ON THE COMBUSTION OF BITUMINOUS COAL CHAR

Thesis by

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To Ma and Baba
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The combustion of chars from pulverized bituminous coals was experimentally and theoretically investigated. The chars were made by pyrolyzing size-graded PSOC 1451 coal particles in nitrogen at temperatures of 1000-1600K. Sized char particles were then used for further experiments. Low temperature reactivities of such cenospheric chars were measured at 800K on a thermogravimetric analyzer. The effects of initial coal size, char size, pyrolysis temperature, and oxygen concentration were investigated. Single particle combustion experiments were done in both air and 50% oxygen ambients at wall temperatures of 1000-1500K in a drop tube laminar flow furnace. Particle temperatures were measured during the entire course of combustion. From the complete temperature-time histories of such burning particles, the apparent activation energy and pre-exponential factors were inferred, using numerical models and statistical modelling techniques. Questions of particle-particle variability were addressed. The ignition transients of single burning particles were studied and a model that predicted delay times observed experimentally was developed. Char samples were also partially oxidized at temperatures in the range 1200-1500K (particle temperatures) and physically characterized. Methods of characterization included optical and electron microscopy, gas adsorption methods for specific surface area and pore volume distributions, and mercury porosimetry for pore volume distribution measurements. The results of these characterizations were compared with those done on chars oxidized at 500°C.

The combustion of single char particles was numerically modelled. A continuum model for asymptotic shrinking-core combustion was developed using apparent
reaction rates and temperature-dependent properties. Simplified assumptions were made regarding the gas-phase combustion. Parametric sensitivity of this model yielded significant insight into the combustion process. A more general continuum model was then developed. This model treated the internal pore structure more realistically, as inferred from experiments. The steady state diffusion equation was solved inside the particle to determine its theoretical temperature-time history. Good agreement with experiments was found. The model was extended to include the effects of some nonlinear kinetic reaction rate expressions. A discrete model for a cenospheric particle was also developed. This model consists of spherical voids randomly placed in a spherical particle. It simulates the combustion by taking into account the connectivity of the internal pore structure. This connectivity influences the access of reactant to the interior of the particle and, therefore, the extent of internal reaction. The changes in the internal connectivity led to a percolation type behavior in most particles.
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All particles were PSOC 1451 1600K char.
Chapter 1

INTRODUCTION
This dissertation deals with some aspects of the combustion of chars made from some U.S. bituminous coals. Bituminous coals are characterized by fixed carbon contents between 69 and 86%. Of course there are wide variations in the contents of volatile matter, moisture and mineral matter between various bituminous coals. While the primary emphasis was on one coal, PSOC 1451, chars from other coals have been used for comparison purposes. The most common method of coal utilization is in the form of pulverized coal for power generation. The particle size used is in the range 40-200µm. When coal particles are heated, moisture and the volatiles are successively expelled leaving behind a carbonaceous char. The volatiles burn in the gas phase on time scales of the order of less than a millisecond while the char burns out in tens of milliseconds. Thus, char combustion is the controlling factor in the overall process and it determines combustor size.

While gas phase combustion reactions involving the volatiles have been extensively studied, the peculiar problems of char combustion are now receiving greater attention. The latter is a much more difficult problem due to the following causes: heterogeneity of the system, internal morphology characterized by the presence of pores with diameters ranging from few angstroms to few microns, diffusion and reaction in such a media, nonavailability of reliable kinetic data on intrinsic chemical reactions of the carbon at high temperatures, and the presence of ash and mineral matter in the solid which have physical and chemical ramifications on the combustion process. All these problems are for single particle combustion. In a real system, the problems of particle-particle interaction, fluid-particle interaction and
mass transfer have also to be accounted for.

Appendix I lists some of the physical and chemical properties of PSOC 1451 including its proximate and ultimate analyses, heating values, elemental composition, and the composition of its ash. While there are many excellent reviews of coal science in the literature, not all of them deal with bituminous char combustion in sufficient detail. Chapter 2 summarizes the important findings from the recent literature in the area of bituminous char combustion. Apart from char reactivities at low and high temperatures, the chapter also discusses models used to represent the internal structure of such chars and the dispersion of mineral matter and ash in single particles. Finally, single particle combustion models are discussed. No attempt has been made to discuss the combustion behaviour of groups consisting of many particles.

Chapter 3 describes the results of oxidation studies on sized char particles at temperatures around 800K. The experiments were done on a thermogravimetric analyzer. In addition to PSOC 1451, chars from two other bituminous coals, PSOC 176 and PSOC 282 were also used in this study. At these low temperatures, it was shown that the effects of diffusion are minimal and that the observed reactivities represent the true rates. Various experiments were done to test the effect of coal type, char pyrolysis temperature, char particle size, parent coal particle size, oxygen concentration, and other variables on reaction rates. Physical characterization of the chars was done using gas adsorption, capillary condensation, and mercury porosimetry. Surface area values were determined for some samples at intermediate conversions. Heating values were determined as a function of carbon conversion
for PSOC 1451 chars. The intrinsic kinetic rates were then determined from the apparent reactivities and the measured surface area values. It was shown that, after accounting for the effects of ash, the intrinsic rate was fairly constant over a wide range of carbon conversion. Appendix X describes in detail the experimental conditions used.

Single particle combustion experiments done in the laminar flow drop tube reactor are described in Chapter 4. These experiments were done at wall temperatures in the range 1000K-1500K. Some experiments were done in air and others in an ambient of 50% oxygen. Complete temperature-time burn histories for each particle were recorded. This was repeated for many particles in a given sample. It was observed that particles from the same sample often produced temperature-time signatures that were quite different. This was primarily due to the different initial particle sizes and shapes. While there are other particle-particle differences, the initial size and shape variations are undoubtedly major causes of later combustion variability. Based on this hypothesis, a statistical model was developed and used to derive the apparent kinetic rates of combustion at these high temperatures. Appendix VIII gives the listings of the programs used in the data acquisition, inversion and modelling. The temperature-time traces for each of the various runs is given in Appendix XII.

Physical characterization experiments of char samples that were partially oxidized at high temperatures in air are described in Chapter 5. The various methods of characterization include optical and electron microscopy, gas adsorption to determine BET specific surface areas, capillary condensation to determine pore volume
distributions of the micro and transition pores, and mercury porosimetry to find the pore volumes of the macro and transition pores. The physical changes occurring in the particles as conversion increases are discussed in great detail in the chapter. The final section compares the changes at high temperatures to those occurring when the conversion is carried out at low temperatures. The temperature of the particles as they burned was also measured at different conversions. Appendix II describes in some detail the design and construction of a two color optical pyrometer employed for particle temperature measurement. The construction of the high temperature reactor is described in Appendix IV. Computer programs used for data acquisition and inversion for the gas adsorption experiments are given in Appendix V. Appendix VI gives similar listings for the programs used for mercury porosimetry data analysis. Finally, programs used to acquire data from the pyrometer and convert the data to particle temperature measurements are given in Appendix VII.

The temperature-time traces from single particle combustion experiments led naturally to questions regarding the ignition transients observed at the earlier stages of combustion. It was observed that while the particle temperature was constant, the light intensity signal from the particles continued to increase. This was attributed to the growth of hot spots on the particle surface. A model that describes the growth of such a spot was developed and its predictions were compared to the experimentally observed delay times. Good agreement was found. This is described in Chapter 6.

Continuum models depicting the combustion of single particles are described in Chapter 7. The simplest model assumes that all the reaction takes place on
the external surface of the particle with the apparent kinetic rates derived earlier. This diffusion limited regime is typical of combustion of large particles at high temperatures and at high oxygen concentrations. While the model does not treat the details of the internal morphology, it does account for the presence of ash in the particle. The gas phase outside the particle is modelled in a simple manner assuming it to be quasi-steady with respect to the solid combustion. The next level of complexity involves accounting for the presence of pores inside the particle. Starting with initially monodisperse spherical pores, a general model that accounts for internal diffusion and reaction is formulated. The internal porosity and specific surface area are allowed to change. The chemical reactions are described by their intrinsic rates. The reaction rate is assumed to be linear with respect to local oxygen concentration. This model is then extended to allow a more realistic description of the internal morphology consisting of pores of three sizes corresponding to micro, transition and macro pores, observed experimentally. The parametric sensitivities of all the models are discussed. The last section deals with the inclusion of nonlinear kinetic expressions in the reaction rates. Two forms corresponding to Langmuir-Hinschelwood and Power law functions of the local oxygen concentration are considered. Appendix IX lists the computer codes of the different models.

While assuming that the interior of a char particle is homogenous and capable of continuum description is a convenience, it is often an over-simplification. There are cases when the internal morphology cannot be described as a continuum due to the presence of voids whose sizes are comparable to the particle radii. A discrete simulation model was developed to describe, in general terms, the combustion of
cenospheric chars like those of PSOC 1451. While most simulation models of this nature are based on lattice geometries, the present model described in Chapter 8, is closer to describing the physical reality. Spherical pores were randomly placed inside a spherical particle leading to void overlap. This model takes into account the connectivity of the pores inside the particle and the connectivity of pores to the outside. The access of oxygen to the interior is constrained by this connectivity. Particle void fraction and conversion are tracked as they change with burn time. Interesting percolation behaviour of the void structure was observed. Examples of the percolation traces are shown in Appendix XI.

Specific surface areas and pore volume distributions obtained by gas adsorption techniques are widely used to characterize porous particles in many different areas including coals and chars. However, there are many questions regarding the applicability of techniques, models, and inversion paradigms commonly used. The suitability of such techniques is discussed in Appendix III. Four solids having different internal morphologies were chosen. Also, three different gases were chosen as the adsorptives. The applicability of the various adsorptive-adsorbate combinations is discussed. The next question involves inversion routines to generate pore volume distributions from the raw data. The standard inversion methods are described and critically analyzed. Finally, methods used specially for microporous solids are studied.

Chapter 9 briefly summarizes the major conclusions of the thesis.
Chapter 2

INTRODUCTION TO
BITUMINOUS COAL CHAR COMBUSTION
2.1 Introduction

Coal has always been a major source of energy for electricity generation. Since the 1960’s, however, it began losing ground as the primary fuel for power generation. Oil and natural gas prices were cheap and nuclear power was poised for rapid growth. In the 1970’s the situation suddenly changed. Oil and gas prices had sky rocketed and safety concerns regarding the nuclear power industry were thwarting its projected growth. All this, coupled with the realization that oil and gas supplies are rapidly dwindling, has created renewed interest in utilization of the vast coal reserves in the world. Of course, coal, like oil, is also a non-renewable source of energy. Eventually, nuclear, solar or some other renewable energy source will be required. But, in the short term, coal and energy conservation offer the best alternatives for meeting our energy demands.

At the very outset it should be recognized that ‘coal’ is a generic term and the solids it refers to are often more dissimilar than alike. This is due to the conditions under which coal was formed. At various times in geological history, due to land subsidence and water inundation, plant debris was gradually covered by silts which shielded it from further degradation. As this debris was buried under increasingly thick inorganic sediments, it was progressively compacted by overburden pressures and chemically altered by heat. Whenever this happened, coal was formed. The fact that coal is so widely distributed shows that it did not require a particular types of debris. It formed from whatever plant life happened to flourish at the time. But the variety of this vegetation and the diverse conditions under which it accumulated and decayed had a profound effect on the kinds of coal that developed
Numerous attempts have been made to organize various types of coal into comprehensive classification schemes primarily to assess their suitability for different applications. *Rank*, as applied to coal, carries the same meaning as extent of maturation and is therefore a qualitative measure of its carbon content. Bituminous coals and anthracites are classified as being high rank while lignites and subbituminous coals are considered to be low rank. However, rank should not be confused with *grade*, which refers to quality. The widely accepted ASTM classification by rank is shown in Table 2.1. For lower rank coals, heating value rather than fixed carbon content is used to classify the coals.

For practical purposes, the chemical composition of coal is always defined in terms of its proximate analysis which determines its moisture, volatile matter, ash, and fixed carbon contents. Upon heating, moisture and the volatiles are lost leaving a solid *char* which contains the carbon and mineral matter. At higher temperatures the char burns. Thus coal combustion involves the combustion of the volatiles in the gas phase and the combustion of the char. For pulverized combustion, in which coal is generally ground to sizes below 200µm, char combustion controls the overall burn time and, therefore, the combustor size.

The scope of this chapter will be limited to combustion and modelling of single bituminous coal or char particles. Reactivity measurements at high and low temperatures and various approaches used to model the internal morphology of char particles will be discussed. Attempts to predict the effects of ash on the combustion of single particles are receiving greater attention now but as yet there is no
consensus on the best approach. Some experimental work on the effects of ash and mineral matter will be reviewed. Finally, some complete models of single particle combustion will be discussed.

Excellent reviews in the general area of pulverized coal combustion are available in the literature. Field and co-workers (1967) described all aspects of combustion of pulverized coal including fluid mechanical, thermal, and chemical kinetic effects. Although most of the material is derived from their own research at the BCURA, they give a succinct review of various topics prior to the mid 1960's. A few years later, Mulcahy and Smith (1969) published a review dealing exclusively with chemical kinetic aspects of pulverized fuel combustion. Laurendeau (1978) describes in great detail much of the progress made in the 1970's in the area of heterogeneous kinetics of coal char combustion. His review gives a complete discussion of the mechanisms and rates of the relevant gas-solid reactions. Mass transfer and diffusion are also discussed. Smith (1982) summarizes the field of char kinetics including a comprehensive attempt to gather the reactivity data for all types of carbons over a wide range of temperatures. He proposed an intrinsic chemical rate expression suitable for all chars. Essenhigh (1981) gives an extensive review of most aspects of coal combustion, with a scope much larger than any of those previously mentioned. Recently, Smoot and Smith (1985) have also published a valuable addition to the field of coal combustion. While most of the references mentioned above deal with the solid phase in greater detail than the gas phase combustion, Libby and Blake (1979) examine the latter in greater detail.
2.2 Low Temperature Kinetic Studies

Although temperatures in the practical combustion systems of interest here are generally high, reactivity studies at lower temperatures can give valuable insight into the various physio-chemical processes occurring during combustion. The influence of diffusion resistance in the gas phase can be minimized by suitable choice of temperature, oxygen partial pressure, and particle size making possible direct observations of chemical effects. In many cases pore diffusion does not limit the reaction rate, at least for the larger feeder pores. Therefore, it is possible, in principle, to determine the intrinsic reactivity of the carbonaceous matter from such experiments. Care must be taken to properly account for the presence of ash or mineral matter in the coal or char since, at lower temperatures, the influence of ash on the chemical kinetic effects can be quite important. The growth and development of the internal morphology (pore growth) is also important at lower temperatures.

The Thermogravimetric Analyzer (TGA) is most commonly used for low temperature reactivity studies. The TGA is convenient because it directly gives the rate of mass loss of a given sample under a specified programmable temperature loading. From the rate of mass loss data the apparent reactivities are easily calculated. Finally, knowing the surface area of the sample and the diffusion limitations of the particular experiment, it is possible to estimate the intrinsic chemical reactivity. Table 2.2 summarizes some of the work in the area of low temperature reactivity measurement. Low temperature reactivity measurements in the present study are discussed in Chapter 3.

In a major study Jenkins et al. (1973) investigated the role of coal rank, pyrol-
ysis temperature, and mineral matter on the reactivity of chars from 21 US coals. For coals pyrolyzed in N₂ at 600-1000°C they found that while reactivity increases with the decreasing coal rank, possibly due to the catalytic effects of mineral matter, it decreases with increasing pyrolysis temperature. They also correlated reactivity with the calcium and magnesium contents in the char. Since reactivity was not well correlated with other known catalysts like iron, they speculated that the form and distribution of mineral matter has an important influence on the reactivity. The role of the internal structure of the chars in determining their reactivities was shown by Dutta and Wen (1977). They found that in the chemical kinetic regime, the reactivity depended more on the degree of gasification and the pore characteristics of the char than it did on the parent coal. In another important study Mahajan et al. (1978) supported the earlier findings of Jenkins et al.. While the latter had used the maximum weight loss as the reactivity parameter in their work, Mahajan et al. suggested that the time to reach a particular fractional burnoff, say 50%, be used as a parameter to correlate reactivity data of different chars. This unification of reactivity data was further proof that the changes in the pore structure with burnoff greatly influences reactivity. More recently, Morgan et al. (1987) have shown that reactivity depends on the maceral content of the chars. Vitrinites are more reactive than inertinites. An important conclusion of their work was that there is maceral segregation in the different size fractions of char. Therefore, char size, in addition to influencing diffusion conditions, also determines intrinsic chemical reactivity.

2.3 High Temperature Kinetic Studies

At higher temperatures, the combustion of particles in the pulverized size range is
usually strongly diffusion limited. There are two major diffusion limitations. The first is the diffusion across the particle boundary layer. The second is pore diffusion. Since the chemical rate is a sensitive function of the particle temperature, the combustion rate is governed by the amount of oxidant that reaches the char surface and then penetrates into the interior of the particle. In most cases, the reaction occurs only in the larger pores and most of the internal area in the smaller pores is not utilized. The particle density and size are both reduced. Since diffusion is such an important aspect of high temperature combustion, it must be treated in any determination of the intrinsic chemical rate parameters. Smith and Tyler (1974) have outlined a first order procedure for determining the intrinsic reactivities.

A number of experimental techniques have been used to measure reactivity at high temperatures. The thermogravimetric analyzer can be used up to 1300K. Most workers have used the laminar flow drop tube reactor. The flow is generally kept laminar to minimize complications in the data interpretation due to fluid mechanics. The heat source can be a flame, plasma, or some type of electric heating. The limitations of using a flame (vitiated combustion) as the heat source are obvious. The temperature depends on the fuel/oxidant mixture ratios and flame stability considerations. The chemistry in the gas phase around the particle is difficult to characterize due to the presence of various radicals and other species. Plasma heating also introduces reactive species. Electric heating allows greater control of the temperature and gas composition. Shock tubes have been used in some studies to determine high pressure reactivities.

The reactivity can be measured either gravimetrically, involving a direct mea-
sure of the carbon mass loss, or inferred from the gas phase composition by monitoring the carbon oxides. In most of the earlier measurements, the particle temperature was calculated from the carbon mass loss data by using an energy balance and making appropriate assumptions regarding the nature of the heterogeneous reaction at the particle surface. More recent studies have employed nonintrusive optical techniques for independent determination of the particle temperature. Table 2.3 summarizes the high temperature reactivity studies of the last two decades. The present work in this area is presented in Chapters 4, 5, and 6.

Direct comparison of the reaction rates or the activation energies from different studies is not possible since the nature of the chars is quite different. While it is certainly true that the influence of char type on the reactivity at higher temperatures is much less than at lower temperatures, Smith (1982) found that the reactivities of different chars at a given temperature varied by as much as four orders of magnitude. His attempt to unify the known reactivities of various carbons over a wide range of temperatures met with limited success. This may be due to the intrinsically different nature of the carbons and their reactivity with oxygen, or due to the different pore structures of the carbons, or both. The chemical influences of ash were not investigated. The measurement of reaction order is also open to question. Mechanisms that have been theoretically proposed for the carbon-oxygen reaction (Nagle and Strickland-Constable, 1962; Essenhigh, 1981) have not been entirely validated (Laurendeau, 1978; Tseng and Edgar, 1985), probably due to incomplete control over experimental conditions. As experimental techniques improve, better understanding will doubtless emerge. The recent simultaneous op-
tical measurements of particle size, velocity, and temperature reported by Mitchell (1987) represent a significant step in this direction.

2.4 Description of Internal Morphology

The description of the internal structure of a char particle is critical to any model that attempts to describe its combustion behaviour. The reaction rate depends on the available internal surface area, which, in turn, depends on the diffusion of reactant into the solid structure. The estimation of the overall porosity and the particle density are also determined by the particular pore structure model. It is quite clear from experiments that pore sizes in pulverized coal or char combustion range from tens of microns to few Angstroms. They are also irregular in shape. However, for reasons of mathematical tractability, simple geometrical pore shapes like cylinders, spheres, and slits are often assumed. A comprehensive pore model should be able to describe the overall features of the pore distribution, i.e. porosity, average pore radius, and pore surface area, as well as the evolution of the pore structure with reaction. Mechanisms of pore formation, growth, and coalescence must be described. Of course, the reaction kinetics are closely coupled with the problem of pore diffusion since the reaction rate is dependent on the local concentration of oxidant at each location inside the particle. Few general models are available that describe these features satisfactorily. Some of the important models will be briefly described below.

Petersen (1957) proposed a simple model of reaction and diffusion in a single cylindrical pore and then extended it to a network of similar pores with random intersections. However, his model predicted values of effective diffusivity that were
an order of magnitude lower than the experimentally observed values. Johnson and Stewart (1965) and later Feng and Stewart (1973) calculated diffusivities using a capillary model containing a size distribution of randomly oriented pores. Cross linking of the pores was assumed. Their models contain adjustable parameters that must be evaluated from experiments. The 'calibrated' models predict reasonably accurate values of diffusivity. Szekely and Evans (1970) describe two simple models of porous solids. Their pore model consists of parallel, regularly spaced cylindrical pores of uniform size. While this may describe some situations in heterogenous catalysis, it is not a suitable model for chars. Their grain model consists of spherical solid particles of uniform radii arranged in a lattice with fixed center separation. Using a population balance method, Hashimoto and Silveston (1973) proposed the first sophisticated model of a porous solid. They also review the relevant catalysis literature regarding homogenous and shrinking core models. Their model includes the effects of pore growth, creation of new pores, and pore coalescence. Surface area, porosity, and mean pore radius were predicted as a function of the extent of reaction. By adjusting the model parameters, they were able to obtain good agreement with experiments. Simons (1982) proposed a pore tree model for chars, postulating that feeder pores that were connected to the external surface branched into smaller and smaller pores as the radius increased. This branching sequence creates a pore network that resembles a tree-like structure. This model cannot predict the change of surface area and other pore structure parameters at the local level that is essential for a predictive model. Gavalas (1980) and Bhatia and Perlmutter (1980) independently proposed similar random pore models for solids.
with cylindrical pores. The model by Gavalas consists of infinitely long cylinders whose radii are drawn from a certain size distribution. The axes of the cylinders are randomly oriented creating pore intersections in a natural manner. Bhatia and Perlmutter consider the random overlap of a set of cylindrical surfaces of different radii. Although their formulation is different, their results closely resemble those obtained by Gavalas.

2.5 Mineral Matter and Ash

In addition to the engineering considerations of deposit formation, fouling, and environmental pollution (Raask, 1985), the presence of mineral matter and its transformation to ash strongly influences the combustion of coal or char.

The application of such methods as low temperature ashing and x-ray diffraction has increased our understanding of ash. Of the hundred or so different minerals that can occur in coal, about 15 are abundant enough to have major influence (Harvey and Ruch, 1984). Different investigations have shown that the presence of CaO in the ash tends to enhance reactivity (Hippo and Walker, 1975). Hippo and Walker (1975) also showed that MgO enhances reactivity when present in concentrations less than 1%. Surprisingly, they found that iron, sodium or potassium do not correlate well with reactivity. Padrick (1984) observed enhancement in the hydrogasification rate when iron-bearing compounds were added to the coal. Pohl (1984) comments on the reactivity enhancement of graphite in the presence of sodium. But, he reports that sodium must be distributed on the molecular level to be effective. These observations suggest that the sodium in real coals may be segregated, reducing its effectiveness as a catalyst. Huffman and Huggins (1984) have concluded
from Mossbauer spectrometry that iron undergoes a number of reactions at high temperatures under both oxidizing and reducing conditions, suggesting that iron compounds may act as catalysts if present in sufficient amounts. The other important effect of iron compounds is on ash emissivity (Raask, 1985) which profoundly affects the radiation balance of the particle and its temperature.

2.6 Modelling of Single Particle Combustion

Although many models have been proposed to describe the combustion of single particles, a few of them will be described here.

The simpler models assume that the particle is impervious to the reactant and that the reaction is lumped at the particle surface. Caram and Amundson (1977) proposed such a boundary layer model for slab and spherical geometries. They also give an excellent review of some previous models. Two heterogeneous reactions at the carbon surface (\(C + \text{O}_2 \rightarrow \text{CO}_2\); \(2C + \text{O}_2 \rightarrow 2\text{CO}\)) and one homogeneous reaction in the gas phase involving oxidation of carbon monoxide were considered. The particle was assumed to be in radiation equilibrium with similar particles. Transport properties were assumed to be independent of temperature. From such a simple model, they nevertheless concluded that Stefan flow was a negligible factor in spherical geometry. More importantly, they found that while larger particles (5mm) burned according to the double-film theory, smaller ones (50\(\mu\)m) burned consistent with single-film theory predictions. In the latter, the primary reaction at the surface produces carbon monoxide which is later oxidized to carbon dioxide far from the particle. Thus there is no flame in the particle boundary layer. Caram and Amundson also predicted the existence of multiple steady states in the solution of the differential
equations, some of which were interpreted as ignition and extinction phenomena. Mon and Amundson (1978) extended the previous work to include the effect of radiative exchange with a wall or enclosure and also assumed varying diffusivities of the gas phase components. They concluded that, for particles in the pulverized coal size range burning in air, CO oxidation always takes place outside the boundary layer and that the only important heterogeneous reaction at the particle surface is

\[ 2C + O_2 \rightarrow 2CO. \]

Srinivas and Amundson (1980, 1981a, 1981b) investigated the effects of intraparticle transport. Although the earlier papers (1980, 1981a) treated the internal structure as invariant (e.g. porosity and surface area as constant) with respect to combustion, this assumption was later relaxed (1981b). They found that the pore structure and its evolution significantly influence all aspects of combustion including burn time, ignition, and extinction. The validity of previous boundary layer models (Caram and Amundson, 1977; Mon and Amundson, 1978) was thus doubtful under any condition.

Thus the internal particle structure must be incorporated into any realistic model although properly formulated shrinking core models could still describe combustion at high temperatures. For these, reaction rates were a crucial input parameter. Sotirchos and Amundson (1984) combined the previous approaches of the boundary layer and the intraparticle models into a single model. Internal surface area, porosity, and diffusivity were functions of the local conversion. They also included the effects of intraparticle thermal gradients. As before, internal pore structure and growth were dominant parameters.

None of the models described above attempt to include the presence of ash in any manner. Some attempts to incorporate the presence of ash in continuum models is described in Chapter 7.
References


### Table 2.1 ASTM Coal classification by rank.

<table>
<thead>
<tr>
<th>Class and Group</th>
<th>Fixed Carbon&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>Volatile Matter&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>Heating Value&lt;sup&gt;b&lt;/sup&gt; (Btu/lb)&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Anthracite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Metaanthracite</td>
<td>&gt;98</td>
<td>&lt;2</td>
<td></td>
</tr>
<tr>
<td>2. Anthracite</td>
<td>92-98</td>
<td>2-8</td>
<td></td>
</tr>
<tr>
<td>3. Semianthracite</td>
<td>86-92</td>
<td>8-14</td>
<td></td>
</tr>
<tr>
<td>II. Bituminous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Low Volatile</td>
<td>78-86</td>
<td>14-22</td>
<td></td>
</tr>
<tr>
<td>2. Medium Volatile</td>
<td>69-78</td>
<td>22-31</td>
<td></td>
</tr>
<tr>
<td>3. High Volatile A</td>
<td>&lt;69</td>
<td>&gt;31</td>
<td></td>
</tr>
<tr>
<td>4. High Volatile B</td>
<td></td>
<td></td>
<td>&gt;14000</td>
</tr>
<tr>
<td>5. High Volatile C</td>
<td></td>
<td></td>
<td>13000-14000</td>
</tr>
<tr>
<td>III. Subbituminous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Subbituminous A</td>
<td></td>
<td></td>
<td>10500-13000</td>
</tr>
<tr>
<td>2. Subbituminous B</td>
<td></td>
<td></td>
<td>9500-10500</td>
</tr>
<tr>
<td>3. Subbituminous C</td>
<td></td>
<td></td>
<td>8300-9500</td>
</tr>
<tr>
<td>IV. Lignite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Lignite A</td>
<td></td>
<td></td>
<td>6300-8300</td>
</tr>
<tr>
<td>2. Lignite B</td>
<td></td>
<td></td>
<td>&lt;6300</td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated on dmmf basis.

<sup>b</sup> Calculated on mmf basis with bed moisture content.

<sup>c</sup> If agglutinating then HVC, else Subbit. A.

<sup>d</sup> 1 Btu/lb = 478.55 J/kg.
<table>
<thead>
<tr>
<th>Authors</th>
<th>Method</th>
<th>Temperature</th>
<th>% O₂</th>
<th>Pressure</th>
<th>Char Type</th>
</tr>
</thead>
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<tr>
<td>Jenkins et. al.</td>
<td>TGA</td>
<td>500°C</td>
<td>21</td>
<td>1 atm</td>
<td>From 21 US Coals pyrolyzed in N₂ at 600-1000°C</td>
</tr>
<tr>
<td>(1973)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dutta et. al.</td>
<td>TGA</td>
<td>424-576°C</td>
<td>21</td>
<td>1 atm</td>
<td>From 2 US Bituminous Coals pyrolyzed in N₂ at 1024°C and 4 process chars</td>
</tr>
<tr>
<td>(1977)</td>
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<td></td>
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</tr>
<tr>
<td>Mahajan et. al.</td>
<td>TGA</td>
<td>405°C</td>
<td>21</td>
<td>1 atm</td>
<td>From 16 US Coals pyrolyzed in N₂ at 1000°C</td>
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<tr>
<td>(1978)</td>
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<tr>
<td>Radovic et. al.</td>
<td>TGA</td>
<td>550-750K</td>
<td>21</td>
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<td>Process Chars</td>
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<td>(1983)</td>
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<tr>
<td>Tseng et. al.</td>
<td>TGA</td>
<td>425-900°C</td>
<td>0.5-100</td>
<td>1 atm</td>
<td>From 1 US Bituminous Coal pyrolyzed in N₂ at 1000°C</td>
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<tr>
<td>(1985)</td>
<td></td>
<td></td>
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<tr>
<td>Knill et. al.</td>
<td>TGA</td>
<td>&lt; 500°C</td>
<td>0-100</td>
<td>1 atm</td>
<td>From hydropyrolysis of sub-bituminous Canadian coals at 600-800°C</td>
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<tr>
<td>(1986)</td>
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<tr>
<td>Morgan et. al.</td>
<td>TGA</td>
<td>450-650°C</td>
<td>21</td>
<td>1 atm</td>
<td>From hydropyrolysis of a British coal at 1400°C</td>
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<tr>
<td>(1986)</td>
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Table 2.2 Low Temperature Reactivity Studies
<table>
<thead>
<tr>
<th>Authors</th>
<th>Method</th>
<th>Temperature</th>
<th>% O₂</th>
<th>Pressure</th>
<th>Char Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field (1969)</td>
<td>Drop Tube</td>
<td>1200-1720°C</td>
<td>5, 10</td>
<td>1 atm</td>
<td>low rank UK Coal (N₂ at 1600K)</td>
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<tr>
<td>Smith (1971)</td>
<td>Drop Tube</td>
<td>1200-1900K</td>
<td>21</td>
<td>1 atm</td>
<td>NZ Bit. Coal (air at 1500K)</td>
</tr>
<tr>
<td>Hamor et al. (1973)</td>
<td>Drop Tube</td>
<td>900-2200K</td>
<td>10, 20</td>
<td>1 atm</td>
<td>Aust. Brown Coal (air at 1600K)</td>
</tr>
<tr>
<td>Smith et al. (1974)</td>
<td>Drop Tube</td>
<td>630-1812K</td>
<td>10, 20</td>
<td>1 atm</td>
<td>Aust. Brown Coal (air at 1600K)</td>
</tr>
<tr>
<td>Dutta et al. (1977)</td>
<td>TGA</td>
<td>834-1106°C</td>
<td>0.2-2</td>
<td>1 atm</td>
<td>US Bit. Coals (N₂ at 1024°C)</td>
</tr>
<tr>
<td>Smith (1978)</td>
<td>See Ref.</td>
<td>See Ref.</td>
<td>See Ref.</td>
<td>1 atm</td>
<td>Different Porous Chars</td>
</tr>
<tr>
<td>Young et al. (1981)</td>
<td>Drop Tube</td>
<td>1000-1800K</td>
<td>5-30</td>
<td>1 atm</td>
<td>Petro. coke</td>
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<tr>
<td>Wells et al. (1984)</td>
<td>Drop Tube</td>
<td>1300-1700K</td>
<td>21</td>
<td>1 atm</td>
<td>Process Chars</td>
</tr>
<tr>
<td>Knill et al. (1986)</td>
<td>Drop Tube</td>
<td>1100°C</td>
<td>21</td>
<td>1 atm</td>
<td>Can. bit. coals (600-800°C)</td>
</tr>
<tr>
<td>Mitchell (1987)</td>
<td>Drop Tube</td>
<td>1300-1800K</td>
<td>0-30</td>
<td>1 atm</td>
<td>Bit. coals/chars</td>
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</tbody>
</table>

Table 2.3 High Temperature Reactivity Studies
Chapter 3

PHYSICAL PROPERTIES AND OXIDATION RATES
OF CHARs MADE FROM THREE BITUMINOUS COALS

Published in Fuel, 67, 1988, 275-283.
Abstract

Intrinsic oxidation rates of coal chars derived from three bituminous coals were measured at 800 K and the effects of char formation temperature, conversion, coal particle size and char particle size on the rates were evaluated. Characterization of the various samples by BET surface area, mercury porosimetry, mercury and helium densities, heating values and in some cases elemental analyses were carried out to better understand the roles and interactions of the various parameters. Optical microscopic observations were also made to verify assumptions wherever possible. The results show that apparent and intrinsic rates as well as heating values are reduced with increasing char formation temperature. N$_2$-BET surface areas increase by an order of magnitude with conversion and exhibit maxima in the range of temperatures considered (1000 K to 1600 K). Of similar sized chars derived from different sizes of coal particles, those from the smaller coal size fractions had higher apparent reaction rates.
3.1 Introduction

The relationship between char reactivity and its physical or chemical properties is a subject of long standing. Several authors have reported on the dependence of the rates of char gasification by O₂, H₂O, and CO₂ on rank or chemical composition of the parent coal,¹⁻³ mineral matter,¹⁻²,⁴,⁵ and thermal pretreatment.¹⁻²,⁴,⁵ These experimental studies have, in most instances, employed sufficiently low temperatures and have taken other suitable precautions in order to minimize or eliminate intraparticle and external diffusion limitations. In the absence of diffusional effects the reaction rate divided by the surface area of the char, e.g. the N₂-BET surface area, provides what is known as the "intrinsic rate" or "intrinsic reactivity." It is well known that both total surface area and reactivity vary with the rank of the parent coal and its thermal pretreatment, although both surface area and reactivity have not always been measured.

Once a char has been prepared under specified and carefully controlled conditions, the gasification rate becomes a function of temperature, gas composition, and char conversion only. From the standpoint of process design, the dependence on conversion is as essential as the dependence on gas composition. Rates of char gasification by O₂, H₂O, and CO₂ have been reported as functions of conversion by several authors.⁶⁻⁹,²⁸ The rate versus conversion curves normalized by the maximum or the initial rate were found, in some cases, to be insensitive to reaction temperature but to vary with the reactant gas. Few workers measured surface area as well as reaction rate as functions of conversion to determine whether or not that ratio remained constant, although the assumption of constant ratio has been widely
employed in modelling work. In a recent investigation\textsuperscript{10} oxidation rates of chars from an anthracite and a bituminous coal (hva) were found to be approximately proportional to the surface area determined by CO\textsubscript{2} adsorption at 273K at all conversions. The constancy of the intrinsic rate permitted the analysis of the data by the random pore model.

In addition to their inherent interest, studies as the ones quoted above are useful in the interpretation of gasification or combustion rates under conditions pertinent to applications. At temperatures typical of practical processes, the reactions of char are quite strongly influenced by external heat and mass transfer and by internal pore diffusion. The interpretation and extrapolation of high temperature data must somehow take into account pore diffusion and pore growth. Some progress has been made in this area\textsuperscript{11,12} but the problem is far from having been satisfactorily treated, especially in regard to swelling coal chars. It is hoped, nevertheless, that in many cases the conversion dependence of pore structure characteristics and relative reaction rates measured under diffusion-free conditions can be approximately applied to high temperature reaction conditions.

In this paper we report oxidation rates and physical properties of bituminous coal chars subjected to devolatilization for two seconds at 1000-1600K. The focus is on the variation of surface area, reaction rate, and intrinsic reaction rate with conversion under diffusion-free conditions. Other physical properties reported include pore volume distribution, elemental composition and heating value. The effects of devolatilization temperature and particle size of the char and the parent coal are also examined.
3.2 Experimental Procedure

3.2.1 Char Formation

Chars were made from three bituminous coals with the compositions given in Table 3.1. At first the coals were ground in a mechanized mortar and pestle grinder in air for approximately 30 seconds and then sieved on a mechanical shaker for 10 minutes and classified into the following size fractions: less than 45µm, 45 - 53µm, 53 - 90µm, 90 - 104µm, 104 - 125µm and greater than 125µm.

Chars were then generated from the 45 - 53µm and 104 - 125µm size fractions of coal. These size fractions are narrow enough to minimize the effects of coal size variability while providing adequate sample quantities. The mean sizes 49µm and 114µm were different enough to examine the effects of coal size on subsequent char combustion.

The coals were pyrolysed in an electrically heated drop tube furnace. The furnace consists of an alumina tube having 5 cm. internal diameter heated by Kanthal heating elements placed in a radiation cavity 20 cm. long. Coal particles were entrained in a stream of nitrogen at rates of 2 g/hr using the syringe pump feeder arrangement described by Senior$^{13}$ and were injected into the radiation cavity of the furnace through a wide bore (1 cm) water cooled injector. Furnace wall temperatures were measured by thermocouples attached to the outside of the alumina tube. Gas temperatures were measured using a suction pyrometer. Based on both wall and gas temperatures the particle temperature was deduced from a steady state thermal energy balance. The carrier gas flow rate was adjusted to achieve residence times of 2 seconds. The devolatilization loss for the coals ranged between 30-50 %,
depending on the temperature, and varied from coal to coal.

The chars were collected on a filter. To eliminate any tars that might have condensed, the chars were washed repeatedly with tetrahydrofuran and then dried at room temperature for 1 hour. Finally the tar-free chars were sieve-classified into the following size fractions: less than 45 µm, 45 - 53 µm, 53 - 90 µm, 90 - 104 µm, 104 - 125 µm, 125 - 147 µm and greater than 147 µm.

3.2.2 Rate Measurements with TGA

A DuPont model 920 electrodynamic balance was used to measure the weight loss of a char sample oxidized at 800 K. In all cases the samples were heated in nitrogen at 50 K/min until the final temperature of 800 K was reached at which instant oxygen was admitted. The flow rates of the initial nitrogen stream and the oxidizing stream (17 % oxygen by volume) were kept at 100 cm³/min STP for all runs. This low flowrate was used to avoid entrainment of the extremely low density samples. The sample was placed on a platinum pan and its temperature was monitored with a thermocouple placed directly above. The mass loss, rate of mass loss, and the sample temperature were continuously recorded by a computerized data acquisition system. The initial sample masses were in the range 5 - 10 mg.

3.2.3 Surface Area and Helium Density Measurement

Surface areas were measured by a pseudo-static technique by acquiring gas adsorption isotherms using continuous addition of adsorbate gas (N₂ at 77 K) as described by Northrop et al.¹⁴ BET and capillary condensation analyses were carried out on the resulting isotherms. Calibration of the apparatus was carried out using various standardized samples of alumina and graphite. Helium densities were determined
on vacuum-dried samples by helium displacement at room temperature. Sample quantities of at least 0.8 g were used to obtain reliable density values.

### 3.2.4 Mercury Porosimetry

Pore volume distributions were determined by mercury penetration. An Autoscan porosimeter, Model 33 was used. Low pressure penetration (101 kPa) was implemented to fill the interparticle voids and intraparticle voids with openings larger than 7 µm. High pressure, to a maximum of 227 MPa (30000 psi), was used to penetrate pores having diameters larger than 6 nm. The Washburn equation\(^\text{15}\) was used to calculate pore volume distribution as a function of pore radius from pressure and intrusion volume measurements under the assumption of cylindrical pores.

### 3.3 Results and Discussion

#### 3.3.1 Physical Characteristics

Apparent densities, \(\sigma_A\); mercury densities, \(\sigma_{Hg}\), corresponding to the solid plus pores below 6 nm in diameter; and helium densities, \(\sigma_{He}\), for the uncombusted chars are listed in Table 3.2. Total porosity, \(\epsilon_A\), and porosity of pores below 64 Å, \(\epsilon\), can be estimated from the density values. Pore diffusivities for the initial materials were calculated based on mercury porosimetry, nitrogen capillary condensation and helium density data. Values of mean pore radii \(r_p\) were determined from the porosimetry plots or calculated from the microporosity values. Figure 3.1 shows the volume and surface area distributions for the 1200 K and 1600 K chars of PSOC-1451. These were obtained from mercury intrusion and nitrogen capillary condensation measurements. An interesting feature of the pore volume and area distributions
is that chars obtained by devolatilization at higher temperatures (1600 K) developed trimodal distributions while the low temperature (1200 K) chars developed bimodal ones. As is evident from the surface area curves in the same figure, pores below 100 Å in diameter account for most of the area while contributing very little to the total volume. On the other hand the presence of the pores above 1000 Å in diameter is manifested in the volume distribution. Therefore the presence of different pore ranges can be inferred by examining both the volume and surface area distributions. For the 1200 K char the distribution is bimodal showing appreciable pore volume in the macropore region and significant surface area in the micropore region. The same peaks are also evident for the 1600 K char. In addition there is a distinct peak around 500 Å showing development of accessible porosity in the transitional region. The 1000 K and 1400 K chars for this coal exhibit characteristics similar to the 1200 K char.Chars of the other coals also exhibited similar behaviour. The total pore volume penetrated by mercury, $V_{Hg}$, along with the pore size distribution is a good indication of the extent of connectivity of the macro and the transitional pores. The corresponding pore area, $A_{Hg}$ is calculated assuming cylindrical pores. Also listed are initial BET surface areas, heating values and elemental composition, expressed as mass fractions, for some of the chars. Data for partially combusted PSOC-176 1600 K char at 80% conversion are also tabulated. The apparent density of the partially combusted char has diminished while its porosity and the pore volume have increased.

### 3.3.2 Heating Values

Higher heating values (HHV) were measured using the 1341 Parr oxygen bomb
calorimeter. The results obtained were reproducible to within 250 J/g or about 1%. The values obtained for the PSOC-1451 coal and chars are plotted in Figure 3.2 as a function of charring temperature both on a total weight basis and on a dry ash-free basis. For both cases the heating values decrease with the increase in pyrolysis temperature. The reduction of heating value is obviously related to the loss of hydrogen at higher devolatilization temperatures as shown by the elemental analysis values listed in Table 3.2. Dulong\textsuperscript{16} gives an empirical relationship between coal heating value and C,H,O and S content. Experimental values agree very well with Dulong's formula as shown in the figure. There appears to be some disagreement for the 1600 K char. This might be due to a small error in the C:H ratio measurement.

3.2.9 Rate Calculations

The variation of sample mass with time in the TGA experiments was normalized with its value at the moment oxygen was admitted. There was some mass loss due to tar release as the sample was heated. The chars formed at relatively low temperature (1000 K and 1200 K) lost considerable mass during this period. For the 1400 K and 1600 K chars, almost all the volatiles were expelled during char formation, so that the loss during the heat up period was less than 3%.

In Figure 3.3 the apparent reaction rate $\rho_m$ is plotted versus carbon conversion. The conversion, $X$, at any given time is the mass of carbon reacted divided by the mass of initial carbon.

$$X = \frac{m_{\text{initial}} - m}{m_{\text{initial}} - m_{\text{ash}}} \quad (3.1)$$

The apparent reaction rate normalized per unit instantaneous mass, $m$, of carbon,
\[ \rho_m, \text{ is defined as} \]
\[ \rho_m = \frac{1}{m - m_{ash}} \frac{dm}{dt} \]  
(3.2)

The mass of ash, \( m_{ash} \), was measured in each run by carrying out oxidation until there was no further mass loss.

Another common way to plot the data is also shown in Figure 3.3 where \( \rho_{mo} \) is defined by normalizing with respect to the initial mass.

\[ \rho_{mo} = \frac{1}{m_{initial} - m_{ash}} \frac{dm}{dt} \]  
(3.3)

Plotted in this fashion the reaction rate exhibits a distinct maximum at a certain conversion that varies with char type, and particle size.

Figure 3.4 shows the reaction rate \( \rho_m \), as a function of conversion for two sizes of the 1600 K char of PSOC-1451. The two curves are indistinguishable, consistent with the absence of diffusion limitations concluded from the calculations given in the discussion below. Optical microscope photographs of PSOC-176 1600 K char at conversions of 0, 65 and 90% show that the particle size is independent of conversion as would be expected for regime I reaction.

### 3.3.4 Surface Areas

The surface area, \( A_T \), for the PSOC-176 1600 K char is shown in Figure 3.5 as a function of conversion. The area reported corresponds to the carbonaceous matter in as much as the surface area of the ash was measured to be only 2 - 3m\(^2\)/g, in good agreement with values reported by Smith and Tyler\(^{17}\). It can be seen that the surface area increases rapidly with conversion and at about 60% conversion, reaches a maximum value of 450m\(^2\)/g which is almost higher by an order of magnitude than
the initial value 50m$^2$/g. At higher conversions the area stays constant or decreases slightly. Similar trends have been observed for other coals$^{18}$. Surface areas of the three chars are plotted as a function of char pyrolysis temperature in Figure 3.6. The top three curves give the areas of the chars after partial oxidation to 50% conversion while the fourth curve shows the variation of the uncombusted area of the PSOC-176 char; areas for the other two 1600 K uncombusted chars are also shown. The area of the PSOC-176 char at zero conversion increases with pyrolysis temperature. There are two competing effects that affect surface area. While volatiles and tars released at higher temperatures leave a larger pore volume accessible to nitrogen, thermal annealing and structural reorganisation of the carbon matrix at higher pyrolysis temperatures leads to closing of pore mouths and pore coalescence thus reducing surface area. Which effect will dominate is not predictable a priori. In the present case experimental evidence suggests that for PSOC-176 the former does. The surface areas of partially combusted PSOC-176 and 1451 chars initially increase with pyrolysis temperature, reach a maximum and then drop. The high surface area of the PSOC-176 char indicates that it has more small pores accessible to N$_2$ at 77 K. In contrast, the surface area of the PSOC-282 char is approximately constant initially but later increases with pyrolysis temperature. Reduction of areas at higher charring temperatures may result from closure of the finer pores due to structural ordering of the carbon that increases with temperature of exposure. This hypothesis is supported by X-ray diffraction studies on semi-anthracite reported by Smith and Tyler$^{17}$. The anomaly presented by the 1000 K char is probably due to the presence of heavy tars in the material.
3.9.5 Diffusion Limitations

Three distinct processes must be examined to insure that the measured rates are free of diffusional limitations. They are diffusion in the boundary layer between the flowing oxidizer stream and the bed of particles, diffusion through the particle bed, and pore diffusion inside the particles. Each shall be examined briefly.

1. Bed Boundary Layer Diffusion: As a very simple approximation, the flow of oxidizer over the pan was modelled as flow past a flat plate, neglecting the effects of the pan walls, pan leading edge and the confining reactor tube walls. For the conditions of the experiment, the Reynolds number (based on average velocity at the reactor temperature and pan length) is about 1.5 and hence the flow is laminar. The time for diffusion across the boundary layer is negligible compared to the characteristic reaction time computed as $\rho^{-1}$ (see Table 3.3). Therefore it is safe to assume that there is no limitation imposed by diffusion in the bed boundary layer.

2. Bed Diffusion: Although sample quantities were small and spread uniformly over the pan, the effect of bed diffusion could become important at high temperatures. A modified Thiele modulus based on bed parameters and the apparent reaction rate can be formulated as shown below

$$K = \frac{\dot{N}}{C_0D_B} \frac{H^2}{C_0D_B} \quad (3.4)$$

where $\dot{N}$ is the apparent reaction rate per unit bed volume ($g/cm^3$), $C_0$ is the oxygen concentration in the ambient ($g/cm^3$), $H$ is the bed thickness (cm) and $D_B$ is the bed diffusion coefficient ($cm^2/s$), given by Satterfield as

$$D_B = \frac{D_m\epsilon_0}{\tau} \quad (3.5)$$
where $D_m$ is the molecular or bulk binary diffusion coefficient of oxygen in nitrogen at the proper temperature, $\epsilon_0$ is the void fraction of the bed normally in the range 0.35 - 0.4 and $\tau$ is the bed tortuosity, commonly taken equal to 2. Bed diffusion is negligible\textsuperscript{23} for $K < 1$. For the 45 - 53 $\mu$m size fraction of the PSOC-1451 1600 K char the sample size was 5 mg. and its apparent particle density was 0.98 g/cm$^3$. The apparent rate was $25 \times 10^{-4}$ g/cm$^3$-s. The pan area was 0.3 cm$^2$. Hence, the thickness of the bed, $H$, was 0.017 cm. Assuming a mean particle size of 50 $\mu$m, the average bed depth was only 3.4 particles. At 800 K the value of $D_m$ is 1.88 cm$^2$/s and, therefore, $D_B$ is 0.33 cm$^2$/s, assuming $\epsilon_0$ to be 0.35. At an oxygen mole fraction of 0.17 $C_0$ is $6.03 \times 10^{-5}$ g/cm$^3$. The resulting Thiele modulus, $K$, is $3.64 \times 10^{-4}$, hence bed diffusion does not significantly influence the reaction in these experiments.

3. Pore Diffusion: The present chars are extremely porous, having pore openings with length scales ranging from few microns down to few angstroms. The type of diffusion taking place covers the range from bulk diffusion in the macropores to Knudsen diffusion in the smaller meso and micropores with a combination of the two in pores of intermediate size. It is essential, therefore, to know the pore size distribution of the material before the pore diffusional resistance can be assessed. In the present study all micro and meso pore diameters were smaller than the mean free path of oxygen, approximately 0.3$\mu$m for the experimental conditions and thus, the diffusivity was that corresponding to Knudsen diffusion\textsuperscript{25},

$$D_K = 9.7 \times 10^3 r_p \left( \frac{T}{M} \right)^{0.5} \quad (3.6)$$
For the pores that have diameters comparable to the mean free path of oxygen, the transition regime diffusivity was applied i.e.\(^{26}\),

\[
\frac{1}{D_p} = \frac{1}{D_m} + \frac{1}{D_K}
\]  

(3.7)

Finally the total effective diffusivity was calculated by adding the contributions from the different pore sizes and the resulting values varied from 0.02 to 0.2.

3.9.6 Reaction Rate

As shown in Figure 3.3, \(\rho_m\) increases sharply during the first 3-4\% carbon conversion. The principal reason for this phenomenon is that the gas composition over the bed gradually changes from pure nitrogen to a final mixture of 17\% \(\text{O}_2\) in nitrogen. Jenkins\textit{ et al.}\(^1\) also suggest that oxygen complex formation at the surface and char activation may also be important at this early stage of conversion. After this initial delay the oxygen concentration reaches a steady value and the apparent rate increases slowly with conversion until the completion of combustion.

Following the procedure outlined by Smith\(^{19}\) an effectiveness factor \(\eta\) defined as the ratio of actual reaction rate to the rate found in the absence of restrictions due to pore diffusion can be calculated as:

\[
\eta \phi^2 \frac{(m + 1)}{2} = \frac{\gamma^2 \rho_m \sigma_A (m + 1)}{4D_e C_s}
\]  

(3.8)

where \(\phi\) is the pore Thiele modulus and \(\gamma\) is the characteristic length defined as the ratio of particle volume to external area. Thus the right side of equation (3.8) can be calculated and \(\eta\) can be calculated by the relationships between \(\eta\) and \(\eta \phi^2(m + 1)/2\) given by Mehta and Aris\(^{20}\). The effectiveness factors calculated for the uncombusted
chars using suitable diffusion parameters are equal to unity, in agreement with findings by Knill and others\textsuperscript{21} for similar conditions. This calculation also shows that there are no pore diffusion limitations. The order of magnitude increase in the surface area after partial combustion indicates the opening of a vast micropore network. A worst case calculation assuming that all pores have diameters of 10 Å, yielded an effectiveness factor \( \eta \) which was still close to unity.

Since the particles oxidize in the kinetically controlled regime I as shown earlier, an intrinsic reaction rate \( \rho_i \) can be defined by

\[
\rho_i = \frac{\rho_m}{A_T} \tag{3.9}
\]

Table 3.3 shows the intrinsic rate of PSOC-176 1600 K char at various degrees of conversion. Values for the areas were taken from Figure 3.5 and values of the apparent rate from Figure 3.3. It can be seen that after approximately 5\% of conversion the intrinsic rate becomes essentially independent of conversion providing a justification for employing the N\textsubscript{2}-BET surface area \( A_T \) for the definition of \( \rho_i \). Approximately constant intrinsic rates after the first 5\% conversion were obtained for the PSOC-1451 chars as well. The small increase in the rate at the highest conversions could be attributed to experimental error particularly in the area measurement of very small samples. It could also be due to the decrease in the particle conductivity with increasing porosity, causing local hot spots with high reaction rates.

The fact that the intrinsic rate is nearly constant with conversion makes possible the comparison of the intrinsic reactivities of chars at any conversion for which surface area values are available. In the present study all rates have been compared
at 50% conversion. Figure 3.7 shows the apparent reaction rate at 50% conversion for the three chars for two size cuts, 104-125µm and 45-53µm. It is evident that the reaction rates of all chars increase with decreasing pyrolysis temperature, possibly due to the residual volatile matter of higher reactivity or to less complete structural ordering which leaves a larger number of sites available for reaction with oxygen. The figure also shows that the apparent rate is independent of char particle size.

The effect of parent coal size on the apparent combustion rate was investigated for PSOC-1451 chars for the two size cuts 45-53 and 90-104 µm, both produced from coal size cuts 53-90 µm, and from coal fines below 45 µm in diameter. This effect of parent coal size can be quite important as the fractionation of coal leads to selective segregation of the different maceral types in certain sizes\(^22\). The presence of macerals of different chemical compositions affects the morphology, structure and reactivity of the char. Figure 3.8 shows the oxidation rates of chars derived from different size fractions of the parent coal. The oxidation rates of the char fraction derived from smaller coal particles appear to be 10-20% higher. This fraction was characterized by a more pronounced cenospheric structure and higher mineral matter content, the latter possibly causing some catalytic enhancement of the oxidation rate.

Intrinsic reaction rates for two size cuts of the three chars are presented in Figure 3.9. The intrinsic rate for two of the chars decreases with pyrolysis temperature, most probably due to the increased structural ordering of the carbon matrix with temperature. The rate of the PSOC-1451 char decreases the least, suggesting minimal structural changes. It is interesting to note that the intrinsic rates of the
three chars are equal at the lowest devolatilization temperature but deviate as much as 30% at higher devolatilization temperatures. One reason may be that structural ordering at the lower temperature is minimal in all three chars while as the temperature increases changes become more pronounced and differentiated among the chars. The fact that the intrinsic rate follows similar trends with the heating value of the chars suggests that the loss of hydrogen at higher devolatilization temperatures reduces the number of active sites for oxidation. This is in agreement with results reported by Khan\textsuperscript{27} showing a correlation between hydrogen content and rate of oxidation.

3.4 Conclusions

Increasing the pyrolysis temperature of three bituminous coals from 1000 K to 1600 K resulted in (i) decrease of the H:C ratio of the resulting char by a factor of 2 to 2.5 (ii) decrease of the heat of combustion of the char by 10-15% (iii) change in the pore volume and pore surface distributions from bimodal to trimodal with the creation of porosity in the mesopore range. The apparent oxidation rate (at 800K) decreased by about 50% as the pyrolysis temperature increased from 1000 K to 1600 K.

The N\textsubscript{2}-BET surface areas of the char increased from 10-50 m\textsuperscript{2}/g in the first few percent of conversion to 300-500 m\textsuperscript{2}/g at the highest conversions measured. The surface area at 50% conversion varied irregularly with the pyrolysis temperature.

The intrinsic char oxidation rate defined in terms of the N\textsubscript{2}-BET surface area was approximately the same for all coals pyrolysed at 1000 K but varied with the parent coal for the higher pyrolysis temperatures. The intrinsic reaction rate after
the first 5% of conversion was found to be approximately independent of conversion for all chars examined.

Char particles in the same size fraction obtained from coal of different size fractions differ in properties. The cenospheric char produced from the smaller coal particles was 10-15% more reactive than the char of equal size produced from the larger coal particles.

3.5 Acknowledgements

This work was supported by the US Department of Energy under their contract DE-AC2284FC70915. Thanks are due to Mr. P. S. Northrop for help in constructing and testing the BET apparatus and for carrying out some of the surface area measurements. The authors are also grateful to the reviewers for their useful suggestions and comments.
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28. Tseng H.P. and Edgar T.F. Fuel, 64, 1985, 373
List of Symbols

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<td>specific Mercury area [N$_2$-BET]</td>
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<td>specific total area</td>
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<td>$C_g$</td>
<td>ambient oxygen concentration</td>
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<td>particle diameter</td>
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Table 3.1 Properties of the three bituminous coals devolutilized to produce the chars used in the experiments.
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<th>$\sigma_\text{A}$ (g/cm$^3$)</th>
<th>$\sigma_\text{Hg}$ (g/cm$^3$)</th>
<th>$\sigma_\text{He}$ (g/cm$^3$)</th>
<th>$\epsilon_\text{A}$ % &lt; 7µm</th>
<th>$\epsilon_\text{A}$ % &lt; 32Å</th>
<th>$V_{\text{Hg}}$ (cm$^3$/g)</th>
<th>$S_{\text{Hg}}$ (m$^2$/g)</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
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<th>H (%)</th>
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Table 3.2 Properties of coals and chars.
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<th>INTRINSIC RATE $\rho_i$ (g/cm²-sec)</th>
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<td>90</td>
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Table 3.3 Variation of rates with conversion for PSOC-176, 1600K char.
Figure 3.1 Pore volume and surface area distributions for PSOC-1451 chars (a) 1200 K (b) 1600 K
Figure 3.2 Heating Values of PSOC-1451 coal and chars versus pyrolysis temperature.
Figure 3.3 Apparent rates, $\rho_m$ and $\rho_{mo}$ versus conversion, $X$, for PSOC-176 1600 K char.
Figure 3.4 Apparent rates, $\rho_m$ versus conversion, $X$, for PSOC 1451 1600K char, (a) 45-53 and (b) 104-125 $\mu$m.
Figure 3.5 Surface areas of PSOC-176 1600 K char versus conversion.

Line is smooth fit.
Figure 3.6 Initial surface areas and surface areas after 50% conversion for all chars versus pyrolysis temperature.
Figure 3.7 Apparent reaction rates at 50% conversion for 45-53 and 104-125 µm sizes of all chars versus pyrolysis temperature.
Figure 3.8 Apparent reaction rates at 50% conversion for 45-53 and 104-125 μm char sizes derived from PSOC-1451 coal sizes (a) less than 45 μm (b) 53-90 μm versus pyrolysis temperature.
Figure 3.9 Intrinsic reaction rates at 50 % conversion for 45-53 and 104-125 \( \mu m \) sizes of all chars versus pyrolysis temperature.
Chapter 4

CHAR COMBUSTION: MEASUREMENT AND ANALYSIS OF PARTICLE TEMPERATURE HISTORIES

Accepted for publication in

*Combustion Science and Technology*
Abstract

Single particle combustion experiments were carried out with 50 - 100µm char particles derived from one lignite and one HVA bituminous coal. Reactor wall temperatures in the range 1050 K to 1450 K and oxygen partial pressures of 0.21 and 0.5 were used. The complete temperature-time histories of individual burning particles were measured using two-color optical pyrometry techniques. Apparent combustion rate parameters of the chars were then estimated using a model of single particle combustion and taking into account the random particle-to-particle property variation.
4.1 Introduction

The entrained flow reactor is the standard experimental system for the measurement of pulverized char combustion rates. Measurements that can be carried out in this system include (i) carbon conversion and characterization of physical properties (size, density, etc.) of partially burned char withdrawn at the reactor outlet or at intermediate axial positions using a cooled probe (ii) reactor wall temperature and gas temperature at various axial locations. The measurement techniques and procedures for data analysis have been described in the well known papers of Field (1969) and Smith and coworkers (Hamor and Smith, 1973). In analyzing their data these authors estimated particle temperatures by a steady-state energy balance using the measurements of reaction rates and gas and wall temperatures. Ayling and Smith (1972) used two-color pyrometry to determine directly the temperature of a stream of burning particles and found fair agreement between measured and calculated temperatures. Such measurements and calculations involve averages over many particles which, even when carefully sized, can differ considerably in shape, density, mineral content and other properties. This averaging is quite reasonable from the engineering point of view but it introduces an as yet unexplored uncertainty in the reported apparent or intrinsic reaction rate parameters.

More recently various workers have been able to measure the temperature of individual burning particles by two-color pyrometry (McLean et al., 1981; Mitchell and McLean, 1982; Timothy et al., 1982; Jorgensen and Zuiderwyk, 1985). The key element in this technique is the introduction of an extremely dilute stream of particles into the reactor so that the optical volume sampled by a pyrometer
equipped with a very sensitive detector, contains a single particle. The measure-
ments involve either a particle at a particular location along the furnace, i.e. at
a particular instant during its burning history (McLean et al., 1981; Mitchell and
McLean, 1982), or the complete temperature-time history of the particle (Timothy
et al., 1982; Jorgensen and Zuiderwyk, 1985). The interpretation of single parti-
cle temperature-time traces using some suitable particle combustion model requires
specification of particle properties. As mentioned earlier, these properties vary con-
siderably from particle to particle and this variation poses a major problem in the
analysis of the data. The experimental technique of Mitchell and McLean (1982)
provides simultaneous information about particle size and particle temperature at
a fixed location but is not applicable in its present form to the measurement of a
complete temperature-time trace.

In this paper we report measurements of temperature-time traces of single
char particles derived from a narrow sieve cut. A particle combustion model is
then used to analyze the temperature traces and estimate the apparent combustion
rate parameters. The analysis uses a simple approach to account for the random
particle-to-particle property variation.

4.2 Experimental Procedure

4.2.1 Char Formation

Chars were made from one high-volatile A bituminous coal (PSOC 1451) and one
lignite coal (PSOC 1443). The coals were ground in a mechanized mortar and
pestle grinder in air for approximately 30 seconds and then sieved on a mechanical
shaker for 10 minutes into the following size fractions: less than 45µm, 45 - 53µm,
53 - 74\mu m, 74 - 104\mu m, 104 - 125\mu m and greater than 125\mu m.Chars were then generated from the 53 - 74\mu m size fraction of coal.

The coals were pyrolysed in an electrically heated drop tube furnace. The furnace consists of an alumina tube of 5 cm. internal diameter heated by Kanthal heating elements placed in a radiation cavity 20 cm. long. Coal particles were entrained in a stream of nitrogen at rates of 2 g/hr using the syringe pump feeder arrangement described by Senior and Flagan (1984) and were injected into the alumina tube through a wide bore (1 cm) water cooled injector. Furnace wall temperatures were measured by thermocouples attached to the outside of the alumina tube. Gas temperatures were measured using a suction pyrometer. The carrier gas flow rate was adjusted to achieve residence times of 2 seconds. The devolatilization loss for the coals ranged between 30-50%, depending on the coal type.

The chars were collected on a filter. To eliminate any tars that might have condensed, the chars were washed repeatedly with tetrahydrofuran and then dried at room temperature for 1 hour. Finally the tar-free chars were sieve-classified into the following size fractions: less than 45\mu m, 45 - 53 \mu m, 53 - 90 \mu m, 90 - 104 \mu m, 104 - 125 \mu m, 125 - 147 \mu m and greater than 147 \mu m. A few chemical and physical characteristics of the coals are given in Table 4.1. Some properties of the derived chars are shown in Table 4.2.

4.2.2 Optical Pyrometry

The temperature of the burning char particles was measured by two-color optical pyrometry in the near infrared. The radiation from the burning particles was focussed onto a bifurcated optical fibre and transmitted to two silicon photodetectors
via medium band (70nm) filters centered at 800 and 1000nm. The voltage signals from each channel were read by a high speed, computerized data acquisition system. Details of pyrometer construction are given elsewhere (Levendis and Flagan, 1987). By using Planck's law of radiation the temperature of each particle can be deduced from the ratio of the two signals as a function of time. The system was calibrated at the melting point of pure platinum (2045 K). The pyrometer was aligned along the direction of flow of the particles and thus was able to 'see' each particle for its entire burning history.

4.2.3 Experimental Conditions

Experiments were carried out with char particles of different sizes at various wall temperatures and in different ambients. For the bituminous coal (PSOC 1451), char sizes 45-53 and 104-125 µm were used. Both fractions were derived from sieving the char produced from the 53-74 µm coal fraction. Char sizes of 45-53 µm and 53-74 µm were derived from 45-63 µm and 63-75 µm fractions of raw lignite, respectively. Ambients were air and 50% O₂ for the bituminous char and air for the lignite char. Wall temperature was varied from 1000 K to 1500 K. In all cases the gas velocity was roughly 0.1 m/s, so the particles burned within a few millimeters after igniting. Since the distance between the point of injection and the detector was 0.3 m., the detector effectively saw 'stationary' particles.

4.3 Experimental Results

4.3.1 Temperature versus Time Traces

Intensity-time traces were measured for at least twenty particles for each set of
experimental conditions. Figures 4.1a-d show the intensity-time traces and the calculated temperature-time traces for a few particles. The temperature-time traces show widely different qualitative behaviour from particle to particle. While some burn at almost constant temperature (Figure 4.1a), many particles show temperature maxima (Figure 4.1b) or even monotonic behavior, both increasing (Figure 4.1c) and decreasing (Figure 4.1d). This variability is particularly pronounced in the case of the bituminous char. Temperature traces for lignite char showed maxima at intermediate times in most cases.

4.3.2 Data Analysis

The observed variability of the temperature-time traces is due partly to experimental error and partly to the variability in the initial properties of individual particles: size or shape, density, pore structure, maceral and mineral content. Pyrometry measurements on uniform spherical particles of synthetic char (Levendis, 1987) using the same reactor and pyrometer have yielded much more uniform traces of intensity and temperature. Most of the observed variation in the traces of the bituminous and lignite chars must, therefore, be due to differences in the properties of individual particles.

The obvious approach to estimating combustion rate parameters from a set of temperature traces is to postulate a spherical particle having average size, density etc. and to assign to that particle a single temperature-time trace obtained by averaging the measured individual traces. This straightforward approach would entail loss of the detailed information contained in the individual traces. Moreover, calculating an ‘average’ trace is not very meaningful because of the different
burnout times of the individual traces. In this study we have followed a different approach whereby the rate parameters are estimated from the individual temperature traces treating the properties of individual particles as random variables. While the particle-to-particle variation involves several properties, the level of experimental accuracy and the need for mathematical tractability suggests a highly simplified approach. We assume that the properties of the $i^{th}$ particle are characterized by two random variables: its initial radius, $r_{0i}$, assuming spherical shape, and the apparent Arrhenius pre-exponential factor $A_{ai}$. The apparent reaction rate is assumed to be of the form

$$R_a = A_a e^{-E_a/RT_p m}$$

This is based on the external surface area of the particle. The reaction order, $m_i$, is assumed to be one, but other types of kinetics can be treated without difficulty.

Using an effective radius (i.e. assuming spherical particles) is a clear necessity in view of the impracticability of carrying out mathematical calculations for particles of irregular and unknown shape. The second random variable $A_a$ is assumed to account for particle-to-particle variations in reactivity and porosity, the latter affecting $A_a$ (and not $E_a$) as discussed by Gavalas (1981). Variations in mineral and maceral content affect $E_a$ as well as $A_a$. Nevertheless, the accuracy of the data does not warrant using more than one or two parameters that vary from trace to trace. Therefore, we have treated $E_a$ as an unknown parameter common to all traces. The other properties of the particle, namely density, heat capacity, and mineral content are treated as known constants. Under these assumptions, the temperature
of the $i^{th}$ particle may be expressed as

$$T_i(t) = f(t; E_a, A_{ai}, r_{0i}) + \epsilon_i(t)$$

(4.2)

where $\epsilon_i(t)$ is the error in the measurement of the temperature. The dependence on the known properties (e.g. particle density and heat capacity) is not shown explicitly. The function $f$ is defined by some suitable combustion model. The model that has been used in the present study is discussed briefly in the following section.

The analysis of the data proceeds as follows. For each trace we define a quantity

$$J_i = \sum_{j=1}^{n} [f(t_j; E_a, A_{ai}, r_{0j}) - T_{i}^{exp}(t_j)]^2 + w(f_0 - r_{0i})^2$$

(4.3)

where the first term represents the deviation of experimental and calculated temperatures over a suitable discrete set of times and the second term represents the deviation of the random radius from the known mean radius (the mean of the appropriate sieve size cut). The weighting coefficient $w$ must be chosen in accordance with the expected error in the temperature measurement ($\epsilon_i(t)$) and the spread in particle size. It is given by $\sigma_T^2/\sigma_r^2$ where $\sigma_T$ is the standard deviation in the particle temperature measurement and $\sigma_r$ is the standard deviation in the initial radius measurement. The error in the temperature measurement can be calculated from the spread observed over many calibration runs. It was taken as $\sigma_T \sim 50K$. The experimental error in the radius measurement was calculated by two independent means: (i) from optical size measurements over many particles (ii) from ASTM sieve standards for wire mesh sieves. Both methods give similar results, $\sigma_r \sim 12\mu m$. The values of $A_{ai}$ and $r_{0i}$ that minimize $J_i$ are denoted by $A_{ai}^*$ and $r_{0i}^*$.
by \( J_i^* \) the minimum value of \( J_i \). The three quantities \( A_{a_i}^*, r_{0i}^*, \) and \( J_i^* \) are clearly functions of \( E_a \).

We now calculate the minimum with respect to \( E_a \) of the quantity

\[
Q = \sum_{i=1}^{N} J_i^*(E_a) \tag{4.4}
\]

obtained by summing over all \( N \) traces. If we denote by \( \hat{E}_a \) the minimizing value of \( E_a \) then the quantities

\[
\hat{r}_{0i} = r_{0i}(\hat{E}_a) \tag{4.5}
\]

\[
\hat{A}_{ai} = A_{ai}(\hat{E}_a) \tag{4.6}
\]

are the best estimates of radius and pre-exponential factor for the \( i^{th} \) particle. A mean preexponential factor can then be defined by the arithmetic mean

\[
\bar{A}_a = \frac{1}{N} \sum_{i=1}^{N} \hat{A}_{ai} \tag{4.7}
\]

A mean particle size is not needed since this can be directly determined by simple observation. However, comparison of the range of \( \hat{r}_{0i} \) values with the directly observed range of particle sizes provides a general consistency check.

The cumulative sum \( Q \) of the \( J_i \)'s over all particles versus activation energy is shown in Figure 4.2: Figures 4.2a and 4.2b show the minimization with respect to \( E_a \) for the bituminous char and lignite char, respectively. The estimated apparent rates for these two chars are given by

\[
R_a = 107.1 \exp(-17000/RT) \quad \text{gcm}^{-2}\text{s}^{-1}\text{atm}^{-1} \tag{4.8}
\]

\[
R_a = 20.8 \exp(-14000/RT) \quad \text{gcm}^{-2}\text{s}^{-1}\text{atm}^{-1} \tag{4.9}
\]
The estimated apparent activation energy for the bituminous char is in good agreement with that reported by Field (1969) but lower than the value of 21400 cal/gmole that follows from the collective correlation given by Smith (1982). The apparent activation energy for the lignite char is somewhat lower than the value of 16300 cal/gmole that is obtained from Australian brown coal chars reported by Smith and Tyler (1974). The values for preexponential factors reported here are arithmetic means over many traces. The spread of these factors was rather large, as shown in the histograms given in Figures 4.3a and 4.3b. A similar, though smaller spread of values was obtained for the estimated particle diameters. The average of the diameter estimates was 45µm for the lignite char and 57µm for the bituminous char. Taking into account the irregular shape of the particles, the estimated equivalent sphere diameters are in fair agreement with the sieve sizes (45-53µm) and the sizes observed by microscopy.

4.4 Particle Combustion Model

4.4.1 Model Description and Comparison with Experimental Data

The particle combustion model described by Loewenberg et al. (1987) was employed for the calculations after being extended to include the effects of ash. The ash is initially uniformly distributed throughout the particle, but as the carbonaceous material is oxidized, the exposed ash particles accumulate on the surface as a porous layer of increasing thickness. Scanning electron microscopy of individual particles at various conversions has shown the accumulation of ash but does not exclude the possibility of some ash loss to the gas phase. The ash layer is assumed to add a mass transfer resistance in series with the resistance across the film or boundary layer.
around the particle. However, it does not create an additional thermal resistance. To calculate the resistance to mass transfer, the ash layer is regarded as a stagnant packed bed with effective diffusivity equal to the bulk gas phase diffusivity multiplied by the ash layer void fraction (~0.4) and divided by a tortuosity factor (~2).

The complete particle combustion model includes a detailed description of intraparticle diffusion and pore growth. However, the calculations reported here used a limiting form of the model wherein the reaction takes place in a thin outer shell (Gavalas (1981); Loewenberg et al. (1987)). Simulations have shown that this limiting form of the model is adequate for the range of particle temperatures encountered in the experiments. In this case the mass and energy balances can be written as

\[
\frac{d}{dt}[m_c + m_{ash}] = -4\pi r^2 R_a
\]  \hspace{1cm} (4.10)

\[
\frac{d}{dt}[m_c C_{pc} + m_{ash} C_{pash}]T = 4\pi r^2 (R_a \Delta H - e_c - e_r)
\]  \hspace{1cm} (4.11)

where \(r\) is the radius of the particle including the ash layer; \(m_c, C_{pc}\) and \(m_{ash}, C_{pash}\) are mass and heat capacity of the total carbon and the total ash within the particle; \(R_a\) is the apparent rate; \(\Delta H\) is the heat of the combustion reaction; and \(e_c, e_r\) are heat fluxes from the particle by conduction and radiation, respectively.

The radiative term was based on a constant overall emissivity without provision for any effects of the accumulating ash. The apparent rate \(R_a\) depends on the intrinsic kinetics as well as on the pore structure of char (Gavalas (1981); Loewenberg et al. (1987)). From the standpoint of parameter estimation, however, all that is needed is a functional form as given by Eq.(4.1) where \(A_a\) and \(E_a\) are treated as apparent rate parameters.
Equations (4.10) and (4.11) are coupled to the equations of diffusion and heat transfer from the particle surface to the free stream. The latter equations, which include Stefan flow and temperature dependent properties are given in Lowenberg et al. (1987). The coupled system of equations is solved to yield the radius and temperature of the particle and the oxygen partial pressure $p_a$ at the surface of the particle, all as functions of time.

Sample comparisons between calculated and experimental temperatures are shown for two particles in Figures 4.4a and 4.4b. For each particle the calculated curve was obtained using the optimal parameters $E_a, A_{ai}(E_a), \text{ and } r_{oi}(E_a)$. The fits are good, indicating the ability of the simple model to describe particle combustion using the estimated rate parameters.

### 4.4.2 Parametric Studies

Calculations were carried out to determine the effect of various properties on the particle temperature. Figure 4.5a shows that the predominant effect of increasing initial particle size is to increase the burn time and slightly decrease the maximum temperature. The increase in burn time varies approximately as the square of the particle radius as expected from the 'shrinking core' particle combustion. Increasing the apparent density of the particle (Figure 4.5b) increases only the burn time and does not affect the maximum temperature reached. The presence of ash affects the shape of the temperature trace dramatically (Figure 4.5c). At high conversions, the particle consists mainly of ash so that its thermal inertia is higher and, hence, its temperature does not fall as quickly as it would have if ash was not present. The effect of carbon emissivity (Figure 4.5d) is straightforward: for a fixed wall
emissivity, a particle with higher carbon emissivity burns at a lower maximum temperature due to increased radiative loss. However, the decrease in temperature is not dramatic and the burn time increases only marginally. The most dramatic effect on the temperature-time traces are caused by changing the reaction rate parameters. For example, the effects of the frequency factor at constant activation energy are shown in Figure 4.5e.

4.5 Conclusions

Single particle temperature-time traces measured by optical pyrometry show considerable variability due to different size, shape, pore structure and mineral content of individual particles. A novel technique is introduced to analyze the traces by treating size and preexponential factor of each particle as random variables. This technique was used in conjunction with a particle combustion model assuming that the heterogenous reaction is limited to a thin surface layer of the particle in order to estimate the apparent kinetic parameters. The estimated values of the apparent preexponential factor varied significantly from particle to particle. Using the estimated parameters provided good agreement between calculated and experimental temperature-time traces.

4.6 Acknowledgements

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References


Table 4.1 Properties of parent coals.

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<th>PSOC 1451</th>
<th>PSOC 1443</th>
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<td><strong>RANK</strong></td>
<td>HVAB</td>
<td>SUB-BIT C/ LIGNITE</td>
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<tr>
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<td><strong>SEAM NAME</strong></td>
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<td>LOWER WILCOX</td>
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<td><strong>PROXIMATE ANALYSIS (%)</strong> (AS REC'D)</td>
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<tr>
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</tr>
<tr>
<td>* EXCLUDES MOISTURE</td>
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<td></td>
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<td><strong>FREE SWELLING INDEX</strong></td>
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</tr>
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<td>Coal Rank</td>
<td>HVA Bituminous</td>
<td>Lignite</td>
</tr>
<tr>
<td>-----------</td>
<td>----------------</td>
<td>--------</td>
</tr>
<tr>
<td>C (wt %)</td>
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</tr>
<tr>
<td>H (wt %)</td>
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<tr>
<td>Ash (wt %)</td>
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</tr>
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<td>Surface Area (m²/g)</td>
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<tr>
<td>Density (g/cm³)</td>
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</tr>
<tr>
<td>Pore Volume (cm³/g)</td>
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<td>0.5</td>
</tr>
<tr>
<td>Particle Diameter (µm)</td>
<td>45-53, 90-104</td>
<td>45-53, 61-74</td>
</tr>
</tbody>
</table>

* after 5% conversion at 450°C

Table 4.2 Properties of the Chars.
Figure 4.1a Intensity vs. Time and Temperature vs. Time during the combustion of one bituminous char particle in air at reactor wall temperature of 1450K.
Figure 4.1b Intensity vs. Time and Temperature vs. Time during the combustion of one bituminous char particle in air at reactor wall temperature of 1450K.
Figure 4.1c Intensity vs. Time and Temperature vs. Time during the combustion of one bituminous char particle in air at reactor wall temperature of 1450K.
Figure 4.1d Intensity vs. Time and Temperature vs. Time during the combustion of one bituminous char particle in air at reactor wall temperature of 1450K.
Figure 4.2a Minimization of the sum of residuals with respect to activation energy for bituminous char.
Figure 4.2b Minimization of the sum of residuals with respect to activation energy for lignite char.
Figure 4.3a Histogram of pre-exponential factors for bituminous char.
Figure 4.3b Histogram of pre-exponential factors for lignite char.
Figure 4.4a Comparison of experimental and calculated temperature-time history for a bituminous char particle.
Figure 4.4b Comparison of experimental and calculated temperature-time history for a lignite char particle.
Figure 4.5a The effect of initial particle size as predicted by the model.
Figure 4.5b The effect of apparent particle density as predicted by the model.
Figure 4.5c The effect of initial ash content as predicted by the model.
Figure 4.5d The effect of carbon emissivity as predicted by the model.
Figure 4.5e The effect of pre-exponential factor as predicted by the model.
Chapter 5

COMBUSTION OF CHARS AT HIGH TEMPERATURES
5.1 Introduction

Particle temperatures in large pulverized coal combustion systems are often greater than 1000K and may be in excess of 2000K. Many of the published measurements of coal or char combustion rates were made at temperatures much lower than this (Essenhigh, 1981; Tseng and Edgar, 1984). The low temperature data are useful and can be obtained with relative ease, but, given the complex nature of coal or char and the combustion process, it is not obvious that low temperature combustion data can be used to predict behavior at higher temperatures.

The entrained flow reactor is the most common experimental system for the study of high temperature pulverized char combustion. Measurements typically made in combustion experiments include (i) carbon conversion and characterization of physical properties (size, density, etc.) of partially burned char withdrawn at the reactor outlet or at intermediate axial positions using a cooled probe (ii) reactor wall temperature and gas temperature at various axial locations (Field, 1969; Hamor and Smith, 1973).

Prior to understanding combustion behavior, it is imperative that the physical and structural changes of the char be well characterized. This chapter describes experiments that were carried out to physically characterize bituminous chars combusted at high temperatures. These results are then compared to those from similar experiments done on the same chars combusted at lower temperatures.
5.2 Experimental Procedure

5.2.1 Char Formation

Chars were made from PSOC 1451. The chemical and physical properties of this coal are summarized in Table 5.1. The coal was ground in a mechanized mortar and pestle grinder in air for approximately 30 seconds and then sieve classified on a mechanical shaker for 10 minutes. Chars were generated from the 53 - 74\(\mu\)m size fraction of the coal.

The coal was pyrolysed in an electrically heated drop tube furnace. The furnace consists of an alumina tube of 5 cm. internal diameter heated by Kanthal Super 33 heating elements placed in a radiation cavity 20 cm. long. Coal particles were entrained in a stream of nitrogen at rates of 2 g/hr using a syringe pump feeder and were injected into the alumina tube through a wide bore (1 cm) water cooled injector. The furnace wall temperature was maintained at a temperature of approximately 1650K, in order to achieve gas temperatures of 1600K. Furnace wall temperatures were measured by thermocouples attached to the outside of the alumina tube. Gas temperatures were measured using a suction pyrometer. Based on wall and gas temperatures the particle temperature was deduced from a steady state thermal energy balance. The carrier gas flow rate was adjusted to achieve residence times of about 2 seconds. The mass loss during devolatilization of the coals ranged from 30-40\%, depending on the coal particle size.

The char particles were collected on a filter. To eliminate any tars that might have condensed, the chars were washed repeatedly with tetrahydrofuran and then dried at room temperature for 1 hour. Finally, the tar-free chars were sieve-classified
into the following size fractions: less than 45µm, 45 - 53µm, 53 - 90µm, 90 - 104µm, 104 - 125µm, 125 - 147µm and greater than 147µm. The 45-53µm and 90-104µm char size fractions were used for the combustion studies described in this chapter.

Combustion experiments were performed in the high temperature flow reactor shown in Figure 5.1. Preheater wall temperatures of 1475K and 1675K were used to heat the primary air stream. However, due to heat losses in the section between the pre-heater and the reactor, the gas temperature at the entrance to the reactor was lower. The particle temperature was measured by a split-beam two-color optical pyrometer. Particle temperatures were generally higher than the gas temperature at the same axial location. For each value of the pre-heater wall temperature, partially burned particles were collected for analysis at three axial locations using a moveable water-cooled, N₂-quenched collection probe. The residence time upstream of the collection point in the reactor was also estimated in each case by knowing the velocity of the laminar carrier gas flow. The collected samples were then analyzed as described in a later section.

5.2.2 Experimental Conditions

Experiments were carried out using two sizes of char particles at two reactor temperatures. Char sizes of 45-53 and 90-104µm were used. The first two sets of experiments were performed at a preheater wall temperature of 1475K using the two char sizes. For the third set of experiments, the preheater temperature was 1675K, and the initial char size was 90-104µm. In the first two sets of experiments the gas velocity was roughly 0.7 m/s. In the last set it was about 0.9 m/s. In all cases the particles travelled several centimeters before burning out. Partially
burned samples were collected at three different axial locations. While every effort was made to collect samples of widely differing conversions, *a priori* control of conversion at the sampling locations was not possible. The quantities of char collected were small since the original samples were themselves small due to the narrow size cuts chosen.

5.2.3 Particle Temperature Determination

The particle temperatures as a function of axial location were measured in a dilute stream using the two-color pyrometer. The detector optics was mounted on a 3-degree of freedom translator so that any volume in the test section could be probed. The pyrometer was focussed at the center of the particle stream on the axis of the reactor. The whole assembly was moved vertically to the desired axial location. The view volume of the detector optics was about 0.4 to 0.8 millimeters at its narrowest. At the flow rates used, the particle residence time in the view volume was 0.3 to 0.6 ms. Since the view volume was so small, and the particle stream so dilute, the probability of more than one particle occupying the view volume at the same time was negligible. A high-speed data acquisition system was used to gather the temperature data. Average particle temperatures were determined by observing many particles at each location. The pyrometer was calibrated using a Type S thermocouple bead placed in the hot gas flow within the view volume of the detector optics.

Table 5.2 shows the average particle temperatures measured in each case. The spread of measurements as well as the average is shown. The temperature data are consistent with model predictions that the temperature of the particles remains
reasonably constant over the burnout period. The drop in temperature at the highest conversions is attributed to heat losses from the test section since it was not completely insulated. The particle temperatures of the 1675K preheater wall temperature samples are smaller than the 1475K case because they were collected further downstream than the latter and thus suffered more heat losses. Given the uncertainties in calibration and measurement, it is impossible to infer minor trends with conversion. The data suggest that the particle temperature was approximately constant throughout the combustion process for each case.

5.2.4 Collection of Partially Oxidized Chars

A water-cooled probe was used to collect the partially oxidized material. The particles were quenched with a large flow of nitrogen to ensure that oxidation did not take place in the probe and on the filter downstream. A schematic diagram of the collector is shown in Figure AIV.6 (Appendix IV).

5.3 Conversion Determination

The single most important variable in characterizing the partially oxidized samples is the carbon conversion or burnoff. The conversion is most commonly determined gravimetrically from mass measurements made before and after combustion. Assuming that there are no sampling losses the extent of conversion is easily estimated. However, in most cases sampling losses are unavoidable so this method is relatively inaccurate.

In the present system, while most of the particle stream was captured, there were thermophoretic losses at the cold entrance region of the collector. These losses
are difficult to estimate. Therefore, the ash was used as a tracer to estimate the quantity of carbon represented by a particular char sample. This assumes that the ash is not lost due to devolatilization during char formation. Even at combustion temperatures, volatilization is minimal, amounting to less than a few percent of the ash (Flagan and Friedlander, 1978). Since the chars were made at 1600K, ash volatilization is expected to be a very small correction. Thus the ash-tracer technique is well suited for measuring carbon conversion in chars used in this study. The drawbacks of this method are that the char sample must be destroyed to determine the ash content and that, for reasons of accuracy, the sample size should be as large as possible. Therefore, all char characterization tests were performed on the sample before its ash content was determined by incineration and subsequent weighing. Rapid heating rates were used in char ashing to prevent graphitization of the carbon. This is necessary since the resulting graphitic structure is difficult to oxidize except at very high temperatures. Graphitic residues left with the ash could lead to erroneous carbon conversion values.

Let the mass fractions of ash in the unburned and partially burned chars be $x_0$ and $x$ respectively. Let the total masses in the beginning and at the end of partial combustion be $m_0$ and $m$ respectively. Since, the mass of ash is assumed to be constant, we have

$$m_0 x_0 = mx \quad (5.1)$$

Also, the mass of carbon burnt, $m_{loss}$ is

$$m_{loss} = m_0 - m \quad (5.2)$$

The experimental carbon conversion, $X_{expt}$, is defined as the mass of carbon burnt
divided by the initial mass of carbon. Thus,

\[ X_{\text{expt}} = \frac{m_{\text{loss}}}{m_0(1-x_0)} \]  

(5.3)

Combining equations (5.1), (5.2) and (5.3), and eliminating \( m \) and \( m_0 \), we have,

\[ X_{\text{expt}} = \frac{x-x_0}{x(1-x_0)} \]  

(5.4)

Thus, knowing the mass fractions \( x \) and \( x_0 \), conversion \( X_{\text{expt}} \) can be calculated.

5.4 Experimental Methods and Results

5.4.1 Optical Microscopy

Particle size was determined visually under the optical microscope. Since the particles were generally irregular, the following procedure was used: the length along the major axis and the greatest length along its perpendicular were measured. The average particle size was computed as the arithmetic mean of these lengths. This was randomly repeated for 25 particles in each sample. Figure 5.2 shows the distributions of the average particle sizes for the unburned 90-104\( \mu \)m sieve cut char. This figure clearly shows that char sizes were bigger than expected from the particular sieve size cut. Similar size distributions were also measured for one group of the partially burned samples (1675K wall, 90-104\( \mu \)m parent size). They are shown in Figures 5.3-5.5 in order of increasing carbon conversion. The size distribution shifts to smaller sizes at higher conversions. However, the decrease in particle size is smaller than would be expected from diffusion limited combustion conditions. Thus, there must be some internal combustion to explain the observed carbon loss. This will be discussed more fully later on. Figure 5.6 shows the variation of the average particle size as a function of conversion.
Observations using the optical and electron microscopes have shown that the bituminous char is cenospheric, i.e. it is almost spherical and contains large bubble-like voids (Lightman and Street, 1967). The free swelling index (FSI) of the parent coal (7.5) also indicates its propensity to swell on devolatilization. An indicator of the irregularity of shape of a particle is its aspect ratio, which is defined as the ratio of the major to the minor dimension. The average aspect ratio for the unburned 90-104 µm bituminous char particles is 1.18. Since this is not too different from unity, it shows that the char of this size is indeed roughly spherical. However, aspect ratio measurements on the partially burned chars do not show any systemic variation. This also indirectly supports the contention that there is internal combustion. The argument is as follows: Let each particle be an ellipse. Further, let the external surface recede at a constant velocity all around the particle, as would be expected for diffusion limited combustion. The aspect ratio of the particle should then increase monotonically. Since this is not observed, there must be some penetration of oxidant into the particle causing internal reaction.

5.4.2 Electron Microscopy

Figure 5.7 is an electron micrograph of an unburned char particle from the 90-104µm sieve cut. It is a typical cenosphere. The outer surface is smooth though quite convoluted. In addition to the large pore in the upper part of the figure, other pore mouths are clearly visible. Some mineral matter agglomerates are also seen on the surface of the particle. Figure 5.8 is a higher magnification picture of the lower part of the same particle. The smooth nature of the surface is again clearly visible. At the top right hand corner of this figure, pore mouths about 1µm in diameter are
seen. Fine mineral matter is also dispersed on the particle surface.

Figures 5.9 and 5.10 show two different magnifications of a particle converted to 17.4% at the 1475K preheater wall temperature. The striking changes even at such small conversions should be noted. The particle surface is very convoluted now, with deep recesses, and shows the enlarged mouths of the bigger pores. On the small scale, however, the surface is still very smooth. Large ash agglomerates are clearly seen. The effect that such an ash agglomerate might have on reactant access to the interior of the particle is unknown. However, 5-8µm diameter pore mouths, beyond the ash, are seen in Figure 5.10. It seems plausible that the ash particle grows by physical agglomeration as the carbon surface recesses with combustion, thus bringing together the smaller ash particles. The ash itself appears fairly loosely bound and there is no evidence of ash melting. Figure 5.11 shows another particle converted to 17.4% at 1475K. From this picture it seems that there is hardly any change from the unburned material, but the morphology on the blind side is hard to guess. A closer look at the particle (Figure 5.12) shows that loose physical agglomeration of ash has taken place like in Figure 5.10. Yet another particle converted to 17.4% is shown in Figure 5.13. Although not much ash is visible, the hollow nature of the particle is striking. Clearly, in such a particle, there is little difference between the external and internal surfaces as far as reactant access is concerned. The pores in the interior surface are also visible.

Figures 5.14 and 5.15 show two particles, from the 45-53µm size fraction burned to 46.6% conversion at a preheater wall temperature of 1475K. The presence of large voids in the particle is obvious. Ash also appears in forms similar to those in the
larger particles. In general, the smaller particles are not as rounded as the bigger ones. They also have more ash. The ash bridge on the particle in figure 5.14 is an interesting feature.

The ash in the char may catalyze combustion (Walker and Nichols, 1957) and/or limit access of oxygen to the particle surface. The catalytic effects of ash are expected to be more important at lower temperatures than at higher temperatures. However, the physical effects of ash are important at higher conversions at all temperatures. It appears from examination of the micrographs that much of the ash remains associated with the particle. While some ash may be lost due to fragmentation or attrition, this is probably of minor importance at these conversions as indicated by the absence of separate ash fragments on the filter.

5.4.3 Surface Area Measurement

Adsorption isotherms on all samples were obtained using nitrogen at 77K as the adsorptive gas. The Brunauer-Emmett-Taylor (BET) theory (Brunauer et al., 1938) was then used to infer specific surface areas of unburned and partially oxidized samples from these isotherms. The procedure and details are described later (Appendix III).

Although most of the pore volume in these porous chars is present in the macro and larger transition pores, it is well known that the micropores account for most of the surface area. The areas normalized per unit total mass are shown in Table 5.3. Since the weight percent ash is also given in the same table, the area per unit carbon mass can also be easily obtained.

In all cases, there is a significant decrease in the area compared to the unburned
material at very low conversions. This can only be attributed to closure of the small pores due to thermal annealing at these high temperatures (Smith, 1972). For the 45-53µm char, the trend with respect to conversion appears to be anomalous. But this is most probably due to an erroneous data point at 5.6% conversion. In the other cases, the surface area, after the initial drop, appears to rise with conversion, reaches a maximum (90-104µm, 1675K wall temperature case) and then decreases again. The final drop is due to pore coalescence at the higher conversions. While the trends are correct, the actual values may not be exact because sample sizes were small in most cases.

5.4.4 Pore Volume Distribution: Capillary Condensation

Pore volume distributions for pores with radii between 20 and 200 Å were obtained from measurement of capillary condensation of nitrogen in the pores of the chars. This corresponds to relative pressures of 0.35 to 0.975 of the isotherms. Since multilayer adsorption occurs over the entire range of pressures, the pore radii and volumes had to be adjusted accordingly. The algorithm given by Yan and Zhang (1986) was used for the calculations. Details of the inversion are given in Appendix III.

Results are given in Figure 5.16 for one case and tabulated in Table 5.3 for all cases. As before, the total volume in this range of pore sizes is appreciably smaller after few percent conversion at high temperatures compared to the unburned material indicating thermal annealing effects in pores of this range. The effect of conversion is best illustrated by Figure 5.16. The pore volume distributions shown are for the 90-104µm parent material converted at 1675K wall temperature. There
is very little decrease of the volume with conversion and no shift of the distribution at all. This shows that pores of this size do not participate in combustion because of diffusion limitations. The figure also shows that the char has very few pores with radii in the range 30-50Å radius. However, minor growth of the smaller pores creates some pores of this size at the higher conversions.

5.4.5 Pore Volume Distribution: Mercury Porosimetry

Mercury porosimetry experiments were performed on an Autoscan-33 porosimeter capable of applying pressures up to 33000 psig. This means that the smallest pores that can be detected are around 32Å in radius. The raw data were in the form of cumulative volume versus applied pressure. Although both intrusion and extrusion curves can be interpreted to derive pore sizes, the intrusion branch was used in our experiments. The many problems of data interpretation including hysteresis and pore geometry are discussed by Lowell and Shields (1979). The pore radius penetrated at a given pressure is calculated from the Washburn equation:

\[
\tau_p = \frac{2\gamma \cos \theta}{P}
\]  

(5.5)

where \( \tau_p \) is the pore radius, \( \gamma \) is the surface tension of mercury normally taken to be 480 ergs/cm², \( \theta \) is the angle of contact between mercury and the char, and \( P \) is the applied pressure. The contact angle is conventionally assumed to be 140°. This equation assumes that the pores are cylindrical in shape. Thus, while the results may not have any intrinsic value in describing the present char which is cenospheric, their value as a comparative tool is well accepted. Figure 5.17 shows an example of the raw data derived from a porosimetry run. The abscissa is the volume
in cubic centimeters and the ordinate is the pressure in psig. The intrusion and
eextrusion curves are both shown. The former is shown in two parts, the scale being
expanded at lower pressures for better accuracy in that range. This cumulative
curve (intrusion branch) was numerically differentiated to give the pore volume
distribution shown in Figure 5.18 for the 90-104µm size fraction of the unburned
material. A dead volume correction was applied before the numerical differentiation.

The distribution for the unburned material shows that there is significant tran-
sition porosity (200-1000Å radius) as well as macroporosity in this char. Pores
larger than 1.76µm in radius are penetrated at pressures below 60 psig and are
assumed to be interparticle spaces rather than internal porosity. Of course, it is not
possible to rule out the presence of cracks and voids of these sizes or even larger
ones within particles. Indeed electron micrographs do show the presence of voids of
this size in the particles. Thus, at these low pressures it is impossible to resolve the
controversy regarding the relative contributions of the inter and intraparticle voids
to the total voidage, particularly in a material that has large voids.

Figure 5.19 shows the pore volume distribution of the 90-104µm parent char
after 65.9% conversion at 1675K preheater wall temperature. Comparing with figure
5.18, it is clear that there is less transitional porosity in the burned char. This
indicates that these pores are accessible to oxygen at these temperatures. There is
some resulting increase in the macroporosity. Table 5.3 shows the pore volumes in
the ranges 32-500Å and 500-17600Å. 32Å is normally taken as the micro-transitional
boundary and 500Å is the transitional-macropore boundary in the literature. Due
to sample size limitations, porosimetry was done on samples having the highest
conversion in each group. In the 1675K 90-104µm group we see that while the transitional pore volume decreases, the macroporosity increases showing oxygen accessibility in the transitional range. The same trend is observed in the sample with big particles burned at 1475K wall temperature.

5.4.6 Conclusions from High Temperature Combustion

This section will summarize the observations from all the characterization experiments described earlier. Although there is a noticeable decrease in the particle size with conversion at high temperatures indicating the possibility of diffusion-limited combustion, this decrease by itself is insufficient to account for the total carbon loss. Thus there is internal burning in these char particles which is not surprising considering that there are macropores as large as 8µm in diameter visible on the char surface. These obviously act as feeder pores allowing oxygen to penetrate into the particle. The only question that remains to be answered is the extent of the oxygen penetration.

Capillary condensation and mercury porosimetry together indicate quite clearly that while pores above 200Å in radius do grow during combustion, those smaller than this size remain unaffected. Thus pores below 200Å are diffusion limited. This is also indirectly seen from the small values of surface area present in the samples. Since most of the surface area is in the micropores below 200Å in radius, it is clearly not accessible. One cause of the lack of penetration into pores of this size may be that their pore mouths are closed by some thermal annealing mechanism as the particle is heated to these temperatures. That thermal annealing occurs is indicated in the drop in the surface area value compared to that of the unburned
material.

The presence of ash on the surface of the burned materials is quite evident from the electron micrographs. The ash appears to be present as loosely bound globules of very small size that are drawn together as the carbon surface below them recedes. There is no evidence to show ash melting at the temperatures used.

5.5 Comparison of High and Low Temperature Combustion

Table 5.4 shows data on chars burned to various conversions at 500°C. There are two major sets of data corresponding to the 104-125µm and 90-104µm size fractions. Porosimetry experiments were done on the bigger samples for reasons of greater sample availability. However, since the sizes are similar, the results should also be indicative of the 90-104µm size fraction.

The main difference between high and low temperature combustion is seen in the surface area values. Table 5.4 and Figure 5.20 show the change of the surface area with conversion at 500°C. The areas at the lower temperature are at least an order of magnitude larger than those from the high temperature experiments. This indicates that most or all of the micropores are accessible at low temperatures and that diffusion is not a factor. Thus combustion takes place in the kinetic limited regime. Figure 5.20 shows the surface area normalized with total and carbon masses. The rapid initial rise in the surface area is due to the opening of the pore mouths. Thereafter, the rise is smaller, reaching a maximum at some carbon conversion and finally the area decreases due to pore coalescence.

Pore volume distributions from capillary condensation are shown in Figure 5.21. This shows that the volume in this range increases with conversion and drops
slightly at the last point. This reinforces the conclusion that even these small pores are accessible to oxygen, unlike burning during high temperatures (Figure 5.16).

The pore volume data from porosimetry on the 104-125µm samples show that pore volumes in all size ranges increase with conversion. The pore volume distribution of a char converted to 70.6% at 500°C is shown in Figure 5.22. Comparing with the pore volumes of the unburned material (Figure 5.18) and that burned at 1675K wall temperature (Figure 5.19) to a similar conversion we see that although the total volume is not very different, there is little volume in the small pores (indicating their growth) and somewhat more porosity in the larger pores and cracks. Figure 5.23 is a plot of the pore volumes versus conversion at low temperature.

Thus the major difference between the combustion of the char at low and high temperatures is the absence of diffusion limitations in the micropores and their resulting accessibility to the oxidizer at lower temperatures. There is also no evidence of thermal annealing at the low temperature.
References

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Table 5.1 Properties of raw coal.
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Table 5.2 Particle temperature measurements.
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Table 5.3 Characterization of PSOC 1451 1600K chars burned at high temperatures.
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Chapter 6

IGNITION TRANSIENTS IN THE COMBUSTION
OF SINGLE CHAR PARTICLES

Submitted to Fuel
Abstract

The temperature-time history of single char particles burning at temperatures above 1500 K have been measured by two-color near infrared pyrometry techniques. Two coal chars and a synthetic char consisting of spherical glassy carbon particles of uniform size were used in the experiments. The results indicate that in the regime of lean combustion and low-to-medium temperatures, the char particles do not ignite over their whole external surface, but exhibit preferential ignition at specific sites. These hot-spots probably involve regions where the material exhibits strong inhomogeneities, either on or below the surface. Following ignition, the reaction may propagate over the particle surface. At elevated combustor temperatures and/or high oxygen partial pressures, ignition spreads quickly over the entire particle surface and the importance of the hot-spots diminishes. A simple model is used to estimate the rate of growth of a hot-spot under various experimental conditions.
6.1 Introduction

The structural complexity of coal is well-documented. The organic components have been mixed with sedimentary strata, compacted, variably subjected to decay and chemically altered by geological processes. In addition to the organic components, the coal microstructure incorporates small and large pores and a plethora of minerals. The particles produced during the grinding process have irregular shapes, and contain cracks and loosely bound material on the surface. Because of this variable surface morphology and the physical and chemical inhomogeneities, there is no reason to expect the particles to ignite and burn uniformly over their surface. In the customary mathematical analysis of char combustion the particles are assumed to have spherical shape and spatially uniform properties, density, pore structure etc. Real particles of course, have irregular shapes and gross spatial inhomogeneities ( pores, cracks, minerals) but these irregularities cannot be described mathematically in any reasonable fashion. Nevertheless it is quite clear that these irregularities in char particles cause significant particle-to-particle variations in particle temperature and burnout time. Variations in ignition behavior due to these irregularities can also be expected.

Efforts to understand the ignition mechanism of coal particles date back to Semenov. Thereafter studies on the ignition of clouds of particles and packed beds of particles have been conducted but studies concerning the ignition behavior of single particles are rare. Ignition of coal particles has been assumed to be either homogeneous where emitted volatiles ignite first or heterogeneous where ignition occurs at the particle surface. Recent studies on ignition of single coal particles
suggest that ignition switches from being homogeneous to heterogeneous as the reactor temperature increases. The ignition of char particles is heterogeneous, in view of the absence of volatiles. Ignition occurs with\textsuperscript{9} or without\textsuperscript{10} a temperature jump and the measured ignition temperature has been observed to increase with decreasing particle size.\textsuperscript{9}

Previous modelling work has utilized steady or unsteady energy balances assuming that the particle ignites uniformly over its surface.\textsuperscript{9–12} In this paper we shall present experimental observations that suggest that ignition does not occur uniformly over the particle surface but, rather, occurs in small localized regions. Reaction fronts then propagate over the particle surface. A theoretical description of a reaction front propagation is developed.

\textbf{6.2 Experimental}

The coal chars used in the combustion experiments were derived from the two high volatile bituminous coals, listed in Table 6.1, by devolatilization at 1600 K, for 2 s, and in nitrogen. Experiments were also conducted with glassy carbon chars for comparison purposes. These glassy carbons were synthesized from polymer materials\textsuperscript{13} in the form of mineral-free, homogeneous, uniformly sized spheres. The char particles were sized by sieving, with the aid of a mechanical shaker. The size and surface morphology of the particles were examined by optical and scanning electron microscopy (SEM). Physical properties and chemical composition of the particles were measured as described elsewhere.\textsuperscript{13,14}

Both coal pyrolysis and char combustion were performed in an externally heated, laminar flow, drop-tube furnace capable of reaching centerline temperatures
of 1600 K. Pyrolysis was performed in a stream of pure nitrogen and combustion in O₂-N₂ mixtures at oxygen partial pressures varying between 0.21 (air) and 1.0 atm. Particle temperatures were monitored with a two-color pyrometer, with broadband filters centered in the near-infrared at 800 and 1000 nm, respectively, and employing silicon photocell detectors. Details of the combustion apparatus and the pyrometer are given elsewhere.¹³ For the present experiments, only one particle at a time was introduced into the combustion chamber making it possible to record the two-color radiation intensity traces throughout the combustion life of a single particle. Employing a Planck-law analysis, temperature-time profiles were derived from the ratio of the two intensity signals.

6.3 Results and Discussion

Typical intensity-time traces and the corresponding calculated temperatures for the two coal chars are shown in Figures 6.1-6.3. The combustion atmosphere and wall temperatures were as indicated in the figures while the gas temperature was 1100 K for all cases. Since the oxidation took place at furnace temperatures (centerline and wall) lower than the temperatures used for the pyrolysis process, no devolatilization is anticipated during the char combustion experiments. In Figure 6.1, the particle temperature is approximately constant throughout combustion, but the emission intensities rise through a large fraction of the burn time (region 1) and then decrease throughout the remaining time (region 2). The behavior in region 2 can be attributed to the decreasing particle cross section as the char particle shrinks during the final stages of combustion. In short, the increase in intensity in region 2 is a purely geometrical effect.
The behavior in region 1, where the intensity increases while the temperature remains approximately constant is more difficult to explain. We first ascertained that this behavior is not an artifact generated by the pyrometer electronics. This possibility can be eliminated by the following observations: (a) The silicon photocell detectors used, Hamamatsu S1356-5GQ, are very fast, having a nominal rise time of 0.2 $\mu$s, and exhibit a linear response. (b) The 'slew' rate of the amplifiers is very fast, 2 V/$\mu$s. (c) The response of the two channels of the pyrometer was verified to be the same, by swapping the filters. (d) Radiation intensity traces obtained by Sarofim and coworkers$^{16,17}$ exhibit similar behavior, even though a totally different system was used for data acquisition. The pyrometer used in their work employed photomultiplier tubes (PMT) that exhibited a rise time of 15 ns. (e) The peak occurred at different times for different particles and, moreover, a late peak occurred only for particles burning in air, in contrast to particles burning at high $O_2$ partial pressures, where the intensity rise is almost instantaneous. Thus, it can be safely concluded that the intensity increase must be a characteristic of the combustion behavior of the chars.

It is proposed that the gradual increase in intensity at constant temperature is caused by the spread of the reacting region from one or more localized ignition sites at the particle surface. The intensity of the radiation that is received by the detectors depends on three parameters: (i) the luminosity of the light source that is directly related to its temperature; (ii) the size of the light source, and (iii) the distance between the source and the detector. The distance did not vary significantly in our experiments since, at the furnace flowrates used, a particle travels at most 2 to
4 mm during its burntime (velocity \( \approx 10^{-1} \) mm/ms), which is much smaller than the distance between the particle and the detector (\( \approx 300 \) mm). Hence, the detectors see a particle that is almost stationary during its entire combustion history. Further, if distance were responsible for the intensity variation at constant temperature, the intensity traces would monotonically decrease, since the particles travel away from the detector. Such behavior was not observed for any particles. The second parameter, luminosity at some fixed wavelength, is a function of temperature via the temperature dependence of Planck's law and by the temperature dependence of the emissivity. However, if the temperature of the particle remains constant, as observed, the luminosity of the particle should also remain constant. Therefore, the recorded intensity variations must be due to variations in the radiating area of the particle projected in the direction of the detector. The increase in the radiating area could be attributed to either an increase in the total area, radiating uniformly, or an increase of the radiating fraction of a roughly constant physical area. In view of prior devolatilization, the total area could not increase by swelling. Therefore, the area of the particle that is radiating increases with time in region (1). It is proposed that a few reactive regions on the char surface ignite first, and thereafter combustion fronts propagate over the rest of the particle. Thus, the radiating area of the particle can increase without an associated increase in temperature, if the ignited regions or hot-spots have roughly the same temperature. Progressive ignition on the particle surface has also been observed by photographic techniques.\(^{17}\)

The higher reactivity in localized regions on the particle surface could result from a number of causes. One possibility is local mineral concentrations that cat-
alyze and accelerate reaction. Previous investigations\textsuperscript{18} have shown that the reactivity is greatly enhanced in the presence of impurities, particularly magnesium and calcium. Reactive spots could also be due to localized macro- and transitional pores that serve as feeders to the micropores and enhance reactivity. In Figure 6.4a the scanning electron micrograph of a char particle reveals an irregular particle shape, various surface cavities, and large pores and protrusions that usually appear (by the degree of darkness in BSE-SEM) to be rich in ash and could contribute to localized ignition.

Whatever the cause of the localized ignition, particles of the same char would be expected to become fully ignited more rapidly in oxygen-enriched atmospheres than at lower oxygen levels because the combined effect of the oxygen availability and the resulting higher temperatures accelerate the reaction. Hence, the observed delay times, i.e., the duration of region (1), should be short. This is seen by comparing Figures 6.1-6.3. Clearly, the rate of intensity increase in region (1) increases with oxygen level. The short delay observed in the high O\textsubscript{2} level experiments was usually associated with the period of increasing temperature. Ignition in pure oxygen was almost instantaneous.

Combustion of spherical synthetic char particles such as that shown in Figure 6.4b provides a sharp contrast to coal char combustion. These particles are highly uniform and are mineral-free, hence catalytic effects are minimal. These particles are not expected to have important reactive sites. Instead of undergoing localized ignition, such a particle may be uniformly heated close to the ignition temperature before rapid reaction begins. Once ignited, the particle would rapidly be engulfed
in flame. This was confirmed in the experiments whenever it occurred. Combustion of the synthetic chars, proceeded rapidly. Any delay in reaching peak intensities was associated with rising temperatures. The temperature and intensity profiles for combustion of a typical synthetic char particle is shown in Figure 6.5.

Some coal char particles exhibited another interesting phenomenon that is shown in Figure 6.6. The intensities undergo roughly periodic fluctuations. In Figure 6.6a, the intensity in each channel fluctuates periodically for three complete cycles while following an overall decreasing trend. The temperature of the particle is almost constant over that period of time. We attribute these oscillations to the tumbling motion of the particle that changes the projected burning area that is viewed by the detector. Another set of measurements is shown in Figure 6.6b. In this case the periodically varying signal is superimposed on an increasing trend suggesting that tumbling is taking place while hot-spots are growing.

Pyrometry traces were also obtained for a lignite char. These are not shown here but they exhibit similar ignition delay times as those observed for the chars of the two bituminous coals. Similar pyrometry results on lignite have also been obtained by others.\textsuperscript{15,16}

6.4 Analysis of the Growth of a Hot Spot

In this section we examine the growth of a single local ignited region in an attempt to explain the gradual intensity rise while the particle temperature remains constant. We postulate that a hot, burning region propagates on the comparatively cooler particle surface without delving into the reasons of how such a region was ignited in the first place. The burning region, assumed circular and locally two-dimensional
(Figure 6.7), dissipates heat to the surroundings and the rest of the particle while spreading on the surface at the same time. Using a quasi-one-dimensional analysis and thermal balance arguments, we calculate the growth of the burning region and determine the time required for the ignited region to engulf a hemisphere of the entire particle. This time turns out to be larger than the experimental ignition delay time indicating that ignition involves several rather than one spot on the particle surface.

Assuming the burning region to be a spherical sector, its area $A_s$ is given as:

$$A_s = 2\pi r_p^2 \left( 1 - \sqrt{1 - (r/r_p)^2} \right) \quad (6.1)$$

where $r$ and $r_p$ are the radii of the burning region and the particle, respectively. The area of a differential element is then given by:

$$dA_s = 2\pi r \frac{r_p}{\sqrt{r_p^2 - r^2}} \, dr \quad (6.2)$$

The growth of the burning region is controlled by the balance between heat generation and heat dissipation:

$$\tilde{d} \sigma_a c_p (T_s - T_p) \frac{dA_s}{dt} = Q_G - Q_D \quad (6.3)$$

where $Q_G$ and $Q_D$ are the heat generation and dissipation terms, respectively, $c_p$ the heat capacity and $\sigma_a$ the apparent density. The thickness, $\tilde{d}$, and the temperature, $T_s$, of the burning region are assumed to be constant. The temperature $T_s$ is taken equal to the temperature measured by pyrometry. The thickness, $\tilde{d}$, is estimated by the procedure followed in reaction-diffusion problems in the limit of large Thiele modulus. It is given by:

$$\tilde{d} = \frac{r_p}{\phi} \quad (6.4)$$
where $r_p$ is the particle radius and $\phi$ is the Thiele modulus of the particle given as:

$$\phi = \frac{r_p}{3} \left[ A_T \sigma_a R_i C_*^{m-1} D_e^{-1} \right]^{1/2} \quad (6.5)$$

$A_T$ is the pore surface area per unit mass, averaged over the course of combustion, obtained from BET measurements or other equivalent techniques; $\sigma_a$ is the apparent density of the solid; $R_i$ is the intrinsic reaction rate coefficient; $C_*$ is the oxygen concentration at the particle surface; $m$ is the true reaction order, taken as unity in the present calculations, and $D_e$ is the effective diffusivity in the porous particle. Thus the value of $\phi$ can be estimated using information about the porous structure of the particle and measured combustion rates.

The heat generated by the burning region can be expressed as:

$$Q_G = A_i \exp(-E_i/RT_*) C_* A_T \tilde{d} A_\sigma \sigma_a \Delta H \quad (6.6)$$

where $E_i$ is the activation energy of the reaction, $A_i$ is the pre-exponential factor, and $C_*$ is the oxygen concentration at the particle surface. $\Delta H$ is the heat of combustion at temperature $T_*$ assuming that the heterogeneous reaction at the surface produces CO exclusively.

Heat dissipation consists of three contributions: conduction into the core of the particle, convection to the surrounding gas, and radiation to the furnace walls.

The convection to the ambient gas can be calculated from:

$$k_{gas} \frac{T_s - T_{gas}}{r_p} A_s \quad (6.7)$$

where $k_{gas}$ is the thermal conductivity of the gas at the film temperature. This assumes that the Nusselt number is 2, since the Reynolds number, based on the
slip velocity between the particle and the gas is very small. The radiation to the furnace enclosure is:

\[ \sigma (\varepsilon_s T_s^4 - T_w^4) A_s \]  

where \( \sigma \) is the Stefan-Boltzmann constant and \( \varepsilon_s \) and \( \varepsilon_w \) are the emissivities of the hot-spot and the wall respectively.

Conduction from the surface layer to the interior of the particle is a complicated unsteady two-dimensional problem coupled with the overall propagation problem. For the purpose of this analysis we assume that heat conduction occurs only perpendicular to the surface in an unsteady fashion. The heat flux from an element of the burning region is then given by:

\[ \frac{k_c (T_s - T_p)}{\sqrt{\alpha_{eff}(t - \hat{t})}} \]  

where \( k_c \), \( \alpha_{eff} \) are the thermal conductivity and the effective thermal diffusivity of the particle core, \( t \) is the current time, and \( \hat{t} \) is the time at which burning first reached the surface element in question. The conduction heat flux over the entire burning region is then given by:

\[ (T_s - T_p) \int_0^r \frac{k_c d\hat{A}_s}{\sqrt{\alpha_{eff}(t - \hat{t})}} \]  

where now \( \hat{A}_s \) is the area of the burning region at time \( \hat{t} \) and \( r \) is the radius at time \( t \).

Combining Eqs. (6.3),(6.6)-(6.8) and (6.10) we obtain the heat balance equation for the burning region:

\[ A_i \exp(-E_i/RT_s) C_s A_T \tilde{d}A_s \sigma_a \Delta H = \sigma_a d c_p (T_s - T_p) \frac{dA_s}{dt} + \frac{k_{gas}}{\tau_p} (T_s - T_{gas}) A_s + \sigma (\varepsilon_s T_s^4 - T_w^4) A_s + \frac{k_c (T_s - T_p)}{\sqrt{\alpha_{eff}}} \int_0^r \frac{d\hat{A}_s}{\sqrt{t - \hat{t}}} \]  

(6.11)
In equation (6.11), the time $t$ for the front to propagate to radius $r$ is given by

$$t = \int_0^r \frac{d\tilde{r}}{S(\tilde{r})}$$

(6.12)

where $S(r) = \frac{dr}{dt}$ is the velocity of propagation of the burning region. Similarly $t_f$ is given by Eq. (6.12), replacing $r$ in the upper limit of the integral with $\tilde{r}$. Thus Eq. (6.11) is an integro-differential equation in $r(t)$ which must be solved numerically. Once $r(t)$ has been computed, the total time taken by the burning region to cover the hemispherical surface of the particle (visible to the detector) can be found as that value of $t$ for which $r(t) = r_p$. This time, which will be denoted as $t_b$, should be the upper bound of the experimentally observed delay time, $t_D$, that elapses before the peak in the pyrometer signals occurs. For the present calculations the temperature of the burning region was taken equal to the temperature deduced from the pyrometer traces, assumed constant, and the temperature of the rest of the particle was assumed equal to the combustor wall temperature. The total surface area of the layer was deduced from BET area measurements on partially combusted samples, assuming that the burning region had the same average surface per unit mass as that of the char after partial burning. Details of the variation of total surface area with burnout are not included in the present analysis but are given elsewhere. The effective conductivity was estimated using the correlation of Butt, while the heat capacity by a relationship given by Kelley. The intrinsic kinetics used were determined for the present chars from other experiments employing the same experimental setup and analyzing the results using the capillary model of Gavalas to describe the evolution of pores. For the PSOC-1451 1600 K char the activation energy, $E_i$, was estimated to be 34000 cal/mole and the pre-exponential factor $A_i$.
was $8.6 \times 10^5$ cm/s. Smith's kinetics$^{24} (E_i = 42800 \text{ cal/mole} \text{ and } A_i = 1.46 \times 10^6 \text{ cm/s})$ give similar values.

Figure 6.8 shows the calculated variation of $t_b$ with oxygen partial pressure. The predicted ignition transient times are higher by a factor of almost five compared to those observed experimentally. For the case of the particle shown in Figure 6.1, the experimentally observed delay time is 12 ms while the theoretically determined delay time (corresponding to an oxygen partial pressure of 0.12) is around 60 ms. This suggests that there are more than one such spots propagating over the particle surface. As expected, $t_b$ decreases with increasing oxygen partial pressure and with decreasing particle size.

The speed of propagation of the spot increases rapidly as the radius expands, reaches a maximum and falls off as the particle radius is reached. This is shown in Figure 6.9. If several hot-spots are growing simultaneously as suggested by the experimental ignition delay times then only the first part of the speed versus radius curve is physically significant. The values assumed for the emissivities of both the particle and the wall had negligible effects in the calculation, indicating the minor importance of the radiation heat loss in the cases examined. Likewise, the apparent particle density does not seem to be an important factor. Finally, $t_b$ is inversely proportional to the pore surface area of the char.

6.5 Conclusions

The ignition behavior of coal chars at various oxygen partial pressures and combustion chamber temperatures has been observed by means of near-infrared optical pyrometry techniques. It has been concluded that at mild combustion conditions
(combustor temperatures around/or below 1300 K and oxygen partial pressures at/or below 0.21), the char particles undergo preferential ignition at localized reactive sites leading to the development of hot-spots. The reaction zones take a finite time to engulf and ignite the whole particle. These reactive sites can be due to of mineral matter catalysis, enhanced porosity or favorable surface morphology. At elevated combustor temperatures and/or high O₂ concentrations the ignition proceeds almost instantaneously because of temperature-dependent kinetics. An energy balance was used to estimate the time required for the spreading of a local hot spot. Comparison of the estimated times and measured ignition times suggest that several spots are spreading over the particle surface simultaneously.

6.6 Acknowledgements

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References


### Notation

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Table 6.1 Properties of parent coals.

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</tbody>
</table>
Figure 6.1 Intensity signals and particle temperature profiles of a PSOC-1451 100µm coal char particle burning at a combustor wall temperature of 1300 K and $p_{O_2} = 0.21$. 

0.25

0.20

0.15

0.10

0.05

0.00

0.20

0.15

0.10

0.05

0.00

0

5

10

15

20

25

30

TIME (m sec.)

0

1000

2000

3000

4000

TEMPERATURE (K)

INTENSITY (VOLTS)
Figure 6.2 Intensity signals and particle temperature profiles of a PSOC-176 50µm coal char particle burning at a combustor wall temperature of 1300 K and $p_{O_2} = 0.50$. 
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Figure 6.6b Intensity signals and particle temperature profiles of a PSOC-1451 100μm coal char particle burning at a combustor wall temperature of 1300 K and $p_{O_2} = 0.21$. Particle exhibits tumbling behavior.
Figure 6.7 Schematic representation of the hot spot assumed in the model.
Figure 6.8 Results of the mathematical modelling: the effect of oxygen partial pressure on the flame spreading delay time $t_b$. 
Figure 6.9 Results of the mathematical modelling: velocity of propagation of the burning region as a function of its radius.
Chapter 7

CONTINUUM MODELLING
7.1 Introduction

This chapter will describe, in detail, the models that were developed to describe char particle combustion. All the models assume that the particle is spherical and has internal spherical symmetry. The internal morphology is assumed to be a continuum of fine pores, thereby allowing diffusion and reaction inside the particle to be described by differential equations. Models that consider larger discrete pores are described in the next Chapter.

Most of the attention has been focussed on the changes in the internal solid structure of the particle and its effect on combustion variables. Reasonable assumptions were made regarding the description of the solid morphology. Pore structure parameters were estimated from gas adsorption and mercury porosimetry data. Thermodynamic and transport properties were assumed to be functions of temperature within the particle and in the gas phase. The reactions in the gas phase were not considered.

The simplest model which assumes that all the reaction occurs at the particle surface and none inside is described in detail in the next section. While this may seem too restrictive at first, it is applicable to many situations of combustion at high temperatures and high oxygen concentrations since, in these situations, there is very little penetration of oxygen into the particle as will be shown later. The computational burden is light, and the model can describe fairly accurately the proper temperature-time histories observed in the experiments.

Section 7.3 describes the general model involving a simplistic internal geometry which is later extended in Section 7.4 to more realistic internal morphologies. The
diffusion equation inside the particle is solved to accurately predict the internal oxygen concentration profiles which then determine the carbon flux, void fraction, specific surface area, etc.

The influence of nonlinear reaction kinetics such as the Langmuir-Hinschelwood and Power law are discussed briefly in the last section.

The effects of parametric variations are discussed in detail in all cases. Limitations and applicability of the various models are stated as necessary.

Computer code listings for all the major programs are given in Appendix IX. The programs were written in standard Fortran 77 and the actual simulations were done on IBM and compatible personal computers.

7.2 Asymptotic Model with Lumped Surface Reaction

The simplest model of char combustion considered is a homogenous particle that reacts only at its exterior surface. The solid particle is assumed to be spherical and to contain internal voids and ash particles distributed uniformly throughout its entire volume. Details of the internal morphology, such as pore volume distribution and ash size and distribution, are not important in this model since the reaction is assumed to occur only at the particle surface. However, the presence of the voids changes the particle density. Let the volume fraction of the voids and ash in the particle be $\epsilon$ and $\epsilon_A$ respectively. Assuming that the densities of carbon and ash are $\rho_C$ and $\rho_A$, a mass balance gives,

$$\rho_a = \epsilon_A (\rho_A - \rho_C) + \rho_C (1 - \epsilon)$$

(7.1)

where $\rho_a$ is the apparent density of the particle.
The reaction at the particle surface is assumed to be the heterogenous reaction, 
\[ 2C + O_2 \rightarrow 2CO \] since it has been shown that, at high temperatures, the heterogenous reaction leading to \( CO_2 \) formation is not as important (Mitchell, 1986). Also, the reaction of carbon with water vapor has been neglected since the amounts of water vapor in the experimental systems used in this study were negligible.

Once the carbon monoxide is formed, it is assumed to oxidize in the gas phase, far from the particle. Thus, in this model details of the gas phase combustion are not considered. The gas phase is also assumed to be quasi-steady with respect to solid phase combustion.

The particle is also assumed to be isothermal. The reaction rate used in this model is based on the external area of the particle, i.e. it is the apparent rate. All thermodynamic and transport properties are assumed to be temperature dependent. This is a significant improvement over models that assume constant or average property values over wide ranges of temperature variation.

Assumptions regarding the effects of ash on combustion are based on experimental observations from electron microscopy as discussed in Chapter 5. As the carbon is oxidized, the ash particles are exposed at, then accumulate on the surface. The thickness of the ash layer increases as combustion proceeds, and it is assumed that none of the ash is lost. This porous ash layer presents a diffusional resistance to the oxygen transport in series with the gas phase diffusional resistance. The presence of ash also manifests itself in the energy balance of the particle, increasing its thermal inertia and altering its radiative properties. A detailed study of the radiative properties of the combined carbon-ash layer has not been undertaken.
Instead, an overall emissivity of the particle is used.

In an early version of the model, the effect of ash was accounted for differently. Instead of forming a porous layer on the particle, patches of ash were assumed to cover parts of the surface of the carbon. Reaction was allowed to take place only on those parts not blocked by the ash. The fraction of surface blocked was equal to the ash mass fraction in the particle. The computer code for this model is also given in Appendix IX.

7.2.1 Equations

The particle mass balance can be written in terms of the apparent reaction rate as:

\[ \frac{dm_C}{dt} = -A_a e^{-E_a/RT_p} Y_{1*} 4\pi r^2 \]  \hspace{1cm} (7.2)

where \( m_C \) is the mass of carbon, \( A_a \) and \( E_a \) are the apparent Arrhenius reaction rate parameters, \( R \) is the universal gas constant, \( Y_{1*} \) is the mass fraction of oxygen at the carbon surface, \( r \) is radius of the carbon sphere (Figure 7.1), and \( T_p \) is the particle temperature. The negative sign implies that mass decreases with time.

The reaction kinetics are assumed to be first order with respect to surface oxygen concentration. The value of \( Y_{1*} \) is determined as follows: at first the oxygen mass fraction outside the ash layer, \( Y_{1p} \), is determined and then by properly accounting for diffusion in the ash layer, we get \( Y_{1*} \).

The particle energy balance can be written as:

\[ \frac{d}{dt} \left( m_C H_C + m_A H_A \right) = \text{Energy Generation Rate} - \text{Energy Loss Rate} \]  \hspace{1cm} (7.3)

where \( m \) and \( H \) are the mass and enthalpy, respectively. The subscripts \( C \) and \( A \)
denote carbon and ash. The energy generation rate is given by

\[- \frac{dm_C}{dt} \Delta H_{\text{comb}}(T_p) \] (7.4)

where \(\Delta H_{\text{comb}}\) is the enthalpy of combustion of the heterogeneous reaction at the particle temperature. The rate of mass loss can be rewritten using the carbon mass flux per unit external area at the particle surface, \(N_p\), as

\[- \frac{dm_C}{dt} = 4\pi r_p^2 N_p \] (7.5)

The energy generation term can be written in terms of the enthalpies and the mass fluxes of the gas phase components \((O_2=1; CO=2; N_2=3)\) as

\[-4\pi r_p^2 \sum_{i=1}^{3} N_i H_i \bigg|_{r=r_p} \] (7.6)

In equation (7.6), \(N_i\) and \(H_i\) are, respectively, the mass flux away from the particle and specific enthalpy of the gas phase component \(i\). From stoichiometry we have

\[N_{1p} = -\frac{4}{3} N_p, \quad N_{2p} = \frac{7}{3} N_p, \quad N_{3p} = 0 \] (7.7)

There are two heat loss terms accounting for conduction and radiation. The heat loss by conduction is given by

\[\epsilon_{\text{cond}} = -4\pi r_p^2 k \frac{dT}{dr} \bigg|_{r=r_p} \] (7.8)

where \(k\) is the thermal conductivity of the gas phase. The heat loss due to radiation from the particle to its surroundings is given by

\[\epsilon_{\text{rad}} = 4\pi r_p^2 \sigma \left\{ \epsilon_o T_p^4 - \epsilon_\infty T_\infty^4 \right\} \] (7.9)
where \( \sigma \) is the Stefan-Boltzmann constant of radiation, \( \varepsilon_0 \) is the emissivity of the particle, \( \varepsilon_\infty \) is the emissivity of the wall or radiating environment far from the particle, and \( T_\infty \) is the temperature of the wall. The unsteady term on the left hand side of equation (7.3) can be expanded using the chain rule. Also the enthalpy \( H \) of either carbon or the ash can be written as

\[
H = H_0 + \int_{T_0}^{T_p} c_p dT
\]

(7.10)

where \( H_0 \) is the enthalpy at some reference temperature \( T_0 \). Using the chain rule, equation (7.10) and equation (7.5), the unsteady term in equation (7.3) becomes

\[
(m_C c_{pC} + m_A c_{pA}) \frac{dT_p}{dt} = 4\pi r_p^2 N_p H_C
\]

(7.11)

Therefore combining equations (7.11), (7.6), (7.8) and (7.9), the particle energy balance becomes

\[
(m_C c_{pC} + m_a c_{pa}) \frac{dT_p}{dt} = 4\pi r_p^2 \left[ N_p H_C - \sum_{i=1}^{3} N_i H_i \right]_{r=r_p} \]

\[
+ k \frac{dT}{dr} \bigg|_{r=r_p} - \sigma \{ \varepsilon_0 T_p^4 - \varepsilon_\infty T_\infty^4 \}
\]

(7.12)

Defining

\[
\varepsilon_p = \left[ -k \frac{dT}{dr} + \sum_{i=3}^{3} N_i H_i \right]_{r=r_p}
\]

(7.13)

and

\[
\gamma_p = \frac{\varepsilon_p}{N_p}
\]

(7.14)

the energy balance becomes

\[
(m_C c_{pC} + m_A c_{pA}) \frac{dT_p}{dt} = 4\pi r_p^2 \left[ N_p H_C - N_p \gamma_p - \sigma \{ \varepsilon_0 T_p^4 - \varepsilon_\infty T_\infty^4 \} \right]
\]

(7.15)
Transport in the gas phase is described by the Stefan-Maxwell equations:

\[
\frac{dY_i}{dr} = \sum_j \frac{(Y_i N_j - Y_j N_i)}{\rho_g D_{ij}}
\]  

(7.16)

where \( Y_i \) is the mass fraction of species \( i \), \( N_i \) is the mass flux of \( i \), \( \rho_g \) is the density of gas and \( D_{ij} \) is the diffusivity of component \( i \) in component \( j \). Here, in our 3-component system: species 1 = O\(_2\), 2 = CO, and 3 = N\(_2\). Since these molecules are similar in size, the binary diffusion coefficients \( D_{ij} \) are assumed equal. This simplifies (7.16) to

\[
N_i = -\rho_g D \frac{dY_i}{dr} + NY_i
\]  

(7.17)

where \( N \) is the total mass flux \( \sum_i N_i \) which satisfies

\[
r^2 N = r_p^2 N_p
\]  

(7.18)

where the subscript \( p \) denotes values at the surface of the particle. Loewenberg et al. (1987) have shown that the equations (7.17) for the various species can be combined to give

\[
\frac{d(Y_1/4 + Y_2/7)}{dY_3} = \frac{Y_1/4 + Y_2/7}{Y_3}
\]  

(7.19)

From this, along with boundary conditions at \( r \to \infty \) and the fact that \( \sum_i Y_i = 1 \), \( Y_2 \) and \( Y_3 \) are obtained in terms of \( Y_1 \) as given below:

\[
Y_3 = \frac{3/28Y_1 + 1/7}{1/Y_3\infty(Y_1\infty/4 + Y_2\infty/7) + 1/7}
\]  

(7.20)

\[
Y_2 = 1 - Y_1 - Y_3
\]  

(7.21)

where the subscript \( \infty \) denotes values far from the particle.
The energy balance for the gas phase is:

\[ r^2 \{-k \frac{dT}{dr} + \sum_i N_i H_i\} = r^2_p e_p \] (7.22)

From the stoichiometric relations (7.19) and overall mass balance (7.18),

\[ r^2 k \frac{dT}{dr} = r^2_p \left( \frac{N_p}{3} (h(T) - e_p) \right) \] (7.23)

with \( h(T) = \{7H_2 - 4H_1\}/3 \). The boundary conditions are:

\[ r = r_p : T = T_p; r \to \infty : T \to T_\infty \] (7.24)

Integrating (7.23) gives

\[ r_p N_p = \int_{T_\infty}^{T_p} \frac{kdT}{\gamma_p - h(T)} \] (7.25)

This is an algebraic expression for mass flux at the surface. Combining (7.25) with the mass balance for oxygen (7.23) yields

\[ r^2 \rho_g D \frac{dY_1}{dr} = r^2_p N_p \left\{ Y_1 + \frac{4}{3} \right\} \] (7.26)

Dividing (7.26) by (7.23) gives

\[ \frac{\rho_g D}{k} \frac{dY_1}{dT} = \frac{Y_1 + 4/3}{h(T) - \gamma_p} \] (7.27)

Assuming that the temperature and mass fraction of oxygen far from the particle are \( T_\infty \) and \( Y_{1\infty} \) equation (7.27) can be integrated to yield

\[ \ln \frac{Y_{1\infty} + 4/3}{Y_{1p} + 4/3} = \int_{T_\infty}^{T_p} \frac{kdT}{\rho_g D \{\gamma_p - h(T)\}} \] (7.28)

This is a quadrature for the energy flux at the particle surface. Equations (7.25) and (7.28) were solved numerically to obtain the particle temperature and the oxygen mass fraction at the external surface of the ash layer as a function of time.
Once the oxygen mass fraction outside the ash layer, \( Y_{1p} \), is obtained, its mass fraction, \( Y_{1*} \), at the carbon surface can be determined. The ash layer is assumed to be at the same temperature as the particle. Let \( h_{mgas} \) and \( h_{mash} \) be the mass transfer coefficients in the boundary layer outside the particle and in the ash layer respectively. Then, the mass balance across the various layers can be written as

\[
4\pi r^2 A_o e^{-E_o/RT_p} Y_{1*} = 4\pi r^2 h_{mash} (Y_{1p} - Y_{1*}) \frac{fM_{O_2}}{RT_p} \\
= 4\pi (r + t)^2 h_{mgas} (Y_{1\infty} - Y_{1p}) \frac{fM_{O_2}}{RT_p}
\]

where, \( t \) is the thickness of the ash layer, \( f \) is a stoichiometric factor relating the number of grams of carbon to the number of grams of oxygen, \( M_{O_2} \) is the molecular weight of oxygen and \( T_f \) is the boundary layer film temperature. Eliminating \( Y_{1p} \) from (7.29) we get

\[
Y_{1*} = \frac{XY_{1\infty}}{(M + 1)(X + 1) - 1}
\]

where \( M \) and \( X \) are given by the relations below:

\[
X = \frac{h_{mgas}}{h_{mash}} \left(1 + \frac{t}{r}\right)^2
\]

\[
M = \frac{A_o e^{-E_o/RT_p}}{h_{mash} \frac{fM_{O_2}}{RT_p}}
\]

The mass transfer coefficients, assuming spherical geometry and negligible Reynolds number, are given by

\[
h_{mgas} = \frac{D}{r + t}
\]

and

\[
h_{mash} = \frac{\epsilon A D}{\tau_A} \ln \left(1 + \frac{t}{r}\right)
\]
In equation (7.34), the void fraction, \( \epsilon_A \), and tortuosity, \( \tau_A \), in the ash layer are assumed to be 0.35 and 2, respectively. The bulk diffusivities \( D \) in the gas and the ash layers are calculated at the film and particle temperatures respectively. The thickness of the ash layer, \( t \), is calculated from a mass balance of the total ash in the particle, assuming that none of it is lost.

\[
t = \left[ r^3 + \frac{x_0 (r_0^3 - r^3)}{1 - 0.35} \right]^{0.33} - r
\]  

(7.35)

where, \( x_0 \) is the initial volume fraction of ash in the particle and 0.35 is the void fraction in the ash layer. The mass fraction \( Y_1 \), is then used in the carbon flux calculation.

7.2.2 Parametric Sensitivity

Since so many different parameters have to be known in advance as inputs to the model, it is important to find out the effect of some of the major parameters on crucial combustion variables such as particle temperature and burnout time.

Figure 7.2 shows the temperature-time histories for three different initial particle radii. While the bigger particles appear to burn at slightly lower temperatures due to increased radiative heat loss, the burnout times scale approximately as the square of the size. The radiating area also explains the increase in particle temperature with time. As the particle becomes smaller, the radiation loss decreases. The ash volume fraction was arbitrarily assumed to be 1% for all three cases. Wall temperature was kept at 1600K and the apparent densities of all particles were assumed to be 0.9 g/cc (900 kg m\(^{-3}\)). The ambient was air. The initial particle temperature was 1000K. Emissivities of the wall and the particle were taken to be
0.8 at all temperatures. The apparent activation energy was 17000 cal/mole (71.4 kJ/mole) and the pre-exponential factor was 46 g cm\(^{-2}\)s\(^{-1}\) (460 kg m\(^{-2}\)s\(^{-1}\)) in all three cases.

The influence of the apparent density of the particle is shown in Figure 7.3 for combustion of 25\(\mu\)m radius particles. It has no effect on the maximum particle temperature, but the burn time increases linearly with density as expected. Figure 7.4 shows the effect of wall temperature keeping all other parameters the same. Not unexpectedly, the particle burns faster and at higher temperatures if the wall is hotter. This is due to higher radiant heat transfer to the particle. Particle emissivity is not a very influential parameter for the combustion of such small particles, as seen in Figure 7.5. Decreasing the emissivity from 0.8 to 0.6 increased the maximum temperature by only 4%, with hardly any change in the burntime.

The apparent reaction kinetics profoundly influence combustion. For a constant apparent activation energy of 17000 cal/mole, calculations for variation in the pre-exponential factor from 23 to 92 g cm\(^{-2}\)s\(^{-1}\) are shown in Figure 7.6. The burn time decreases with increasing frequency factor as expected. At high rates, the particle burns isothermally over a significant part of its history, with a relatively brief initial rise and final burnout phase. At lower rates, however, there is no isothermal region. Instead, the temperature begins to fall immediately after the initial heatup period.

Figure 7.7 shows the dramatic influence of ash on the combustion. Since the final mass of the particle does not go to zero, the ash residue eventually reaches a steady-state temperature in radiative and conductive equilibrium with its surroundings. In reality, this steady-state may not be physically attainable since frag-
mentation of the particle would most likely have occurred before this. The density of the ash was taken as 2 g/cc and the carbon density was 1.5 g/cc. The fact that all three curves have similar heatup characteristics deserves special comment. While particles with higher ash contents should have more thermal inertia, this is not the case since the value of specific heat of the ash is not very different from that of carbon over the temperature range of interest. Figure 7.8 shows the effect of ash density. As expected, higher density implies a higher thermal inertia and consequently a higher burnout time. In order to emphasize this effect, the initial ash volume fraction was assumed to be 20%.

7.3 General Case: Monodisperse Internal Voids

The model described in the previous section does not treat the problem of diffusion and reaction inside the particle. Only at very high temperatures or at high oxygen concentrations, can reaction be assumed to proceed only at the exterior surface of the char particle. Under these special conditions, the particle is pore diffusion limited and the penetration of oxygen is limited to a fairly thin outer shell of the particle.

In general, however, internal reaction within the pores of the particle must be accounted for. This requires a suitable model for the internal structure of the particle. Pore sizes in coal char may vary over four orders of magnitude (Chapter 5). However, as a first step in modelling this internal structure, a relatively simple pore model will be used. As in any continuum model, the porosity will be assumed to be homogenous within the particle. However, as combustion proceeds, variations in the radial distribution of pores will develop. In this model, the initial porosity
is assumed to be due to monodisperse spherical voids present in the particle. The radius of the void and the void volume fraction (or porosity) are the two parameters that characterize the initial porosity. Let $a_0$ be the initial radius of the spherical voids and let there be $\lambda$ voids per unit particle volume. Then, accounting for pore overlap (Gavalas, 1985), the initial void fraction in a solid of infinite extent is

$$\epsilon_{\text{init}} = 1 - e^{-\frac{4}{3} \pi a_0^3}$$

(7.36)

The void fraction of a finite particle will be larger due to edge effects.

In the present analysis, temperature has been assumed to vary with time but to be constant throughout the particle. The maximum difference between the external particle temperature and that at its center is estimated to be 25-50K (Field, 1967). Thus, the particle can reasonably be taken to be spatially isothermal.

The presence of ash has been neglected in this model because: (i) the bituminous char does not have as much ash as many other coals and chars and thus it is not as significant; and (ii) the main purpose of the modelling effort was to test the effect of the internal structure as the particle burns. Without knowing the various details of how the ash behaves inside the particle, its inclusion in any model but the very simplest (like the one in the previous section) would be meaningless. Moreover, it would obscure those parts of the model that do correspond to physical reality. At the present moment our knowledge of ash behavior do not justify its inclusion in this model.

Since the reaction can take place inside the particle, the kinetic parameters used in the model are the intrinsic Arrhenius parameters derived from single particle experiments described in Chapter 4. These are based on the total surface area per
unit mass of the particle (e.g. N$_2$-BET area). The reaction kinetics will be assumed to be first order with respect to local oxygen concentration.

The overall scheme of the solution is as follows. The steady state diffusion equation is solved within the particle to determine the oxygen concentration as a function of radius. Since the problem is linear in oxygen concentration, the diffusion equation can be solved with an arbitrary boundary concentration at the exterior surface of the particle. Once the concentration profile is determined, it is scaled such that the external concentration matches the concentration determined from the transport outside the particle. This scaling is possible due to the linearity of the reaction rate.

### 7.9.1 Equations

The diffusion equation inside the particle is

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \phi_e \frac{\partial c}{\partial r} \right) = \frac{1}{\rho_C} A_i e^{-E_i/RT} S(r)c$$

(7.37)

where $c$ is the oxygen concentration, $\phi_e$ is the effective diffusion coefficient, $\rho_C$ is the density of carbon, $A_i$ and $E_i$ are the intrinsic Arrhenius parameters, and $S$ is the internal surface area per unit volume. The boundary conditions for this equation are

$$r = 0 : \frac{\partial c}{\partial r} = 0$$

(7.38a)

and

$$r = r^* : c = c^*$$

(7.38b)

The first condition is from spherical symmetry. $r^*$ and $c^*$ are the external radius and oxygen concentration respectively. $c^*$ is determined from the gas phase equations.
and is the matching condition at the boundary.

Based on the oxygen concentration inside the particle, the local carbon recession $q$ is determined by

$$q(r, t) = \int_0^t \frac{A_i e^{-E_i / RT_x(t)}}{\rho_c} c(r) \, dt$$  

(7.39)

This important equation determines the depth of carbon burned at any given radial location as a function of time. It is assumed that the void radius grows by the amount $q$ with time. Thus, knowing $q$, the void fraction $\epsilon$ can be determined as

$$\epsilon(r) = 1 - e^{-\lambda \frac{4}{3} \pi [a_0^3 + q(r)]}$$  

(7.40)

Once the void fraction is known, the local surface area, $S$, is given by

$$S(r) = [1 - \epsilon(r)] 4\pi \lambda (a_0 + q(r))^2$$  

(7.41)

This surface area is then used in the reaction rate term of the diffusion equation (7.37).

In calculating the external radius of the particle, the effect of surface crumbling must be taken into account. Once the void fraction at the surface reaches a critical value, the surface becomes too porous to retain its structural integrity. The char particle then crumbles, shedding some carbon and decreasing in radius to the point where the void fraction is below the critical value. This becomes the fresh surface and the cycle repeats. The fragments of carbon burn in the gas phase transferring some or all heat to the particle. If the model is run at fine enough time intervals the magnitude of the shedding is small and the radius appears to decrease smoothly. The time resolution is based on the penetration of oxygen and depends on the
porosity at the exterior surface. Therefore, the radius of the particle is calculated as follows:

\[
\begin{align*}
&\text{for } \epsilon_{\text{ext}} < \epsilon_{\text{crit}} : r^* = r_0 - q(\text{ext}) \\
&\text{for } \epsilon_{\text{ext}} \geq \epsilon_{\text{crit}} : r^* = r^{*\text{old}} - \frac{d\epsilon}{dt}\bigg|_{\epsilon_{\text{ext}}} \Delta t 
\end{align*}
\]

where the subscript \text{ext} refers to the external surface of the particle and \epsilon_{\text{crit}} denotes the critical value of the void fraction at which crumbling starts. \epsilon_{\text{crit}} was assumed to be 0.8 in the model.

The effective diffusivity in equation (7.37) was calculated from the void fraction using

\[
D_e(r) = \frac{1}{\tau} D\epsilon(r)
\]

where, \tau is a tortuosity factor, commonly taken as 2, and \( D \) is the bulk diffusion coefficient at the particle temperature.

Clearly, the above equations are strongly coupled with each other and with the external gas phase equations. The particle energy equation and all the gas phase transport equations derived in the previous section can be applied to this formulation. The particle was radially discretized into fifty shells of equal radial thickness. Conditions were assumed to be uniform inside each shell. As the radius decreased with time, the number of remaining shells correspondingly decreased. The position of the external surface was calculated as a function of time by interpolating between shells. Hence, the resolution in calculating the radius was not limited by the number of shells chosen.

The overall carbon flux for the particle was the sum of all the fluxes at the various radii. This flux, in conjunction with the gas phase, determined the new external oxygen concentration. This was used to recalculate new internal profiles of
the various quantities. This iterative process was continued until convergence was achieved at each time step. Then the overall energy balance was used to calculate the new particle temperature and a new particle radius was also calculated. This was repeated over as many time steps as needed to achieve preset final conversion values.

7.9.2 Parametric Sensitivity

Figure 7.9 shows the size of the particle as a function of time. A typical particle, having an initial radius of $25\mu m$ and an initial void fraction of 0.1 consisting of $0.1\mu m$ diameter voids, was used. The density of the solid carbon was assumed to be 2.0g/cc. The initial particle and wall temperatures were both 1500K and the critical void fraction was 0.8. The wall and the particle emissivities were 0.9 and 0.8 respectively. The figure shows three distinct regions. At first, the external radius of the particle decreases very slowly because the surface void fraction is below the critical void fraction and the radius can only change by reaction. When the surface void fraction does reach the critical value, crumbling starts and the radius reduces as a faster rate. As the particle burns, however, oxygen penetrates further and more of the outer shell reaches the critical value and is shed. This causes the radius to decrease faster. Finally, when the particle becomes quite small, there is complete oxygen penetration and it burns in the kinetic limited regime. The shedding thickness becomes smaller and the radius decrease is arrested. Eventually, the entire particle reaches the critical void fraction and disintegrates. This happens when the radius is around $3\mu m$. Therefore the final radius is not zero. Figure 7.10 shows the variation of conversion versus time. The particle temperature is
shown in Figure 7.11. The heat up period, the almost isothermal phase, the rapid decrease and finally the kinetic regime are all shown. In the kinetic regime the particle is in thermal equilibrium with its environment. In fact the kinetic regime is seen because of the preceding temperature drop. Figure 7.12 shows the variation of the surface oxygen partial pressure. The initial surface partial pressure, 0.145, is lower than that in the free stream, 0.21, because of the diffusional resistance in the particle boundary layer. During the heat up period, the reaction rate increases and the oxygen concentration drops. For most of the burning period, the oxygen concentration at the surface is quite low, indicating near diffusion limited conditions. Finally, as the particle size decreases, the external concentration rises, approaching the ambient partial pressure. The flux of carbon from the particle is shown in Figure 7.13. The fluctuations are due to the numerical method employed and the choice of each time step interval. The temporal resolution in various runs was 0.1 milliseconds. Figure 7.14 shows the surface and total void fractions of the particle as a function of time. Since the critical void fraction is chosen as 0.8, the surface void fraction increases to 0.8 and then remains constant throughout most of the combustion. The drop at the start of the kinetic regime is due to computational inaccuracies. The total void fraction starts from the value of the initial void fraction (0.1). At first it rises because the radius is not changing and there is some reaction. As soon as shedding begins, it starts decreasing because the particle loses its most porous external shell. However, the thickness of the outer layer that crumbles decreases with time, and the particle void fraction decreases to a relative minimum. Eventually, the particle size becomes small enough that oxygen
penetrates throughout the particle. The accelerating reaction then increases the particle void fraction monotonically till the critical void fraction is reached when the entire particle crumbles.

The effect of particle radius on the combustion temperature plot is shown in Figure 7.15. The burn times again scale approximately as the square of the size because of the aforementioned shrinking core type of behavior. The peak temperature is almost the same for the two particle sizes examined. The initial void fraction and void radius, were, in both cases, 0.1 and 0.05µm, respectively. The wall and initial particle temperatures were both 1500K. The intrinsic pre-exponential factor was $10^5$ kg m$^{-2}$s$^{-1}$ and the intrinsic activation energy was 179740 J/mole (43000 cal/mole). Figure 7.16 shows that the carbon density affects only the burn time and not the peak temperature. The lower density particle also heats more rapidly due to its low thermal inertia. The influence of carbon emissivity is shown in Figure 7.17. Again, the change in the temperature is small and the higher the emissivity, the lower the final particle temperature. In both cases the wall emissivity was assumed to be 0.9. In Figure 7.18, the influence of the pre-exponential factor is demonstrated. The nature of the variation is as expected. The initial rate of rise is not commensurate with the rise in reaction rate, but the duration of time the particle spends in the final kinetic regime is dramatically increased with decreasing reaction rate. The curves in Figure 7.19 show the effect of initial void size. The initial void fraction in all cases was 0.1, so the number concentration of voids decreased with increasing void size. The specific surface area increases as the void size decreases, so the net reaction rate also increases. Since the radiative heat loss is the same in
all cases, the particles with the smaller voids tend to reach higher temperatures and consequently burn out faster. The influence of the initial void fraction is shown in Figure 7.20. The initial void size in all cases was 0.05µm in radius. The smaller the void fraction, the larger the particle mass and therefore the longer the burn time. The particle temperature does not vary significantly with void fraction. In all the cases discussed above, the energy released by the core particle and the burning fragments was completely fed back to the particle. However, not all the energy of combustion is necessarily available for the remaining particle. Burning fragments expelled from the particle may burn far from the particle. To simulate such a situation, various fractions of energy released by the exterior crumbling shell were fed back to the particle and the effect on its combustion behavior noted. Figure 7.21 shows two cases involving no (0%) and 50% feedback. The particle burns at almost 100K high in the second case. The final comparison (Figure 7.22) involves various wall temperatures. The heat up period is longer when the wall is cool, but the latter part of the combustion is similar in both cases.

Figures 7.23-7.29 show the oxygen concentration profiles inside the particle as a function of time for different values of reaction rate, initial void size and initial void fraction. Figure 7.23 shows the case with a pre-exponential factor of 10^5 kg m^{-2}s^{-1}, initial void radius of 0.05 µm, and initial void fraction of 0.1. The first profile is labelled 0 ms. It shows that after the first time step, the radius of the particle is still 25 µm and the external oxygen partial pressure is 0.12. There is no penetration below 10 µm radius, implying that the oxygen is confined to an outer layer 15 µm thick. The profiles are drawn every 2 ms and labelled every 10 ms for clarity.
Twenty milliseconds after the start of combustion, the profile shows that the particle radius is around \(18 \mu m\) and the penetration depth is only \(3 \mu m\). The surface partial pressure is 0.025. As combustion continues, the external concentration rises, and the radius decreases. The penetration depth remains around \(3 \mu m\). At about 42 ms after the start of combustion, the concentration at the center of the particle becomes non-zero for the first time and the particle is in the kinetic regime. Although there is some drop in concentration inside the particle, the penetration of oxygen is not limited to a layer on the outside. Figures 7.24 and 7.25 show similar profiles for a lower and a higher pre-exponential factor, respectively. When the reaction rate is lower, there is better penetration of oxygen into the particle and also the concentration at the exterior is higher. The opposite is true for the high reaction rate (Figure 7.25). The influence of the initial void fraction on the profiles are shown in Figures 7.26, 7.23 and 7.27 which have initial void fractions of 0.05, 0.1 and 0.15 respectively. All three cases have the same initial void size and reaction rate. The higher the void fraction, the greater the void surface area (this is only true for small void fractions; at much larger void fractions, void coalescence actually reduces the area) and effectively, higher the reaction rate. Hence, there is better penetration of oxygen at lower void fractions. The influence of initial void size are shown in Figures 7.28, 7.23 and 7.29 respectively. All three cases have the same initial void fraction (0.1) and reaction rate. Clearly, for a given void fraction there are more numbers of smaller voids leading to larger surface areas and therefore higher reaction rates. Therefore there is very little penetration and the surface concentrations are the least for the smallest void sizes (Figure 7.28).
7.4 General Case: Polydisperse Internal Voids

In general coal chars have a distribution of void sizes. We now extend the spherical void model to a more realistic representation of the internal structure. Three different void sizes, corresponding to micro, transition, and macro pores were used. The sizes of the voids and the void fraction for each size were determined from mercury porosimetry. (see Chapters 5 for examples). The surface area and diffusion calculations were modified to account for the presence of the different size voids. All other equations are essentially unchanged from the ones given in the previous sections.

Input data for the internal pore morphology assumed in this model were the average radii of pores in the micro, transition, and macro ranges, assumed to be 0.001 μm, 0.01 μm, and 0.1 μm, respectively. The void fractions in the three pore types were also specified. At first, the void number density, $\lambda_i$, was determined. This is the number of voids of a particular type per unit particle volume. The number densities were then held constant while the pore radii were allowed to grow by reaction. Let $\epsilon_{i,0}$ be the initial void fractions of the macro ($i=1$), transition ($i=2$), and micro ($i=3$) pores. If $a_{i,0}$ are the initial radii, then let

$$\omega_{i,0} \equiv \frac{4}{3} \pi \lambda_i a_{i,0}^3 \quad i = 1, 2, 3$$ (7.43)

Assuming overlap of micro pores with the other two types we have

$$\epsilon_{3,0} = 1 - e^{-\omega_{3,0}}$$ (7.44)

Also, assuming overlap of transition pores with macro pores but not with micro pores we have

$$\epsilon_{2,0} = e^{-\omega_{3,0}} - e^{-\omega_{2,0} - \omega_{3,0}}$$ (7.45)
Finally assuming no overlap of the macro pores with the other two types we get

\[ \epsilon_{1,0} = e^{-\omega_{2,0} - \omega_{3,0}} - e^{-\omega_{1,0} - \omega_{2,0} - \omega_{3,0}} \]  \hspace{1cm} (7.46)

Equations (7.44), (7.45), and (7.46) successively determine \( \lambda_3 \), \( \lambda_2 \) and \( \lambda_1 \) respectively. Once the void number concentrations are known, the void fractions at any time can be determined by knowing the surface recession, \( q \). Let

\[ \omega_i = \frac{4}{3} \pi \lambda_i (a_{i,0} + q)^3 \quad i = 1, 2, 3 \]  \hspace{1cm} (7.47)

Then the void fractions are given by

\[ \epsilon_3 = 1 - e^{-\omega_3} \]
\[ \epsilon_2 = e^{-\omega_3} - e^{-\omega_2 - \omega_3} \]  \hspace{1cm} (7.48)
\[ \epsilon_1 = e^{-\omega_2 - \omega_3} - e^{-\omega_1 - \omega_2 - \omega_3} \]

The total void fraction, \( \epsilon \), is given by

\[ \epsilon = \epsilon_1 + \epsilon_2 + \epsilon_3 \]  \hspace{1cm} (7.49)

The surface area, \( S(q) \), is given by

\[ S(q) = (1 - \epsilon)4\pi \sum_{i=1}^{3} \lambda_i (a_{i,0} + q)^2 \]  \hspace{1cm} (7.50)

The result of varying the different void fractions in the various sizes is shown in Figure 7.30. The total initial void fraction is kept constant in all cases. Figure 7.31 shows the specific surface area of the particle as a function of carbon conversion. The shape of the curves is very similar to those obtained experimentally, including the maximum observed at some intermediate conversion. This is an indicator of the
capability of such a model to describe accurately the combustion behavior of single particles.

7.5 General Case: Polydisperse Voids and Nonlinear Kinetics

The condition of first order Arrhenius kinetics was relaxed to test the effects of various non-linear reaction rate expressions on the combustion history. The presence of ash was neglected in these formulations.

The introduction of non-linearity makes the problem more difficult to solve numerically. Various shooting and adaptive-grid techniques were used to make the numerical aspects tractable, accurate, and efficient since scaling was no longer possible. Computation times increased by about one order of magnitude.

The first non-linear expression used was of the Langmuir-Hinschelwood type. The intrinsic reaction rate was assumed to be of the form

\[ R = A_i e^{-E_i/RT_p} \frac{c}{1 + Cc} \]  

(7.51)

where \( c \) is the oxygen concentration and \( C \) is a constant. The effect of varying \( C \) is shown in Figure 7.32. The results are also compared to the temperature-time history obtained from linear kinetics in Figure 7.33.

Figure 7.34 shows the internal oxygen concentration profiles when the intrinsic reaction rate is of the form

\[ R = A_i e^{-E_i/RT_p} c^m \]  

(7.52)

where \( m \) is between 0 and 1. If \( m \) is smaller than 0.8, the problem becomes numerically stiff and difficult to solve. However, in those cases it is seen from the figure that the penetration of oxygen is confined to a very thin shell on the outside of the
particle. In such situations, the asymptotic formulation given in Section 7.2 can be used without much error.
References


4. Mitchell, R.E., Experimentally Determined Overall Burning Rates of Coal Chars, Presented at the combined Canadian and Western States Section Technical Meeting of the Combustion Institute, Banff, Canada (1986).
Figure 7.1 Schematic diagram of a single char particle with ash.
Figure 7.2 Asymptotic Model: Effect of initial particle radius, \( r_p \). \( \epsilon_A = 0.01 \), \( \rho_A = 2000 \text{ kg m}^{-3} \), \( T_\infty = 1600 \text{ K} \), \( T_{pi} = 1000 \text{ K} \), \( \rho_a = 900 \text{ kg m}^{-3} \), \( P_{O_2,\infty} = 0.21 \), \( \epsilon_\infty = \epsilon_0 = 0.8 \), \( E = 71060 \text{ J/mole} \), \( A_a = 460 \text{ kg m}^{-2} \text{ s}^{-1} \)
Figure 7.3 Asymptotic Model: Effect of apparent particle density, $\rho_a$. $r_p=25 \mu m$, $\epsilon_A=0.01$, $\rho_A=2000$ kg m$^{-3}$, $T_\infty=1600$ K, $T_{pi}=1000$ K, $p_{O_3,\infty}=0.21$, $\epsilon_\infty=\epsilon_0=0.8$, $E=71060$ J/mole, $A_a=460$ kg m$^{-2}$ s$^{-1}$.
Figure 7.4 Asymptotic Model: Effect of wall temperature, $T_\infty$. $r_p=25 \ \mu m$, $\epsilon_A=0.01$, $\rho_A=2000 \ \text{kg m}^{-3}$, $\rho_a=900 \ \text{kg m}^{-3}$, $T_p=1000 \ \text{K}$, $p_{O_2,\infty}=0.21$, $\epsilon_\infty=\epsilon_0=0.8$, $E=71060 \ \text{J/mole}$, $A_a=460 \ \text{kg m}^{-2} \ \text{s}^{-1}$
Figure 7.5 Asymptotic Model: Effect of particle emissivity, $\epsilon_0$. $r_p=25$ $\mu$m, $\epsilon_A=0.01$, $\rho_A=2000$ kg m$^{-3}$, $\rho_a=900$ kg m$^{-3}$, $T_{pi}=1000$ K, $pO_2,\infty=0.21$, $\epsilon_\infty=0.8$, $T_\infty=1600$ K, $E=71060$ J/mole, $\Lambda_a=460$ kg m$^{-2}$ s$^{-1}$
Figure 7.6 Asymptotic Model: Effect of the apparent Arrhenius pre-exponential factor, \( A_\alpha \). \( r_p=25 \mu m, \epsilon_A=0.01, \rho_A=2000 \text{ kg m}^{-3}, \rho_a=900 \text{ kg m}^{-3}, T_{pr}=1000 \text{ K}, p_{O_2,\infty}=0.21, \epsilon_\infty=\epsilon_0=0.8, T_\infty=1600 \text{ K}, E=71060 \text{ J/mole}, \)
Figure 7.7 Asymptotic Model: Effect of initial ash volume fraction in the particle, $\epsilon_A$. $r_p=25 \ \mu m$, $\rho_A=2000 \ \text{kg m}^{-3}$, $\rho_a=900 \ \text{kg m}^{-3}$, $T_{pi}=1000 \ \text{K}$, $p_{O_2,\infty}=0.21$, $\epsilon_\infty=\epsilon_0=0.8$, $T_\infty=1600 \ \text{K}$, $E=71060 \ \text{J/mole}$, $A_a=460 \ \text{kg m}^{-2} \ \text{s}^{-1}$
Figure 7.8 Asymptotic Model: Effect of ash density, $\rho_A$. $\epsilon_A=0.2$, $r_p=25$ $\mu$m, $\rho_a=900$ kg m$^{-3}$, $T_{pi}=1000$ K, $p_{O_2,\infty}=0.21$, $\epsilon_{\infty}=\epsilon_0=0.8$, $T_\infty=1600$ K, $E_r=71060$ J/mole, $A_a=460$ kg m$^{-2}$ s$^{-1}$
Figure 7.9 General Model with initially monodisperse voids: Particle radius versus time. $r_p=25 \, \mu m$, $\epsilon=0.1$, $a_0=0.05 \, \mu m$, $\rho_C=2000 \, \text{kg m}^{-3}$, $T_{pi}=T_{\infty}=1500 \, \text{K}$, $\epsilon_{crit}=0.8$, $\epsilon_\infty=0.9$, $\epsilon_0=0.8$, $p_{O_2,\infty}=0.21$, $E=179740 \, \text{J/mole}$, $A_i=10^5 \, \text{kg m}^{-2} \, \text{s}^{-1}$, 0% feedback.
Figure 7.10 General Model with initially monodisperse voids: Carbon conversion versus time. Parameters as in Figure 7.9.
Figure 7.11 General Model with initially monodisperse voids: Particle temperature versus time. Parameters as in Figure 7.9.
Figure 7.12 General Model with initially monodisperse voids: Oxygen partial pressure at the particle surface versus time. Parameters as in Figure 7.9.
Figure 7.13 General Model with initially monodisperse voids: Carbon flux versus time. Parameters as in Figure 7.9.
Figure 7.14 General Model with initially monodisperse voids: Total and Surface void fractions versus time. Parameters as in Figure 7.9.
Figure 7.15 General Model with initially monodisperse voids: Effect of initial particle radius, $r_p$. Parameters as in Figure 7.9.
Figure 7.16 General Model with initially monodisperse voids: Effect of carbon density, $\rho_C$. Parameters as in Figure 7.9.
Figure 7.17 General Model with initially monodisperse voids: Effect of particle emissivity, $\varepsilon_0$. Parameters as in Figure 7.9.
Figure 7.18 General Model with initially monodisperse voids: Effect of intrinsic Arrhenius pre-exponential factor, $\Lambda_i$. Parameters as in Figure 7.9.
Figure 7.19 General Model with initially monodisperse voids: Effect of initial void radius, $a_0$. Parameters as in Figure 7.9.
Figure 7.20 General Model with initially monodisperse voids: Effect of initial void fraction, $\epsilon$. Parameters as in figure 7.9.
Figure 7.21 General Model with initially monodisperse voids: Effect of energy feedback. Parameters as in Figure 7.9.
Figure 7.22 General Model with initially monodisperse voids: Effect of wall temperature, $T_\infty$. Parameters as in Figure 7.9.
Figure 7.23 General Model with initially monodisperse voids: Internal oxygen partial pressure profiles at various times for $A_i=10^5$ kg m$^{-2}$ s$^{-1}$. Other parameters as in Figure 7.9.
Figure 7.24 General Model with initially monodisperse voids: Internal oxygen partial pressure profiles at various times for $A_i=3 \times 10^4$ kg m$^{-2}$ s$^{-1}$. Other parameters as in Figure 7.9.
Figure 7.25 General Model with initially monodisperse voids: Internal oxygen partial pressure profiles at various times for $A_i=1.67\times10^5$ kg m$^{-2}$ s$^{-1}$. Other parameters as in Figure 7.9.
Figure 7.26 General Model with initially monodisperse voids: Internal oxygen partial pressure profiles at various times for $\epsilon=0.05$. Other parameters as in Figure 7.9.
Figure 7.27 General Model with initially monodisperse voids: Internal oxygen partial pressure profiles at various times for $\epsilon=0.15$. Other parameters as in Figure 7.9.
Figure 7.28 General Model with initially monodisperse voids: Internal oxygen partial pressure profiles at various times for \( a_0 = 0.01 \) µm. Other parameters as in Figure 7.9.
Figure 7.29 General Model with initially monodisperse voids: Internal oxygen partial pressure profiles at various times for \( a_0 = 0.1 \) \( \mu m \). Other parameters as in Figure 7.9.
Figure 7.30 General Model with initially polydisperse voids: Effect of void fraction distribution in the three void radii 0.1 µm, 0.01 µm, and 0.001 µm respectively. Case A: 0.05, 0.09, 0.03; Case B: 0.10, 0.04, 0.03; Case C: 0.10, 0.05, 0.02; Case D: 0.10, 0.06, 0.01; Case E: 0.10, 0.07, 0.00. Total initial void fraction in all cases = 0.17. Other parameters as in Figure 7.9.
Figure 7.31 General Model with initially polydisperse voids: Specific surface area versus carbon conversion for cases with varying void fractions in the different void sizes. Case A: 0.05, 0.09, 0.03; Case B: 0.10, 0.04, 0.03; Case C: 0.10, 0.05, 0.02; Case D: 0.10, 0.06, 0.01; Case E: 0.10, 0.07, 0.00. Total initial void fraction in all cases = 0.17. Other parameters as in Figure 7.9.
Figure 7.32 General Model with initially polydisperse voids: Effect of the parameter C in the Langmuir-Hinschelwood reaction rate expression. Other parameters as in Figure 7.30 Case A.
Figure 7.33 General Model with initially polydisperse voids: Comparison of the linear rate with the Langmuir-Hinschelwood rate with C=1.
Figure 7.34 General Model with initially polydisperse voids: Internal oxygen partial pressure profiles at $t=0$ for different powers in the power law reaction rate expression. Other parameters as in Figure 7.30 Case A.
Chapter 8

DISCRETE SIMULATION OF
CENOSPHERIC COAL-CHAR COMBUSTION

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A phenomenological model of structural transformations during pulverized coal char combustion is presented. The random geometry of the voids is modelled realistically by means of a random assemblage of spheres in a spherical particle. Pore connectedness and growth are accounted for as the combustion proceeds. The percolation behaviour of the void space is dramatically demonstrated. The effects of different initial voidfractions and of the random nature of the structure itself, at a given initial voidfraction are shown. This sheds some light on our ability to realistically model the solid. The limitation of shrinking core models of combustion of cenospheric chars are demonstrated. In this initial application, the model is limited to isothermal combustion with no diffusional limitations.
8.1 Introduction

Recent theoretical research in coal combustion and gasification has emphasized the role of intraparticle reaction, diffusion, and pore morphology evolution. Two approaches have been taken. In the first approach [1-8], the carbonaceous matter is treated as a continuum and the material and energy balances governing the combustion process are formulated as differential equations. These equations contain coefficients, such as specific surface area and internal diffusivity, which are generally functions of carbon conversion and vary with time and intraparticle position. The relations between surface area, diffusivity and conversion were either based on the random pore model [1,5,6], treated as directly measurable properties [2-4], or derived using results from percolation theory [7,8]. Regardless of the particular form or origin of these functional relationships, the use of local average properties presumes that the largest length scale characteristic of the porous structure is much smaller than the characteristic length associated with concentration gradients. It is not necessary, for our present purposes, to define these length scales more precisely except to note that the characteristic length of the porous structure could be considerably larger than the pore diameter itself. It is easy to verify that the relation between the length scales necessary to justify the continuum description is not satisfied under conditions of pulverized combustion where the oxygen penetration depth of a few microns is on the same order of magnitude as the largest length scale characteristic of the porous structure. Chars of softening coals often possess a sponge-like structure containing large voids, several micrometers in diameter, as well as smaller pores all the way down to one nanometer. For such chars
the continuum description is particularly unsuitable.

In the second approach that has been used to describe intraparticle processes in combustion, the porous structure is represented by a lattice where, for example, the presence or absence of a bond signifies the solid and the void phases respectively. This approach, sometimes known as 'discrete simulation', has been used by several authors particularly as a means of exploring the role of connectivity and the onset of fragmentation. Sandmann and Zygourakis [9] have developed a detailed discrete simulation approach to describe char gasification. The char particle is represented by a two-dimensional lattice whereon voids of different sizes are constructed according to some geometric rule to simulate mercury porosimetry data. To simulate pure kinetic control, they assumed that all voids are accessible and grow at the same rate in discrete increments. In another limiting case examined, only those voids accessible to the external particle surface were allowed to grow, all at the same rate. This diffusion-reaction regime would be applicable to a material having a macropore-micropore structure where the Thiele modulus for the micropores is very high but that for the macropores is low.

Sahimi and Tsotsis [10] have represented the porous structure on a three-dimensional lattice, using a percolation cluster to represent a char particle. Only those solid sites accessible to the particle surface were allowed to react, at an uniform rate. Their simulations provide detailed information about fragmentation as well as the rate of conversion history of a burning particle.

effect of intraparticle diffusion. Sahimi and Tsotsis [12] have extended their model to include the effect of diffusion, simulated by random walks of the oxidizer molecules towards the particle.

The near percolation structure used to represent the char particle in papers [10-12] is not suitable for representing a material with macropore-micropore morphology or one having a more complex pore structure. Nevertheless, this limitation can be overcome by adopting the approach of Sandmann and Zygourakis [9]. Thus representation of the pore structure on a three-dimensional lattice in conjunction with random walks to describe diffusion provides, in principle, a very general and flexible approach to modelling char gasification and combustion.

The use of the lattice is computationally attractive because it allows use of efficient searching and sorting routines. Many results from graph theory and percolation theory developed for lattices are also applicable. However, quantitative applications and predictions would have to employ three-dimensional and relatively fine grids involving large-scale computations.

In this paper we present an alternative non-lattice representation of the porous structure which is computationally simpler although not quite as general as the lattice representation.

8.2 Pore Structure Model

As a model of a cenospheric char particle, consider a spherical char particle with spherical voids randomly distributed throughout its volume. The voids may overlap and, therefore, be connected to one another, or they may be isolated. Thus, connectivity to other voids and the external particle surface are built into the geometry.
Two voids overlap when their center separation is less than the sum of their radii. Similarly, a void is connected to the outside when the distance between its center and the instantaneous external surface is less than its radius. Figure 8.1 illustrates the initial geometry, and that corresponding to a later time when considerable reaction has already occurred. Voids that are connected together form clusters. A cluster is connected to the outside if any one of its constituent voids is connected to the outside. A cluster may be multiply-connected to the outside via more than one void.

The size of the initial particle, the initial number, volume, and size distribution of the voids and the initial random distribution of the void centers are parameters in this geometry. We have chosen a particle size of 50µm in diameter. For simplicity the initial void sizes are taken to be monodisperse and 5µm in diameter. This assumption is easily relaxed to introduce a variety of void sizes, but the essential results of the model are captured by assuming an initially monodisperse set of voids. Initial void fractions are then varied by changing the number of void centers in the particle.

The particle combustion is modelled as follows. Analogous to Gavalas [1] we postulate a surface recession velocity, q, such that every surface that is connected to the outside, either directly or indirectly (being part of a cluster that is connected to the outside) recedes by the amount \( \delta = q \Delta t \) in time, \( \Delta t \). The effects of temperature and reaction rates are lumped into the parameter q. In the simplest case we have assumed that q is constant with time and with radius. Physically this corresponds to an isothermal, homogeneous particle burning with no diffusional re-
sistances. The motivation for this study was to determine the structural dynamics of a burning cenospheric char particle. Hence, as a first approximation we minimized the complications introduced by diffusion, composition inhomogeneities, and the energy balance. However, diffusion can be taken into account by varying q with radius.

It is clear that, if we take discrete steps of magnitude \( \delta \), the smaller we take \( \delta \) the better the temporal resolution of the simulation. That is, when \( \delta \) is small the surface area of an accessible cluster will change smoothly without abrupt jumps. However making \( \delta \) too small increases the simulation time considerably. We have taken q to be 0.05 \( \mu m/time \) step and the simulations have been carried out till \( \delta/R_0 \) was 0.25. Since the particle was burning internally, this was sufficient to reach void fractions as high as 0.95.

The main variable that is measured at each step is void fraction. By randomly distributing a large number (typically 3000 or more) of probe points in the particle and counting that fraction which lies in the voids we can measure the void fraction and conversion very accurately. As the exterior of the particle also recedes at the rate q, the particle radius is defined accurately at all times. We also record some other geometrical parameters defined in the next section that shed light on the dynamics.

The simulation is terminated after a given number of time steps. The values of conversion at the end of the runs were in the range 0.8-1.0. For some of the runs clearly fragmentation must have occurred. This paper will not address the challenging questions posed by fragmentation.
It is clear that the results will depend on the quality of the random number generator used. We have used a generator in the IMSL library after rigorously testing its output for independence of sequence entries and repartisation. To avoid the possibility of creating N-tuples for some starting seed numbers the random numbers were re-randomised by randomly mixing two strings [13].

8.3 Model Parameters

The voidfraction is defined as the volume fraction of voids in a particle. It is denoted by \( \varepsilon \). This parameter is directly obtained from the simulation by counting the number of probe points. The carbon conversion is calculated knowing the initial and final void fractions and radii of the particle. This assumes that there is no mineral matter or ash in the particle. The final radius of the particle is the external radius of the particle at the termination time step. The conversion in percent is given by

\[
\varepsilon = 100 \left[ 1 - \frac{R_f^3(1 - \varepsilon_f)}{R_0^3(1 - \varepsilon_0)} \right]
\]

where \( R_f^3 \) and \( R_0^3 \) are the final and initial radii of the particle and \( \varepsilon_f \) and \( \varepsilon_0 \) are the final and initial voidfractions. The density of the solid phase is assumed to stay constant throughout the process. Another interesting parameter is the conversion rate. This is the instantaneous slope of the conversion versus time curve, i.e., the rate of mass loss. The relation between number of steps in the simulation and real time for an isothermally burning particle is

\[
t = \frac{MqN}{R\rho}
\]

where \( t \) is time, \( M \) is the molecular weight of carbon, \( N \) is the number of steps,
q is the surface recession velocity (µm/step), ρ is the particle density, R is the reaction rate in moles-sec/cm² (assumed invariant with temperature) and N is an unit conversion constant.

For a particle whose temperature is uniform but varies with time, the relation is given by the following integral

$$t = N \int_0^T \frac{Mq}{R(r) \rho} dN dr$$  \hspace{1cm} (8.3)

where T is the particle temperature and $\frac{dN}{dr}$ is derived from an energy balance.

A preliminary effort has been made to model the effects of diffusion by varying the parameter q with radius. An exponential function was chosen such that the value of q was 0.05µ/step at the instantaneous surface of the particle and 0.005µ/step at the particle center. However, results pertaining to diffusion will not be given in this paper.

Apart from the above, another important variable is the size of the largest void cluster. Due to overlap and given the fact that the clusters do not grow in geometrically regular shapes we denote size by the number of void centers in a given cluster. As will be seen later this parameter shows interesting percolation properties. One other important variable is the radial distribution of voidfraction as a function of conversion. This clearly shows the depth of the combustion zone on the particle surface. If this depth is small, modelling of the process by a ‘shrinking core’ model can be justified. Hence, our model helps to identify those types of solid structures that can be modelled with traditional and simple models.
8.4 Results

Table 8.1 shows the run numbers, number of initial voids and initial void fractions of the various runs. There are five groups of runs with around 50 (group E), 70 (group C), 100 (group B), 165 (group A) and 215 (group D) voids in the particle initially for each run. Due to the random nature of specifying the voids it was not possible to have exactly the same number of voids in the particle for each run in a given group. Moreover, void overlap leads to additional variation in the initial void fraction. However we believe that the variances in the initial number of voids within a group do not significantly affect our conclusions. We shall study in detail those runs where in fact there are exactly the same number of initial voids (e.g. runs D1, D2, D13, D14, D17, D18 — all having 216 voids initially). The other runs are given for the sake of completeness.

Table 8.2 compares the initial void fractions obtained from the simulation and those calculated using the method given in Gavalas [1]. The void fractions calculated from theory are higher because the theory assumes an infinitely large particle and thus tends to overestimate the effects of voids whose centers are near or just outside the outer surface of the particle.

Figure 8.2 is a plot of the void fraction versus number of steps for run D14. Plots for the other runs are similar. At first the rate of increase of the void fraction from the initial void fraction, accelerates with conversion. The rate then levels off and decreases slowly till the termination of the simulation. Initially, only those few voids that are connected to the outside can grow. As time progresses, the number of voids connected to the outside increases due to the capture of inaccessible voids by
the growing externally-connected clusters. Some other voids also become externally connected as the particle radius decreases. Eventually, most of the voids become externally connected and, therefore, can grow. The void fraction then grows rapidly. Finally, void collapse becomes dominant and the rate of growth of void fraction decreases. Void collapse occurs when the surface of a given void no longer exists, having been merged with other neighboring voids.

Figures 8.3 and 8.4 show conversion and conversion rate plotted against time, respectively. There is a slight maximum in Figure 8.4. The location and height of this maximum varies from run to run and, in some cases there is only a monotonic decrease as in Figure 8.5. This is consistent with previous experimental and theoretical observations of the variation of the reaction rate with time (or conversion). Since there are no composition heterogeneities in the model solid, this variation is due to pore growth and collapse. The fact that different realizations show different behaviour underscores the importance of the random nature of the pore structure and its effects on the combustion.

Figure 8.6 shows the ratio of the number of voids in the largest cluster (XLAR) to the total number of voids (RTOT) as a function of the void fraction. The percolation of the void cluster through the particle occurs at various void fractions and finally all voids belong to one large cluster by 60% void fraction. This ratio of the number of voids in the largest cluster to the total number of voids can be thought of as a percolation probability. However, although all runs showed similar behaviour, there are important differences. The discrete jumps in the curve are capture events when growing clusters merge, creating larger clusters. Thus, in this
example at 40% void fraction nearly 70% of the voids already belong to the largest cluster. However, in Figure 8.7 (run D13) at 40% void fraction nearly 90% of the voids belong to the largest cluster. The only difference between runs D13 and D14 is that they are different members (realizations) of the same ensemble. There are similar examples in the other groups of runs where major differences are observed simply by changing only the random ordering of the voids in the particle.

The strong influence of the initial random nature of the solid and the importance of connectivity and growth of the solid in the combustion process cannot be overemphasized. Given this variability between 'similar' particles we have to be careful in defining and using 'average' values. In Figures 8.6 and 8.7 we see that the major transition takes place at a given void fraction. Figures 8.8 and 8.9 plot the void fraction when the percolation probability is 80% and 50% respectively as a function of the total number of voids in each run. Although there is variability the average values point to a definite trend. The variability also does not exceed the 1σ limits which are plotted in the figures. From those figures it seems that the asymptotic (when the number of voids → ∞) void fractions when the percolation probability is 80% and 50% are 0.4 and 0.32 respectively.

The solid fraction is shown in Figure 8.10 as a function of the radius of the particle from run D14 at two different instants as it is burning. The curve A is at the start of the run and shows that except for deep inside the particle there are voids scattered throughout the particle such that the solid fraction at any radius is around 75% - 95%. The curve is jagged because the particle was divided into 50 spherical shells in order to calculate the radial solid fraction and reflects numerical noise.
Curve B corresponds to 70% conversion when combustion has penetrated quite deep into the particle leaving deep pits in the external surface. These pits account for the greatly reduced solid fraction at larger radii. A pictorial representation of this particle is shown in Figure 8.1. In this instance the assumption of a shrinking core model would not be valid. That was the general observation in most of the runs.

8.5 Discussion and Conclusions

Some additional comments are necessary regarding the percolation behaviour demonstrated by the void space with change in conversion. It should be quite evident that the process described here does not correspond to a simple percolation process in which the changes occur homogeneously through the domain under consideration. Here, only those voids connected to the outside grow and therefore this connectivity driven growth alters the phenomena and does not permit direct comparison with results from percolation theory (like critical voidfractions and critical exponents). Sahimi and Tsotsis have discussed this issue in considerable detail for their lattice representation.

The assumption of an initially monodisperse set of voids is oversimplified. It is clear that the model can readily be applied to other pore size distributions since, from the second step of the simulation onwards, the voids become poly disperse due to the external connectivity-growth constraint. Far more important is the role of multiple scales of voids that are present in an actual particle. A real particle typically has voids whose length scales differ by as much as four orders of magnitude. The number of the smallest voids is also very large. While, in principle, our model
can be extended to simulate such a case the computational cost and time make such an approach impractical. Renormalisation to account for the various length scales is a more elegant approach but it is still an open problem particularly for the non-lattice random geometry described here. The connectivity problem further complicates the issue.

Our calculations did not include diffusion and as such they are restricted to the following to physical situations. The first is a solid with a narrow pore size distribution burning in the kinetics controlled regime. The second is a bimodal macropore-micropore solid with large Thiele modulus for the micropores and small Thiele modulus for the macropores. In this case, the micropores need not be described explicitly, although their effect is manifested via an apparent rate expressed per unit macropore surface area.Chars of softening coals contain macropores, as large as $5\mu m$ in diameter, and micropores. However they sometimes contain transitional pores as well. Under conditions of pulverized combustion the micropore Thiele modulus is large but the macropore Thiele modulus is not always small. To describe this situation more realistically, diffusion has to be incorporated in any such discrete model.
References

Table 8.1 Initial conditions for various runs. The number in brackets is the initial number of voids in the particle and the other number shows the initial void fraction.
Table 8.2 Comparision of the initial void fractions as calculated from theory and from the simulation for Group D runs.
Figure 8.1 Geometry of the simulation showing the voids and clusters in the particle initially (A) and after significant conversion (B). The hatched area is solid carbon.
Figure 8.2 Void fraction versus $\delta/R_0$ for run D14.
Figure 8.3 Carbon conversion versus $\delta / R_0$ for run D14.
Figure 8.4 Carbon conversion rate versus $\delta/R_0$ for run D14.
Figure 8.5 Carbon conversion rate versus $\delta/R_0$ for run D3.
Figure 8.6 Percolation probability versus void fraction for run D14.
Figure 8.7 Percolation probability versus void fraction for run D13.
Figure 8.8 Void fraction versus number of initial voids for percolation probability = 80%.
Figure 8.9 Void fraction versus number of initial voids for percolation probability = 50%.
Figure 8.10 Solid fraction versus radius of the particle at two different conversions. A: 0% conversion. B: 70% conversion.
Chapter 9

CONCLUSIONS
Factors that govern the low and high temperature reactivities of coal chars were examined. The size of the parent coal particles had a significant influence. The cenospheric char produced from the smaller coal particles was 10-15% more reactive than char of equal size produced from larger coal particles. This is partly due to maceral segregation in the coal particle as a function of their size. Chars were formed by pyrolyzing the coals in nitrogen at temperatures ranging from 1000K to 1600K. Increasing the pyrolysis temperature reduced the H:C ratio in the char by a factor of almost 2.5 and the heat of combustion by 10-15%. The apparent oxidation rate (at 800K) decreased by as much as 50% as the pyrolysis temperature was increased. The pore size distribution in the chars changed from being bimodal at a pyrolysis temperature of 1000K, to trimodal at 1600K. Transitional porosity was evident at the higher pyrolysis temperatures. The impact of carbon conversion on char reactivity was investigated. The N₂-BET surface areas of the bituminous chars increased from 10-50 m²/g in the first few percent of conversion to 300-500 m²/g at the highest measured conversions, but the intrinsic oxidation rate defined in terms of the N₂-BET area was found to be almost constant after the initial 5% of conversion for all of the chars examined. The intrinsic rate was same for chars from different coals pyrolyzed at 1000K but showed significant variations as the pyrolysis temperature was increased. Care was taken to account for diffusion effects in the interpretation of the reactivity results. It was shown that at 800K, diffusion is not
important.

Single particle experiments were performed in a drop-tube reactor at wall temperatures ranging from 1050K to 1450K. Complete temperature-time histories were measured for individual particles. These traces show considerable variability due to the different size, shape, pore structure and mineral content of individual particles. Even though narrow size fractions of char were used, it was not possible to eliminate such variability. A novel technique was, therefore, used to analyze the traces by treating size and pre-exponential factor of each particle as a random variable. This technique was used in conjunction with an asymptotic combustion model to determine the apparent Arrhenius kinetic parameters. Using the estimated parameters provided good agreement between calculated and experimental temperature-time traces.

Chars were also partially oxidized to various conversions at high temperatures. Physical characterization of these partially oxidized samples showed that while there is some decrease in the particle size, that reduction is insufficient to account for the total carbon conversion. Thus, there is internal combustion as well. Capillary condensation and mercury porosimetry indicate that while pores greater than 200Å in radius grow during combustion, those smaller than this size remain unaffected. The surface area, which is mostly present in the micropores, is almost constant. The micropores may be inaccessible due to pore mouth closure induced by a thermal annealing mechanism. The above results from high temperature conversion are in marked contrast to those obtained from characterization of samples converted at lower temperatures (∼ 500°C). The latter indicate that there is complete penetra-
tion of oxygen into the particle at the lower temperatures. Surface areas increase significantly with early conversion as the smallest pores become accessible.

The ignition behaviour of chars was observed from the temperature-time traces of single particles. Comparing the temperature traces with the intensity traces, it was concluded that under mild oxidation conditions (wall temperatures below 1300K and oxygen partial pressures at/or below 0.21), the char particles undergo localized ignition at reactive sites leading to the development of hot-spots. These hot spots then grow, taking a finite time to engulf the whole particle. A model was proposed to explain this behaviour. Delay times predicted by the model agree closely with experimentally observed delay times.

Continuum and discrete models of single particle combustion were developed. While the continuum models assume that the reaction-diffusion problem inside the particle can be formulated in terms of differential equations which are then solved subject to appropriate boundary and initial conditions, the discrete models take into account the non-homogenous and non-symmetric nature of the actual particles. Results of parametric variations of the continuum models indicate the relative importance of different parameters like particle size, density, reaction rate, emissivity, and ash content on the burn time of each particle. Burn times predicted by the various models are similar to those observed experimentally. By proper adjustment of the key parameters, good agreement was obtained between the experimental and theoretical temperature-time traces. The discrete models show the importance of void connectivity inside the particle. While the discrete models did not consider intraparticle diffusion, they pointed out the existence of percolation in the void space.
with increase in carbon conversion.

The total surface area and pore volume distribution obtained from gas adsorption experiments are widely used to characterize porous materials. A critical analysis of the various experimental methods used and the results obtained therefrom, was performed. Algorithms commonly used to invert pressure-volume raw data into pore volume distributions with respect to pore radius were critically examined. The suitability of different gas-solid pairs was also analyzed. Special methods used to probe microporous solids were also studied.
Appendix I

PROPERTIES OF PSOC 1451 COAL
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## CHEMICAL DATA

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## ASH COMPOSITION

Ashing at 750°C

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<td>Al₂O₃</td>
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<td>V</td>
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<tr>
<td>SO₃</td>
<td>Zn</td>
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### Major Compounds
- SiO₂: 54.40 %
- Al₂O₃: 24.50 %
- TiO₂: 1.14 %
- Fe₂O₃: 9.16 %
- MgO: 0.85 %
- CaO: 2.97 %
- Na₂O: 0.61 %
- K₂O: 2.02 %
- P₂O₅: 0.34 %
- SO₃: 2.30 %

### Trace Elements
- Ba: 540 ppm
- Be: 7 ppm
- Cr: 150 ppm
- Cu: 80 ppm
- Mn: 140 ppm
- Ni: 65 ppm
- Rb: 100 ppm
- Sr: 590 ppm
- V: 200 ppm
- Zn: 85 ppm
- Zr: 240 ppm

## PETROGRAPHIC DATA

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## PHYSICAL PROPERTIES

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## ASH FUSION ANALYSIS

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Appendix II

OPTICAL PYROMETER DESIGN
AII.1 Objective

To elucidate the kinetics of char oxidation, it is necessary to know the relationship between the particle mass loss rate and its temperature. In this report, we describe a two-color optical pyrometer designed to measure the temperature of individual burning particles.

AII.2 Theory

From Planck's law for spectral distribution of radiation from a black body at temperature $T$, the intensity of radiation in the wavelength range $[\lambda, \lambda + d\lambda]$ is given by

$$i_{\lambda,\beta} = \frac{2C_1}{\lambda^5 (e^{C_2/\lambda T} - 1)}$$

where $C_1$ and $C_2$ are the first and second radiation constants. The temperature of an emitting object can be estimated by measuring its absolute emission intensity at one wavelength (typically 650 nanometers) or by measuring the relative emission intensities at two or more different wavelengths. The former approach, called brightness pyrometry, requires knowledge of the emissivity and geometry of the emitting object. The latter method is better suited to the measurement of temperatures of burning particles of microscopic size since it only requires that the particles be gray, i.e., that their emissivity not vary significantly over the wavelength range examined. The different wavelengths can be selected with monochromators or narrow band-pass filters. The signal recorded by a detector is determined by the contributions of all wavelengths that reach the detector, i.e.,

$$s_t = \int_{\lambda_t}^{\lambda_h} \epsilon_\lambda \mathcal{F}_\lambda i_{\lambda,\beta} d\lambda$$

(AII.2)
where $s_i$ is the response of the $i^{th}$ detector, $\varepsilon_\lambda$ is the emissivity, and $F_\lambda$ is the wavelength dependent response function of the optical system and detector. $\lambda_L$ and $\lambda_H$ are the low and high wavelengths allowed by the filter. The ratio of two such signals is used to estimate the temperature of the object being observed. In the special case of extremely narrow band pass measurements centered about $\lambda_1$ and $\lambda_2$, this ratio reduces to

$$R = K \left( \frac{\varepsilon_{\lambda_2}/\lambda_2 T - 1}{\varepsilon_{\lambda_1}/\lambda_1 T - 1} \right)$$

(AII.3)

where $K$ is the calibration constant into which the optical inefficiencies and emissivity factors have been lumped. $K$ is determined by calibrating the instrument at a known temperature (e.g. melting point of a pure metal like platinum). It is then assumed to be independent of temperature. This last assumption is permissible only if the source is a gray body. There is also a geometrical factor in the intensity expression if the source distance from the detector is rapidly changing. This is not necessary in the present case as the burning particle is quasi-static in relation to the detector given the short burning time and relatively slow particle velocity.

**AII.3 System Specifications**

The size of particles to be burnt is in the range 50-300µm. Expected burning temperatures are in the range 1000 K to 2500 K. Particle flow velocity is around 10 cm/s, corresponding to a cold gas flow rate of around 2 l min$^{-1}$ heated to 1500 K. The viewing dimension of the optics, 330µm was chosen to accommodate the largest particles expected. Based on the above flow rate, particle residence time in the view
volume is close to 4 ms. This sets the lower limit of the frequency response of the signal processing and real-time data acquisition systems.

AII.4 Wavelength Selection

Black bodies emit radiation whose spectral behaviour is governed by Planck's law. While coal or char particles are not expected to be black emitters, to a first approximation they shall be assumed to be gray bodies. The spectral response of a black body is shown in Figure AII.1 for various temperatures. The intensity maxima and the temperature are related by Wien's displacement law. Clearly, in order to attain maximum sensitivity, wavelengths that are smaller than the wavelength at maximum intensity, $\lambda_{\text{max}}$ should be selected. The smallest $\lambda_{\text{max}}$ occurs at the highest temperature. This then sets a natural upper limit for the choice of wavelengths. However, it should be mentioned that it is definitely possible to use wavelengths higher than $\lambda_{\text{max}}$ if loss of resultant signal strength is compensated later in the signal processing stage.

In the present case, since $T_{\text{max}}$ was 2500 K, $\lambda_{\text{max}}$ was calculated to be 1.16\,\mu m. The second criterion for choosing wavelengths is that the two wavelengths chosen be sufficiently apart to minimize experimental error and to enhance the sensitivity in temperature measurement. This implies, of course, that the smaller wavelength be quite small. The lower limit, however, is set by the intensity of the signal at the lowest design temperature, at that wavelength, that can be detected. Apart from the black body radiation, it must be kept in mind that the signal is attenuated in passing through the various optical elements before reaching the detector where it can be amplified. The last consideration regarding wavelength choice is the commercial
availability of suitable filters. Based on all these considerations, wavelengths around 1000nm and 800nm were chosen. The filters chosen had bandwidths of 70nm and their spectral responses are shown in Figures AII.2 and AII.3.

AII.5 Detector Selection

This is governed by the following considerations:

(i) Maximum sensitivity (Amps/Watts) at the desired wavelengths.

(ii) It is desirable that the detector have similar sensitivity at both wavelengths.

(iii) Low dark current.

(iv) Reasonably large detector area.

(v) Linearity of response over wide input power signals.

The detector selected was the Hamamatsu S1336-5BQ. Its spectral response characteristics are shown in Figure AII.4.

AII.6 Preamplifier Selection and Design

As soon as the optical signal is converted at the detector to a feeble voltage signal, it is essential that this small voltage signal be amplified carefully (without amplifying the noise) before it can be processed and stored. For a variety of reasons that will become clear shortly, it is desirable to have the detector and the preamplifier physically close to each other and hence the design of the detector-preamplifier package is of paramount importance. For small signals, having the detector and the preamp separated means that additional wiring has to carry the signal to the amplifier and apart from noise, the stray capacitance induced in the wiring may seriously limit the frequency response of the circuit.
The amplifier gain is a crucial parameter. The gain has to be determined from considerations below and then a suitable amplifier capable of that gain along with the desired frequency bandwidth has to be selected.

The gain is decided based on detectability of the signals. It is convenient to have signals that are at least tens of millivolts so that they can be detected easily and also input directly into the data acquisition system. It is therefore necessary to determine the optical signal strength of a typical burning particle.

For a 50µm particle with emissivity one, burning at 1000 K, the radiant energy reaching the detector after filtering at 800 nm is $1.12 \times 10^{-4}$ watts. The detector sensitivity is 0.6 amps/watt and therefore the detector signal will be $6.72 \times 10^{-5}$ amps. Accounting for various optical losses we expect microamp signals. Therefore, a gain of at least 1000 is necessary to convert this into a millivolt signal (an op-amp converts amps to volts). Of course, signal levels are more manageable at higher temperatures.

The detector amplifier circuit is shown in Figure AII.5. The single most important parameter of the detector is its junction capacitance, $C_{jn}$, which is 65 picofarads for the S1336-5BQ. $R_F$, the feedback resistance and $C_F$, the feedback capacitance of the amplifier will now be determined. An amplifier has to be chosen at this point. If the gain, frequency bandwidth, and noise criteria cannot be simultaneously satisfied then a different amplifier has to be used and the process repeated. As a start the LF357 amplifier is chosen.

**Determination of $R_F$**

The gain bandwidth of the LF357 amplifier is 12MHz (although its specifications
mention 20MHz, a conservative value is chosen). Since the time resolution required is of the order of milliseconds, it is necessary to have a frequency bandwidth of around 10kHz. Now

\[
\text{Available Gain} = \frac{\text{Gain bandwidth}}{\text{Frequency bandwidth}} \quad (AII.4)
\]

\[
\text{Available Gain} = \frac{12\text{MHz}}{10\text{kHz}} \quad (AII.5)
\]

Thus the available gain is 1200. The impedance of the junction capacitance at 10kHz, \(Z_{jn}\) is 240kΩ. Also \(\text{Gain} = \frac{R_F}{Z_{jn}} \quad (AII.6)\)

Therefore, \(R_F\) is 1200x240kΩ or 288MΩ. A conservative value of 100MΩ is chosen for \(R_F\).

**Determination of \(C_F\)**

Once the feedback resistance has been fixed, the breakpoint frequency, \(f_1\) and the gain amplitude \(A_2\) (Figure AII.6) can be determined as follows:

\[
f_1 = \frac{1}{2\pi R_F C_{jn}} \quad (AII.7)
\]

\[
A_2 = \frac{\text{Gain bandwidth}}{f_1} \quad (AII.8)
\]

Thus \(f_1\) and \(A_2\) are calculated to be 24.5Hz and 480000 respectively. The frequency \(f_2\) is defined as

\[
f_2 = f_1 \sqrt{A_2} \quad (AII.9)
\]

and therefore \(f_2\) is 17.3 kHz. The frequency \(f_3\) is chosen such that it is larger than or equal to the frequency bandwidth but smaller than \(f_2\). Let \(f_3\) be 10 kHz. Finally
\( C_F \) is defined as follows

\[
C_F = \frac{1}{2\pi R_F f_3}
\]

Putting in the appropriate values for \( R_F \) and \( f_3 \), \( C_F \) is computed to be 0.16 pico-farads.

**Noise Considerations**

The electronic noise in the circuit can be expressed in the following form

\[
\text{Noise} = 2ei + 4kT/R_F + i_n^2 + e_n^2/R_F^2
\]

The units of each term are in am^2/Hz. The last two terms are device noise terms while the first two are unavoidable intrinsic noise factors. Neglecting the device terms, minimum noise is achieved when the first two terms are set equal and is only a function of temperature.

\[
iR_{F_{\text{min}}} = 2kT/e
\]

The device noise terms are tabulated in the specifications. In the present design the choice of \( R_F \) ensures that the overall noise is manageable.

**AII.7 Additional Features**

In addition to the preamplifier, the circuit includes a programmable gain amplifier with gain factors of 10 and 100 for further signal enhancement. A divide circuit is also present in case the signal ratio is desired directly. Finally, a log-ratio circuit is also present. Of course, signal processing can always be done via software after the raw intensity signals have been acquired. To help conserve the system memory, the data acquisition system is enabled only if the signal on a particular channel
(selected by the user) exceeds a certain reference signal. This is done in the trigger circuit. Actual data acquisition is done by a Data Translation DT-2801A board at up to 20kHz rates and the digital signal is input directly into the memory of a Zenith 148 PC converted for data acquisition purposes. Then the signal is read by software and processed. A schematic of the pyrometer is shown in Figure AII.7 and the circuit is shown in Figure AII.8. Device specifications for the essential chips used in the circuit can be obtained from the respective manufacturers' catalogues: DIV 100, LOG 100, and PGA 102 (Burr Brown); LF 356, LF 357, and LM 393 (Motorola).
Figure AII.1 Spectral response of a black body.
Figure AII.2 Spectral response of the 1000nm filter.
Figure AII.3  Spectral response of the 800nm filter.
Figure AII.4 Spectral response of the Hamamatsu S1336-5BQ detector.
Figure AII.5 Circuit diagram of the detector preamplifier.
Figure AII.6 Determination of $C_F$. 

\[ A_2 \]

\[ f_1 \quad f_3 \quad f_2 \quad 12\text{MHz} \]
Figure AII.7 Schematic layout of the pyrometer.
Figure AII.8 Pyrometer electronics circuit diagram.
Appendix III

A CRITICAL ANALYSIS OF
GAS-SOLID PHYSIOSORPTION

To be submitted to the Journal of Colloid and Interface Science
Abstract

The internal morphology of three porous solids (\(\gamma\)-alumina, a partially oxidized synthetic char and PSOC-190 coal) was studied in detail using gas adsorption. Four gases (nitrogen, argon, carbon dioxide and Freon-21) were used to observe specific adsorbent-adsorbate interactions in each solid. BET surface areas and \(C\) values were determined in each case. Several methods of determining pore volume distributions (Cranston-Inkley, Yan-Zhang and Brunauer's Modelless method) in the meso and macropore range from the isotherms were examined and compared. The pore volume distribution in the micropore range was interpreted according to the M-P and Medek methods. Micropore volumes were obtained from the Dubinin-Radushkevich-Kaganer method.
AIII.1 Introduction

The use of gas adsorption to probe the internal structure of porous solids is presently an accepted and widely used experimental technique. One reason for this is that the measurement of the extent of adsorption of a gas on a solid under a given set of conditions is relatively easy. Also, physical adsorption is reversible (except for porous solids which exhibit hysteresis) and non-destructive.

The amount of gas adsorbed on a solid surface depends on the temperature of the system, the partial pressure of the particular adsorptive, and of course, the nature of the solid. Ordinarily, the extent of adsorption is measured as a function of pressure of the adsorptive at a fixed temperature. For this reason, the resulting plot is known as an isotherm.

Since physical adsorption is rather non-specific, various gas-solid pairs give similar isotherms. Brunauer et al. (1) identified five basic types of isotherms. Porous solids usually give type III isotherms, but also psuedo-type I and more rarely type V. For types III and V, enhanced adsorption at relative pressures greater than 0.4 is attributed to capillary condensation of adsorbate in the small pores of the solid. This is the region of the isotherm where information about pore size distribution can be obtained.

It has been found that desorption isotherms do not coincide with adsorption isotherms for porous materials. This phenomenon of hysteresis is attributed to different physical states of the gas-solid system which occur during the processes of evaporation and condensation. Hysteresis may be used to obtain information about pore shape; however, it is debatable as to how accurate this information is, insofar
as actual pores are rarely, if ever, describable by regular geometrical shapes.

Since the dynamics of adsorption and the exact nature of solid surfaces on the molecular level are not well understood, interpretation of experimental data is rather open to question. Even more questionable is the interpretation of data in the regime of capillary condensation. A variety of simplifying assumptions have been made in the attempt to develop models which attempt to elucidate the nature of the underlying porous structure of the solid (Wheeler (7), Brunauer, et al. (14), Kaganer (16)). In these models, some ideal pore shape is assumed \textit{a priori}. Pores are often assumed to be cylindrical or slit-shaped. In spite of the overly simplistic structures assumed, some models do, at least qualitatively, describe the particle morphology. The purpose of this paper is to examine a few of these models and apply them to isotherms of several gas-solid pairs. The models will be evaluated in light of what is known about the solid and the gas. An attempt will be made to correlate the properties of the adsorbate and adsorbent with the most suitable model.

Given the complexity of any solid surface it is not surprising that the interaction of different gases with the same solid may lead to divergent interpretations as to the underlying solid structure. With sufficient information about the adsorbing gas, however, it should be possible to draw conclusions about the fundamental nature of the solid consistent with all observations. Thus, it may be preferable to infer the pore morphology of a given solid based on its interactions with a number of different gases rather than a single one. Some attempts in that direction shall be made in the present study.
The analysis of particle morphology in the microporous region is extremely difficult because of the presence of strong overlapping pore potentials from pore walls. Also, the concept of rigid pore geometry is unrealistic at molecular dimensions. Moreover, little is known about actual potential distributions in a real solid. Some of the more common methods for analysing the pore structure in this regime are compared in the present analysis and conclusions as to their suitability are drawn therefrom.

AIII.2 Experimental Procedure

All isotherms were obtained using a system into which a continuous flow of adsorbate was introduced (Northrop, et al. (2)). The adsorptive was admitted through a 10µ diameter orifice. The flow rate was very carefully calibrated for a given set of conditions by monitoring the pressure increase in a well defined volume. Generally, flow rates were kept at about 1.0 cm³/min (STP).

During the experimental run, the system pressure was periodically recorded with the aid of a computerised data acquisition system. The pressure was measured with an MKS Baratron 270A Digital pressure gage whose output signal was recorded in a Zenith 152 computer converted for data acquisition purposes.

After the run was completed, the “dead-volume” of the system including the sample tube was measured using helium, assuming that the ideal gas law holds. Knowledge of the system dead-volume and pressure at a given time allowed calculation of the amount of adsorptive in the gas phase. The difference between the amount of adsorptive which had passed through the orifice and the amount remaining in the gas phase was the amount adsorbed at that time. The system can also
be used to obtain desorption isotherms; however, only the adsorption branch was obtained and used in this series of experiments. For further details on apparatus and procedure consult ref. (2).

Experiments were performed using four different adsorbates on three porous adsorbents. The gases used were: nitrogen at 77K, argon at 77K, carbon dioxide at 195K, and Freon-21 at 273K. Carbon dioxide at 298K was also used to obtain data for the Dubinin-Radushkevich-Kaganer (DKR) theory. The solids examined were: a γ-alumina, a partially oxidized synthetic char, and a raw coal (PSOC-190). The unique interactions of each adsorptive-adsorbent pair are important in determining the type of isotherm for that pair. Table AIII.1 lists some of the properties of the adsorptives used.

AIII.3 Inversions

Though the primary interest is in adsorption on porous materials, it will be useful to first consider multilayer adsorption on flat surfaces. Many models have been developed to explain physical adsorption on a free surface. For example, Halsey and Hill (3), Young and Crowell (4) and Sircar (5) have presented such models. However, none of these has been as successful as the theory developed by Brunauer, et al. (6).

The BET theory is based on the assumptions of a homogeneous surface and no adsorbate-adsorbate interaction. These assumptions are difficult to justify, yet the model gives a good fit to experimental data for a wide variety of gas-solid pairs over a limited range of relative pressures. Furthermore, the theory predicts the amount of adsorbate required to form a layer one molecule thick over the surface. Knowledge
of the molecular cross-sectional area allows calculation of an overall surface area. The model also gives a measure of the strength of the gas-solid interaction through the $C$ value. $C$ is defined by $\exp\{(\epsilon - \epsilon_v)/RT\}$, where $\epsilon$ is the energy of adsorption per mole of adsorbate, and $\epsilon_v$ is the energy of vaporization per mole. The BET surface area and $C$ value are useful for comparison between experiments; hence, they will be given for all gas-solid pairs (Table AIII.2).

Capillary condensation occurs in porous solids below the vapor pressure of the adsorbate. The reason for this is that a pressure difference exists across the curved meniscus of the condensed vapor. The relationship between the size of the capillary and pressure is given by the Kelvin equation:

$$\ln(P/P^0) = 2\gamma\hat{V}\cos\theta/LRT$$  \hspace{1cm} (AIII.1)

where $\gamma$ is the surface tension, $\hat{V}$ is the molar volume, $\theta$ is the angle of contact, $R$ is the gas constant and $T$ is the absolute temperature. $L$ is a measure of the width of a pore; for a cylinder, it is the radius, while for a slit it is half the distance between walls.

Wheeler (7) considered a model for capillary condensation which included multilayer adsorption. He deduced a relation between specific pore volume $V(r)$ and the volume of nitrogen desorbed over a small segment on the desorption branch of the isotherm $v(r)$:

$$v(r) = \frac{(r - t(r))^2}{r^2} V(r) + \frac{dt}{dr} \int_r^{r_0} \frac{2r' - t(r')}{r'^2} V(r')dr'$$  \hspace{1cm} (AIII.2)

where $r$ is the radius of the pore, and $t$ is the thickness of the adsorbed layer of gas. The first term on the right accounts for liquid evaporated from the pore cores, while the second term represents the amount of gas desorbed from free surfaces.
The thickness of the layer was obtained from what is known as a t-curve (8). This is simply a plot of volume of adsorptive divided by BET surface area at monolayer coverage versus relative pressure for a non-porous substance. Thus, it is a relation between the thickness of the adsorbed layer and the relative pressure. It has been pointed out that a t-curve of a material with a similar C value must be used to obtain the proper t values (9).

In principle, both the Kelvin radius and the average thickness of adsorbate can be calculated for a given relative pressure. The appropriate values can then be used in the integral equation (AIII.2). However, Wheeler was not able to come up with an iterative scheme for calculating V(r).

Several authors have developed methods for calculating V(r). Among them are Pierce (10), Dollimore and Heal (11), and Cranston and Inkley (12). The inversion method of Cranston and Inkley was difficult to carry out when it was first introduced, however the calculations are quite easy with any type of computer. For a finite adsorption step from pressure P1 (corresponding to radius r1) to P2 (radius r2) the amount of nitrogen adsorbed is

\[ v_{12} = \int_{r_1}^{r_2} \frac{(r' - t_1)^2}{r'^2} V_{r'} dr' + (t_2 - t_1) \int_{r_2}^{\infty} \frac{V_{r'} (2r' - t_1 - t_2)}{r'^2} dr' \]  (AIII.3)

where \( t_1 \) and \( t_2 \) are the adsorbed layer thicknesses at the respective pressures and \( V_{r'} \) is the volume of pores with radii in the interval \( r_1 \) to \( r_2 \). It has been shown (12) that \( V_{12} \) can be approximated by

\[ V_{12} = R_{12} \left( v_{12} - 4 (t_2 - t_1) \sum_{r_2 + \delta r}^{r_{\text{max}}} \frac{(r - 1/2 (t_1 + t_2))}{2r^2} V_r \Delta r \right) \]  (AIII.4)
Yan and Zhang (13) have also developed a means of calculating pore volume distribution based on Wheeler's model. The volume of pores of mean radius \( r_i \) is given by

\[
\Delta V_i = R_i \left( \Delta v_i - 2 \Delta t_i \sum_{j=1}^{i-1} \frac{\Delta V_j}{r_j} + 2 \ell_i \Delta t_i \sum_{j=1}^{i-1} \frac{\Delta V_j}{r_j^2} \right)
\]

where \( \ell_i \) refers to the pore group and the overbar denotes average values. They have shown that this method gives essentially the same results as the Cranston-Inkley method. In fact, the only difference is that \( R_{12} \) is essentially a log mean of \( r_1 \) and \( r_2 \), while \( r_i \) is an arithmetic mean. Yan-Zhang's method is more compact, however.

A rather different line of thought was used by Brunauer (14) to develop his "modelless" theory. This model is based on the thermodynamic identity

\[
\gamma dS = \mu da
\]

This equation relates change in surface area \( dS \) of the adsorbate to the free energy change \( da \) through the surface tension \( \gamma \) and the chemical potential \( \mu \). Integration yields

\[
S = \frac{1}{\gamma} \int A_n da = \frac{1}{\gamma} \int RT \ln(P/P^0) dn
\]

where \( R \) is the ideal gas constant, \( T \) is the absolute temperature, \( P^0 \) is the vapor pressure, \( dn \) is the incremental number of moles of adsorbate and \( A_n \) is the free energy of adsorption. The method is called modelless because it uses the hydraulic
radius as a characteristic length parameter for the cores instead of the more usual core 'radius'. (The core is the volume of the pore which is not occupied by adsorbed gas.) The hydraulic radius is defined as follows:

\[ r_h = \frac{V}{S} \quad (AIII.9) \]

where \( V \) is the volume of adsorbate and \( S \) is the wetted surface area.

Again, both the gas evaporating from the cores and the gas desorbing from open surfaces must be accounted for. Unfortunately, one must assume a shape for the pores to calculate the free surface area.

An example of the calculations is as follows: for relative pressure from 1 to 0.95, \( V_1 = (n_{1.0} - n_{0.95})\nu \) where \( \nu \) is the molar volume of liquid. Then, \( S_1 \) is obtained from equation (AIII.8). The definition of hydraulic radius is then used to obtain a measure of average core size in this range of relative pressures. For the next step, \( V_2 = (n_{0.95} - n_{0.90})\nu - V'_2 \). The second term is the correction for gas which is desorbing from the free surface. If the pores are assumed to be parallel slits, \( V'_2 = (t_1 - t_2)S_110^{-4} \), for \( t \) in Å, \( S \) in m\(^2\) and \( V \) in cm\(^3\). The correction for cylindrical pores is more complicated but it does not change the result significantly.

As it stands, the modelless method describes the size and volume distributions of the cores. In order to compare its results with those of other inversions, the pore size and pore volume distributions are needed. However, in going from cores to pores some assumption regarding geometry must be made; hence, the resulting method is no longer modelless. In the present analysis the statistical thickness calculated at the appropriate partial pressure was added to the core hydraulic radius to determine the pore radius. The core volume was also increased by an amount \( S_i t_i \).
to determine the pore volume. These modifications were made in order to facilitate comparison of the now ‘modelless’ method with the other schemes.

The procedures above pertain to pores in which capillary condensation takes place. The lower limit of applicability of the Kelvin equation (AIII.1) occurs at a relative pressure of about 0.4, which corresponds to a radius of 16 Å. Below this, the concept of bulk surface tension becomes difficult to justify. Of course, smaller pores may be present in the solid. Thus, it is necessary to consider analyses which deal with these micropores.

One such method is known as the MP method(15). This theory is rooted in the concept of the t-curve described above. A v-t curve is a plot of the liquid volume uptake versus a statistical thickness which is obtained from a t-curve. It is imperative that a t-curve of a similar C value be used.

A v-t plot for a non-porous adsorbent will be a straight line with a slope equal to the surface area (8). A microporous adsorbent will show a downward deviation at lower relative pressures, as shown later. The reason for this is the following: at the lowest pressures, adsorption occurs over the entire surface. As more adsorption occurs, some of the micropores become filled with adsorbate. Thus, less surface is available for adsorption. This is reflected in the v-t curve by a decrease in slope, and hence, apparent surface area.

Actually, surface area in pores of this size cannot be strictly defined because the pore dimensions are similar to the size of individual molecules. Whether the pore is cylindrical or slit-shaped, the total area “covered” by a molecule will be quite different from that which it covers on a free surface.
Dubinin and Radushkevich originally developed a theory for micropore volume analysis of carbonaceous solids; however, Kaganer (16) extended it to surface area analysis. The following assumptions are made concerning microporous materials:

1. The potential distribution is of the form

\[ N = N_0 \exp(-KE_0^2) \]  \hspace{1cm} (AIII.10)

where \( N \) is the number of moles of gas adsorbed, \( N_0 \) the total number of moles at monolayer coverage, \( E_0 \) is the energy of adsorption of the reference adsorbate and \( K \) is a constant characteristic of the system.

2. All adsorbates can be scaled to a single reference adsorbate

\[ N = F(E/\beta) \]  \hspace{1cm} (AIII.11)

where \( \beta = E/E_0 \).

The work required to isothermally compress a gas from \( P \) to \( P_0 \) is

\[ E = RT \ln(P_0/P) \]  \hspace{1cm} (AIII.12)

Simple substitution of (AIII.11) and (AIII.12) into (AIII.10) gives

\[ N = N_0 \exp(-K(RT)^2 \ln^2(P_0/P)/\beta^2) \]  \hspace{1cm} (AIII.13)

or, taking logarithms,

\[ \log N = \log N_0 - 2.303K(RT/\beta)^2 \log^2(P_0/P) \]  \hspace{1cm} (AIII.14)

A plot of \( \log N \) vs. \( \log^2(P_0/P) \) should give a straight line, from which the number of moles at monolayer coverage can be obtained. Given a molecular cross-sectional area, the total surface area for the sample can be calculated. Again, it is
debatable as to what to use for the value of the the area of a molecule sitting on a particular surface.

Medek (17) extended this theory to determine pore size distributions. Working from Dubinin's equation (AIII.10), he assumed that the potential inside of a pore could be expressed as \( \phi = kr_{eq}^3 \), where \( k \) is a constant and \( r_{eq} \) is the equivalent radius of the pore. Substitution into (AIII.10) yields:

\[
\frac{N}{N_0} = \exp\left(\frac{-\kappa}{E}\right)^{n r_{eq}^{-3n}}
\]  

(AIII.15)

where \( \kappa \) is related to \( k \) and the exponent \( n \) is close to 2 (but treated as a parameter in the Medek analysis). This expression can be differentiated to get the distribution.

AIII.4 Results

AIII.4.1 Isotherms

The isotherms for nitrogen (N), argon (A), carbon dioxide at 195K (C) and Freon (F) on \( \gamma \)-alumina are shown in Figure AIII.1. They are plotted as a function of relative pressure (\( P/P^0 \), where \( P^0 \) is the vapor pressure of adsorptive at the system temperature) so that they can be compared on a single plot. All isotherms on the \( \gamma \)-alumina are typical Type IV isotherms. This indicates that the solid is porous, with most pores being in the meso- to macro-pore range (i.e. more than 16 Å in diameter). The similarity between the nitrogen and argon isotherms is to be expected since both molecules are similar in size. The small difference in shapes is due to the slight difference in the relative rates of gas admission in the two cases. Carbon dioxide (196K) and Freon also produce similar isotherms. Since these molecules are larger, the total molar amounts adsorbed are smaller. Multiplication
of the respective molar volumes shows that the total pore volume is nearly 0.40 cm$^3$/g in all four cases. The isotherm for carbon dioxide on γ-alumina at 298K is shown in Figure AIII.2. It appears as though there is Type I behavior followed by further adsorption. It is possible that at very low relative pressures, carbon dioxide is adsorbed only by the most active sites. At higher pressures, there is more general adsorption.

The nitrogen, argon and carbon dioxide at 195K isotherms on oxidized char are classic examples of pseudo-Type I isotherms (see Figure AIII.3). This shows that the char contains a very large number of micropores. Once these micropores are filled, there is very little subsequent adsorption. Surprisingly, the amount of argon adsorbed is significantly greater than the amounts of the other gases, contrary to the expectation that nitrogen and CO$_2$ should be adsorbed to a greater extent due to their smaller minimum molecular dimensions and significant quadrupole moments. While the Freon also produces a Langmuir type of isotherm, it is evident that there are two distinct regimes of adsorption (as manifested by the different slopes). This suggests that the char-Freon interaction is site specific and points to the existence of two distinct types of active sites. Given the larger size of the Freon molecule molecular sieve effects may affect its penetration into the very smallest pores. The pore volumes of the char are (in cm$^3$/g) 0.039 (N$_2$), 0.033 (CO$_2$), 0.05 (Freon) and 0.06 (Ar). Incorporating effects of multilayer adsorption in the Freon case will reduce its pore volume but no simple explanation can explain the anomalous argon result. Figure AIII.2 shows the resulting isotherm for carbon dioxide at 298K on the partially oxidized char.
The nitrogen and argon isotherms on PSOC-190 (Figure AIII.4) showed rather unusual behavior. At the lowest pressures there was very little adsorption. However when the relative pressure reached a critical value (0.04 for N$_2$ and 0.08 for Ar) adsorption increased significantly. The reason for this appears to be lack of equilibration time in the dynamic adsorption apparatus used in this study. At some higher partial pressure there was significant adsorbate uptake at constant partial pressure indicating the establishment of a pseudo-steady state. This is not due to pressure drop in the bed as the particle size was 425µ and the bed was free flowing. Equilibration is not a limiting factor for CO$_2$ or Freon possibly due to their more complex interactions with the surface. CO$_2$ adsorbed most strongly on the coal. Freon gave a typical type IV isotherm.

**AIII.4.2 BET Plots**

The BET plots for nitrogen (N), argon (A), carbon dioxide at 195K (C), and Freon (F) on γ-alumina are shown in Figure AIII.5. All are quite linear, and give reasonably consistent surface areas. The areas were calculated using molecular cross-sectional areas obtained from Lowell and Shields (18), and Gregg and Sing (19). The computed specific areas for this method are 207 m$^2$/g (N), 174 m$^2$/g (A), 200 m$^2$/g (C) and 205 m$^2$/g (F).

Figure AIII.6 shows the BET plots for the same adsorbates on oxidized char. It is interesting to note the similar shapes of the nitrogen, argon and carbon dioxide plots. The upward deviation at higher relative pressures is due to the fact that there is so little additional adsorption in this region. Once the micropores of the solid are filled with adsorbate, the solid appears virtually non-porous. The specific
areas were found to be: \(400 \text{ m}^2/\text{g} \) (N), \(573 \text{ m}^2/\text{g} \) (A), \(430 \text{ m}^2/\text{g} \) (C) and \(433 \text{ m}^2/\text{g} \) (F).

In Figure AIII.7 the BET plots on the coal are shown. The specific areas were: \(23.1 \text{ m}^2/\text{g} \) (N), \(22.8 \text{ m}^2/\text{g} \) (A), \(147.5 \text{ m}^2/\text{g} \) (C) and \(151.6 \text{ m}^2/\text{g} \) (F).

The \(C\) values for these isotherms (as calculated from the BET plots) are shown in Table AIII.2.

### AIII.4.3 Pore Volume Distributions

The inversions described above (Cranston-Inkley, Yan-Zhang and Modelless — hereinafter referred to as CI, YZ and ML, respectively) were applied to each of the isotherms to determine the pore volume distributions in each case. Pore volume distributions were chosen instead of pore surface area distributions due to the following reasons: (a) Fundamentally, the concept of surface area in porous (or microporous) solids is nebulous on close scrutiny. Surface areas are useful only as a comparison between different materials; therefore, their intrinsic value has been questioned by many researchers (20). (b) Geometrical assumptions, often simplistic, must be made to derive surface area distributions from the experimental data. (c) Most inversions naturally lend themselves to pore volume distribution determinations.

In this section, all plots are in the form \(dV/d\log r\) vs. \(\log r\). The reason for this is that it is easy to visually integrate to obtain total void volume, and to view the contributions of different size intervals to the total porosity.

The CI and YZ distributions in all cases showed virtually identical results, as shown in Figures AIII.8a-d. As discussed earlier, both methods are essentially the same. In order to observe the effect of the calculation, two approximations for the
thickness have been used in each method: (a) a polynomial function of the relative pressure \( C \sim 130 \) and (b) the Halsey expression \( C \sim 100 \). For a given expression of thickness, the two methods gave indistinguishable results (Figures AIII.8a,c or Figures AIII.8b,d). This shows that the method of calculation of mean radius (log mean vs. arithmetic mean) is unimportant. Figure AIII.9 shows thickness as a function of relative pressure for these two approaches. Note that the appropriate range of relative pressure is 0.4 to 0.95. The use of the Halsey thickness resulted in total pore volumes which were about 5% lower than those from the polynomial approximation. The reason for this is that the Halsey thickness was slightly smaller than that calculated by the polynomial approximation.

Pore volume distributions were obtained for the different adsorptives on two different solids using the CI method (see Figures AIII.10a,b). The char did not show appreciable volumes in this range of pore sizes, so they will not be considered here. For alumina (Figure AIII.10a), the distributions from the nitrogen and Freon isotherms were strikingly similar. Counterintuitively, the distribution from argon is different. While total pore volumes (equal to area under the curve) are similar, the argon distribution is skewed toward larger pore sizes. The argon was admitted at a higher relative rate than the nitrogen; hence, there was less time for equilibration of the gas with the liquid in the pores. Thus, adsorption took place at higher relative pressures. This shows the importance of allowing adequate times for equilibration. The similarity of the nitrogen and Freon results may seem surprising. However, if the pores are sufficiently large, and if the interaction with the surface is similar, the result is reasonable. Freon has a higher dipole moment, yet it appears to have
little influence on the surface interaction. This may indicate that the nature of the adsorption is rather non-specific, and that the adsorbent is relatively passive. It is also possible that the Freon interaction is very strong on a local level. This interaction may be so localized that there is no overall orientation effect.

The pore volume distributions for PSOC-190 are shown in Figure AIII.10b. Here, the nitrogen and argon distributions differ for the same reasons as described above. Freon, on the other hand, gives a much larger total pore volume. It appears as though Freon has a strong specific interaction with the coal. This may lead to orientation of the adsorbate, which in turn may lead to enhanced adsorption.

The modelless method was applied only to the nitrogen isotherms. The resulting distributions are shown along with those of CI (Figures AIII.11a-c). Recall that the hydraulic core radii calculated by the method were augmented by the adsorbed layer thickness as calculated by the Halsley equation (3). The pore radii in the two methods cannot be directly compared because CI has assumed a cylindrical pore geometry, while the modelless method uses the hydraulic radius. Since the hydraulic radius of a cylinder is half of its radius, the radii from the modelless method could be multiplied by two to obtain some comparison.

AIII.4.4 Microporosity Analysis

The v-t plots for nitrogen adsorption on the porous solids are shown in Figure AIII.12. The slope for the alumina (for t=3 to 5 Å) gave an area of 211 m²/g, which was quite close to the BET area. The v-t plot gave an area of 34 m²/g for the PSOC-190. This area was significantly higher than the corresponding BET area. This is an unusual case where the two methods do not agree even though the
v-t plot does not show significant microporosity.

The area for the char had to be estimated from the slope of a line passing through the origin tangent to the plot. This resulted in an area of 750 m²/g, which was not even close to the nitrogen BET area. These plots show that only the char has significant microporosity. Therefore, the MP analysis was applied only to the char.

The MP method result is shown in Figure AIII.13. According to this analysis, the vast majority of pores have radii between 3.5 and 5 Å. This seems quite reasonable in light of the original isotherm.

The DRK Theory was applied to the isotherms of carbon dioxide at 298K (see Figure AIII.14). Strictly speaking, this theory was developed for carbonaceous solids with micropores. Since the assumptions are not too stringent, the theory was applied to the alumina as well. The plot for PSOC-190 (C) was quite linear; those for γ-alumina (A) and oxidized char (O) were less so. The region of lower log N was used in the calculation of specific area. The areas calculated by this method were: 161 m²/g for alumina, 1400 m²/g for char, and 162 m²/g for PSOC-190. The values for γ-alumina and PSOC 190 are similar to those calculated from the BET method for CO₂. The value for char is significantly greater.

The Medek method was applied to these isotherms in addition to several others. Figures AIII.15a-b show the results for CO₂ and Freon on the porous solids. The form of the curve is the same in all cases; only the magnitude and position of the maxima are different.
AIII.5 Discussion

For the materials studied, the continuous flow method gives isotherms similar to those obtained by the traditional method in a fraction of the time. Any discrepancy is due to the non-equilibration of the gas phase with the adsorbed phase.

The adsorptives were selected because of their different molecular characteristics. Nitrogen, generally regarded as the “standard adsorbate”, is non-polar and axially symmetric. Argon, another commonly used adsorptive, is also non-polar, but is spherically symmetric. Carbon dioxide has a strong quadrupole, and is easily polarizable. Freon is larger than the others, and possesses a permanent dipole. In some orientations, however, its minimum dimension is comparable with that of nitrogen or argon.

In spite of these differences, there was little effect on the overall form of the isotherm for a given adsorbent. The only significant exceptions were Freon on char and CO$_2$ on PSOC-190. The former was probably due to slow diffusion of large Freon molecules into the small micropores, as explained above. The latter was likely due to specific adsorbate-adsorbent interaction, a small minimum dimension, and high absolute temperature.

The areas calculated for the microporous char are rather questionable. The models used assume that the adsorbate molecule sits on a locally flat surface. However, when a molecule is in a pore which has a diameter on the order of molecular dimensions, it will cover a much larger area. The discrepancy between the nitrogen and argon areas shows that the way in which the molecules are packed into the pores is also an important consideration.
It was interesting to see that the DRK model gave an area for γ-alumina that was consistent with the other methods. As described previously, the model was developed from a theory of micropore adsorption. The alumina has few micropores, but it is rich in oxygen. It is possible that the carbon dioxide interaction with oxygen-containing groups is similar in magnitude to its interaction with the walls of a micropore. That the total area obtained is close to the others may be fortuitous.

As mentioned above, the Medek method gave curves which appeared to be self-similar for all adsorbents and adsorptives. Furthermore, it showed significant microporosity for the alumina, which is rather questionable. It seems as though this method simply transforms a given isotherm into a log normal curve.

Alumina is one of the most studied and relatively “well-characterised” material of all the solids considered in this study. According to the present experimental findings, conclusions can be drawn regarding its morphology by applying a unified analysis of surface area, pore volume and pore volume distribution. The BET surface area was around 200 m²/g for all gases except argon, which gave a lower value, possibly due to non-equilibration effects. The v-t plot gave a surface area which was very close to the BET values; it also indicated an absence of micropores. While the Medek method gave a micropore distribution, its validity is doubtful.

Considering the similarity of the nitrogen and Freon CI pore size distributions, they are likely to give a reasonable picture of the true porosity. The modelless method is difficult to interpret without having some idea about pore shape. Unfortunately, it is difficult to infer anything about pore shape without a desorption isotherm.
The partially oxidized synthetic char is not a common material, but it gives isotherms similar to many other microporous substances, like molecular sieves or activated charcoals. In this case, the micropores were large enough so that diffusion was not a problem. Not surprisingly, the microporous nature of the material precluded the use of CI and YZ. The MP method gave what appears to be a reasonable distribution. The Medek method gave distributions with much larger pore volumes and radii.

The PSOC-190 is a typical bituminous coal. As with many raw coals, reliable determination of particle morphology is difficult at best. The existence of micropores which are of the order of molecular dimensions causes molecular sieve effects to be extremely important. Also, diffusion into pores of this size may be via an activated process. To counter these effects, an adsorptive with small minimum molecular dimension and high critical point is generally used for determining the isotherm. CO$_2$ at 196 or 298K is usually the adsorptive(21) of choice for these coals (Figure AIII.3). However, applying the BET analysis to the CO$_2$ at 196K isotherm, it is seen that, while the adsorptive uptake is quite high, the $C$ value is quite small (Table AIII.2). Since the $C$ value indicates the strength of the gas-solid interaction, the only possible conclusion that can be drawn is that CO$_2$ adsorbs strongly on itself. Care must be taken to interpret surface areas in this case.

AIII.6 Conclusions

Examination of the isotherms shows that the form of the isotherm is essentially independent of the type of adsorptive (for small enough molecules) for a given solid.
The BET areas were generally consistent with areas calculated by other methods for non-microporous solids. When micropores are present, the agreement was not as good. Of course, interpretation of area on this level is fraught with uncertainty.

The equivalent methods of CI and YZ appear to be the most suitable means of obtaining pore size distributions in the mesopore range. The modelless method is also quite useful; however, additional information regarding pore shape must be obtained or assumed in order to formulate a reasonable picture of the internal structure.

The MP analysis is the method of choice for pore size distributions in the micropore range. The Medek method is somewhat questionable.

AIII.7 Acknowledgements

This work was supported by DOE Grant No. DE-AC2284FC70915.


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<th>q</th>
<th>$V_{liq}$ (cm$^3$/g mol)</th>
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Table AIII.1 Properties of the adsorptive gases.
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Table AIII.2 Summary of adsorptive-adsorbate interactions.
Figure AIII.1 Nitrogen, Argon, CO$_2$ (196K), and Freon-21 isotherms on $\gamma$-alumina.
Figure AIII.2 CO₂ isotherms at 298K on γ-alumina, oxidised char and PSOC-190.
Figure AIII.3 Nitrogen, Argon, CO₂ (196K), and Freon-21 isotherms on oxidized char.
Figure AIII.4 Nitrogen, Argon, CO₂ (196K), and Freon-21 isotherms on PSOC-190 Coal.
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Figure AIII.6 BET plots for oxidised char.
Figure AIII.7 BET plots for PSOC-190 coal.
Figure AIII.8a Pore volume distribution of $\gamma$-alumina from nitrogen — Cranston-Inkley inversion with polynomial thickness.
Figure AIII.8b Pore volume distribution of γ-alumina from nitrogen — Yan-Zhang inversion with polynomial thickness.
Figure AIII.8c Pore volume distribution of γ-alumina from nitrogen — Cranston-Inkley inversion with Halsley thickness.
Figure AIII.8d Pore volume distribution of γ-alumina from nitrogen — Yan-Zhang inversion with Halsey thickness.
Figure AIII.9 Comparision of polynomial and Halsley thicknesses as a function of relative pressure.
Figure AIII.10a Pore volume distributions of \( \gamma \)-alumina from different adsorptive gases using the Cranston-Inkley inversion.
Figure AIII.10b Pore volume distributions of PSOC-190 coal from different adsorptive gases using the Cranston-Inkley inversion.
Figure AIII.11a Comparision of pore volume distributions of γ-alumina by nitrogen using the Cranston-Inkley (—) and Modelless Inversions (— - -).
Figure AIII.11b Comparison of pore volume distributions of oxidized char by nitrogen using the Cranston-Inkley (—) and Modelless Inversions (− − −).
Figure AIII.11c Comparision of pore volume distributions of PSOC 190 coal by nitrogen using the Cranston-Inkley (—) and Modelless Inversions (— —).
Figure AIII.12 V-t plots with nitrogen.
Figure AIII.13 MP distribution with nitrogen on oxidised char.
Figure AIII.14 DRK plots with nitrogen.
Figure AIII.15a Pore volume distributions of several solids using CO$_2$ at 196K and the Medek Inversion.
Figure AIII.15b  Pore volume distributions of several solids using Freon and the Medek Inversion.
Appendix IV

HIGH TEMPERATURE REACTOR

EQUIPMENT DETAILS
AIV.1 Introduction

This appendix provides details, specifications, and other information on the construction of the high temperature reactor. Manufacturers’ names, addresses and part numbers are also given.

The major components of the reactor are as follows: the structural frame, the air preheater furnace, power supply for the furnace, temperature controller, air preheater tube, test section, particle feeder, water-cooled particle injector, and particle collector probe. In addition, the following supporting equipment was used: the optical pyrometer, suction pyrometer, disappearing filament pyrometer, and the data acquisition system. Other minor parts include the vacuum pump, condenser unit, slide, various pressure gages, flowmeters, thermocouples, valves, cooling water lines and air lines.

The details of the electronic design of the pyrometer are described in Appendix II. The part numbers of the optical equipment will be given in this Appendix. The overall layout schematic of the system is shown in Figure AIV.1.

AIV.2 Structural Frame

The furnace and the test section are mounted on a steel frame that was designed and fabricated at Caltech. It is shown in Figure AIV.2. The structural members are angle iron, the various dimensions of which are shown in the figure. The joints are arc-welded for integrity. Levelling screws are provided to align the structure.

AIV.3 Air Preheater Furnace

This furnace was purchased from Applied Test Systems, Butler, PA 16003. It
is a series 3310 tube type furnace with a maximum temperature rating of 3000°F (1650°C). Its tube and external diameters are 4.5in (114.3mm) and 16in (406.4mm) respectively. Its height is 21in (533.4mm) inclusive of the insulation layers at the top and bottom. It uses 8 Kanthal Super 33 heating elements (Kanthal Corporation, Bethel, CT 06801). These 3/6 style elements are capable of prolonged service at temperatures as high as 3200°F (1760°C). The elements are 11in (279.4mm) long. The eight elements are connected in two parallel banks of four elements each.

The furnace has a single heating zone 11in (279.4mm) in length. The power required to run the furnace is 5.25kW at 58 volts (90.5amps). The insulation around the radiation cavity is a low "K" factor cast ceramic fiber, capable of service to 3000°F (1650°C). There is a thin stainless steel shell on the outside of the furnace with one thermocouple port via which the Type B control thermocouple (Pt-6%Rh/Pt-30%Rh) can be introduced into the heating zone.

The approximate heat-up time of the furnace, from room temperature to 1600°C is about 45 minutes.

AIV.4 Furnace Power Supply

The furnace power supply was procured from NWL Transformers, Bordentown, NJ 08505. The schematic of the transformer and the regulating system is shown in Figure AIV.3. The unit consists of a 8kW, single phase, 60Hz transformer with a Thyristor phase angle controller. For safety purposes, the unit is equipped with a current limiting device. The level of the output power is determined by the signal from the temperature controller (0-5V, D.C.). The magnitude of this signal depends on the difference between the control thermocouple signal and the desired
set temperature.

The whole unit is housed in a NEMA I enclosure designed to operate with natural convection cooling. Additional fan cooling is not necessary.

**AIV.5 Temperature Controller**

The temperature controller was purchased from Omega Engineering Inc., Stamford, CT 06907 (Part Number CN-2001A B-DC1). It is a microprocessor-based controller that accepts the voltage signal from the Type B thermocouple and generates a 0-5 volt D.C. signal. The magnitude of this signal depends on the difference between the thermocouple output and the furnace set temperature. The controller signal is sent to the power supply.

**AIV.6 Air Preheater Tube**

Primary air at room temperature is heated in the furnace heating zone before entering the test section. It flows through the heating zone in a cast ceramic tube made by the Carborundum Company, Keasbey, NJ 08832 (Matl: Refrax 20). It is 36in (914.4mm) long. Its internal and external diameters are 4in (101.6mm) and 4.5in (114.3mm) respectively. This tube is capable of withstanding high temperatures while maintaining reasonably high thermal conductivity at those temperatures. Moreover, since its radial thermal conductivity is much higher than its axial conductivity, there is not much heat loss to the outside.

**AIV.7 Test Section**

The actual test section, in which the char is mixed with the hot primary air and combusted, is a cylindrical hollow tube 12in (304.8mm) long with a 2in (50.8mm)
internal diameter. The wall thickness is 0.5in (12.7mm). It is made of light weight, high temperature (up to 1650°C), fibrous ceramic: ZAL 15 (85% alumina; 15% silica), supplied by Zircar Fibrous Ceramics, Florida, NY 10921. This material is very easily machinable.

In order to have optical access to the test section, two ground and polished plate quartz windows, 9in (228.6mm) long, 0.75in (19mm) wide, and 0.25in (6.4mm) thick are mounted in the walls of the ceramic tube diametrically opposite each other. The windows allow the light signal from the burning char particles to fall on the pyrometer detector and thereafter their temperature can be determined. The quartz plates were supplied by U.S. Fused Quartz (Brea, CA 92621). They are glued to the ceramic using high temperature alumina cement from Zircar Fibrous Ceramics (see address above).

AIV.8 Particle Feeder

This fluidized entrainment apparatus was designed and built at Caltech. A schematic diagram is shown in Figure AIV.4. The char sample to be injected into the furnace is put in a glass test-tube 6in (152.4mm) long with an internal diameter of 0.5in (12.7mm). The tube is then sealed from the top with an aluminum adaptor that allows entrainment air to be injected into the test-tube. This air flow rate is adjusted to give desired char feed rate. The entrained char then leaves the tube via a 0.125in (3.175mm) outer diameter steel tube that leads it directly into the test section. Since the level of the char in the test-tube decreases with time, the tube is mounted on a simple apparatus that moves it up at the desired rate so as to keep the level of char constant with respect to the lower edge of the entrainment tube.
This apparatus consists of a screw, powered by a small motor (0-120V, 1.5amp, 2000rpm) via pulleys and belts. The motor rpm is reduced significantly by two reduction gears with a combined ratio of 1:60. Motor speed control is achieved by controlling the input voltage using a simple transformer. All the small parts for this apparatus were obtained from Winifred M. Berg, Fort Rockaway, NY, 11518. The base and adaptor were machined at Caltech.

AIV.9 Particle Injector

The narrow tube carrying the char particles is introduced to the test section by passing it concentrically down the air preheater ceramic tube. To keep the char at room temperature, the injector tube is water cooled by a double water jacket. The length of the water cooled injector is 42in (1066.8mm). Its outer wall is then insulated using ZAL 15 insulating board cut to the proper geometry. Cooling water is introduced directly at the pressure of the mains, without using a pump. Since the volume of water needed is not significant, a open loop system is used, the waste water being returned to the drain. Diagrams of the injector are shown in Figures AIV.5a-c.

AIV.10 Particle Collector Probe

This is a triple jacket probe with an outer diameter of 1.0in (25.4mm) and an internal diameter of 0.5in (12.7mm). It can be moved to any axial location inside the test section tube in order to collect partially burned char at various carbon conversions. The two outer jackets carry cooling water. The innermost jacket provides a path for a quenching gas (nitrogen or argon) to be introduced along with the char so
that the chemical reaction is terminated immediately upon entry of the char into the probe. The quenching gas and the sample are drawn into the probe by suction provided by a vacuum pump. The char is collected on a glass fibre filter 47mm in diameter (Gelman, Type A/E). This filter sample is then removed and analyzed. The length of the probe is 22in (558.8mm). It is attached to a rack and pinion type axial slide. A diagram is shown in Figure AIV.6. The steel tubes for the probe and the injector were obtained from Tube Sales, Los Angeles, CA 90040.

**AIV.11 Pyrometers**

The design of the Optical Pyrometer has been described earlier. The optical rails, carriers, lens holders, and posts were obtained from Newport Corporation, Fountain Valley, CA 92708. The lenses, beam splitter, and precision pin holes were from Melles Griot, Irvine, CA 92714. The filters, beam probes, and optical fibres were brought from Oriel Corporation, Stratford, CT 06497. The linear positioning slides were manufactured by Daedal Corporation (Harrison City, PA 15636). Two such stages (Model 4804 M) were used at right angles to give precise control in the X and Y directions. A 24in (609.6mm) vertical slide was built at Caltech and used as the adjustable Z axis. The various parts, part numbers and the suppliers are listed in Table AIV.1.

The suction pyrometer was designed and built at Caltech. It uses a Type S thermocouple (Omega Engineering Inc.)

The disappearing filament pyrometer was used to find the temperature of a fairly dense stream of particles. This was used to verify the temperature obtained from the optical pyrometer.
AIV.12 Additional Minor Equipment

These include the vacuum pump, condenser unit, pressure gages, flow meters, thermocouples, valves, cooling water lines, air and gas lines, and the exhaust hood.

The condenser unit was fabricated and built to extract any condensed moisture in the line before it passed through the vacuum pump. Various flow meters were used to monitor the flow rates of the primary, entrainment, and dilution gas streams. Matheson flow meters (Dwyer Instruments Inc., Anaheim, CA 92806) as well as pressure drop flow meters were used. The latter were used for their flexibility. Pressure gages were from Dwyer (Magnahelic type). While 0.25in poly-flo lines were used for the gas lines, water lines were of copper. The exhaust hood was fabricated at Caltech.

AIV.13 Data Acquisition

The light intensity signals from the burning char particles were converted to voltage signals in the optical pyrometer. After suitable noise filtering and amplification, these signals were sent to the data acquisition system. This consists of a Zenith 148 Personal Computer with 640K RAM and two 360K floppy drives. The computer was equipped with a 8087-2 math co-processor for speed. For data acquisition purposes, it was equipped with an A/D converter and a Data Translation DT-2801A board rated at 20kHz. Data from the pyrometer was dumped via DMA into the computer’s RAM and later retrieved for analysis. Finally, software programs written in Fortran-77 were used to convert the data into temperature measurements. Suitable calibration data was used at this point.
<table>
<thead>
<tr>
<th>PART NAME</th>
<th>PART NUMBER</th>
<th>MANUFACTURER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filters</td>
<td>57670, 57750</td>
<td>Oriel Corp.</td>
</tr>
<tr>
<td>Beam Probes</td>
<td>77646</td>
<td>Oriel Corp.</td>
</tr>
<tr>
<td>Fused Silica Lens</td>
<td>41254</td>
<td>Oriel Corp.</td>
</tr>
<tr>
<td>Plano-Convex Lens</td>
<td>01 LPX 219</td>
<td>Melles Griot</td>
</tr>
<tr>
<td>Plano-Convex Lens</td>
<td>01 LPX 113</td>
<td>Melles Griot</td>
</tr>
<tr>
<td>Plano-Convex Lens</td>
<td>01 LPX 041</td>
<td>Melles Griot</td>
</tr>
<tr>
<td>Cube Beam Splitter</td>
<td>02 BSC 029</td>
<td>Melles Griot</td>
</tr>
<tr>
<td>Precision Pin Holes</td>
<td>04 PIP 013</td>
<td>Melles Griot</td>
</tr>
<tr>
<td>Optical Rails</td>
<td>MRL-6, MRL-12</td>
<td>Newport Corp.</td>
</tr>
<tr>
<td>Carriers</td>
<td>MTC, MTF</td>
<td>Newport Corp.</td>
</tr>
<tr>
<td>Lens Holders</td>
<td>LH1-P, LH1-1</td>
<td>Newport Corp.</td>
</tr>
<tr>
<td>Lens Mounts</td>
<td>LM-1</td>
<td>Newport Corp.</td>
</tr>
<tr>
<td>Posts</td>
<td>MSP-1</td>
<td>Newport Corp.</td>
</tr>
<tr>
<td>Post Holders</td>
<td>MPH-1</td>
<td>Newport Corp.</td>
</tr>
<tr>
<td>Silicon Photodiodes</td>
<td>S1336-5BQ</td>
<td>Hamamatsu Corp.</td>
</tr>
<tr>
<td>Linear Slides</td>
<td>4804 M</td>
<td>Daedal Corp.</td>
</tr>
</tbody>
</table>

Table AIV.1 Details of the Optical Pyrometer components.
Figure AIV.1 Schematic of the high temperature reactor.
Figure AIV.2 Structural frame for the high temperature reactor.
Figure AIV.3 High temperature reactor power supply schematic.
Figure AIV.4 Schematic of the char particle feeder.
Figure AIV.5a Schematic of the particle injector.
Figure AIV.5b Detail of particle injector nozzle.

A: 0.500in O.D., 0.020in wall
B: 0.313in O.D., 0.006in wall
C: 0.188in O.D., 0.028in wall
D: 0.125in O.D., 0.020in wall
Figure AIV.5c Detail of a cooling water adaptor at injector base.
Length = 21 in

I: 0.500in O.D., 0.049in wall
II: 0.813in O.D., 0.035in wall
III: 1.000in O.D., 0.020in wall
IV: 1.188in O.D., 0.035in wall

Figure AIV.6 Schematic of the char particle collector.
Appendix V

PROGRAMS FOR
GAS ADSORPTION EXPERIMENTS
This Appendix gives the listings of the various computer programs used in the data acquisition and interpretation of gas adsorption data.

Two similar but distinct systems were used for the gas adsorption experiments. Both systems were used to determine BET surface areas, pore volume distributions, and densities of various char samples. Basically this involved monitoring the pressure in the sample volume as a function of time (data points every 10 seconds or so) for a period of approximately two hours. The speed of data acquisition was not important. In each system, an analog pressure signal (0-5V) from the pressure transducer was first digitized and then stored in the computer.

The first system used a DASCON1 data acquisition board manufactured by Metrabyte Corporation, Taunton, MA 02780. It was driven by a Zenith 150 series PC. The other system used a Zenith 148 series PC to drive a DT2801-A board made by Data Translation Inc., Marlborough, MA 01752. The specifications of both boards are given in Table AV.1.

Software programs provided by the respective manufacturers were modified to adapt them to the existing hardware. The modified driver programs for the DASCON1 and DT2801-A boards are RT2.BAS and GETBET.BAS, respectively. Once the raw data are obtained, further manipulation is carried out according to the scheme shown in Figure AV.1. The relevant program listings follow.
Table AV.1 Specifications of the Data Acquisition Boards.

<table>
<thead>
<tr>
<th>Feature</th>
<th>DT2801-A</th>
<th>DASCON1</th>
</tr>
</thead>
<tbody>
<tr>
<td>A/D Inputs</td>
<td>16SE/8DI</td>
<td>4SE/4DI</td>
</tr>
<tr>
<td>A/D Resolution</td>
<td>12-bits</td>
<td>12-bits</td>
</tr>
<tr>
<td>Voltage Input</td>
<td>±10V</td>
<td>±2V</td>
</tr>
<tr>
<td>Prog. Gain</td>
<td>1,2,4,8</td>
<td>No</td>
</tr>
<tr>
<td>A/D Throughput</td>
<td>27.5kHz</td>
<td>30Hz</td>
</tr>
<tr>
<td>D/A Channels</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>D/A Resolution</td>
<td>12-bits</td>
<td>12-bit</td>
</tr>
<tr>
<td>D/A Throughput</td>
<td>33kHz</td>
<td>30Hz</td>
</tr>
<tr>
<td>Digital I/O</td>
<td>16 lines</td>
<td>12 lines</td>
</tr>
<tr>
<td>Screw panel</td>
<td>DT707</td>
<td>STA01</td>
</tr>
<tr>
<td>DMA</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Prog. Clock</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Ext. Trigger</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Figure AV.1 Flow Diagram for the analysis of gas adsorption experiments.
AV.1 RT2.BAS

REAL TIME PLOTTING AND LOGGING PROGRAM

This program drives the METRABYTE DASCON1 data acquisition system. Note that the DEF SEG values occurring here had to be changed to accommodate the ZENITH 152 PC. This program allows the user to select which A/D are to be displayed for real-time plotting on the screen. The user may also store data from each channel in user-specified files.

The program requires a *.SCN file plus a *.PAR file which are created by MAKEGRAP.BAS. It also requires the presence of LINPLT.BAS, RLINPLT.LNK DASCON1.ADR and DASCON1.BIN.

CLEAR, 32768!
N = 6 * 60 * 5 'size of storage arrays.

KEY OFF
TRUE = 1:FAL = 0
CLS:SCREEN 0,0,0
PRINT " ---REAL TIME ANALOG I/O PLOT---"
LOCATE 5,1
INPUT "ENTER SCREEN FILE AS [dsk:] filename (no extension) ":FILX$
IF FILX$ = "" THEN 170
LOCATE 8,1
DIM C%(4)
PRINT " CHANNEL(S) TO BE DISPLAYED ---"
INPUT " CHANNEL 0 (Yes or No) ":CHO$
IF MID$(CHO$,1)="Y" THEN C%(0)=TRUE ELSE C%(0)=FAL
INPUT " CHANNEL 1 (Yes or No) ":CH1$
IF MID$(CH1$,1)="Y" THEN C%(1)=TRUE ELSE C%(1)=FAL
INPUT " CHANNEL 2 (Yes or No) ":CH2$
IF MID$(CH2$,1)="Y" THEN C%(2)=TRUE ELSE C%(2)=FAL
INPUT " CHANNEL 3 (Yes or No) ":CH3$
IF MID$(CH3$,1)="Y" THEN C%(3)=TRUE ELSE C%(3)=FAL
LOCATE 16,1:PRINT SPACE$(78);:LOCATE 16,1
INPUT " ENTER SCAN RATE IN SECONDS [1 to 3600] ":SCANRATE%
IF SCANRATE% < 1 OR SCANRATE% > 3600 THEN 340
' Setup the display and load the display program and scale parameters.
DEF SEG = &H2000
BLOAD "DASCON1.BIN",0
DASCON1 = 0
DIM DIO%(8) 'data array ANALOG I/O
MD% = 0 'free scan mode 4 channels
OPEN "I",#1,"DASCON1.ADR";INPUT #1,BASADD%;CLOSE #1 'base address
CH% = 0 'not used in mode 0
470 'Load the screen display and set the parameters for data scaling
480
500 CLS:SCREEN 2
510 DEF SEG = &HB800
520 BLOAD FILX$+.SCN
530 DEF SEG
540 OPEN FILX$+.PAR* AS #1 LEN=30
550 FIELD #1,15 AS PARX$, 15 AS PARY$
560 GET #1,1
570 SX = CVS(PARX$):SY = CVS(PARY$)
580 GET #1,2
590 DX = CVS(PARX$):DY = CVS(PARY$)
600 GET #1,3
610 X2 = CVS(PARX$):Y2 = CVS(PARY$)
620 GET #1,4
630 X1 = CVS(PARX$):Y1 = CVS(PARY$)
640 GET #1,5
650 QX = CVS(PARX$):QY = CVS(PARY$)
660 GET #1,6
670 OX = CVS(PARX$):OY = CVS(PARY$)
680 GET #1,7
690 XA = CVS(PARX$):YA = CVS(PARY$)
700 GET #1,8
710 XE = CVS(PARX$):YE = CVS(PARY$)
720 CLOSE #1
740 'graphics display segment
750 .SCN is the screen display
760 'single precision fields
770 'scale factors
780 'slope variables for axis
790 'X, Y maximum values on graph
800 'X, Y minimum values on graph
810 'X, Y screen scale factor
820 'graph starting point
830 'data positional scale factors
840 'scale x,y resolution
850 'This is the section where the data is scanned and plotted for each
860 'channel. The display sets a different graphic character for each
870 'channel. This is added to the screen on line 23.
880 'One second delay loop
890
900 DEF SEG = SG
910 XAXIS = 0
920 GOTO 1000
930 GOTO 1000
940 FOR SECDLY% = 1 TO SCANRATE%
950 STIME$ = TIME$:STDATE$ = DATE$ 'start time/date
960 LOCATE 23,10;PRINT "START TIME IS ";STIME$;" START DATE IS ";STDATE$;
970 LOCATE 25,1;PRINT SPACE$(78);LOCATE 25,1
980 PRINT "Fl= SAVE SCREEN  F2 = END";
990 ON KEY(1) GO TO 1200
1000 ON KEY(2) GO TO 1580
1010 KEY(1) ON:KEY(2) ON
1020
1030 'One second delay loop
1040
1050 DEF SEG = SG
1060 XAXIS = 0
1070 GOTO 1000
1080 FOR SECDLY% = 1 TO SCANRATE%
1090 TEMT$ = RIGHT$(TIME$,2)
1100 IF RIGHT$(TIME$,2)=TEMT$ THEN GOTO 970
1110 NEXT SECDLY%
990 
1000 DEF SEG = &H2000
1010 CALL DASCON1 (MD%, CH%, DIO%(0), DIO%(8), BASADD%)  
1020 FOR I = 0 TO 3
1030 IF C%(I) = FALSE THEN 1110
1040 PS = 1
1050 X = XA + SX * XAXIS * SCANRATE%
1060 Y = YA - SY * DIO%(I)
1070 IF X < 9 OR Y < 9 THEN PS = 0
1080 IF X > 271 OR Y > 151 THEN PS = 0
1090 IF PS = 0 THEN 1110
1100 CIRCLE (QX*X+OX,QY*Y+OY),I
1110 NEXT I
1120 XAXIS = XAXIS + 1
1130 IF XAXIS = 32766 THEN GOTO 1580
1140 TIME%(XAXIS) = (XAXIS - 1) * SCANRATE%
1150 OUT0%(XAXIS) = DIO%(0)
1160 OUT1%(XAXIS) = DIO%(1)
1170 OUT2%(XAXIS) = DIO%(2)
1180 OUT3%(XAXIS) = DIO%(3)
1190 GOTO 950
1200 LOCATE 25,1:PRINT SPACE$(78); LOCATE 25,1
1210 INPUT ;"ENTER SCREEN NAME AS [dsk:] filename (no extension) - ";SFLX$
1220 OPEN SFLX$+.PAR AS #1 LEN=30
1230 FIELD #1,15 AS PARX$,15 AS PARY$
1240 FOR XX%=1 TO 14:LSET PARX$ ="XXX":LSET PARY$ ="YYY"
1245 PUT #1,XX%:NEXT XX%:CLOSE #1
1250 OPEN SFLX$+.PAR AS #1 LEN=30
1260 FIELD #1,15 AS PARX$,15 AS PARY$
1270 LSET PARX$ = MKS$(SX)
1280 LSET PARY$ = MKS$(SY)
1290 PUT #1,1
1300 LSET PARX$ = MKS$(DX)
1310 LSET PARY$ = MKS$(DY)
1320 PUT #1,2
1330 LSET PARX$ = MKS$(X2)
1340 LSET PARY$ = MKS$(Y2)
1350 PUT #1,3
1360 LSET PARX$ = MKS$(X1)
1370 LSET PARY$ = MKS$(X2)
1380 PUT #1,4
1390 LSET PARX$ = MKS$(QX)
1400 LSET PARY$ = MKS$(QY)
1410 PUT #1,5
1420 LSET PARX$ = MKS$(OX)
1430 PUT #1,6
1440 LSET PARX$ = MKS$(XA)
1450 LSET PARY$ = MKS$(YA)
1460 PUT #1,7
XE = 1/ABS(X2-X1):LSET PARX$ = MKS$(XE)
XE = 1/ABS(Y2-Y1):LSET PARY$ = MKS$(YE)
PUT #1,8
CLOSE #1
LOCATE 25,1:PRINT SPACE$(78);;LOCATE 25,1
DEF SEG = &HB800 'screen buffer
BSAVE SFLX$+".SCN",0,&H4000 '16 k buffer
DEF SEG
PRINT "FILE ";SFLX$;"SAVED HIT ANY KEY TO GO ON";;LOCATE 20,1
KX$ = INKEY:IF KX$ = "" THEN 1560
RETURN 1580
LOCATE 25,1:PRINT SPACE$(78);;LOCATE 25,1
PRINT " TERMINATED AT ";TIME$;" ON ";DATE$;;LOCATE 23,1
'This is the part of the program which stores the data on disk.
'Note that channel 3 is automatically stored.
KEY1) OFF:KEY2) OFF
CLS:SCREEN 0,0,0
LOCATE 1,1
INPUT "Should output from channel 0 be stored on disk : ";RESP$
IF RESP$ = "n" GOTO 1840
LOCATE 3,1
INPUT "Enter name of storage data file [dsk:filename.dat] ";FILDAT0$
OPEN FILDAT0$ AS #1 LEN = 30
FIELD #1, 15 AS X$, 15 AS Y$
LOCATE 5,1
INPUT "Line, Dot or No plot mode (L,D,N)? ";A$
IF A$="L" OR A$="1" THEN M=1:GOTO 1750
IF A$="N" OR A$="n" THEN M=2:GOTO 1750
IF A$="D" OR A$="d" THEN M=0:GOTO 1750
LOCATE 11,1:PRINT"RE-ENTER":LOCATE 9,1:PRINT SPC(79):GOTO 1690
CLS:LOCATE 12,24:PRINT"STORING DATA ON DISK"
LSET X$ = MKS$(XAXIS):LSET Y$=MKS$(M)
PUT #1,1
FOR I=2 TO XAXIS+1
LSET X$=MKS$(TIME%[I-1]):LSET Y$=MKS$(OUT0%[I-1])
PUT #1,I
NEXT I
CLOSE #1
CLS
LOCATE 3,1
INPUT "Should output from channel 1 be stored on disk. ";RESP$
IF RESP$ = "n" GOTO 2060
LOCATE 5,1
INPUT "Enter name of storage data file [dsk:filename.dat] ";FILDAT1$
OPEN FILDAT1$ AS #1 LEN = 30
FIELD #1, 15 AS X$, 15 AS Y$
LOCATE 7,1
1920 INPUT "Line, Dot or No plot mode (L,D,N)?"; A$
1930 IF A$="L" OR A$="1" THEN M=1:GOTO 1970
1940 IF A$="N" OR A$="n" THEN M=2:GOTO 1970
1950 IF A$="D" OR A$="d" THEN M=0:GOTO 1970
1960 LOCATE 11,1:PRINT "RE-ENTER":LOCATE 9,1:PRINT SPC(79):GOTO 1910
1970 CLS:LOCATE 12,24:PRINT "STORING DATA ON DISK"
1980 LSET X$ = MKS$(XAXIS):LSET Y$=MKS$(M)
1990 PUT #1,1
2000 FOR I=2 TO XAXIS+1
2010 LSET X$=MKS$(TIME%(I-1)):LSET Y$=MKS$(OUT1%(I-1))
2020 PUT #1,I
2030 NEXT I
2040 CLOSE #1
2050 CLS
2060 LOCATE 5,1
2070 INPUT "Should output from channel 2 be stored on disk. " ;RESP$
2080 IF RESP$ = "n" GOTO 2290
2090 LOCATE 7,1
2100 INPUT "Enter name of storage data file [disk]:filename.dat";FILDAT1$
2110 OPEN FILDAT1$ AS #1 LEN = 30
2120 FIELD #1, 15 AS X$, 15 AS Y$
2130 LOCATE 9,1
2140 INPUT "Line, Dot or No plot mode (L,D,N)?"; A$
2150 IF A$="L" OR A$="1" THEN M=1:GOTO 2190
2160 IF A$="N" OR A$="n" THEN M=2:GOTO 2190
2170 IF A$="D" OR A$="d" THEN M=0:GOTO 2190
2180 LOCATE 11,1:PRINT "RE-ENTER":LOCATE 9,1:PRINT SPC(79):GOTO 2140
2190 CLS:LOCATE 12,24:PRINT "STORING DATA ON DISK"
2200 LSET X$ = MKS$(XAXIS):LSET Y$=MKS$(M)
2210 PUT #1,1
2220 FOR I = 2 TO XAXIS+1
2230 LSET X$=MKS$(TIME%(I-1)): LSET Y$=MKS$(OUT2%(I-1))
2240 PUT #1,I
2250 NEXT I
2260 CLOSE #1
2270 CLS
2280 LOCATE 9,1
2290 PRINT "Output from channel 3 will be stored on disk."
2300 LOCATE 10,1
2310 INPUT "Enter name of storage data file [disk]:filename.dat";FILDAT1$
2320 OPEN FILDAT1$ AS #1 LEN = 30
2330 FIELD #1, 15 AS X$, 15 AS Y$
2340 INPUT "Line, Dot or No plot mode (L,D,N)?"; A$
2350 IF A$="L" OR A$="1" THEN M=1:GOTO 2390
2360 IF A$="N" OR A$="n" THEN M=2:GOTO 2390
2370 IF A$="D" OR A$="d" THEN M=0:GOTO 2390
2380 LOCATE 11,1:PRINT "RE-ENTER":LOCATE 9,1:PRINT SPC(79):GOTO 2340
2390 CLS:LOCATE 12,24:PRINT "STORING DATA ON DISK"
2400 LSET X$ = MKS$(XAXIS):LSET Y$=MKS$(M)
2410 PUT #1,1
2420 FOR I=2 TO XAXIS+1
2430 LSET X$=MKS$(TIME%(I-1)):LSET Y$=MKS$(OUT3%(I-1))
2440 PUT #1,I
2450 NEXT I
2460 CLOSE #1
2470 CLS:LOCATE 12,28:PRINT"DONE":LOCATE 25,1
2480 END
AV.2 GETBET.BAS

10 ' SLOW REAL TIME PLOTTING AND LOGGING PROGRAM
20 ' FEBRUARY 20 1986
30 'This program drives the DATA TRANSLATION board DT 2801-A on the
40 'Zenith 148 system. It is used to obtain data from the SETRA Digital
50 'Pressure Gage for gas adsorption measurements. It plots the data
60 'points (pressure as a function of time) in real time on screen using
70 'MAKEGRAF.BAS which makes PRES.SCN and PRES.PAR. It acquires data
80 'from 8 A/D channels by sequentially scanning them. Data from selected
90 'channels can be stored in user defined files.
100 'CLEAR, 32768!
110 N = 360 'size of storage array for actual input data.
120 GAIN(0)=1: GAIN(1)=2: GAIN(2)=4: GAIN(3)=8
130 ADSCHANNEL=0: ADECHANNEL=7
140 NCONVERSIONS#=8
150 INPUT 'A/D GAIN (TYPE 0,1,2 OR 3)';ADGAIN
160 IF ADGAIN < 0 THEN GOTO 200
170 IF ADGAIN > 3 THEN GOTO 200
180 KEY OFF
190 TRUE=1: FAL=0
200 CLS:SCREEN 0,0,0
210 PRINT "REAL TIME ANALOG I/O PLOT"
220 LOCATE 5,1
230 INPUT 'ENTER SCREEN DISPLAY FILE [dsk:] filename (no extension) ';FILX$ 
240 IF FILX$ = .. THEN 260
250 DIM C%(8)
260 PRINT "CHANNEL(S) TO BE DISPLAYED"
270 INPUT "CHANNEL 0 (Yes or No) " ;CH0$
280 IF MID$(CH0$,1,1)="Y" THEN C%(0)=TRUE ELSE C%(0)=FAL
290 INPUT "CHANNEL 1 (Yes or No) " ;CH1$
300 IF MID$(CH1$,1,1)="Y" THEN C%(1)=TRUE ELSE C%(1)=FAL
310 INPUT "CHANNEL 2 (Yes or No) " ;CH2$
320 IF MID$(CH2$,1,1)="Y" THEN C%(2)=TRUE ELSE C%(2)=FAL
330 INPUT "CHANNEL 3 (Yes or No) " ;CH3$
340 IF MID$(CH3$,1,1)="Y" THEN C%(3)=TRUE ELSE C%(3)=FAL
350 INPUT "CHANNEL 4 (Yes or No) " ;CH4$
360 IF MID$(CH4$,1,1)="Y" THEN C%(4)=TRUE ELSE C%(4)=FAL
370 INPUT "CHANNEL 5 (Yes or No) " ;CH5$
380 IF MID$(CH5$,1,1)="Y" THEN C%(5)=TRUE ELSE C%(5)=FAL
- 362470
480
490
500
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580

INPUT"
CHANNEL 6 (Yes or No)" ;CH6$
IF MID$(CH6$,1,l)="Y" THEN C%(6}=TRUE ELSE C%(6)=FAL
INPUT"
CHANNEL 7 (Yes or·No)" ;CH7$
IF MID$(CH7$,1,l)="Y" THEN C%(7)=TRUE ELSE C%(7)=FAL
LOCATE 20,l:PRINT SPACE$(78);:LOCATE 20,1
INPUT "ENTER SCAN RATE IN SECONDS [1to3600] ";SCANRATE%
IF SCANRATE% < 1 OR SCANRATE% > 3600 THEN 510
'
'Setup the display and load the display program and scale parameters.
'
DEF SEG = &H2000
OPEN "I" ,#1,"GET.ADR":INPUT #1,BASADD%:CLOSE #1 'boards base address

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940
950

'Load the screen display and set the parameters for data scaling
'
CLS:SCREEN 2
'graphics display segment
DEF SEG = &HB800
'.SCN is the screen display
BLOAD FILX$+" .SCN"
DEF SEG
'parameter file for .SCN
OPEN FILX$+" .PAR" AS #1 LEN=30
'Bingle prescion fields
FIELD #1,15 AS PARX$, 15 AS PARY$
GET #1,1
'scale factors
SX = CVS(PARX$):SY = CVS(PARY$)
GET #1,2
'slope variables for axis
DX = CVS(PARX$):DY = CVS(PARY$)
GET #1,3
'X, Y maximum values on graph
X2 = CVS(PARX$):Y2 = CVS(PARY$)
GET #1,4
'X, Y minimum values on graph
Xl = CVS(PARXS):Yl = CVS(PARY$)
GET #1,5
'X, Y saeen scale factor
QX = CVS(PARX$):QY = CVS(PARY$)
GET #1,6
'graph starting point
OX = CVS(PARX$):0Y = CVS(PARY$)
GET #1,7
'data positional scale factors
XA = CVS(PARX$):YA = CVS(PARY$)
GET #1,8
'scale x,y resolution
XE= CVS(PARX$):YE = CVS(PARY$)
CLOSE #1
,
'
'This is the section where the data is scanned and plotted for each
'channel. The display sets a different graphic character for each
'channel. This is added to the screen on line 23.
'
'
DIM OUTO%(N) , TIME%(N) , OUT1%(N) , OUT2%(N) , OUT3%(N)
DIM OUT4%(N),OUT5%(N),OUT6%(N),OUT7%(N),ADH%(8),ADL%(8)
STIME$ = TIME$:SDATE$ = DATE$
'start time/date
LOCATE 23,lO:PRINT "START TIME IS ";STIME$;" START DATE IS ";SDATE$;


LOCATE 25,1:PRINT SPACE$(78);:LOCATE 25,1
PRINT *F1 = SAVE SCREEN     F2 = END*;
ON KEY(1) GOSUB 1370
ON KEY(2) GOSUB 1760
KEY(1) ON:KEY(2) ON
' One second delay loop
DEF SEG = SG
XAXIS =0
GOTO 1130
'Start loop :
FOR SECDLY% = 1 TO SCANRATE%
TEMT$=RIGHT$(TIME$,2)
IF RIGHT$(TIME$,2)=TEMT$ THEN GOTO 1100
NEXT SECDLY%
DEF SEG = &H2000
GOSUB 3570
FOR I = 0 TO 7
X = XA + SX * XAXIS * SCANRATE%
Y = YA - SY * (ADL%(I+1)+ ADH%(I+1) * 256)
IF X < 9 OR Y < 9 THEN PS = 0
IF X > 271 OR Y > 151 THEN PS = 0
IF PS = 0 THEN 1240
CIRCLE (QX* X+OX,QY* Y+OY),I
NEXT I
XAXIS = XAXIS + 1
IF XAXIS = 32766 THEN GOTO 1760
TIME%(XAXIS) = (XAXIS - 1) * SCANRATE%
OUT0%(XAXIS) = ADL%(1)+ADH%(1) * 256
OUT1%(XAXIS) = ADL%(2)+ADH%(2) * 256
OUT2%(XAXIS) = ADL%(3)+ADH%(3) * 256
OUT3%(XAXIS) = ADL%(4)+ADH%(4) * 256
OUT4%(XAXIS) = ADL%(5)+ADH%(5) * 256
OUT5%(XAXIS) = ADL%(6)+ADH%(6) * 256
OUT6%(XAXIS) = ADL%(7)+ADH%(7) * 256
OUT7%(XAXIS) = ADL%(8)+ADH%(8) * 256
GOTO 1080
LOCATE 25,1:PRINT SPACE$(78);:LOCATE 25,1
INPUT ;"ENTER SCREEN NAME AS [dsk:] filename (no ext.) --- *;SFLX$
OPEN SFLX$+.PAR" AS #1 LEN=30
FIELD #1,15 AS PARX$,15 AS PARY$
FOR XX%=1 TO 14: LSET PARX$="XXX*
LSET PARY$="YYY": PUT #1,XX%; NEXT XX%; CLOSE #1
OPEN SFLX$+.PAR" AS #1 LEN=30
FIELD #1,15 AS PARX$,15 AS PARY$
LSET PARX$ = MKS$(SX)
LSET PARY$ = MKS$(SY)
PUT #1,1
LSET PARX$ = MKS$(DX)
LSET PARY$ = MKS$(DY)
PUT #1,2
LSET PARX$ = MKS$(X2)
LSET PARY$ = MKS$(Y2)
PUT #1,3
LSET PARX$ = MKS$(X1)
LSET PARY$ = MKS$(X2)
PUT #1,4
LSET PARX$ = MKS$(QX)
LSET PARY$ = MKS$(QY)
PUT #1,5
LSET PARX$ = MKS$(OX)
PUT #1,6
LSET PARX$ = MKS$(XA)
LSET PARY$ = MKS$(YA)
PUT #1,7
XE = 1/ABS(X2-X1):LSET PARX$ = MKS$(XE)
YE = 1/ABS(Y2-Y1):LSET PARY$ = MKS$(YE)
PUT #1,8
CLOSE #1
LOCATE 25,1:PRINT SPACE$(78);:LOCATE 25,1
DEF SEG = &HB800 'screen buffer
BSAVE SFLX$+ •.SCN",0,&H4000 '16 k buffer
DEF SEG
PRINT "FILE ".SFLX$:" SAVED HIT ANY KEY TO GO ON":LOCATE 20,1
KX$ = INKEY$:IF KX$ = "n" GOTO 2020
LOCATE 3,1
INPUT "Enter name of storage data file !dsk:Jfilename.dat";FILDATO$
OPEN FILDATO$ AS #1 LEN = 30
FIELD #1, 15 AS X$, 15 AS Y$
LOCATE 5,1
INPUT "Line, Dot or No plot mode (L,D,N) ";A$
IF A$="L" OR A$="1" THEN M=1:GOTO 1930
IF A$="D" OR A$="n" THEN M=2:GOTO 1930
IF A$="D" OR A$="d" THEN M=0:GOTO 1930
LOCATE 11,1:PRINT"RE-ENTER":LOCATE 9,1:PRINT SPC(79):GOTO 1870
CLS:LOCATE 12,24:PRINT"STORING DATA ON DISK"
1940 LSET X$ = MKS$(XAXIS):LSET Y$=MKS$(M)
1950 PUT #1,1
1960 FOR I=2 TO XAXIS+1
1970 LSET X$=MKS$(TIME%(I-1)):LSET Y$=MKS$(OUT0%(I-1))
1980 PUT #1,1
1990 NEXT I
2000 CLOSE #1
2010 CLS
2020 LOCATE 3,1
2030 INPUT *Should output from channel 1 be stored on disk. * ;RESP$
2040 IF RESP$ = "n" GOTO 2240
2050 LOCATE 5,1
2060 INPUT *Enter name of storage data file [dsk:]file.dat*;FILDAT1$
2070 OPEN FILDAT1$ AS #1 LEN = 30
2080 FIELD #1, 15 AS X$, 15 AS Y$
2090 LOCATE 7,1
2100 INPUT *Line, Dot or No plot mode (L,D,N) * ;A$
2110 IF A$="L" OR A$="l" THEN M=1:GOTO 2150
2120 IF A$="N" OR A$="n" THEN M=2:GOTO 2150
2130 IF A$="D" OR A$="d" THEN M=0:GOTO 2150
2140 LOCATE 11,1:PRINT"RE-ENTER":LOCATE 9,1:PRINT SPC(79):GOTO 2090
2150 CLS:LOCATE 12,24:PRINT"STORING DATA ON DISK"
2160 LSET X$ = MKS$(XAXIS):LSET Y$=MKS$(M)
2170 PUT #1,1
2180 FOR I=2 TO XAXIS+1
2190 LSET X$=MKS$(TIME%(I-1)):LSET Y$=MKS$(OUT1%(I-1))
2200 PUT #1,1
2210 NEXT I
2220 CLOSE #1
2230 CLS
2240 LOCATE 5,1
2250 INPUT *Should output from channel 2 be stored on disk. * ;RESP$
2260 IF RESP$ = "n" GOTO 2460
2270 LOCATE 7,1
2280 INPUT *Enter name of storage data file [dsk:]file.dat*;FILDAT2$
2290 OPEN FILDAT2$ AS #1 LEN = 30
2300 FIELD #1, 15 AS X$, 15 AS Y$
2310 LOCATE 9,1
2320 INPUT *Line, Dot or No plot mode (L,D,N) * ;A$
2330 IF A$="L" OR A$="l" THEN M=1:GOTO 2370
2340 IF A$="N" OR A$="n" THEN M=2:GOTO 2370
2350 IF A$="D" OR A$="d" THEN M=0:GOTO 2370
2360 LOCATE 11,1:PRINT"RE-ENTER":LOCATE 9,1:PRINT SPC(79):GOTO 2090
2370 CLS:LOCATE 12,24:PRINT"STORING DATA ON DISK"
2380 LSET X$ = MKS$(XAXIS):LSET Y$=MKS$(M)
2390 PUT #1,1
2400 FOR I = 2 TO XAXIS+1
2410 LSET X$=MKS$(TIME%(I-1)): LSET Y$=MKS$(OUT2%(I-1))
2420 PUT #1,1
2430 NEXT I
2440 CLOSE #1
2450 CLS
2460 LOCATE 7,1
2470 INPUT "Should output from channel 3 be stored on disk?" ; RESP$
2480 IF RESP$ = "n" GOTO 2660
2490 LOCATE 11,1
2500 INPUT "Enter name of storage data file [dsk:]file.dat" ; FILDAT3$ 
2510 OPEN FILDAT3$ AS #1 LEN = 30
2520 FIELD #1, 15 AS X$, 15 AS Y$
2530 INPUT "Line, Dot or No plot mode (L,D,N) " ; A$
2540 IF A$ = "L" OR A$ = "l" THEN M = 1: GOTO 2580
2550 IF A$ = "N" OR A$ = "n" THEN M = 2: GOTO 2580
2560 IF A$ = "D" OR A$ = "d" THEN M = 0: GOTO 2580
2570 LOCATE 11,1: PRINT "RE-ENTER" : LOCATE 9,1: PRINT SPC(79): GOTO 2090
2580 CLS: LOCATE 12,24: PRINT "STORING DATA ON DISK"
2590 LSET X$ = MKS$(XAXIS): LSET Y$ = MKS$(M)
2600 PUT #1, 1
2610 FOR I = 2 TO XAXIS + 1
2620 LSET X$ = MKS$(TIME%(I - 1)): LSET Y$ = MKS$(OUT3%(I - 1))
2630 PUT #1, I
2640 NEXT I
2650 CLOSE #1: CLS
2660 LOCATE 9,1
2670 INPUT "Should output from channel 4 be stored on disk? " ; RESP$
2680 IF RESP$ = "n" GOTO 2880
2690 LOCATE 11,1
2700 INPUT "Enter name of storage data file [dsk:]file.dat" ; FILDAT4$
2710 OPEN FILDAT4$ AS #1 LEN = 30
2720 FIELD #1, 15 AS X$, 15 AS Y$
2730 LOCATE 13,1
2740 INPUT "Line, Dot or No plot mode (L,D,N) " ; A$
2750 IF A$ = "L" OR A$ = "l" THEN M = 1: GOTO 2790
2760 IF A$ = "N" OR A$ = "n" THEN M = 2: GOTO 2790
2770 IF A$ = "D" OR A$ = "d" THEN M = 0: GOTO 2790
2780 LOCATE 11,1: PRINT "RE-ENTER" : LOCATE 9,1: PRINT SPC(79): GOTO 2730
2790 CLS: LOCATE 12,24: PRINT "STORING DATA ON DISK"
2800 LSET X$ = MKS$(XAXIS): LSET Y$ = MKS$(M)
2810 PUT #1, 1
2820 FOR I = 2 TO XAXIS + 1
2830 LSET X$ = MKS$(TIME%(I - 1)): LSET Y$ = MKS$(OUT0%(I - 1))
2840 PUT #1, I
2850 NEXT I
2860 CLOSE #1
2870 CLS
2880 LOCATE 11,1
2890 INPUT "Should output from channel 5 be stored on disk? " ; RESP$
2900 IF RESP$ = "n" GOTO 3100
2910 LOCATE 13,1
INPUT "Enter name of storage data file [dsk:]ile.dat";FILDAT5$
OPEN FILDAT5$ AS #1 LEN = 30
FIELD #1, 15 AS X$, 15 AS Y$
LOCATE 15, 1
INPUT "Line, Dot or No plot mode (L,D,N) ";A$
IF A$="L" OR A$="1" THEN M=1:GOTO 3010
IF A$="N" OR A$="n" THEN M=2:GOTO 3010
IF A$="D" OR A$="d" THEN M=0:GOTO 3010
LOCATE 11,1:PRINT"RE-ENTER";LOCATE 9,1:PRINT SPC(79):GOTO 2950
CLS:LOCATE 12,24:PRINT"STORING DATA ON DISK"*
LSET X$ = MKS$(XAXIS):LSET Y$=MKS$(M)
PUT #1,1
FOR I=2 TO XAXIS+1
LSET X$=MKS$(TIME%(I-1)): LSET Y$=MKS$(OUT1%(I-1))
PUT #1,I
NEXT I
CLOSE #1
CLS
LOCATE 13,1
INPUT "Should output from channel 6 be stored on disk. ";RESP$
IF RESP$ = "n" GOTO 3310
LOCATE 15,1
INPUT "Enter name of storage data file [dsk:]ile.dat";FILDAT6$
OPEN FILDAT6$ AS #1 LEN = 30
FIELD #1, 15 AS X$, 15 AS Y$
LOCATE 17,1
INPUT "Line, Dot or No plot mode (L,D,N) ";A$
IF A$="L" OR A$="1" THEN M=1:GOTO 3230
IF A$="N" OR A$="n" THEN M=2:GOTO 3230
IF A$="D" OR A$="d" THEN M=0:GOTO 3230
LOCATE 11,1:PRINT"RE-ENTER";LOCATE 9,1:PRINT SPC(79):GOTO 2950
CLS:LOCATE 12,24:PRINT"STORING DATA ON DISK"*
LSET X$ = MKS$(XAXIS):LSET Y$=MKS$(M)
PUT #1,1
FOR I = 2 TO XAXIS+1
LSET X$=MKS$(TIME%(I-1)): LSET Y$=MKS$(OUT2%(I-1))
PUT #1,I
NEXT I
CLOSE #1
CLS
LOCATE 15,1
INPUT "Should output from channel 7 be stored on disk. ";RESP$
IF RESP$ = "n" GOTO 3510
LOCATE 17,1
INPUT "Enter name of storage data file [dsk:]ile.dat";FILDAT7$
OPEN FILDAT7$ AS #1 LEN = 30
FIELD #1, 15 AS X$, 15 AS Y$
INPUT "Line, Dot or No plot mode (L,D,N) ";A$
IF A$="L" OR A$="1" THEN M=1:GOTO 3430
IF A$="N" OR A$="n" THEN M=2:GOTO 3430
3410 IF A$="D" OR A$="d" THEN M=0:GOTO 3430
3420 LOCATE 11,1:PRINT"RE-ENTER":LOCATE 9,1:PRINT SPC(79):GOTO 2950
3430 CLS:LOCATE 12,24:PRINT"STORING DATA ON DISK"
3440 LSET X$=MKS$(XAXIS):LSET Y$=MKS$(M)
3450 PUT #1,1
3460 FOR I=2 TO XAXIS+1
3470 LSET X$=MKS$(TIME%(I-1)):LSET Y$=MKS$(OUT3%(I-1))
3480 PUT #1,1
3490 NEXT I
3500 CLOSE #1
3510 CLS:LOCATE 12,28:PRINT"DONE":LOCATE 25,1
3520 END
3530 'The following part of the program reads the board. The board is
3540 'set up for SE BIPOLAR operation.
3550 'Define constants for the board.
3560 'BASE.ADDRESS=&:H2EC
3570 COMMAND.REGISTER=BASE.ADDRESS+1
3580 STATUS.REGISTER=BASE.ADDRESS+1
3590 DATA.REGISTER=BASE.ADDRESS
3600 COMMAND.WAIT=&:H4
3610 WRITE.WAIT=&:H2
3620 READ.WAIT=&:H5
3630 CCLEAR=&:H1
3640 CCLOCK=&:H3
3650 CSAD=&:HD
3660 CRAD=&:HE
3670 CSTOP=&:HF
3680 PERIOD# =40000!
3690 BASE.FACTOR# =4096
3700 BASE.CHANNELS=8
3710 NCONVERSIONS# =8
3720 GAIN(0)=1: GAIN(1)=2: GAIN(2)=4: GAIN(3)=8
3730 'Stop and clear the DT2801-A board.
3740 '
3750 OUT COMMAND.REGISTER, CSTOP
3760 TEMP = INP(DATA.REGISTER) .
3770 WAIT STATUS.REGISTER, COMMAND.WAIT
3780 OUT COMMAND.REGISTER, CCLEAR
3790 '
3800 'Set clock rate.
3810 '
3820 '
3830 WAIT STATUS.REGISTER, COMMAND.WAIT
3840 OUT COMMAND.REGISTER, CCLOCK
3850 '
3860 PERIODH =INT(PERIOD#/256)
3870 PERIODL =PERIOD# − PERIODH* 256
3880 WAIT STATUS.REGISTER, WRITE.WAIT, WRITE.WAIT
3890 OUT DATA.REGISTER, PERIODL
3900 WAIT STATUS.REGISTER, WRITE.WAIT, WRITE.WAIT
3910 OUT DATA.REGISTER, PERIODH
3920 WAIT STATUS.REGISTER, COMMAND.WAIT
3930 OUT COMMAND.REGISTER, CSAD
3940 WAIT STATUS.REGISTER, WRITE.WAIT, WRITE.WAIT
3950 OUT DATA.REGISTER, ADGAIN
3960 WAIT STATUS.REGISTER, WRITE.WAIT, WRITE.WAIT
3970 OUT DATA.REGISTER, ADSCHANNEL
3980 WAIT STATUS.REGISTER, WRITE.WAIT, WRITE.WAIT
3990 OUT DATA.REGISTER, ADECHANNEL
4000 '
4010 NUMBERH = INT(NCONVERSIONS#/256)
4020 NUMBERL = NCONVERSIONS# - NUMBERH* 256
4030 '
4040 WAIT STATUS.REGISTER, WRITE.WAIT, WRITE.WAIT
4050 OUT DATA.REGISTER, NUMBERL
4060 WAIT STATUS.REGISTER, WRITE.WAIT, WRITE.WAIT
4070 OUT DATA.REGISTER, NUMBERH
4080 WAIT STATUS.REGISTER, COMMAND.WAIT
4090 OUT COMMAND.REGISTER, CRAD
4100 '
4110 FOR LOOP = 1 TO NCONVERSIONS#
4120 WAIT STATUS.REGISTER, READ.WAIT
4130 ADL%(LOOP) = INP(DATA.REGISTER)
4140 WAIT STATUS.REGISTER, READ.WAIT
4150 ADH%(LOOP) = INP(DATA.REGISTER)
4160 NEXT LOOP
4170 '
4180 WAIT STATUS.REGISTER, COMMAND.WAIT
4190 STATUS = INP(STATUS.REGISTER)
4200 IF (STATUS AND &H80) THEN GOTO 4230
4210 RETURN
4220 RETURN
4230 'Board Error.
4240 PRINT
4250 PRINT "Error"
4260 RETURN
4270 END
AV.3 INST.BAS

10 ' CREATE ADSORPTION INFORMATION FILES
20 ' 30 'This program is used to invert the raw data (pressure versus time) of adsorption.
40 'It calculates the isotherm, the BET, and pore volume distribution
50 'plots. The required inputs are the raw data file, the run number (#),
60 'the temperature during the run, the dead volume, room temperature
70 'and the coefficients of the polynomial fit to the flow rate (POLY2.BAS on INFLO.BAS).
80 'Outputs are: the isotherm file (iso#.dat), BET file (bet#.dat), and the pore size
90 'distribution file (pore#.dat).
100 '
110 ' 120 PGH(0)=.5 : PGH(1)=1 : PGH(2)=2 : PGH(3)=4
130 N = 1500 ' size of the arrays
140 '
150 CLS:SCREEN 0,0,0:KEY OFF
160 LOCATE 1,1
170 INPUT "What was the gain "; GAIN#
180 IF GAIN#<0 OR GAIN#>3 GOTO 160
190 FACTOR=PGH(GAIN#)
200 LOCATE 3,1
210 INPUT "Enter name of data file to be read as [dsk:]file.dat";FILOLD$
220 LOCATE 5,1
230 PRINT "The new data files will be sent to drive b:"
240 LOCATE 7,1
250 INPUT "Enter run number of this experiment ";RUNNUM$
260 FILNEW1$ = "b:iso"+RUNNUM$+.dat"
270 FILNEW2$ = "b:bet"+RUNNUM$+.dat"
280 FILNEW3$ = "b:pore"+RUNNUM$+.dat"
290 DIM X(N) , Y(N) , COEF(6) , Z(N)
300 LOCATE 9,1
310 PRINT "Reading data..."
320 OPEN FILOLD$ AS #1 LEN = 30
330 FIELD #1, 15 AS X$, 15 AS Y$
340 GET #1,1
350 NPTS = CVS(X$)
360 M = CVS(Y$)
370 FOR I = 1 TO NPTS
380 GET #1,1+1
390 X(I) = CVS(X$)
400 Y(I) = CVS(Y$)
410 NEXT I
420 CLOSE #1
430 LOCATE 11,1
440 PRINT "Smoothing data..."
450 FOR K = 1 TO NPTS
460 Z(K) = Y(K)
470 NEXT K
480 ' Smooth the data by using appropriate weights of local points.
500 '
510 NMOD = NPTS - 2
520 FOR N = 3 TO NMOD
530 Y(N) = (-3*Z(N-2)+12*Z(N-1)+17*Z(N)+12*Z(N+1)-3*Z(N+2))/35
540 NEXT N
550 '
560 'Now that the data is smoothed, calculate the isotherm.
570 '
580 LOCATE 13,1
590 INPUT "Enter initial temperature in k " ; TEMPI
600 LOCATE 14,1
610 INPUT "Enter final temperature in k " ; TEMP2
620 LOCATE 15,1
630 INPUT "Enter total effective volume in ml " ; VOL
640 LOCATE 16,1
650 INPUT "What was the vapor pressure of adsorbate ";PFIN
660 LOCATE 17,1
670 '
680 'Read coefficients for instantaneous flow rate as a function of pressure:
690 '
700 INPUT "Enter first rate coefficient ";COEF(1)
710 INPUT "Enter second coefficient ";COEF(2)
720 INPUT "Enter third coefficient ";COEF(3)
730 INPUT "Enter fourth coefficient ";COEF(4)
740 INPUT "Enter fifth coefficient ";COEF(5)
750 INPUT "Enter sixth coefficient ";COEF(6)
760 CLS
770 LOCATE 13,1
780 PRINT "Computing Isotherm..."
790 '
800 'Pressure = bits/4096*20psi*0.01934torr/psi
810 '
820 P0 = Y(1)/(3.96017*FACTOR)
830 DVOL=32.96
840 '
850 'The initial amount of gas is that in the dead volume at t=0.
860 '
870 TOTMOL=P0*DVOL*16.0364/TEMPI
880 TIME = X(2)-X(1)
890 FOR I = 2 TO NPTS
900 P = Y(I)/(3.96017*FACTOR)
910 Q = COEF(6)
920 FOR CNT% = 5 TO 1 STEP - 1
930 Q = Q * P + COEF(CNT%)
940 NEXT CNT%
960 TEMP = TEMP1 + (TEMP2 - TEMP1)*(X(I) - X(O))/(X(NPTS) - X(O))
970 TOTMOL = TOTMOL + Q * TIME
980 ADSMOL = TOTMOL - P * VOL * 16.0364/TEMP
990 X(I) = P
1000 Y(I) = ADSMOL
1010 NEXT I
1020 X(1) = P0 : Y(1) = 0
1030 LOCATE 19,1
1040 PRINT "Creating data files:"
1050 OPEN FILNEW1$ AS #1 LEN = 30
1060 FIELD #1, 15 AS X$, 15 AS Y$
1070 LSET X$ = MKS$(NPTS) : LSET Y$ = MKS$(M)
1080 PUT #1,1
1090 FOR I = 1 TO NPTS
1100 LSET X$ = MKS$(X(I)) : LSET Y$ = MKS$(Y(I))
1110 PUT #1,1+1
1120 NEXT I
1130 CLOSE #1
1140 PRINT FILNEW1$
1150 ' 
1160 'Now create a BET file."
1170 ' 
1180 OPEN FILNEW1$ AS #2 LEN = 30
1190 FIELD #2, 15 AS X$, 15 AS Y$
1200 GET #2,1
1210 NPTS = CVS(X$)
1220 M = CVS(Y$)
1230 NNEW = 1
1240 FOR I = 1 TO NPTS
1250 GET #2, I+1
1260 X(NNEW) = CVS(X$)
1270 Y(NNEW) = CVS(Y$)
1280 PHI = .314*PFIN
1290 PL0 = .04*PFIN
1300 IF X(NNEW) > PHI OR X(NNEW) = PHI GOTO 1330
1310 IF X(NNEW) > PLO OR X(NNEW) = PLO THEN NNEW = NNEW + 1
1320 NEXT I
1330 CLOSE #2
1340 OPEN FILNEW2$ AS #1 LEN = 30
1350 FIELD #1, 15 AS X$, 15 AS Y$
1360 LSET X$ = MKS$(NNEW) : LSET Y$ = MKS$(M)
1370 PUT #1,1
1380 FOR I = 1 TO NNEW
1390 X(I) = X(I)/PFIN
1400 Y(I) = X(I)/(Y(I) * (1 - X(I))) * 1000000!
1410 LSET X$ = MKS$(X(I))
1420 LSET Y$ = MKS$(Y(I))
1430 PUT #1,1+1
1440 NEXT I
Now create volume distribution file.

OPEN FILNEW1$ AS #1 LEN = 30
FIELD #1, 15 AS X$, 15 AS Y$
GET #1, 1
NPTS = CVS(X$)
M = CVS(Y$)
NNEW = 1
FOR N = 1 TO NPTS
GET #1, N+1
X(NNEW) = CVS(X$)
Y(NNEW) = CVS(Y$)

HIEND = .92*PFIN
LOEND = .5*PFIN
IF X(NNEW) > HIEND OR X(NNEW)=HIEND GOTO 1650
IF X(NNEW) > LOEND OR X(NNEW)=LOEND THEN NNEW=NNEW+1
NEXT N
CLOSE #1
OPEN FILNEW2$ AS #2 LEN = 30
FIELD #2, 15 AS X$, 15 AS Y$
LSET X$ = MKS$(NNEW): LSET Y$ = MKS$(M)
PUT #2, 1
FOR J = 1 TO NNEW
Z(J) = Y(J)
NEXT J
NLAST = NNEW - 2
Y(1)=0.X(1)=0.Y(2)=0.X(2)=0
Y(NLAST+2)=0.X(NLAST+2)=0.Y(NLAST+1)=0.X(NLAST+1)=0
FOR I=3 TO NLAST
ARG = X(I)/PFIN
IF ARG < 0 OR ARG = 0 THEN GOTO 1930
PRAD = 1.018E-07 /DEN
FOR freon, gamma = 18 dynes/cm, v=73.15cm$^3$/gmole, T=282 K.

This routine uses the method developed by Yan and Zhang.

Surface Tension nitrogen = 8.5 dynes/cm, v = 34.65 cm$^3$/gmole.

PRAD = 1.123E-07/DEN
X(I) = LOG(PRAD)/2.303 + 6
Y(I) = (Z(I-2)-8*Z(I-1)+8*Z(I+1)-Z(I+2))*3.465E-05/(12*(X(I)-X(I-1)))
LSET X$ = MKS$(X(I))
LSET Y$ = MKS$(Y(I))
PUT #2, I-1
NEXT I
CLOSE #2
PRINT FILNEW3$
SCREEN 0,0,0
DIM FL$(1)
'User has the option to plot isotherm or BET file immediately.

INPUT "Do you wish to plot the isotherm ";ANS$
IF ANS$="y" OR ANS$="Y" THEN FL$(1)=FILNEW1$ ELSE GOTO 2060
YLBS$= "Micromoles"
XLBS$= "Pressure (torr)"
GOTO 2100
INPUT "Do you wish to see the BET plot "; ANS$
IF ANS$="y" OR ANS$="Y" THEN FL$(1)=FILNEW2$ ELSE GOTO 2370
YLBS$= "BET plot"
XLBS$= "Rel. Pres. (P/P0)"
PRINT "Working...."
NOF = 1
'This part of the program sets the parameters required for plotting
'the data.

OPEN "RLINPLT.LNK" AS #1 LEN = 30
FIELD #1, 30 AS RFLD$
FOR I= 1 TO 21:LSET RFLD$ = "XXXXXXXXX":PUT #1,I:NEXT !:CLOSE #1
OPEN "RLINPLT.LNK" AS #1 LEN = 30
GET #1,1
LSET RFLD$ = MKI$(NOF)
PUT #1,1
GET #1,2
LSET RFLD$ = YLBL$
PUT #1,2
GET #1,3
LSET RFLD$ = XLBS$
PUT #1,3
FOR I = 1 TO NOF
GET #1,I+3
LSET RFLD$ = FL$(I)
PUT #1,I+3
NEXT I
CLOSE #1
CHAIN "LINPLT.BAS"
END
AV.4 INFLO.BAS

10 ' INSTANTANEOUS ORIFICE FLOW PROGRAM
20 ' This program computes the instantaneous flow rate for given
30 ' pressure and temperature of the system.
40 ' Input data file is the raw data for the blank run.
50 ' Output file is user named containing flow rate in micromoles/s
60 ' versus downstream pressure in torr.
70 ' Input data file is the raw data for the blank run.
80 ' Input data file is the raw data for the blank run.
90 PGH(0)=.5 : PGH(1)=1 : PGH(2)=2 : PGH(3)=4
100 N = 1500 'size of the arrays
110 '
120 CLS:SCREEN 0,0,0:KEY OFF
130 LOCATE 3,1
140 INPUT "What was the gain"; GAIN#
150 FACTOR = PGH(GAIN#)
160 LOCATE 5,1
170 INPUT "Enter data to be differentiated as [dsk]:file.dat"; FILOLD$
180 LOCATE 7,1
190 INPUT "Enter name of output file as [dsk]:filename.dat"; FILNEW$
200 FF X(N) , Y(N) , Z(N)
210 LOCATE 9,1
220 INPUT "What was the temperature during calibration"; TEMP
230 LOCATE 11,1
240 PRINT "Reading old file..."
250 OPEN FILOLD$ AS #1 LEN = 30
260 FIELD #1, 15 AS X$, 15 AS Y$
270 GET #1,1
280 NPTS = CVS(X$)
290 M = CVS(Y$)
300 FOR I = 1 TO NPTS
310 GET #1,I+1
320 X(I) = CVS(X$)
330 Z(I) = CVS(Y$)
340 NEXT I
350 CLOSE #1
360 '
370 LOCATE 13,1
380 PRINT "Computing modifications..."
390 DEN = 12*(X(3)-X(2))*FACTOR
400 NEND = NPTS - 2
410 '
420 FOR I = 3 TO NEND
430 '
440 'For 5 micron with nitrogen, vol. = 40.00 cc. For micromoles/sec,
450 'and psia gage, const. = 20 psi/10volt*51.7149 torr/psia *30.4 ml
460 '/82.05 ml atm/gmol k /760torr/atm *10e6 micromoles/mole =12.701
\[ Y(I) = \frac{(Z(I-2)-8*Z(I-1)+8*Z(I+1)-Z(I+2))*160.5655*30.4}{(DEN*TEMP*40!)} \]

'Conversion factor for millibar gage is 3.96017'

\[ X(I) = \frac{Z(I)}{(3.96017*FACTOR)} \]

NEXT I

NTOT=NPTS-5

LOCATE 15,1

PRINT "Writing new file..."

OPEN FILNEW$ AS #1 LEN = 30

FIELD #1, 15 AS X$, 15 AS Y$

LSET X$ = MKS$(NTOT) : LSET Y$ = MKS$(M)

NEND=NEND-1

PUT #1,1

FOR I = 3 TO NEND

LSET X$ = MKS$(X(I)) : LSET Y$ = MKS$(Y(I))

PUT #1,1-1

NEXT I

CLOSE #1

LOCATE 17,1

PRINT "Done."

LOCATE 24,1

END
AV.5 MONO.BAS

10 ' MONOLAYER COVERAGE CALCULATION PROGRAM
20 '
30 'This program calculates the BET surface area and 'C' value from the
40 'BET data file. The data are fit with a straight line using a modified
50 'form of POLY2.BAS. The slope and intercept of this line are used to
60 'calculate the desired quantities. Input is the BET file, output is
70 'to the screen. The values are, respectively: intercept, slope, surface
80 'area (assuming nitrogen), micromoles at monolayer coverage, 'C' value
90 'and sum of residuals.
100 'The polynomial fit is described in more detail in POLY2.BAS.
110 '
120 SCREEN 0,0,0:KEY OFF:CLS:LOCATE 25,1:PRINT"POLYNOM";
130 DIM COEF(6), MTX(6,7), SM(10), RT(6)
140 '
150 'This is the regression part of the program.
160 '
170 NP= 2000
180 LOCATE 2,1
190 INPUT "Enter name of file to be read as [dsk:]filename.dat ":FILOLD$
200 DIM X(NP), Y(NP)
210 OPEN FILOLD$ AS #1 LEN = 30
220 FIELD #1, 15 AS XS, 15 AS Y$
230 GET #1,1
240 N = CVS(X$)
250 DUM = CVS(Y$)
260 FOR I = 1 TO N
270 GET #1,1+1
280 X(I) = CVS(X$)
290 Y(I) = CVS(Y$)
300 PRINT I,X(I),Y(I)
310 NEXT I
320 CLOSE #1
330 '
340 'This is the regression part of the program.
350 '
360 CLS:LOCATE 25,1:PRINT"POLYNOM — PERFORMING LINEAR REGRESSION";
370 ORD = 1
380 LOCATE 10,20:PRINT"WAIT — REGRESSION ANALYSIS IN PROGRESS"
390 FOR I=1 TO 2*ORD
400 SM(I)=0
410 NEXT I
420 FOR I = 1 TO ORD+1
430 RT(I)=0
440 NEXT I
450 FOR PNT = 1 TO N
460 FOR I= 1 TO ORD+2
470 SM(I) = SM(I) + X(PNT) * I
480 NEXT I
490 FOR I = 1 TO ORD + 1
500 IF I = 1 THEN RT(I) = RT(I) + Y(PNT)
510 IF I <> 1 THEN RT(I) = RT(I) + Y(PNT) * (X(PNT)^ (I - 1))
520 NEXT I
530 NEXT PNT
540 MTX(1, 1) = N
550 FOR I = 1 TO ORD + 1
560 MTX(I, ORD + 2) = RT(I)
570 FOR J = 1 TO ORD + 1
580 IF I + J <> 2 THEN MTX(I, J) = SM(I + J - 2)
590 NEXT J
600 NEXT I
610 FOR K = 1 TO ORD
620 KTMP = K + 1
630 L = K
640 FOR I = KTMP TO ORD + 1
650 IF ABS(MTX(I, K)) > ABS(MTX(L, K)) THEN L = I
660 NEXT I
670 IF L = K THEN GOTO 730
680 FOR J = K TO ORD + 2
690 TMP = MTX(K, J)
700 MTX(K, J) = MTX(L, J)
710 MTX(L, J) = TMP
720 NEXT J
730 FOR I = KTMP TO ORD + 1
740 FTR = MTX(I, K) / MTX(K, K)
750 FOR J = KTMP TO ORD + 2
760 MTX(I, J) = MTX(I, J) - FTR * MTX(K, J)
770 NEXT J
780 NEXT I
790 NEXT K
800 COEF(ORD + 1) = MTX(ORD + 1, ORD + 2) / MTX(ORD + 1, ORD + 1)
810 I = ORD
820 ITMP = I + 1
830 TOT = 0
840 FOR J = ITMP TO ORD + 1
850 TOT = TOT + MTX(I, J) * COEF(J)
860 NEXT J
870 COEF(I) = (MTX(I, ORD + 2) - TOT) / MTX(I, I)
880 I = I - 1
890 IF I >= 1 THEN GOTO 820
900 'Display data.
910 'CLS:LOCATE 1, 1
920 FOR I = 1 TO ORD + 1
930 PRINT "COEF(", I, ") = ", COEF(I)
960 NEXT I
970 RECIP = 1/(COEF(1)+COEF(2))
980 AREA = 16.2 * 6022 * RECIP
990 NM = RECIP
1000 C = COEF(2)/COEF(1) + 1
1010 RESID = 0
1020 FOR I = 1 TO N
1030 RESID = RESID + ABS(Y(I) - COEF(2)*X(I) - COEF(1))
1040 NEXT I
1050 PRINT AREA, RECIP, C, RESID
1060 END
AV.6 POLY2.BAS

10 ' FIFTH-ORDER LEAST-SQUARES POLYNOMIAL FIT PROGRAM
20 ',
30 ',
40 'This program evaluates the coefficients C1—6 for the polynomial
50 'approximation:-
60 ';
70 ' Y = C1 + C2*X + C3*X^2 + C4*X^3 + C5*X^4 + C6*X^5
80'
90 'such that the sum of the squares of the errors between the actual
100 'value of Y and the polynomial value of Y for all data points entered
110 'is minimised (i.e. curve fitting).
120 'This approximation is useful for linearizing transducer outputs.
130 'e.g. flowmeters, thermocouples, tacho-generators etc.. The transducer
140 'output is obtained from the A/D converter (suitably scaled if required)
150 'as variable X and the linearized output from the transducer e.g. flow,
160 'temperature, velocity etc. is calculated as variable Y. The coefficients
170 'C1—6 are calculated from a set of Y,X data or calibration points.
180 'Type RUN[CR] to run the program. The prompts are self explanatory.
190 'The data are assumed to be X,Y in the file. The program then proceeds to perform
200 'a regression analysis to calculate the coefficients of the polynomial.
210 'You are prompted to select the order required, up to 5th. order. Usually
220 '5th. order is the best option unless you want to experiment with trying
230 'a lower order. After the analysis is finished, the coefficients are
240 'displayed and you can check the conformance by inputting various values
250 'of X and seeing how accurate Y is. If you wish, before exiting the
260 'program, you can run the regression at another order on the same data
270 'to see how good the conformance is with a different order polynomial.
280 ';
290 'Once the coefficients are evaluated the polynomial can be inserted
300 'into your programs as a subroutine. The neatest way is to use a loop to
310 'evaluate it as follows:-
320 ',
330 ' xxx00 Y = COEF(1)
340 ' xxx10 FOR CNT% = 5 TO 1 STEP - 1
350 ' xxx20 Y = Y + COEF(CNT% + 1) * X ^ CNT%
360 ' xxx30 NEXT CNT%
370 ' xxx40 RETURN
380 ',
390 ',
400 '—- START - INITIALIZATION SECTION —-..............................
410 SCREEN 0,0,0:KEY OFF:CLS:LOCATE 25,1:PRINT"POLYNOM";
420 DIM COEF(6), MTX(6,7), SM(10), RT(6)
430 '—- DATA POINT ENTRY —-...........................................
440 CLS:LOCATE 25,1:PRINT"POLYNOM - DATA FILE ENTRY";
450 NP= 2000
460 LOCATE 2,1
 INPUT "Enter name of file to be read as [dsk:]filename.dat ";FILOLD$
480 DIM X(NP) , Y(NP)
490 OPEN FILOLD$ AS #1 LEN = 30
500 FIELD #1, 15 AS X$, 15 AS Y$
510 GET #1,1
520 N = CVS(X$)
530 DUM = CVS(Y$)
540 FOR I = 1 TO N
550 GET #1,I
560 X(I) = CVS(X$)
570 Y(I) = CVS(Y$)
580 PRINT I,X(I),Y(I)
590 NEXT I
600 CLOSE #1
610 '—— PERFORM LINEAR REGRESSION ———
620 CLS:LOCATE 25,l:PRINT"POLYNOM - PERFORMING LINEAR REGRESSION";
630 LOCATE 2,l:INPUT"ORDER OF ANALYSIS REQUIRED (0-5)? ",ORD
640 IF ORD <0 OR ORD>5 THEN GOTO 630
650 LOCATE 10,20:PRINT"WAIT - REGRESSION ANALYSIS IN PROGRESS"
660 FOR I=1 TO 2*ORD
670 SM(I)=0
680 NEXT I
690 FOR I = 1 TO ORD+1
700 RT(I)=0
710 NEXT I
720 FOR PNT = 1 TO N
730 FOR I= 1 TO ORD+2
740 SM(I)=SM(I) + X(PNT)*I
750 NEXT I
760 FOR I = 1 TO ORD+1
770 IF I=1 THEN RT(I)=RT(I) + Y(PNT)
780 IF I<>I THEN RT(I) = RT(I) + Y(PNT)*(X(PNT)*(I-1))
790 NEXT I
800 NEXT PNT
810 MTX(1,1)=N
820 FOR I=1 TO ORD+1
830 MTX(I,ORD+2)=RT(I)
840 FOR J=1 TO ORD+1
850 IF I+J<=2 THEN MTX(I,J)=SM(I+J-2)
860 NEXT J
870 NEXT I
880 FOR K = 1 TO ORD
890 KTMP=K+1
900 L=K
910 FOR I=KTMP TO ORD+1
920 IF ABS(MTX(I,K))>ABS(MTX(L,K)) THEN L=I
930 NEXT I
940 IF L=K THEN GOTO 1000
950 FOR J=K TO ORD+2
960  TMP = MTX(K, J)
970  MTX(K, J) = MTX(L, J)
980  MTX(L, J) = TMP
990  NEXT J
1000 FOR I = KTMP TO ORD + 1
1010  FTR = MTX(I, K) / MTX(K, K)
1020  FOR J = KTMP TO ORD + 2
1030  MTX(I, J) = MTX(I, J) - FTR * MTX(K, J)
1040  NEXT J
1050  NEXT I
1060  NEXT K
1070  COEF(ORD + 1) = MTX(ORD + 1, ORD + 2) / MTX(ORD + 1, ORD + 1)
1080  I = ORD
1090  ITMP = I + 1
1100  TOT = 0
1110  FOR J = ITMP TO ORD + 1
1120  TOT = TOT + MTX(I, J) * COEF(J)
1130  NEXT J
1140  COEF(I) = (MTX(I, ORD + 2) - TOT) / MTX(I, I)
1150  I = I - 1
1160 IF I > 1 THEN GOTO 1090
1170  '____ DISPLAY COEFFICIENTS __________________________
1180  CLS: LOCATE 1, 1
1190  FOR I = 1 TO ORD + 1
1200  PRINT "COEF("; I; ") = "; COEF(I)
1210  NEXT I
1220  RESID = 0
1230  FOR I = 1 TO NPTS
1240  P = X(I)
1250  Q = COEF(6)
1260  FOR CNT% = 5 TO 1 STEP - 1
1270  Q = Q * P + COEF(CNT%)
1280  NEXT CNT%
1290  RESID = RESID + ABS( Y(I) - Q )
1300  NEXT I
1310  PRINT RESID
1320  '____ TEST FIT __________________________
1330  LOCATE 25, 1: PRINT SPC(79): LOCATE 25, 1: PRINT "POLYNOM - TEST FIT";
1340  LOCATE 9, 1: PRINT "TEST CONFORMANCE": PRINT "_________
1350  LOCATE 12, 1: PRINT SPC(79)
1360  LOCATE 12, 1: INPUT "X VALUE (type Q to quit)? ", A$
1370  IF A$ = "Q" OR A$ = "q" THEN GOTO 1470
1380  X = VAL(A$)
1390  Y = COEF(1)
1400  FOR CNT% = 5 TO 1 STEP - 1
1410  Y = Y + COEF(CNT% + 1) * X^ CNT%
1420  NEXT CNT%
1430  LOCATE 14, 1: PRINT SPC(79)
1440  LOCATE 14, 1: PRINT "Calculated Y (output) = "; Y; " for X (input) = "; X
1450 GOTO 1360
1460 LOCATE 14,1: PRINT SPC(79)
1470 LOCATE 14,1: INPUT "TRY DIFFERENT REGRESSION ORDER (Y/N)? ", A$
1480 IF A$="y" OR A$="Y" THEN GOTO 1500
1490 LOCATE 25,1: PRINT SPC(79): LOCATE 20,1: END
1500 ERASE SM, MTX, RT, COEF
1510 DIM COEF(6), MTX(6,7), SM(10), RT(6)
1520 GOTO 610
1530 END
AV.7 MPLOT.BAS

10 ' PROGRAM TO MAKE/READ A LINEAR PLOT CONTROL FILE
20 '  
30 '  
40 'This routine allows the user to make or read a plot control file and  
50 'execute it if desired. This program links the program LINPLT.BAS and  
60 'runs the program. The LINPLT.BAS program uses the file called RLINPLT.BAS  
70 'as a control file. The RLINPLT.BAS control file contains:  
80 '  
90 '  A. THE NUMBER OF FILES TO BE PLOTTED  
100 '  B. THE 'X' AXIS LABEL [ 30 CHARACTERS LONG ]  
110 '  C. THE 'Y' AXIS LABEL [ 20 CHARACTERS LONG ]  
120 '  D. FILES TO BE PLOTTED (n records following)  
130 '  
140 SCREEN 0,0,0:CLS:KEY OFF  
150 DIM FL$(15)  
160 PRINT TAB(20);"MAKE / READ A LINEAR PLOT FILE"  
170 PRINT  
180 PRINT "Do you wish to (R)ead or (M)ake a plot file ";  
190 RS = INKEY$: IF RS = " " THEN 190  
200 IF RS="R" THEN 220 ELSE IF RS="M" OR RS="m" THEN 500 ELSE CLS  
210 GOTO 160  
220 OPEN "RLINPLT.LNK" AS #1 LEN=30  
230 FIELD #1, 30 AS RFLD$  
240 GET #1,1  
250 NOF = CVI(RFLD$)  
260 GET #1,2  
270 YLBL$ = RFLD$  
280 GET #1,3  
290 XLBL$ = RFLD$  
300 FOR I = 1 TO NOF  
310 GET #1,1+3  
320 FL$(I) = RFLD$  
330 NEXT I  
340 CLOSE #1  
350 CLS  
360 PRINT TAB(20);"READ A LINEAR PLOT CONTROL FILE"  
370 LOCATE 3,1  
380 PRINT "NUMBER OF DATA FILES TO BE PLOTTED [15 max] = ";NOF  
390 LOCATE 5,1  
400 PRINT "X - AXIS LABEL [ 30 characters maximum ] ";XLBL$  
410 LOCATE 7,1  
420 PRINT "Y - AXIS LABEL [ 16 characters maximum ] ";YLBL$  
430 LOCATE 9,1  
440 FOR I%= 1 TO NOF  
450 LOCATE 9+I%−1,1  
460 PRINT "DATA FILE NAME ";
PRINT USING "##";I%;PRINT "[DSK:] FILENAME.EXT ";FL$(I%);
NEXT I%
GOTO 880
CLS
PRINT TAB(20);" MAKE A LINEAR PLOT FILE ">
LOCATE 3,1
INPUT "NUMBER OF DATA FILES TO BE PLOTTED [15 MAX] = ",NOF
IF NOF <1 OR NOF >15 THEN LOCATE 3,1:PRINT SPACE$(78);:GOTO 520
LOCATE 5,1
INPUT "ENTER 'X' AXIS LABEL [30 characters maximum]: ",XLBL$
LOCATE 7,1
INPUT "ENTER 'Y' AXIS LABEL [16 characters maximum] 
LOCATE 9,1
FOR I%= 1 TO NOF
PRINT "DATA FILE NAME 
PRINT USING "##";I%;PRINT" [DSK:j FILENAME.EXT 
INPUT;FL$(I%)
IF FL$(I%) ="" THEN LOCATE 9+I%-1,1:PRINT SPACE$(78);:LOCATE9+I%-1,1
GOTO 630
NEXT I%
OPEN "RLINPLT.LNK" AS #1 LEN= 30
FIELD #1, 30 AS RFLD$
FOR I= 1 TO 21:LSET RFLF$ = "XXXXXXX":PUT #1,I:NEXT I:CLOSE #1
OPEN "RLINPLT.LNK" AS #1 LEN= 30
FIELD #1, 30 AS RFLD$
GET #1,1
LSET RFLD$ = MKI$(NOF)
PUT #1,1
GET #1,2
LSET RFLD$ = YLBL$
PUT #1,2
GET #1,3
LSET RFLD$ = XLBL$
PUT #1,3
FOR I = 1 TO NOF
GET #1,1+3
LSET RFLD$ = FL$(I)
PUT #1,1+3
NEXT I
CLOSE #1
LOCATE 25,1:PRINT SPACE$(70);:LOCATE 25,1
INPUT;"UPDATE ENTRY Nof, X axis,Y axis, File#, Exit, Plot 
ERC$=LEFT$(ERC$,1)
IF ERC$ = "N" OR ERC$ = "n" THEN 1010
IF ERC$ = "X" OR ERC$ = "x" THEN 1050
IF ERC$ = "Y" OR ERC$ = "y" THEN 1090
IF ERC$ = "F" OR ERC$ = "f" THEN 1130
IF ERC$ = "E" OR ERC$ = "e" THEN cls:NEW:END
960 IF ERC$ <>"P" OR ERC$ <>"p" THEN 990
970 GOTO 880
980 CLS
990 CHAIN "LINPLT.BAS"
1000 
1010 LOCATE 3,1:PRINT SPACE$(78);:LOCATE 3,1
1020 INPUT *NUMBER OF DATA FILES TO BE PLOTTED [15 MAX] = *,NOF
1030 IF NOF < 1 THEN 1010 ELSE IF NOF > 15 THEN 1010
1040 GOTO 680
1050 LOCATE 5,1:PRINT SPACE$(78);:LOCATE 5,1
1060 INPUT *ENTER 'X' AXIS LABEL [30 characters maximum]: *,XLBL$
1070 IF LEN(XLBL$) > 30 THEN 1050
1080 GOTO 680
1090 LOCATE 7,1:PRINT SPACE$(78);:LOCATE 7,1
1100 INPUT *ENTER 'Y' AXIS LABEL [16 characters maximum]: *,YLBL$
1110 IF LEN(YLBL$) >16 THEN 1090
1120 GOTO 680
1130 LOCATE 25,1:PRINT SPACE$(78);:LOCATE 25,1
1140 INPUT,*ENTER FILE NUMBER TO BE CHANGED = *,NFC
1150 IF NFC > NOF THEN 1130 ELSE IF NFC > 15 THEN 1130
1160 LOCATE 8+NFC,1:PRINT SPACE$(79);:LOCATE 8+NFC,1
1165 PRINT *DATA FILE NAME *;
1170 PRINT USING **DSK;FILENAME.EXT **;
1180 INPUT;FILX$:IF FILX$="" THEN 1160 ELSE FL$(NFC)=FILX$
1190 GOTO 680
1200 END
AV.8 LINPLT.BAS

10 ' LINEAR PLOT PROGRAM
20 '
30 '
40 'This program will plot from one to 15 data files with the same scale
50 'factors for all the files. The program also has a save screen command
60 'which allows the user to save the resultant plot for future reference.
70 'The program also allows the user to chain an additional set of data
80 'files to be plotted on the already data files shown. Printing of the
90 'screen is done by entering the option as directed, then SHFT PrtSc key.
100 'The user must have the graftrax option active.
110 '
120 'This section is where the starting graph coordinates and screen scale
130 'ratio is set. OX, OY = starting point of graph. QX, QY = screen scale x:y.
140 '
150 KEY OFF:SCREEN 0,0,0
160 OX=70:OY=0:QX=1.8:QY=.9000001
170 DIM X(100),Y(100),F$(15)
180 CLS:LOCATE 12,30:COLOR 31,0,0:PRINT "COMPUTING GRAPHICS FILES"
190 '
200 'This is the main link to the plotting program. The file RLINPLT.LNK
210 'has the file name and disk of the file(s) to be plotted.
220 '
230 OPEN "RLINPLT.LNK" AS #1 LEN = 30
240 FIELD #1, 30 AS RLINK$
250 GET #1,1
260 NF = CVI(RLINK$)
270 GET #1,2
280 YLB$ = RLINK$
290 GET #1,3
300 XLB$ = RLINK$
310 IP = 1
320 FOR I = 1 TO NF
330 GET #1,1+3
340 F$(IP) = RLINK$
350 IP = IP + 1
360 NEXT I
370 CLOSE
380 '
390 'This loop scans the data files and sets the X,Y Max/Min values so
400 'all the data files are on the same scale.
410 '
420 X1=0
430 X2=0
440 Y1=0
450 Y2=0
460 FOR I=1 TO NF
IC=0
OPEN F$(1) AS #1 LEN=30
FIELD #1, 15 AS XVAL$, 15 AS YVAL$
GET #1,1
NL=CVS(XVAL$)
FOR J=1 TO NL
IC=IC+1
GET #1,IC+1
A=CVS(XVAL$)
B=CVS(YVAL$)
IF A < X1 THEN X1=A
IF A > X2 THEN X2=A
IF B < Y1 THEN Y1=B
IF B > Y2 THEN Y2=B
NEXT J
CLOSE #1
NEXT I

'This section establishes the actual scale factors used to plot the
'data as the files are read. These values are also the same values saved
'on the disk when a Save command is executed.

CLS:COLOR 7,0,0:SCREEN 2
DX=ABS(CINT((X2-X1)/25+.5))
DY=ABS(CINT(((Y2-Y1)/25)+.5))
SX=260/(X2-X1)
SY=140/(Y2-Y1)

'This section locates the Axis x,y and plots them out with the small
tick marks identifying the scale. The axis labels are also printed.

IF Y2<=0 THEN YA=10:GOTO 830
IF Y1=>0 THEN YA=150:GOTO 830
YA=10+SY*Y2

SET the range limits

IF X2<=0 THEN XA=270:GOTO 880
IF X1=>0 THEN XA=10:GOTO 880
XA=10-SX*X1
FOR YLBL = 1 TO 16
LOCATE 2+YLBL,6:PRINT MID$(YLB$,YLBL,1);
NEXT YLBL
LOCATE 1,1:PRINT USING ";#.## " ;Y2;
LOCATE 19,1:PRINT USING ";#.## " ;Y1;
LOCATE 20,10:PRINT USING ";#.## " ;X1;
LOCATE 20,68:PRINT USING ";#.## " ;X2;
PSET (QX*0+OX,QY*0+OY)
Mark the x axis ticks.

K=0
B=YA-2
C=YA+2
K=K+1
A=DX*K
AA=XA+SX*A
IF AA>271 GOTO 1140
LINE (QX*AA+OX,QY*B+OY)-(QX*AA+OX,QY*C+OY)
GOTO 1080

K=0
K=K+1
A=DX*K
AA=XA-SX*A
IF AA<9 GOTO 1240
LINE (QX*AA+OX,QY*B+OY)-(QX*AA+OX,QY*C+OY)
GOTO 1150

Mark the y axis ticks.

K=0
A=XA-2
C=XA+2
K=K+1
B=DY*K
BB=YA-SY*B
IF BB<9 GOTO 1330
LINE (QX*A+OX,QY*BB+OY)-(QX*C+OX,QY*BB+OY)
GOTO 1270

K=0
K=K+1
B=DY*K
BB=YA+SY*B
IF BB>151 GOTO 1400
LINE (QX*A+OX,QY*BB+OY)-(QX*C+OX,QY*BB+OY)
GOTO 1340

LOCATE 22,1
PRINT " X TICK=",INT(DX);" Y TICK=",INT(DY);" File#1 is ";F$(1)
LOCATE 20,22:PRINT XLBS;:LOCATE 22,1

This section recalls all the files and plots them one by one.
1450  
1460  FOR I=1 TO NF
1470  IC=0
1480  JC=0
1490  OPEN F$(I) AS #1 LEN=30
1500  FIELD #1, 15 AS XVAL$, 15 AS YVAL$
1510  GET #1,1
1520  NI = CVS(XVAL$): DOT = CVS(YVAL$)
1530  FOR J=1 TO 100
1540  IC=IC+1
1550  GET #1,IC+1
1560  X(J)=CVS(XVAL$)
1570  Y(J)=CVS(YVAL$)
1580  IF J = 1 AND IC = 1 THEN XIN = X(J); YIN = Y(J): GOTO 1600
1590  IF J = 100 THEN XTMP = X(J); YTMP = Y(J)
1600  IF IC = NI GOTO 1620
1610  NEXT J
1620  FOR J=1 TO 100
1630  JC=JC+1
1640  PS = 0
1650  IF J = 1 AND JC=1 THEN XTMP=XIN: YTMP= YIN: GOTO 1680
1660  IF J = 1 THEN GOTO 1680
1670  XTMP = X(J-1); YTMP= Y(J-1)
1680  AA = XA + SX * X(J)
1690  AT = XA + SX * XTMP
1700  BB = YA - SY * Y(J)
1710  BT = YA - SY * YTMP
1720  IF AA < 9 OR BB < 9 THEN PS = 1
1730  IF AA > 271 OR BB > 151 THEN PS = 1
1740  IF PS GOTO 1810
1750  IF INT(DOT + .5) = 2 THEN GOTO 1810 'No plot
1760  IF INT(DOT+.5)=0 THEN GOTO 1790 'Dot plot
1770  LINE (QX*AT+OX,QY*BT+OY) - (QX*AA+OX,QY*BB+OY) 'Line plot
1780  CIRCLE (QX*AA+OX, QY*BB+OY),2 :GOTO 1810
1790  IDOT = I
1800  CIRCLE (QX*AA+OX,QY*BB+OY),IDOT
1810  IF JC=NI GOTO 1840
1820  NEXT J
1830  GOTO 1530
1840  CLOSE #1
1850  NEXT I
1860  
1870  'This is the conversational part of the program where the user may
1880  'save the plot/graph or add more data or print plot/graph.
1890  
1900  LOCATE 24,1:INPUT ;"ENTER OPTION Save, Make plot, Exit "; OPTX$
1910  IF OPTX$="S" OR OPTX$="s" THEN 1970
1920  IF OPTX$="M" OR OPTX$="m" THEN 2110
1930  IF OPTX$="E" OR OPTX$="e" THEN Locate 24,1:PRINT SPACE$(78);
LOCATE 23,1:END
LOCATE 24,1:PRINT SPC(79):LOCATE 24,1:GOTO 1900
1960 'Save screen routine.
1970 'Save screen routine.
1980 LOCATE 25,1:PRINT SPACE$(78);:LOCATE 25,1
2000 INPUT ;"ENTER IDSK:J filename (NO EXTENSION) ";FIL$
2010 OPEN FIL$+".PAR" AS #1 LEN=30
2020 GOSUB 2170
2030 LOCATE 24,1:PRINT SPACE$(78);:LOCATE 25,1:PRINT SPACE$(78);:LOCATE 23,1
2040 DEF SEG =&HB800
2050 BSAVE FIL$+".SCN",0,&H4000
2060 DEF SEG
2070 LOCATE 25,1:PRINT "FILE ";CHR$(34);FIL$;CHR$(34);" SAVED ";
2080 LOCATE 23,1:END
2090 LOCATE 24,1:PRINT SPACE$(78);:LOCATE 23,1
2100 END
2110 LOCATE 24,1:PRINT SPACE$(78);:LOCATE 24,1
2120 FLX$="mplot.bas"
2130 GOSUB 2160
2140 GOTO 2440
2150 GOTO 2440
2160 OPEN "CHAINDAT.PAR" AS #1 LEN = 30
2170 FIELD #1, 15 AS XPAR$,15 AS YPAR$
2180 LSET XPAR$ = MKS$(SX)
2190 LSET XPAR$ = MKS$(SX)
2200 PUT #1,1
2210 LSET XPAR$ = MKS$(DX)
2220 LSET XPAR$ = MKS$(DY)
2230 PUT #1,2
2240 LSET XPAR$ = MKS$(X2)
2250 LSET XPAR$ = MKS$(Y2)
2260 PUT #1,3
2270 LSET XPAR$ = MKS$(X1)
2280 LSET XPAR$ = MKS$(Y1)
2290 PUT #1,4
2300 LSET XPAR$ = MKS$(QX)
2310 LSET XPAR$ = MKS$(QX)
2320 PUT #1,5
2330 LSET XPAR$ = MKS$(OX)
2340 LSET XPAR$ = MKS$(OX)
2350 PUT #1,6
2360 LSET XPAR$ = MKS$(XA)
2370 LSET XPAR$ = MKS$(YA)
2380 PUT #1,7
2390 XE = 1/ABS(X2-X1):LSET XPAR$ = MKS$(XE)
2400 YE = 1/ABS(Y2-Y1):LSET XPAR$ = MKS$(YE)
2410 PUT #1,8
2420 CLOSE 1
2430 RETURN
2440 CHAIN FLX$
2450 END
AV.9 MAKEGRAF.BAS

10 ' MAKE A LINEAR X,Y GRAPH
20 ' This program allows the user to make an x,y linear graph on the
30 ' graphics monitor with the x and y axis labeled. The graph is generated
40 ' via LINPLT.BAS program which calls file RLINPLT.LNK. The RLINPLT.LNK
50 ' file has the x and y labels and the data file which this program makes.
60 '
70 ' 90 CLS:KEY OFF
80 ' 100 XLOOP = 0
90 ' 110 GOTO 580
100 ' 120 OPEN "RLINPLT.LNK" AS #1 LEN = 30
110 ' 130 FIELD #1,30 AS RFLD$
120 ' 140 GET #1,1
130 ' 150 LSET RFLD$ = MKI$(1)
140 ' 160 PUT #1,1
150 ' 170 GET #1,2
160 ' 180 LSET RFLD$ = YLBL$
170 ' 190 PUT #1,2
180 ' 200 GET #1,3
190 ' 210 LSET RFLD$ = XLBL$
200 ' 220 PUT #1,3
210 ' 230 GET #1,4
220 ' 240 LSET RFLD$ = FILX$
230 ' 250 PUT #1,4
240 ' 260 CLOSE #1
250 ' 270 OPEN FILX$ AS #1 LEN = 30
260 ' 280 FIELD #1,15 AS X$,15 AS Y$
270 ' 290 FOR I = 1 TO 14:LSET X$ = "XXX":LSET Y$ = "YYY":PUT #1,I:
280 ' NEXT I:CLOSE #1
290 ' 300 OPEN FILX$ AS #1 LEN = 30
300 ' 310 FIELD #1,15 AS X$,15 AS Y$
310 ' 320 GET #1,1
320 ' 330 LSET X$ = MKS$(2):LSET Y$ = MKS$(2)
330 ' 340 PUT #1,1
340 ' 350 GET #1,2
350 ' 360 LSET X$ = MKS$(XMAX):LSET Y$ = MKS$(YMAX)
360 ' 370 PUT #1,2
370 ' 380 GET #1,3
380 ' 390 LSET X$ = MKS$(XMIN):LSET Y$ = MKS$(YMIN)
390 ' 400 PUT #1,3
400 ' 410 LOCATE 25,1
410 ' 420 PRINT SPACES$(78);:LOCATE 25,1
420 ' 430 PRINT "ENTER OPTION Plot, End ";
430 ' 440 YN$ = INKEY$: IF YN$ ="" THEN 440
440 ' 450 IF YN$ ="E" OR YN$ = "e" THEN CLS:NEW:END
460 IF YN$ = "P" OR YN$ = "p" THEN CLOSE #1:CHAIN "LINPLT.BAS" ELSE 410
470 LOCATE 25,1:PRINT SPACES(78):LOCATE 25,1:XLOOP = 1
480 INPUT;"ENTER FIELD CHANGE XMAX, XMIN, YMAX, YMIN, XLAB, YLAB, FILE, RUN ;","EF$
490 IF EF$ = "XMAX" OR EF$ = "xmax" THEN 580
500 IF EF$ = "YMAX" OR EF$ = "ymax" THEN 640
510 IF EF$ = "XMIN" OR EF$ = "xmin" THEN 610
520 IF EF$ = "YMIN" OR EF$ = "ymin" THEN 670
530 IF EF$ = "XLAB" OR EF$ = "xlab" THEN 700
540 IF EF$ = "YLAB" OR EF$ = "ylab" THEN 730
550 IF EF$ = "FILE" OR EF$ = "file" THEN 760
560 IF EF$ = "RUN" OR EF$ = "run" THEN 120
570 GOTO 470
580 LOCATE 3,1:PRINT SPACES(78):LOCATE 3,1
590 INPUT;"ENTER 'X' MAXIMUM VALUE = ",XMAX
600 IF XLOOP = 1 THEN GOTO 470 ELSE 610
610 LOCATE 4,1:PRINT SPACES(78):LOCATE 4,1
620 INPUT;"ENTER 'X' MINIMUM VALUE = ",XMIN
630 IF XLOOP = 1 THEN GOTO 470 ELSE 640
640 LOCATE 6,1:PRINT SPACES(78):LOCATE 6,1
650 INPUT;"ENTER 'Y' MAXIMUM VALUE = ",YMAX
660 IF XLOOP = 1 THEN GOTO 470 ELSE 670
670 LOCATE 7,1:PRINT SPACES(78):LOCATE 7,1
680 INPUT;"ENTER 'Y' MINIMUM VALUE = ",YMIN
690 IF XLOOP = 1 THEN GOTO 470 ELSE 700
700 LOCATE 9,1:PRINT SPACES(78):LOCATE 9,1
710 INPUT;"ENTER 'X' LABEL [30 characters]: ",XLBL$
720 IF XLOOP = 1 THEN GOTO 470 ELSE 730
730 LOCATE 10,1:PRINT SPACES(78):LOCATE 10,1
740 INPUT;"ENTER 'Y' LABEL [16 characters]: ",YLBL$
750 IF XLOOP = 1 THEN GOTO 470 ELSE 760
760 LOCATE 12,1:PRINT SPACES(78):LOCATE 12,1
770 INPUT;"ENTER DATA FILE NAME dsk:filename.ext — ",FILX$
780 GOTO 470
Appendix VI

PROGRAMS FOR
POROSIMETRY EXPERIMENTS
Two short programs used in the inversion of data from the mercury porosimetry experiments are given in this Appendix.

The raw data from a porosimetry run are in the form of intrusion pressures versus intrusion volumes. This is plotted on graph paper in real-time. That data is digitized either by hand or by any other suitable means and a digitized data file is made. The program HGINV.BAS reads the digitized data file and after suitable manipulations, produces a file containing the pore volume and pore surface area distributions. The dead volume correction as provided by the porosimeter manufacturer is incorporated in the program.

The HGVOLPRT.BAS program computes the specific volumes and surface areas from the respective distribution data in the three pore size ranges corresponding to micro, transitional, and macro pores. The appropriate ranges are user defined.
AVI.1 HGINV.BAS

10 ' MERCURY INTRUSION INVERSION PROGRAM
20 '
30 'This program reads the digitized data file and creates a file containing
40 'r(P), dV/d(log r) and dS/d(log r). The distribution curves are plotted
50 'versus log r. The dead volume correction is included.
60 KEY OFF
70 CLS
80 'Polynomial corrections for blank volume:
90 'These coefficients are from the run performed on 2/13/87.
100 'Intrusion 0—3000 psi
110 '
120 C0=−.000762 : C1=−9.243701E−07 : C2=1.59553E−10
130 '
140 'Intrusion 3000—33000 psi
150 '
160 D0=−.002943 : D1=1.560229E−07 : D2=−1.902453E−12
170 '
180 'Extrusion 25—3000 psi
190 '
200 E0=.0015 : E1=0! : E2=0!
210 '
220 'Extrusion 3000—33000 psi
230 '
240 F0=.001016 : F1= 1.43002E−07 : F2=−4.873868E−12
250 '
260 DIM VOLLOG(NN),SURLOG(NN),DV(NN),DP(NN),P(NN),V(NN)
270 DIM R(NN),RR(NN),VRAW(NN),VCOR(NN),RAV(NN)
280 INPUT *NO.OF PRESSURE POINTS*;NN
290 INPUT *NAME OF DATA FILE*;N$
300 INPUT *MASS OF SAMPLE*;M
310 INPUT *NAME OF OUTPUT FILE*;FILI$
320 INPUT *Intrusion (0) or extrusion (1)*;FLAG
330 IF (FLAG=0 OR FLAG=1)GOTO 340 ELSE GOTO 320
340 OPEN *1*,#1,N$
350 FOR I = 1 TO NN
360 INPUT #1,P(I),VRAW(I)
370 NEXT I
380 CLOSE #1
390 IF FLAG = 1 THEN GOTO 490
400 '
410 'The first point correction is different.
420 '
430 FOR I=2 TO NN
440 IF P(I)<3000 THEN VCOR(I)=C0+P(I)*(C1+P(I)*C2)
450 IF P(I)>3000 THEN VCOR(I)=D0+P(I)*(D1+P(I)*D2)
460 NEXT I
470 VCOR(1)=0!
480 GOTO 540
490 FOR I=2 TO NN
500 IF P(I)<3000 THEN VCOR(I)=E0+P(I)*(E1+P(I)*E2)
510 IF P(I)>3000 THEN VCOR(I)=F0+P(I)*(F1+P(I)*F2)
520 NEXT I
530 VCOR(1)=0.0035
540 FOR I=1 TO NN
550 V(I)=VRAW(I)-VCOR(I)
560 NEXT I
570 R(I)=106.66/(P(I)+14.7): DV(I)=V(I)/M : DP(I)=P(I)+14.7
580 RAV(I)=2*106.66/(P(I)+14.7)
590 TOTSURF=0
600 FOR I = 2 TO NN
610 R(I)=106.66/(P(I)+14.7)
620 RAV(I)=(R(I)+R(I-1))/2
630 DV(I)=(V(I)-V(I-1))/M
640 IF DV(I)<0 THEN DV(I)=0
650 DP(I)=P(I)-P(I-1)
660 VOLLOG(I)=2.303*P(I)*DV(I)/DP(I)
670 SURLOG(I)=VOLLOG(I)*2/RAV(I)
680 SURF=2*DV(I)*10000!/RAV(I)
690 TOTSURF=TOTSURF+SURF
700 NEXT I
710 VFIN=V(1)/M
720 LOCATE 11,1
730 PRINT "Total volume intruded was (cc/g)" : PRINT VFIN
740 LOCATE 13,1
750 PRINT "Total surface area was (sq. cm/g)" :PRINT TOTSURF
760 LOCATE 15,1
770 PRINT "Writing new files..." 
780 OPEN FIL1$ FOR OUTPUT AS #1
790 FOR I=1 TO NN
800 RAV(I)=RAV(I)*10000
810 WRITE #1, RAV(I),VOLLOG(I),SURLOG(I)
820 NEXT I
830 CLOSE #1
840 LOCATE 17,1
850 PRINT "DONE."
860 END
POROSIMETRY DATA PARTITIONING PROGRAM

This program computes the specific volume and surface area from pore volume and pore surface distributions in three pore size ranges corresponding to external, macro, and transition pores. The ranges are defined by the user.

Suggested ranges are: < 500 Å for transitional—macro boundary and < 17600 Å for macro—interparticle boundary (60 psi).

This program also calculates a mean pore radius for each range.

DIM R(200), VLOG(200), SLOG(200), DVDR(200), DSDR(200)
DIM DELVOL(200), DELSURF(200), RVOL(200)
CLS

INPUT "What is the name of the input file ";FILI$
INPUT "What is the file name you will write to ";N$
INPUT "Number of points in file ";NPTS

FOR J=2 TO NPTS
IF R(J) > R2 THEN EXTVOL=EXTVOL+DELVOL(J)
IF R(J) > R[J] THEN EXTSUR=EXTSUR+DELSURF(J)
IF R(J) < R2 AND R(J) > R1 THEN MACVOL=MACVOL+DELVOL(J)
IF R(J) < R2 AND R(J) > R1 THEN MACSUR=MACSUR+DELSURF(J)
470 IF R(J) < R1 THEN TRNVOL = TRNVOL + DELVOL(J)
480 IF R(J) < R1 THEN TRNSUR = TRNSUR + DELSURF(J)
490 NEXT J
500 EXTSUMRV = 0: MACSUMRV = 0: TRNSUMRV = 0
510 FOR J = 2 TO NPTS
520 IF R(J) > R2 THEN EXTSUMRV = EXTSUMRV + RVOL(J)
530 IF R(J) < R2 AND R(J) > R1 THEN MACSUMRV = MACSUMRV + RVOL(J)
540 IF R(J) < R1 THEN TRNSUMRV = TRNSUMRV + RVOL(J)
550 NEXT J
560 EXTRAV = EXTSUMRV / EXTVOL
570 MACRAV = MACSUMRV / MACVOL
580 TRNRAV = TRNSUMRV / TRNVOL
590 VOLSUM = EXTVOL + MACVOL + TRNVOL
600 SURSUM = EXTSUR + MACSUR + TRNSUR
610 OPEN N$ FOR OUTPUT AS #1
620 WRITE #1, RTRANS, TRNVOL, TRNSUR
630 WRITE #1, RMACRO, MACVOL, MACSUR
640 WRITE #1, RINTRP, EXTVOL, EXTSUR
650 PRINT RTRANS, TRNVOL, TRNSUR
660 PRINT RMACRO, MACVOL, MACSUR
670 PRINT RINTRP, EXTVOL, EXTSUR
680 PRINT
690 PRINT , VOLSUM, SURSUM
700 PRINT
710 PRINT
720 PRINT EXTRAV, MACRAV, TRNRAV
730 CLOSE #1
740 END
Appendix VII

PROGRAMS FOR
HIGH TEMPERATURE PYROMETRY
The programs used to acquire particle temperature data from the high temperature reactor pyrometer are given in this Appendix.

The data acquisition program is GETTEMP.BAS. It uses the DT2801-A board and an external trigger to gather the signals from the 1000nm and 800nm channels of the pyrometer. The signals are digitized and stored in the computer RAM via a DMA procedure. PYRO.BAS reads in the raw signal data and creates the actual signal data for temperature inversion. Basically, this involves separating the DMA data into their respective channels, calculating the baselines averages and finally, calculating the signal strengths above their respective baselines. MTEMP.FOR uses suitable calibration data and Planck law analysis to generate the particle temperature-time data.

Figure AVII.1 shows the sequence of steps just outlined. Program listings follow.
Figure AVII.1 Flow Diagram for the analysis of optical pyrometry data.
AVII.1 GETTEMP.BAS

10 ' DIRECT MEMORY ACCESS PROGRAM
20 '  
30 '  
40 '  
50 'This program is used to gather pyrometry data from the high  
60 'temperature reactor. Channels 0 and 1 collect the  
70 'signals from wavelengths 1000 and 800 nm.
80 'It performs fast data acquisition (20kHz) by driving  
90 'the DT2801−A data acquisition board (DATA TRANSLATION INC.).
100 'The system is externally triggered when the voltage on channel 0/1
110 'rises above an adjustable threshold. A fixed number points  
120 'user specified) are obtained from each channel.
130 'These data are printed sequentially on the screen, and then plotted  
140 'by chaining to MPlOT.BAS, thence to LINPLT.BAS via RLINPLT.LNK.
150 'The memory allocation specifications etc. are for the Zenith 148.
160 CLEAR ,25000
170 '  
180 DEFINT A−Z
190 BASE ADDRESS = &H2EC
200 COMMAND REGISTER = BASE ADDRESS + 1
210 STATUS REGISTER = BASE ADDRESS + 1
220 DATA REGISTER = BASE ADDRESS
230 COMMAND WAIT = &H4
240 WRITE WAIT = &H2
250 READ WAIT = &H5
260 CSTOP = &HF
270 CCLEAR = &H1
280 CERROR = &H2
290 CCLOCK = &H3
300 CSAD = &HD
310 CRAD = &HE
320 MIN CONV = 3
330 MAX CONV = 20000!
340 CDMA = &H10
350 DUMMY = 5
360 FREQUENCY# = 800000!
370 PERIOD# = 40
380 EXT TRIGGER = &H80
390 '  
400 'A/D parameter constants.
410 '  
420 FACTOR# = 4096
430 '  
440 'The memory to be used for DMA starts at memory address &HF800
450 'on memory page 0.
460 '  

DMACHANNEL = 1
DMAMODE = &H45
BASEREG = 2
COUNTREG = 3
PAGEREG = &H83
DMABASEL = 0
DMABASEH = &HO
DMAPAGE = 3

'Check for legal Status Register.
STATUS = INP(STATUS.REGISTER)
IF NOT((STATUS AND &H70) = 0) THEN GOTO 2540

'Stop and clear the DT2801-A.
OUT COMMAND.REGISTER, CSTOP
TEMP = INP(DATA.REGISTER)
WAIT STATUS.REGISTER, COMMAND.WAIT
OUT COMMAND.REGISTER, CCLEAR
COMMAND = COMMAND + EXT.TRIGGER

GAIN(0) = 1 : GAIN(1) = 2
GAIN(2) = 4 : GAIN(3) = 8

'Range and Offset are set for unipolar differential outputs.
RANGE = 10 : OFFSET = 0
CLS
INPUT "What is the name of the file series ";FILSER$

'Print out conversion rate.
PRINT USING "#####";FREQUENCY#/PERIOD#;: PRINT " Hertz."

'Get A/D gain.
PRINT "Legal values for gain are ";GAIN(0), ";GAIN(1);PRINT ", ";GAIN(2), ";GAIN(3);."
INPUT "Gain value = ";Y
FOR GAIN.CODE = 0 TO 3 : IF GAIN(GAIN.CODE) = Y THEN GOTO 950
NEXT GAIN.CODE

PRINT " Please use legal gain value."
GOTO 860

START.CHANNEL = 0 : END.CHANNEL = 1
'Get number of conversions to do.

PRINT : PRINT : PRINT ";

PRINT "Legal values for number of conversions are ";MIN.CONV;

PRINT " through ";MAX.CONV;

INPUT " Number of conversions value = ";NUM.CONV

IF (NUM.CONV >= MIN.CONV AND NUM.CONV <= MAX.CONV)
THEN GOTO 1090

GOTO 960

PRINT "Please use legal number of conversions value."

GOTO 960

'Set up the A/D converter.

'Write SET A/D PARAMETERS command.

WAIT STATUS.REGISTER, COMMAND.WAIT
OUT COMMAND.REGISTER, CSAD

'Write A/D gain byte.

WAIT STATUS.REGISTER, WRITE.WAIT, WRITE.WAIT
OUT DATA.REGISTER, GAIN.CODE

'Write A/D start channel byte.

WAIT STATUS.REGISTER, WRITE.WAIT, WRITE.WAIT
OUT DATA.REGISTER, START.CHANNEL

'Write A/D end channel byte.

WAIT STATUS.REGISTER, WRITE.WAIT, WRITE.WAIT
OUT DATA.REGISTER, END.CHANNEL

'Write two bytes, dummy number of conversions.

WAIT STATUS.REGISTER, WRITE.WAIT, WRITE.WAIT
OUT DATA.REGISTER, DUMMY

'Write two bytes, dummy number of conversions.

WAIT STATUS.REGISTER, WRITE.WAIT, WRITE.WAIT
OUT DATA.REGISTER, DUMMY

'Set internal clock rate.

'Set internal clock rate.

WAIT STATUS.REGISTER, COMMAND.WAIT
OUT COMMAND.REGISTER, CCLOCK
'Write high and low bytes of PERIOD#.

PERIODH = INT(PERIOD#/256)
PERIODL = PERIOD# - PERIODH * 256

WAIT STATUS.REGISTER, WRITE.WAIT, WRITE.WAIT
OUT DATA.REGISTER, PERIODL
WAIT STATUS.REGISTER, WRITE.WAIT, WRITE.WAIT
OUT DATA.REGISTER, PERIODH

'Set-up DMA controller

DMACOUNT = (NUM.CONV * 2) - 1
DMACOUNTH = INT(DMACOUNT/256)
DMACOUNTL = DMACOUNT - DMACOUNTH * 256

OUT 11,DMAMODE ' set DMA mode
OUT 12,0 ' clear byte flip-flop
OUT BASEREG,DMABASEL ' set DMA memory base address
OUT BASEREG,DMABASEH 'OUT COUNTREG,DMACOUNTL ' set DMA byte count
OUT COUNTREG,DMACOUNTH 'OUT PAGereg,DMAPAGE ' set DMA memory page
OUT COUNTREG,DMACOUNTL ' set DMA byte count
OUT COUNTREG,DMACOUNTH 'OUT PAGereg,DMAPAGE ' set DMA memory page
OUT 10,DMACHANNEL ' enable DMA channel mask
OUT 10,DMACHANNEL ' enable DMA channel mask

'Check for ERROR.

WAIT STATUS.REGISTER, COMMAND.WAIT
STATUS = INP(STATUS.REGISTER)
IF (STATUS AND &H80) THEN GOTO 2320

'Write READ A/D WITH DMA command.

PRINT : PRINT * Starting conversions.* : PRINT

WAIT STATUS.REGISTER, COMMAND.WAIT
OUT COMMAND.REGISTER, CRAD + CDMA + COMMAND

'Check for ERROR.

WAIT STATUS.REGISTER, COMMAND.WAIT
STATUS = INP(STATUS.REGISTER)
PRINT "TRIGGERED"
IF (STATUS AND &H80) THEN GOTO 2320

'Calculate and print the A/D readings in volts.

PRINT

DEF SEG = &H3000
1930  SUFF=MAIN+97
1940  RUNNUM$=CHR$(SUFF)
1950  
1960  FILNEW$=FILSER$+RUNNUM$+".dat"
1970  OPEN FILNEW$ AS #1 LEN=30
1980  FIELD #1, 15 AS X$, 15 AS Y$
1990  LSET X$=MK$(NUM.CONV) : LSET Y$=MK$(0)
2000  PUT #1,1
2010  FOR LOOP = 1 TO NUM.CONV
2020    ADDRESS= (LOOP - 1) * 2
2030    DATA.VALUE#= PEEK(ADDRESS)
2040    DATA.VALUE#= DATA.VALUE#+ PEEK(ADDRESS + 1) * 256
2050    VOLTS#=((RANGE*DATA.VALUE#/FACTOR#)-OFFSET)/
2060                  GAIN(GAIN.CODE)
2070    TIME#=(LOOP-1)*.05
2080    LSET X$ =MK$(TIME#): LSET Y$ =MK$(VOLTS#)
2090  PUT #1, LOOP+1
2100  PRINT " CHANNEL "; PRINT USING "##";CHANNEL;
2110  PRINT "="; PRINT USING "###.######";VOLTS#;
2120  IF CHANNEL = END.CHANNEL THEN PRINT
2130  NEXT LOOP
2140  CLOSE #1
2150  PRINT
2160  PRINT FILNEW$
2170  GOTO 2700
2180  PRINT : PRINT
2190  INPUT " Do you want to do more conversions (Y/N)";Y$
2200  IF Y$ = "N" OR Y$ = "n" THEN GOTO 2230
2210  IF Y$ = "Y" OR Y$ = "y" THEN GOTO 760
2220  
2230  GOSUB 2270 : GOTO 2160
2240  
2250  PRINT : PRINT
2260  PRINT " READ A/D WITH DMA Operation Complete"
2270  GOTO 2610
2280  'Respond to query with 'Y' or 'N'.
2290  
2300  PRINT : PRINT " Please respond with 'Y' or 'N' only."
2310  RETURN
2320  
2330  'Fatal board error.
2340  
2350  PRINT
2360  PRINT "FATAL BOARD ERROR"
2370  PRINT "STATUS REGISTER VALUE IS ";HEX$(STATUS);" HEXIDECIMAL"
2380  PRINT : BEEP : BEEP : GOSUB 2430
2390  PRINT "ERROR REGISTER VALUES ARE:
2400  PRINT " BYTE 1 — ";HEX$(ERROR1);" HEXIDECIMAL"
PRINT " BYTE 2 — ";HEX$(ERROR2);" HEXIDECIMAL"
PRINT : GOTO 2610
'Read the Error Register.

OUT COMMAND.REGISTER, CSTOP : TEMP = INP(DATA.REGISTER)
WAIT STATUS.REGISTER, COMMAND.WAIT
OUT COMMAND.REGISTER, CERROR
WAIT STATUS.REGISTER, READ.WAIT
ERROR1 = INP(DATA.REGISTER)
WAIT STATUS.REGISTER, READ.WAIT
ERROR2 = INP(DATA.REGISTER)
RETURN

'Illegal Status Register.

PRINT "FATAL ERROR — ILLEGAL STATUS REGISTER VALUE"
PRINT "STATUS REGISTER VALUE IS ";HEX$(STATUS);" HEXIDECIMAL"
BEEP : BEEP
PRINT : PRINT

INPUT " Run program again (Y/N)"; Y$
IF Y$ = "Y" OR Y$ = "y" THEN RUN
IF Y$ = "N" OR Y$ = "n" THEN GOTO 2690

' This part of the program sets the parameters for plotting the data.

SCREEN 0,0,0:CLS:KEY OFF
DIM FL$(1)
NOF = 1
XLBL$ = "TIME"
YLBL$ = "VOLTS"
FL$(1) = FILNEW$
OPEN "RLINPLT.LNK" AS #1 LEN = 30
FIELD #1, 30 AS RFLD$
FOR I = 1 TO 21:LSET RFLD$ = "XXXXXXXXX":PUT #1,I:NEXT I:CLOSE #1
OPEN "RLINPLT.LNK" AS #1 LEN = 30
FIELD #1, 30 AS RFLD$
GET #1,1
LSET RFLD$ = MKI$(NOF)
PUT #1,1
GET #1,2
LSET RFLD$ = YLBL$
PUT #1,2
GET #1,3
2900  LSET RFLD$ = XLBL$
2910  PUT #1,3
2920  FOR I = 1 TO NOF
2930  GET #1,I+3
2940  LSET RFLD$ = FL$(I)
2950  PUT #1,I+3
2960  NEXT I
2970  CLOSE #1
2980  CLS
2990  CHAIN "LINPLT.BAS"
3000  
3010  END
PYROMETRY INVERSION PROGRAM

This program takes the pyrometry signal file (from GETTEMP.BAS) and first separates the signals into their respective channels. It then computes the baseline average (over the last 15 points) signal in each channel. Finally, it computes the actual signal (input-average) in each channel and the ratio of the signals (rat). The output file, readable by zplot (ASCII) contains the actual signals, their ratio and also the raw signals and time. This output file is read by MTEMP.EXE (from MTEMP.FOR) to deduce the temperature from the signal ratio.

N = 200 'size of the arrays

CLS:SCREEN 0,0,0:KEY OFF
LOCATE 5,1

'Enter input file from GETTEMP.BAS
INPUT "Enter name of file to be modified as [dsk:]filename.dat ";FILOLD$
LOCATE 7,1
INPUT "Enter name of new file as [dsk:]filename.dat ";FILNEW$
DIM X(N),Y(N),Y1(N),Y2(N),Y1SIG(N),Y2SIG(N),RAT(N)
LOCATE 9,1
PRINT "Reading old file..."
OPEN FILOLD$ AS #1 LEN = 30
FIELD #1, 15 AS X$, 15 AS Y$
GET #1,1
NPTS = CVS(X$)
M = CVS(Y$)
FOR I = 1 TO NPTS
GET #1,I+1
X(I) = CVS(X$)
Y(I) = CVS(Y$)
NEXT I
CLOSE #1
IC=1

'Separate the signals into proper channels.
FOR I=NPTS TO 2 STEP -2
Y1(IC)=Y(I)
Y2(IC)=Y(I-1)
X(IC)=(IC-1)*.1
IC=IC+1

'Calculate baseline average in each channel.

FOR J = 1 TO 15
  SUM1 = SUM1 + Y1(J)
  SUM2 = SUM2 + Y2(J)
NEXT J

Y1AV = SUM1 / 15!
Y2AV = SUM2 / 15!

'Find the actual signal level in each channel and the signal ratio.

FOR K = 1 TO NNEW
  Y1SIG(K) = Y1(K) - Y1AV
  Y2SIG(K) = Y2(K) - Y2AV
  RAT(K) = Y1SIG(K) / Y2SIG(K)
  IF RAT(K) < 1! THEN RAT(K) = 1! / RAT(K)
  PRINT RAT(K)
NEXT K

PRINT "Computing modifications..."

'Write to output file.

OPEN FILNEW$ FOR OUTPUT AS #1
FOR I = 1 TO NNEW
  WRITE #1, X(I), Y1(I), Y2(I), Y1SIG(I), Y2SIG(I), RAT(I)
NEXT I
CLOSE #1

PRINT "Done."
AVII.3 MTEMP.FOR

This program calculates the particle temperature from the high temperature pyrometry experiments. Its input is the file from PYRO.BAS that has the ratio of the signals in the two wavelengths. Using that ratio and a calibration factor the particle temperature is calculated from a Planck law analysis.

DIMENSION X(50),Y1(50),Y2(50),Y1S(50),Y2S(50)
DIMENSION RAT(50),TEMP(50),TIME(50)
CHARACTER*15 OLDFILE,NEWFILE

WRITE(*,10)
10 FORMAT(1X,'ENTER OLDFILE:')
READ(*,12)OLDFILE
12 FORMAT(A15)
WRITE(*,14)
14 FORMAT(1X,'ENTER NEWFILE')
READ(*,12)NEWFILE
WRITE(*,16)
16 FORMAT(1X,'ENTER RATIO')
READ(*,*)RATIO

OPEN(1,FILE=OLDFILE,STATUS='OLD',FORM='FORMATTED')
DO 100 I=1,50
READ(1.*,END=101)X(I),Y1(I),Y2(I),Y1S(I),Y2S(I),RAT(I)
CONTINUE
CONTINUE
CLOSE(1)
CAL=-1.0*ALOG(RATIO/26.3114)
DO 200 J=1,50
IF (RAT(J) .EQ. 0.0)GOTO 201
TIME(J)=(J-1)*0.1
TEMP(J)=3597.0/(ALOG(RAT(J))+CAL)
CONTINUE
CONTINUE
OPEN(2,FILE=NEWFILE,STATUS='NEW')
DO 300 K=1,50
IF(Y1S(K) .NE. 0.0)THEN
WRITE(2,400)TIME(K),TEMP(K),Y1S(K),Y2S(K),RAT(K)
ELSE
CONTINUE
ENDIF
CONTINUE
CLOSE(2)
STOP
END
Appendix VIII

PROGRAMS FOR
KINETIC PARAMETER ESTIMATION
The experimental and theoretical procedure used to get the chemical kinetic parameters at high temperatures is outlined in Figure AVIII.1. First, single particle experiments are done and individual temperature-time traces depicting the particle combustion histories are obtained. The program AD2.FOR is used for data acquisition purposes. The raw data containing the light intensity voltage values are converted to particle temperatures in the program RETEMP.FOR.

Once the experimental time histories are known, the kinetic parameter estimation program VARASH.FOR is used to determine the kinetic parameters. Individual traces are fit by polynomial functions and the polynomial coefficients are used as inputs in the VARASH program. VARASH also contains a suitable particle combustion model (VARNU.FOR, see Appendix IX) to interpret the traces. Details of the procedure are given in Chapter 4. Temperature-time traces of most of the runs are collected in Appendix XII.
Figure AVIII.1 Flow diagram for kinetic parameter estimation.
AVIII.1 AD2.FOR

ROUINE AD2 (date acquisition)
DIMENSION IRAM1(1200),IRAM2(1200)
DIMENSION X(1200),Y(1200)
BYTE FILE (20),AVSH
VCON = 10. / 4096.
RMAX = 1500
ICH1 = 2
ICH2 = 3
TYPE 10. ICH1, ICH2
10 FORMAT(('ICL.'Dual A/D Fast Sampling Program -- ',
1 'Sampling Channels ',2,' & ',2,' //'))
12 TYPE 15
15 FORMAT('Enter the Number of A/D Samples to Take: ')
ACCEPT *, KOUNT
IF (KOUNT.LE.0 .OR. KOUNT.GT.RMAX) GOTO 12
EDIM=KOUNT
TYPE 30
30 FORMAT('Enter threshold (00-w=40) : ')
ACCEPT *, IEVC
TYPE 35
35 FORMAT('Enter # of baseline points: ')
ACCEPT *, NAVG
TYPE 50
50 FORMAT('Hit RETURN to start sampling: ')
ACCEPT 55, JUNK
55 FORMAT(A1)
59 ITE=0
60 CALL GTIM(TINTB)
61 CALL ADSET2(ICH1, ICH2,KOUNT,IRAM1,IRAM2)
CALL GTIM(TINTE)
SEC = ELAPSE(TINTB,TINTE)
CALL PFEAK(IRAM2,EDIM,IEVC,NAVG,IAVG,IECN,IN5,1N6)
ITEM=ITEM+1
TYPE 70. ITEM,IECN,IAVG
70 FORMAT(15,5X,'PEAK AT :',14,
8 5X,'BASELINE SIGNAL :',14)
IF (ITEM.EQ.50) GO TO 222
IF (IECN.EQ.-1) GO TO 60
IF (IECN.EQ.-2) GO TO 60
IF (IECN.EQ.-3) GO TO 60
TYPE 150, SEC, KOUNT
150 FORMAT(' The Elapsed Time Is',F10.3,' seconds for',14,)
TYPE 160, IECN,1N6
160 FORMAT(15,5X,'SIGNAL STARTS AT:',14,5X,'SIGNAL ENDS AT:',14)
CALL ISTAT(KOUNT,IRAM1,AV1,ED1,SL1)
AV1 = AV1 * VCON
ED1 = VCON + ED1
SL1 = SL1 * VCON
CALL ISTAT(KOUNT,IRAM2,AV2,ED2,SL2)
AV2 = AV2 * VCON
ED2 = ED2 * VCON
SL2 = SL2 * VCON
TYPE 200, 1,AV1,ED1,SL1
TYPE 200, 2,AV2,ED2,SL2
200 FORMAT(' For Channel 1,13,' 'Average=',F8.4,' Std.Dev.=',
1 F8.4,' Slope=',F9.5,' Volts')
DO 7 J=1,KOUNT
Y(J) = FLOAT(VCON*IRAM1(J))
X(J) = FLOAT(I)
7 CONTINUE
ISTIME = 0.0
INCN = 0
INAX = KOUNT
205 IXOUNT=IMAX-IMIN-1
C CALL RANGES (IXOUNT, X(IMIN), Y(IMIN), XMIN, XMAX, YMIN, YMAX)
XMIN=X(IMIN)
XMAX=X(IMAX)
YMIN=Y(IMIN)
YMAX=Y(IMAX)
IF (XMIN.EQ.1) XMIN=0.
DO 212 IM=IMIN,IMAX
   IF (Y(IM).LT.YMIN) YMIN=Y(IM)
   IF (Y(IM).GT.YMAX) YMAX=Y(IM)
212 CONTINUE
YMIN=YMIN-0.001
YMAX=YMAX+0.001
CALL VSETS(YMIN, YMAX, XMIN, XMAX, D)
210 CALL VXPL0T(0, X, Y)
ISTEP = (IMAX-IMIN+1)/100
IF (ISTEP.LT.1) ISTEP = 1
DO 220 IM=IMIN, IMAX, ISTEP
   CALL VXADD(1, X(IM), Y(IM))
220 CONTINUE
CALL VPUT (24, 1)
222 TYPE 225
225 FORMAT ("Select M to magnify, S to Save, R to Repeat, ", 1 ", I to Initialise, Q to Quit: ")
ACCEPT 226, ANSW
226 FORMAT (A1)
   IF (ANSW.EQ.'S') GOTO 240
   IF (ANSW.EQ.'R') GOTO 400
   IF (ANSW.EQ.'M') GOTO 229
   GOTO 222
228 TYPE 230
230 FORMAT ('Enter IMIN,IMAX : ')
ACCEPT IMIN, IMAX
IF (IMIN.GE.IMAX .OR. IMAX.GT.IMIN) GOTO 229
GOTO 205
240 CALL ASFAIL (3, FILE)
CALL ASSIGN (3, FILE)
DO 300 IM=IMIN, IMAX
   WRITE (3, 333) VCON*IRAM1(IM),VCON*IRAM2(IM)
333 FORMAT (',2F8.4)
300 CONTINUE
CLOSE (UNIT=3)
400 CALL VINIT
GO TO 59
401 STOP
END
SUBROUTINE PEAK (IBUF, IDIM, IE XC, NAVG, IAVG, ICEN, INS, INE)

THIS ROUTINE IS USED TO DETECT SIGNALS EMITTED BY BURNING
COAL PARTICLES AND RECORDED BY A TWO COLOR PYROMETER
(THE APPROXIMATE CENTER OF THE PEAK CAN ALSO BE FOUND)

METHOD: THE CENTER OF THE PEAK IS DEFINED AS THE POINT WHICH
GIVES THE MAXIMUM CORRELATION OF THE SIGNAL AND A WINDOW
OF CONSTANT VALUE.

NOTE: THIS ROUTINE ASSUMES THAT THE FIRST "NAVG" DATA POINTS
REPRESENT A ZERO LEVEL IN THE SIGNAL AND THAT THE PEAK
OCCURS "IW IN" POINTS BEFORE THE END SPECIFIED BY "IDIM"

INPUT: IBUF- ARRAY CONTAINING THE SIGNAL
       IDIM- LENGTH OF ARRAY

OUTPUT: ICEN- INDEX TO APPROXIMATE CENTER OF THE PEAK
       INS- FIRST OCCURRENCE WHEN SIGNAL EXCEEDS THRESHOLD
            STARTING FROM THE BEGINNING OF THE SIGNAL
       INE- FIRST OCCURRENCE WHEN SIGNAL EXCEEDS THRESHOLD
            STARTING FROM THE END OF THE SIGNAL

ERRORS: ICEN- SET TO -1 IF NO PEAK FOUND

PARAMETERS: NAVG- # OF POINTS TO FIND AVERAGE OVER ZERO LEVEL
                IN SIGNAL

IW IN- WIDTH OF WINDOW TO FIND PEAK

IEXC- ABSOLUTE VALUE THE SIGNAL MUST CHANGE BY
      BEFORE SEARCH FOR PEAK IS MADE
      100mv IS 41.

INTEGER*2 IBUF (IDIM)
VIRTUAL IBUF (IDIM)

GET ZERO LEVEL FOR START OF SIGNAL

AVG=0.
DO 10 J=1, NAVG
   AVG=AVG+IBUF (J)
2  IAVG=AVG/NAV G

FIND ENDING ZERO LEVEL

AVG=0.
DO 15 J=IDIM-NA VG+1, IDIM
   AVG=AVG+IBUF (J)
2  IAVG=AVG/NAV G

IWIN=IDIM-NA VG+2

TWO STATEMENTS THAT SET ERROR FLAGS FOLLOW

IF (IW IN .GT. 20) GO TO 19
   ICEN=-2
RETURN
IF (IBUF(IDIM) .LT. IEXC/2) GO TO 19
ICEN=3
RETURN

FINITE STARTING INDEX WHERE SIGNAL EXCEEDS THRESHOLD

19 INS=1
20 IF ( IABS(IBUF(INS)-IAVG) .GT. IEXC ) GO TO 25
INS=INS+1
IF ( INS .LT. IWIN ) GO TO 20
ICEN=1
RETURN

SET ERROR IF SIGNAL "DOESN'T EXCEED THRESHOLD"

FINITE ENDING INDEX WHERE SIGNAL EXCEEDS THRESHOLD

25 INE=IDIM
28 IF ( IABS(IBUF(INE)-IAVG) .GT. IEXC ) GO TO 30
INE=INE-1
GO TO 28
INE=INE-IWIN/2
30 XMAX=0
GO 50 K=INS,INE
THAX=0
40 THAX=THAX+IABS(IBUF(K)-IAVG)
IF ( THAX .LE. XMAX ) GO TO 50
ICEN=K
XMAX=THAX
50 CONTINUE
RETURN
END
.TITLE ADSET2 -- TAKES 2 SETS OF A/D READINGS
.GLOBAL ADSET2

; FORTRAN USAGE: CALL ADSET2(ICH1,ICH2,KOUNT,IAAR1,IAAR2)
; ICH1 = FIRST A/D CHANNEL NUMBER (0-15 NORMALLY)
; ICH2 = SECOND A/D CHANNEL NUMBER (0-15)
; KOUNT = NUMBER OF READINGS TO TAKE
; IAAR1 = FIRST INTEGER ARRAY SPACE FOR RAW A/D VALUES
; IAAR2 = SECOND INTEGER ARRAY SPACE FOR RAW A/D VALUES
; NOTE THAT ICH1, ICH2, AND KOUNT ARE INTEGER*2 VARIABLES, AND
; IAAR1 AND IAAR2 ARE INTEGER*2 ARRAYS DIMENSIONED TO AT LEAST KOUNT

CIDSTAT=170400
GNCCHAD=170402
ADDATA=170402

ADSET2:
TST (R5)+ ; IGNORE # OF ARGUMENTS
MOV @ (R5)+,R1 ; R1 = ICH1
MOV @ (R5)+,R2 ; R2 = ICH2
MOV @ (R5)+,R0 ; R0 = KOUNT
MOV (R5)+,R3 ; R3 = ADDRESS OF IAAR1
MOV (R5)+,R4 ; R4 = ADDRESS OF IAAR2

NEXT:
MOV R1,#GNCCHAD ; START CONVERSION

LOOP1:
TST #CIDSTAT ; A/D CONVERSION DONE?
BGE LOOP1 ; LOOP UNTIL DONE
MOV #ADDATA,(R3)= ; SAVE RAW DATA IN IAAR1
MOV R2,#GNCCHAD ; START IGN2 CONVERSION

LOOP2:
TST #CIDSTAT ; A/D CONVERSION DONE?
BGE LOOP2
MOV #ADDATA,(R4)= ; SAVE RAW DATA IN IAAR2
DEC R0 ; DECREMENT KOUNT
BNE NEXT ; NEXT SAMPLE UNLESS R2=0
RETURN
.END
This program calculates the ratio of the two signals generated by the combustion of a char particle. First the magnitudes of the two signals are computed then the ratio is taken and finally the temperature is calculated.

```
CHARACTER*15 INFIL,OUTFIL
REAL*4 A1(1000),A2(1000),DA(1000),AA1(1000),AA2(1000)
REAL*4 TIME(1000),T(1000)

Read in data from the input file.
```

```
WRITE(*,2)
FORMAT(2X,' ENTER INPUT DATA FILENAME :'\)
READ(*,50)INFIL
FORMAT(A15)

OPEN ( 1, FILE=INFIL,FMT='FORMATTED',STATUS='OLD')

DO 100 I=1,1000
  READ(1,99,END=101) A1(I),A2(I)
CONTINUE
CONTINUE
FORMAT(1X,2F8.4)
```
DO 102 I=1,15
    WRITE(*,99) A1(I),A2(I)
102    CONTINUE

C Enter flag corresponding to furnace wall temperature.

WRITE(*,33)
33 FORMAT(' ENTER FLAG : FLAG=1 FOR 10.3MV ELSE 0:"
READ(*,*)FLAG

C Compute the baseline average in each channel.

A1SUM=0.
A2SUM=0.
DO 110 I=1,15
    A1SUM=A1(I)+A1SUM
    A2SUM=A2(I)+A2SUM
110 CONTINUE

A1BCK=A1SUM/15.
A2BCK=A2SUM/15.
WRITE(*,111)A1BCK,A2BCK
111 FORMAT(//,2X,' A1BCK = ',F8.4,3X,' A2BCK = ',F8.4)

C Calculate the signal average in each channel.

DO 200 I=1,1000
    AA1(I)=A1(I)-A1BCK
AA2(I) = A2(I) - A2BCK

DO 300 I=1,1000
   IF(AA1(I) .LT. 0.000001) GOTO 300
   DA(I) = AA2(I) / AA1(I)
300 CONTINUE

Calculate the temperature.

IF(FLAG .EQ. 1.) THEN
   DO 310 I=1,1000
      IF(DA(I) .LE. 0.0) GOTO 311
      IF(DA(I) .GT. 0.0) GOTO 312
311 T(I) = 0.0
   GO TO 310
312 T(I) = (3597) / (ALOG(DA(I)) + 1.0921929)
310 CONTINUE
ELSE
   DO 410 I=1,1000
      IF(DA(I) .LE. 0.0) GOTO 411
      IF(DA(I) .GT. 0.0) GOTO 412
411 T(I) = 0.0
   GO TO 410
412 T(I) = (3597) / (ALOG(DA(I)) + 1.2033064)
CONTINUE
ENDIF

Write to output file.
Time(i) is in milliseconds, assuming 1000/0.1sec rate.

WRITE(*,320)
FORMAT(2X,' ENTER OUTPUT FILENAME : '
READ(*,50)OUTFIL
OPEN(2,FILE=OUTFIL,FORM='FORMATTED',STATUS = 'NEW')
DO 350 I=1,1000
   TIME(I)=0.1*I
   WRITE (2,330)I,TIME(I),AA1(I),AA2(I),DA(I),T(I)
350 CONTINUE
330 FORMAT(1X,I4,1X,5F10.4)

CLOSE(1)
CLOSE(2)
GOTO 999
990 WRITE(*,991)
991 GOTO 999
992 WRITE(*,993)
993 FORMAT(' ERROR IN OPENING INPUT FILE')
994 STOP
END
This program is used to determine the apparent Arrhenius kinetic parameters from single particle temperature-time traces. The experiments were done in the drop-tube reactor at high temperatures.

Since there is significant particle to particle variability even when experimental conditions are the same, this is attributed to variation in the particle initial size and the particle shape. Both parameters are lumped in the initial particle radius.

The experimental temperature trace is first fit with a fifth order polynomial using the program POLY2.BAS. These coefficients are inputs to this program. The average initial particle radius, guesses for the pre-exponential factor and activation energy, wall temperature, and oxygen partial pressure are the other inputs.

Using the guessed kinetic parameters, the particle burning model (asymptotic version VARNU.FOR) is run. This predicts a temperature-time trace. The pre-exponential factor is adjusted till the experimental and model burn times match.

Then a least squares residual is computed that represents the difference between the model and experimental traces.
The above procedure is repeated with different initial particle radii and activation energies. For each trace, the residual is computed for many values of activation energies and initial radii. That value of activation energy (and the associated pre-exponential factor) and initial radius is chosen which minimizes the residual.

The process is then repeated for many traces. Finally the activation energy that minimizes the sum of the minimum residuals of each trace is chosen as the correct parameter.

---

Declarations.

```
IMPLICIT REAL*4(A-H,O-Z)
REAL*8 CHRON0(800),CALOR(800)
REAL*8 TFAC,PEMMIS
CHARACTER*15 OFIL
DIMENSION CTIME(10),CTEMP(10),ATEMP(10),PLTEMP(10)
DIMENSION ER(10),VARER(15),PHTEMP(10)
INTEGER IER,NCOUNT
EXTERNAL QCR,VARNU
COMMON /BIG/ EPSO,RHOC,RINIT,RFINAL,PINF,AERR,RERR,
    TWALL,DUM,RBAR,NCOUNT,ENG,PTS,NDEG,EPSF,Asho,A(3)
COMMON /DATA/CHRONO,CALOR
COMMON /TI/TSTART,TEND
```
530 COMMON /TF,TFAC,PEMMIS

540 C

550 C-----------------------------------------------

560 C

570 C Parameter inputs.

580 C

590 WRITE(*,306)

600 306 FORMAT(1X,'ENTER THE OUTPUT FILE NAME:')

610 READ(*,305)OFL

620 305 FORMAT(A15)

630 WRITE(*,310)

640 310 FORMAT(1X,'ENTER START AND END TIMES (ms):')

650 READ(*,*)TSTART,TEND

660 WRITE(*,312)

670 312 FORMAT(1X,'ENTER INIT ASH AND VOID FRACTIONS, PEMMIS:')

680 READ(*,*)ASHO,EPSO,PEMMIS

690 WRITE(*,315)

700 315 FORMAT(1X,'ENTER INITIAL RAD(mic), TWALL AND O2 P.P:')

710 READ(*,*)RINIT,TWALL,PINF

720 WRITE(*,317)

730 317 FORMAT(1X,'ENTER INIT., FINAL ACT. ENERGIES, INCREMENT:')

740 READ(*,*)E,FAE,DELE

750 WRITE(*,320)

760 320 FORMAT(1X,'ENTER THE INIT. GUESS FOR A AND THCK FACTOR:')

770 READ(*,*)GUESSA,TFAC

780 WRITE(*,325)

790 325 FORMAT(1X,'ENTER NUMBER OF COEFF.S (MAX=5):')
800 READ(*,*)NDEG
810 DO 340 IT=1,NDEG
820 WRITE(*,330)IT
830 330 FORMAT(1X,'ENTER COEFF. ',I2)
840 READ(*,*)A(IT)
850 340 CONTINUE
860 C
870 C ASH0=0.12
880 C EPS0=0.58
890 RHOC=1.5
900 OPEN(2,FILE=OFIL,STATUS='NEW')
910 C
920 DELRINIT=1.0*1.0E-04
930 E=E-DELE
940 XACC=0.0001
950 XACC2=0.025
960 RINIT=RINIT*1.0E-04
970 RFINAL=RINIT*(ASHO/(1.0-EPS0))**0.333333
980 INDEX=(FAE-E)/DELE
990 C
1000 C Main program main loop begins.
1010 C
1020 DO 370 I=1,INDEX
1030 E=E+DELE
1040 GUESS1=1.7*GUESSA
1050 GUESS2=3.0*GUESSA
1060 C
DUMR=RINIT
X1=GUESS1
X2=GUESS2
CALL QCR(E,X1,DUMR,FX1)
WRITE(*,*)FX1
CALL QCR(E,X2,DUMR,FX2)
WRITE(*,*)FX2
DO 350 J=1,100
GUESS3=GUESS1+(GUESS1-GUESS2)*FX1/(FX2-FX1)
CALL QCR(E,GUESS3,DUMR,FX3)
WRITE(*,*)FX1,FX2,FX3
350 CONTINUE
FX1=FX2
FX2=FX3

FREQ=GUESS3
GUESSA=FREQ
WRITE(*,*)FREQ

DELCHRO=(TEND-TSTART)/11.0
DO 400 J=1,10
DUMJ=TSTART+DELCHRO*J
DO 450 K=1,800
IF (CHRONO(K) .GT. DUMJ) THEN
CTIME(J)=CHRONO(K)
450 CONTINUE
400 CONTINUE

The following two program blocks perform numerical differentiation with respect to initial radius.

RLOW=RINIT-DELRINIT
CALL QCR(E,FREQ,RLOW,FUNT)
DO 500 J=1,10
DUMJ=TSTART+DELCHRO*J
DO 550 K=1,800
   IF (CHRONO(K) .GT. DUMJ) THEN
      PLTEMP(J)=CALOR(K)
      GOTO 501
   ENDIF
550 CONTINUE
501 CONTINUE
500 CONTINUE

RHIGH=RINIT+DELRINIT
CALL QCR(E,FREQ,RHIGH,FUNT)
DO 600 J=1,10
DUMJ=TSTART+DELCHRO*J
600 CONTINUE
601 CONTINUE
600 CONTINUE
DO 650 K=1,800
IF (CHRONO(K) .GT. DUMJ) THEN
  PHTEMP(J)=CALOR(K)
  GOTO 601
ENDIF
CONTINUE
CONTINUE
CONTINUE
SUMER=0.0
DO 700 IL=1,10
  ATEMP(IL)=0.0
  DO 710 JK=1,NDEG
    ATEMP(IL)=ATEMP(IL)+A(JK)*(CHRONO(IL)*1.0E-03)**(JK-1)
  CONTINUE
  DERIV=(PHTEMP(IL)-PLTEMP(IL))/(2.0*DELRINIT)
  ER(IL)=(ATEMP(IL)-CTEMP(IL))/DERIV
  SUMER=SUMER+ER(IL)
CONTINUE
VARSUM=0.0
ERBAR=SUMER/10.0
DO 800 KL=1,10
  VARSUM=VARSUM+(ER(KL)-ERBAR)*(ER(KL)-ERBAR)
CONTINUE

Write to file.

VARER(I)=VARSUM/9.0

WRITE(2,380)E,FREQ,VARER(I)
WRITE(*,380)E,FREQ,VARER(I)

CONTINUE

FORMAT(1X,2F12.5,1X,1F18.12)
CLOSE(2)
STOP
END

This is the calling program for VARNU.

SUBROUTINE QCR(EM,P,DUMR,FUNT)
IMPLICIT REAL*4(A-H,O-Z)
REAL*8 RHOP,DTWAL,TPINIT,DP,C1INF,DRINIT
REAL*8 ASHINIT,ACEN,TTOT
EXTERNAL VARNU
COMMON /BIG/ EPSO,RHOC,RINIT,RFINAL,PINF,AERR,RERR,
TWALL,DUM,RBAR,NCOUNT,ENG,PTS,NDEG,EPSF,ASHO,A(3)
COMMON /TI/TSTART,TEND

C
RHOP = (1.0 - EPSO - ASHO) * RHOC

DTWAL = TWALL

TMPR = 0.0

DO 75 K = 1, NDEG

    TMPR = TMPR + A(K) * (TSTART * 1.0E-03)**(K-1)

CONTINUE

TPINIT = TMPR

DP = P

C1INF = PINF

DRINIT = DUMR * 1.0D04

ASHINIT = ASHO

ACEN = EM

CALL VARNU(RHOP, DTWAL, TPINIT, DP, C1INF, DRINIT, ASHINIT, ACEN, TTOT)

FUNT = TTOT - (TEND - TSTART)

RETURN

END

SUBROUTINE VARNU(AZ1, BZ1, CZ1, DZ1, EZ1, FZ1, GZ1, HZ1, TBURN)

IMPLICIT REAL*8(A-H, O-Z)

REAL*8 NMAX

REAL*8 K11, K12, K13, K14, K21, K22, K23, K24

REAL*4 TSTART, TEND
DIMENSION CHRON0(800),CALOR(800)

EXTERNAL EC,ECH,CPC,CPCH
EXTERNAL FLUX,ENERGY
EXTERNAL GAMMA,RTBIS,RADIUS,SOLID

COMMON /FIRST/T,GAM,TWALL,FP
COMMON /R/RHOC,XFAC,ACEN
COMMON /Y1S/Y1S,Y1INF
COMMON /ASH/ASHFRAC,RHOASH,ASHINIT,
           1 RPINIT,CPASH,AMMIS,THCK
COMMON /DATA/CHRONO,CALOR
COMMON /TI/TSTART,TEND
COMMON /TF/TFAC,PEMMIS

Initialization.

RHOC=AZ1
TWALL=BZ1
TPINIT=CZ1
XFAC=DZ1
C1INF=EZ1
RPINIT=FZ1
ASHINIT=GZ1
ACEN=HZ1
RHOASH=2.5
NMAX=2000
ES1=1.0D-6
ES2=1.0D07
XACC=0.0001
STEP0=0.0001
DELT=20
WEMMIS=0.8
PEMMIS=0.8
AMMIS=0.8

Y1INF=(C1INF * 32.0)/(C1INF * 32.0 +(1.0 - C1INF)*28.0)
A = (1.0 / (1.0 - Y1INF)) * (Y1INF / 4.0)

TP = TPINIT
RP = RPINIT
C1S = C1INF
TIME = 0.0
DTDR = 0.0
FP=0.0
THCK=0.0
ASHFRAC = ASHINIT

WRITE(*, 900) TIME, RP, TP, C1S, FP
FORMAT(1X,5G12.4)
X1 and X2 are appropriate brackets for GAM.

Typically, ES1 is 0(1D-6), while ES2 is 0(1D11).

```
IF ( TPINIT .LT. TWALL) THEN
    X1 = ( -2331.5425 + 0.3388749*TPINIT) - ES2
    X2 = ( -2331.5425 + 0.3388749*TPINIT) - ES1
ELSE
    X1 = ( -2331.5425 + 0.3388749*TPINIT) + ES1
    X2 = ( -2331.5425 + 0.3388749*TPINIT) + ES2
ENDIF
```

Main loop in VARNU begins.

```
JMAX = NMAX
DO 1000 I = 1, JMAX
    STEP=STEPO
    T = TP
    RR = RP * 1D-04
    THCK=(RP**3.0+(ASHINIT*(RPINIT**3.0-RP**3.0))/0.65)**
         1 (1.0/3.0)-RP + 1.0D-08
    THCK=THCK*1.0D-04*TFAC
    CALL RTBIS(GAMMA,X1,X2,XACC,RR,GAM)
    DUMC = (1.0/(-1.0/7.0 + 8.0/(7.0*Y1S)))
    CALL FLUX(DUMC,RR)
    FP1 = -1.3333 * FP
    FP2 = 2.3333 * FP
    EP = GAM * FP
```
CALL SOLID(RR)
CALL RUNG(RADIUS,ENERGY,DUMC,STEP,EP,
PEMMIS,WEMMIS,RR,RNEW,TNEW)
!
C
!

IF(DABS((RNEW-RR)/RR) .LT. 0.0001)THEN
IF(RNEW .LE. 0.0001)THEN
TBURN=TIME
GOTO 1001
END IF
RP = 1.0D4*RNEW
TP = TNEW
TIME = TIME + 1.0D3*STEP
!

REDUCING BRACKETS FOR THE NEXT CALL OF GAM.
!

IF ( TP .LT. TWALL) THEN
X1 = GAM - DABS(1000.0*GAM)
X2 = ( -2331.5425 + 0.3388749*TP ) - ES1
ELSE
X1 = ( -2331.5425 + 0.3388749*TP ) + ES1
X2 = GAM + DABS(1000.0*GAM)
ENDIF
!

CONTINUE
CONTINUE
Main loop in VARNU ends.

---

Property values.

EC and ECH calculate the enthalpy of the solid in cal/g.

Data from the Coal Data Book.

```fortran
REAL*8 FUNCTION EC(D)
IMPLICIT REAL*8(A-H,O-Z)
COMMON /FIRST/T,GAM,TWALL,FP
CPCO = 0.024
CPC1 = 6.953D-04
CPC2 = -2.841D-07
EC = CPCO*(D - 298) + (CPC1 / 2.0)*(D*D - 298*298)
1 + (CPC2 / 3.0)*(D*D*D - 298*298*298)
RETURN
END
```

```fortran
REAL*8 FUNCTION ECH(D)
IMPLICIT REAL*S(A-H,0-Z)
COMMON /FIRST/T,GAM,TWALL,FP
CPCHO = 0.36
```
CPC and CPCH calculate heat cap. of the solid in cal/g-K.
Data from Coal Data Book.

REAL*8 FUNCTION CPC(D)
IMPLICIT REAL*8(A-H,O-Z)
COMMON /FIRST/T,GAM,TWALL,FP
CPCO = 0.024
CPC1 = 6.953D-04
CPC2 = -2.841D-07
CPC = CPCO + CPC1 * D + CPC2 * D * D
RETURN
END

REAL*8 FUNCTION CPCH(D)
IMPLICIT REAL*8(A-H,O-Z)
COMMON /FIRST/T,GAM,TWALL,FP
CPCHO = 0.36
CPCH1 = 6.931D-05
CPCH = CPCHO + CPCH1 * D
RETURN
END
This routine finds the fraction of solid covered by ash (ASHFRAC). (ASHFRAC --> 1.0 as RR --> RMIN).

```
SUBROUTINE SOLID(RR)
IMPLICIT REAL*8(A-H,O-Z)
COMMON /ASH/ASHFRAC,RHOASH,ASHINIT,
RPINIT,CPASH,AMMIS,THCK
ASHFRAC = ASHINIT*(1.0D-4*RPINIT/RR)**3.0
RETURN
END
```

Root finder by the method of bisection for function TET.

```
SUBROUTINE RTBIS(TET,X1,X2,XACC,R2,XMID)
IMPLICIT REAL*8(A-H,O-Z)
EXTERNAL TET
COMMON /FIRST/T,GAM,TWALL,FP
PARAMETER (JMAX = 500)
CALL TET(X1,FX1,R2)
CALL TET(X2,FX2,R2)
IF(FX2*FX1 .GE. 0.0) PAUSE 'BRACKET ROOT IN VARNU'
```
DX = X2 - X1  
DO 200 J = 1, JMAX  
    DX = DX * 0.5  
    XMID = X1 + DX  
    CALL TET(XMID,FMID,R2)  
    IF (FMID * FX1 .GT. 0.0) THEN  
        X1 = XMID  
        FX1 = FMID  
    ELSE  
        X2 = XMID  
        FX2 = FMID  
    ENDIF  
    IF (DABS(DX/XMID) .LT. XACC) RETURN  
CONTINUE  
PAUSE 'TOO MANY BISECTIONS IN VARNU'  
END

SUBROUTINE FLUX(B,R)
IMPLICIT REAL*8(A-H,O-Z)
COMMON /ASH/ASHFRAC,RHOASH,ASHINIT,
1 RPINIT,CPASH,AMMIS,THCK
COMMON /FIRST/T,GAM,TWALL,FP
COMMON /R/RHOC,XFAC,ACEN

Calculation of solid flux in g/m²/cm²-s. (Smith 1974)
Older calculation of FP.

CASH = B - FP * R * R(1/(R+T) - 1/R) / C * M02 * DASH

FP = XFAC * DEXP(-1.0 * ACEN / (1.98 * T)) * CASH

DASH = 0.35 * 3.13 * (T/1500.0)**1.75 / 2.0

PF = XFAC * DEXP(-1.0 * ACEN / (1.98 * T))

FP = PF * B / (1.0 + 82.05 * T * PF * R * THCK / ((R+THCK) * (32.0 * DASH)))

TEST = PF * B

RETURN

END

This routine calculates the value of the integrated equations from TWALL to TP based on GAM1.

SUBROUTINE GAMMA(GAM1, F, R1)

IMPLICIT REAL*8(A-H,O-Z)

COMMON /ASH/ASHFRAC, RHOASH, ASHINIT,

1 RPINIT, CPASH, AMMIS, THCK

COMMON /FIRST/ T, GAM, TWALL, FP

COMMON /R/RHOC, XFAC, ACEN

COMMON /Y1S/Y1S, Y1INF

C
4850  
4860  
4870  
4880  
4890  
4900  
4910  
4920  
4930  
4940  
4950  
4960  
4970  
4980  
4990  
5000  
5010  
5020  
5030  
5040  
5050  
5060  
5070  
5080  
5090  
5100  
5110  

CC = -3.0043D-05
DASH=0.35*3.13*(T/1500.0)**1.75/2.0

IF (T .LT. TWALL) THEN

    HH = DSQRT(DABS(-2331.5425 - GAM1)/0.3388749)

    IF (GAM1 .GT.-2331.5425) THEN

        AR1=-1.0*CC * ((DSQRT(TWALL) - DSQRT(T)) + HH/2.0 *
        (DLOG((DSQRT(TWALL) - HH)*(DSQRT(T) + HH)/
        ((DSQRT(TWALL) + HH)*(DSQRT(T) - HH))))

        HM = (2331.5425 + GAM1)/0.3388749

        Y1S=(Y1INF+4.0/3.0)*((T-HM)/
        (TWALL-HM))**0.8095478-4.0/3.0

        CONC=(1.0/(-1.0/7.0 + 8.0/(7.0*Y1S)))

        PF=XFAC*DEXP( -1.0*ACEN/(1.98 * T))

        FFP=PF*CONC/(1.0+82.05*T*PF*R1*THCK/((R1+THCK)*
        (32.0•DASH)))

    F = AR1-R1* FFP

ELSE

    AR2=-1.0*CC*((DSQRT(TWALL)-DSQRT(T))-HH*
    (DATAN(DSQRT(TWALL)/HH)-DATAN(DSQRT(T)/HH)))

    HM = (2331.5425 + GAM1)/0.3388749

    Y1S=(Y1INF+4.0/3.0)*((T-HM)/(TWALL-HM))**

    0.8095478-4.0/3.0

    CONC=(1.0/(-1.0/7.0 + 8.0/(7.0*Y1S)))

    PF=XFAC*DEXP( -1.0*ACEN/(1.98 * T))

    FFP=PF*CONC/(1.0+82.05*T*PF*R1*THCK/((R1+THCK)*
    (32.0•DASH)))

    F = AR2-R1* FFP
ENDIF

ELSE

FF = DSQRT(DABS(2331.5425 + GAM1)/0.3388749)

IF (GAM1 .LT.-2331.5425) THEN

AR3 = CC*((DSQRT(T)-DSQRT(TWALL))-FF*
(DATAN(DSQRT(T)/FF)-DATAN(DSQRT(TWALL)/FF)))

C3 = (2331.5425 + GAM1)/0.3388749
Y1S=(Y1INF+4.0/3.0)*((T-C3)/(TWALL-C3))**

CONC=(1.0/(-1.0/7.0 + 8.0/(7.0*Y1S)))
PF=XFAC*DEXP( -1.0*ACEN/(1.98 * T))
FFP=PF*CONC/(1.0+82.05*T*PF*R1*THCK/((R1+THCK)*(32.0*DASH)))

F = AR3-R1* FFP

ELSE

AR4 = CC* ((DSQRT(T) - DSQRT(TWALL)) + FF/2.0 *
(DLOG((DSQRT(T) - FF) *(DSQRT(TWALL) + FF))/
((DSQRT(T) + FF) *(DSQRT(TWALL) - FF))))

C3 = (2331.5425 + GAM1)/0.3388749
Y1S=(Y1INF+4.0/3.0)*((T-C3)/(TWALL-C3))**

CONC=(1.0/(-1.0/7.0 + 8.0/(7.0*Y1S)))
PF=XFAC*DEXP( -1.0*ACEN/(1.98 * T))
FFP=PF*CONC/(1.0+82.05*T*PF*R1*THCK/((R1+THCK)*(32.0*DASH)))

F = AR4-R1* FFP

ENDIF
SUBROUTINE ENERGY(EP,PEMMIS,WEMMIS,RR,DUM2,ANST)
IMPLICIT REAL*8(A-H,O-Z)
EXTERNAL CPC,EC,CPCH,ECH
COMMON /FIRST/ T,GAM,TWALL,FP
COMMON /R/RHOC,XFAC,ACEN
COMMON /ASH/ASHFRAC,RHOASH,ASHINIT.
1 RPINIT,CPASH,AMMIS,THCK
Note that RHOC=1.5*(1-ASHINIT- EPSINIT)=Apparent density
SIG = 1.595D-12
IF (DUM2 .LT. 1350) THEN
    CPSOL= CPC(DUM2)
    VAL = EC(DUM2)
ELSE
    CPSOL= CPCH(DUM2)
    VAL = ECH(DUM2)
ENDIF
CPASH = 0.183 + 0.111D-3*T
ANST=3.0*(RR+THCK)*(RR+THCK)*(FP*VAL-EP-SIG*
1 (PEMMIS*DUM2**4-WEMMIS*TWALL**4))/
2 (RR*RR*RR*(CPSOL*RHOC + CPASH*RHOASH* 
3 (ASHINIT+0.65*((1+THCK/RR)**3.0-1.0))))
RETURN
END

Fourth order Runge-Kutta method for solving
TEST1 and TEST2 for each time step.

SUBROUTINE RUNG(TEST1,TEST2,DUMC,STEP,EP,
1 PEMMIS,WEMMIS,RR,RNEW,TNEW)
IMPLICIT REAL*8(A-H,O-Z)
REAL*8 K11,K12,K13,K14,K21,K22,K23,K24
EXTERNAL TEST1,TEST2,ENERGY,RADIUS
COMMON /FIRST/ T,GAM,TWALL,FP
COMMON /R/RHOC,XFAC,ACEN
DUM1=RR
DUM2=T
CALL TEST1(DUMC,DUM1,DUM2,DRDT)
CALL TEST2(EP,PEMMIS,WEMMIS,DUM1,DUM2,DTDT)
K11=DRDT
K21=DTDT
DUM1 = RR + K11*STEP/2.0
DUM2 = T + K21*STEP/2.0
CALL TEST1(DUMC,DUM1,DUM2,DRDT)
CALL TEST2(EP,PEMMIS,WEMMIS,DUM1,DUM2,DTDT)
K12 = DRDT
K22 = DTDT
DUM1 = RR + K12*STEP/2.0
DUM2 = T + K22*STEP/2.0
CALL TEST1(DUMC,DUM1,DUM2,DRDT)
CALL TEST2(EP,PEMMIS,WEMMIS,DUM1,DUM2,DTDT)
K13 = DRDT
K23 = DTDT
DUM1 = RR + K13*STEP
DUM2 = T + K23*STEP
CALL TEST1(DUMC,DUM1,DUM2,DRDT)
CALL TEST2(EP,PEMMIS,WEMMIS,DUM1,DUM2,DTDT)
K14 = DRDT
K24 = DTDT
RNEW = RR + STEP*(K11 + 2.0*K12 + 2.0*K13 + K14)/6.0
TNEW = T + STEP*(K21 + 2.0*K22 + 2.0*K23 + K24)/6.0
RETURN
END

Mass balance.

SUBROUTINE RADIUS(B,DUM1,DUM2,ANS)
IMPLICIT REAL*8(A-H,O-Z)

COMMON /FIRST/ T,GAM,TWALL,FP
COMMON /R/RHOC,XFAC,ACEN
COMMON /ASH/ASHFRAC,RHOASH,ASHINIT.

1 RPINIT,CPASH,AMMIS,THCK

Note that RHOC=1.5*(1-ASHINIT-EPSINIT)=Apparent density

DASH=0.35*3.13*(DUM2/1500.0)**1.75/2.0
PF= XFAC*DEXP( -1.0*ACEN/(1.98 * DUM2))
FFP=PF*B/(1.0+82.05*DUM2*PF*DUM1*THCK)
1 /((DUM1+THCK)*(32.0*DASH)))
ANS =-1.0*FFP/RHOC
RETURN
END
Appendix IX

NUMERICAL MODELS
Program listings of various numerical models are gathered in this Appendix. Every effort has been made to document the programs with generous comments whereever applicable. All programs were written in DOS FORTRAN 3.3 and run on IBM PC/AT's or clones.

IGNIT2 is the model used to determine ignition delay times for single particle combustion. The model is described in Chapter 6.

MENU and VARNU are two versions of the asymptotic model for single particles. While VARNU has been described in detail (Chapter 7), MENU differs from it only in the way the presence of ash is accounted for. While VARNU treats the ash as a diffusion layer around the particle, MENU treats ash as forming patches on the particle. The ash patches prevent reactant access to portions of the particle they cover.

3VOIDS is the general single particle combustion program described in Chapter 7. It describes the internal morphology with three different sized voids. It uses linear kinetics. This model is extended to include power law kinetics in PCONC. A similar extension to include Langmuir-Hinschelwood kinetics was done in another program that is not listed here for reasons of space.

An example of the discrete approach to modelling char combustion is CEN-MOD21 (Chapter 8).
PROGRAM IGNIT2

IMPLICIT REAL*4(A-H,O-Z)

CHARACTER*15 IFILE

DIMENSION RADMIC(100),ARAT(100)

COMMON /S/S(100)

COMMON /R/RAD(100)

COMMON /A/A1,A2,A3,A4

COMMON /CS/A11,B11

EXTERNAL SUM,FUNT

WRITE(*,7)

FORMAT(1X,'ENTER PART.RAD (cm), DOD (cm):')

READ(*,*)RP,DOD

WRITE(*,8)

FORMAT(1X,'ENTER E,ARR,CMAX,CMIN:')

READ(*,*)E,ARR,CMAX,CMIN

WRITE(*,9)

FORMAT(1X,'ENTER ETA,RHOAP,EPS,TS:')

READ(*,*)ETA,RHOAP,EPS,TS

WRITE(*,11)

FORMAT(1X,'ENTER THE DATA FILENAME')

READ(*,12)IFILE

FORMAT(A15)
SBET=3500000
RP0AP=0.5
DEPH=2340*4.187
CSURF=0.15
B11=LOG(CMAX/CMIN)/RP
A11=CMAX
A1=ETA*ARR*EXP(-E/(1.98*TS))*SBET*DOD*RP0AP*DEPH
CPCARB=1.880
TC=1200
A2=2.0*RP0AP*DOD*CPCARB*(TS-TC)
SIG=5.667E-012
EMMS=0.25
TINF=1150
TWALL=1250
EPS=0.75
CCARB=10.0E-02
CAIR=0.0891E-02
CEFF=CCARB*(1.0-EPS)**2.0 + CAIR*(EPS**2.0)
Alternate values for CCARB: 57.4(1000K); 60.2(1300K); 0.71(3300K); 5.9(300K)
TFILM=(TS+TINF)/2.0
RADP=RP
A3=SIG*EMMS*(TS**4-TWALL**4) + CAIR*(TS-TINF)/RADP
DBULK = 3.13 * (TFILM / 1500) ** 1.75
PORER2 = 1.0E-07
PORER3 = 25E-07
DK2 = 9700 * PORER2 * SQRT(TS / 32.0)
DK3 = 9700 * PORER3 * SQRT(TS / 32.0)
DEFF2 = 1.0 / (1.0 / DBULK + 1.0 / DK2)
DEFF3 = 1.0 / (1.0 / DBULK + 1.0 / DK3)
DEFF = 0.5 * (EPS1 * DBULK + EPS2 * DEFF2 + EPS3 * DEFF3)
ALPHAeff = CEFF / (RHOAP * CPCARB)

DO 50 I = 1, 100
   S(I) = 0.0
50 CONTINUE

OPEN(2, FILE=IFILE, STATUS='NEW')
XACC = 0.001
GAP = RP / 99.0

DO 300 I = 2, 99
   GUESSL = 1.0E-10
300 CONTINUE
RAD(I) = (I-1) * GAP

R = RAD(I)

CALL FUNT(I, GAP, RADP, GUESSL, FX1, R)

CALL FUNT(I, GAP, RADP, GUESSH, FX2, R)

IF (FX2 * FX1 .GE. 0.0) PAUSE 'BRACKET ROOT IN MAIN'

DX = GUESSH - GUESSL

DO 200 J = 1, 500

DX = DX * 0.5

ANSW = GUESSL + DX

CALL FUNT(I, GAP, RADP, ANSW, FMID, R)

IF (FMID * FX1 .GT. 0.0) THEN

GUESSL = ANSW

FX1 = FMID

ELSE

GUESSH = ANSW

FX2 = FMID

ENDIF

IF (ABS(DX/ANSW) .LT. XACC) GOTO 111

CONTINUE

PAUSE 'TOO MANY BISECTIONS IN MAIN'

S(I) = ANSW

WRITE(*,*) I, RAD(I), S(I)

CONTINUE

TAU = 0.0

DO 400 I = 2, 99
- 457 -

1070  RADMIC(I)=RAD(I)*1E04
1080  ARAT(I)=RAD(I)**2/RAD(99)**2
1090  TAU=TAU + GAP/S(I)
1100  WRITE(2,*)TAU,RADMIC(I),S(I),ARAT(I)
1110  400  CONTINUE
1120  WRITE(*,*)TAU
1130  C
1140  CLOSE(2)
1150  STOP
1160  END
1170  C
1180  C-----------------------------------------------
1190  C
1200  SUBROUTINE FUNT(I,GAP,RADP,X,FX,R)
1210  IMPLICIT REAL*4(A-H,O-Z)
1220  COMMON /A/A1,A2,A3,A4
1230  COMMON /CS/A11,B11
1240  EXTERNAL SUM
1250  C
1260  CALL SUM(I,GAP,X,ANS,RADP)
1270  DUMSUM=ANS
1280  FX=A2*R*X*RADP/(SQRT(RADP**2-R**2))+
1290  1  (A3-A1*A11*EXP(-B11*R))*2.0*(RADP**2) ·
1300  2  *(1.0-SQRT(1.0-(R/RADP)**2)))*A4*DUMSUM
1310  RETURN
1320  END
1330  C
SUBROUTINE SUM(I,GAP,X,ANS,RADP)
IMPLICIT REAL*4(A-H,O-Z)
COMMON /S/S(100)
COMMON /R/RAD(100)

ANS=0.0
DO 100 J=2,I
   IF(I.EQ.2)THEN
      SUM1=GAP/X
   ELSE
      SUM1=0.0
   END IF
   DO 200 K=J,I-1
      SUM1=SUM1+GAP/S(K)
   CONTINUE
   SUM1=SUM1+GAP/X
   ANS=ANS+(RADP/(SQRT(RADP**2-RAD(J)**2)))*
        ((RAD(J)*GAP)/(SQRT(SUM1)))
   CONTINUE
100 CONTINUE
RETURN
END
This program simulates the combustion of a single solid carbon particle with no internal structure. The particle is assumed to be isothermal. The gas phase is assumed to be in a quasi-steady state relative to the solid for a given time step. The reaction at the solid is $2C + O_2 \rightarrow 2CO$ and in the gas phase the oxidation is assumed to be far enough from the particle so as to have no effect on it. The gas phase equations include the Stefan flow term. Gas phase property values are calculated using the kinetic theory of gases. The integral equations are then solved analytically.

Ash is assumed to be distributed uniformly inside the particle, initially. However, as the particle burns, its radius shrinks and the ash fraction in the particle increases as only the carbon burns. It is assumed that at each step, the fraction of ash covering the surface is the same as the ash volume fraction in the particle. The presence of ash affects the access of oxygen to the particle (blockage effect), the effective emissivity of the particle (since ash has an emissivity different from carbon), and the thermal inertia of the particle (assuming some heat capacity for ash). These effects have been taken into account.
Declarations.

IMPLICIT REAL*8(A-H,O-Z)
REAL*8 NMAX
REAL*8 K11,K12,K13,K14,K21,K22,K23,K24
CHARACTER*15 IFILE
CHARACTER*1 QRESP

EXTERNAL RHOG,DIFF,EC,ECH,CPC,CPCH
EXTERNAL RLAMB,E0X,ECO,FLUX,MFRC,ENERGY
EXTERNAL GAMMA,RTBIS,RADIUS,SOLID

COMMON T,GAM,TWALL,FP
COMMON /R/RHOC,XFAC,ACEN
COMMON /Y1S/Y1S,Y1INF
COMMON /ASH/ASHFRAC,RHOASH,ASHINIT,RPINIT,CPASH,AMMIS

Interactive program parameter inputs.
530 C
540 WRITE(*,9)
550 9 FORMAT(1x,'WANT TO READ THE MENU.INP FILE (Y OR N)?')
560 READ(*,8)QRESP
570 8 FORMAT(A1)
580 IF((QRESP .EQ. 'y') .OR. (QRESP .EQ. 'Y')) GOTO 2000
590 C
600 OPEN(1,FILE='MENU.INP',STATUS='NEW')
610
620 WRITE(*,10)
630 10 FORMAT(1x,'ENTER PARTICLE AND ASH DENSITIES IN G/CC')
640 READ(*,*)RHOC,RHOASH
650 WRITE(1,*)RHOC,RHOASH
660
670 WRITE(*,11)
680 11 FORMAT(1x,'ENTER WALL AND INIT. PARTICLE TEMPS. IN K')
690 READ(*,*)TWALL,TPINIT
700 WRITE(1,*)TWALL,TPINIT
710
720 WRITE(*,12)
730 12 FORMAT(1x,'ENTER THE INITIAL ASH VOLUME FRACTION')
740 READ(*,*)ASHINIT
750 WRITE(1,*)ASHINIT
760
770 WRITE(*,13)
780 13 FORMAT(1x,'ENTER THE INIT. PART. RADIUS IN MICRONS')
790 READ(*,*)RPINIT
800        WRITE(1,*)RPINIT
810
820        WRITE(*,14)
830   14    FORMAT(1x,'ENTER THE O2 PART. PRES. IN THE AMBIENT')
840        READ(*,*)C1INF
850        WRITE(1,*)C1INF
860
870        WRITE(*,15)
880   15    FORMAT(1x,'ENTER THE WALL, CARBON AND ASH EMMISIVITIES')
890        READ(*,*)WEMMIS,PEMMIS,AMMIS
900        WRITE(1,*)WEMMIS,PEMMIS,AMMIS
910
920        WRITE(*,16)
930   16    FORMAT(1x,'ENTER THE MAXIMUM TEMPERATURE INCREMENT')
940        READ(*,*)DELTEMP
950        WRITE(1,*)DELTEMP
960
970        WRITE(*,17)
980   17    FORMAT(1x,'ENTER FACTOR XFAC, ACEN AND TIMESTEP')
990        READ(*,*)XFAC,ACEN,STEPO
1000       WRITE(1,*)XFAC,ACEN,STEPO
1010
1020        WRITE(*,18)
1030   18    FORMAT(1x,'ENTER ES1,ES2,XACC (0 < ES1 << ES2 )')
1040        READ(*,*)ES1,ES2,XACC
1050        WRITE(1,*)ES1,ES2,XACC
1060
1070 WRITE(*,19)
1080 19 FORMAT(1x,'ENTER THE NUMBER OF Timesteps')
1090 READ(*,*)NMAX
1100 WRITE(1,*),NMAX
1110
1120 WRITE(*,21)
1130 21 FORMAT(1x,'WRITE OUTPUT FILENAME (NOT MENU.INP !)')
1140 READ(*,22)IFILE
1150 22 FORMAT(A16)
1160
1170 CLOSE(1)
1180 GOTO 3000
1190
1200 2000 OPEN(1,FILE='MENU.INP',STATUS='OLD')
1210 READ(1,*),RHOC,RHOASH,TWALL,TPINIT,ASHINIT,RPINIT,C1INF,
1220 1 WEMMIS,PEMMIS,AMMIS,DELTEMP,XFAC,ACEN,STEPO,ES1,ES2,
1230 2 XACC,NMAX
1240 CLOSE(1)
1250
1260 WRITE(*,30)RHOC,RHOASH
1270 30 FORMAT(1x,'1. PARTICLE AND ASH DENSITIES IN G/CC:
1280 1 ',F8.4,3X,F8.4,/)  
1290
1300 WRITE(*,31)TWALL,TPINIT
1310 31 FORMAT(1x,'2. WALL AND INIT. PART. TEMPS.IN K: ',
1320 1 F10.4,3X,F10.4,/)  
1330
WRITE(*,32)ASHINIT
32 FORMAT(1x,'3. THE INIT. ASH VOLUME FRACTION: ',F8.4,/) 

WRITE(*,33)RPINIT
33 FORMAT(1x,'4. THE INIT. PART. RAD. IN MICRONS: ',F8.4,/) 

WRITE(*,34)C1INF
34 FORMAT(1x,'5. THE O2 PART. PRES. (AMBIENT): ',F8.4,/) 

WRITE(*,35)WEMMIS,PEMMIS,AMMIS
35 FORMAT(1x,'6. THE WALL, CARBON AND ASH EMMISIVITIES: ', 
1  F6.4,3X,F6.4,3X,F6.4,/) 

WRITE(*,36)DELTTEMP
36 FORMAT(1x,'7. THE MAXIMUM TEMP. INCREMENT: ',F8.2,/) 

WRITE(*,37)XFAC,ACEN,STEPO
37 FORMAT(1x,'8. THE FACTOR XFAC, ACEN AND TIMESTEP: ', 
1  F8.4,3X,F10.4,3X,F8.6,/) 

WRITE(*,38)ES1,ES2,XACC
38 FORMAT(1x,'9. ES1,ES2,XACC (0 < ES1 << ES2): ', 
1  E9.4,3X,E9.4,3X,E9.4,/) 

WRITE(*,39)NMAX
39 FORMAT(1x,'10. THE NUMBER OF TIMESTEPS: ',F10.2,/)
WRITE(*.41)

FORMAT( 1x, 'WRITE OUTPUT FILENAME (NOT MENU.INP !)')

READ(*.42)IFILE

FORMAT(A15)

WRITE(*.43)

FORMAT(1X, 'WRITE ENTRY NO. TO BE ALTERED (0 TO RUN)'

READ(*,*)NALT

IF(NALT .EQ. 0)GOTO 2500

IF(NALT .EQ. 1)GOTO 2010

IF(NALT .EQ. 2)GOTO 2020

IF(NALT .EQ. 3)GOTO 2030

IF(NALT .EQ. 4)GOTO 2040

IF(NALT .EQ. 5)GOTO 2050

IF(NALT .EQ. 6)GOTO 2060

IF(NALT .EQ. 7)GOTO 2070

IF(NALT .EQ. 8)GOTO 2080

IF(NALT .EQ. 9)GOTO 2090

IF(NALT .EQ. 10)GOTO 2100

GOTO 1990

WRITE(*,10)

READ(*,*)RHOC,RHOASH

GOTO 1990

WRITE(*,11)

READ(*,*).TWALL,TPINIT
1880  GOTO 1990
1890
1900  2030  WRITE(*,12)
1910  READ(*,*)ASHINIT
1920  GOTO 1990
1930
1940  2040  WRITE(*,13)
1950  READ(*,*)RPINIT
1960  GOTO 1990
1970
1980  2050  WRITE(*,14)
1990  READ(*,*)C1INF
2000  GOTO 1990
2010
2020  2060  WRITE(*,15)
2030  READ(*,*)WEMMIS,PEMMS,AMMIS
2040  GOTO 1990
2050
2060  2070  WRITE(*,16)
2070  READ(*,*)DELTEMP
2080  GOTO 1990
2090
2100  2080  WRITE(*,17)
2110  READ(*,*)XFAC,ACEN,STEPO
2120  GOTO 1990
2130
2140  2090  WRITE(*,18)
2150       READ(*,*)ES1,ES2,XACC
2160       GOTO 1990
2170
2180       WRITE(*,19)
2190       READ(*,*)NMAX
2200       GOTO 1990
2210
2220       OPEN(1,FILE='MENU.INP',STATUS='NEW')
2230       WRITE(1,*)RHOC,RHOASH,TWALL,TPINIT,ASHINIT,RPINIT,C1INF,
2240 1  WEMMIS,PEMMIS,AMMIS,DELTEMP,XFAC,ACEN,STEPO,ES1,ES2,
2250 2  XACC,NMAX
2260       CLOSE(1)
2270       C
2280       C------------------------------------------
2290       C------------------------------------------
2300       C
2310       C       Main program.
2320       C
2330       C       After initialization, the main loop begins. Timestep
2340       C       (STEP) is set to its original value. Radii are converted
2350       C       to centimeters for the actual calculation but are written
2360       C       out in microns. GAM is found by the method of bisection.
2370       C       The coupled gas and solid phase equations are solved to
2380       C       get GAM. Flux is calculated based on a reaction rate by
2390       C       Smith. Property values in the gas phase are functions of
2400       C       temperature. DUMC is the mole fraction of O2 at the
2410       C       external surface of the particle. X1, X2 are initial
guesses for GAM and XACC is the error tolerance. DTDR is the temperature gradient at the surface.

Subroutine SOLID calculates the ash coverage of the particle. The reaction takes place on that portion of the solid that is free of ash. Ash is assumed to be at the same temperature as the rest of the particle.

Subroutine RUNG solves the coupled equations of mass and energy for a given time step. If the temperature change in the time step is larger than DELTEMP, the time step is halved and the process is repeated.

Every tenth data point is written to file and screen.

Initialization.

\[
Y_{1\text{INF}} = \frac{C_{1\text{INF}} \times 32.0}{C_{1\text{INF}} \times 32.0 + (1.0 - C_{1\text{INF}}) \times 28.0}
\]

\[
A = \frac{1.0}{1.0 - Y_{1\text{INF}}} \times \left(\frac{Y_{1\text{INF}}}{4.0}\right)
\]

\[
T_P = T_{P\text{INIT}}
\]

\[
R_P = R_{P\text{INIT}}
\]

\[
C_{1S} = C_{1\text{INF}}
\]

\[
T_M = 0.0
\]

\[
D_{TDR} = 0.0
\]
FP=0.0
ASHFRAC = ASHINIT

OPEN(2,FILE=IFILE,STATUS='NEW')
WRITE(2, 900) TIME, RP, TP, C1S, FP
WRITE(*, 900) TIME, RP, TP, C1S, FP
900 FORMAT(1X,5G12.4)

X1 and X2 are appropriate brackets for GAM.
Typically, ES1 is 0(1D-6), while ES2 is 0(1D11).

IF ( TPINIT .LT. TWALL) THEN
    X1=( -2331.5425 + 0.3388749*TPINIT) - ES2
    X2=( -2331.5425 + 0.3388749*TPINIT) - ES1
ELSE
    X1=( -2331.5425 + 0.3388749*TPINIT) + ES1
    X2=( -2331.5425 + 0.3388749*TPINIT) + ES2
ENDIF

Main loop begins.

JMAX = NMAX
DO 1000 I = 1, JMAX
    STEP=STEP0
    T = TP
    RR = RP* 1D-04
    CALL RTBIS(GAMMA,X1,X2,XACC,RR,GAM)
DUMC = (1.0/(-1.0/7.0 + 8.0/(7.0*Y1S)))

CALL FLUX(DUMC)

FP1 = -1.3333 * FP
FP2 = 2.3333 * FP

EP = GAM * FP

DTDR=-1.0D-4*(EP-FP1*EOX(T)-FP2*ECO(T))/RLAMB(T)

CALL SOLID(RR)

CALL RUNG(RADIUS,ENERGY,DUMC,STEP,EP,PEMMIS,WEMMIS,RR,RNEW,TNEW)

DELR=(RR-RNEW)/RR

IF((ASHFRAC .GE. 1.0).0R.(DELR .LT. 0.00001))GOTO 1001

IF(ABS(TNEW - TP) .GT. DELTEMP)THEN

STEP = STEP/2.0

GOTO 991

ENDIF

RP = 1.0D4*RNEW

TP = TNEW

TIME = TIME + 1.0D3*STEP

Writing to file.

IF(MOD(I,10) .EQ. 0)THEN

WRITE(2, 900) TIME, RP, TP, DUMC ,FP

WRITE(*, 900) TIME, RP, TP, DUMC ,FP

ENDIF

Reducing the brackets for the next call of GAM.
3230 C
3240 IF ( TP .LT. T WALL) THEN
3250 X1 = GAM - DABS(1000.0*GAM)
3260 X2 = ( -2331.5425 + 0.3388749*TP ) - ES1
3270 ELSE
3280 X1 = ( -2331.5425 + 0.3388749*TP ) + ES1
3290 X2 = GAM + DABS(1000.0*GAM)
3300 ENDIF
3310 C
3320 1000 CONTINUE
3330 1001 CLOSE(2)
3340 STOP
3350 END
3360 C
3370 C Main loop and main program end.
3380 C
3390 C-------------------------------------------------------------
3400 C-------------------------------------------------------------
3410 C
3420 C Property values.
3430 C
3440 C
3450 C Gas diffusivity is calculated for an N2-O2 system over a
3460 C range of 300K to 3000K. Units are cm^2/s.
3470 C
3480 REAL*8 FUNCTION DIFF(D)
3490 IMPLICIT REAL*8(A-H,O-Z)
COMMON T, GAM, TWALL, FP

DIFFO = -0.099
DIFF1 = 6.910D-04
DIFF2 = 1.070D-06
DIFF3 = -6.04D-11
DIFF = DIFFO + DIFF1*D + DIFF2*(D*D) + DIFF3*(D*D*D)
RETURN
END

C

Gas density is found using the ideal gas law in g/cc.
Average molecular weight for air is taken as 29.0.

REAL*8 FUNCTION RHOG(D)
IMPLICIT REAL*8(A-H,O-Z)
COMMON T, GAM, TWALL, FP
RHOG = 29.0/(82.05*D)
RETURN
END

C

Gas thermal conductivity coeffs. are in W/m-K for D in K.
Data from Eckert (300K to 2500K). RLAMB is converted
to cal/cm-K.

REAL*8 FUNCTION RLAMB(D)
IMPLICIT REAL*8(A-H,O-Z)
REAL*8 LGO, LG1, LG2, LG3, D
COMMON T, GAM, TWALL, FP
The enthalpies for the gases are in cal/mol for D in K.
Ref state = 0 at 298K (except CO); Data from Smith and VanNess (298K to 2500K). Heat capacities are assumed to be constant to obtain reasonable integrable forms.

```fortran
REAL*8 FUNCTION EOX(D)
IMPLICIT REAL*8(A-H,O-Z)
COMMON T,GAM,TWALL,FP
CPOXO = 7.16
CPOX1 = 0.001
CPOX2 = -40000.0
EOX = (CPOXO*(D - 298) + (CPOX1 / 2.0)*(D*D - 298*298) + CPOX2*(1.0/D - 1.0/298) / 32.0
RETURN
END

REAL*8 FUNCTION ECO(D)
IMPLICIT REAL*8(A-H,O-Z)
COMMON T,GAM,TWALL,FP
```
4040
CPCO0 = 6.79
4050
CPC01 = 0.00098
4060
CPC02 = -11000.0
4070
DELH = -26416.0
4080
EC0 = (DELH + CPC00 * (D - 298) + (CPC01 / 2.0) * (D*D - 298*298))
4090
1 + CPC02 * (1.0/D - 1.0/298))/28.0
4100
RETURN
4110
END

4120 C

4130 REAL*8 FUNCTION EN(D)
4140 IMPLICIT REAL*8(A-H,0-Z)
4150 COMMON T,GAM,TWALL,FP
4160 CPNO = 6.83
4170 CPN1 = 0.0009
4180 CPN2 = -12000.0
4190 EN = (CPNO * (D - 298) + (CPN1 / 2.0) * (D*D - 298*298))
4200 1 + CPN2 * (1.0/D - 1.0/298))/28.0
4210 RETURN
4220 END

4230 C

4240 C EC and ECH calculate the enthalpy of the solid in cal/g.
4250 C Data from coal data book.
4260 C

4270 REAL*8 FUNCTION EC(D)
4280 IMPLICIT REAL*8(A-H,0-Z)
4290 COMMON T,GAM,TWALL,FP
4300 CPCO = 0.024
CPC1 = 6.9530D-04
CPC2 = -2.841D-07
EC = CPC0*(D - 298) + (CPC1 / 2.0)*(D*D - 298*298)
1 + (CPC2 / 3.0)*(D*D*D - 298*298*298)
RETURN
END

REAL*8 FUNCTION ECH(D)
IMPLICIT REAL*8(A-H,O-Z)
COMMON T,GAM,TWALL,FP
CPCHO = 0.36
CPCH1 = 6.9310D-05
ECH = CPCHO*(D - 298) + (CPCH1 / 2.0)*(D*D - 298*298)
RETURN
END

CPC and CPCH calculate the heat capacity of the solid in cal/g-K. Data from coal data book.

REAL*8 FUNCTION CPC(D)
IMPLICIT REAL*8(A-H,O-Z)
COMMON T,GAM,TWALL,FP
CPCO = 0.024
CPC1 = 6.953D-04
CPC2 = -2.841D-07
CPC = CPC0 + CPC1 * D + CPC2 * D * D
- 476 -

     RETURN
  4590     END
  4600 c
  4610     REAL*8 FUNCTION CPCH(D)
  4620     IMPLICIT REAL*8(A-H,O-Z)
  4630     COMMON T,GAM,TWALL,FP
  4640     CPCHO = 0.36
  4650     CPCH1 = 6.931D-05
  4660     CPCH = CPCHO + CPCH1 * D
  4670     RETURN
  4680     END
  4690 c
  4700 c------------------------------------------
  4710 c
  4720 c     This routine calculates the fraction of solid covered by
  4730 c     ash (ASHFRAC). (ASHFRAC --> 1.0 as RR --> RMIN)
  4740 c
  4750     SUBROUTINE SOLID(RR)
  4760     IMPLICIT REAL*8(A-H,O-Z)
  4770     COMMON /ASH/ASHFRAC,RHOASH,ASHINIT,RPINIT,CPASH,AMMIS
  4780 c
  4790     ASHFRAC = ASHINIT*(1.0D-4*RPINIT/RR)**3.0
  4800     RETURN
  4810     END
  4820 c
  4830 c------------------------------------------
Root finder by the method of bisection for function TET.

SUBROUTINE RTBIS(TET,X1,X2,XACC,R2,XMID)

IMPLICIT REAL*8(A-H,O-Z)

EXTERNAL TET

COMMON T,GAM,TWALL,FP

PARAMETER (JMAX = 500)

CALL TET(X1,FX1,R2)

CALL TET(X2,FX2,R2)

IF(FX2*FX1 .GE. 0.0) PAUSE 'BRACKET ROOT IN RTBIS'

DX = X2 - X1

DO 200 J = 1, JMAX

   DX = DX * 0.5

   XMID = X1 + DX

   CALL TET(XMID,FMID,R2)

   IF (FMID * FX1 .GT. 0.0) THEN

      X1 = XMID

      FX1 = FMID

   ELSE

      X2 = XMID

      FX2 = FMID

   ENDIF

   IF (DABS(DX/XMID) .LT. XACC) RETURN

CONTINUE

PAUSE 'TOO MANY BISECTIONS'

END
Calculation of solid flux in gmc/cm\(^2\)-s. (Smith 1974)

```
SUBROUTINE FLUX(B)
IMPLICIT REAL*8(A-H,O-Z)
COMMON /ASH/ASHFRAC,RHOASH,ASHINIT,RPINIT,CPASH,AMMIS
COMMON T,GAM,TWALL,FP
COMMON /R/RHOC,XFAC,ACEN

FP=(1.0-ASHFRAC)*XFAC*9.3*DEXP(-ACEN/(1.98*T))*B
RETURN
END
```

This routine calculates the value of the fully integrated equations from TWALL to TP based on GAM1.

```
SUBROUTINE GAMMA(GAM1,F,R1)
IMPLICIT REAL*8(A-H,O-Z)
COMMON T, GAM, TWALL,FP
COMMON /R/RHOC,XFAC,ACEN
COMMON /Y1S/Y1S,Y1INF

CC = -3.0043D-05
```
5390 IF (T .LT. TWALL) THEN
5400 HH = DSQRT(DABS(-2331.5425 - GAM1)/0.3388749)
5410 IF (GAM1 .GT. -2331.5425) THEN
5420 AR1=-1.0*CC*((DSQRT(TWALL) - DSQRT(T))+HH/2.0*
5430 (DLOG((DSQRT(TWALL) - HH)*(DSQRT(T) + HH)/
5440 ((DSQRT(TWALL) + HH)*(DSQRT(T) - HH))))
5450 HM = (2331.6425 + GAM1)/0.3388749
5460 Y1S=(Y1INF+4.0/3.0)*((T-HM)/(TWALL-HM))**0.8095478-4.0/3.0
5470 F = AR1-R1* XFAC*9.3*DEXP(-ACEN/(1.98*T))*
5480 1 (1.0/(-1.0/7.0 + 8.0/(7.0*Y1S)))
5490 ELSE
5500 AR2 = -1.0*CC*((DSQRT(TWALL)-DSQRT(T))-HH*
5510 (DATAN(DSQRT(TWALL)/HH)-DATAN(DSQRT(T)/HH)))
5520 HM = (2331.5425 + GAM1)/0.3388749
5530 Y1S=(Y1INF+4.0/3.0)*((T-HM)/(TWALL-HM))**0.8095478-4.0/3.0
5540 F = AR2-R1* XFAC*9.3*DEXP(-ACEN/(1.98*T))*
5550 1 (1.0/(-1.0/7.0 + 8.0/(7.0*Y1S)))
5560 ENDIF
5570 ELSE
5580 FF = DSQRT(DABS(2331.5425 + GAM1)/0.3388749)
5590 IF (GAM1 .LT. -2331.5425) THEN
5600 AR3 = CC*((DSQRT(T)-DSQRT(TWALL))-FF*
5610 (DATAN(DSQRT(T)/FF)-DATAN(DSQRT(TWALL)/FF)))
5620 C3 = (2331.5425 + GAM1)/0.3388749
5630 Y1S=(Y1INF+4.0/3.0)*((T-C3)/(TWALL-C3))**0.8095478-4.0/3.0
5640 F = AR3-R1* XFAC*9.3*DEXP(-ACEN/(1.98*T))*
5650 1 (1.0/(-1.0/7.0 + 8.0/(7.0*Y1S)))
ELSE

AR4 = CC * ((DSQRT(T) - DSQRT(TWALL)) + FF/2.0 * 
1 (DLOG((DSQRT(T) - FF)*(DSQRT(TWALL) + FF)/ 
2 ((DSQRT(T) + FF)*(DSQRT(TWALL) - FF))))

C3 = (2331.5425 + GAM1)/0.3388749

Y1S=(Y1INF+4.0/3.0)*((T-C3)/(TWALL-C3))**0.8095478-4.0/3.0

F = AR4-R1* XFAC*9.3*DEXP(-ACEN/(1.98*T))*

1 (1.0/(-1.0/7.0 + 8.0/(7.0*Y1S)))

ENDIF

ENDIF

RETURN

END

C

Energy equation.

SUBROUTINE ENERGY(EP,PEMMIS,WEMMIS,RR,DUM2,ANST)

IMPLICIT REAL*8(A-H.O-Z)

EXTERNAL CPC,EC,CPCH,ECH

COMMON T, GAM, TWALL,FP

COMMON /R/RHOC,XFAC,ACEN

COMMON /ASH/ASHFRAC,RHOASH,ASHINIT,RPINIT,CPASH,AMMIS

SIG = 1.595D-12

IF (DUM2 .LT. 1350) THEN

CPSOL= CPC(DUM2)
VAL = EC(DUM2)
ELSE
CPSOL = CPCH(DUM2)
VAL = ECH(DUM2)
ENDIF
CPASH = 0.183 + 0.111D-3*T
ANST = 3.0*RR*RR*(FP*VAL - EP - SIG* ((ASHFRAC*AMMIS +
1.0-ASHFRAC)*PEMMIS)*DUM2**4-WEMMIS*TWALL**4))/
(RHOC*RR*RR*RR*CPSOL +
CPASH*RHOASH*ASHINIT*((1.0D-4*RPINIT)**3.0))
RETURN
END

Fourth order Runge-Kutta method for solving TEST1 and
TEST2 for one time step.

SUBROUTINE RUNG(TEST1, TEST2, DUMC, STEP, EP,
1 PEMMIS, WEMMIS, RR, RNEW, TNEW)
IMPLICIT REAL*8(A-H,O-Z)
REAL*8 K11, K12, K13, K14, K21, K22, K23, K24
EXTERNAL TEST1, TEST2, ENERGY, RADIUS
COMMON T, GAM, TWALL, FP
COMMON /R/RHOC, XFAC, ACEN
DUM1 = RR
6200      DUM2=T
6210      CALL TEST1(DUMC,DUM1,DUM2,DRDT)
6220      CALL TEST2(EP,PEMMIS,WEMMIS,DUM1,DUM2,DTDT)
6230      K11=DRDT
6240      K21=DTDT
6250      DUM1 = RR + K11*STEP/2.0
6260      DUM2 = T + K21*STEP/2.0
6270      CALL TEST1(DUMC,DUM1,DUM2,DRDT)
6280      CALL TEST2(EP,PEMMIS,WEMMIS,DUM1,DUM2,DTDT)
6290      K12 = DRDT
6300      K22 = DTDT
6310      DUM1 = RR + K12*STEP/2.0
6320      DUM2 = T + K22*STEP/2.0
6330      CALL TEST1(DUMC,DUM1,DUM2,DRDT)
6340      CALL TEST2(EP,PEMMIS,WEMMIS,DUM1,DUM2,DTDT)
6350      K13 = DRDT
6360      K23 = DTDT
6370      DUM1 = RR + K13*STEP
6380      DUM2 = T + K23*STEP
6390      CALL TEST1(DUMC,DUM1,DUM2,DRDT)
6400      CALL TEST2(EP,PEMMIS,WEMMIS,DUM1,DUM2,DTDT)
6410      K14 = DRDT
6420      K24 = DTDT
6430      RNEW = RR + STEP*(K11 + 2.0*K12 + 2.0*K13 + K14)/6.0
6440      TNEW = T + STEP*(K21 + 2.0*K22 + 2.0*K23 + K24)/6.0
6450      RETURN
6460      END
Particle mass balance.

SUBROUTINE RADIUS(B,DUM1,DUM2,ANS)
IMPLICIT REAL*8(A-H,O-Z)
COMMON T, GAM, TWALL, FP
COMMON /R/RHOC,XFAC,ACEN
COMMON /ASH/ASHFRAC,RHOASH,ASHINIT,RPINIT,CPASH,AMMIS
ANS=(((-1.0*(XFAC*9.3*DEXP(-ACEN/(1.98 * DUM2))* B)))*
  (1.0-ASHFRAC))/((RHOASH*ASHFRAC + RHOC*(1.0-ASHFRAC))
  +((RHOC -RHOASH)*ASHINIT*((1.0D-4*RPINIT)**3.0)/
  (DUM1**3.0)))
RETURN
END
AIX.3 VARNU.FOR

10 C This program simulates the combustion of a single solid carbon particle with no internal structure. The particle is assumed to be isothermal.
40 C The gas phase is assumed to be in a quasi-steady state relative to the solid for a given time step. The hetero reaction at the solid is 2C + O_2 --> 2CO and in the gas phase the oxidation is assumed to be far enough from the particle so as to have no effect on it. The gas phase equations include the Stefan flow term. Gas phase properties are calculated using the kinetic theory of gases. The integral equations are then solved analytically.
90 C Ash is assumed to be distributed uniformly inside the particle, initially. However, as the particle burns, the carbon shrinks and the ash fraction in the particle rises. It is assumed that none of the ash is lost; it accumulates on the carbon surface. The ash layer affects the access of oxygen to the particle (blockage effect), the effective emissivity of the particle (since ash has an emissivity different from carbon), and the thermal inertia of the particle (assuming some heat capacity for ash). These effects have been taken into account.
260 C Declarations.
270 C
280 C
290 IMPLICIT REAL*8(A-H,O-Z)
300 REAL*8 NMAX
310 REAL*8 K11,K12,K13,K14,K21,K22,K23,K24
320 CHARACTER*15 IFILE
330 CHARACTER*1 QRESP
340 C
350 EXTERNAL EC,ECH,CPC,CPCH
360 EXTERNAL FLUX,ENERGY
370 EXTERNAL GAMMA,RTBIS,RADIUS,SOLID
380 C
390 C
400 COMMON /FIRST/T,GAM,TWALL,FP
410 COMMON /R/RHOC,XFAC,ACEN
420 COMMON /Y1S/Y1S,Y1INF
430 COMMON /ASH/ASHFRAC,RHOASH,ASHINIT,
440 1 RPINIT,CPASH,AMMIS,THCK
450 COMMON /TF/TFAC,PEMMIS
460 C
470 C---------------------------------------------
480 C
490 C Interactive program parameter inputs.
500 C
510 C
520 WRITE(*,9)
530  9  FORMAT(1X,'WANT TO READ THE VARNU.INP FILE (Y OR N)?')
540     READ(*,8)QRESP
550   8  FORMAT(A1)
560      IF((QRESP .EQ. 'y') .OR. (QRESP .EQ. 'Y'))goto 2000
570
580     OPEN(1,FILE='VARNU.INP',STATUS='NEW')
590
600     WRITE(*,10)
610  10  FORMAT(1X,'ENTER VOID FRC. AND THICKNESS FACTOR')
620     READ(*,*)EPSO,TFAC
630     WRITE(1,*)EPSO,TFAC
640
650     WRITE(*,11)
660  11  FORMAT(1X,'ENTER WALL AND INIT. PART. TEMPS. IN K')
670     READ(*,*)TWALL,TPINIT
680     WRITE(1,*)TWALL,TPINIT
690
700     WRITE(*,12)
710  12  FORMAT(1X,'ENTER THE INITIAL ASH VOLUME FRACTION')
720     READ(*,*)ASHO
730     WRITE(1,*)ASHO
740
750     WRITE(*,13)
760  13  FORMAT(1X,'ENTER THE INIT. PART. RADIUS IN MICRONS')
770     READ(*,*)RINIT
780     WRITE(1,*)RINIT
790
800 WRITE(*,14)
810 14 FORMAT(1X,'ENTER THE O2 PART. PRES. IN THE AMBIENT')
820 READ(*,*)PINF
830 WRITE(1,*)PINF
840
850 WRITE(*,15)
860 15 FORMAT(1X,'INPUT WALL, CARBON AND ASH EMMISIVITIES')
870 READ(*,*)WEMMIS,PEMMIS,AMMIS
880 WRITE(1,*)WEMMIS,PEMMIS,AMMIS
890
900 WRITE(*,16)
910 16 FORMAT(1X,'ENTER THE MAXIMUM TEMPERATURE INCREMENT')
920 READ(*,*)DELTEMP
930 WRITE(1,*)DELTEMP
940
950 WRITE(*,17)
960 17 FORMAT(1X,'ENTER XFAC, ACEN AND TIMESTEP')
970 READ(*,*)XFAC,ACEN,STEPO
980 WRITE(1,*)XFAC,ACEN,STEPO
990
1000 WRITE(*,18)
1010 18 FORMAT(1X,'ENTER ES1,ES2,XACC (0 < ES1 << ES2)')
1020 READ(*,*)ES1,ES2,XACC
1030 WRITE(1,*)ES1,ES2,XACC
1040
1050 WRITE(*,19)
1060 19 FORMAT(1X,'ENTER THE NUMBER OF TIMESTEPS')
READ(*,*)NMAX
WRITE(1,*)NMAX
WRITE(*,21)
FORMAT(1X,'ENTER THE OUTPUT FILENAME (NOT VARNU.INP!)')
READ(*,22)IFILE
FORMAT(A15)
CLOSE(1)
GOTO 3000
OPEN(1,FILE='VARNU.INP',STATUS='OLD')
READ(1,*)EPSO,TFAC,TWALL,TPINIT,ASHO,RINIT,PINF,WEMMIS.
PEMMIS,AMMIS,DELTEMP,XFAC,ACEN,STEPO,ES1,ES2,XACC,NMAX
CLOSE(1)
WRITE(*,30)EPSO,TFAC
FORMAT(1X,'1. PARTICLE VOID FRAC. AND TFAC: 
1  ',F8.4,3X,F8.4,/
WRITE(*,31)TWALL,TPINIT
FORMAT(1X,'2. WALL AND INIT. PART. TEMPS. IN K: 
1  F10.4,3X,F10.4,/
WRITE(*,32)ASHO
FORMAT(1X,'3. THE INIT. ASH VOLUME FRACTION: 
1  F8.4,/ 

1340 WRITE(*,33)RINIT
1350 33 FORMAT(1X,'4. THE INIT. PART. RADIUS IN MIC.: ',F8.4,/) 
1360
1370 WRITE(*,34)PINF
1380 34 FORMAT(1X,'5. THE O2 PART. PRES. (AMBIENT): ',F8.4,/) 
1390
1400 WRITE(*,35)WEMMIS,PEMMIS,AMMIS
1410 35 FORMAT(1X,'6. THE WALL, CARBON AND ASH EMISIVITIES: ',
1420 1 F6.4,3X,F6.4,3X,F6.4,/) 
1430
1440 WRITE(*,36)DELTEMP
1450 36 FORMAT(1X,'7. THE MAXIMUM TEMP: INCREMENT: ',F8.2,/) 
1460
1470 WRITE(*,37)XFAC,ACEN,STEPO
1480 37 FORMAT(1X,'8. THE FACTOR XFAC, ACEN AND TIMESTEP: ',
1490 1 F8.4,3X,F12.2,2X,F8.6,/) 
1500
1510 WRITE(*,38)ES1,ES2,XACC
1520 38 FORMAT(1X,'9. ES1,ES2,XACC (0 < ES1 << ES2): ',
1530 1 E9.4,3X,E9.4,3X,E9.4,/) 
1540
1550 WRITE(*,39)NMAX
1560 39 FORMAT(1X,'10. THE NUMBER OF TIMESTEPS: ',F10.2,/) 
1570
1580 WRITE(*,41)
1590 41 FORMAT(1X,'ENTER THE OUTPUT FILENAME (NOT VARNU.INP!)')
1600 READ(*,42)IFILE
42    FORMAT(A15)

WRITE(*,43)
FORMAT(1X, 'ENTRY NO. TO BE ALTERED (0 TO RUN)')
READ(*,*)NALT
IF(NALT .EQ. 0)GOTO 2500
IF(NALT .EQ. 1)GOTO 2010
IF(NALT .EQ. 2)GOTO 2020
IF(NALT .EQ. 3)GOTO 2030
IF(NALT .EQ. 4)GOTO 2040
IF(NALT .EQ. 5)GOTO 2050
IF(NALT .EQ. 6)GOTO 2060
IF(NALT .EQ. 7)GOTO 2070
IF(NALT .EQ. 8)GOTO 2080
IF(NALT .EQ. 9)GOTO 2090
IF(NALT .EQ. 10)GOTO 2100
GOTO 1990

WRITE(*,10)
READ(*,*)EPSO,TFAC
GOTO 1990

WRITE(*,11)
READ(*,*)TWALL,TPINIT
GOTO 1990

WRITE(*,12)
1880  READ(*,*)ASHO
1890  GOTO 1990
1900
1910  2040  WRITE(*,13)
1920  READ(*,*)RINIT
1930  GOTO 1990
1940
1950  2050  WRITE(*,14)
1960  READ(*,*)PINF
1970  GOTO 1990
1980
1990  2060  WRITE(*,15)
2000  READ(*,*)WEMMIS,PEMMIS,AMMIS
2010  GOTO 1990
2020
2030  2070  WRITE(*,16)
2040  READ(*,*)DELTEMP
2050  GOTO 1990
2060
2070  2080  WRITE(*,17)
2080  READ(*,*)XFAC,ACEN,STEPO
2090  GOTO 1990
2100
2110  2090  WRITE(*,18)
2120  READ(*,*)ES1,ES2,XACC
2130  GOTO 1990
2140
2150 2100 WRITE(*,19)
2160 READ(*,*)NMAX
2170 GOTO 1990
2180
2190 2500 OPEN(1,FILE='VARNU.INP',STATUS='NEW')
2200 WRITE(1,*),EPSO,TFAC,TWALL,TPINIT,ASHO,RINIT,PINF,WEMMIS,
2210 1 PEMMIS,AMMIS,DELTEMP,XFAC,ACEN,STEPO,ES1,ES2,XACC,NMAX
2220
2230 C
2240 C------------------------------------------------------------
2250 C
2260 C  Main program.
2270 C
2280 C  After initialization, the main loop begins. STEP (timestep)
2290 C  is set to its original value. Radii are converted to cms.
2300 C  for actual calculation but are written out in microns. GAM
2310 C  is found by bisection. The coupled gas and solid phase
2320 C  equations are solved to get GAM. Flux is calculated based on
2330 C  a reaction rate by Smith. Property values in the gas phase
2340 C  are functions of temperature. DUMC is the mole fraction of
2350 C  O2 at the external surface of the particle. X1, X2 are
2360 C  initial guesses for GAM and XACC is the error tolerance.
2370 C  DTDR is the temperature gradient at the surface.
2380 C
2390 C  Subroutine SOLID finds the ash fraction of the particle.
2400 C  Ash is assumed to be at the same temperature as the rest
2410 C  of the particle.
Subroutine RUNG solves the coupled equations of mass and energy for a given time step. If the temperature change in a time step is larger than DELTEMP, the time step is halved and the process is repeated.

Every tenth data point is written to file and screen.

Initialization.

RHOC = 1.5 * (1 - ASHO - EPSO)
C1INF = PINF
RPINIT = RINIT
ASHINIT = ASHO

RHOASH = 2.0
NMAX = 2000
ES1 = 1.0D-6
ES2 = 1.0D07
XACC = 0.0001
STEP0 = 0.0001
DELTTEMP = 20
WEMMIS = 0.8
PEMMIS = 0.8
AMMIS = 0.8
Y1INF = (C1INF * 32.0) / (C1INF * 32.0 + (1.0 - C1INF) * 28.0)
A = (1.0 / (1.0 - Y1INF)) * (Y1INF / 4.0)

TP = TPINIT
RP = RPINIT
C1S = C1INF
TIME = 0.0
DTDR = 0.0
FP = 0.0
THCK = 0.0
ASHFRAC = ASHINIT

OPEN(2, FILE=IFILE, STATUS='NEW')
WRITE(*, 900) TIME, RP, TP, C1S, FP
WRITE(2, 900) TIME, RP, TP, C1S, FP
FORMAT(1X, 5G12.4)

X1 and X2 are appropriate brackets for GAM.
Typically, ES1 is 0(1D-6), while ES2 is 0(1D11).

IF (TPINIT .LT. TWALL) THEN
    X1 = (-2331.5425 + 0.3388749*TPINIT) - ES2
    X2 = (-2331.5425 + 0.3388749*TPINIT) - ES1
ELSE
    X1 = (-2331.5425 + 0.3388749*TPINIT) + ES1
    X2 = (-2331.5425 + 0.3388749*TPINIT) + ES2
ENDIF

C Main loop begins.

C

JMAX = NMAX

DO 1000 I = 1, JMAX

STEP=STEP0

T = TP

RR = RP * 1D-04

THCK=(RP**3.0+(ASHINIT*(RPINIT**3.0-RP**3.0))/0.65)**(1.0/3.0)-RP + 1.0D-08

THCK=THCK*1.0D-04*TFAC

CALL RTBIS(GAMMA,X1,X2,XACC,RR,GAM)

DUMC = (1.0/(-1.0/7.0 + 8.0/(7.0*Y1S)))

CALL FLUX(DUMC,RR)

FP1 = -1.3333 * FP

FP2 = 2.3333 * FP

EP = GAM * FP

CALL SOLID(RR)

CALL RUNG(RADIUS,ENERGY,DUMC,STEP,EP.

991 CALL RUNG(RADIUS,ENERGY,DUMC,STEP,EP.

PEMMIS,WEMMIS,RR,RNEW,TIME)

IF(RNEW .LE. 0.0001)THEN

TBURN=TIME

GOTO 1001

ENDIF

RP = 1.0D4*RNEW

TP = TNEW
3230 TIME = TIME + 1.0D3*STEP
3240 C
3250 C Writing to file.
3260 C
3270 IF(MOD(I,10) .EQ. 0)THEN
3280 WRITE(*, 900) TIME, RP, TP, DUMC ,FP
3290 WRITE(2, 900) TIME, RP, TP, DUMC ,FP
3300 ENDIF
3310 C
3320 C Reducing the brackets for the next call of GAM.
3330 C
3340 IF ( TP .LT. TWALL) THEN
3350 X1 = GAM - DABS(1000.0*GAM)
3360 X2 = ( -2331.5425 + 0.3388749*TP ) - ES1
3370 ELSE
3380 X1 = ( -2331.5425 + 0.3388749*TP ) + ES1
3390 X2 = GAM + DABS(1000.0*GAM)
3400 ENDIF
3410 C
3420 1000 CONTINUE
3430 1001 CONTINUE
3440 CLOSE(2)
3450 END
3460 C
3470 C Main loop and main program end.
3480 C
3490 C------------------------------------------
Property values.

EC and ECH calculate the enthalpy of the solid in cal/g.

Data from coal data book.

REAL*8 FUNCTION EC(D)
IMPLICIT REAL*8(A-H,O-Z)
COMMON /FIRST/T.GAM,TWALL,FP
CPCO = 0.024
CPC1 = 6.953D-04
CPC2 = -2.841D-07
EC = CPCO*(D - 298) + (CPC1 / 2.0)*(D*D - 298*298)
1 + (CPC2 / 3.0)*(D*D*D - 298*298*298)
RETURN
END

REAL*8 FUNCTION ECH(D)
IMPLICIT REAL*8(A-H,O-Z)
COMMON /FIRST/T.GAM,TWALL,FP
CPCHO = 0.36
CPCH1 = 6.931D-05
ECH = CPCHO*(D - 298) + (CPCH1 / 2.0)*(D*D - 298*298)
RETURN
END
CPC and CPCH calculate the heat capacity of the solid in cal/g-K. Data from coal data book.

REAL*8 FUNCTION CPC(D)
IMPLICIT REAL*8(A-H,O-Z)
COMMON /FIRST/T,GAM,TWALL,FP
CPCO = 0.024
CPC1 = 6.953D-04
CPC2 = -2.841D-07
CPC = CPCO + CPC1 * D + CPC2 * D * D
RETURN
END

REAL*8 FUNCTION CPCH(D)
IMPLICIT REAL*8(A-H,O-Z)
COMMON /FIRST/T,GAM,TWALL,FP
CPCHO = 0.36
CPCH1 = 6.9310-05
CPCH = CPCHO + CPCH1 * D
RETURN
END

This routine calculates the fraction of ash in the solid. (ASHFRAC --> 1.0 as RR --> RMIN)
SUBROUTINE SOLID(RR)
IMPLICIT REAL*8(A-H,0-Z)
COMMON /ASH/ASHFRAC,RHOASH,ASHINIT,
        RPINIT,CPASH,AMMIS,THCK
ASHFRAC = ASHINIT*(1.0D-4*RPINIT/RR)**3.0
RETURN
END

C-------------------------------------------------
C-------------------------------------------------
C-------------------------------------------------
C-------------------------------------------------
C-------------------------------------------------
C-------------------------------------------------
C-------------------------------------------------
C-------------------------------------------------
C-------------------------------------------------
C-------------------------------------------------

Root finder by the method of bisection for function TET.

SUBROUTINE RTBIS(TET,X1,X2,XACC,R2,XMID)
IMPLICIT REAL*8(A-H,0-Z)
EXTERNAL TET
COMMON /FIRST/T,GAM,TWALL,FP
PARAMETER (JMAX = 500)
CALL TET(X1,FX1,R2)
CALL TET(X2,FX2,R2)
IF(FX2*FX1 .GE. 0.0) PAUSE 'BRACKET ROOT IN MENU'
DX = X2 - X1
DO 200 J = 1, JMAX
     DX = DX * 0.6
     XMID = X1 + DX
200       CONTINUE
CALL TET(XMID,FX3,R2)
CALL TET(XMID,FMID,R2)

IF (FMID * FX1 .GT. 0.0) THEN
  X1 = XMID
  FX1 = FMID
ELSE
  X2 = XMID
  FX2 = FMID
ENDIF

IF (DABS(DX/XMID) .LT. XACC) RETURN

CONTINUE

PAUSE 'TOO MANY BISECTIONS IN MENU'
END

---------------------------------------------------------------------

Calculation of solid flux in gmc/cm^2-s.(Smith 1974)

SUBROUTINE FLUX(B,R)
IMPLICIT REAL*8(A-H,O-Z)
COMMON /ASH/ASHFRAC,RHOASH,ASHINIT,
     RPINIT,CPASH,AMMIS,THCK
COMMON /FIRST/T,GAM,TWALL,FP
COMMON /R/RHOC,XFAC,ACEN
C
Older approach to calculate FP.

CASH=B-FP*R*R(1/(R+T)-1/R)/C*MD2*DASH
This routine calculates the value of the fully integrated equations from TWALL to TP based on GAM1.

SUBROUTINE GAMMA(GAM1,F,R1)
IMPLICIT REAL*8(A-H,O-Z)
COMMON /ASH/ASHFRAC,RHOASH,ASHINIT,
1 RPINIT,CPASH,AMMIS,THCK
COMMON /FIRST/ T,GAM,TWALL,FP
COMMON /R/RHOC, XFAC, ACEN
COMMON /Y1S/Y1S,Y1INF
CC = -3.0043D-05
DASH=0.35*3.13*(T/1500.0)**1.75/2.0
IF (T .LT. TWALL) THEN
HH = DSQRT(DABS(-2331.5425 - GAM1)/0.3388749)
IF (GAM1 .GT. -2331.5425) THEN
  AR1 = -1.0*CC*((DSQRT(TWALL) - DSQRT(T)) + HH/2.0 * 
  (DLOG(((DSQRT(TWALL) - HH)*(DSQRT(T) + HH) /
  2) 
  ((DSQRT(TWALL) + HH)*(DSQRT(T) - HH)))))
  HM = (2331.5425 + GAM1)/0.3388749
  Y1S = (Y1INF +4.0/3.0)*((T-HM)/(TWALL-HM))**
  1 0.8095478-4.0/3.0
  CONC = (1.0/(1.0/7.0 + 8.0/(7.0*Y1S)))
  PF = XFAC*DEXP(-1.0*ACEN/(1.98 * T))
  FFP = PF*CONC/(1.0+82.05*T*PF*R1*THCK/
  1 ((R1+THCK)*(32.0*DASH)))
  F = AR1 - R1* FFP
ELSE
  AR2 = -1.0*CC*((DSQRT(TWALL) - DSQRT(T)) - HH* 
  (DATAN(DSQRT(TWALL)/HH) - DATAN(DSQRT(T)/HH)))
  HM = (2331.5425 + GAM1)/0.3388749
  Y1S = (Y1INF +4.0/3.0)*((T-HM)/(TWALL-HM))**
  1 0.8095478-4.0/3.0
  CONC = (1.0/(1.0/7.0 + 8.0/(7.0*Y1S)))
  PF = XFAC*DEXP(-1.0*ACEN/(1.98 * T))
  FFP = PF*CONC/(1.0+82.05*T*PF*R1*THCK/
  1 ((R1+THCK)*(32.0*DASH)))
  F = AR2 - R1* FFP
ENDIF
ELSE
  FF = DSQRT(DABS(2331.5425 + GAM1)/0.3388749)
IF (GAM1 .LT. -2331.5425) THEN
AR3 = CC*((DSQRT(T)-DSQRT(TWALL))-FF*(DATAN(DSQRT(T)/FF)-DATAN(DSQRT(TWALL)/FF)))
C3 = (2331.5425 + GAM1)/0.3388749
Y1S=(Y1INF+4.0/3.0)*((T-C3)/(TWALL-C3))**0.8095478-4.0/3.0
CONC=(1.0/(-1.0/7.0 + 8.0/(7.0*Y1S)))
PF= XFAC*DEXP( -1.0*ACEN/(1.98 * T))
FFP=PF*CONC/(1.0+82.05*T*PF*R1*THCK/(R1+THCK)*(32.0*DASH)))
F = AR3-R1* FFP

ELSE
AR4 = CC * ((DSQRT(T) - DSQRT(TWALL)) + FF/2.0 * (DLOG((DSQRT(T) - FF)*(DSQRT(TWALL) + FF)/((DSQRT(T) + FF)*(DSQRT(TWALL) - FF))))
C3 = (2331.5425 + GAM1)/0.3388749
Y1S=(Y1INF+4.0/3.0)*((T-C3)/(TWALL-C3))**0.8095478-4.0/3.0
CONC=(1.0/(-1.0/7.0 + 8.0/(7.0*Y1S)))
PF= XFAC*DEXP( -1.0*ACEN/(1.98 * T))
FFP=PF*CONC/(1.0+82.05*T*PF*R1*THCK/(R1+THCK)*(32.0*DASH)))
F = AR4-R1* FFP
ENDIF
ENDIF
RETURN
END
Energy balance.

SUBROUTINE ENERGY(EP,PEMMIS,WEMMIS,RR,DUM2,ANST)

IMPLICIT REAL*8(A-H,O-Z)

EXTERNAL CPC,EC,CPCH,ECH

COMMON /FIRST/ T,GAM,TWALL,FP

COMMON /R/RHOC,XFAC,ACEN

COMMON /ASH/ASHFRAC,RH0ASH,ASHINIT.

1 RPINIT,CPASH,AMMIS,THCK

Note that RH0C=1.5*(1-ASHINIT-EPSINIT) = Apparent density

SIG = 1.595D-12

IF (DUM2 .LT. 1350) THEN

CPSOL= CPC(DUM2)

VAL = EC(DUM2)

ELSE

CPSOL= CPCH(DUM2)

VAL = ECH(DUM2)

ENDIF

CPASH = 0.183 + 0.111D-3*T

ANST=3.0*(RR+THCK)*(RR+THCK)*(FP*VAL-EP-SIG*

(PEMMIS*DUM2**4-WEMMIS*TWALL**4))/

(RR*RR*RR*(CPSOL*RHOC + CPASH*RHOASH* 

ASHINIT+0.65*((1+THCK/RR)**3.0-1.0))))
Fourth order Runge-Kutta method for solving TEST1 and TEST2 for one time step.

```fortran
SUBROUTINE RUNG(TEST1, TEST2, DUMC, STEP, EP, PEMMIS, WEMMIS, RR, RNEW, TNEW)

IMPLICIT REAL*8(A-H,O-Z)

REAL*8 K11, K12, K13, K14, K21, K22, K23, K24

EXTERNAL TEST1, TEST2, ENERGY, RADIUS

COMMON /FIRST/ T, GAM, TWALL, FP
COMMON /R/ RHOC, XFA, ACEN

DUM1 = RR
DUM2 = T

CALL TEST1(DUMC, DUM1, DUM2, DRDT)
CALL TEST2(EP, PEMMIS, WEMMIS, DUM1, DUM2, DTDT)
K11 = DRDT
K21 = DTDT
DUM1 = RR + K11*STEP/2.0
DUM2 = T + K21*STEP/2.0
CALL TEST1(DUMC, DUM1, DUM2, DRDT)
CALL TEST2(EP, PEMMIS, WEMMIS, DUM1, DUM2, DTDT)
K12 = DRDT
```

RETURN
END
K22 = DTDT
DUM1 = RR + K12*STEP/2.0
DUM2 = T + K22*STEP/2.0
CALL TEST1(DUMC,DUM1,DUM2,DRDT)
CALL TEST2(EP,PEMMIS,WEMMIS,DUM1,DUM2,DTDT)
K13 = DRDT
K23 = DTDT
DUM1 = RR + K13*STEP
DUM2 = T + K23*STEP
CALL TEST1(DUMC,DUM1,DUM2,DRDT)
CALL TEST2(EP,PEMMIS,WEMMIS,DUM1,DUM2,DTDT)
K14 = DRDT
K24 = DTDT
RNEW = RR + STEP*(K11 + 2.0*K12 + 2.0*K13 + K14)/6.0
TNEW = T + STEP*(K21 + 2.0*K22 + 2.0*K23 + K24)/6.0
RETURN
END

C-------------------------------------------------
C
C
Subroutine radius(b, dum1, dum2, ans)

Implicit Real*8(a-h, o-z)

Common /First/ T, Gam, Twall, FP
Common /r/rhoc, xfac, acen
Common /ash/ashfrac, rhoash, ashinit.
Note that $RHOC = 1.5 \times (1 - ASHINIT - EPSINIT) = \text{Apparent density}$

$DASH = 0.35 \times 3.13 \times (DUM2/1500.0)^{1.75}/2.0$

$PF = XFAC \times \text{DEXP}(-1.0 \times ACEN/(1.98 \times DUM2))$

$FFP = PF \times B/(1.0 + 82.05 \times DUM2 \times PF \times DUM1 \times THCK)$

$ANS = -1.0 \times FFP/RHOC$

RETURN

END
This program simulates the combustion of a single porous carbon particle. The particle is assumed to be isothermal internally. It has spherical voids distributed inside. Three sizes of voids corresponding to macro, transition and micro pores are used to describe the internal structure. As combustion proceeds, the local recession, which is a function of the local oxygen concentration and the particle temperature is computed at 50 fixed points within the particle. This local recession, Q, determines the local void fraction and the local surface area at any radial location. The bulk diffusion coefficient is used throughout. It is modified to account for the local void fraction according to the Satterfield relation. The diffusion equation is solved inside the particle to determine the oxygen profile inside the particle. The boundary conditions are zero gradient at the particle center and known surface concentration determined by solving the gas phase equations. The particle radius changes in two ways. Until the external void fraction reaches the user-set value, radius
changes due to reaction. However, once the external void fraction reaches the critical value, that portion of the solid in which the void fraction exceeds or equals the critical value is shed. The particle temperature is determined by an overall energy balance including radiation conduction and convection terms.

The gas phase is assumed to be quasi-steady relative to the solid for a given time step. The heterogeneous reaction at the solid is $2C + O_2 \rightarrow 2CO$ and in the gas phase, the CO oxidation is assumed to be far enough from the particle so as to have no thermal effect on the particle. The gas phase equations include the Stefan flow term. Gas phase properties are calculated using kinetic theory of gases. The integral equations are solved analytically.

The reaction rate is assumed to be linear with respect to the surface oxygen concentration.

No attempt has been made to simulate the presence of ash in this version.
Declarations.

IMPLICIT REAL*8(A-H,O-Z)

CHARACTER*15 IFILE

CHARACTER*1 QRESP

DIMENSION WK(54)

EXTERNAL EC,ECH,CPC,CPCH,RLAMB,EOX,ECO

EXTERNAL RTBIS,GAMMA,RUNG,PROF,RADIUS,ENERGY,QUE

EXTERNAL STROBE,RTBISOL,RUNGSOL,EQN1,EQN2

EXTERNAL QCR

COMMON T,TWALL

COMMON /R/RHOC,FRAC,RPINIT

COMMON /SOL/VOID1,EPS1,DLAMB1,EPSOUT,EPSOLD,FSHED.

1 EPSCRIT,VOID2,EPS2,DLAMB2,VOID3,EPS3,DLAMB3

COMMON /MISC/C,XLOW,AO,BO,XFAC,ACEN

COMMON /ARR/X(50),R(50),Y1(50),Y2(50)

COMMON /CS/CSTAR,TAU,XACC,SURFSUM
- 511 -

680 COMMON /Q$Q(4,50)$,DQDR$$(4,50),QINT,QBAR,QCRIT$

690 COMMON /AQ/AQ(50),ADQDR(50)

700 COMMON /Y1/Y1S,Y1INF

710 C

720 C

730 C-----------------------------------------------

740 C

750 C Interactive program parameter inputs.

760 C

770 C

780 WRITE(*,9)

790 9 FORMAT(i1,'WANT TO READ THE 3VOIDS.INP FILE (Y OR N)?')

800 READ(*,8)QRESP

810 8 FORMAT(A1)

820 IF((QRESP .EQ. 'y') .OR. (QRESP .EQ. 'Y'))GOTO 2000

830

840 WRITE(*,10)

850 10 FORMAT(i1,'ENTER SOLID DENSITY IN G/CC')

860 READ(*,*)RHOC

870

880 WRITE(*,11)

890 11 FORMAT(i1,'ENTER WALL AND INIT. PARTICLE TEMPS. IN K')

900 READ(*,*)T_WALL,TPINIT
WRITE(*,12)

FORMAT(1x,'ENTER THE CRITICAL VOLUME FRACTION')
READ(*,*)EPSCRIT

WRITE(*,13)

FORMAT(1x,'INIT. PART. VOID RADII(mu) AND VOIDFRACCTS (BIG --> SMALL)')
READ(*,*)RPINIT,VOID1,VOID2,VOID3,EPS1,EPS2,EPS3

WRITE(*,14)

FORMAT(1x,'ENTER THE O2 PARTIAL PRES. IN THE AMBIENT')
READ(*,*)C1INF

WRITE(*,15)

FORMAT(1x,'ENTER THE WALL AND CARBON EMMISIVITIES')
READ(*,*)WEMMIS,PEMMIS

WRITE(*,16)

FORMAT( 1x,'ENTER FRAC AND SWITCH(1:1 VOID;0:2/3 VOIDS)')
READ(*,*)FRAC,SWITCH

WRITE(*,17)
1140  17  FORMAT( 1x,'ENTER FACTOR XFAC, ACEN AND TIMESTEP')
1150  READ(*,*)XFAC,ACEN,STEPO
1160
1170  WRITE(*,18)
1180  18  FORMAT(1X,'ENTER ES1,ES2,XACC (0 < ES1 << ES2 ) ')
1190  READ(*,*)ES1,ES2,XACC
1200
1210  WRITE(*,19)
1220  19  FORMAT( 1x,'ENTER THE NO. OF TIMESTEPS, TAU AND CSTAR')
1230  READ(*,*)NMAX,TAU,CSTAR
1240
1250  WRITE(*,21)
1260  21  FORMAT( 1x,'ENTER THE OUTPUT FILENAME (NOT *.INP !)')
1270  READ(*,22)IFILE
1280  22  FORMAT(A15)
1290
1300  GOTO 2500
1310
1320  2000 OPEN(1,FILE='3VOIDS.INP',STATUS='OLD')
1330  READ(1,*,END=129)RHOC,TWALL,TPINIT,EPSCRIT,RPINIT,VOID1.
1340  1 VOID2,VOID3,EPS1,EPS2,EPS3,C1INF,WEMMIS,PEMMIS,FRAC.
1350  2 SWITCH,XFAC,ACEN,STEPO,ES1,ES2,XACC,NMAX,TAU,CSTAR
1360  CLOSE(1)
WRITE(*,30)RHOC

FORMAT(1x,'1. SOLID DENSITY IN G/CC:
1 ,F8.4,/) 

WRITE(*,31)TWALL,TPINIT

FORMAT(1x,'2. WALL AND INIT. PARTICLE TEMPS. IN K: ',
1 F10.4,3X,F10.4,/) 

WRITE(*,32)EPSCRIT

FORMAT(1x,'3. THE CRITICAL VOLUME FRACTION: ',F8.4,/) 

WRITE(*,33)RPINIT,VOID1,VOID2,VOID3,EPS1,EPS2,EPS3

FORMAT(1x,'4. INIT. PART.,VOID RADII(mu) AND VOIDFRAC.:'
1 ,/7G10.4,/) 

WRITE(*,34)C1INF

FORMAT(1x,'5. THE O2 PART. PRES. (AMBIENT):',F8.4,/) 

WRITE(*,35)WEMMIS,PEMMIS

FORMAT(1x,'6. THE WALL AND CARBON EMMISIVITIES: ',
1 F6.4,3X,F6.4,/) 


WRITE(*,36)FRAC,SWITCH
FORMAT( 1x,'7. FRAC AND SWITCH: ',2F8.2,/) 

WRITE(*,37)XFAC,ACEN,STEPO
FORMAT( 1x,'8. THE FACTOR XFAC, ACEN AND TIMESTEP: ', 
1650 1 F9.4,3X,F10.2,2X,F8.6,/) 

WRITE(*,38)ES1,ES2,XACC
FORMAT(1X,'9. ES1,ES2,XACC (0 < ES1 <= ES2): ', 
1690 1 E9.4,3X,E9.4,3X,E9.4,/) 

WRITE(*,39)NMAX,TAU,CSTAR
FORMAT( 1x,'10. THE NO. OF STEPS, TAU, CSTAR: 
1730 1 ',I8,2X,2F12.4,/) 

WRITE(*,41)
FORMAT( 1X,'ENTER THE OUTPUT FILENAME (NOT *.INP !)') 
READ(*,42)IFILE

WRITE(*,43)
FORMAT(1X, 'ENTER # OF ENTRY TO BE ALTERED (0 TO RUN)') 
READ(*,*)NALT
1830 IF(NALT .EQ. 0) GOTO 2500
1840 IF(NALT .EQ. 1) GOTO 2010
1850 IF(NALT .EQ. 2) GOTO 2020
1860 IF(NALT .EQ. 3) GOTO 2030
1870 IF(NALT .EQ. 4) GOTO 2040
1880 IF(NALT .EQ. 5) GOTO 2050
1890 IF(NALT .EQ. 6) GOTO 2060
1900 IF(NALT .EQ. 7) GOTO 2070
1910 IF(NALT .EQ. 8) GOTO 2080
1920 IF(NALT .EQ. 9) GOTO 2090
1930 IF(NALT .EQ. 10) GOTO 2100
1940 GOTO 1990
1950
1960 2010 WRITE(*,10)
1970 READ(*,*) RHOC
1980 GOTO 1990
1990
2000 2020 WRITE(*,11)
2010 READ(*,*) TWALL, TPINIT
2020 GOTO 1990
2030
2040 2030 WRITE(*,12)
2050 READ(*,*) EPSCRIT
2060      GOTO 1990

2070

2080  2040      WRITE(*,13)

2090      READ(*,*)RPINIT,VOID1,VOID2,VOID3,EPS1,EPS2,EPS3

2100      GOTO 1990

2110

2120  2050      WRITE(*,14)

2130      READ(*,*)C1INF

2140      GOTO 1990

2150

2160  2060      WRITE(*,15)

2170      READ(*,*)WEMMIS,PEMMIS

2180      GOTO 1990

2190

2200  2070      WRITE(*,16)

2210      READ(*,*)FRAC,SWITCH

2220      GOTO 1990

2230

2240  2080      WRITE(*,17)

2250      READ(*,*)XFAC,ACEN,STEPO

2260      GOTO 1990

2270

2280  2090      WRITE(*,18)
2290 READ(*,*)ES1,ES2,XACC
2300 GOTO 1990
2310
2320 2100 WRITE(*,19)
2330 READ(*,*)NMAX,TAU,CSTAR
2340 GOTO 1990
2350
2360 2500 OPEN(1,FILE='3VOIDS.INP',STATUS='NEW')
2370 WRITE(1,*)RHOC,TWALL,TPINIT,EPSCRIT,RPINIT,VOID1,VOID2,
2380 1 VOID3,EPS1,EPS2,EPS3,C1INF,WEMMIS,PEMMIS,FRAC,
2390 2 SWITCH,XFAC,ACEN,STEP0,ES1,ES2,XACC,NMAX,TAU,CSTAR
2400 CLOSE(1)
2410 C
2420 C------------------------------------------------------------
2430 C------------------------------------------------------------
2440 C
2450 C Main Program.
2460 C
2470 C After initialisation of various parameters, the main
2480 C loop begins. C1INF and Y1INF are the mole and mass
2490 C fractions of oxygen far from the particle. A is used
2500 C to calculate the mass fractions of the other species.
2510 C EPSCRIT is the critical voidfraction at which shedding
starts. QINT is the interval between the 50 fixed points where Q's are calculated.

The porosity in the solid is characterized by the three parameters EPS, VOID and DLAMB for each void size. The porosity is obtained by polydisperse spherical voids whose initial sizes are VOID1, VOID2 and VOID3 microns. The initial void fractions are EPS1, EPS2 and EPS3 respectively. From the EPS's and VOID's, the DLAMB's (the number densities of the voids (#/vol)) are obtained. DLAMB's remain constant thereafter.

Factors of 1D4 or 1D-4 occur in converting from cms. to microns and back.

RTBIS is called to calculate the carbon flux from the solid. It calls GAMMA which in turn calls SOLID. SOLID solves for the oxygen concentration profile inside the particle using EQN1 and EQN2. It uses a scaling method to solve the two-point boundary value problem for the profile.

The routine RUNG uses a fourth order Runge-Kutta scheme
to solve the simultaneous equations for particle radius
and temperature. It calls ENERGY and RADIUS. The latter
calls SOLID and QUE to actually calculate DR/DT. The
routine QUE calculates the recession at points inside
the particle and checks to see if the critical recession
(calculated from EPSCRIT) is reached at the surface.
The concentration profiles in the particle are written
into a file called PRO.DAT at every 20th step.
After a profile has been calculated, PLACE is called.
This routine rearranges the R's such that more points
are put in the region where the profile has steeper
gradients.
The reaction rate expression is from Smith's paper (1974).
It is based on the external surface area.
XFAC multiplies the pre-exponential factor and can be
adjusted.
RATE= XFAC*305*DEXP(-ACEN/(1.98*T))*CONC [G/CM^-2-S]
Initialization.

Initially equally spaces R's

DO 153 I=1,50
   FIX=I-1
   R(I)=FIX*RPINIT/49.0
CONTINUE

DO 156 L=1,50
   AQ(L)=O.O
   ADQDR(L)=O.O
CONTINUE

Y1INF=(C1INF*32.0)/(C1INF * 32.0 +(1.0 - C1INF )*28.0)
A = (1.0 / (1.0 - Y1INF)) * (Y1INF / 4.0)

FP=O.O
TIME = 0.0
DTDR = 0.0
FLAG=1.0
CONV=O.O
QINT=RPINIT/49.0
\text{\bf T = TPINIT}

\text{\bf TPOLD = TPINIT}

\text{\bf RP = RPINIT}

\text{\bf ROLD = RPINIT*1.0D-04}

\text{\bf C1S = C1INF}

\text{\bf Y1OLD = Y1INF}

\text{\bf Y1S = Y1INF}

\text{\bf DLAMB3 = -1.0*DLOG(1.0-\text{EPS3})/(4.2*VOID3*VOID3*VOID3)}

\text{\bf DLAMB2 = \{-1.0*DLOG(1.0-\text{EPS3-\text{EPS2}})-DLAMB3*(4.2*VOID3*VOID3*VOID3)}

\text{\bf DLAMB1 = \{-1.0*DLOG(1.0-\text{EPS3-\text{EPS2-\text{EPS1}})-DLAMB3*4.2*VOID3**3}}

\text{\bf EPS = 1.0-DEXP((-4.2*DLAMB1*(VOID1)**3)+(-4.2*DLAMB2*(VOID2)**3)+(-4.2*DLAMB3*(VOID3)**3))}

\text{\bf SURF = \{(1.0-\text{EPS})*12.6*(DLAMB1*VOID1**2 + DLAMB2*VOID2**2 + DLAMB3*VOID3**2))} /

\text{\bf ((1.0-\text{EPS})*RHO*CG)}

\text{\bf EPSOLD = EPS}

\text{\bf EPSOUT = EPS}

\text{\bf EPSINIT = EPS}

\text{\bf \text{\bf C}}

\text{\bf \text{\bf C}}
OPEN(2,FILE=IFILE,STATUS='NEW',FORM='FORMATTED')
OPEN(3,FILE='PRO.DAT',STATUS='NEW',FORM='FORMATTED')
WRITE(2, 900)TIME,CONV,RP,T,C1S,FP,SURF,EPSOLD,EPSOUT
WRITE(*, 900)TIME,CONV,RP,T,C1S,FP,SURF,EPSOLD,EPSOUT
FORMAT(1X,3F9.4,1X,F7.2,1X,2F8.6,1X,F6.2,1X,
F6.4,1X,F6.4)

X1 and X2 are appropriate brackets for GAM.
Typically, ES1 is 0(1D-6), while ES2 is 0(1D11).

IF ( TPINIT .LT. TWALL) THEN
  X1 = ( -2331.5425 + 0.3388749*TPINIT) - ES2
  X2 = ( -2331.5425 + 0.3388749*TPINIT) - ES1
ELSE
  X1 = ( -2331.5425 + 0.3388749*TPINIT) + ES1
  X2 = ( -2331.5425 + 0.3388749*TPINIT) + ES2
ENDIF

Calculation of QCRIT.

IF(SWITCH .EQ. 1) THEN
  QCRIT=(-1.0*DLOG(1.0-EPSCRIT)/(DLAMB1•4.2))••.33-VOID1
ELSE
GUESS1 = \(-1.0 \cdot \text{DLOG}(1.0 - \text{EPSCRIT})/\text{DLAMB1} \times 4.2\) \times 0.33 - VOID1

GUESS2 = 0.0

CALL RTBIS0L(QCR, GUESS2, GUESS1, XACC, RSLT)

QCRIT = RSLT

ENDIF

WRITE(*,*) QCRIT

C

Main loop begins.

C

DO 1000 I = 1, NMAX

SWIT = 0.0

STEP = STEPO

RR = RP \times 1.0D-04

CALL RTBIS(GAMMA, X1, X2, XACC, STEP, PEMMIS, WEMMIS, RR, RNEW.

1 TNEW, FP, ANSW, SWIT)

FP1 = -1.3333 \times FP

FP2 = 2.3333 \times FP

EPF = ANSW \times FP

DTDR = \(-1.0D-4 \times (\text{EPF} \times \text{FP1} \times \text{EPX}(T) - \text{FP2} \times \text{EC0}(T)))/\text{RLAMB}(T)

DUMC = (1.0/(\-1.0/7.0 + 8.0/(7.0\times Y1S)))

RBAR = (ROLD + RNEW)/2.0

FSHED = 0.333 \times (1.0 - \text{EPSOUT}) \times \text{RHOC}*

(ROLD \times 3.0 - RNEW \times 3.0)/(STEP \times RBAR \times 2.0)
3900 \text{ ROLD=RNEW}
3910 \text{ RP = 1.0D4*RNEW}
3920 \text{ CONV=1.0-((RP/RPINIT)**3.0)*((1.0-EPSOLD)/(1.0-EPSINIT))}
3930 \text{ SURF=SURFSUM*1.0D-12/(4.2*RNEW**3.0*(1.0-EPSOLD)*RHOC)}
3940 \text{ T = TNEW}
3950 \text{ TIME = TIME + 1.0D3*STEP}
3960 \text{ TPO LD=T}
3970 \text{ C}
3980 \text{ C Writing profiles to PRO.DAT}
3990 \text{ C}
4000 \text{ IF(MOD(I,20) .EQ. 0)THEN}
4010 \text{ DO 148 LI=1,50}
4020 \text{ WRITE(3,147)R(LI),Y1(LI)}
4030 \text{ 148 CONTINUE}
4040 \text{ EN DIF}
4050 \text{ 147 FORMAT(6X,2G12.4)}
4060 \text{ C}
4070 \text{ C Writing results to DATA file.}
4080 \text{ C}
4090 \text{ IF(MOD(I,10) .EQ. 0)THEN}
4100 \text{ WRITE(2,900)TIME,CONV,RP,T,DUMC,FP,SURF,EPSOLD,EPSOUT}
4110 \text{ WRITE(*,900)TIME,CONV,RP,T,DUMC,FP,SURF,EPSOLD,EPSOUT}
4120 \text{ EN DIF}
C Equispacing R's

DO 157 KI=1,50

FIX=KI-1

R(KI)=FIX*RP/49.0

157 CONTINUE

DO 158 LI=1,50

AQ(LI)=Q(4,LI)

ADQDR(LI)=DQDR(4,LI)

158 CONTINUE

Reducing brackets for next call of ANS.

IF ( T .LT. TWALL) THEN

X1 = ANSW - DABS(10.0*ANSW)

X2 = (-2331.5425 + 0.3388749*T) - ES1

ELSE

X1 = (-2331.5425 + 0.3388749*T) + ES1

X2 = ANSW + DABS(10.0*ANSW)

ENDIF

C
4360 C Program exit condition.

4370 C

4380 IF((EPSOLD .GE. EPSCRIT) .OR. 1 (R(50) .LE. 0.0))GOTO 1001

4400 C

4410 1000 CONTINUE

4420 C

4430 1001 CLOSE(2)

4440 CLOSE(3)

4450 CONTINUE

4460 STOP

4470 END

4480 C

4490 C Main loop and main program end.

4500 C

4510 C

4520 C-----------------------------------------------

4530 C-----------------------------------------------

4540 C

4550 C Property subprograms.

4560 C

4570 C RLAMB: gas thermal conductivity (cal/cm-K) [300-2500K]

4580 C from Eckert. The COEFFS are in W/m-K for D in K
Form NOT used here.

EOX : oxygen enthalpy (cal/gmol). Ref. state is 0.0 at 298K. Valid for 298-2500K. Heat capacities assumed constant. From Smith and Van Ness. Form NOT used.

ECO : CO enthalpy. As above except ref. state.

EC : Carbon enthalpy (cal/g) [LT 1350K] (COAL DATA BOOK)
ECH : Carbon enthalpy (cal/g) [GE 1350K] (COAL DATA BOOK)
CPC : Carbon heat cap. (cal/g-K) [LT 1350K] (COAL DATA BOOK)
CPCH : Carbon heat cap. (cal/g-K) [GE 1350K] (COAL DATA BOOK)

REAL*8 FUNCTION RLAMB(D)

IMPLICIT REAL*8(A-H,O-Z)

REAL*8 LGO,LG1,LG2,LG3

LGO = -1.333D-03
LG1 = 1.036D-04
LG2 = -4.715D-08
LG3 = 1.341D-11

RLAMB = (1.0/418.0)*(LGO+LG1*D+LG2*(D*D)+LG3*(D*D*D))

RETURN
END
REAL*8 FUNCTION EOX(D)

IMPLICIT REAL*8(A-H,O-Z)

CPOXO = 7.16
CPOX1 = 0.001
CPOX2 = -40000.0

EOX = (CPOXO*(D - 298) + (CPOX1 / 2.0)*(D*D - 298*298) + CPOX2*(1.0/D - 1.0/298)) / 32.0

RETURN

END

REAL*8 FUNCTION ECO(D)

IMPLICIT REAL*8(A-H,O-Z)

CPC00 = 6.79
CPC01 = 0.00098
CPC02 = -11000.0
DELH = -26416.0

ECO = (DELH*CPC00*(D-298)+(CPC01/2.0)*(D*D-298*298) + CPC02*(1.0/D - 1.0/298))/ 28.0

RETURN

END
REAL*8 FUNCTION EC(D)
IMPLICIT REAL*8(A-H,O-Z)
CPO = 0.024
CPC1 = 6.953D-04
CPC2 = -2.841D-07
EC = CPC0*(D - 298) + (CPC1 / 2.0)*(D*D - 298*298)
1 + (CPC2 / 3.0)*(D*D*D - 298*298*298)
RETURN
END

REAL*8 FUNCTION ECH(D)
IMPLICIT REAL*8(A-H,O-Z)
CPCHO = 0.36
CPCH1 = 6.931D-05
ECH = CPCHO*(D - 298) + (CPCH1 / 2.0)*(D*D - 298*298)
RETURN
END

REAL*8 FUNCTION CPC(D)
IMPLICIT REAL*8(A-H,O-Z)
CPO = 0.024
CPC1 = 6.953D-04
CPC2 = -2.841D-07
CPC = CPCO + CPC1 * D + CPC2 * D * D
RETURN
END

REAL*8 FUNCTION CPCH(D)
IMPLICIT REAL*8(A-H,O-Z)
CPCHO = 0.36
CPCH1 = 6.931D-05
CPCH = CPCHO + CPCH1 * D
RETURN
END

SUBROUTINE RTBISOL(TET,X1,X2,XACC,XMID)
IMPLICIT REAL*8(A-H,O-Z)
EXTERNAL TET
PARAMETER (JMAX = 500)
CALL TET(X1,FX1)
CALL TET(X2,FX2)
IF(FX2*FX1.GE.0)PAUSE 'ROOT MUST BE BRACKETED IN RTBISOL'
DO 200 J = 1, JMAX

DX = DX * 0.5
XMID = X1 + DX
CALL TET(XMID,FMID)
IF (FMID * FX1 .GT. 0.0) THEN
X1 = XMID
FX1 = FMID
ELSE
X2 = XMID
FX2 = FMID
ENDIF
IF (DABS(DX) .LT. XACC) RETURN
CONTINUE
PAUSE 'TOO MANY BISECTIONS IN RTBISOL'
END

SUBROUTINE QCR(P,FUNT)
IMPLICIT REAL*8(A-H,O-Z)
COMMON /SOL/VOID1,EPS1,DLAMB1,EPSOUT,EPSOLD,FSHED,
EPSCRIT,VOID2,EPS2,DLAMB2,VOID3,EPS3,DLAMB3
FUNT = DLAMB1*(VOID1+P)**3 + DLAMB2*(VOID2+P)**3 + DLAMB3*(VOID3+P)**3 + DLOG(1.0-EPSCRIT)/4.2

RETURN

END

SUBROUTINE PROF(ITER,RPIN,T,BETA)

IMPLICIT REAL*8(A-H,O-Z)

EXTERNAL STROBE,RTBISOL,RUNGSOL,EQN1,EQN2

COMMON /ARR/X(50),R(50),Y1(50),Y2(50)

COMMON /MISC/C,XLOW,AO,BO,XFAC,ACEN

AO=0.0

BO=R(50)

RP=RPIN*1.0D4

Y1INIT=1.0

Y2INIT=0.0

CALL STROBE(T,Y1INIT,Y2INIT,ANS)
FACTOR=BETA/Y1(50)

DO 181 I=1,50

Y1(I)=FACTOR*Y1(I)

Y2(I)=FACTOR*Y2(I)

X(I)=R(I)

CONTINUE

RETURN

END

---------------------------------------------------

SUBROUTINE STROBE(T,Y1INIT,Y2INIT,SHOT)

IMPLICIT REAL*8(A-H,O-Z)

EXTERNAL RTBISOL,RUNGSOL,EQN1,EQN2

EXTERNAL DCADRE,IFLSQ

COMMON /ARR/X(60),R(60),Y1(60),Y2(60)

Y1(1)=Y1INIT

Y2(1)=Y2INIT

DO 600 I=1,49

RINIT=R(I)

Y1INIT=Y1(I)

Y2INIT=Y2(I)
H = R(I+1) - R(I)

CALL RUNGSOL(T, EQN1, EQN2, RINIT, Y1INIT, Y2INIT, H, ANS, ANSP)

Y1(I+1) = ANS
Y2(I+1) = ANSP

CONTINUE

SHOT = Y1(50)
RETURN

END

SUBROUTINE RUNGSOL(T, TST1, TST2, RINIT, Y1INIT, Y2INIT, H, ANS, ANSP)

IMPLICIT REAL*8(A-H,O-Z)

REAL*8 K11, K12, K13, K14, K21, K22, K23, K24

EXTERNAL TST1, TST2, EQN1, EQN2, DCADRE, IFLSQ

XP = RINIT
DUM1 = Y1INIT
DUM2 = Y2INIT

CALL TST1(DUM1, DUM2, DY1DT)
CALL TST2(T, XP, DUM1, DUM2, DY2DT)
K11 = DY1DT
K21 = DY2DT
XP = XP + H/2.0
DUM1 = Y1INIT + K11*H/2.0
DUM2 = Y2INIT + K21*H/2.0
CALL TST1(DUM1, DUM2, DY1DT)
CALL TST2(T, XP, DUM1, DUM2, DY2DT)
K12 = DY1DT
K22 = DY2DT
DUM1 = Y1INIT + K12*H/2.0
DUM2 = Y2INIT + K22*H/2.0
CALL TST1(DUM1, DUM2, DY1DT)
CALL TST2(T, XP, DUM1, DUM2, DY2DT)
K13 = DY1DT
K23 = DY2DT
XP = XP + H/2.0
DUM1 = Y1INIT + K13*H
DUM2 = Y2INIT + K23*H
CALL TST1(DUM1, DUM2, DY1DT)
CALL TST2(T, XP, DUM1, DUM2, DY2DT)
K14 = DY1DT
K24 = DY2DT
ANS = Y1INIT + H*(K11 + 2.0*K12 + 2.0*K13 + K14)/6.0
ANSP = Y2INIT + H*(K21 + 2.0*K22 + 2.0*K23 + K24)/6.0
SUBROUTINE EQN1(DUM1,DUM2,DY1DT)
IMPLICIT REAL*8(A-H,O-Z)

DY1DT = DUM2
RETURN
END

SUBROUTINE EQN2(T,XP,DUM1,DUM2,DY2DT)
IMPLICIT REAL*8(A-H,O-Z)

COMMON /MISC/C,XLOW,AO,BO,XFAC,ACEN
COMMON /SOL/VOID1,EPS1,DLAMB1,EPSOUT,EPSOLD,FSHED,
     1 EPSCRIT,VOID2,EPS2,DLAMB2,VOID3,EPS3,DLAMB3
COMMON /QS/Q(4,50),DQDR(4,50),QINT,QBAR,QCRIT
COMMON /CS/CSTAR,TAU,XACC,SURFSUM
COMMON /R/RHOC,FRAC,RPINIT

C

KL=INT(XP/QINT)+1

QBARL=Q(4,KL)+((XP-(KL-1)*QINT)/QINT)*(Q(4,KL+1)-Q(4,KL))

DQBARL=DQDR(4,KL)+((XP-(KL-1)*QINT)/QINT)*(DQDR(4,KL+1)-

1 DQDR(4,KL))

EPS=1.0-DEXP((-DLAMB1*4.2*(VOID1+QBARL)**3)+(-DLAMB2*4.2*

1 (VOID2+QBARL)**3)+(-DLAMB3*4.2*(VOID3+QBARL)**3))

SQ=(1.0-EPS)*12.6*(DLAMB1*(VOID1+QBARL)**2 + DLAMB2*(VOID2+QBARL)**2 + DLAMB3*(VOID3+QBARL)**2)

FREQ=305.0

DIFF=3.13*(T/1500.0)**1.75

E=ACEN/1.98

RHOG=1.0/(82.05*T)

C1=TAU*FREQ*XFAC/(24.0*DIFF*RHOG)

IF(XP .GT. CSTAR)THEN

DY2DT = C1*DEXP(-E/T)*SQ*1D-04*DUM1/EPS-2.0*DUM2/XP

1 -SQ*DQBARL*DUM2/EPS

ELSE

DY2DT = C1*DEXP(-E/T)*SQ*1D-04*DUM1/EPS-

1 SQ*DQBARL*DUM2/EPS

ENDIF

RETURN
SUBROUTINE QUE(T,DELT,DRDT,ITER,FP)
IMPLICIT REAL*8(A-H,O-Z)
DIMENSION Y1BAR(50),Y2BAR(50)
COMMON /ARR/X(50),R(50),Y1(50),Y2(50)
COMMON /MISC/C,XLOW,A0,BO,XFAC,ACEN
COMMON /SOL/VOID1,EPS1,DLAMB1,EPSOUT,EPSOLD,FSHED,
     1 EPSCRIT,VOID2,EPS2,DLAMB2,VOID3,EPS3,DLAMB3
COMMON /QS/Q(4,50),DQDR(4,50),QINT,QBAR,QCRIT
COMMON /R/RHOC,FRAC,RPINIT
COMMON /CS/CSTAR,TAU,XACC,SURFSUM
COMMON /AQ/AQ(50),ADQDR(50)

FREQ=305.0
E=ACEN/1.98
C2=FREQ*XFAC/RHOC
RXN = C2*DEXP(-E/T)*1.0D04

Q’s are in microns for the above expression of reaction
The inner J-loop finds the position of Q(I) just below
R(J). Y1BAR and Y2BAR are the interpolated values of mass fraction and its gradients at the fixed locations where Q's are calculated.

Y1BAR(1)=Y1(1)
Y2BAR(1)=Y2(1)

DO 300 I=2,50
DIST = QINT*(I-1)

DO 360 J=1,49
IF((R(J).LT.DIST).AND.(R(J+1).GE.DIST))THEN
Y1BAR(I)=Y1(J)+((DIST-R(J))/(R(J+1)-R(J)))*(Y1(J+1)-Y1(J))
Y2BAR(I)=Y2(J)+((DIST-R(J))/(R(J+1)-R(J)))*(Y2(J+1)-Y2(J))
ELSEIF (DIST .GT. R(50)) THEN
Y1BAR(I)=Y1(50)
Y2BAR(I)=Y2(50)
ENDIF

Q(ITER,1)=AQ(1)+DELT*RXN*Y1BAR(1)
DQDR(ITER,1)=ADQDR(1)+DELT*RXN*Y2BAR(1)
DO 310 I=2,50
Q(ITER,I)=AQ(I)+DELT*RXN*Y1BAR(I)
DQDR(ITER,I)=ADQDR(I)+DELT*RXN*Y2BAR(I)
750 IF((Q(ITER,I).GE.QCRIT).AND.(Q(ITER,I-1).LT.QCRIT))THEN
RCRIT=QINT*(I-2)+((QCRIT-Q(ITER,I-1))/(Q(ITER,I)-
1 Q(ITER,I-1)))*QINT
DQDT=RXN*Y1AVG
DRDT=-1D-04*(R(50)-RCRIT)/DELT
FLAG=0.0
GOTO 940
310 CONTINUE

KL=INT(R(50)/QINT)+1
IF(KL .EQ. 50) THEN
QBAR=Q(ITER,50)
DQDRP=DQDR(ITER,50)
ELSE
QBAR=Q(ITER,KL)+((R(50)-(KL-1)*QINT)/QINT)*(Q(ITER,KL+1)
1 -Q(ITER,KL))
DQDRP=DQDR(ITER,KL)+((R(50)-(KL-1)*QINT)/QINT)*
(DQDR(ITER,KL+1)-DQDR(ITER,KL))
ENDIF
QLAST = AQ(KL) + ((R(50) - (KL - 1) * QINT) / QINT) * (AQ(KL + 1) - AQ(KL))

1

DRDT = -1D-04 * (QBAR - QLAST) / DELT

FLAG = 1.0

C

Flux (fp) is calculated using mole fraction gradient

C at the surface Y2(50), diffusivity, and stoichiometric

C coefficient 24.0 [gm/cm-^2-s]. The expression for

diffusivity is from Field's book.

C

IF (FLAG .EQ. 1.0) THEN

IF (R(50) .EQ. RPINIT) THEN

QBAR = Q(ITER, 50)

ELSE

KL = INT(R(50)/QINT) + 1

QBAR = Q(ITER, KL) + ((R(50) - (KL - 1) * QINT) / QINT) * 

1

(Q(ITER, KL + 1) - Q(ITER, KL))

ENDIF

EPSOUT = 1.0 - DEXP((-4.2 * DLAMB1 * (VOID1 + QBAR)**3) + 

-4.2 * DLAMB2 * (VOID2 + QBAR)**3) + (-4.2 * DLAMB3 * 

VOID3 + QBAR)**3))

ELSE

KL = INT(R(50)/QINT) + 1
QSUP = Q(ITER,KL) + ((R(50) - (KL-1)*QINT)/QINT) *
1 (Q(ITER,KL+1) - Q(ITER,KL))
EPSSUP = 1.0 - DEXP((-4.2*DLAMB1*(VOID1+QSUP)**3) +
1 (-4.2*DLAMB2* (VOID2+QSUP)**3) + (-4.2*DLAMB3*
2 (VOID3+QSUP)**3)))
EPSOUT = (EPSCRIT + EPSSUP)/2.0
END IF
C
SUM = 0.0
VOLSUM = 0.0
SURFSUM = 0.0
KL = INT(R(50)/QINT) + 1
DO 560 I = 2, KL
QSHELL = (Q(ITER,I) + Q(ITER,I-1))/2.0
AQSHELL = (AQ(I) + AQ(I-1))/2.0
EPSSHELL = 1.0 - DEXP((-4.2*DLAMB1*(VOID1+QSHELL)**3) +
1 (-4.2*DLAMB2* (VOID2+QSHELL)**3) + (-4.2*DLAMB3*
2 (VOID3+QSHELL)**3)))
SQSHELL = (1.0 - EPSSHELL) * 12.6 * (DLAMB1*(VOID1+QSHELL)**2 +
1 DLAMB2*(VOID2+QSHELL)**2 +
2 DLAMB3*(VOID3+QSHELL)**2)
ROUT = QINT*(I-1)
RIN = QINT*(I-2)
FPSHELL = 4.2*(ROUTE**3.0 - RIN**3.0)*SQSHELL*

1
(QSHELL - AQ SHEL)

SURFSUM = SURFSUM + 4.2*(ROUTE**3.0 - RIN**3.0)*SQSHELL

SUM = SUM + FPSHELL

IF(QSHELL .LT. QCRI T) THEN

VOLSUM = VOLSUM + EPSHELL*(4.2*(ROUTE**3.0 - RIN**3.0))

ENDIF

CONTINUE

QR50 = Q(ITER, KL) + 0.5*(((R(50) - (KL-1)*QINT)/QINT)*

1
(Q(ITER, KL+1) - Q(ITER, KL)))

AQR50 = AQ(KL) + 0.5*(((R(50) - (KL-1)*QINT)/QINT)*(AQ(KL+1)

1
-AQ(KL)))

EPSR50 = 1.0 - DEXP((-4.2*DLAMB1*(VOID1+QR50)**3) +

1
(-4.2*DLAMB2* (VOID2+QR50)**3) + (-4.2*DLAMB3*

2
(VOID3+QR50)**3))

SQR50 = (1.0 - EPSR50) * 12.6*(DLAMB1*(VOID1+QR50)**2

1
+ DLAMB2* (VOID2+QR50)**2 + DLAMB3*(VOID3+QR50)**2)

FPQ50 = 4.2*(R(50)**3.0 - (QINT*(KL-1)**3.0)*

1
SQR50*(QR50 - AQR50)

VOLR50 = EPSR50*(R(50)**3.0 - (QINT*(KL-1)**3.0)*4.2

SURFSUM = SURFSUM + SQR50*(R(50)**3.0 -

1
(QINT*(KL-1)**3.0)*4.2

EPSOLD = (VOLSUM + VOLR50)/(4.2*R(50)**3.0)
This routine uses the method of bisection to find the root of the function described by TET. X1 and X2 are the bounds of the root and must be input into the routine. When the relative accuracy specified by XACC is reached, the root is returned as XMID.

SUBROUTINE RTBIS(TET,X1,X2,XACC,STEP,PEMMIS,WEMMIS,R2,RNEW,TNEW,FP,XMID,SWIT)

EXTERNAL TET
EXTERNAL EC,ECH,CPC,CPCH,RLAMB,EOX,ECO
EXTERNAL GAMMA,RUNG,PROF,RADIUS,ENERGY,QUE
EXTERNAL STROBE,RTBISOL,RUNGSOL,EQN1,EQN2
COMMON T,TWALL
PARAMETER (JMAX = 500)
8730       DXACC=XACC
8740       CALL TET(X1,FX1,R2,STEP,PEMMIS,WEMMIS,RNEW,TNEW,FP,SWIT)
8750       CALL TET(X2,FX2,R2,STEP,PEMMIS,WEMMIS,RNEW,TNEW,FP,SWIT)
8760       IF(FX2*FX1 .GE. 0.0)PAUSE 'YOU BRACKET ROOT IN RTBIS'
8770       DX = X2 - X1
8780       DO 200 J = 1, JMAX
8790
8800
8810
8820
8830
8840
8850
8860
8870
8880
8890
8900
8910
8920
8930
8940
8950 C
SUBROUTINE GAMMA(GAM1,F,R1,STEP,PEMMIS,WEMMIS,RNEW,
TNEW,FP,SWIT)
IMPLICIT REAL*8(A-H,O-Z)
EXTERNAL EC,ECH,CPC,CPCH,RLAMB,E0X,EC0
EXTERNAL RUNG,PROF,RADIUS,ENERGY,QUE
EXTERNAL STROBE,RTBISOL,RUNGSOL,EQN1,EQN2
COMMON T, TWALL
COMMON /Y1/Y1S,Y1INF
CC = -3.00430D-05
C3 = (2331.6425 + GAM1)/0.3388749
Y1S=(Y1INF+4.0/3.0)*((T-C3)/(TWALL-C3))**0.8095478-4.0/3.0
C1SURF= (1.0/(-1.0/7.0 + 8.0/(7.0*Y1S)))
CALL RUNG(RADIUS,ENERGY,C1SURF,STEP,PEMMIS,WEMMIS,
GAM1,R1,RNEW,TNEW,FP,SWIT)

IF (T .LT. TWALL) THEN
HH = DSQRT(DABS(-2331.5425 - GAM1)/0.3388749)
IF (GAM1 .GT.-2331.6425) THEN
AR1 = -1.0*CC*((DSQRT(TWALL)-DSQRT(T))+HH/2.0)*
1
(DLOG((DSQRT(TWALL) - HH) * (DSQRT(T) + HH) /)
2
((DSQRT(TWALL) + HH) * (DSQRT(T) - HH))))
F = AR1 - R1 * FP
ELSE
AR2 = -1.0 * CC * ((DSQRT(TWALL) - DSQRT(T)) - HH * 
1
(DATAN(DSQRT(TWALL)/HH) - DATAN(DSQRT(T)/HH))
F = AR2 - R1 * FP
ENDIF
ELSE
FF = DSQRT(DABS(2331.5425 + GAM1) / 0.3388749)
IF (GAM1 .LT. -2331.5425) THEN

AR3 = CC * ((DSQRT(T) - DSQRT(TWALL)) - FF * 
1
(DATAN(DSQRT(T)/FF) - DATAN(DSQRT(TWALL)/FF))
F = AR3 - R1 * FP
ELSE

AR4 = CC * ((DSQRT(T) - DSQRT(TWALL)) + FF * 
1
(DLOG((DSQRT(T) - FF) * (DSQRT(TWALL) + FF) / 
2
((DSQRT(T) + FF) * (DSQRT(TWALL) - FF))))
F = AR4 - R1 * FP
ENDIF
ENDIF
RETURN
END
SUBROUTINE ENERGY(EP, PEMMIS, WEMMIS, RR, DUM2, ANST)
IMPLICIT REAL*8(A-H,O-Z)
EXTERNAL EC, ECH, CPC, CPCH, RLAMB, EOX, ECO
COMMON T, TWALL
COMMON /R/RHOC, FRAC, RPINIT
COMMON /SOL/ VOID1, EPS1, DLAMB1, EPSOUT, EPSOLD, FSHED,
1 EPSCRIT, VOID2, EPS2, DLAMB2, VOID3, EPS3, DLAMB3
SIG = 1.695D-12
IF (DUM2 .LT. 1350) THEN
   CPSOL = CPC(DUM2)
   VAL = EC(DUM2)
ELSE
   CPSOL = CPCH(DUM2)
   VAL = ECH(DUM2)
ENDIF
ANST = (3.0/(1.0-EPSOLD))*(FP+(1.0-FRAC)*FSHED)*
1 VAL-EP-SIG* (PEMMIS*DUM2**4-WEMMIS*TWALL**4))/
2 /(RR*RHOC*CPSOL)
RETURN
This routine solves the coupled equations TEST1 and TEST2 for one time step. It is a standard first order Runge Kutta algorithm.

SUBROUTINE RUNG(TEST1,TEST2,DUMC,STEP,PEMMIS,WEMMIS,GAM1,RR,RNEW,TNEW,FP,SWIT)
IMPLICIT REAL*8(A-H,O-Z)
REAL*8 K11,K12,K13,K14,K21,K22,K23,K24
EXTERNAL TEST1,TEST2
EXTERNAL EC,ECH,CPC,CPCH,RLAMB,EOX,ECO
EXTERNAL PROF,RADIUS,ENERGY,QUE
EXTERNAL STROBE,RTBISOL,RUNGSOL,EQN1,EQN2
COMMON T,TWALL
COMMON /ARR/X(50),R(50),Y1(50),Y2(50)
COMMON /SOL/VOID1,EPS1,DLAMB1,EPSOUT,EPSOLD,FSHED
COMMON /R/RHOC,FRAC,RPINIT
COMMON /CS/CSTAR,TAU,XACC,SURFSUM
IF(SWIT .EQ. 0.0) THEN
    ITER=4
    CALL PROF(ITER,R1,T,DUMC)
    DIFF=3.13*(T/1500)**1.75
    FP=1.0D04*Y2(50)*DIFF*EPSOUT*24.0/(TAU*82.05*T)
RETURN
ENDIF
DUM1=RR
DUM2=T
ITER=4
CALL PROF(ITER,DUM1,DUM2,DUMC)
CALL TEST1(STEP,DUM2,ITER,DRDT,FP)
EP=FP*GAM1
CALL TEST2(EP,Pemmis,Wemmis,DUM1,DUM2,DTDT)
K11=DRDT
K21=DTDT
RNEW = RR + STEP*K11
TNEW = T + STEP*K21
RETURN
END

C------------------------------------------------
SUBROUTINE RAQUS(TMSTP,DUM2,ITER,ANS,FP)

IMPLICIT REAL*8(A-H,O-Z)

EXTERNAL QUE

C

CALL QUE(DUM2,TMSTP,DRDT,ITER,FP)

ANS=DRDT

RETURN

END

C

C-----------------------------------------------
This program simulates the combustion of a single porous carbon particle. The particle is assumed to be isothermal internally. It has spherical voids distributed inside.

Three sizes of voids corresponding to macro, transition and micro pores are used to describe the internal structure.

The reaction rate has a nonlinear dependence on the oxygen concentration at the particle surface. This function is a $m$-th power expression where $m$ can be varied between 0 and 1. For small values of $m$, the problem becomes very stiff and concentration is zero inside of the particle except in a thin outer shell. Thus the asymptotic model MENU can be used for those cases with proper reaction rate expressions.

As combustion proceeds, the local recession, which is a function of the local oxygen concentration and the particle temperature is computed at 50 fixed points within the particle. This local recession, $Q$, determines the local void fraction and the local surface area at any radial
location. The bulk diffusion coefficient is used throughout. It is modified to account for the local void fraction according to the Satterfield relation. The diffusion equation is solved inside the particle to determine the oxygen profile inside the particle. The boundary conditions are zero gradient at the particle center and known surface concentration determined by solving the gas phase equations.

The particle radius changes in two ways. Until the external void fraction reaches the user-set value, radius changes due to reaction. However, once the external void fraction reaches the critical value, that portion of the solid in which the void fraction exceeds or equals the critical value is shed. The particle temperature is determined by an overall energy balance including radiation conduction and convection terms.

The gas phase is assumed to be quasi-steady relative to the solid for a given time step. The heterogeneous reaction at the solid is \( 2C + O_2 \rightarrow 2CO \) and in the gas phase, the CO oxidation is assumed to be far enough from the particle so as to have no thermal effect on the particle.

The gas phase equations include the Stefan flow term.
Gas phase properties are calculated using kinetic theory of gases. The integral equations are solved analytically.

No attempt has been made to simulate the presence of ash in this version.

Declarations.

```
IMPLICIT REAL*8(A-H,O-Z)

CHARACTER*15 IFILE
CHARACTER*1 QRESP

DIMENSION WK(64)

EXTERNAL EC,ECH,CPC,CPCH,RLAMB,EOX,ECO
EXTERNAL GAMMA,PROF,RADIUS,ENERGY,QUE
EXTERNAL STROBE,RTBISOL,EQN1,EQN2
EXTERNAL QCR,SHOOT

COMMON T,TWALL
COMMON /R/RHOC,FRAC,RPINIT
```
Interactive program parameter inputs.

WRITE(*,9)
9 FORMAT(1x,'WANT TO READ THE PCONC.INP FILE (Y OR N)?')
READ(*,8)QRESP
8 FORMAT(A1)
IF((QRESP .EQ. 'y') .OR. (QRESP .EQ. 'Y')) GO TO 2000
WRITE(*,10)
10 FORMAT(1x,'ENTER SOLID DENSITY IN G/CC')
READ(*,*) RHOC

WRITE(*,11)

FORMAT(1x,'ENTER WALL AND INIT. PART. TEMPS IN K')

READ(*,*) TWALL, TINIT

WRITE(*,12)

FORMAT(1x,'ENTER THE CRITICAL VOLUME FRACTION')

READ(*,*) EPSCRIT

WRITE(*,13)

FORMAT(1x,'INIT PART., VOID RADI (mu) AND VOIDFRACTIONS (BIG --> SMALL)')

READ(*,*) RPINIT, VOID1, VOID2, VOID3, EPS1, EPS2, EPS3

WRITE(*,14)

FORMAT(1x,'ENTER THE O2 PART. PRES. IN THE AMBIENT')

READ(*,*) C1INF

WRITE(*,15)

FORMAT(1x,'ENTER THE WALL AND CARBON EMISIVITIES')

READ(*,*) WEMMIS, PEMMIS

110

1110
WRITE(*,16)
FORMAT( 1x,'ENTER FRAC,POW ')
READ(*,*)FRAC,POW
WRITE(*,17)
FORMAT( 1x,'ENTER XFAC, ACEN AND TIMESTEP')
READ(*,*)XFAC,ACEN,STEPO
WRITE(*,18)
FORMAT(1X,'ENTER ES1,ES2,XACC (0 < ES1 << ES2) ')
READ(*,*)ES1,ES2,XACC
WRITE(*,19)
FORMAT( 1x,'ENTER THE NO. OF TIMESTEPS, TAU AND CSTAR')
READ(*,*)NMAX,TAU,CSTAR
WRITE(*,21)
FORMAT( 1x,'ENTER THE OUTPUT FILENAME (NOT *.INP !)')
READ(*,22)IFILE
FORMAT(A15)
GOTO 2500
OPEN(1,FILE='PCONC.INP',STATUS='OLD')

READ(1,*,END=129)RHOC,TWALL,TPINIT,EPSCRIT,RPINIT,VOID1,
VOID2,VOID3,EPS1,EPS2,EPS3,C1INF,WEMMIS,PEMMIS,FRAC,
POW,XFAC,ACEN,STEP0,ES1,ES2,XACC,NMAX,TAU,CSTAR

CLOSE(1)

WRITE(*,30)RHOC

FORMAT(1x,'1. SOLID DENSITY IN G/CC: ',/)

WRITE(*,31)TWALL,TPINIT

FORMAT(1x,'2. WALL AND INIT. PARTICLE TEMPS. IN K: ',/)

WRITE(*,32)EPSCRIT

FORMAT(1x,'3. THE CRITICAL VOLUME FRACTION: ',/)

WRITE(*,33)RPINIT,VOID1,VOID2,VOID3,EPS1,EPS2,EPS3

FORMAT(1x,'4. INIT. PART., VOID RADII(mu) AND VOIDFRAC.:'/)

WRITE(*,34)C1INF
1600 34 FORMAT(1x,'5. THE O2 PART. PRES. (AMBIENT): ',F8.4,/) 
1610 
1620 WRITE(*,35)WEMMIS,PEMMIS 
1630 35 FORMAT(1x,'6. THE WALL AND CARBON EMMISIVITIES: ', 
1640 1 F6.4,3X,F6.4,/) 
1650 
1660 WRITE(*,36)FRAC,POW 
1670 36 FORMAT( 1x,'7. FRAC ,POW : ',F8.2,2X,E9.4,/) 
1680 
1690 WRITE(*,37)XFAC,ACEN,STEPO 
1700 37 FORMAT( 1x,'8. THE FACTOR XFAC, ACEN AND TIMESTEP: ', 
1710 1 F10.4,3X,F10.2,3X,F8.6,/) 
1720 
1730 WRITE(*,38)ES1,ES2,XACC 
1740 38 FORMAT(1X,'9. ES1,ES2,XACC (0 < ES1 << ES2): ', 
1750 1 E9.4,3X,E9.4,3X,E9.4,/) 
1760 
1770 WRITE(*,39)NMAX,TAU,CSTAR 
1780 39 FORMAT(1x,'10. NO. OF STEPS, TAU, CSTAR: ',I8,2X,2F12.4,/) 
1790 
1800 WRITE(*,41) 
1810 41 FORMAT( 1x,'ENTER THE OUTPUT FILENAME (EXCEPT *.INP !)') 
1820 READ(*,42)IFILE
1830 FORMAT(A15)

1850 WRITE(*,43)
1860 FORMAT(1X, 'ENTRY NO. TO BE ALTERED (0 TO RUN)'
1870 READ(*,*)NALT
1880 IF(NALT .EQ. 0) GOTO 2500
1890 IF(NALT .EQ. 1) GOTO 2010
1900 IF(NALT .EQ. 2) GOTO 2020
1910 IF(NALT .EQ. 3) GOTO 2030
1920 IF(NALT .EQ. 4) GOTO 2040
1930 IF(NALT .EQ. 5) GOTO 2050
1940 IF(NALT .EQ. 6) GOTO 2060
1950 IF(NALT .EQ. 7) GOTO 2070
1960 IF(NALT .EQ. 8) GOTO 2080
1970 IF(NALT .EQ. 9) GOTO 2090
1980 IF(NALT .EQ. 10) GOTO 2100
1990 GOTO 1990
2000
2010 WRITE(*,10)
2020 READ(*,*)RHOC
2030 GOTO 1990
2040
2050 WRITE(*,11)
READ(*,*) TWALL, TPINIT
GOTO 1990

WRITE(*,12)
READ(*,*) EPCRIT
GOTO 1990

WRITE(*,13)
READ(*,*) RPINIT, VOID1, VOID2, VOID3, EPS1, EPS2, EPS3
GOTO 1990

WRITE(*,14)
READ(*,*) CI INF
GOTO 1990

WRITE(*,15)
READ(*,*) WEMMIS, PEMMIS
GOTO 1990

WRITE(*,16)
READ(*,*) FRAC, POW
GOTO 1990
WRITE(*,17)
READ(*,*)XFAC,ACEN,STEPO
GOTO 1990

WRITE(*,18)
READ(*,*)ES1,ES2,XACC
GOTO 1990

WRITE(*,19)
READ(*,*)NMAX,TAU,CSTAR
GOTO 1990

OPEN(1,FILE='PCONC.INP',STATUS='NEW')
WRITE(1,*)RHOC,TWALL,TPINIT,EPSCRIT,RPINIT,VOID1,VOID2,
VOID3,EPS1,EPS2,EPS3,C1INF,WEMMIS,PENMIS,FRAC,
POW, XFAC, ACEN, STEPO, ES1, ES2, XACC, NMAX, TAU, CSTAR
CLOSE(1)

Main Program.
After initialization of various parameters, the main loop begins. $C_{1INF}$ and $Y_{1INF}$ are the mole and mass fractions of oxygen far from the particle. $A$ is used to calculate the mass fractions of the other species. $EPSCRIT$ is the critical void fraction at which shedding starts. $QINT$ is the interval between the 50 fixed points where $Q$'s are calculated.

The porosity in the solid is characterized by the three parameters $EPS$, $VOID$ and $DLAMB$ for each void size. The porosity is obtained by polydisperse spherical voids whose initial sizes are $VOID1$, $VOID2$ and $VOID3$ microns. The initial void fractions are $EPS1$, $EPS2$ and $EPS3$ respectively. From the $EPS$'s and $VOID$'s, the $DLAMB$'s (the number densities of the voids ($#/vol$)) are obtained. $DLAMB$'s remain constant thereafter.

Factors of $1D4$ or $1D-4$ occur in converting from cms. to microns and back.

$RTBIS$ is called to calculate the carbon flux from the solid. It calls $GAMMA$ which in turn calls $SOLID$. $SOLID$ solves for the oxygen concentration profile inside the
particle using EQN1 and EQN2. It uses a shooting method to solve the two-point boundary value problem for the profile.

The routine RUNG uses a fourth order Runge-Kutta scheme to solve the simultaneous equations for particle radius and temperature. It calls ENERGY and RADIUS. The latter calls SOLID and QUE to actually calculate DR/DT. The routine QUE calculates the recession at points inside the particle and checks to see if the critical recession (calculated from EPSCRIT) is reached at the surface.

The concentration profiles in the particle are written into a file called PRO.DAT at every 20th step.

After a profile has been calculated, PLACE is called. This routine rearranges the R's such that more points are put in the region where the profile has steeper gradients.

The reaction rate expression is from Smith's paper (1974). It is based on the external surface area.

XFAC multiplies the pre-exponential factor and can be
adjusted. The concentration is raised to the \( m \)-th power.

\[
\text{RATE} = \text{XFAC} \cdot \text{DEXP}(-\text{ACEN} / (1.98 \cdot \text{T})) \cdot \text{CONC}^m \quad \text{[G/CM}^2\text{-S]}
\]

Initialization.

Initially equally spaced R's

DO 163 I=1.50
   FIX=I-1
   R(I)=FIX*RPINIT/49.0
163 CONTINUE

DO 166 L=1,60
   AQ(L)=O.O
   ADQDR(L)=O.O
166 CONTINUE

\[
\text{Y1INF} = \frac{\text{C1INF} \cdot 32.0}{\text{C1INF} \cdot 32.0 + (1.0 - \text{C1INF}) \cdot 28.0} \\
A = \left(1.0 / (1.0 - \text{Y1INF})\right) \times (\text{Y1INF} / 4.0)
\]

FP=0.0
TIME = 0.0
DTDR = 0.0
FLAG = 1.0
CONV = 0.0
LIE = 1
QINT = RPINIT/49.0
T = TPINIT
TPOLD = TPINIT
RP = RPINIT
R0LD = RPINIT*1.0D-04
C1S = C1INF
Y10LD = Y1INF
Y1S = Y1INF

C

DLAMB3 = -1.0*DLOG(1.0-EPS3)/(4.2*VOID3*VOID3*VOID3)
DLAMB2 = (-1.0*DLOG(1.0-EPS3-EPS2)-DLAMB3)*
(4.2*VOID3*VOID3*VOID3)/(4.2*VOID2*VOID2*VOID2)
DLAMB1 = (-1.0*DLOG(1.0-EPS3-EPS2-EPS1)-DLAMB3*4.2*VOID3**3
(4.2*VOID2*VOID2*VOID2))/(4.2*VOID1**3)
EPS = 1.0-DEXP((-4.2*DLAMB1*(VOID1)**3)+(-4.2*DLAMB2*
(VOID2)**3)+(-4.2*DLAMB3*(VOID3)**3))
SURF = ((1.0-EPS)*12.6*(DLAMB1*VOID1**2
+DLAMB2*VOID2**2+DLAMB3*VOID3**2))/(RHOC*(1.0-EPS))
3440             EPSOLD=EPS
3450             EPSOUT=EPS
3460             EPSINIT=EPS
3470             C
3480             C
3490             OPEN(2,FILE=IFILE,STATUS='NEW',FORM='FORMATTED')
3500             OPEN(3,FILE='PRO.DAT',STATUS='NEW',FORM='FORMATTED')
3510             WRITE(2,900)TIME,CONV,RP,T,C1S,FP,SURF,EPSOLD,EPSOUT
3520             WRITE(*,900)TIME,CONV,RP,T,C1S,FP,SURF,EPSOLD,EPSOUT
3530             900 FORMAT(1X,3F9.4,1X,F7.2,1X,2F8.6,1X,F6.2,1X,
3540             1             F6.4,1X,F6.4)
3550             C
3560             C X1 and X2 are appropriate brackets for GAM.
3570             C Typically, ES1 is 0(1D-6), while ES2 is 0(1D11).
3580             C
3590             IF ( TPINIT .LT. TWALL) THEN
3600             X1 = ( -2331.5425 + 0.3388749*TPINIT) - ES2
3610             X2 = ( -2331.5425 + 0.3388749*TPINIT) - ES1
3620             ELSE
3630             X1 = ( -2331.5425 + 0.3388749*TPINIT) + ES1
3640             X2 = ( -2331.5425 + 0.3388749*TPINIT) + ES2
3650             ENDIF
3660             C
Calculation of QCRIT.

GUESS1 = (-1.0*DLOG(1.0-EPSCRIT)/(DLAMB1*4.2))**.33-VOID1

GUESS2 = 0.0

CALL RTBISOL(QCR,GUESS2,GUESS1,XACC,RSLT)

QCRIT = RSLT

Main loop begins.

DO 1000 I = 1, NMAX

SWIT = 0.0

STEP = STEPO

RR = RP * 1.0D-04

RTBIS merged here.

DXACC = XACC

CALL GAMMA(X1,FX1,RR,STEP,PEMMIS,WEMMIS, RNEW,TNEW,FP,SWIT)

1

CALL GAMMA(X2,FX2,RR,STEP,PEMMIS,WEMMIS, RNEW,TNEW,FP,SWIT)

1
IF (FX2*FX1 .GE. 0.0) PAUSE 'BRACKET ROOT IN MAIN'

DX = X2 - X1

DO 200 J = 1, 500

DX = DX * 0.5

ANSW = X1 + DX

CALL GAMMA(ANSW, FMID, RR, STEP, PEMMIS, WEMMIS, RNEW, TNEW, FP, SWIT)

IF (FMID * FX1 .GT. 0.0) THEN

X1 = ANSW

FX1 = FMID

ELSE

X2 = ANSW

FX2 = FMID

ENDIF

IF (DABS(DX/ANSW) .LT. 0.20) SWIT = 1.0

IF (DABS(DX/ANSW) .LT. DXACC) GOTO 111

CONTINUE

PAUSE 'TOO MANY BISECTIONS IN MAIN'

FP1 = -1.3333 * FP

FP2 = 2.3333 * FP

EPF = ANSW * FP
DTDR=-1.0D-4*(EPF-1*EGX(T)-FP2*ECO(T))/RLAMB(T)

DUMC= (1.0/(-1.0/7.0 + 8.0/(7.0*Y1S)))

RBAR=(ROLD+RNEW)/2.0

FSHED=0.333*(1.0-EPSOUT)*RHOC*

(ROLD**3.0-RNEW**3.0)/(STEP*RBAR**2.0)

ROLD=RNEW

RP = 1.0D4*RNEW

CONV=1.0-((RP/RPINIT)**3.0)*((1.0-EPSOLD)/(1.0-EPSINIT))

SURF=SURFSUM*1.0D-12/(4.2*RNEW**3.0*(1.0-EPSOLD)*RHOC)

T = TNEW

TIME = TIME + 1.0D3*STEP

TPOLD=T

Writing profiles to PRO.DAT

IF(MOD(I,10) .EQ. 0)THEN

DO 148 LI=1,50

WRITE(3,147)R(LI),Y1(LI)

CONTINUE

ENDIF

Writing results to data file.
WRITE(2,900)TIME,CONV,RP,T,DUMC,FP,SURF,EPSOLD,EPSOUT
WRITE(*,900)TIME,CONV,RP,T,DUMC,FP,SURF,EPSOLD,EPSOUT

C Equispacing R's

DO 157 KI=1,50
   FIX=KI-1
   R(KI)=FIX*RP/49.0
157 CONTINUE

DO 158 LI=1,50
   AQ(LI)=Q(4,LI)
   ADQDR(LI)=DQDR(4,LI)
158 CONTINUE

Reducing brackets for next call of ANS.

IF ( T .LT. TWALL) THEN
   X1 = ANSW - DABS(4.0*ANSW)
   X2 = ( -2331.5425 + 0.3388749*T ) - ES1
ELSE
   X1 = ( -2331.5425 + 0.3388749*T ) + ES1
4590 \( X2 = \text{ANSW} + \text{DABS}(4.0 \times \text{ANSW}) \)

4600 ENDIF

4610 C

4620 C Program exit condition.

4630 C

4640 IF((\text{EPSOLD} \geq \text{EPSCRIT}) \text{ OR.}

4650 \( (R(50) \leq 0.0) \) GOTO 1001

4660 C

4670 1000 CONTINUE

4680 C

4690 1001 CLOSE(2)

4700 CLOSE(3)

4710 CONTINUE

4720 STOP

4730 END

4740 C

4750 C Main loop and main program end.

4760 C

4770 C--------------------------------------------------------------

4780 C--------------------------------------------------------------

4790 C

4800 C Property subprograms.

4810 C
RLAMB: gas thermal conductivity (cal/cm-K) [300-2500K] from Eckert. The COEFFS are in W/m-K for D in K

Form NOT used here.

EOX: oxygen enthalpy (cal/gmol). Ref. state is 0.0 at 298K. Valid for 298-2500K. Heat capacities assumed constant. From Smith and VanNess. Form NOT used.

ECO: CO enthalpy. As above except ref. state.

EC: Carbon enthalpy (cal/g) [LT 1350K] (COAL DATA BOOK)

ECH: Carbon enthalpy (cal/g) [GE 1350K] (COAL DATA BOOK)

CPC: Carbon heat cap. (cal/g-K) [LT 1350K] (COAL DATA BOOK)

CPCH: Carbon heat cap. (cal/g-K) [GE 1350K] (COAL DATA BOOK)

real*8 function rlamb(d)
implicit real*8(a-h,o-z)
real*8 lgo,lgi,lg2,lg3
lgo = -1.3330d-03
lg1 = 1.0360d-04
lg2 = -4.7150d-08
lg3 = 1.3410d-11
rlamb = (1.0/418.0)*(lgo+lg1*d+lg2*(d*d)+lg3*(d*d*d))
return
end
5050 C
5060 C
5070 REAL*8 FUNCTION EOX(D)
5080 IMPLICIT REAL*8(A-H,O-Z)
5090 CPOX0 = 7.16
5100 CPOX1 = 0.001
5110 CPOX2 = -40000.0
5120 EOX = (CPOX0*(D - 298) + (CPOX1 / 2.0)*(D*D - 298*298)
5130 1 + CPOX2* (1.0/D - 1.0/298)) / 32.0
5140 RETURN
5150 END
5160 C
5170 C
5180 REAL*8 FUNCTION ECO(D)
5190 IMPLICIT REAL*8(A-H,O-Z)
5200 CPC00 = 6.79
5210 CPC01 = 0.00098
5220 CPC02 = -11000.0
5230 DELH = -26416.0
5240 ECO = (DELH+CPC00*(D-298)+(CPC01/2.0)*(D*D - 298*298)
5250 1 + CPC02* (1.0/D - 1.0/298))/ 28.0
5260 RETURN
5270 END
REAL*8 FUNCTION EC(D)
IMPLICIT REAL*8(A-H,O-Z)
CPCO = 0.024
CPC1 = 6.953D-04
CPC2 = -2.841D-07
EC = CPCO*(D - 298) + (CPC1 / 2.0)*(D*D - 298*298) + (CPC2 / 3.0)*(D*D*D - 298*298*298)
RETURN
END

REAL*8 FUNCTION ECH(D)
IMPLICIT REAL*8(A-H,O-Z)
CPCHO = 0.36
CPCH1 = 6.931D-05
ECH = CPCHO*(D - 298) + (CPCH1 / 2.0)*(D*D - 298*298)
RETURN
END

REAL*8 FUNCTION CPC(D)
IMPLICIT REAL*8(A-H,O-Z)
CPCO = 0.024
CPC1 = 6.9530-04
CPC2 = -2.8410-07
CPC = CPCO + CPC1 * D + CPC2 * D * D
RETURN
END

REAL*8 FUNCTION CPCH(D)
IMPLICIT REAL*8(A-H,O-Z)
CPCHO = 0.36
CPCH1 = 6.9310-05
CPCH = CPCHO + CPCH1 * D
RETURN
END

C

SUBROUTINE RTBISOL(TET,X1,X2,XACC,XMID)
IMPLICIT REAL*8(A-H,O-Z)
EXTERNAL TET
PARAMETER (JMAX = 500)
CALL TET(X1,FX1)
CALL TET(X2,FX2)
IF(FX2*FX1 .GE. 0.0) PAUSE 'BRACKET ROOT IN RTBISOL'
DX=X2-X1
DO 200 J = 1, JMAX
   DX = DX * 0.5
   XMID = X1 + DX
   CALL TET(XMID,FMID)
   IF (FMID * FX1 .GT. 0.0) THEN
      X1 = XMID
      FX1 = FMID
   ELSE
      X2 = XMID
      FX2 = FMID
   ENDIF
   IF (DABS(DX) .LT. XACC) RETURN
CONTINUE
PAUSE 'TOO MANY BISECTIONS IN RTBISOL'
END

C------------------------------------------------
C
SUBROUTINE QCR(P,FUNT)
IMPLICIT REAL*8(A-H,O-Z)
COMMON /SOL/VOID1,EPS1,DLAMB1,EPSOUT,EPSOLD,FSHED,

1 EPSCRIT,VOID2,EPS2,DLAMB2,VOID3,EPS3,DLAMB3

FUNT=DLAMB1*(VOID1+P)**3+DLAMB2*(VOID2+P)**3+

1 DLAMB3*(VOID3+P)**3 + DLOG(1.0-EPSCRIT)/4.2

RETURN

END

C------------------------------------------------

SUBROUTINE PROF(LIE,ITER,RPIN,T,BETA)

IMPLICIT REAL*8(A-H,O-Z)

EXTERNAL SHOOT,STROBE,RTBISOL,EQN1,EQN2

COMMON /ARR/X(50),R(50),Y1(50),Y2(50)

COMMON /MISC/C,XLOW,AO,BO,XFAC,ACEN

COMMON /JW/JWARN

RSTART=R(LIE)

BO=R(50)

Y1BASE=BETA
ALPHAB=1.0D-04
ALPHAA=0.0
GRADO=0.0
CALL SHOOT(T,GRADO,ALPHAA,ALPHAB,Y1BASE,RSTART,LIE)
IF(Y1(1) .GE. 1.0D-10) RETURN
C
DO 201 J=1,10
DO 101 I=1,49
IF ((Y1(I).LT.1.0D-10) .AND. (Y1(I+1).GE.1.0D-10)) THEN
RSTART=R(I)
LIE=I
Y1BASE=BETA
ALPHAB=Y1(LIE+1)+1.0D-07
ALPHAA=0.0
GRADO=0.0
CALL SHOOT(T,GRADO,ALPHAA,ALPHAB,Y1BASE,RSTART,LIE)
IF(JWARN .NE. 100) RETURN
ENDIF
101 CONTINUE
201 CONTINUE
RETURN
END
SUBROUTINE SHOOT(T,GRADO,ALPHAA,ALPHAB,Y1BASE,RSTART,LIE)
IMPLICIT REAL*8(A-H,O-Z)
EXTERNAL STROBE,EQN1,EQN2,RTBISOL
COMMON /JW/JWARN

Y1INIT=ALPHAA
Y2INIT=GRADO
CALL STROBE(T,Y1INIT,Y2INIT,RSTART,LIE,ANS)
VOUTA=ANS

Y1INIT=ALPHAB
Y2INIT=GRADO
CALL STROBE(T,Y1INIT,Y2INIT,RSTART,LIE,ANS)
VOUTB=ANS

TOLR=0.0001
DO 100 J=1,100
JWARN=J
ALP=ALPHAA+(ALPHAB-ALPHAA)*(Y1BASE-VOUTA)/(VOUTB-VOUTA)
Y1INIT=ALP
Y2INIT=GRADO
CALL STROBE(T,Y1INIT,Y2INIT,RSTART,LIE,ANS)
VALOUT=ANS
IF(DABS((VALOUT-Y1BASE)/Y1BASE) .LT. TOLR) THEN
   GOTO 201
ELSEIF(VALOUT .GT. Y1BASE) THEN
   ALPHAB=ALP
   VOUTB=VALOUT
   GOTO 199
ELSEIF(VALOUT .LT. Y1BASE) THEN
   ALPHAA=ALP
   VOUTA=VALOUT
   GOTO 199
ENDIF
199 CONTINUE
100 CONTINUE
201 RETURN
END

C------------------------------------------------

SUBROUTINE STROBE(T,Y1INIT,Y2INIT,RSTART,LIE,SHOT)
IMPLICIT REAL*8(A-H,O-Z)
REAL*8 K11,K12,K13,K14,K21,K22,K23,K24
EXTERNAL RTBISOL,EQN1,EQN2
COMMON /ARR/X(50),R(50),Y1(50),Y2(50)
IF(RSTART .EQ. 0.0) THEN
  Y1(1) = Y1INIT
  Y2(1) = Y2INIT
  L = 2
ELSE
  DO 200 J = 1, LIE
  Y1(J) = 0.0
  Y2(J) = 0.0
  CONTINUE
  Y1(LIE+1) = Y1INIT
  Y2(LIE+1) = Y2INIT
  L = LIE + 2
END IF
DO 600 I = L, 50
  RINIT = R(I-1)
  Y1INIT = Y1(I-1)
  Y2INIT = Y2(I-1)
  H = R(I) - R(I-1)
C
Following is the old RUNGSOL routine now absorbed here.
C
XP = RINIT
DUM1 = Y1INIT
DUM2 = Y2INIT
CALL EQN1(DUM1, DUM2, DY1DT)
CALL EQN2(T, XP, DUM1, DUM2, DY2DT)
K11 = DY1DT
K21 = DY2DT
XP = XP + H/2.0
DUM1 = Y1INIT + K11*H/2.0
DUM2 = Y2INIT + K21*H/2.0
CALL EQN1(DUM1, DUM2, DY1DT)
CALL EQN2(T, XP, DUM1, DUM2, DY2DT)
K12 = DY1DT
K22 = DY2DT
DUM1 = Y1INIT + K12*H/2.0
DUM2 = Y2INIT + K22*H/2.0
CALL EQN1(DUM1, DUM2, DY1DT)
CALL EQN2(T, XP, DUM1, DUM2, DY2DT)
K13 = DY1DT
K23 = DY2DT
XP = XP + H/2.0
DUM1 = Y1INIT + K13*H
DUM2 = Y2INIT + K23*H
CALL EQN1(DUM1, DUM2, DY1DT)
CALL EQN2(T,XP,DUM1,DUM2,DY2DT)
K14 = DY1DT
K24 = DY2DT
ANS = Y1INIT + H*(K11 + 2.0*K12 + 2.0*K13 + K14)/6.0
ANSP = Y2INIT + H*(K21 + 2.0*K22 + 2.0*K23 + K24)/6.0

Y1(I)=ANS
Y2(I)=ANSP
CONTINUE
SHOT=Y1(50)
RETURN
END

DY1DT is in molfrac/micron.

SUBROUTINE EQN1(DUM1,DUM2,DY1DT)
IMPLICIT REAL*8(A-H,O-Z)
DY1DT = DUM2
RETURN
END
SUBROUTINE EQN2(T,XP,DUM1,DUM2,DY2DT)

IMPLICIT REAL*8(A-H,O-Z)

COMMON /MISC/C,XLOW,AO,BO,XFAC,ACEN

COMMON /SOL/VOID1,EPS1,DLAMB1,EPSOUT,EPSOLD,FSHED,

1

EPSCRIT,VOID2,EPS2,DLAMB2,VOID3,EPS3,DLAMB3

COMMON /QS/Q(4,50),DQDR(4,50),QINT,QBAR,QCRIT

COMMON /CS/CSTAR,TAU,XACC,SURFSUM

COMMON /R/RHOC,FRAC,RPINIT

COMMON /POW/POW

KL=INT(XP/QINT)+1

QBARL=Q(4,KL)+((XP-(KL-1)•QINT)/QINT)*(Q(4,KL+1)-Q(4,KL))

DQBARL=DQDR(4,KL)+((XP-(KL-1)•QINT)/QINT)*(DQDR(4,KL+1)-

1

DQDR(4,KL))

EPS=1.0-DEXP((-DLAMB1*4.2*(VOID1+QBARL)**3)+(-DLAMB2*4.2*

1

(VOID2+QBARL)**3)+(-DLAMB3*4.2*(VOID3+QBARL)**3))

SQ=(1.0-EPS)*12.6*(DLAMB1*(VOID1+QBARL)**2 +

1

DLAMB2*(VOID2+QBARL)**2 + DLAMB3*(VOID3+QBARL)**2)

FREQ=305.0

DIFF=3.13*(T/1500.0)**1.75
- 587 -

7810  \( E = \frac{\text{ACEN}}{1.98} \)

7820  \( \text{RHOG} = \frac{1.0}{(82.05 \times T)} \)

7830  \( C_1 = \text{T}\text{AU} \times \text{FREQ} \times \text{XFAC} / (24.0 \times \text{DIFF} \times \text{RHOG}) \)

7840  IF(XP .GT. CSTAR) THEN

7850  \( \text{DY2DT} = C_1 \times \text{DEXP}(-E/T) \times SQ \times 1D-04 \times \text{DUM1}**\text{POW}/\text{EPS} \)

7860  1  \( -2.0 \times \text{DUM2}/\text{XP} - SQ \times \text{DQBARL} \times \text{DUM2}/\text{EPS} \)

7870  ELSE

7880  \( \text{DY2DT} = C_1 \times \text{DEXP}(-E/T) \times SQ \times 1D-04 \times \text{DUM1}**\text{POW}/\text{EPS} \)

7890  1  \( -SQ \times \text{DQBARL} \times \text{DUM2}/\text{EPS} \)

7900  ENDIF

7910  RETURN

7920  END

7930  C

7940  C-----------------------------------------------

7950  C

7960  SUBROUTINE QUE(T,DELT,DRDT,ITER,FP)

7970  IMPLICIT REAL*8(A-H,O-Z)

7980  DIMENSION Y1BAR(50),Y2BAR(50)

7990  COMMON /ARR/X(50),R(50),Y1(50),Y2(50)

8000  COMMON /MISC/C,XLOW,AO,BO, XFAC,ACEN

8010  COMMON /SOL/VOID1,EPS1,DLAMB1,EPSOUT,EPSOLD,FSHED

8020  1  \( \text{EPSCRIT}, \text{VOID2}, \text{EPS2}, \text{DLAMB2}, \text{VOID3}, \text{EPS3}, \text{DLAMB3} \)

8030  COMMON /QS/Q(4,50),DQDR(4,50),QINT,QBAR,QCRIT
COMMON /R/RHOC,FRACT,RPINIT
COMMON /CS/CSTAR,TAU,XACC,SURFSUM
COMMON /AQ/AQ(50),ADQDR(50)
COMMON /POW/POW

FREQ=305.0
E=ACEN/1.98
C2=FREQ*XFAC/RHOC

RXN = C2*DEXP(-E/T)*1.0D04

Q's are in microns for the above expression of RXN.
The inner J-loop finds the position of Q(I) just below R(J). Y1BAR and Y2BAR are the interpolated values of mass fraction and its gradient at the fixed locations where Q's are calculated.

Y1BAR(1)=Y1(1)
Y2BAR(1)=Y2(1)

DO 300 I=2,50

DIST = QINT*(I-1)

DO 350 J=1,49

IF((R(J).LT.DIST).AND.(R(J+1).GE.DIST))THEN

Y1BAR(I)=Y1(J)+((DIST-R(J))/
8270 1 \((R(J+1)-R(J))\)*(Y1(J+1)-Y1(J))
8280 \(Y2_{BAR}(I)=Y2(J)+\left((DIST-R(J))\right)/\)
8290 1 \((R(J+1)-R(J))\)*(Y2(J+1)-Y2(J))
8300 ELSEIF (DIST .GT. R(50)) THEN
8310 \(Y1_{BAR}(I)=Y1(50)\)
8320 \(Y2_{BAR}(I)=Y2(50)\)
8330 ENDIF
8340 350 CONTINUE
8350 300 CONTINUE
8360 C
8370 IF(Y1BAR(1) .EQ. 0)THEN
8380 \(Q(ITER,1)=AQ(1)\)
8390 \(DQDR(ITER,1)=ADQDR(1)\)
8400 ELSE
8410 \(Q(ITER,1)=AQ(1)+\\DELTA*R*X*N*Y1_{BAR}(1)*^{POW}\)
8420 \(DQDR(ITER,1)=ADQDR(1)+\\DELTA*R*X*N*Y2_{BAR}(1)*^{POW}\)
8430 1 \(POW*Y1_{BAR}(1)^{POW}(POW-1.0)\)
8440 ENDIF
8450 C
8460 DO 310 I=2,50
8470 IF(Y1BAR(I) .EQ. 0)THEN
8480 \(Q(ITER,I)=AQ(I)\)
8490 \(DQDR(ITER,I)=ADQDR(I)\)
ELSE
Q(ITER, I) = AQ(I) + DELT*RXN*Y1BAR(I)**POW
DQDR(ITER, I) = ADQDR(I) + DELT*RXN*Y2BAR(I)*
     1 POW*Y1BAR(I)**(POW-1.0)
ENDIF
C
IF((Q(ITER, I).GE.QCRIT).AND.(Q(ITER, I-1).LT.QCRIT))THEN
    RCRIT = QINT*(I-2) + ((QCRIT-Q(ITER, I-1))/(Q(ITER, I) -
     1 Q(ITER, I-1)))*QINT
    DRDT = -1D-04*(R(60)-RCRIT)/DELT
    FLAG = 0.0
    GOTO 940
ENDIF
310 CONTINUE
C
KL = INT(R(60)/QINT)+1
IF(KL .EQ. 50) THEN
    QBAR = Q(ITER, 50)
    DQDRP = DQDR(ITER, 50)
ELSE
    QBAR = Q(ITER, KL)*((R(60)-(KL-1)*QINT)/QINT)*(Q(ITER, KL+1)
     1 - Q(ITER, KL))
    DQDRP = DQDR(ITER, KL)*((R(60)-(KL-1)*QINT)/QINT)*
Flux (FP) is calculated using mole fraction gradient at the surface Y2(50), diffusivity, and stoichiometric coefficient 24.0 [gm/cm^2-s]. The expression for diffusivity is from FIELD's book.
ELSE

KL=INT(R(50)/QINT)+1

QSUP=Q(ITER,KL)*((R(50)-(KL-1)*QINT)/QINT)*

1 (Q(ITER,KL+1)-Q(ITER,KL))

EPSSUP=1.0-DEXP((-4.2*DLAMB1*(VOID1+QSUP)**3)+

1 (-4.2*DLAMB2*(VOID2+QSUP)**3)+

2 (-4.2*DLAMB3*(VOID3+QSUP)**3))

EPSOUT=(EPSCRIT+EPSSUP)/2.0

ENDIF

C

SUM=0.0

VOLSUM=0.0

SURFSUM=0.0

KL=INT(R(50)/QINT)+1

DO 560 I=2,KL

QSH=Q(ITER,I)+Q(ITER,I-1))/2.0

AQSHEL=(AQ(I)+AQ(I-1))/2.0

EPSSH=1.0-DEXP((-4.2*DLAMB1*(VOID1+QSH)**3)+

1 (-4.2*DLAMB2*(VOID2+QSH)**3)+

2 (-4.2*DLAMB3*(VOID3+QSH)**3))

SQSHEL=(1.0-EPSSH)*12.6*(DLAMB1*(VOID1+QSH)**2

+DLAMB2*(VOID2+QSH)**2+DLAMB3*(VOID3+QSH)**2)

ROUT=QINT*(I-1)
RIN = QINT*(I-2)

FPSHELL = 4.2*(ROUT**3.0-RIN**3.0)*SQSHELL*

SURFSUM = SURFSUM + 4.2*(ROUT**3.0-RIN**3.0)*SQSHELL

SUM = SUM + FPSHELL

IF(QSHELL .LT. QCRT) THEN
  VOLSUM = VOLSUM + EPSSHELL*(4.2*(ROUT**3.0-RIN**3.0))
END IF

CONTINUE

QR50 = Q(ITER,KL)+0.6 *((R(50)-(KL-1)*QINT)/QINT)*

AQR50 = AQ(KL)+0.5 *((R(50)-(KL-1)*QINT)/QINT)*(AQ(KL+1)

EPSR50 = 1.0 - DEXP((-4.2*DLAMB1*(VOID1+QR50)**3)+

SQR50 = (1.0-EPSR50)*12.6*(DLAMB1*(VOID1+QR50)**2

FPQ50 = 4.2*(R(60)**3.0-(QINT*(KL-1))**3.0)*

VOLR50 = EPSR50*(R(60)**3.0-(QINT*(KL-1))**3.0)*4.2

SURFSUM = SURFSUM + SQR50*(R(50)**3.0-(QINT*(KL-1))**3.0)*4.2

EPSOLD = (VOLSUM+VOLR50)/(4.2*R(50)**3.0)
FP=(SUM+FPQ50)*RHOC*1.0D-04/(DELT*12.6*R(50)**2.0)
RETURN
END

C------------------------------------------------

SUBROUTINE GAMMA(GAM1,F,R1,STEP,PEMMIS,WEMMIS,RNEW,TNEW,
FP,SWIT)

IMPLICIT REAL*8(A-H,O-Z)
REAL*8 K11,K12,K13,K14,K21,K22,K23,K24
EXTERNAL EC,ECH,CPC,CPCH,RLAMB,EOX,ECO
EXTERNAL PROF,RADIUS,ENERGY,QUE,SHOOT
EXTERNAL STROBE,RTBISOL,EQN1,EQN2
COMMON T,TWALL
COMMON /MISC/C,XLOW,AO,BO,XFAC,ACEN
COMMON /ARR/X(60),R(50),Y1(50),Y2(60)
COMMON /SOL/VOID1,EPS1,DLAMB1,EPSCOUT,EPSOLD,FSHED,
EPSCRIT,VOID2,EPS2,DLAMB2,VOID3,EPS3,DLAMB3
COMMON /R/RHOC,FRAC,RPINIT
COMMON /CS/CSTAR,TAU,XACC,SURFSUM
COMMON /Y1/Y1S,Y1INF

CC = -3.0043D-05
C3 = (2331.5425 + GAM1)/0.3388749
Y1S=(Y1INF+4.0/3.0)*((T-C3)/(TWALL-C3))**0.8095478-4.0/3.0
C1SURF= (1.0/(-1.0/7.0 + 8.0/(7.0*Y1S)))
IF(C1SURF .LT. 0.0)THEN
   F=1.0
   RETURN
ENDIF

RUNG merged here.

LIE=1
IF(SWIT .EQ. 0.0)THEN
   ITER=4
   CALL PROF(LIE,ITER,R1,T,C1SURF)
   DIFF=3.13*(T/1500)**1.75
   FP=1.0D0*Y2(50)*DIFF*EPSOUT*24.0/(TAU*82.05*T)
   GO TO 111
ENDIF

DUM1=R1
DUM2=T
ITER=4
CALL PROF(LIE,ITER,DUM1,DUM2,C1SURF)
CALL RADIUS(STEP,DUM2,ITER,DRDT,FP)
EP = FP * GAM1

CALL ENERGY(EP, PEMMIS, WEMMIS, DUM1, DUM2, DTDT)

K11 = DRDT

K21 = DTDT

RNEW = R1 + STEP * K11

TNEW = T + STEP * K21

C

C

111 IF (T .LT. TWALL) THEN

HH = DSQRT(DABS(-2331.5425 - GAM1)/0.3388749)

IF (GAM1 .GT. -2331.6426) THEN

AR1 = -1.0 * CC * ((DSQRT(TWALL) - DSQRT(T)) + HH/2.0 * DLOG((DSQRT(TWALL) - HH)*(DSQRT(T) + HH)/(DSQRT(TWALL) + HH)*(DSQRT(T) - HH))))

F = AR1 - R1 * FP

ELSE

AR2 = -1.0 * CC * ((DSQRT(TWALL) - DSQRT(T)) - HH* (DATAN(DSQRT(TWALL)/HH) - DATAN(DSQRT(T)/HH)))

F = AR2 - R1 * FP

ENDIF

ELSE

FF = DSQRT(DABS(2331.5425 + GAM1)/0.3388749)

IF (GAM1 .LT. -2331.5425) THEN
AR3 = CC*(((DSQRT(T)-DSQRT(TWALL))-FF)*
          (DATAN(DSQRT(T)/FF)-DATAN(DSQRT(TWALL)/FF)))

F = AR3-R1* FP

ELSE

AR4 = CC * ((DSQRT(T) - DSQRT(TWALL)) + FF/2.0 *
          1 (DLOG((DSQRT(T) - FF)*(DSQRT(TWALL) + FF)/
          2 ((DSQRT(T) + FF)*(DSQRT(TWALL) - FF))))

F = AR4-R1* FP

ENDIF

ENDIF

RETURN

END

SUBROUTINE ENERGY(EP,PEMMIS,WEMMIS,RR,DUM2,ANST)
IMPLICIT REAL*8(A-H,O-Z)
EXTERNAL EC,ECH,CPC,CPCH,RLAMB,EOX,ECO

COMMON T,TWALL

COMMON /R/RHOC,FRAC,RPINIT

COMMON /SOL/VOID1,EPS1,DLAMB1,EPSOUT,EPSOLD,FSHED,

1 EPSCRIT,VOID2,EPS2,DLAMB2,VOID3,EPS3,DLAMB3

C
SIG = 1.595D-12

IF (DUM2 .LT. 1350) THEN
  CPSOL = CPC(DUM2)
  VAL = EC(DUM2)
ELSE
  CPSOL = CPCH(DUM2)
  VAL = ECH(DUM2)
ENDIF

ANST = (3.0/(1.0-EPSOLD))*(FP+(1.0-FRAC)*FSHED)*VAL-EP-SIG*
  1 (PEMMIS*DUM2**4-WEMMIS*TWALL**4))/(RR*RHOC*CPSOL)
RETURN
END

SUBROUTINE RADIUS(TMSTP,DUM2,ITER,ANS,FP)
IMPLICIT REAL*8(A-H,O-Z)
EXTERNAL QUE
C
CALL QUE(DUM2,TMSTP,DRDT,ITER,FP)
ANS=DRDT
RETURN
END
This program describes the growth of the internal structure of a char particle containing polydisperse spherical voids randomly distributed in it. It is a phenomenological model and does not consider actual effects of chemical kinetics, temperature and diffusion. Instead it simulates the burning of the char particle. The focus is on how the pores grow, coalesce etc; ultimately fragmenting the particle at high conversions.

The voids are randomly distributed in the particle. Their sizes are also randomly selected. Once the void centers fixed, they remain unchanged. Only void size can grow by reaction. Clearly, due to the random placement, voids may intersect each other and might have access to the outside. Two voids intersect if the sum of their radii is less than their center separation. Similarly, a void is connected to the outside if its center lies closer to the particle surface than its radius.

Reaction is simulated by allowing those voids that are either directly or indirectly (via other voids) connected
to the outside to grow a certain amount in each time step. The external surface is also assumed to reduce in each time step. In this program diffusion is not taken into account and thus voids grow the same amount no matter where they are present as long as they have access to the outside. However, diffusion can be simulated by allowing the growth parameter to be a function of radius.

Thus, after many time steps, the particle void fraction will reach large values and the particle may fragment. The user sets both the growth parameter and the number of time steps.

This discrete model keeps track of the connectivity of individual voids. It computes the void fraction at each time step and calculates conversion. Other parameters of interest are the number fraction of voids connected to the outside, and the number fraction of voids in the largest void cluster.

---------------------------

Declarations.
PARAMETER (ND1=430,NDIM=1290,ID1=3200,IDIM=9600,NCON=151)

PARAMETER (ND=220,ID=2000,NDEL=50)

REAL RVX(ND1),RVY(ND1),RVZ(ND1),RVA(ND1)

REAL RPX(ID1),RPY(ID1),RPZ(ID1)

REAL C(ND1,3),VC(ND,3),RS,VS,DIST1,RC

REAL DIST2,Q,IN,OUT,PC1(ID1,3),PC(ID,3)

REAL Q1,Q2,COUNTIN,COUNTOUT,RCOUNTOUT,RTOTAL,RTOT

REAL DIST,RSO,VDIAO,QCONV,CCOUNT,VOID(ND),XLARGE

REAL VDIA(ND),VDIAM(ND1),VOIDF(NCON),CONV(NCON)

REAL SUMX,SUMY,SUMZ,SUMM,SUMR,RADGY,USED(ID)

REAL CMASSX,CMASSY,CMASSZ,DCON(NCON)

REAL CF,RLN,QLN,Q3,RNDEL

REAL RTO(NDEL),RSOLID(NDEL),RBIG(NDEL)

REAL RSMALL(NDEL),RMEAN(NDEL),RRATIO(NDEL)

INTEGER ICON(ND,ND),ICLUSTER,IDCON(1,ND),MOUT,NOUT

INTEGER MAT(ND,ND),IMAP(1,ND),LICLU
REAL*8 DSEED1,DSEED2,DSEED3,DSEED4,DSEED5,DSEED6
REAL*8 DSEED7

OPEN(9,FILE='FOR.DAT',STATUS='NEW')
OPEN(8,FILE='MOD.DAT',STATUS='NEW')
OPEN(7,FILE='RAD.DAT',STATUS='NEW')

WRITE(*,89)
FORMAT(3X,'ENTER THE VALUES OF DSEEDS 1-6 like xxxx.DX')
READ(*,*)DSEED1,DSEED2,DSEED3,DSEED4,DSEED5,DSEED6

WRITE(*,88)
FORMAT(3X,'ENTER THE VALUE OF DSEED7')
READ(*,*)DSEED7

RS0=25.0
VDIA0=5.0
QCONV=0.05
VS=VDIA0-2.0*QCONV
RC=RS0+VDIA0/2.0
RS=25.0+QCONV

C
Random number generation for void centers. Separate strings for x, y and z coordinates.

\[ \begin{align*}
I_1 &= N_{D1} \\
I_2 &= N_{DIM} \\
\text{CALL GGUBS(DSEED1,ND1,RVX)} \\
\text{CALL GGUBS(DSEED2,ND1,RVY)} \\
\text{CALL GGUBS(DSEED3,ND1,RVZ)}
\end{align*} \]

Creating the void centers in the cube.

\[ \begin{align*}
\text{DO 200 J=1,ND1} \\
C(J,1) &= \text{RVX}(J) \times R_C \times 2.0 \\
C(J,2) &= \text{RVY}(J) \times R_C \times 2.0 \\
C(J,3) &= \text{RVZ}(J) \times R_C \times 2.0
\end{align*} \]

Random number generation for probe points.

\[ \begin{align*}
I_3 &= I_{D1} \\
I_4 &= I_{DIM} \\
\text{CALL GGUBS(DSEED4,ID1,RPX)} \\
\text{CALL GGUBS(DSEED5,ID1,RPY)}
\end{align*} \]
CALL GGUBS(DSEED6,ID1,RPZ)

Creating probe centers in the cube.

DO 700 J1=1,ID1
   PC1(J1,1)=RPX(J1)*RSO*2.0+VDIA0/2.0
   PC1(J1,2)=RPY(J1)*RSO*2.0+VDIA0/2.0
   PC1(J1,3)=RPZ(J1)*RSO*2.0+VDIA0/2.0
700 CONTINUE

Setting the initial diameters of the voids.

CALL GGUBS(DSEED7,ND1,RVA)

DO 91 I31=1,II
   VDIAM(I31)=VDIA0*RVA(I31)
91 CONTINUE

Ordering the void centers in the sphere. Since this does not change, this part is outside the main loop.

OUT=0.0
IN=0.0
INC=0
INC1=0

DO 300 J10=1,I1

Q=SQRT((C(J10,1)-RC)**2+(C(J10,2)-RC)**2+
1 (C(J10,3)-RC)**2)

IF(Q.GT.(VDIAM(J10)/2.0+RS))THEN
OUT=OUT+1
ELSE
IN=IN+1
INC=INC+1
INC1=INC1+1
VC(INC,1)=C(J10,1)
VC(INC,2)=C(J10,2)
VC(INC,3)=C(J10,3)
VDIA(INC)=VDIAM(J10)
ENDIF

300 CONTINUE

WRITE (*,11)INC
11 FORMAT(10X,I4)

C Ordering the probe centers in the original sphere.
C
DO 334 M1=1,ID
USED(M1)=0.0
IPIN = 0
IPIN1 = 0
DO 800 J9 = 1, ID1
Q1 = SQRT((PC1(J9,1) - RC)**2 + (PC1(J9,2) - RC)**2 +
          (PC1(J9,3) - RC)**2)
IF(Q1 .LE. RSO) THEN
   IPIN = IPIN + 1
   IPIN1 = IPIN1 + 1
   PC(IPIN,1) = PC1(J9,1)
   PC(IPIN,2) = PC1(J9,2)
   PC(IPIN,3) = PC1(J9,3)
ELSE
   CONTINUE
ENDIF
800 CONTINUE

C Initialisation.
C
DO 333 M = 1, NCON
VOIDF(M) = 0.0
CONV(M) = 0.0
333 CONTINUE
Main loop starts here.

DO 5000 I17=1,NCON
RS=RS-QCONV
VS=VS+2.0*QCONV
DO 801 J9=1,IPIN
Q2=SQRT((PC(J9,1)-RC)**2+(PC(J9,2)-RC)**2+(PC(J9,3)-RC)**2)
IF(Q2 .GT. RS)THEN
USED(J9)=1.0
IPIN1=IPIN1-1
ELSE
CONTINUE
END IF
801 CONTINUE

Initialization for connectivity matrix.

DO 2000 JCON=1,INC
DO 2000 KCON=1,INC
IF(JCON .EQ. KCON)THEN
ICON(JCON,KCON)=1
ELSE
ICON(JCON,KCON)=0
ENDIF
2090 2000 CONTINUE
2100 WRITE(*,12)INC
2110 12 FORMAT(10X,I4)
2120 C
2130 C  Internal connectivity calculation.
2140 C
2150 DO 3000 JCON=1,INC
2160 DO 3000 KCON=1,INC
2170 DIST1=SQRT((VC(JCON,1)-VC(KCON,1))**2+
2180  1  (VC(JCON,2)-VC(KCON,2))**2
2190  2  +(VC(JCON,3)-VC(KCON,3))**2)
2200 IF(DIST1 .LT. (VDIA(JCON)+VDIA(KCON))/2.0)THEN
2210 ICON(JCON,KCON)=1
2220 ELSE
2230 CONTINUE
2240 ENDIF
2250 3000 CONTINUE
2260 C
2270 C  External connectivity calculation.
2280 C
IN3=INC+1
DO 4000 JCON=1,INC
   DIST2=SQRT((VC(JCON,1)-RC)**2+(VC(JCON,2)-RC)**2 + (VC(JCON,3)-RC)**2)
   IF(ABS(RS-DIST2) .LT. VDIA(JCON)/2.0) THEN
      ICON(JCON,IN3)=1
   ELSE
      ICON(JCON,IN3)=0
   ENDIF
4000 CONTINUE
C
Initializing the diagonal of the connectivity matrix ICON.
DO 400 JCON=1,INC
   ICON(JCON,JCON)=0
400 CONTINUE
C
Writing to screen.
WRITE(*,998)RS,VS
998 FORMAT(5X,'RS=',1PE10.3,6X,'VS=',1PE10.3/)
C
Calculating connected clusters and those connected to
the outside. Results in MAT(ICLUSTER,KCON).

DO 70 JCON=1,INC
   IF((ICON(JCON,JCON).EQ.0).AND.(IDCON(1,KCON).EQ.1))THEN
      DO 80 KCON1=1,INC
         IF((IDCON(1,KCON1).EQ.1).OR.(ICON(KCON,KCON1) .EQ. 1))THEN
            IDCON(1,KCON1)=1
         ELSE
            IDCON(1,KCON1)=0
         END IF
   ELSE
      IDCON(1,KCON1)=0
   ENDIF
CONTINUE

ICON(KCON,KCON)=ICLUSTER

MAT(ICLUSTER,KCON)=1

IF(ICON(KCON,IN3) .EQ. 1) THEN
    MAT(ICLUSTER,IN3)=1
    MOUT=1
ELSE
    MOUT=0
ENDIF

IF(KCON .NE. JCON) THEN
    WRITE(*,1) ICLUSTER,KCON,MOUT
ELSE
    CONTINUE
ENDIF
GOTO 10
ELSE
    CONTINUE
ENDIF
GOTO 10

CONTINUE

ICON(JCON,JCON)=ICLUSTER

MAT(ICLUSTER,JCON)=1

IF(ICON(JCON,IN3) .EQ. 1) THEN
    MAT(ICLUSTER,IN3)=1
Calculating the number of clusters, number of clusters connected to the outside, number of voids in the largest cluster, number of voids connected to the outside.

XLARGE=0.0
LICLU=0
KOUNT=0

DO 705 ICLU=2,ICLUSTER
    IF(MAT(ICLU,IN3) .EQ. 1) THEN
        DO 710 KCON=1,INC
            IF(MAT(ICLU,KCON) .EQ. 1) THEN
                KOUNT=KOUNT+1
            ELSE
3210          CONTINUE
3220          ENDIF
3230          CONTINUE
3240          ELSE
3250          CONTINUE
3260          ENDIF
3270          CONTINUE
3280          KOUNT1=KOUNT
3290          DO 36 ICLU=2,ICLUSTER
3300          VOID(ICLU)=0.0
3310          CONTINUE
3320          ICLUSTER1=ICLUSTER-1
3330          CCOUNT=1.0
3340          DO 37 ICLU=2,ICLUSTER
3350          IF(MAT(ICLU,IN3) .EQ. 1)THEN
3360          CCOUNT=CCOUNT+1.0
3370          ELSE
3380          CONTINUE
3390          ENDIF
3400          DO 38 KCON=1,INC
3410          IF(MAT(ICLU,KCON) .EQ. 1)THEN
3420          VOID(ICLU)=VOID(ICLU)+1.0
3430          ELSE
3440       CONTINUE
3450       ENDIF
3460 38    CONTINUE
3470 IF(VOID(ICLU) .GT. XLARGE) THEN
3480     XLARGE=VOID(ICLU)
3490     LICLU=ICLU
3500 ELSE
3510      CONTINUE
3520      ENDIF
3530 37    CONTINUE
3540     XLN= ALOG(XLARGE)
3550 C
3560 C
3570 C
3580     CMASSX=0.0
3590     CMASSY=0.0
3600     CMASSZ=0.0
3610     RADGY=0.0
3620 DO 49 KCON=1,ND
3630     IMAP(1,KCON)=0
3640 49    CONTINUE
3650 DO 51 KCON=1,INC
3660     IMAP(1,KCON)=MAT(LICLU,KCON)
Calculating the center of mass of the largest cluster.

```
51 CONTINUE

C

Calculating the center of mass of the largest cluster.

C

SUMX=0.0
SUMY=0.0
SUMZ=0.0
SUMM=0.0

DO 52 KCON=1,INC

IF(IMAP(1,KCON) .EQ. 1) THEN
  SUMX=SUMX+((VDIA(KCON)**3)*VC(KCON,1)
  SUMY=SUMY+((VDIA(KCON)**3)*VC(KCON,2)
  SUMZ=SUMZ+((VDIA(KCON)**3)*VC(KCON,3)
  SUMM=SUMM+VDIA(KCON)**3
ELSE
  CONTINUE
ENDIF

52 CONTINUE

CMASSX=SUMX/SUMM
CMASSY=SUMY/SUMM
CMASSZ=SUMZ/SUMM

C

Finding the radius of gyration of the largest cluster.
```
3900 C
3910 SUMR=0.0
3920 DO 53 KCON=1,INC
3930 IF(IMAP(1,KCON) .EQ. 1) THEN
3940 SUMR=SUMR+(((VC(KCON,1)-CMASSX)**2)+
3950 1 ((VC(KCON,2)-CMASSY)**2)+
3960 2 +((VC(KCON,3)-CMASSZ)**2))*(VDIA(KCON)**3)
3970 ELSE
3980 CONTINUE
3990 ENDIF
4000 53 CONTINUE
4010 RADGY=SQRT(SUMR/SUMM)
4020 RLN=ALOG(RADGY)
4030 C
4040 C Writing to file.
4050 C
4060 WRITE(9,1007)ICLUSTER1,CCOUNT,XLARGE,RADGY,KOUNT1,SUMM
4070 1007 FORMAT(5X,'NO. OF CLUSTERS=',I5/
4080 1 5X,'NO. OF CLUSTERS CONNECTED TO THE OUTSIDE=',E10.4/
4090 2 5X,'NO. OF VOIDS IN THE LARGEST CLUSTER=',E10.4/
4100 3 5X,'RADIUS OF GYRATION OF THE LARGEST CLUSTER=',E10.4/
4110 4 5X,'NO. OF VOIDS CONNECTED TO THE OUTSIDE=',I5/
4120 5 5X,'NONOVERLAP VOL. OF THE LARGEST CLUSTER=',E10.4)
Finding the probe points that are outside all the voids.

DO 61 I=1,NDEL

RSOLID(I)=0.0
RTO(I)=0.0
RMEAN(I)=0.0

61 CONTINUE

RNDEL=NDEL

DO 62 IP=1,IPIN

DO 63 I=1,NDEL

RBIG(I)=RS-((I-1)*RS/RNDEL)
RSMALL(I)=RS-(I*RS/RNDEL)
RMEAN(I)=(RBIG(I)+RSMALL(I))/2.0

Q3=SQRT((PC(IP,1)-RC)**2+(PC(IP,2)-RC)**2+

(Q3.LE.RBIG(I)).AND.(Q3.GT.RSMALL(I)))THEN

IF((Q3.LE.RBIG(I)).AND.(Q3.GT.RSMALL(I)))THEN

RTO(I)=RTO(I)+1.0

ELSE

ENDIF
CONTINUE

ENDIF

ELSE

CONTINUE

ENDIF

CONTINUE

CONTINUE

COUNTIN=0.0

COUNTOUT=0.0

RCOUNTOUT=0.0

RTOTAL=IPIN1

RTOT=INC1

DO 900 IP=1,IPIN

IF(USED(IP) .EQ. 0.0)THEN

DO 90 I=1,NDEL

Q3=SQRT((PC(IP,1)-RC)**2+(PC(IP,2)-RC)**2+

1

(PC(IP,3)-RC)**2)

IF((Q3.LE.RBIG(I)).AND.

1

(Q3.GT.RSMALL(I)))THEN

DO 13 MC=1,INC

DIST=SQRT((VC(MC,1)-PC(IP,1))**2+

1

(VC(MC,2)-PC(IP,2))**2+

2

(VC(MC,3)-PC(IP,3))**2)
IF(DIST .GE. VDIA(MC)/2.0) THEN
  COUNTOUT = COUNTOUT + 1.0
ELSE
  COUNTIN = COUNTIN + 1.0
  USED(IP) = 1.0
ENDIF

WRITE(*,*) COUNTOUT, COUNTIN
IF(COUNTIN .EQ. 0) THEN
  ELSE
    RSOLID(I) = RSOLID(I) + 1.0
  ELSE
    CONTINUE
  ENDIF
ELSE
  CONTINUE
ENDIF

CONTINUE
COUNTOUT = 0.0
CONTINUE
COUNTIN = 0.0

ELSE
  CONTINUE
ENDIF

CONTINUE
RCOUNTOUT=0.0
I16=I17-1
DO 92 I=1,NDEL
   RCOUNTOUT=RCOUNTOUT+RSOLID(I)
   IF(RTO(I) .NE. 0.0) THEN
      RRATIO(I)=RSOLID(I)/RTO(I)
   ELSE
      RRATIO(I)=1.0
   ENDIF
   IF((I16 .EQ. 0) .OR. (I16 .GE. 10)) THEN
      IF(MOD(I16,10).EQ.0) THEN
         WRITE(7,93) RMEAN(I), RRATIO(I)
         FORMAT(5X,E10.4,5X,E10.4)
      ELSE
         CONTINUE
      ENDIF
   ELSE
      CONTINUE
   ENDIF
92 CONTINUE
WRITE(*,*) RCOUNTOUT, RTO, RTOTAL
CF=XLARGE/RTOT
Calculate and write void fraction and conversion.

I12 = I17 - 5

VOIDF(I17) = 1.0 - (RCOUNTOUT/RTOTAL)

CONV(I17) = 1.0 - ((1.0 - VOIDF(I17)) / (1.0 - VOIDF(1))) * ((RS/RSO)**3)

IF(I16 .GE. 5) THEN
    DCON(I17) = CONV(I17) - CONV(I12)
ELSE
    DCON(I17) = 0.0
ENDIF

WRITE(9,1111)I16

1111 FORMAT(5X,'STEP='I5/)  
WRITE(9,1002)RS,VS,VOIDF(I17),INC1,

1 IPIN1,ND,CONV(I17),DCON(I17)

1002 FORMAT(5X,'RS=',E10.4,2X,'VS=',E10.4,2X,'VOIDF=',E10.4,

5X,'INC1=',I5,2X,'IPIN1=',I5,2X,'ND=',I5/

5X,'CONVERSION=',E10.4,2X,'DELTA CONVER=',E10.4///)

WRITE(8,444)I16,VOIDF(I17),CONV(I17),

444 FORMAT(1X,I4,1X,E9.4,1X,E9.4,1X,E9.4,1X,E9.4,1X,E9.4)

C
Increasing void diameters if they are connected to the outside.

```
5310       DO 905 ICLU=2,ICLUSTER
5320          IF((MAT(ICLU,IN3) .EQ. 1))THEN
5330             DO 910 KCON=1,INC1
5340                IF((MAT(ICLU,KCON) .EQ. 1))THEN
5350                   VDIA(KCON)=VDIA(KCON)+2.0*QCONV
5360                ELSE
5370                   CONTINUE
5380             ENDIF
5390       910       CONTINUE
5400          ELSE
5410       CONTINUE
5420       ENDIF
5430       905       CONTINUE
5440       IPIN1=IPIN
5450       5000       CONTINUE
5460 C
5470 C       Main loop ends.
5480 C
5490       STOP
5500       CLOSE(7)
```
5510   CLOSE(8)
5520   CLOSE(9)
5530   END
Appendix X

TGA EXPERIMENTAL CONDITIONS
This Appendix shows the details of the experimental conditions for the different sets of TGA experiments that were done. All the chars used were derived from PSOC 1451 coal. Experiments done on other chars are not reported in this thesis.

Table AX.6 shows the organization of a typical data file after the raw data have been converted to suitable form. Time, in seconds, is shown in column 1. Data points were collected every six seconds by a computerized data acquisition system. Column 2 shows the normalized carbon mass of the sample. The normalizing factor is the carbon mass at the moment the oxidizer reaches the sample. Column 3 shows the rate of loss of carbon normalized by the instantaneous carbon mass. Sample temperature, as recorded by a thermocouple is shown in column 4. Finally, the carbon conversion is shown in the last column. Since all samples were burned until there was no further weight loss, the final mass was taken to be the mass of ash.

Table AX.1 shows two sets of similar experiments done at TGA temperatures of 800K and 1100K. In each set, two char sizes (45-53μm and 90-104μm) were used. Finally, four different pyrolysis temperatures (1000K, 1200K, 1400K, and 1600K) were used for each size and TGA temperature. The parent coal was also used. In all experiments, the total flow rate (110 cc/min) and oxygen concentration (17%) was kept constant. All chars used for experiments in Table AX.1 were made from parent coal of size 53-90μm. The experiments in Table AX.2 were exactly like those in Table AX.1, the only difference being the parent coal size. The effect of initial mass was investigated in the runs shown in Table AX.3. The behaviour of chars made from large size coal particles was investigated in the runs reported
in Table AX.4. Finally, Table AX.5 shows experiments in which only the oxygen concentration was varied.
<table>
<thead>
<tr>
<th>RUN NAME</th>
<th>COAL SIZE</th>
<th>CHAR SIZE</th>
<th>PYROLYSIS TEMPERATURE</th>
<th>OXYGEN CONCENTRATION</th>
<th>INITIAL MASS</th>
<th>TGA TEMPERATURE</th>
<th>COMMENTS</th>
<th>TGA TEMPERATURE</th>
<th>COMMENTS</th>
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<td>17</td>
<td>13.403</td>
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<td>13.403</td>
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<td>104-125</td>
<td>1600</td>
<td>17</td>
<td>13.403</td>
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<td>1600</td>
<td>17</td>
<td>13.403</td>
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<td>104-125</td>
<td>1600</td>
<td>17</td>
<td>13.403</td>
<td>1100</td>
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<td>CAN34.DAT</td>
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<td>13.403</td>
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<td>1100</td>
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Table AX.1 TGA runs on chars from PSOC 1451 53-90µm coal.
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<th>RUN NAME</th>
<th>COAL SIZE</th>
<th>CHAR SIZE</th>
<th>PYROLYSIS TEMPERATURE</th>
<th>OXYGEN CONCENTRATION</th>
<th>INITIAL MASS</th>
<th>TGA TEMPERATURE</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAN1.DAT</td>
<td>L.T. 45</td>
<td>45-53</td>
<td>1600</td>
<td>17</td>
<td>6.543</td>
<td>1100</td>
<td>(In all runs the total flow rate was 110 cc/min)</td>
</tr>
<tr>
<td>DAN2.DAT</td>
<td>L.T. 45</td>
<td>45-53</td>
<td>1400</td>
<td>17</td>
<td>5.078</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DAN3.DAT</td>
<td></td>
<td></td>
<td>1200</td>
<td>17</td>
<td>5.176</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DAN4.DAT</td>
<td></td>
<td></td>
<td>1000</td>
<td>17</td>
<td>5.884</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DAN5.DAT</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>DAN11.DAT</td>
<td>L.T. 45</td>
<td>104-125</td>
<td>1600</td>
<td>17</td>
<td>10.742</td>
<td>1100</td>
<td>(Total flow rate = 110 cc/min)</td>
</tr>
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<td>DAN12.DAT</td>
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<td>17</td>
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<td>17</td>
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<td>DAN15.DAT</td>
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<td>DAN21.DAT</td>
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<td>45-53</td>
<td>1600</td>
<td>17</td>
<td>5.542</td>
<td>800</td>
<td>(Total flow rate = 110 cc/min)</td>
</tr>
<tr>
<td>DAN22.DAT</td>
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<td>1400</td>
<td>17</td>
<td>5.762</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DAN23.DAT</td>
<td></td>
<td></td>
<td>1200</td>
<td>17</td>
<td>5.151</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DAN24.DAT</td>
<td></td>
<td></td>
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<td>17</td>
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<tr>
<td>DAN25.DAT</td>
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</tr>
<tr>
<td>DAN31.DAT</td>
<td>L.T. 45</td>
<td>104-125</td>
<td>1600</td>
<td>17</td>
<td>5.347</td>
<td>800</td>
<td>(Total flow rate = 110 cc/min)</td>
</tr>
<tr>
<td>DAN32.DAT</td>
<td></td>
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<td>1400</td>
<td>17</td>
<td>5.151</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DAN33.DAT</td>
<td></td>
<td></td>
<td>1200</td>
<td>17</td>
<td>4.785</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DAN34.DAT</td>
<td></td>
<td></td>
<td>1000</td>
<td>17</td>
<td>4.712</td>
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<td></td>
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<td>DAN35.DAT</td>
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Table AX.2 TGA runs on chars from PSOC 1451 <45µm coal.
<table>
<thead>
<tr>
<th>RUN NAME</th>
<th>COAL SIZE</th>
<th>CHAR SIZE</th>
<th>PYROLYSIS TEMPERATURE</th>
<th>OXYGEN CONCENTRATION</th>
<th>INITIAL MASS</th>
<th>TGA TEMPERATURE</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAN1.DAT</td>
<td>90-125</td>
<td>125-147</td>
<td>1600</td>
<td>17</td>
<td>5.762</td>
<td>1100</td>
<td>(In all runs the total flow rate was 110cc/min)</td>
</tr>
<tr>
<td>MAN2.DAT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAN3.DAT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAN4.DAT</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAN5.DAT</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<td>MAN6.DAT</td>
<td></td>
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</tr>
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</table>

Table AX.3 Effect of initial sample mass on TGA runs.

<table>
<thead>
<tr>
<th>RUN NAME</th>
<th>COAL SIZE</th>
<th>CHAR SIZE</th>
<th>PYROLYSIS TEMPERATURE</th>
<th>OXYGEN CONCENTRATION</th>
<th>INITIAL MASS</th>
<th>TGA TEMPERATURE</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAN1.DAT</td>
<td>90-125</td>
<td>L.T. 53</td>
<td>1600</td>
<td>17</td>
<td>5.078</td>
<td>1100</td>
<td>(Flow rate=110cc/min)</td>
</tr>
<tr>
<td>FAN11.DAT</td>
<td>125-147</td>
<td></td>
<td></td>
<td></td>
<td>5.371</td>
<td>800</td>
<td>(Flow rate=110cc/min)</td>
</tr>
<tr>
<td>FAN21.DAT</td>
<td>90-125</td>
<td>L.T. 53</td>
<td>1600</td>
<td>17</td>
<td>5.762</td>
<td>1100</td>
<td>=MAN1.DAT</td>
</tr>
<tr>
<td>FAN31.DAT</td>
<td>125-147</td>
<td></td>
<td></td>
<td></td>
<td>5.029</td>
<td>800</td>
<td></td>
</tr>
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</table>

Table AX.4 Effect of char size and TGA temperature.
<table>
<thead>
<tr>
<th>RUN NAME</th>
<th>COAL SIZE (µm)</th>
<th>CHAR SIZE (µm)</th>
<th>PYROLYSIS TEMPERATURE (K)</th>
<th>OXYGEN CONCENTRATION (%)</th>
<th>INITIAL MASS (mg)</th>
<th>TGA TEMPERATURE (K)</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAN1.DAT</td>
<td>90-125</td>
<td>125-147</td>
<td>1600</td>
<td>21.0</td>
<td>4.883</td>
<td>1100</td>
<td>(Total flow rate = 110 cc/min) = MAN1.DAT</td>
</tr>
<tr>
<td>GAN2.DAT</td>
<td>125</td>
<td>175</td>
<td>1600</td>
<td>19.1</td>
<td>4.980</td>
<td>1100</td>
<td></td>
</tr>
<tr>
<td>GAN3.DAT</td>
<td>150-200</td>
<td>125</td>
<td>1600</td>
<td>17.0</td>
<td>5.762</td>
<td>1100</td>
<td></td>
</tr>
<tr>
<td>GAN4.DAT</td>
<td>150</td>
<td>150</td>
<td>1600</td>
<td>15.3</td>
<td>5.273</td>
<td>1100</td>
<td></td>
</tr>
<tr>
<td>GAN5.DAT</td>
<td>150</td>
<td>150</td>
<td>1600</td>
<td>11.5</td>
<td>5.200</td>
<td>1100</td>
<td></td>
</tr>
<tr>
<td>GAN6.DAT</td>
<td>50-75</td>
<td>100</td>
<td>1600</td>
<td>0.7</td>
<td>4.980</td>
<td>1100</td>
<td></td>
</tr>
<tr>
<td>GAN7.DAT</td>
<td>80-120</td>
<td>125</td>
<td>1600</td>
<td>81.9</td>
<td>5.176</td>
<td>1100</td>
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<td>GAN8.DAT</td>
<td>125-150</td>
<td>150</td>
<td>1600</td>
<td>45.5</td>
<td>5.249</td>
<td>1100</td>
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Table AX.5 Effect of oxygen concentration on TGA runs.

<table>
<thead>
<tr>
<th>TIME (s)</th>
<th>$\frac{M_e}{M_{e,i}}$</th>
<th>$\frac{1}{M_e} \frac{dM_e}{dt}$</th>
<th>SAMPLE TEMPERATURE (K)</th>
<th>CARBON CONVERSION (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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</tr>
</tbody>
</table>

Table AX.6 Data file format for TGA experiments.
Appendix XI

DETAILS OF

CENOSPHERE SIMULATION RUNS
The initial conditions of all the simulation runs are shown in Tables in this Appendix. The Figures that follow show the variation of the void percolation probability (P) as a function of particle void fraction (ε) for the different cases.

The structure of the primary data file (MODrunname.DAT) produced by each simulation run is shown in Table AXI.1. Number of steps, void fraction, conversion and the rate of change of conversion are shown in columns 1-4, respectively. Column 5 shows the void percolation probability. The total number of voids connected to the outside of the particle, KOUNT1, is shown in the next column. Column 7 is the natural logarithm of the radius of gyration of the largest void cluster (RLN) and the last column is the natural logarithm of the number of voids in that cluster (XLN).

Tables AXI.2 and AXI.3 show the five main sets of simulations that were done. The initial number of voids in each case was kept reasonably similar and varied from set to set. In these runs the void size initially was monodisperse. Due to the random nature of the void placement process, particles having the same number of initial voids often have different initial void fractions. Table AXI.4 shows runs in which the size of the initial voids was randomly selected in the range 0-5 units while Table AXI.5 shows the runs where the initial size of the void was either 1 or 5 units, subject to the constraint that 90% of the voids be of the smaller size.

The effect of an assumed diffusion mechanism was tested in the runs shown in Table AXI.6. In each of the relevant Tables, the parent Fortran program name is also shown. A listing of one of the programs (CENMODE21.FOR) is given in
Appendix IX. The other programs are similar.
### Table AXI.1 Typical data file organization (MODrun name.DAT).

<table>
<thead>
<tr>
<th>RUN NAME</th>
<th>NO. OF VOIDS</th>
<th>INITIAL VOID FRAc.</th>
<th>PROGRAM</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1.DAT</td>
<td>169</td>
<td>0.119</td>
<td>CENMOD20</td>
<td>Initially, voids were monodisperse.</td>
</tr>
<tr>
<td>A2.DAT</td>
<td>162</td>
<td>0.111</td>
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<td></td>
</tr>
<tr>
<td>A3.DAT</td>
<td>158</td>
<td>0.117</td>
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<tr>
<td>A4.DAT</td>
<td>169</td>
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<td>A5.DAT</td>
<td>171</td>
<td>0.128</td>
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<td>A6.DAT</td>
<td>167</td>
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<td>A7.DAT</td>
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<td>0.0607</td>
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<td>0.0575</td>
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<tr>
<td>C7.DAT</td>
<td>66</td>
<td>0.0569</td>
<td></td>
<td></td>
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<td>CENMOD20</td>
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<td>E18.DAT</td>
<td>53</td>
<td>0.0294</td>
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</table>

Table AXI.2 Basic simulation runs. Initially monodisperse voids.
<table>
<thead>
<tr>
<th>RUN NAME</th>
<th>NO. OF VOIDS</th>
<th>INITIAL VOID FRAC.</th>
<th>PROGRAM</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>108</td>
<td>0.0807</td>
<td>CENMOD20</td>
<td>Initially, voids were monodisperse.</td>
</tr>
<tr>
<td>B2</td>
<td>104</td>
<td>0.0814</td>
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<tr>
<td>B3</td>
<td>110</td>
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<td></td>
</tr>
<tr>
<td>B4</td>
<td>117</td>
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<td>B5</td>
<td>106</td>
<td>0.0814</td>
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<td>B6</td>
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<td>120</td>
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<td>105</td>
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<td>0.0861</td>
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</tr>
<tr>
<td>B16</td>
<td>106</td>
<td>0.0872</td>
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<td></td>
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<tr>
<td>B17</td>
<td>107</td>
<td>0.0835</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B18</td>
<td>104</td>
<td>0.0780</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D1</td>
<td>216</td>
<td>0.143</td>
<td>CENMOD20</td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>216</td>
<td>0.161</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D3</td>
<td>215</td>
<td>0.154</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D4</td>
<td>212</td>
<td>0.139</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D5</td>
<td>218</td>
<td>0.148</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D6</td>
<td>214</td>
<td>0.152</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D7</td>
<td>214</td>
<td>0.159</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D11</td>
<td>215</td>
<td>0.147</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D12</td>
<td>215</td>
<td>0.136</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D13</td>
<td>216</td>
<td>0.148</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D14</td>
<td>216</td>
<td>0.139</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D15</td>
<td>212</td>
<td>0.139</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D16</td>
<td>214</td>
<td>0.141</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D17</td>
<td>216</td>
<td>0.168</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D18</td>
<td>216</td>
<td>0.163</td>
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<td></td>
</tr>
</tbody>
</table>

Table AXI.3 Basic simulation runs. Initially monodisperse voids.
<table>
<thead>
<tr>
<th>RUN NAME</th>
<th>NO. OF VOIDS</th>
<th>INITIAL VOID FRAC.</th>
<th>PROGRAM</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>B21</td>
<td>105</td>
<td>0.0225</td>
<td>CENMOD21</td>
<td>Initially, voids were randomly sized in the range 0-5. Particle diameter=50. True for all runs below.</td>
</tr>
<tr>
<td>B22</td>
<td>107</td>
<td>0.0260</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B23</td>
<td>107</td>
<td>0.0283</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B24</td>
<td>106</td>
<td>0.0206</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B25</td>
<td>105</td>
<td>0.0233</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B26</td>
<td>104</td>
<td>0.0274</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D21</td>
<td>120</td>
<td>0.0564</td>
<td>CENMOD21</td>
<td></td>
</tr>
<tr>
<td>D22</td>
<td>104</td>
<td>0.0479</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D23</td>
<td>105</td>
<td>0.0472</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D24</td>
<td>107</td>
<td>0.0453</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table AXI.4 Simulations with initially random sized voids.

<table>
<thead>
<tr>
<th>RUN NAME</th>
<th>NO. OF VOIDS</th>
<th>INITIAL VOID FRAC.</th>
<th>PROGRAM</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>G21</td>
<td>172</td>
<td>0.0192</td>
<td>CENMOD22</td>
<td>Bimodal voids: 90% were 5 and 10% were 1 in diameter. Particle diameter=50.</td>
</tr>
<tr>
<td>G22</td>
<td>175</td>
<td>0.0153</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G23</td>
<td>177</td>
<td>0.0158</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G24</td>
<td>172</td>
<td>0.0120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G25</td>
<td>177</td>
<td>0.0140</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table AXI.5 Simulations with initially bimodal voids.

<table>
<thead>
<tr>
<th>RUN NAME</th>
<th>NO. OF VOIDS</th>
<th>INITIAL VOID FRAC.</th>
<th>PROGRAM</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1D</td>
<td>105</td>
<td>0.0833</td>
<td>CENMOD20D</td>
<td>Void diameter=5. Particle diameter=50. With diffusion.</td>
</tr>
<tr>
<td>B2D</td>
<td>097</td>
<td>0.0646</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3D</td>
<td>101</td>
<td>0.0749</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B4D</td>
<td>104</td>
<td>0.0774</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B5D</td>
<td>104</td>
<td>0.0883</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B4N</td>
<td>104</td>
<td>0.0774</td>
<td>CENMOD20N</td>
<td>Without diffusion.</td>
</tr>
<tr>
<td>B5N</td>
<td>104</td>
<td>0.0883</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table AXI.6 Simulations showing the effect of diffusion.
Appendix XII

SINGLE PARTICLE EXPERIMENTS:
TEMPERATURE-TIME TRACES
Single particle drop-tube experiments were done under a variety of conditions. Only the temperature-time traces are shown in this Appendix. The intensity-time traces from which these were derived are not shown due to space limitations. The derived area-ratio is also not shown.

At the top of each Figure is a line that describes the conditions of that experiment. The first two words are 1451 and 1600K indicating that the chars were derived from the bituminous PSOC 1451 coal, after pyrolysis at 1600K. The next number, e.g. 45-53 indicates the char size in microns. Following that is the value of the wall temperature in degrees Celsius. 1000W means the wall temperature was 1000°C. Finally the particular filename.ext is given. The starting letter of the filename indicates whether the experiment was carried out in air or in 50% oxygen. Filenames starting with A, P, R, X, and Y denote experiments in air and those starting with L, S, T, and V are for experiments in 50% oxygen.

Two additional comments are in order. The file series starting with the letter P shows data from chars oxidized to 13% conversion at 500°C. This is indicated in the top header for those files. All other chars are initially unburnt. The files starting with the letters X and Y are from the same char but belong to two density classified fractions — D for the denser and L for lighter fraction. This is also indicated in their respective top headers.

Table AXII.1 shows the organization of each data file. Time, in milliseconds, is in column 1. Columns 2 and 3 show the signal intensities in Volts in the wavelength ranges centered around 800nm and 1000nm respectively. Column 4 shows
the particle temperature in degrees Kelvin. Finally, columns 5 and 6 show the area ratios (projected area of the particle along the detector line-of-sight as a function of time, divided by the initial projected area) as obtained from the 800nm and the 1000nm signals. Table AXII.2 summarizes the experimental conditions for runs in air while Table AXII.3 does the same for runs in 50% oxygen.

Figure AXII.1 is a flow diagram showing the sequence of steps involved in gathering and interpreting the data from the experiments. The various steps are discussed in Chapter 4. Figure AXII.2 shows the calibration sensitivity curve. It shows how sensitive the particle temperature is to the value of the experimentally determined calibration constant, C. The sensitivity depends on the ratio of the signals at the two wavelengths. Various curves are for different signal-ratios as shown. The subsequent Figures show the temperature-time traces of the various runs. The calibration runs are also shown in the first few Figures labelled CAL*.DAT.
Table AXII.1 Data file format for single particle experiments.

<table>
<thead>
<tr>
<th>Time (ms)</th>
<th>800nm signal</th>
<th>1000nm signal</th>
<th>Particle Temperature</th>
<th>Area ratio (800nm)</th>
<th>Area ratio (1000nm)</th>
</tr>
</thead>
</table>

Table AXII.2 Details of single particle experiments in air. All particles were PSOC 1451 1600K char.

<table>
<thead>
<tr>
<th>RUN NAME</th>
<th>CHAR SIZE</th>
<th>WALL TEMPERATURE</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>R16B 1,2,4, 6-10,12-14</td>
<td>90-104</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>R16S 1-14</td>
<td>45-53</td>
<td>1000</td>
<td>Dense particles</td>
</tr>
<tr>
<td>X16B 2-7</td>
<td>90-104</td>
<td>1000</td>
<td>Light particles</td>
</tr>
<tr>
<td>Y16B 1-14</td>
<td>90-104</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>P16S 1,4,5,8, 9,13,14,16,17</td>
<td>45-53</td>
<td>1000</td>
<td>13% B.O. at 500°C</td>
</tr>
<tr>
<td>A16S 1-16</td>
<td>45-53</td>
<td>800</td>
<td></td>
</tr>
</tbody>
</table>

Table AXII.3 Details of single particle experiments in 50% O₂. All particles were PSOC 1451 1600K char.

<table>
<thead>
<tr>
<th>RUN NAME</th>
<th>CHAR SIZE</th>
<th>WALL TEMPERATURE</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>S16B 2,6-9,11, 13,15,16,18,21</td>
<td>90-104</td>
<td>1200</td>
<td></td>
</tr>
<tr>
<td>S16S 1-3,5,7-9, 12,14,16,17,20</td>
<td>45-53</td>
<td>1200</td>
<td></td>
</tr>
<tr>
<td>T16B 1,4,9, 10,12</td>
<td>90-104</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>T16S 3,4,6,8, 11,13,14</td>
<td>45-53</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>L16S 1-6,8-16, 19-21</td>
<td>45-53</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>V16S 1,3,4,6,8,9, 12-15,17-21</td>
<td>45-53</td>
<td>700</td>
<td></td>
</tr>
</tbody>
</table>
Figure XII.1 Procedure for obtaining temperature-time traces from single particle drop tube experiments.
Figure XII.2 Calibration sensitivity curve for pyrometry inversion.
1451 1600K 45-53 1200W S16S9.FIN

TEMPERATURE K

TIME ms.

1451 1600K 45-53 1200W S16S12.FIN

TEMPERATURE K

TIME ms.
TEMPERATURE K

TIME ms.
- 740 -

1451 1600 90–104 1000W T16B9.FIN

 TEMPERATURE K

0 5 10 15 20 25 30
TIME ms.

1451 1600 90–104 1000W T16B10.FIN

 TEMPERATURE K

0 5 10 15 20 25 30
TIME ms.