=PSUM1/PSUM2	00111000
	FFU=1.00-PSUM3	00111100
	MCH=MC*(1.00-FFU)	00111200
C	MGM=MGG*(1.00-DEXP(-(TIME/TCH))	00111300
	B1611=TIME/TCH	00111400
	IF(B1611.LE.2.00) MGM=MGG*(1.00-DCOS(PIE*B1611/2.00))/2.00	00111500
	IF(B1611.GT.2.00) MGM=MGG	00111600
	MGM3 = 0.00	00111700
C	IF(ISTAGE.EQ.1.AND.TIME.GT.T3DEL) MGM3=MGG*(1.00-DEXP(-(TIME-	00111800
C	1 T3DEL)/TCH3))	00111900
	B1622=0.00	00112000
	IF(ISTAGE.EQ.1.AND.TIME.GT.T3DEL) B1622=(TIME-T3DEL)/TCH3	00112100
	IF(B1622.LE.2.00) MGM3=MGG*(1.00-DCOS(PIE*B1622/2.00))/2.00	00112200
	IF(B1622.GT.2.00) MGM3=MGG	00112300
	GMGM3 = MGM + MGM3	00112400
	MP=MGM+MC+MK-MCH + MGM3	00112500
C	CALCULATE FRACTION OF CARBON UTILIZED	00112600
	SUMCH=0.00	00112700
	SUM=0.00	00112800
	DO 110 J=1,4	00112900
110	SUM=SUM+XJ(J)	00113000
	DO 111 J=1,4	00113100
	XJ(J)=XJ(J)/SUM	00113200
	ZGM(J)=MGM*XJ(J)	00113300
	ZGM3(J) = MGM3* XJ(J)	00113400
	GZGM3(J) = ZGM(J) + ZGM3(J)	00113500
	ZP(J)=MP*XJ(J)	00113600

ZCH(J)=ZGM(J)+ZC(J)+ZK(J)-ZP(J)+ZGM3(J)	00113700
ZZCH(J) = 0.00	00113800
DO 112 I = 1,IRDIUS	00113900
112 ZZCH(J) = ZZCH(J) + ZCHH(J,I)	00114000
111 SUMCH=SUMCH+ZCH(J)	00114100
DO 3113 J = 1,4	00114200
3113 XJCH(J)=ZCH(J)/SUMCH	00114300
FCU=1.-ZCH(2)	00114400
C PRINTOUT CHECK	00114500
C	00114600
C ORIGINALLY 7.5D-3	00114700
IF (TIME.EQ.1.0D-6) GO TO 5555	00114800
IDAM=IDAM+1	00114900
C	00115000
IF (IDAM.EQ.NPRINT) GO TO 5555	00115100
IF (TIME.LT.CHEC) GO TO 150	00115200
CHEC=CHC+TPRINT	00115300
NSTEPS=INCREM	00115400
INCREM=0	00115500
KK=1	00115600
IF (TGAS.LT.TTRANS) GO TO 580	00115700
IF (INDEX.EQ.1) GO TO 580	00115800
560 GO TO 1105	00115900
580 CONTINUE	00116000
C	00116100
C PRINTOUT	00116200
C	00116300
5555 CONTINUE	00116400
IDAM=0	00116500
C	00116600
EMWT=2.0D*YFH2+18.0D*YFH20+28.0D*YFC0+44.0D*YFC02+32.0D*YF02+	00116700
128.0D*YFN2+12.0D*YFC+16.0D*YFU+YFH+17.0D*YF0H+16.0D*YFCH4+26.0D*	00116800
2YFC2H2+30.0D*YFND+44.0D*YFN20	00116900
DENS=EMWT*PRESS/GASCUN/TGAS	00117000
DO 600 J=1,4	00117100
600 YYVOL(J)=(XJ1(J)*FVOL1+XJ2(J)*FVOL2)/AJ(J)	00117200
YYVOL(3)=YYVOL(4)	00117300
SUM=0.00	00117400
DO 607 M=1,3	00117500
607 SUM=SUM+YYVOL(M)	00117600
DO 602 M=1,3	00117700
602 YYVOL(M)=YYVOL(M)/SUM	00117800
C	00117900
YYCH(2)=ZCH(2)/AJ(2)	00118000
YYCH(1)=ZCH(1)/AJ(1)	00118100
YYCH(3)=ZCH(4)/AJ(4)	00118200
SUM=0.00	00118300
DO 603 M=1,3	00118400
603 SUM=SUM+YYCH(M)	00118500
DO 604 M=1,3	00118600
604 YYCH(M)=YYCH(M)/SUM	00118700
C	00118800
YYP(1)=YJ(1)	00118900
YYP(2)=YJ(2)	00119000
YYP(3)=YJ(4)	00119100
SUM=0.00	00119200
DO 605 M=1,3	00119300
605 SUM=SUM+YYP(M)	00119400
DO 606 M=1,3	00119500
606 YYP(M)=YYP(M)/SUM	00119600

	PHIAB=FASH/(FASH+FC)	00119700
	PRINT 91,TIME,TGAS,F,FC,PHIAB,HHH,VOLYLO,CPAV,NSTEPS	00119800
	PRINT 97,SOOT1,SOOT2,FC1,FC2,FCGAS,HSENS,CGAS,TBB,IT	00119900
	PRINT 95,MGM,MC,MK,MP,MCH,DENS,MGM3,GMGM3	00120000
	PRINT 89,SUMQR,SUMMR,SUMQE,SUMMQE,SUMXX,FGM3,HGM3,SUMX1	00120100
	PRINT 920,(ZGM(J),J=1,4)	00120200
	PRINT 925,(GZGM3(J),J=1,4)	00120300
	PRINT 915,(YYVOL(M),M=1,3)	00120400
	PRINT 921,(ZCHI(J),J=1,4)	00120500
	PRINT 923,(ZZCH(J),J=1,4)	00120600
	PRINT 916,(YYCH(M),M=1,3)	00120700
	PRINT 922,(ZP(J),J=1,4)	00120800
	PRINT 98,YJ(1),YJ(2),YJ(3),YJ(4),FVOL1,FVOL2,FCU,FFU,LL	00120900
	PRINT 917,(YYP(M),M=1,3)	00121000
	PRINT 910,YFH2,YFH20,YFCO,YFCO2,YFO2,YFN2,YFC,YFCC,YFO,YFH,YFCH,	00121100
	1YFCH4,YFC2H2,YFNO,YFN20,EMWT,NSHIFT	00121200
	PRINT 311	00121300
	DO 875 I=1,IRDIUS	00121400
	PRINT 94,I,R(I),RHOCOR(I),TEMP(I),XM(I),XM1(I),XM2(I),XCC(I),	00121500
	*VELP(I)	00121600
875	CONTINUE	00121700
	PRINT 311	00121800
	IT=0	00121900
	DO 880 J=1,4	00122000
	IF(XJ(J).GT.100.00)GO TO 881	00122100
880	CONTINUE	00122200
	GO TO 883	00122300
881	PRINT 882,(XJ(J),J=1,4)	00122400
882	FORMAT(2X,'XJ(J)=' ,2X,1P4E12.4)	00122500
	GO TO 99	00122600
883	CONTINUE	00122700
C		00122800
	DO 123 I=1,IRDIUS	00122900
	IF(DABS(TEMPO(I)-TEMP(I)).GE.100.00)PRINT 2007,I,TEMPO(I),TEMP(I)	00123000
2007	FORMAT(2X,'2007',2X,'I=' ,2X,I2,2X,'TEMPO=' ,2X,1PE12.4,'TEMP=' ,2X,	00123100
	*E12.4)	00123200
	TEMPO(I)=TEMP(I)	00123300
	IF(TGAS.GT.6000.00)GO TO 99	00123400
C		00123500
	IF(TGAS.GT.6000.00.OR.TEMP(I).GT.6000.00) GO TO 99	00123600
C		00123700
	IF(TGAS.LT.250.00.OR.TEMP(I).LT.250.00) GO TO 99	00123800
123	CONTINUE	00123900
311	FORMAT(/)	00124000
98	FORMAT(2X,'YJ.....',1PE11.4,3X,E11.4,3(3X,E11.4),5X,E11.4,4X,E11.4,	00124100
	*4X,E11.4,19)	00124200
97	FORMAT(2X,'SOOT...',1PE11.4,3X,E11.4,3(3X,E11.4),5X,E11.4,4X,E11.4,	00124300
	*4X,E11.4,19)	00124400
920	FORMAT(2X,'ZGM...',1PE11.4,3X,E11.4,2(3X,E11.4))	00124500
925	FORMAT(2X,'GZGM3...',1PE11.4,3X,E11.4,2(3X,E11.4))	00124600
921	FORMAT(2X,'ZCH...',1PE11.4,3X,E11.4,2(3X,E11.4))	00124700
923	FORMAT(2X,'ZZCH...',1PE11.4,3X,E11.4,2(3X,E11.4))	00124800
922	FORMAT(2X,'ZP...',1PE11.4,3X,E11.4,2(3X,E11.4))	00124900
915	FORMAT(2X,'YYVOL...',1PE11.4,3X,E11.4,17X,E11.4)	00125000
916	FORMAT(2X,'YYCH...',1PE11.4,3X,E11.4,17X,E11.4)	00125100
917	FORMAT(2X,'YYP...',1PE11.4,3X,E11.4,17X,E11.4)	00125200
91	FORMAT(2X,'TIME...',1PE11.4,3X,E11.4,3(3X,E11.4),5X,E11.4,4X,E11.4,	00125300
	*4X,E11.4,19)	00125400
95	FORMAT(2X,'M.....',1PE11.4,3X,E11.4,3(3X,E11.4),5X,3(E11.4,4X))	00125500
89	FORMAT(2X,'SUM...',1PE11.4,3X,E11.4,3(3X,E11.4),5X,3(E11.4,4X))	00125600
910	FORMAT(2X,'YF...',1PE11.4,3X,E11.4,3(3X,E11.4),5X,E11.4,4X,E11.4,	
	14X,E11.4,7,8X,E11.4,3X,E11.4,3(3X,E11.4),5X,E11.4,2(4X,E11.4),19)	

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94 FORMAT(7X,I3,7X,1PE11.4,3(4X,E11.4),5X,E11.4,5X,E11.4,5X,E11.4,1X,00125700
1E9.2) 00125800
GO TO 150 00125900
C 00126000
P2161B EQUILIBRIUM PROGRAM 00126100
C 00126200
1105 TGUSS=TGAS 00126300
C 00126400
COMPUTE ELEMENTAL MOLE FRACTIONS FOR USE IN P2161B EQUIL. PACKAGE 00126500
SCALE BY A FACTOR OF TEN FOR RAPID CONVERGENCE 00126600
C 00126700
SUM=0.00 00126800
DO 310 J=1,4 00126900
310 SUM=SUM + (XJ(J)/AJ(J)) 00127000
DO 315 J=1,4 00127100
315 YJ(J)=(XJ(J)/AJ(J))/SUM 00127200
IF (YJ(2).EQ.0.00) GO TO 1130 00127300
YJSAVE=YJ(2) 00127400
DO 1130 J=1,4 00127500
YJ(J)=YJ(J)/YJSAVE 00127600
1130 CONTINUE 00127700
H=10.00*YJ(1) 00127800
C=10.00*YJ(2) 00127900
N=10.00*YJ(3) 00128000
O=10.00*YJ(4) 00128100
TMP=TGUSS 00128200
C 00128300
IP=1 00128400
DO 1117 IP=1,NOPAIR 00128500
PMP=PRES(IP) 00128600
HOMWX=HCPG(IP) 00128700
PMP=PRESS 00128800
IT=0 00128900
NOSC=0 00129000
IF (NCOMB.GT.0) GO TO 1110 00129100
HOMWX=HHH 00129200
CALL HPCHEM(TMP,PMP,PERT,SPNUM,NSAME,IPOX,HOMWX,SOMWX,RCGGX, 00129300
1ACPSX,SUMMWX,SUMNIX,ZX,DHDTX,DHDPX,DSOTX,DSOPX,DRDTX,DRDPX,XMU, 00129400
2RTP,RPP,NELEX,IGASEX,ICONEX,EPST,MIT,IGCOF,HFINAL,D,XNAM1,XNAM2, 00129500
3NGTH,TOL5,IT,NOSC) 00129600
IPOX=IPR21 00129700
799 CONTINUE 00129800
IF (IGCOF.GT.0) 00129900
1PRINT 800,IGCOF 00130000
800 FORMAT(2X,'TROUBLE IN PTCHEM SUBROUTINE',/,2X,'IGCOF=',I6) 00130100
IF (IGCOF-1)1117,1107,1108 00130200
1107 WRITE(6,9000) 00130300
GO TO 1115 00130400
1108 IF (IGCOF-2)1109,1109,1115 00130500
1109 WRITE(6,9001) 00130600
GO TO 1115 00130700
1110 CONTINUE 00130800
IPROX=1 00130900
PRINT 1125, H,C,N,O 00131000
C1125 FORMAT(/,10X,'H'=',1PE12.4,5X,'C'=',E12.4,5X,'N'=',E12.4,5X, 00131100
* 'O'=',E12.4/) 00131200
C 00131300
1111 CALL PTCHEM(TMP,PMP,PERT,SPNUM,NSAME,IPOX,HOMWX,SOMWX,RCGGX, 00131300
1ACPSX,SUMMWX,SUMNIX,ZX,DHDTX,DHDPX,DSOTX,DSOPX,DRDTX,DRDPX,XMU, 00131400
2RTP,RPP,NELEX,IGASEX,ICONEX,IGCOF,D,XNAM1,XNAM2,NGTH,TOL5,IT, 00131500
3NOSC) 00131600

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GO TO 799	00131700
1115 TMP=TGUESS	00131800
XMU(11)=0.000	00131900
DO 1116 11=1,NELEX	00132000
1116 CONTINUE	00132100
1117 CONTINUE	00132200
9001 FORMAT(1X,24HTEMP TOO LOW, SKIP CASE)	00132300
9000 FORMAT(1X,24HTEMP TOO HIGH, SKIP CASE)	00132400
C	00132500
TGUESS =TMP	00132600
TGAS21=TMP	00132700
IF (CSUBP.LT..0100) GO TO 1120	00132800
CPSCAL=CPEQLB/CSUBP	00132900
CPAV=CSUBP	00133000
1120 CONTINUE	00133100
TSCALE=TEQLB/TMP	00133200
TGAS=TMP	00133300
INDEX=1	00133400
ITITER=1	00133500
YFC=ZX(1)	00133600
YFCH4=ZX(2)	00133700
YFCO=ZX(3)	00133800
YFCO2=ZX(4)	00133900
YFC2H2=ZX(5)	00134000
YFH=ZX(6)	00134100
YFOH=ZX(7)	00134200
YFH2=ZX(8)	00134300
YFH2O=ZX(9)	00134400
YFNO=ZX(10)	00134500
YFN2=ZX(11)	00134600
YFN2O=ZX(12)	00134700
YFO=ZX(13)	00134800
YFO2=ZX(14)	00134900
YFCC=ZX(15)	00135000
IF(NCUMB.EQ.1) GO TO 51	00135100
IF(NCUMB.EQ.3) GO TO 53	00135200
IF(INCREM.EQ.0)GO TO 500	00135300
GO TO 420	00135400
9992 PRINT 9993	00135500
9993 FORMAT(' CARBON CONTENT IN COAL NOT UNITY')	00135600
GO TO 99	00135700
9996 PRINT 9998,GTOTAL,XJOTOT,XJITOT,XJITOT,XJ2TOT	00135800
9998 FORMAT(2X,'A SUM OF INPUT MASS FRACTIONS OR INPUT SIZE DISTRIBUTION	00135900
INS DOES NOT EQUAL 1.0',/5X,5(E12.5,2X))	00136000
99 GO TO 1	00136100
610 STOP	00136200
C	00136300
DEBUG UNIT(6),SUBCHK	00136400
END	

SUBROUTINES

EQUILIB (Basic Thermochemistry)

LINES 1365–1487

FUNCTION EMQI (Particle Energy Balance)

LINES 1579–1635

VLCOMP (Volatile Composition)

LINES 2947–3016

NB. PROGRAM STATEMENTS 1488–1578 AND 1636–2946 TREAT THE COMPLETE THERMOCHEMISTRY. SINCE THIS IS A STANDARD FORM OF THERMOCHEMISTRY CODE, IT IS NOT DETAILED HERE.

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SUBROUTINE EQU18IT,HSENS,MCHENI
IMPLICIT REAL*8(A-M,O-Z)
COMMON/READ/TRANS
COMMON/EDB/NN
COMMON/AJ/XJ(4),AJ(4),YJ(4)
COMMON/B/YFN2,YFM2,YFCO,YFCO2,YFN2,YFC,YFO2
COMMON/C/YFO,YFM,YFOM
COMMON/D/D1
SUM=0.000
DO 10 I=1,4
SUM=SUM+XJ(I)/AJ(I)
10 CONTINUE

DO 20 I=1,4
YJ(I)=(XJ(I)/AJ(I))/SUM
20 CONTINUE
PRINT 100,(XJ(I),I=1,4)
C 100 FORMAT(2X,1X(I=1,4),4(2X,1PE14.4))
A=0.5*YJ(1)+0.2*YJ(2)-YJ(4)
IF(A.LE.0.000)GO TO 30
C=YJ(2)*YJ(2)-YJ(4)
IF(C.LE.0.000)GO TO 50
GO TO 40
30 YN2=0.5*YJ(3)
PRINT 101
C 101 FORMAT(4X,30)
YH20=0.5*YJ(1)
YCO2=YJ(2)
Y02=0.500*(YJ(4)-2.00*YJ(2)-0.500*YJ(1))
IF(Y02.LT.0.00) Y02=0.00
YCO=0.000
YH2=0.000
YC=0.000
GO TO 70
40 YN2=0.5*YJ(1)
PRINT 102
C 102 FORMAT(4X,40)
YH20=0.5*YJ(1)
YCO=YJ(4)
YC=YJ(2)-YJ(4)
YCO2=0.000
YH20=0.000
Y02=0.000
GO TO 70
50 PK=0.00391500*T-3.1900
PRINT 103
C 103 FORMAT(4X,50)
A=PK-1.00
B=PK*(1.300*YJ(1)+YJ(2)-YJ(4))+YJ(4)
ARG=B*0.2-D0*ASC
PRINT 104,ARG
C 104 FORMAT(1X,ARG,...,1PE14.4)
IF(ARG.LE.0.000)GO TO 60
YCO2=1050RT(ARG)-81/2.00*A)
YCO=YJ(2)-YCO2
IF(YCO.LT.0.00) YCO=0.000
YH20=YJ(1)-YJ(2)-YCO2
IF(YH20.LT.0.0) YH20=0.00
IF(YH20.LT.0.00)YH20=0.00
YH2=0.5*YJ(1)-YH20
IF(YH2.LT.0.00) YH2=0.00
YH2=0.500*YJ(3)
Y02=0.000
YC=0.000
NN=50
GO TO 70
60 YCO2=YJ(4)-0.500*YJ(1)-YJ(2)
PRINT 105
C 105 FORMAT(4X,60)
IF(YCO2.LT.0.00) YCO2=0.00
IF(YCO.LT.0.00) YCO=0.00
YCO=2.00*YJ(2)+0.500*YJ(1)-YJ(4)
Y02=0.00

YN2=0.500*YJ(3)
YH2=0.00
YH20=0.500*YJ(1)
YC=0.00
NN=60
70 D2=YH2+YH20+YCO+YCO2+Y02+YN2+YC
PRINT 106,YH20,YCO2,YCO,...,3(2X,1PE14.4),/)
C 106 FORMAT(1X,YH20,YCO2,YCO,...,3(2X,1PE14.4),/)
YFH2=YH2/D2
YFH20=YH20/D2
YFCO=YCO/D2
YFCO2=YCO2/D2
YFO2=Y02/D2
YFN2=YN2/D2
YFC=YC/D2
YF=HNSUR(YFH2)=1402.400*DEXP(-27328.00/T)
YFO=D5QRT(YFO2)=3179.300*DEXP(-30527.00/T)
PRINT 900,YFM2,YFM20,YFCO,YFCO2,YFO2,YFN2,YFC,YFM,YFO
C 900 FORMAT(1X,EQU18I,/,1PE15.5)
YFOH=1.2600*(YFH20+15.66700)+1.0163.000*DEXP(-35188.00/T))*
*0.66700)
D6=1.00+YFO+YFOM+YFM
YFH2=YFH2/D6
YFH20=YFH20/D6
YFCO=YFCO/D6
YFCO2=YFCO2/D6
YFO2=YFO2/D6
YFO2=YFH2/D6
YFC=YFC/D6
YFM=YFM/D6
YFO=YFO/D6
YFOM=YFOM/D6
D1=2.00*YFH2+18.00*YFH20+28.00*YFCO+44.00*YFCO2+32.00*YFO2
1+2.00*YFN2+12.00*YFC+YFM+18.00*YFO+17.00*YFOM
H02=(1.00+2.4600*DEXP(-1600.00/T))*
H02=(1.00+2.6000*DEXP(-5700.00/T))*
H02=(1.00+2.8000*DEXP(-2630.00/T))*
H02=(1.00+2.6200*DEXP(-2320.00/T))*
H02=(1.3700+7.7500*DEXP(-1090.00/T))*
H02=(1.7500+5.3500*DEXP(-2130.00/T))*
HCL=1077.00*DEXP(1/953.00)
H0=4.9700*T
H0=(5.3900-0.3800*DEXP(-320.00/T))*T
H0H=(7.0800+2.8300*DEXP(-3880.00/T))*T
HCHM=(57103.00*YFH20+93965.00*YFCO2+27200.00*YFCO)/D1
1+(5162.100*YFM+8989.00*YFO+9289.00*YFOM)/D1
HSENS=YFN2*H02+YFH20*H02+YFCO2*H02+YFH2*H02+YFO2*H02+
1YFCO*H0+YFC*HCL+YFH*H0+YFO*H0+YFOM*H0)/D1
RETURN
C DEBUG UNIT(6),SUBCHK,SUBTRACE
END

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```

FUNCTION EMQ1(EMC,R,X1DT,X2DT,TEMP,REV)
IMPLICIT REAL*8(A-H,O-Z)
DOUBLE PRECISION MC,HV,KCAP(5),MCJJ(5),MOX
COMMON/B/VFN2,VFN20,VFC0,VFC02,VFN2,VFC,VF02
COMMON/C/VFO,VFOH
COMMON/D/D1
COMMON/E/EJ(6),XNUJJ(6),ROD,PIE,RHOG,CAPR,SHAPES,EXPNT
COMMON/G/WV1,WV2
DIMENSION VJJ(5),VINFI(5)
VMD=18.00*VFN2/D1
YC0=48.00*VFC0/D1
Y02=32.00*VFC02/D1
YOM=17.00*VFOH/D1
YQ=16.00*VFO/D1
VINFI(1)=Y0
VINFI(2)=YOM
VINFI(3)=Y02
VINFI(4)=YH20
VINFI(5)=YC02
MC=EMC/(4.00*PIE*ROD*R)
MV=(X1DT*X2DT)/(4.00*PIE*ROD*R)
DO 10 JJ=1,5
  KJJ(JJ)=BJJ(JJ)*DEXP(-(EJ(JJ)/(CAPR*TEMP)))
  KCAP(JJ)=KJJ(JJ)*[R*RHOG/(ROD*(1.00+0.300*REV**0.500*SHAPES**
    *EXPNT))]
  IF((MC*MV).LE.0) MV=1.0D-20
  PART2=DEXP(-(MC*MV))
  PART2=1.00*(KCAP(JJ)/(MC*MV))+(1.00-PART2)
  VJJ(JJ)=VINFI(JJ)*(PART1/PART2)
  MCJJ(JJ)=KJJ(JJ)*VJJ(JJ)*XNUJJ(JJ)
  *ORHOG=1.00*PIE*R*2*SHAPES
10 CONTINUE
MOX=16.00*(X1DT/MV1*X2DT/MV2)
DO 20 JJ=1,5
  IF(TEMP.E.0.00)GO TO 21
  MCJJ(JJ)=0.00
20 MCJJ(JJ)=--TEST
GO TO 20
21 ISAY=JJ
DO 22 JJ=1,5
  EMC=0.000
  GO TO 23
22 SUM=0.000
  DO 30 JJ=ISAY,5
    SUM=SUM+MCJJ(JJ)
30 CONTINUE
  EMC=7500*SUM
23 CONTINUE
C 02--NO HEAT OF FORMATION
  EMQ1=MCJJ(1)*3823.100+MCJJ(2)*580.600+MCJJ(5)*4172.300-
  *MCJJ(4)*3464.400+EMC*2265.00
RETURN
C 900
  DEBUG UNIT(6),SUBCHK,SUBTRACE
C -
  END

```

```

SUBROUTINE VLCOMP(ALF,MPYR,CMBN,VMB1,VMB2,K,MCOAL,CAB,CHMB,HCHAR)
IMPLICIT REAL*8(A-H,O-Z)
DIMENSION CMBN(4),CAB(4),CAB(4),CHAB(4),CHMB(4),VAB(4),VMB(4)
ALF(2),MPYR(2),MCVOL(2),VAB(4),VAB(4),VMB(2),DMVOL(2)
COMMON/A/XJ(4),AJ(4),VJ(4)
COMMON/G/WV1,WV2
COMMON/H/DELHVI,DELHVV
PRINT 10
10 FORMAT(1H1)
SUM=0.00
DO 40 J=1,4
  SUM=SUM+CMBN(J)
40 CONTINUE
DO 50 J=1,4
  CMB(J)=CMBN(J)/SUM
  CAB(J)=SUM*CMB(J)*AJ(2)/(CMBN(2)*AJ(J))
  CHAB(J)=CHMB(J)*AJ(2)/(CMBN(2)*AJ(J))
50 CONTINUE
MCOAL=AJ(2)/CMB(2)
MCHN=MCOAL/AJ(2)
MCHAR=AJ(2)/CHMB(2)
HCHAR=MCHAR*HCHAR*CHAB(1)*500+57798.00-CHAB(2)*94054.00
HFCOAL=MCOAL*MCOAL-CAB(1)*500+57798.00-CAB(2)*94034.00
PRINT 55,(CMB(J),J=1,4),(CAB(J),J=1,4),(CHMB(J),J=1,4),
  (CHAB(J),J=1,4)
55 FORMAT(5X,'COMPOSITION ON MASS AND ATOM BASIS',FOR COAL AND CH
  *AR,M,C,H,O,/,5X,'CMB(1)=',1PE12.4,X,'CMB(2)=',1PE12.4,X,
  *CMB(3)=',1PE12.4,X,'CMB(4)=',1PE12.4,X,'CAB(1)=',1PE12.4,X,'CAB(2)=',1PE12.4,X,
  *CAB(3)=',1PE12.4,X,'CAB(4)=',1PE12.4,X,'CHMB(1)=',1PE12.4,X,
  *CHMB(2)=',1PE12.4,X,'CHMB(3)=',1PE12.4,X,'CHMB(4)=',1PE12.4,X,
  *CHAB(1)=',1PE12.4,X,'CHAB(2)=',1PE12.4,X,'CHAB(3)=',1PE12.4,X,
  *CHAB(4)=',1PE12.4,X,/,)
56 PRINT 56,HFCOAL,HFCOAL,MCHAR,MCHN,MCOAL
56 FORMAT(5X,'HFCOAL= ',1PE11.4,X,'HFCOAL= ',1PE11.4,X,
  *HFCOAL= ',1PE11.4,X,'HFCOAL= ',1PE11.4,X,
  *HFCOAL= ',1PE11.4,X,/,)
DO 70 I=1,4
  ALFA=1/F(I)
  IF(DABS(ALF(I))-LT.1.0D-06)ALFA=0.800
  ALFA=1.0D-(1.0D-ALFA)*MCOAL/MCHAR
  IF(ALFA.LT.0.00)GO TO 999
  MVOL(1)=ALFA*MCOAL/ALFA
  DMVOL(1)=MPYR(1)*HFCOAL/(MCOAL*ALFA)-HFCOAL*(1.0D-ALFA)/(
  *ALFA*MCHAR)
  MVOL(1)=HFCOAL-HCHAR*(1.0D-ALFA)/ALFA-MPYR(1)
  DO 60 J=1,4
    VAB(J)=(CAB(J)-(1-ALFA)*CHAB(J))/ALFA
    VMB(J)=VAB(J)*AJ(J)/DMVOL(1)
    IF(1.EQ.1)VMB(1)=VMB(J)
60 CONTINUE
  IF(1.EQ.2)VMB(2)=VMB(J)
60 PRINT 65,ALFA,MVOL(1),MVOL(1),VAB(J),J=1,4)
65 FORMAT(5X,ALFA(ATOM)=',1PE12.4,X,'V-VOLATILES=',1PE12.4,X,
  *MC-VOLAT= ',1PE12.4,X,'VAB(1)=',1PE12.4,X,'VAB(2)=',1PE12.4,X,
  *VAB(3)=',1PE12.4,X,'VAB(4)=',1PE12.4,X,/,)
70 CONTINUE
WV1=DMVOL(1)
WV2=DMVOL(2)
DELHVI=DMVOL(1)
DELHVV=DMVOL(2)
RETURN
999 CONTINUE
VOLMIN=(CAB(1)*0.0100+CAB(3)*0.0100+CAB(4)*0.0100)/MCOAL
PRINT 75,VOLMIN
75 FORMAT(5X,'MINIMUM VOLATILE YIELD MUST BE =',1PE12.4,X,' SO THAT',
  *ONLY CARBON REMAINS',/)
STOP
C
  DEBUG UNIT(6),SUBCHK,SUBTRACE
  END

```

SAMPLE CASE PRINTOUT

SAMPLE CASE PRINTOUT

B) RECIRCULATION GAS PROPERTIES

```
ALFA(ATUM) = 2.67410D-01 W-VOLATILES = 2.19170D+01 MC-VOLAT = 7.94900D+03
VAB(1) = 3.08120D+00 VAB(2) = 1.00000D+00 VAB(3) = 4.40100D-02 VAB(4) = 3.88730D-01

ALFA(ATUM) = 7.55800D-01 W-VOLATILES = 1.53590D+01 MC-VOLAT = 7.88650D+03
VAB(1) = 1.09010D+00 VAB(2) = 1.00000D+00 VAB(3) = 1.55710D-02 VAB(4) = 1.37540D-01
```

ILL. 04 TLST 0/23/83

COAL DEVOLATILIZATION INPUTS

-208-

D) RECIRCULATION GAS PROPERTIES

THERMO-CHEMICAL CALCULATIONS PROBLEM 1313

TOTAL PRESSURE = 1.000000D+00 TEMP = 1.700000D+03
 TOTAL VOLUME = 9.008941D+06 HT(REF) = 0.0 SUM N = 1.433073D+02
 H 8.309179D+00 C 1.000000D+01 N 9.795721D+01 O 2.704106D+01
 XMU(1) = 1.500655D+01 2.844338D+01 1.302867D+01 1.569762D+01
 D(XBAR)/DT = 5.062957D-05 -1.534335D-02 1.126957D-03 1.217459D-03
 D(XBAR)/DP = -2.090521D-03 -5.795443D-04 -5.000162D-01 -4.998409D-01
 D(MU)/DP = -2.502956D-01 -5.795443D-04 -5.000162D-01 -4.998409D-01
 N CONSERVATION = 4 N GAS = 14 N CONDENSED = 1 ITER = 26 ITERMA = 5 IT = 0 NOSC = 0

NO. GASEOUS SPECIES	N(K) MOLES	X(K) MOLE FRAC	P(K) ATM	LOG10(P(K))	MOLECULES/CC	RMO(K) GM/CC	RMO/RMU ZERO	G(K) STD FR ENGY
1 C	5.0694D-24	7.8496D-26	7.8496D-26	-2.5105D+01	3.3892D-07	6.7587D-30	5.2268D-27	-2.9163D+01
2 CH4	2.3981D-23	3.7133D-25	3.7133D-25	-2.4430D+01	1.8033D-06	4.2706D-29	3.1026D-26	-3.2217D+01
3 CO	4.3780D-03	7.0916D-05	7.0916D-05	-4.1493D+00	3.0619D-14	1.4243D-08	1.1912D-09	-3.4587D+01
4 CO2	9.9954D+00	1.5417D-01	1.5417D-01	-8.0103D-01	6.4825D+17	4.8830D-05	3.1762D-02	-5.7973D+01
5 C2H2	1.0400D-30	1.6104D-32	1.6104D-32	-3.1793D+01	6.9511D-14	3.0059D-36	2.2266D-33	-1.1694D+01
6 H	2.7897D-08	4.3196D-09	4.3196D-09	-8.3648D+00	1.8811D+12	2.1214D-12	2.4139D-09	-3.3163D+01
7 OH	1.0940D-02	1.6948D-04	1.6948D-04	-6.7709D+00	1.8811D+12	2.1214D-12	1.9980D-09	-1.2021D+01
8 H2	5.0092D-04	8.6834D-06	8.6834D-06	-3.0612D+00	3.1810D+13	1.2332D-10	6.7070D-08	-1.8350D+01
9 H2O	4.1485D+00	6.4237D-02	6.4237D-02	-1.1922D+00	2.7715D+17	8.2962D-06	6.4158D-03	-1.2966D+01
10 NO	6.3654D-12	9.8983D-04	9.8983D-04	-1.0063D+00	3.4724D+18	2.1203D-07	1.6397D-04	-1.1804D+01
11 N2	4.8947D+01	7.5790D-01	7.5790D-01	-1.1035D+01	3.4724D+18	1.1221D-04	1.1771D-01	-3.5780D+01
12 N2O	3.2338D-06	5.0383D-08	5.0383D-08	-1.2977D+01	2.1734D+11	1.3897D-11	1.1224D-08	-1.4951D+01
13 O	4.2405D-04	6.5661D-06	6.5661D-06	-1.1887D+00	4.8134D+13	7.5312D-10	3.8291D-07	-1.1640D+01
14 O2	1.4110D+00	2.1849D-02	2.1849D-02	-1.6606D+00	4.4336D+16	5.0120D-06	3.8760D-03	-2.7572D+01

NO. CONDENSED SPECIES	N(K) MOLES	X(K) MOLE FRAC	G(K) STD FR ENGY
15 C	0.0	0.0	-2.3985D+00

GASEOUS SUM H	H/RT	H/MW	H/RTZERO	S/R	MW	SUM N(K)	M	S/MW
KCAL		KCAL/GM					GM	
-2.5700D+02	-1.1779D+00	-1.3293D-01	-7.3311D+00	3.1492D+01	2.9936D+01	6.4582D+01	1.9333D+03	2.0905D+00

MOLECULES/CC	RMU GM/CC	RMO SLUGS/CC FT	RMO/RMU ZERO	CP CAL/GM DEG	GAMMA	Y/M CC/GM	A FT/SEC
4.3177D+18	2.1460D-04	4.1639D-04	1.6596D-01	3.2399D-01	1.2885D+00	4.6598D+03	2.5290D+03

CONDENSED SUM H	H/RT	H/MW	H/RTZERO	S/R	MW	SUM N(K)	M	S/MW
KCAL		KCAL/GM					GM	
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TOTAL SUM H	H/RT	H/MW	H/RTZERO	S/R	MW	SUM N(K)	M	S/MW
KCAL		KCAL/GM					GM	
-2.5700D+02	-1.1779D+00	-1.3293D-01	-7.3311D+00	3.1492D+01	2.9936D+01	6.4582D+01	1.9333D+03	2.0905D+00

CP(FROZEN)	CV(FROZEN)	GAMMA(FROZEN)	A(FROZEN)	A
CAL/GM DEG	CAL/GM DEG		CM/SEC	CM/SEC
3.17669733D-01	2.51282176D-01	1.26417933D+00	7.72584385D+04	7.70841311D+04

COMBUSTION GAS PROPERTIES

CAPMO=-1.3293D+02 YFM2= 8.6854D-06 YFM2D= 6.4237D-02 YFCO= 7.0916D-05 YFCO2= 1.5477D-01 YFM2= 7.5790D-01 YFC= 7.8496D-26
 YFO2= 2.1849D-02 YFO= 6.5661D-06 YFM= 4.3196D-07 YFOM= 1.6948D-04 YFCC= 0.0
 MOLWT= 2.9921D+01GM/MOLE DENS= 2.1449D-04GM/CC

E) AIR AND CARRIER GAS PROPERTIES

THERMO-CHEMICAL CALCULATIONS PROBLEM 1313

TOTAL PRESSURE = 1.000000+00 TEMP = 5.000000+02
 TOTAL VOLUME = 1.078030+13 MT(REF) = 0.0 SUM M = 8.3250010+08
 M 1.200000+02 C 1.000000+01 N 6.600000+08 O 1.725000+08

XMU(1) = 4.0861390+01 1.1154730+02 1.0787650+01 1.2275570+01
 O(XBARI)/DT = 3.015750-06
 U(XBARI)/DT = -5.200550-02 -1.8775120-01 3.5006070-03 3.5495260-03
 D(XBARI)/DP = -1.2930510-05
 D(XBARI)/DP = -2.5000000-01 -2.3283060-10 -5.0000000-01 -5.0000000-01
 N CONSERVATION = 4 M GAS = 14 M CONDENSED = 1 ITER = 20 ITERMR = 6 IT = 0 MOSC = 0

NO. GASEOUS SPECIES	N(K) MOLES	X(K) MOLE FRAC	P(K) ATM	LOG10(P(K))	MOLECULES/CC	RMO(K) CM/CC	RMU/RMO ZERO	G(K) STD FR ENGY
1 C	0.0	0.0	0.0	-5.00000+02	0.0	0.0	0.0	1.52950+02
2 CH4	0.0	0.0	0.0	-5.00000+02	0.0	0.0	0.0	-3.65880+01
3 CO	0.7690-25	0.0	0.0	-3.2020+01	7.32400-14	0.0	0.0	-4.94450+01
4 CO2	1.00000+01	2.0240-08	2.48240-08	-9.21930+00	3.32290+11	3.32290-11	2.63430-33	-1.18550+02
5 C2H2	0.0	0.0	0.0	-5.00000+02	0.0	0.0	0.0	-3.22750+01
6 H2	5.85100-27	1.40560-35	1.40560-35	-3.48520+01	2.06350-16	3.45340-40	2.67070-37	-3.93890+01
7 OH	7.18480-10	1.75360-18	1.75360-18	-1.82500+01	7.11100-09	4.17780-42	1.88320-17	-1.10210+01
8 H2O	1.1820-10	4.13800-10	4.12800-10	-1.38400+01	2.08640+00	4.32850-11	4.80100-08	-7.02460+01
9 H2O	6.03000+01	1.44140-07	1.44140-07	-6.84120+00	2.11400+13	4.32850-11	4.80100-08	-7.02460+01
10 NO	2.78120-01	6.68170-10	6.68170-10	-9.17510+00	9.80870+09	4.88700-13	3.77930-10	-1.93670+00
11 NO	3.37000+08	7.92790-01	7.92790-01	-1.00840-01	1.19280+19	5.41360-04	4.18650-01	-2.13430+01
12 NO	3.37000+08	7.92790-01	7.92790-01	-1.00840-01	1.19280+19	5.41360-04	4.18650-01	-2.13430+01
13 O2	2.16830-19	4.23770-34	4.23770-34	-2.32740+01	7.71830-05	2.05040-17	1.58560-24	4.13270+01
14 O2	8.62500+07	2.07210-01	2.07210-01	-6.83900-01	3.04180+18	1.61610-04	1.24980-01	-2.29770+01

NO. CONDENSED SPECIES	N(K) MOLES	X(K) MOLE FRAC	G(K) STD FR ENGY
15 C	0.0	0.0	-5.80800-01

GASEOUS SUM H	H/RT	H/MW	H/RTZERO	S/R	MW	SUM N(K)	M	S/MW
KCAL	1.43200+09	3.51070+00	1.20950-01	6.42640+00	2.57030+01	2.88420+01	4.16250+08	1.20050+10
KCAL								1.77100+00

MOLECULES/CC	RMO	RMO	RMO	CP	GAMMA	V/M	A
CM/CC	1.46800+19	7.02970-04	1.36400-03	5.43630-01	2.44990-01	1.39130+00	1.42250+03
SLUGS/CC							1.44920+03
FT/SEC							

CONDENSED SUM H	H/RT	H/MW	H/RTZERO	S/R	MW	SUM N(K)	M	S/MW
KCAL	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
KCAL/GM								

TOTAL SUM H	H/RT	H/MW	H/RTZERO	S/R	MW	SUM N(K)	M	S/MW
KCAL	1.43200+09	3.51070+00	1.20950-01	6.42640+00	2.57030+01	2.88420+01	4.16250+08	1.20050+10
KCAL								1.77100+00

CP(FROZEN)	CV(FROZEN)	GAMMA(FROZEN)	A(FROZEN)	A	
CAL/GM DEG	2.4492220-01	1.760894750-01	1.391294010+00	4.476160100+04	4.476114270+04
CM/SEC					

SECONDARY GAS PROPERTIES

CAPMO3 = 1.20950+02 YFM2 = 4.12800-30 YFM20 = 1.44140-07 YFCQ = 4.98950-33 YFCQ2 = 2.40240-08 YFM2 = 7.92790-01 YFC = 0.0
 YFO2 = 2.07210-01 YFO = 3.25770-24 YFM = 1.40560-35 YFOH = 5.25360-19 YFCC = 0.0
 MOLWT = 2.88290+01 GM/MOLE DENS = 7.02650-04 GM/CC

CARRIER GAS PROPERTIES

CAPMK = 7.28730+01 YFM2 = 0.0 YFM20 = 0.0 YFO = 0.0 YFOH = 0.0 YFCQ2 = 0.0 YFM2 = 7.92790-01 YFC = 0.0
 YFO2 = 2.07210-01 YFO = 3.25770-24 YFM = 1.40560-35 YFOH = 5.25360-19 YFCC = 0.0
 MOLWT = 2.88290+01 GM/MOLE

TIME	T GAS
0000	100
0005	100
0010	100
0015	100
0020	100
0025	100
0030	100
0035	100
0040	100
0045	100
0050	100
0055	100
0100	100
0105	100
0110	100
0115	100
0120	100
0125	100
0130	100
0135	100
0140	100
0145	100
0150	100
0155	100
0200	100
0205	100
0210	100
0215	100
0220	100
0225	100
0230	100
0235	100
0240	100
0245	100
0250	100
0255	100
0300	100
0305	100
0310	100
0315	100
0320	100
0325	100
0330	100
0335	100
0340	100
0345	100
0350	100
0355	100
0400	100
0405	100
0410	100
0415	100
0420	100
0425	100
0430	100
0435	100
0440	100
0445	100
0450	100
0455	100
0500	100
0505	100
0510	100
0515	100
0520	100
0525	100
0530	100
0535	100
0540	100
0545	100
0550	100
0555	100
0600	100
0605	100
0610	100
0615	100
0620	100
0625	100
0630	100
0635	100
0640	100
0645	100
0650	100
0655	100
0700	100
0705	100
0710	100
0715	100
0720	100
0725	100
0730	100
0735	100
0740	100
0745	100
0750	100
0755	100
0800	100
0805	100
0810	100
0815	100
0820	100
0825	100
0830	100
0835	100
0840	100
0845	100
0850	100
0855	100
0900	100
0905	100
0910	100
0915	100
0920	100
0925	100
0930	100
0935	100
0940	100
0945	100
0950	100
0955	100
1000	100
1005	100
1010	100
1015	100
1020	100
1025	100
1030	100
1035	100
1040	100
1045	100
1050	100
1055	100
1100	100
1105	100
1110	100
1115	100
1120	100
1125	100
1130	100
1135	100
1140	100
1145	100
1150	100
1155	100
1200	100
1205	100
1210	100
1215	100
1220	100
1225	100
1230	100
1235	100
1240	100
1245	100
1250	100
1255	100

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FOR REASONS OF BREVITY, THE COMPLETE OUTPUT IS NOT INCLUDED. INSTEAD, THE MOST SIGNIFICANT SUBSECTIONS HAVE BEEN INCLUDED FOR TIMES: —

4 msec	36 msec	120 msec
10 "	40 "	150 "
16 "	46 "	200 "
22 "	56 "	250 "
27 "	66 "	300 "
28 "	76 "	400 "
29 "	86 "	500 "
32 "	100 "	

LINE	0.07810-03	3.443E-02	4.84940-02	3.99470-02	1.41300-01	5.98960+01	2.03430-10	2.42900-01	9
SOUT	0.0	0.0	0.0	0.0	8.3340E-12	0.0	3.8620-10	0.0	0
SR.....	8.89490E-02	1.22100+00	1.42370+00	1.48220+00	1.22100+00	1.02170-03	0.0	5.84940-02	
SC.....	3.51520E-04	3.69910E-02	4.15130E-02	4.0970E-02	0.0	0.0	0.0	3.62760-01	
GCZCM	2.51520E-04	3.03350E-03	4.15130E-02	1.30970E-02	0.0	0.0	0.0	0.0	
YVWCL	6.89310E-01	2.23720E-01	1.37300E-02	6.69670E-02	1.38600E-01	0.0	0.0	0.0	
YVCL	6.89310E-01	2.23720E-01	1.37300E-02	1.38600E-01	3.39200E-02	0.0	0.0	0.0	
YVCM	6.89600E-02	1.00000+00	1.37300E-02	1.38600E-01	3.39200E-02	0.0	0.0	0.0	
YVCH	4.27370E-01	3.18710E-01	0.0	0.0	0.0	0.0	0.0	0.0	
YVCH	4.27370E-01	3.18710E-01	0.0	0.0	0.0	0.0	0.0	0.0	
YVCH	2.41620E-03	3.33580E-03	1.88200E-01	3.40560E-01	8.12650-12	1.11020-32	3.49620-10	4.17050-10	1
YVCH	1.15170E-02	1.38610E-02	0.0	0.0	7.4620E-01	0.0	0.0	0.0	
YVCH	1.15170E-02	1.38610E-02	0.0	0.0	7.4620E-01	0.0	0.0	0.0	
YVCH	3.6650E-36	0.0	1.53030-29	0.0	2.00170-01	7.91490E-10	0.0	0.0	
YVCH	3.6650E-36	0.0	1.53030-29	0.0	0.0	6.68170-10	1.24210-13	2.88710+01	0
1	5.00000E-04	1.03040E+00	3.41980E+02	1.00000E+00	6.40960E-07	2.13050E-26	1.39020E-06	1.500E+03	
2	1.00000E-03	1.03040E+00	3.41980E+02	1.00000E+00	6.40960E-07	4.01330E-27	1.530E+03	1.530E+03	
3	1.50000E-03	1.03040E+00	3.424930E+02	1.00000E+00	6.40960E-07	7.39020E-28	2.44800E-07	1.530E+03	
4	2.00000E-03	1.03040E+00	3.42020E+02	1.00000E+00	1.50340E-07	1.51910E-28	1.14470E-07	1.610E+03	
5	2.50000E-03	1.03040E+00	3.42020E+02	1.00000E+00	9.96150E-08	1.73940E-29	4.53880E-08	1.690E+03	
6	3.00000E-03	1.03040E+00	3.42020E+02	1.00000E+00	9.96150E-08	1.73940E-29	4.53880E-08	1.690E+03	
7	4.00000E-03	1.03040E+00	3.42020E+02	1.00000E+00	3.56460E-08	1.12390E-30	1.850E+03	1.850E+03	
8	5.00000E-03	1.03040E+00	3.42020E+02	1.00000E+00	3.56460E-08	1.12390E-30	1.850E+03	1.850E+03	

LINE	1	050420-02	4	011760-02	4	010445-02	3	049476-02	1	113050-01	1	048440-00	3	123600-07	2	430300-01	13
TOTL	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
SUM	3	522550-01	1	122100+00	1	162370+00	1	176000+00	1	122100+00	1	164140-04	0	000000-00	3	522550-01	0
SUM	6	736900+00	0	289930-02	0	289930-02	0	000000-00	0	184000+00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00	0	000000-00	0
GRN	1	514700-03	2	187500-00	2	187500-00	2	249990-01	0	000000-00	0	000000-00	0	000000-00			

	3.73380-24	0.0	8.92520-20	0.0	0.0	6.68170-10	1.24210-13	2.90400+01	0
1.00000-04	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	7.28160-04	1.500+03		
1.00000-03	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	4.40840-04	1.310+03		
1.00000-02	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	2.92010-05	1.150+03		
1.00000-01	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	1.51630-05	1.040+03		
1.00000-00	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	4.61890-06	1.590+03		
1.00000+01	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+02	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+03	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+04	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+05	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+06	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+07	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+08	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+09	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+10	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+11	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+12	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+13	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+14	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+15	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+16	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+17	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+18	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+19	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+20	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+21	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+22	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+23	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+24	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+25	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+26	1.0304+00	4.98400+02	1.00000+00	2.21620-03	2.46900-14	0.0	1.500+03		
1.00000+27	1.0304+00	4.98400+							

[illegible][illegible]

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TOTAL PRESSURE = 9.11000000E+00 TEMP = 1.0303240E+03
TOTAL VOLUME = 9.1120150E+06 MT(REF) = 0.0 SUM M = 2.3049250E+02
M 4.8759320E+00 C 1.0000000E+01 N 1.6570660E+02 O 4.4910060E+01
XMU(1) = 2.0378860E+01 4.7657050E+01 1.2087590E+01 1.3998930E+01
D(XBAR)/DT = 5.7284030E-08
D(MU)/DT = -1.2346190E-02 -4.3175160E-02 1.7673840E-03 1.8399820E-03
D(XBAR)/DP = -7.0000000E-02 -4.941910E-02 1.8399820E-03
D(MU)/DP = -7.0000000E-02 7.3211570E-03 -5.0000000E-03 -5.0000000E-03
N CONSERVATION = 14 M GAS = 14 M CONDENSED = 0 ITER = 1 ITERMAX = 4 IT = 1 MOSC = 0

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NO.	GASEOUS SPECIES	NIK MOLES	X(K) MOLE FRAC	P(K) ATM	LOG10(P(K))	MOLECULES/CC	RHO(K) GR/CC	RHO/RHO ZERO	G(K) STD FR	ENG
1	C ₄ H	7.304E-07	6.777E-09	6.777E-09	-4.81690+01	4.8280D-30	9.62790-53	7.44560-50	6.32560+01	
2	CH ₄	6.3895E-01	5.9275E-03	5.9275E-03	-4.22270+04	4.2227D-24	1.1248E+06	6.6983E-04	-3.9441E+01	
3	CO	5.7620E-09	4.9882E-11	4.9882E-11	-1.03020+01	3.5536D-08	1.6527D-14	1.2781E-11	-7.3941E+01	
4	CO ₂	1.0000E-01	9.2784E-05	9.2784E-05	-1.0325D+00	6.8099E+17	4.8330E-05	3.7352E-02	-7.3729E+01	
5	C ₂ H ₂	4.754E-58	2.7821E-60	2.7821E-60	-1.3600E+02	1.3600D-02	1.6242E+00	1.6242E+00	1.6575E+00	
6	H	2.9850E-12	2.7821E-14	2.7821E-14	-1.3556E+01	1.9826D+05	3.3170E-09	2.0460E-09	1.0460E+00	
7	OH	1.768E-05	1.1724E-07	1.1724E-07	-6.9309D+00	8.3533E-11	2.3588E-11	1.8224E-08	-1.8420E+01	
8	H ₂ O	3.981E-09	3.586E-11	3.586E-11	-1.0502D+01	2.2431E-08	5.5079E-16	5.8601E-13	-1.5676E+01	
9	O	4.9380E-02	3.9814E-04	3.9814E-04	-1.4000E+00	2.2431E-08	5.5079E-16	5.8601E-13	-1.5676E+01	
10	N ₂	3.327D-03	3.1850E-05	3.1850E-05	-4.4969E+00	2.2490D+14	1.1305E-08	8.7442E-04	-1.5733E+01	
11	O ₂	8.2852E-01	7.6873E-01	7.6873E-01	-1.4230E+01	5.4764E+18	2.4764E+04	1.9700E+01	-2.3912E+01	
12	N	2.1182E-09	2.1182E-09	2.1182E-09	-8.6740E+00	1.3099E+10	1.1028E-12	8.2481E-10	-1.8702E+01	
13	D ₂	9.247E-38	9.247E-38	9.247E-38	-1.0332E+02	1.0332D-02	1.0332E+00	1.0332E+00	1.0332E+00	
14	D	9.9443E+00	9.2639E-02	9.2639E-02	-1.0332E+02	6.9996E+17	3.5063E-03	1.1118E-02	-6.6210E+01	

NO. CONDENSED SPECIES	N(K) MOLES	X(K) MOLE FRAC	G(K) STD FR ENGY
19 C	0.0	0.0	-1.43970+00

GASEQUS SUM M KCAL	M/RT	M/MM KCAL/GM	M/RTZERO	S/R	MM	SUM M(K)	M GM	S/MM
-3.75900+02	-1.70340+00	-1.18590-01	-0.42520+00	2.90040+01	2.94110+01	1.07760+02	3.16980+03	1.95980+00

MOLECULES/CC	RHO GM/CC	RHO SLUGS/CF	RHO/RHO ZERO	CP CAL/GM	DEG	GAMMA	V/M CC/GM	FT/SEC
7.1240D+18	3.4788D-04	8.7498D-04	2.6902D-01	2.8914D-01		1.3050D+00	2.8744D+03	2.0227D+03

CONDENSED SUM M	H/RT	H/MW	H/RTZERO	S/R	MW	SUM N(K)	M	S/MW
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LINE#	1.50200-01	1.65910+03	9.83900-01	9.84000-03	4.00490-01	-7.38070+01	5.48660-01	3.21220-01	7
S001...	0.0	0.0	0.0	0.0	8.8960-03	1.2540+02	2.5010+01	1.77200-01	1
NR.....	1.42740+01	-1.22100+00	1.42370+00	3.00640+01	3.00760-01	2.17600-04	1.34460+01	1.77200-01	
SUR.....	1.30280-01	-1.43930+01	0.0	0.0	2.37780+00	4.39900-01	5.32060+01	6.67910-01	
CM.....	6.13790-02	8.86420-01	2.04840+01	3.19600+00	4.28850-02				
CZGML...	5.98440-01	3.26050-01	1.12840-04	7.55030-02					
VF.....	6.60040-06	3.00780-01	-1.32010-06	-1.33950-04					
CZCH...	6.60150-06	1.00030+00	1.86600+01	-3.30890-05					
VYCH...	-2.63400-04	1.00030+00	7.12918+81	9.72298+00	1.00410-02	1.18760-02	6.99220 01	7.53670-01	0
VJ.....	1.00030-01	1.93000-01	6.16680-01	1.30180-01	4.51210-02	7.59310-01	4.58470-02	0.0	
VY.....	1.88300-06	9.49910-02	2.36760-05	1.30180-01	2.03750-02	7.29310-01	6.23310-08	0.0	
VF.....	6.04910-06	1.94820-01	1.52670-04	1.30180-26				7.96240+01	0
1	0.0	3.97770-01	0.0	0.0	0.0	0.0	0.0	0.0	
2	3.34940-01	3.05910-01	1.65100+03	0.6370-02	0.0	0.0	0.0	0.0	1.500+03
3	0.06510-04	4.00370-01	1.63880+03	0.5760-01	0.0	0.0	0.0	0.0	1.500+03
4	1.49050-01	4.05160-01	1.62640+03	1.70770-01	0.0	0.0	0.0	0.0	1.500+03
5	1.49050-01	4.05160-01	1.62640+03	1.70770-01	0.0	0.0	0.0	0.0	1.500+03
6	3.69280-01	3.29030-01	1.57780+03	4.05980-01	0.0	0.0	0.0	0.0	1.500+03
7	6.20260-03	3.60600-01	1.53410+03	4.93410-01	0.0	0.0	0.0	0.0	1.500+03

TGAS, TSCALE, CPSCALE, DELT, TEMP(1), NSTEPS...	1.6853D+03	1.0024D+00	8.6393D-01	3.6415D-04	0.0	1
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118E, 3.00310-01 1.70610+03 9.08350-01 5.07560-03 5.64290-01 -9.36030+01 5.48660-01 3.24080-01 3

TIME: 4.0040D-01 1.7136D+03 9.8969D-01 3.7358D-01 6.3762D-01 -1.0108E+02 3.4500E+01 1.4637E+01

APPENDIX A

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