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INVESTIGATION OF FORMATION OF NITROGEN COMPOUNDS IN COAL COMBUSTION

Final Report

October 1, 1983

Work Performed Under Contract No.: DE-AC21-80MC14061

For
U. S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Exxon Research and Engineering Company
Linden, New Jersey

University of Arizona
Tucson, Arizona

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**For
U. S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26505**

**By
D. W. Blair and I. D. Crane
Exxon Research and Engineering Company
P.O. Box 45
Linden, New Jersey 07036**

**J. O. L. Wendt
University of Arizona
Department of Chemical Engineering
Tucson, Arizona 85720**

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ABSTRACT

This is the final report on DOE contract number DE-AC21-80MC14061. It concerns the formation of nitrogen oxide from fuel-bound nitrogen during coal combustion.

The work reported was divided into three tasks. They addressed problems of time-resolving pyrolysis rates of coal under simulated combustion conditions, the combustion of the tar that results from such pyrolysis, and theoretical modeling of the pyrolysis process. In all of these tasks, special attention was devoted to the fate of coal nitrogen.

The first two tasks, were performed by Exxon Research and Engineering Company. The theoretical modeling was done by the University of Arizona under subcontract to Exxon Research and Engineering Company.

SUMMARY

This report reviews experimental and theoretical results that were directed towards obtaining a fundamental understanding of how nitrogenous pollutants are formed in coal combustion processes. Of specific interest was the determination of the rates at which nitrogenous compounds are evolved during coal devolatilization, and a mathematical description of the relative rates of evolution of nitrogenous and other hydrocarbon constituents. It is believed these relative rates determine the environment in which nitrogenous compounds react in the gas phase, and thus their ultimate conversion to NO and N₂.

The report consists essentially of two parts. The first part covering Tasks 1 and 2 is concerned with the experimental work on time-resolved pyrolysis of coal and coal tar combustion. Additional experiments are required in both areas to provide the necessary interpretable data and make this work complete. Useful guidelines are delineated for execution of these experiments to provide these data if further work is undertaken.

The second part of this report is concerned with the mathematical modeling of coal and coal nitrogen devolatilization. It presents a model framework that allows the combustion of coal to be described in detail. Although additional work still remains to be done, the results presented herein provide a useful approach for other researchers interested in modeling the evolution and fate of trace species during pulverized coal combustion.

The experimental procedure utilized to determine devolatilization rates involved a captive particle technique in which coal particles were heated at high controlled rates on a platinum ribbon. The products were swept out of the reactor by helium flow to appropriate detectors. This report describes limitations and requirements of this experimental configuration if meaningful data are to be obtained. A specific limitation of this technique is that the detector measures a signal which has been distorted during the passage of the carrier gas from the coal particle to the detector. It is shown that this distortion can be quantitatively accounted for, and that the data can be quantitatively interpreted provided that:

1. The mean residence time between the coal particle on the pyroprobe and the detector is kept as short as possible, less than 2 seconds. This yields a measurable difference between the measured devolatilization signal and that resulting from a delta pulse input, and it is this difference which is shown to be interpretable in terms of original devolatilization rates.
2. The response time of the detector/data acquisition system is less than the actual devolatilization time. This is because the difference between the actual signal and that resulting from a pulse is measurable over times comparable to the actual devolatilization times, even though the actual signal may occur over a much longer period of time.

These requirements were explicitly delineated only after much experimental data had been obtained. Therefore, interpretable data on relative devolatilization rates of coal nitrogen and other coal species were not obtained. Rather, this report describes how this experimental approach can be made to work, and leaves it to further research to obtain the required data.

A laboratory scale combustor was designed and built for investigating the combustion behavior of coal tar to determine if tar nitrogen conversion is a function of tar type. This device consisted of a tar diffusion flame centered in a controlled combustion environment from the flat flame of a gas fired laminar premixed burner. Some preliminary tar combustion data were obtained which demonstrated that the system could be made to produce useful quantitative data. However, modifications beyond the scope of the current program were required to improve control of tar flow rates and flame stability. These are identified for future research.

The theoretical results described in this report show how a distributed activation energy model for pyrolysis together with a char oxidation model which includes predictions of solid structural changes can be incorporated into classical kinetic codes and usually reserved for detailed (stiff) homogenous gas phase kinetic mechanisms. The results allow prediction of several phenomena important in determining the fate of coal nitrogen during combustion, namely;

1. Variations in both asymptotic and time reduced yields of volatile and char nitrogen as functions of pyrolysis temperature.
2. The partial conversion of char nitrogen to NO caused by heterogeneous reactions inside the char particle.
3. The interaction between heterogeneous and homogeneous reactions during pulverized coal combustion.

Comparisons between available data and the model are presented and, although promising, show the need for further refinements. These are currently being made in continuing research outside the present contract.

INTRODUCTION

As the combustion of coal provides an ever greater portion of our national energy needs, the absolute tonnage of coal consumed each year will increase dramatically. If not adequately controlled, the environmental problems caused by the combustion of this relatively dirty fuel will grow with its increasing use. It is important that cost effective technology be developed to improve this situation by reducing the pollutant production from coal combustion to acceptable levels. The purpose of this research project was to advance such technological development by improving our fundamental understanding of how nitrogenous pollutants form in coal combustion processes. The experimental findings of the proposed work were to be consolidated into a theoretical model to provide the necessary insight to promote the development of advanced combustion technology for pollutant control.

An important gaseous pollutant which requires attention in the combustion of coal is NO_x . The prevention of NO_x production from fuel nitrogen poses an especially difficult problem. Nitrogen is already "fixed" (in a form other than N_2) in coal. Up to 6 percent nitrogen is found bound within coal structures. Significant amounts of this nitrogen exiting the combustion process as fixed nitrogen in the form of NO_x (HCN and NH_3 may be important precursors) are cause for environmental concern. Systems which focus on prevention of thermal fixation of atmospheric molecular nitrogen are ineffective in reducing the fuel NO_x which results from this source.

Review of Previous Work

Starting in April 1975 under NSF RANN Grant No. AER75-03964 and continuing from October 1977 through November 1979 under DOE Contract No. EF-77-C-01-2650, Exxon Research and Engineering Company and its subcontractor, the University of Arizona, have carried out a combined experimental/theoretical research program on the formation of NO_x and other products from chemically bound nitrogen in coal combustion. The objective was to combine experimentation and theory in an iterative process to develop an understanding of the combustion process to serve as a guide to the design of environmentally acceptable coal combustion systems. To this end, the process of coal particle combustion was viewed as a series of sequential stages, and the conversion of coal nitrogen in these stages was investigated and modeled. These stages were pyrolysis, gas phase combustion of pyrolyzate (tar and gas), and char burnout. Primary emphasis was on the pyrolysis stage with a significant theoretical effort also devoted to the char burnout stage. The experimental work on these projects was conducted at Exxon Research and Engineering Company (Dr. D. W. Blair, Principal Investigator). The theoretical modeling was done at the University of Arizona (Professor J. O. L. Wendt, Principal Investigator).

The work on the pyrolysis stage proceeded along two distinct paths. The first concerned the effect of pyrolysis conditions upon material lost from the solid phase. The object was to discover the nature and quantity of the evolved material, which is the fuel for the gas-phase flame in coal combustion. In this work, pyrolyses were done in a muffle tube furnace with controlled atmospheres (argon, or argon plus 10% CO_2 , 10% CO , or 10% CH_4). The independent variables were coal type and pyrolysis temperature. The pyrolyses were run for one hour, which was sufficient to take them to

completion. The fractions of coal mass, nitrogen, and sulfur evolved were the dependent variables. These experiments were run on twenty-one coals (representing a wide variety from all sections of the U.S.A), two chars, and one petroleum coke. Significant differences were found among coals, but significant similarities were also found. Notably, nitrogen evolution was found to be much more temperature sensitive than was total mass evolution, while sulfur evolution exhibited a plateau (which probably marks the completion of organic sulfur release and the onset of inorganic sulfur release). The high temperature sensitivity of nitrogen release relative to total mass release was common to all of the coals. It was also observed that there was greater similarity of nitrogen release than of total mass release among different coals, even on a dry, ash-free basis. Apparently, the bonding of nitrogen had more in common among the coals than did the bonding of the major elemental species. Practically all of the coal nitrogen was evolved by 1500°C. These data suggested that by regulating the combustion process, control can be exercised over the stage wherein various fractions of coal nitrogen are converted (i.e. in the pyrolyzate combustion or char burnout stages). Such regulation might be exercised through control of particle size or through air scheduling to the flame.

The second experimental path investigated the pyrolyzate itself. It was concerned with finding the distribution of nitrogenous species within the pyrolyzate and with identifying the major pyrolyzate species. These data were obtained as functions of coal type, pyrolysis temperature, and pyrolysis heating rate. The experiments were run by placing small (100-200 μ g) samples of powdered coal on an electrically heated platinum ribbon which served as the heat source. The ribbon could be heated to a maximum temperature of 1650°C at heating rates up to 20000°C/s. This ribbon was located within a small reactor that was part of a gas chromatograph carrier gas (helium) circuit. Pyrolyzate was swept from the sample into a suitable g.c. column. The gas chromatograph was equipped with thermal conductivity, flame ionization, and phosphorous/nitrogen detectors.

It was found that a negligible fraction of coal nitrogen was evolved as molecular nitrogen. Significant fractions (up to approximately ten percent each) were evolved as HCN and NH_3 . Very little was evolved as intermediate boiling point (intermediate molecular weight) species. Much of the nitrogen was evolved as very high boiling point (>500°C) tars. Thus, many important nitrogenous species in the pyrolyzate are very high boiling tar species whose combustion properties are largely unknown. Other, non-nitrogenous, species were more evenly distributed over the intermediate boiling range, although very light species (primarily methane and carbon monoxide) and heavy tars were predominant. Thus, there was a partial segregation by molecular weight between nitrogenous and non-nitrogenous pyrolyzate species. While quantitative results were strongly dependent upon maximum pyrolysis temperature, they were at most only slightly dependent upon heating rate. These data showed that an understanding of the combustion properties of these heavy tars is important to the gas-phase combustion stage.

Because a coal combustor is a flowing system, an interval in time represents a displacement in space. It is, therefore, important to obtain information on the rate of evolution of pyrolyzate species if the scheduling of air addition to the flame is to be adjusted to provide the gas-phase stoichiometry that will cause maximum conversion of fuel nitrogen to molecular

nitrogen. Unfortunately, since the pyrolysis of a coal particle in a combustion environment is a very rapid process, on the order of fractions of a second, time-resolving pyrolysis is difficult because the detector has response times of the same order of magnitude as the process itself. It is, therefore, necessary to somehow retard the process in a well-defined, organized manner. Just such a method was devised as part of this earlier work. It involves replacing the gas chromatographic column with a suitably designed open tube and carrying out pyrolyses in the carrier gas stream. The time-resolved signals from the detectors are related to the evolution rates through a transfer function that characterizes the relatively simple reactor-tube-detector system. A suitable inversion scheme will be able to determine pyrolyzate evolution rates from these signals and, in fact, a numerical inverse Laplace transform computer code (Blair and Wendt, 1978) has been developed to invert the signal data to mass evolution rates.*

A theoretical model of coal pyrolysis was developed to make good use of the time-resolved pyrolysis data. The model is based upon the assumptions of a Gaussian distribution of nitrogen bond energies in the coal matrix, a linear relationship between bond energy and the temperature at which a given bond breaks in the asymptotic (muffle-tube furnace) pyrolysis experiments, and a linear (Semenov) relationship between bond energy and activation energy. The latter two assumptions lead to a linear relationship between activation energy and the temperature at which a given bond breaks. This relationship involves two constants that should be universal among all coals (i.e., coal type independent). The Gaussian distribution of bond energies is characterized by two coal type dependent constants: a mean temperature and a standard deviation about that mean. If this model proves successful, time-resolved and asymptotic experiments on any one coal will determine the two universal constants which can then be used together with asymptotic data on other coals to predict their pyrolysis rate behavior without additional time-resolved pyrolysis experiments. This will prove to be a great simplification in that asymptotic data are far easier to obtain than are time-resolved data.

In addition to predicting the rate of release of pyrolysis products, it is also necessary to obtain an understanding of coal combustion that can assist in the design of combustion systems which maximize conversion of coal nitrogen to molecular nitrogen. Thus, a major portion of further work should include the study of the combustion behavior of pyrolyzate tar, which, as noted above, is a pyrolysis product that contains much of the nitrogen.

Present Program

The contract for the present program (DE-AC21-80MC14061) started October 1, 1980. The program was divided into three tasks. They were:

* This approach also makes a virtue out of necessity in that for any detector that measures material directly flowing through it it is necessary to connect it through a flow system to the reactor. This flow system will inevitably relate the signal to the pyrolysis event through some transfer function.

Task 1: Time-Resolved Coal Pyrolysis

This task comprised two efforts. The first was to experiment with coal pyrolysis to make time-resolved measurements of pyrolysis products evolution rates while the second was to incorporate these rates into the model to calculate the coal-type independent constants.

Task 2: Combustion of Coal Pyrolyzate Tar

The object of this task was to investigate the combustion behavior of coal tar to determine if tar-nitrogen type affects the conversion of that nitrogen under combustion conditions.

Task 3: Analytical Modeling

The objective of this task, which was to be carried out under subcontract by the University of Arizona, was to analytically support the experimental program by providing insight to interpret experimental results and by developing models to generalize the results.

The experimental tasks (Tasks 1 and 2) were conducted at Exxon Research and Engineering Company under the direction of Mr. A. Muenker who reported to Dr. L. A. Ruth. Mr. I D. Crane replaced Dr. Ruth when he transferred to a different ER&E assignment in May 1982. Dr. D. W. Blair served as a consultant during the period when Mr. Muenker was becoming familiar with the project and assuming technical responsibility for it. Mr. R. Kuriskin was the research technician on this project. The analytical modeling (Task 3) was executed by Professor J. O. L. Wendt of the University of Arizona under subcontract to ER&E.

Two principal reports have been written for this project. The first is an interim technical progress report (Muenker, et al., 1982) which covered the period from start of the contract through the experimental phase which ended in August 1982. This interim report presented the experimental results obtained from Tasks 1 and 2 and initial analytical results from Task 3. Mr. Muenker left the project at the end of the experimental phase. The second principal report is this one which is the final report for the period. This report provides an evaluation of the results of the experimental tasks and an extension and interpretation of the analytical results. Dr. Blair returned to the project to assist in writing this final report.

1.0. Task 1: Time Resolved Coal Pyrolysis

1.1 Purpose and Scope

The purpose of this task was to obtain time-resolved measurements of the evolution rate of gaseous products (total mass and CN-containing species) from coal particles under simulated combustion pyrolysis conditions. To accomplish this, it was essential to develop and refine further the apparatus and experimental methods utilized previously (Blair and Wendt, 1978). In this earlier work, 25 separate sets of time-resolved devolatilization data (total mass only) were obtained from a non-optimum system. Through the application of theoretical transfer functions the data was inverted to yield fundamental devolatilization rates. In each case, the distortion of the data was not too large and the devolatilization rates seemed reasonable. This demonstrated that the concept had merit and was feasible.

While progress has been made toward achieving this purpose, further research is required to produce interpretable data. Therefore in preparing this final report, the purpose has become to examine the results obtained to date and to define criteria and guideline for this additional research if this work is continued in the future.

1.2 Apparatus

This section covers a description and analysis of the apparatus used in this experiment. Included in this analysis are a definition of criteria that the apparatus must satisfy in future experiments and an examination of the apparatus used versus these criteria. This examination included using improved modelling techniques developed as part of Task 3.

1.2.1 Description

The apparatus that was used is shown schematically in Figure 1.2.1-1. Coal pyrolysis was carried out on an electrically heated platinum ribbon (the pyroprobe). Its temperature was programmable up to a maximum of 1650°C at maximum controlled linear heating rates of 20,000°C/s. Heating intervals could be controlled from 20 ms to 20 s. The pyrolysis took place in a 1/4 inch I.D. stainless steel reactor. The reactor was connected to a detector (thermal conductivity and/or phosphorous-nitrogen) by a length of stainless steel or glass tubing (to be specified in individual experiments). The reactor, tube, and detector were maintained at 300°C. Helium carrier gas (also preheated to 300°C) was led into and through the reactor, through the tube, through the detector, then to the exhaust.

In principle, pyrolyzate from the coal mixes instantaneously with the carrier gas in the reactor, blows down from the reactor into the tube, undergoes Taylor-Aris diffusion as it passes along the tube, passes through the detector generating a signal (which is recorded on a strip chart recorder) and then passes to the exhaust. The signal/time trace on the recorder is related to the mass evolution time history of the coal by a transfer function. The nature of the transfer function is governed by the processes which link the mass evolution (which applied to a particular chemical species if the detector was species-specific) to the signal generator (the trace). If the linkage processes are particularly simple, the transfer function can be

FIGURE 1.2.1-1. SCHEMATIC OF APPARATUS UTILIZED TO OBTAIN COAL VOLATILIZATION DATA

determined analytically. Transfer functions for more complex processes (such as the combined blowdown-Taylor diffusion) can, upon suitable calibration with known pulses, be calculated numerically.

The proper sizing of reactor and tube was a significant problem that had been examined analytically in the previous program (Blair and Wendt, 1981). In the current program, the proper combination was investigated experimentally. Here, various tube configurations were used with a given reactor, over a range of helium flows to determine the best configuration. The tubes were stainless steel. Tests were made with the thermal conductivity detector attached as closely as possible to the reactor, then with 163 cm lengths of 1/8 or 1/4 inch O. D. stainless steel tubing connecting it to the reactor. Helium carrier gas flowrates ranged from 6 to 160 cc/min. For all tests, and all subsequent work, the reactor, tube, and detector were kept in the range of 300 to 325°C. Wyodak coal was pyrolyzed in these tests and the pyrolysis temperature was 1400°C except for one test at 800°C. The heating rate was 20,000°C/s and the pyrolysis interval (the heating interval including the temperature ramp) was 20 s. The immediate results of these tests (a series of strip chart recorder traces) were compiled in an interim report (Muenker, et. al., 1982). The recorder that was used for these tests and for all subsequent work was an RDK Model B-3061 with 1 s full scale response time.

After these tests, the reactor was connected to the detector via a 1/4 inch O. D. (4 mm ID) helical Pyrex coil 355 cm long. Pyrex was used to reduce tubewall - pyrolyzate interactions, particularly interactions with nitrogenous species. This arrangement was used for subsequent experiments with coal.

1.2.2 System Analysis

The apparatus and results have been analyzed in light of criteria and guidelines which have been established if time-resolved experiments are continued in the future. To extract time-resolved mass and species evolution rates from well-controlled pyrolysis of coal particles it is necessary to meet certain criteria. They are:

1. The pyrolysis system must be one that can produce controllable heating rates and final temperatures. It must be possible to relate these rates and temperatures to particle heating rates and temperatures as opposed to apparatus heating rates and temperatures. These rates and temperatures should be of the order of magnitude of combustion heating rates and temperatures.
2. A method must be designed to convey the evolved pyrolyzate through a suitable detection system or to relate the portion of the material that does pass through the detection system to the whole of the material that is evolved.
3. It must be possible to relate the detector signal either to total mass or to the mass of an of individual species through the detector.
4. The response time of the detector must be short relative to the risetime of the fastest signal that it must detect.
5. A signal recorder must be provided with response times that are short relative to the risetime of the fastest signal that it must record.

The requirement of criteria 1 is obvious. If the experiment is to be useful the thermal conditions imposed upon the particle itself must be known and they should be as representative of the thermal conditions imposed by a combustion environment as possible.

Item 2 is considerably more complex. Somehow, a detector signal must be related to the total evolution of some species evolved from the particle. The signal and evolution must be related in time so that the total evolution may be recovered from the time variation of the signal.

Ideally, the way of achieving this is to have the detector on the particle itself so that its signal exactly follows the evolution in time. In principle, an optical probe can achieve this although serious problems of species-sensitive response must be solved. Also, an optical probe will experience considerable difficulty in detecting the total of any species evolved. It will sample along one line-of-sight over the particle and signals along this line-of-sight must be related to evolution over the entire particle surface. This requires knowledge of the symmetry of evolution over the particle surface and this knowledge is likely to prove very difficult to achieve.

The solution to the problem of criteria 2 chosen for this program is to gather all of the evolved material together as it leaves the particle and transport it to the detector in a manner that does not lose the information regarding the time-variation of evolution. This gathering and transporting of the evolved material inevitably modifies the temporal relation between the evolution and the signal. If nothing else, it introduces a time lag between signal response and evolution response.

Gathering all the evolved material will also introduce other modifications. Physical processes that accompany gathering and transportation will distort the signal-time profile. It is important that these distortions not be such as to lose the evolution rate information. To the extent that the physical processes that produce the distortion are well-understood, and to the extent that the distortions are not too great, a theory may be constructed to deduce the evolution profile from the signal profile. Such a procedure is commonplace in making physical measurements. A simple (static) example is the measurement of hot gas temperature with a thermocouple. The recorder records the thermocouple junction temperature. A theoretical model is required to convert this to the temperature of the gas at that point in the absence of the thermocouple. If the difference between these two temperatures is small, a reasonably accurate theory will give excellent results. If the difference is profound, no theory can produce useful results. This is also the case with this method. With a good theory and tolerable distortion the output signal can be inverted to accurately reproduce the evolution profile.

The application of this method to this work was to locate the coal particle in a reactor which was continually swept with a helium carrier gas. This carrier gas immediately swept gaseous products that evolved from the coal into a capillary tube which conveyed them to the detector. The coal pyrolysis was driven by a suitable heater.

The configuration that was used to produce the data in this report involves placing the particle on an electrically heated ribbon for the purpose

of pyrolysis. The temperature of the ribbon is electronically controlled and its heating rate and maximum temperature may be controlled independently, which is an advantage. This system has several disadvantages. Regarding pyrolysis, the particle is non-uniformly heated, and the heating condition is poorly defined. Particle temperature will closely follow ribbon temperature only if the particle size is quite small (less than 50 μ). Thus, this disadvantage may be partially overcome by using very small particles.

A more serious disadvantage with this method is that the apparatus that holds the ribbon (the assembly including the ribbon is called a pyroprobe) is rather large (1/4 inch dia.). Thus it must fit into a reactor of at least 1/4 inch I.D. This adds another element to the system that collects the pyrolyzate and conveys it to the detector. The helium carrier gas flows through the reactor, over the particle, and out into the capillary which conducts it to the detector. In the reactor the pyrolyzate leaves the particle, mixes with the carrier gas, and this mixture then blows down from the reactor into the smaller capillary tube which conducts it to the reactor. With this approach the physical processes of mixing in the reactor and blowdown into the capillary must be included with the physical processes in the capillary in the theoretical model, which is used to invert the detector profile to produce the evolution profile. For small capillaries the signal distortion is caused by Taylor-Aris diffusion. This is a well-understood physical process which can be accurately modeled to give an accurate inversion of the signal profile to an evolution profile. The mixing process that occurs in the reactor is much less definite. Conceivably, depending upon conditions, it can vary from near-instantaneous mixing of carrier gas and pyrolyzate in the immediate vicinity of the particle to slow mixing with extensive backmixing within the reactor. The process that does occur is not accurately known. For the experiments that were performed in this work it was assumed that perfect mixing occurred in the reactor. Thus the theoretical model that was used to invert the signal profile to the evolution profile was one of perfect mixing, followed by blowdown into a capillary, followed by Taylor-Aris diffusion within the capillary as the sample flowed to the detector.

Another configuration of the heater, which should be considered in the future, would be to eliminate the reactor and have the heater be a preheated section of the capillary tube itself. At time zero, the particle would be injected directly into this section, pyrolysis would commence, and the pyrolyzate would be immediately swept away from the particle, along the tube towards the detector. This pyrolysis arrangement has the advantages that heating rates are geometrically uniform, and the pyrolyzate appears immediately as an input to the capillary flow. The physical model leads to a well-posed theoretical model which can produce an accurate inversion of the signal profile to give the evolution profile. It has the disadvantage that heating rate is linked to final temperature. This disadvantage can be somewhat overcome by using different particle sizes for different final temperatures because heating rate is also influenced by particle size.

Another consideration is the time required for the pyrolyzate to flow through the capillary from the reactor to the detector. If this time is within approximately an order of magnitude of the pyrolysis event, the signal distortion will be sufficiently moderate that it can be inverted to provide an accurate representation of the evolution profile. If, however, the flow time

is several orders of magnitude greater than the time span of the pyrolysis event, then diffusional processes within the capillary will so grossly distort the signal that accurate recovery of the evolution profile by inversion will be impossible. This is analogous to the example of the thermocouple that was given previously. In the limit of infinite transit time, diffusion will uniformly mix the pyrolyzate with the carrier gas throughout the capillary and all information regarding the evolution profile will be destroyed. In these pyrolysis experiments, evolution time spans were the order of 0.1 s. Thus, maximum transit times should not be longer than the order of seconds, certainly not in excess of 10 s.

The requirement of criteria 3 can be readily met with standard commercial detectors. A thermal conductivity detector can be used to measure total mass throughput. Nitrogen compounds which contained CN groups can be selectively detected with a Perkin-Elmer Phosphorous/Nitrogen detector. This detector uses a combination of flame ionization over an iridium bead and electron capture to achieve an extremely high selectivity for CN-compounds. A standard flame ionization detector will selectively detect compounds containing CH groups, if this information is required. Use of these three detectors can in principle detect relative evolution rates of total mass, inorganic species, organic species, and CN-containing compounds. In this research the apparatus was set up only to measure rates for total mass and CN groups.

For the detectors to function, extreme care must be exercised to prevent loss of the compounds within the capillary tubes (or the reactor). This is particularly critical for nitrogen compounds which are notoriously reactive with surfaces. Also, the species must not be adsorbed on the capillary walls (or the reactor walls) if the inversion procedure is to be useful. Nitrogen species tend to adsorb on surfaces.

To avoid these problems (especially with nitrogen species), the capillary must be glass, clean, and hot with no cold spots anywhere from reactor to detector. Otherwise nitrogen species will be lost or their detector signal hopelessly distorted. With coal pyrolyzate there will always be some high-boiling tar that precipitates out on the reactor and capillary. It will pose a severe problem in keeping the apparatus clean, and it must be removed regularly. It will also be lost to the detector, but it should comprise a small percentage of the total mass. Additional techniques would have to be developed in some cases if material balances indicated this was a significant percentage for some coals.

Criteria 4, the requirement that the response time of the detectors be short relative to the risetime of the fastest signal that was anticipated can be met by the above detectors, which have response times of the order of 110 ms or less.

Criteria 5, the requirement for a recorder with a response time that is short relative to the rise time of the fastest event that must be recorded is essential. A pen strip recorder was used to record the data were produced during this project. It had a full-scale response of 1s. It is suitable for recording highly distorted (delayed) signals, but it is unsuitable for recording signals with modest distortion. Below it is shown that these highly distorted signals present severe problems to the inversion process. To record signals with only modest distortion, a full-scale response less than 100 ms is

recommended. This can be readily achieved with digital data recorders with sample times around 5 ms. Furthermore, this type of recorder is desirable because the data is recorded in digital form which is suitable for subsequent analysis on a high speed computer.

Calculations provide some insight into the limits of distortion of the original signal that can be tolerated and still allow the original signal to be recovered. Fig. 1.2.2-1 shows a representative devolatilization rate (produced theoretically by the model to be described in Section 3.1). Here, the original process occurs over 180 milliseconds. If the apparatus uses a large reactor (mean residence time of 3.7 seconds) and a long capillary (mean residence time of 81.3 seconds), the signal to be measured is given by the solid line in Figure 1.2.2-2. If the input were a pulse (delta function), the measured signal is given by the crosses on the same figure. Clearly, the two signals are indistinguishable, indicating that this configuration cannot be utilized to interpret devolatilization rates. If the length of the capillary is decreased to yield a short capillary mean residence time, 0.16 seconds for example, the same input signal produces the measured output signal shown in Fig. 1.2.2-3. The difference between the crosses (pulse input) and the solid line (finite width input) is significant for fractions of a second, and can be interpreted, provided a measuring device has a sufficiently rapid response. From the foregoing it is clear that a distorted signal can be recovered only if the ensuing measured output signal can be distinguished from that resulting from a pulse. Therefore, it is essential that a pulse experiment be performed, to precisely determine the weighting function and thus permit accurate experimental measurement of deviations from it.

1.3 Data Inversion

A detector provides a signal in millivolts that represents the result of a devolatilization pulse that has been distorted prior to reaching the detector. The signal measured does not directly represent events occurring at the particle surface. Rather the original devolatilization signal is distorted by backmixing and by Taylor-Aris diffusion in the capillary leading from the reactor to the detector.

In previous reports it was shown how the weighting function describing the distortion could be theoretically determined, in the absence of experimental determinations. The original input prior to distortion could then be recovered from the distorted output by use of numerical evaluation and inversion of Laplace Transforms.

The weighting function, $W(f)$ is given by

$$W(t) = \frac{1}{2\tau_1} \exp \left\{ M \left(\frac{\tau_2}{\tau_1} \right)^2 + \frac{\tau_2}{\tau_1} \right\} \left[\exp \left(-t/\tau_1 \right) \operatorname{erf} \left(\frac{\tau}{2\tau_2\sqrt{M}} - \sqrt{M} \frac{\tau_2}{\tau_1} - \frac{1}{2\sqrt{M}} \right) \right. \\ \left. - \exp \left(-t/\tau_1 \right) \operatorname{erf} \left(-\sqrt{M} \frac{\tau_2}{\tau_1} - \frac{1}{2\sqrt{M}} \right) \right]$$

where

τ_1 = mean residence time of well stirred reactor
 τ_2 = mean residence time in plug flow

FIGURE 1.2.2-1. REPRESENTATIVE INPUT SIGNAL

COMPLEX W(T), HE FLOW = 0.333 CC/SEC

FIGURE 1.2.2-2. SIGNAL COMPARISON FOR LONG CAPILLARY [SOLID LINE DENOTES MEASURED DEVOLATIZATION RATE; CROSSES DENOTE RESPONSE TO PULSE.]

COMPLEX $W(T)$, HE FLOW = 0.333 CC/SEC

FIGURE 1.2.2-3. MEASURED SIGNAL COMPARED TO WEIGHTING FUNCTION TO SHORT CAPILLARY

$$M = \text{Dispersion Number} \\ = DE/UL$$

with

$$DE = \text{Effective diffusivity, cm}^2/\text{s}$$

and

$$D = DM + \frac{R^2 \bar{U}^2}{48DM}$$

$$\begin{aligned} \bar{U} &= \text{mean velocity in capillary cm/s} \\ R &= \text{capillary radius cm} \\ DM &= \text{molecular diffusivity cm}^2/\text{s} \end{aligned}$$

The Laplace Transform of this is given by:

$$W(s) = \frac{\exp(M_s (1 - \beta))}{(1 - \delta) s \theta + \frac{1 + \beta}{2}}$$

where

$$\begin{aligned} M_s &= 1/2M \\ \theta &= \tau_1 + \tau_2 \\ \delta &= \tau_2/\theta \\ \beta &= \sqrt{1 + 2 \delta s \theta/M_s} \end{aligned}$$

If the transform of the distorted output is given by $O(S)$, that of the input, $I(S)$ is given by

$$I(S) = O(s)/W(s)$$

and

$$I(t) = \mathcal{L}^{-1} I(s)$$

which is obtained numerically using Krylov's method.

In previous work (Blair and Wendt, 1978; Blair and Wendt, 1981), with $\tau_1 = 2.04$ s, $\tau_2 = 3.474$ s and $M_s = 4.27.4$, it was possible to invert 25 separate sets of time resolved coal devolatilization data (total mass measured by thermal conductivity detector) to yield fundamental devolatilization rates. In each of these cases the distortion in the data was not too large and the original devolatilization data was recovered (Blair and Wendt, 1981).

A computer program was utilized to perform the inversions. It completed the following functions:

- Raw data is read in ($O(t)$)
- Raw data is normalized ($O(t)$ norm)
- Normalized data is numerically transformed in Laplace space, using Filon quadrature.
- Transfer function is convoluted in Laplace space.
- Transform of normalized output is divided by transfer function.
- The result is inverted using Krylov's technique, thus providing the normalized input.

1.4 Results From Time-Resolved Evolution Both For Total Mass

In this section, results of work on time resolved evolution of total gaseous species will be assessed. The detector used for this work was a thermal conductivity detector. A number of experiments were run for different coals and conditions (Muenker, et. al., 1982). Two types of experiments were run. In one, the reactor was closely coupled to the detector. In these experiments, delay times from the start of pyrolysis to the peak of the detector output ranged from 0.5 to 5 s. In the second type of experiment, the reactor was connected to the detector with a 355 cm of coil of 4 mm ID glass tubing. In these experiments, delay items from the start of pyrolysis to the peak of the detector output exceeded 80 s. The system was calibrated by injecting (from a hand operated syringe) 0.06 μ l of 5% pyridine in toluene. This calibration served to determine the sensitivity of the system to mass throughput.

Reactor with No Capillary

Figure 1.4-1 shows the measured output, normalized output and calculated input for the case of a direct hook up of the pyroprobe to the TC detector. The coal was a Wyodak coal, heated at 20 k/ms to 1400°C. The helium flow rate was 10 cc/min, yielding $\tau_1 = 7.5$ s. The weighting function was assumed to be:

$$W(t) = \frac{1}{\tau_1} \exp (-t/\tau_1)$$

with the Transform:

$$W(s) = \frac{1}{s\tau_1 + 1}$$

This figure 1.4-1 demonstrates application of the data inversion process and shows that reasonable results should be obtainable from very short capillaries. The input function has been displaced on the time axis due to addition of a hypothetical time lag of approximately 3 seconds. Note that the input signal recovered is much narrower than that measured in the output, thus indicating the applicability of this approach.

The weighting function that was assumed may not be accurate. It is based on assuming a well-stirred reactor with perfect backmixing which in reality may not be the case. A theoretical transfer function will give a good first approximation, but an experimentally determined transfer function will assure a more accurate data inversion. Additional experiments are required to provide an experimental transfer function which would account for both the influence of the reactor itself and the connected tubing. This experimental transfer function can be obtained by using an electric spark from carbon electrodes to provide a pulse (to simulate a delta function) input.

Reactor with Long Capillary

Two sets of data obtained using the capillary configuration were inverted. The helium flow rate and reactor/capillary configuration were maintained constant and the only change was the temperature ($T_{\max} = 1400^\circ\text{K}$,

FIGURE 1.4-1

RECORDED OUTPUTS AND CALCULATED INPUT
WITH DIRECT HOOKUP OF TC DETECTOR TO THE PYROPROBE

800°K) to which the coal was heated. A tube length of 163 cm with an ID ± 0 of 0.46 cm and a helium flow rate of 20 cc/min was used. This gave a capillary mean residence time of 81.3 secs.

Figures 1.4-2 and 1.4-3 show $O(t)$, $O(t)$ normalized and $I(t)$ normalized. In each case only a slowly varying "background" signal representing $I(t)$ was obtained. It is doubtful that this either makes physical sense or that it has physical meaning. It is likely that the long residence times in the capillary (80 seconds) introduced distortions of such an extent that the true devolatilization rates were unrecoverable. In this case, molecular diffusion in the capillary completely washed out any time resolution in the input.

The data on total mass evolved is insufficient to draw conclusions about the coal devolatilization process. The long capillary residence times utilized distorted the signals of the latter to such an extent that the inputs could not be recovered accurately. Even in the cases where the capillary was removed, the data are ambiguous and not self-consistent, and there is no assurance that the reactor did behave as a well-stirred, perfectly backmixed reactor.

As indicated earlier, it was shown in a previous report that this method for the time resolution of rapid coal devolatilization processes could be effective and appeared to have merit. In that work, 25 sets of data for total mass were inverted and interpreted (Blair and Wendt, 1979). The information describing the devolatilization rate was not lost in those cases even though fairly slow response records were utilized. The main difference between that and the present work lies in the length of the capillary in the equipment and the helium flow rates used to sweep the pulse along. In previous work the well-stirred reactor time $\tau_1 = 2.04$ s and that of the capillary $\tau_2 = 3.474$ s. In the current work $\tau_1 = 3.75$ s and $\tau_2 > 81.28$ s, which has been shown to be far too long.

1.5 Results From Time-Resolved Evolution of Nitrogenous Species

In this section the results of work on the time resolved evolution of nitrogenous species are assessed.

The apparatus was the one described previously with the signals for nitrogen species evolution being generated with a P/N detector. Calibration runs were frequently interspersed between coal pyrolysis runs. These calibrations were performed by injecting 0.06 microliter of 5% pyridine by volume in toluene into the head end of the reactor through a septum. A typical trace for the recorder signal is shown in Figure 1.5-1. In this figure the upper trace (trace with the upper baseline) is the record of the P/N signal. The lower trace represents the signal from the thermal conductivity detector. The time of injection is off the figure to the right. Time progresses from right to left and the units are 10 s/inch. The P/N trace with two peaks is a most unusual profile. The first peak starts a gradual rise, followed by an abrupt and precipitous drop back to baseline. This is followed, after 10 s by an equally abrupt and precipitous rise to the second (and major) peak followed by a long tailing return to baseline. The presence of two peaks does not seem to make sense. Pyridine was the only nitrogenous species present. It should have produced only one peak. Also, the abrupt fall off of the first peak does

FIGURE 1.4-2

OUTPUT SIGNALS AND CALCULATED INPUT SIGNAL WITH CAPILLARY CONNECTING
THE TC DETECTOR TO THE PYROPROBE. THE COAL WAS WYODAK, 120 μ g, $T_{\max} = 1400^{\circ}\text{K}$

FIGURE 1.4-3

OUTPUT SIGNALS AND CALCULATED INPUT SIGNAL WITH CAPILLARY
CONNECTING THE TC DETECTOR TO THE PYROPROBE. THE COAL WAS WYODAK, 100 μg , $T_{\text{max}} = 800^\circ\text{C}$

FIGURE 1.5-1

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FIGURE 1.5-2

not make sense. Pyridine might have been expected to produce a tail much like that in the second peak, but certainly not a sharp drop to baseline. Also, for the system to be useful, a method of sharply reducing the tailing behavior of the second peak would have to be devised. These results were repeated in many calibration runs. They indicate severe and complex interaction between the pyridine and the apparatus. Analysis of these results suggested that a dirty system was the source of this behavior. Work at the end of this project showed that severe and careful cleaning of the system with methylene chloride could eliminate the first peak.

Figure 1.5-2 is typical of the many traces from the coal pyrolysis presented in the interim report (Muenker, et. al., 1982). It displays a similar double peaked behavior, but with only about 4 seconds between the peaks. Since results of the calibrations with pyridine showed that the system was malfunctioning regarding nitrogen species, the reliability of coal data was considered unreliable. Therefore the coal data were not inverted and analyzed for nitrogenous species using the data inversion techniques described previously.

The double peaks from coal pyrolyses are probably artifacts of the apparatus, although one cannot be certain of that. If this apparatus is to be useful for the detection of nitrogenous species in the pyrolyzate, significant changes must be made. A short, very clean glass or quartz capillary must be used. Delay times should be short, of the order of 2 or 3 s maximum. The stainless steel reactor should be discarded along with the pyroprobe and the pyrolyses should be performed directly in the capillary. The P/N detector should be close coupled to the capillary with an absolute minimum of metal tubing. The system must be kept scrupulously clean. This probably requires cleaning after each pyrolysis. This will result in very short delays and rise times and a rapid recorder (response time < 10 ms) will be required.

1.6 Conclusions and Recommendations

The experimental procedure utilized to determine coal devolatilization rates involved a captive particle technique in which coal particles were heated at high controlled rates on a platinum ribbon. The products were swept out of the reactor by helium flow to appropriate detectors. A specific limitation of this technique is that the detector measures a signal which has been distorted during the passage of the carrier gas from the coal particle to the detector. It is shown that this distortion can be quantitatively accounted for, and that the data can be quantitatively interpreted provided that:

1. The mean residence time between the coal particle on the pyroprobe and the detector is kept as short as possible (preferably less than 2 seconds and definitely less than 10). This yields a measurable difference between the measured devolatilization signal and that resulting from a delta pulse input, and it is this difference which is shown to be interpretable in terms of original devolatilization rates.
2. The response time of the detector/data acquisition system is less than the actual devolatilization time. This is because the difference between the actual signal and that resulting from a pulse is measurable over times comparable to the actual devolatilization times, even though the actual signal may occur over a much longer period of time.

Additional requirements that must be met for this concept to yield better and more precise data on devolatilization rates include:

1. The weighting function used to invert the data should be experimentally determined by measuring the output of a delta function pulse input such as an electric spark from carbon electrodes. This will permit characterizing the reactor which is probably not a perfect well-stirred reactor.
2. Time resolution of evolution rates for nitrogen species demands extreme care to assure obtaining realistic responses. A short system made of glass tubing should be used. The system should be maintained scrupulously clean which probably means cleaning after each pyrolysis experiment.

These requirements were explicitly delineated after much experimental effort. The data obtained on total mass evolved from coal are insufficient to draw conclusions about the coal devolatilization process. It was possible to recover some input signal using Laplace Transforms, but the rates actually recovered were either not self-consistent or were physically unreasonable. Due to fundamental problems associated with calibration with a known nitrogen compound, none of the time-resolved nitrogen data from coal were inverted. Therefore, additional experiments/according to these requirements are required to obtain interpretable data on relative devolatilization rates of coal nitrogen and other species.

It is the author's conviction that this method can be an effective one for time-resolving evolution rates of nitrogenous species from pyrolyzing coal particles. This conviction is based on improved understanding gained during this research and on the fact that inversions of data for total mass were accomplished previously for a non-optimum system.

2.0. Task 2: Combustion of Coal Pyrolyzation

2.1 Purpose

The purpose of this task was to investigate the combustion behavior of coal pyrolyzate tar.

Coal pyrolyzate tar is a complex and poorly understood material. Its combustion behavior, especially with regard to its fuel nitrogen, is largely unknown, yet it is a significant nitrogen-containing fuel component of pulverized coal combustion systems. The object of this task was to answer two major questions regarding nitrogen conversion in the combustion of this fuel. The first was, whether the nature of the fuel nitrogen species in coal tar combustion is important in determining how the nitrogen is converted. If the answer is no, the details of tar combustion need not be broadly investigated. If the answer is yes, then the second major question must be addressed, to wit, what are the combustion characteristics of pyrolysis tar and how does the nature of the tar and the combustion environment influence those characteristics with regard to the conversion of fuel nitrogen?

To attack these questions, it was necessary to develop laboratory methods of combusting coal tar in a controlled manner. It was also necessary to develop a laboratory scale method of producing tar from selected coals. This was done and the results of these efforts are presented in this section.

2.2 Production of Coal Tar

The initial effort on this task involved developing an apparatus to produce coal tar from a variety of coals. To this end, tests were run on a series of coal tar generators that were assembled during the development process. The details of this effort were reported in (Muenker, et. al., 1982).

The bench-scale coal tar generator that was developed and used in this work is shown in Figure 2.2-1. The apparatus consisted of a 4 inch diameter 2 liter capacity glass resin kettle, a Lindberg crucible furnace, and a dry ice tar collector flask. Typically, a 300 gram charge of powdered coal was placed into the resin kettle. The system was alternately evacuated and filled with helium. This procedure was repeated several times to assure complete removal of oxygen from the system. With a small stream of helium passing through the system, the coal was heated to 600°C. The pyrolysis gases were passed through a water condenser and tar collector flask maintained at dry ice temperature to condense the liquid tar fraction. Noncondensable pyrolysis gases were vented into an exhaust hood. The liquid coal tar products were removed from the condenser and tar collector flask by dissolution in methylene chloride. The low boiling solvent was subsequently stripped from the tar.

A total of six different coals were selected for coal tar generation: four bituminous, one subbituminous and one lignite (Table 2.2-1). Three or four pyrolysis runs were required to collect approximately 100 grams of coal tar. This quantity was sufficient for the tar combustion experiments. Coal tar yields averaged about 10 to 12% based on a dry coal basis. Elemental analyses of the coal tar products are summarized in Table 2.2-2.

FIGURE 2.2-1

THE FINAL CONFIGURATION OF THE
COAL TAR GENERATOR

TABLE 2.2-1

Coals Selected for Coal Tar Generation

<u>Coal</u>	<u>Type</u>	<u>% Tar Yield</u> <u>(600°C Pyrolysis)</u>
Champion Sea Coal	Bituminous	10.8%
Utah	Bituminous	11.8%
Pittsburgh #8	Bituminous	9.8%
Illinois #6	Bituminous	
Wyodak	Sub-Bituminous	
Martin Lake	Texas Lignite	

TABLE 2.2-2

Coal Tar Analyses

<u>Source</u>	<u>%C</u>	<u>% H</u>	<u>% N</u>	<u>% S</u>	<u>% O</u>
Champion Sea Coal	82.08	7.94	1.06	0.58	8.07
Utah	84.80	9.86	0.62	0.26	5.06
*ETSP Coal Liquid	83.61	9.07	0.84	0.84	5.41

*Coal Liquid from East Texas Coal Gasification Pilot Plant.

Because of the difficulty of generating large quantities of coal tar for unit shakedown and initial testing, commercial sources were found. Ten gallons of coal tar were obtained from the Bethel Steel Company and four gallons were obtained from the Exxon East Texas Coal Gasification (ETSP) pilot plant. The analysis of the ETSP tar is included in Table 2.2-1.

2.3 Tar Combustor

A combustor was designed to burn coal tar in a controlled manner. It is shown in Figures 2.3.-1,2,3,4,5. It was a gas fired laminar premixed burner with provision for tar injection at the center of the flame. It was intended to operate as follows. The flat flame combusts a chosen fuel (CH_4 , natural gas, CO, etc) with air to produce the desired combustion environment. Tar is pumped at a constant rate through a steam jacketed stainless steel tube and injected into the combustion gas immediately above the level of the flat flame. The tar pumping rate is adjusted to a rate that just matches the rate of consumption of tar in the flame. The tar should form a constant sized drop at the injection point, and not overflow onto the porous plate flameholder. It was intended that the tar diffusion flame that stabilizes above the drop be probed axially and vertically to determine the distributions of various chemical species, especially the nitrogenous species NO_x , HCN, and NH_3 . Provision was made for on-line analysis of CO, CO_2 , O_2 , NO_x , and unburned hydrocarbons with standard instruments. HCN and NH_3 were determined by combined catalytic conversion, adsorption and difference techniques. In this latter method NO is measured by a standard on-line technique. Then the total fixed nitrogen in the gas is converted to NO by reaction over a catalyst (Hardy, 1982) and measured as NO. Finally, the HCN in the gas is adsorbed on ascarite and the remaining fixed nitrogen is converted to NO and measured.

In the initial tests, an attempt was made to pump the tar through the injection tube with a standard Sage Syringe pump. This attempt failed because the pump was unable to pump the very viscous tar. Consequently a cyclical positive displacement type pump was used. This caused a pulsating tar flow and these pulsations were apparent in extreme pulsations of the tar diffusion flame. These pulsations were greatly reduced by adding a pulse dampener to the pump, but they were never entirely eliminated. No cyclical pump can match the steady and precise flow that is obtainable from a syringe type pump. Syringe type pumps can be made to generate arbitrarily low flow rates, and this work required very low flow rates to balance the tar injection and combustion rates. Any future work with this type of burner should employ a heavy duty high pressure syringe pump which can produce the necessary steady very low tar injection rates.

The tar spattered and caked as it was heated. This made balancing the injection rate with the combustion rate quite difficult. Because of the imbalance between tar injection and combustion rates, the tar spilled over the tip of the injection tube and pooled on the sintered disk around the tube. To compensate for this problem a "tar cup" was formed by placing stainless steel washers around the injector and the tar burned from a "pool" in this cup (Figures 2.3-2,3). The tar diffusion flame still exhibited instabilities which were only partially further suppressed by surrounding the burner with a protective chimney to reduce induced air currents around it.

FIGURE 2.3-1
SECTION VIEW OF
POROUS PLUG TAR BURNER

SCALE: FULL

Figure 2.3-2
OVERALL VIEW OF TAR COMBUSTOR

FIGURE 2.3-3

CLOSEUP VIEW OF TAR COMBUSTOR SHOWING TAR CUP
SITTING ON POROUS BURNER AND COAXIAL WITH TAR INJECTION PORT

FIGURE 2.3-4

TAR COMBUSTOR IN OPERATION WITH CHIMNEY IN PLACE

FIGURE 2.3-5

INLET END OF WATER COOLED QUARTZ SAMPLE PROBE

A quartz lined water cooled probe was used to axially sample the flame. Quartz was used to suppress sample-probe surface reactions, and water cooling was used to quench the reaction gasses immediately at the sample point.

The system that was finally used for the experiments is shown schematically in Figure 2.3-6. The results of preliminary shakedown experiments are shown in Table 2.3-1. The negative values that appear are the result of insufficient precision when using the difference method. This method requires high precision in the direct measurements to give reasonable precision for the values that are obtained by difference. In this regard, direct measurement of all species is superior. However, if the operation of the experiment is improved so that the instability is eliminated the difference method should prove adequate.

The results in Table 2.3-1 show a decrease in both NO and TFN concentrations with increasing height of the sample probe above the plane of the burner. This might be the result of fixed nitrogen destruction progressing with time (as is reasonable to expect under these combustions conditions) but it also might result from increasing dilution of the diffusion flame products with surrounding (premixed flat flame) combustion products as the sample point moves downstream in the flow. It is not possible to ascertain which is the case from these data. However, the data do show that the experimental system can be made to work.

2.4 Conclusions and Recommendations

A laboratory scale combustor was designed and built for investigating the combustion behavior of coal tar to determine if tar nitrogen conversion is a function of tar type. Preliminary tar combustion data have demonstrated that the experimental system can be made to work with additional research. To produce useful quantitative data, several conditions must be met. They are:

1. Problems of flame stability must be solved.
2. Tar flowrates must be significantly reduced.
3. The tar flowrate must be constant, with no pulsations.
4. The gas sampling probe must be very small relative to the dimensions of the tar diffusion flame. Certainly the inlet diameter must not exceed a maximum of about 1 mm.
5. The sampling must be isokinetic.
6. An inert tracer should be used to permit checking of dilution effects.

These are stringent, but achievable requirements. When met, this apparatus will be capable of producing useful information regarding nitrogen conversion in coal tar combustion.

FIGURE 2.3-6

SCHEMATIC FLOW DIAGRAM OF TAR
COMBUSTION APPARATUS

Table 2.3-1

Results from Preliminary Tar Combustion Experiments With ESTP Coal Liquid

25 g/min Air, 0.75 g/min CH₄, 0.075 g/min Tar

Neglecting Tar, Overall $\phi = 0.52$

Including Tar, Overall $\phi = 0.56$

Test #	Species	Concentration, ppm	Concentration, %	Height Above Tar Pool, mm
1	O ₂		6.8	15
1	CO		0.4	15
1	NO	64,68,78,avg. 70		15
1	TFN*	72		15
1	TFN - HCN	78,82,avg. 80		15
	By Difference			
1	HCN	-8		15
1	NH ₃	10		15
2	O ₂		6.8	15
2	CO		0.4	15
2	NO	90,96,72,82,avg. 85		15
2	TFN	105,115,avg. 110		15
2	TFN - HCN	78,82,avg. 80		15
	By Difference			
2	HCN	30		15
2	NH ₃	-5		15
3	O ₂		6.8	11
3	CO		0.5	11
3	NO	120,135,125,avg. 127		11
3	TFN	155,170,avg. 163		11
3	TFN - HCN	140		11
	By Difference			
3	HCN	23		11
3	NH ₃	13		11

*Total Fixed Nitrogen

Table 2.3-1

Results from Preliminary Tar
Combustion Experiments with ESTP Coal Liquid

(Continued)

4	O ₂		6.8	11
4	CO		0.5	11
4	NO	125,145,115,avg. 128		11
4	TFN	160,175,avg. 168		11
4	TFN - HCN	130		11
	By Difference			
4	HCN	38		11
4	NH ₃	2		11
5	O ₂		6.8	11
5	CO		0.5	11
5	NO	175,190,135,avg. 167		11
5	TFN	205,225,avg. 215		11
5	TFN - HCN	150		11
	By Difference			
5	HCN	65		11
5	NH ₃	-17		11

3.0 TASK 3: Analytical Modeling

3.0.1 Purpose and Scope

Theoretical work completed during the period covered by this contract was focused on two areas: i) development of a nitrogen devolatilization model based on a Gaussian distribution of activation energies and ii) development of a coal combustion model framework to allow the devolatilization results obtained to be utilized in a comprehensive coal combustion model.

The purpose of the first topic was to correlate and generalize the experimental results to be obtained from this contract and to provide an engineering model that would predict the relative rates of evolution of nitrogen and other species as functions of temperature, time and coal composition. Determination and prediction of relative rates of nitrogen and other oxygen consuming species is critical in order to predict the amount of coal nitrogen oxidized to form NO in the early portion of the combustion sequence. A distributed activation energy model appeared to be most appropriate and so that is the approach taken in this work.

The second area attacked in this work was to develop a combustion model framework, which is required in order to use the results from this contract to help predict the optimum time, temperature, and environment history necessary for coal particles to minimize conversion of chemically bound nitrogen to NO and other bound nitrogenous species. The model does not concern itself with mixing or aerodynamics; rather, it is a kinetic model that simulates the combustion/pyrolysis behavior of an heterogeneous coal/air mixture as it travels along a stream tube. The model is, therefore, that of a plug flow reactor. The model includes detailed gas phase chemistry (stiff kinetics), devolatilization, char burnout including structural, surface area, internal diffusion and reaction effects, and effects of particle size distributions. Work completed includes the incorporation of a fairly sophisticated heterogeneous char and char nitrogen oxidation model into our multi-purpose gas phase kinetics computer code (REKINET). Results presented below include comparison with available data and other useful predictions of the model. A model framework to allow incorporation of coal devolatilization kinetics is also described.

This portion of the report is divided into two parts. First, Section 3.1 focuses entirely on the modeling of devolatilization processes. In that subsection, the background to the distributed activation energy model is described, the behavior of the model under various choices of parameters and heating rates is presented and its future potential and physical appropriateness is discussed. Unfortunately, lack of experimental data prevented one key aspect of this work from being completed, namely the calibration of the model to fix its parameters and confirmation that it could, in a simple way, account for many of the observed effects of variations of coal composition on conversion of coal nitrogen to nitrogen oxides.

Section 3.2 is concerned wholly with the comprehensive plug flow reactor coal combustion model developed under this contract. First the background and overall modeling approach are described. Then the model development is

delineated in detail, with special emphasis on heterogeneous reaction modeling and devolatilization modeling. Lastly model results are presented, compared to existing data and subsequently discussed. This section is presented in sufficient detail so that other workers in the field can adopt or modify the approach as they see fit. A listing of the pertinent computer code is included in the Appendix.

3.1 DEVOLATILIZATION MODEL

3.1.0 Background

Devolatilization models can fall into three rough categories; namely,

i) competitive reaction models in which the residue is not an unreacted reactant but one of at least two products of reaction,

ii) reactant consumption models in which the residue is not an inert product but rather an unreacted reactant,

iii) combinations of i) and ii) above.

The first model is widely used since it predicts variations in asymptotic yields with temperature and thus appears to have relevance with experimental data. The version by Kobayashi et al. (1977) is most commonly used in current modeling studies. However, based on experiments on the reheating of partially devolatilized coal and coal char described by Blair and Wendt (1981), we believe that model is incorrect and so we favor one in which the residue is an unreacted reactant, namely, the second model described above. This is also the approach taken by Solomon and coworkers (1979) as well as Suuberg, Peters and Howard (1979) at MIT. The truth probably lies in the third approach which is a combination of the first two.

In this work, our approach follows that of workers at Bergbau Forschung in Essen, Germany and subsequently developed by Anthony and Howard (1975). For brevity, we call it the Bond Energy Model.

Model Description and Basis

The Bond Energy model is based on the following assumptions:

1) bond energy pertinent to a nitrogen atom in coal is proportional to the temperature at which the bond connecting that nitrogen to the parent coal ultimately severs,

2) a Semenov relationship between activation energy and bond energy is valid,

3) the preexponential factor in the thermal decomposition is independent of bond broken and is constant for all coals.

Let the quantity of nitrogen released (at time = ∞) between temperatures T and $T + dT$ be given by

$$dN = \phi(T)dT \quad 3.1.0-1$$

where

$$\phi(T) = \frac{1}{\sqrt{2\pi}\sigma_T} \exp \left[-\frac{1}{2} \left(\frac{T-T_m}{\sigma_T} \right)^2 \right] \quad 3.1.0-2$$

and, for a specific coal (Colorado Bituminous, for example)

$$T_m = 1218K \quad 3.1.0-3$$

$$\sigma_T = 363.6K$$

T_m and σ_T can be obtained for each coal from asymptotic data, and can be correlated with coal composition.

Let the mass function held with bond energy between H and $H + dH$ be

$$dN = f(H)dH \quad 3.1.0-4$$

where, according to the first assumption

$$H = aT + b \quad 3.1.0-5$$

where a and b are constants, independent of coal composition.

The Semenov Rule for endothermic reactions is given by

$$E = 11500 + 0.75H \quad 3.1.0-6$$

where E is the activation energy.

Thus,

$$\begin{aligned} E &= 11500 + 0.75b + 0.75aT \\ &= \alpha + \beta T \end{aligned} \quad 3.1.0-7$$

where α and β are constants independent of coal composition.

The mass fraction of nitrogen evolved with activation energy E , between E and $E + dE$ is given by

$$dN = g(E)dE \quad 3.1.0-8$$

where

$$g(E) = \frac{1}{\sqrt{2\pi}\sigma_E} \exp \left[-\frac{1}{2} \left(\frac{E-E_m}{\sigma_E} \right)^2 \right] \quad 3.1.0-9$$

and

$$E_m = \alpha + \beta T_m \quad (\text{e.g., } T_m = 1218\text{K for Colorado Coal})$$

$$\sigma_E = \beta \sigma_T \quad (\sigma_T = 363.6\text{K for Colorado Coal}) \quad 3.1.0-10$$

Finally the nitrogen loss as a function of time is given by

$$W_N(t) = \frac{1}{\sigma_E \sqrt{2\pi}} \int_{-\infty}^{\infty} \exp \left[-k_o \int_0^t \exp \left(-\frac{E}{RT} \right) dt - \frac{1}{2} \left(\frac{E - E_m}{\sigma_E} \right)^2 \right] dE \quad 3.0.1-11$$

There are three unknown parameters: σ_E , E_m , k_o . However, from the preceeding development we can assume

$$\sigma_E = \beta \sigma_T$$

$$E_m = \alpha + \beta T_m$$

where σ_T and T_m are obtained from asymptotic data on nitrogen loss for each coal (or correlation thereof) and α, β are universal constants, i.e., they do not depend on coal composition. Time resolved data from one coal is required to evaluate α , β , and k_o .

This approach takes account of differences in coal structure by tying devolatilization rates to asymptotic yield data, which can be obtained much more easily than rate data. The validity of assumptions used can only be tested with true time resolved nitrogen release data, which are presently unavailable.

3.1.1 Model Development

As noted previously, Equation 3.0.1-11 is a mathematical expression which describes the fraction of nitrogen lost (from pyrolyzing coal) as a function of time. Computer programs have been written for this model to assess its ability to predict experimentally observed cumulative yield trends for both iso and non-isothermal devolatilizations.

The integration is carried out over a Gaussian distribution of activation energies extending from negative to positive infinity. Although negative activation energies are not attainable, the integration limits can be extended to negative infinity for purposes of simplifying the numerical evaluation. This will cause negligible differences in the answers, but care must be taken when estimating the standard deviation σ_E . Given the mean activation energy, E_m , σ_E was estimated to be no larger than that which allowed 99% of the area under the curve of the normal distribution of activation energies to lay on the positive E axis.

For the isothermal case, there is no dependence of temperature on time and the inner integral can be analytically evaluated. This results in the following expression:

$$W_N(t) = \frac{1}{\sigma_E \sqrt{2\pi}} \int_{-\infty}^{+\infty} \exp \left[-k_0 t \exp \left(-\frac{E}{RT} \right) - \frac{1}{2} \left(\frac{E-E_m}{\sigma_E} \right)^2 \right] dE \quad 3.1.1-1$$

For the nonisothermal case, a constant heating rate [where Temperature = (heating rate x time) + initial temperature], followed by an isothermal holding time, τ , is assumed. The equation which results is as follows:

$$W_N(t) = \frac{1}{\sigma_E \sqrt{2\pi}} \int_{-\infty}^{+\infty} \exp \left[-k_0 \int_0^{t'} \exp \left(-\frac{E}{R(mt + T_0)} \right) dt - k_0 \tau \exp \left(-\frac{E}{RT_F} \right) - \frac{1}{2} \left(\frac{E-E_m}{\sigma_E} \right)^2 \right] dE \quad 3.1.1-2$$

where:

$$t'_{\max} = \frac{T_F - T_0}{m}$$

m = heat-up rate

Substituting

$$x = \frac{E-E_m}{\sqrt{2} \sigma_E}; \quad E = \sqrt{2} \sigma_E x + E_m;$$

$$dE = \sqrt{2} \sigma_E dx$$

yields for the isothermal case:

$$W_N(t) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \exp \left[-k_0 t \exp \left(\frac{-\sqrt{2} \sigma_E x - E_m}{RT} \right) \exp (-x^2) \right] dx, \quad 3.1.1-3$$

and for the nonisothermal case:

$$W_N(t) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \exp \left[-k_0 \int_0^{t'} \exp \left(\frac{-\sqrt{2} \sigma_E x - E_m}{R(mt + T_0)} \right) dt - k_0 \tau \exp \left(\frac{-\sqrt{2} \sigma_E x - E_m}{RT_F} \right) \exp (-x^2) \right] dx. \quad 3.1.1-4$$

The outer integral can be solved using a Gaussian-Hermite Quadrature algorithm, i.e.,

$$\int_{-\infty}^{+\infty} f(x) e^{-x^2} dx = \sum_{i=0}^n w_i f(x_i),$$

where e^{-x^2} is the weighting function. The Gaussian-Hermite algorithm was tested on two definite integrals to determine its relative precision. Based on these results a 20 point Hermite algorithm was chosen. The inner integral can be solved using a Gaussian-Legendre Quadrature algorithm. Since this integral evaluates a well behaved function, a 16 pt. algorithm was assumed adequate. As a final check, the cumulative yield curves should asymptotically approach unity.

Prediction of Devolatilization Rates

To predict devolatilization rates the mathematical expression was then differentiated with respect to time. The resulting expressions for both isothermal and nonisothermal devolatilization are:

for the isothermal case,

$$\frac{d}{dt} \left(\frac{V}{V^*} \right) = \frac{k_o}{\sigma_E \sqrt{2\pi}} \int_0^{\infty} \exp [-k_o t] \exp \left(-\frac{E}{RT} \right) - \frac{(E-E_m)^2}{2\sigma_E^2} \exp \left(-\frac{E}{RT} \right) dE$$

3.1.1-5

and in the nonisothermal case, for times during the heat-up period,

$$\begin{aligned} \frac{d}{dt} \left(\frac{V}{V^*} \right) &= \frac{k_o}{\sigma_E \sqrt{2\pi}} \int_0^{\infty} \exp \left[-k_o \int_0^t \exp \left(\frac{-E}{R(mt+T_o)} \right) dt \right. \\ &\quad \left. - \frac{E}{R(mt+T_o)} - \frac{1}{2} \left(\frac{E-E_m}{\sigma_E} \right)^2 \right] dE \end{aligned}$$

3.1.1-6

or for times past the heat-up period,

$$\begin{aligned} \frac{d}{dt} \left(\frac{V}{V^*} \right) &= \frac{k_o}{\sigma_E \sqrt{2\pi}} \int_0^{\infty} \exp \left[-k_o \int_0^t \exp \left(-\frac{E}{R(mt+T_o)} \right) dt \right. \\ &\quad \left. - k_o t \exp \left(\frac{-E}{RT_F} \right) + k_o t' \exp \left(-\frac{E}{RT_F} \right) - \frac{E}{RT_F} - \frac{1}{2} \left(\frac{E-E_m}{\sigma_E} \right)^2 \right] dE \end{aligned}$$

3.1.1-7

Substituting

$$x = \frac{E}{RT_F}; \quad E = xRT_F; \quad dE = RT_F dx, \quad (T_F = T \text{ in isothermal case}),$$

yields, for the isothermal case:

$$\frac{d}{dt} \left(\frac{V}{V^*} \right) = \frac{k_o RT_F}{\sigma_E \sqrt{2\pi}} \int_0^\infty \exp \left[-k_o t \exp(-x) - \frac{(xRT_F - E_m)^2}{2\sigma_E^2} \right] \exp(-x) dx$$

3.1.1-8

and for times during the heat-up period for nonisothermal cases

$$\begin{aligned} \frac{d}{dt} \left(\frac{V}{V^*} \right) &= \frac{k_o RT_F}{\sigma_E \sqrt{2\pi}} \int_0^\infty \exp \left[-k_o \int_0^t \exp \left(\frac{-xT_F}{mt + T_0} \right) dt \right. \\ &\quad \left. - \frac{xT_F}{mt + T_0} - \frac{1}{2} \left(\frac{xRT_F - E_m}{\sigma_E} \right)^2 \right] dx \end{aligned}$$

3.1.1-9

or for times past the heat-up period

$$\begin{aligned} \frac{d}{dt} \left(\frac{V}{V^*} \right) &= \frac{k_o RT_F}{\sigma_E \sqrt{2\pi}} \int_0^\infty \exp \left[-k_o \int_0^{t'} \exp \left(\frac{-xT_F}{mt + T_0} \right) dt - k_o t \exp(-x) \right. \\ &\quad \left. + k_o t' \exp(-x) - x - \frac{1}{2} \left(\frac{xRT_F - E_m}{\sigma_E} \right)^2 \right] dx \end{aligned}$$

3.1.1-10

Note that this numerical evaluation is most easily done over integration limits from zero to infinity.

In these equations the outer integral can be solved using a Gaussian-Laguerre Quadrature algorithm, i.e.,

$$\int_0^\infty f(x) e^{-x} dx = \sum_{i=0}^n w_i f(x_i)$$

where e^{-x} is the weighting function. A 16 pt. formula has been chosen.

If the integral of the above normalized rate expressions is taken over all time, the area under these curves must equal unity. This criteria has been used to test the accuracy of the equation and the precision of the numerics.

3.1.2 Model Results

First estimates of the model's parameters have been chosen based on information available in the literature (Elliott, 1981). These parameters have been varied with both the cumulative yield and rate expressions; and the results have been evaluated to determine if the model is representative.

The following table (3.1.2-1) lists the isothermal cumulative yield computer runs which have been evaluated. Table 3.1.2-2 lists the nonisothermal cumulative yield computer runs which have been evaluated.

Table 3.1.2-1

Test	E_m (Kcal)	σ_E (Kcal)	k_{o-1} (msec ⁻¹)	Temp. (°K)
1	40.0	15.5	1×10^4	1673
2	40.0	15.5	1×10^4	1000
3	40.0	15.5	1×10^4	293
4	40.0	10.0	1×10^4	1673
5	40.0	10.0	1×10^4	1000
6	40.0	10.0	1×10^4	293
7	55.2	15.5	1×10^4	1000

Table 3.1.2-2

Runs 1-9

T_{max} = 1673K and 1200K

$T_{initial}$ = 293K

Heating Rate = 20.0K/msec

Test	E_m (Kcal)	σ_E (Kcal)	k_{o-1} (msec ⁻¹)
1	55.2	21.4	1×10^4
2	55.2	7.13	1×10^4
3	55.2	21.4	1×10^{10}
4	55.2	7.13	1×10^{10}
5	40.0	15.5	1×10^4
6*	40.0	5.17	1×10^4
7	40.0	15.5	1×10^{10}
8	40.0	5.17	1×10^{10}
9**	55.2	5.17	1×10^4

*Also run using a heating rate of 2.0K/msec.

**Only run for T_{max} = 1673K. No run made for T_{max} = 1200K.

An analysis of the previously noted graphs leads to the following conclusions:

Isothermal-Cummulative Yield

1. As anticipated both mathematically and qualitatively, the quantity of nitrogen devolatilized increases asymptotically with time.
2. Also as anticipated, the quantity of nitrogen devolatilized after any given length of time increases with increasing temperature. However, the more significant result is that, for certain values of parameters, the apparent asymptotic yield after long times increases with increasing temperature. This agrees with the experimental data.
3. The behavior of the numerics when the value of σ_E is changed can also be predicted upon examining equation 3.1.1-1. As Figure 3.1.2-1 shows, a comparison of two runs differing only in the value of σ_E indicates an increase in the amount of nitrogen devolatilized with an increase in σ_E , at any given time. In contrast to this, Figure 3.1.2-2 shows that, at long times, the run with the narrower distribution of activation energies can yield more nitrogen. This can be explained as follows: for a given temperature, at each time evaluated, all possible values of E (activation energies) in the given distribution are weighted, and each corresponding reaction devolatilizes a quantity of nitrogen. The narrower the distribution, the smaller is the number of possible reactions contributing relatively significant quantities of nitrogen. Low temperatures will tend to favor reactions with lower activation energies. A wider distribution results in more reactions with low activation energies. Therefore, for a high yield, low temperatures favor a wider distribution, as seen in Figure 3.1.2-1. At early times, no one reaction has had time to contribute a significant quantity of nitrogen--therefore, the more reactions occurring, the greater the quantity of nitrogen released. Even if the temperature is sufficiently high for all possible activation energies to be operative, a wider distribution will tend to allow the yield to rise more rapidly initially then level off as less nitrogen remains to be devolatilized. A narrower distribution will cause the yield to rise more gradually initially. After a given length of time the two curves intersect. At this point the narrower distribution has more reactive nitrogen remaining than that of the wider distribution. Therefore, this curve now rises more rapidly.
4. As seen in Figure 3.1.2-3, increasing the mean activation energy has the same effect as lowering the devolatilization temperature. This follows logically, as reactions having higher activation energies require higher temperatures. If the temperature is not raised along with the activation energies, a lesser number of reactions will occur.

Nonisothermal-Cummulative Yield

1. As anticipated, Figures 3.1.2-4 and 3.1.2-5 show that when the final temperature of the pyrolysis is lowered, the amount of nitrogen devolatilized at any given time also tends to be lower. Also, for

Figure 3.1.2-1. Cumulative Nitrogen Devolatilization Yields for Isothermal Pyrolysis.

Figure 3.1.2-2. Cumulative Nitrogen Devolatilization Yields for Isothermal Pyrolysis: Effect of σ_E .

Figure 3.1.2-3 Cumulative Nitrogen Devolatilization Yields for Isothermal Pyrolysis: Effect of E_m
 Temperature = 1000K; $\sigma_E = 15.5$ Kcal; $k_0 = 1 \times 10^4 \text{ ms}^{-1}$

Figure 3.1.2-4. Monisothermal Cumulative Yields: Final Temperature = 1673K;
 $dT/dt = 20 \text{ K/ms}$ [See text for parameters for curves #1-8].

(FRACTION) NITROGEN DEVOLATILIZATION

Figure 3.1.2-5. Nonisothermal Cumulative Yields: Final Temperature = 1200K; $dT/dt = 20K/ms$ [Curves correspond to those in Fig. 3.1.2-4].

certain values of parameters, the apparent asymptotic yield at moderate times changes with temperature.

2. As expected, the amount of nitrogen devolatilized increases with time.
3. Also, as was previously explained, when a "wider" σ_E is used, the quantity of nitrogen released is initially (when both time and temperature are low) greater than parallel cases using a narrower distribution of activation energies. As time increases and the temperature rises, however, the narrower distribution begins to yield more nitrogen (see Figures 3.1.2-4 and 3.1.2-5).
4. A comparison of Figures 3.1.2-6 and 3.1.2-7 shows that an increase in the mean activation energy causes the yield curve to begin later and rise more slowly. The effect is similar to that of lowering the final temperature.
5. A comparison of Figures 3.1.2-7 and 3.1.2-8 shows the effect of a slower heating rate on the cumulative yield. The devolatilization begins later and takes longer to reach completion. In some respects the behavior is qualitatively similar to use of a wider distribution of activation energies. Given the same final temperature, however, regardless of heat-up rate, the curves should ultimately approach the same value.

Results from Model Expressed in Terms of Devolatilization Rates

Table 3.1.2-3 lists the isothermal devolatilization rate computer runs which have been evaluated. The nonisothermal devolatilization rate computer runs are listed in Table 3.1.2-4.

Table 3.1.2-3

Test	E_m (Kcal)	σ_E (Kcal)	Temp. K
1	40.0	15.5	1673
2	55.2	15.5	1673
3	55.2	21.4	1673
4	55.2	21.4	1000

Figure 3.1.2-6. Nonisothermal Cumulative Yield: Final Temperature = 1673K; $\frac{dT}{dt} = 20.0 \frac{K}{ms}$;
 $E_m = 55.2 \text{ Kcal}$; $\sigma_E = 5.17 \text{ Kcal}$; $k_o = 1 \times 10^4 \text{ ms}^{-1}$.

Figure 3.1.2-7. Nonisothermal Cumulative Yield: Final Temperature = 1673K; $\frac{dT}{dt} = 20 \frac{K}{ms}$;
 $E_m = 40.0 \text{ Kcal}$; $\sigma_E = 5.17 \text{ Kcal}$; $k_o = 1 \times 10^4 \text{ ms}^{-1}$.

Figure 3.1.2-8. Nonisothermal Cumulative Yield: Final Temperature = 1673K; $\frac{dT}{dt} = 2.0 \frac{K}{ms}$;
 $E_m = 40.0 \text{ Kcal}$; $\sigma_E = 5.17 \text{ kcal}$; $k_o = 1 \times 10^4 \text{ ms}^{-1}$.

Table 3.1.2-4

Test	E_m	σ_E	T_F	Heating Rate k/msec
1	40.0	7.5	1673	20
2	40.0	6.0	1673	20
3	40.0	5.0	1673	20
4	55.2	5.0	1673	20
5	40.0	5.0	1673	20
6	40.0	5.0	1673	2.0

An analysis of these graphs leads to the following conclusions:

Normalized Isothermal Devolatilization Rate

1. For very short times, the normalized isothermal curves start at a maximum rate and asymptotically decrease to zero with time. This behavior is predictable from Equation 3.1.1-5 and is theoretically reasonable. The temperature of the devolatilization doesn't increase, therefore the rate should be most rapid when all the coal is present to react.
2. As anticipated both mathematically and conceptually, the lower the temperature, the lower the devolatilization rate. This is clearly shown on Figure 3.1.2-9.
3. A narrower distribution of activation energies (a lower value of σ_E) slows the devolatilization rate, as shown in Figure 3.1.2-10. This is mathematically apparent, as well as theoretically reasonable behavior. As noted previously, a smaller distribution reduces the possible number of reactions. At early times when no single reaction has generated much nitrogen, the amount of reactions significantly effects the devolatilization rate. In time, the smaller distribution containing fewer reactions "catches up" and then will have the higher rate.
4. As shown in Figure 3.1.2-11, increasing the mean activation energy has an effect quantitatively similar to lowering the devolatilization temperature (see Figure 3.1.2-9). As noted previously, this is reasonable behavior.

Normalized Nonisothermal Devolatilization Rates

1. Plots of the data generated from the normalized nonisothermal model, Figures 3.1.2-12 and 3.1.2-13 in some cases show a finite initial rate. This decreases towards zero and then sweeps out a curve of "normally" distributed rates with respect to time. The initial finite rate appearing at short times reflects a normalized isothermal rate curve for temperatures around 293K. The height and area of this first peak is therefore affected by a change in the value of σ_E in the same manner as the change affects the normalized isothermal model. By decreasing the value of σ_E , the peak can virtually be eliminated, as is demonstrated on

Figure 3.1.2-9. Isothermal Devolatilization Rates: Effect of Temperature. $E_m = 55.2$ Kcal;
 $c_E = 21.4$ Kcal; $k_D = 1 \times 10^4$ ms⁻¹.

Figure 3.1.2-10. Isothermal Devolatilization Rates: Effect of σ_E ; Temperature = 1673K; $E_m = 55.2 \text{ Kcal}$; $k_o = 1 \times 10^4 \text{ ms}^{-1}$.

Figure 3.1.2-11. Isothermal Devolatilization Rates: Effect of E_m . Temperature = 1673K; $k_0 = 1 \times 10^4 \text{ ms}^{-1}$; $\sigma_E = 15.5 \text{ Kcal}$.

Figure 3.1.2-12. Nonisothermal Devolatilization Rate. Effect of σ_E ; Final Temperature = 1673K;
 $\frac{dT}{dt} = 20 \frac{K}{ms}$; $E_m = 40.0$ Kcal; $\sigma_E = 10.0$ Kcal; $k_o = 1 \times 10^4 \text{ ms}^{-1}$.

Figure 3.1.2-13. Nonisothermal Devolatilization Rates: Effect of σ_E . Final Temperature = 1673K; $\frac{dT}{dt} = 20 \frac{K}{ms}$; $E_m = 40.0$ Kcal; $k_0 = 1 \times 10^4 \text{ ms}^{-1}$.

Figure 3.1.2-14. Nonisothermal Devolatilization Rates: Effect of σ_E ; Final Temperature 1673K;
 $\frac{dT}{dt} = 20.0 \frac{K}{ms}$; $E_m = 40.0$ Kcal; $k_0 = 1 \times 10^4 \text{ ms}^{-1}$.

Figures 3.1.2-13 and 3.1.2-14. Realistically one would expect a very slow rate and a negligibly small quantity of nitrogen to be released at a temperature of 293K. Data available in literature (Elliott, 1981) in fact suggest this behavior. Therefore, the most appropriate value of σ_E should result in a curve which begins essentially at zero and gradually rises with time, as the temperature of the devolatilization increases. This leads to the choice of $\sigma_E = 5.0$ Kcal for the base parameter. Note that as increasingly large values of σ_E are chosen, the maximum height of the curve is lowered and multiple peaks appear (see Figures 3.1.2-12, 3.1.2-13, 3.1.2-14). The peaks and valleys are due to reaching temperature plateaus. In order for more nitrogen to be devolatilized, a higher temperature must be reached. The peaks are less evident with decreasing value of σ_E because when devolatilization does occur more reactions are available for devolatilization at each given temperature. Therefore, excluding the existence of an initial peak, the shape of the curves are as would be expected, both mathematically and physically. First, as the temperature rises with time, the devolatilization rate also rises. As before, for short times, the greater the distribution of activation energies (i.e., the larger the value of σ_E), the greater the rate. As time passes and the temperature rises further the curve with the smallest value of σ_E has the greatest rate. When the temperature reaches its maximum value, however, the rate begins to decrease. This shows the effect of having less material left to be devolatilized. In time, the curve with the largest value of σ_E again has the greatest rate. The wider distribution causes overall a more gradual devolatilization, and therefore, at this later stage it probably has more reactive nitrogen left than that of the narrower distribution.

2. As shown in Figure 3.1.2-15 the effect of lowering the heating rate is to retard and spread out the devolatilization over time. As clearly shown in Figure 3.1.2-16 the devolatilization curve is distorted in a manner qualitatively similar to that resulting from use of a wider distribution of activation energies. A slower heat-up time could cause various plateaus to be reached. At such times no more nitrogen can be devolatilized until some higher temperature has been reached.
3. Figure 3.1.2-17 shows that use of a larger mean activation energy slows down the devolatilization. As previously noted, the effect is similar in some respects to that of lowering the final temperature (see Figure 3.1.2-18).
4. Finally, as noted above and shown in Figure 3.1.2-18, use of a lower final temperature slows the devolatilization. It also shifts the peak to the left, as the maximum rate occurs at the maximum temperature and the lower maximum temperature is reached more quickly.

3.1.3 Numerical Evaluation of the Convolution Integral

Numerical evaluation of the convolution integral may be difficult, as the time span of the devolatilization and that of the weighting function may be widely disparate. The method of solution may be divided into the two extreme cases:

Figure 3.1.2-15. Nonisothermal Devolatilization Rates: Effect of $\frac{dT}{dt}$. Final Temperature = 1673K; $E_m = 40.0$ Kcal; $\sigma_E = 5.0$ Kcal; $k_o = 1 \times 10^4$ ms $^{-1}$.

Figure 3.1.2-16. Nonisothermal Devolatilization Rate, Final Temperature = 1673K;
 $\frac{dT}{dt} = 2.0 \frac{K}{ms}$; $E_m = 40.0 \text{ Kcal}$; $\sigma_E = 5.0 \text{ Kcal}$; $k_o = 1 \times 10^4 \text{ ms}^{-1}$.

Figure 3.1.2-17. Nonisothermal Devolatilization Rates: Effect of E_m ; Final Temperature = 1673K;

$$\frac{dT}{dt} = 20.0 \frac{\text{K}}{\text{ms}}; \sigma_E = 5.0 \text{ Kcal}; k_0 = 1 \times 10^4 \text{ ms}^{-1}.$$

Figure 3.1.2-18. Nonisothermal Devolatilization Rates: Effect of Final Temperature. $\frac{dT}{dt} = 20.0 \frac{K}{ms}$;
 $E_m = 40.0 \text{ Kcal}$; $\sigma_E = 5.0 \text{ Kcal}$; $k_o = 1 \times 10^4 \text{ ms}^{-1}$.

- I. Suppose for the conditions of interest that the devolatilization is 99 percent complete after 0.8 sec., and the weighting function begins to be "significant" at 50 sec. and essentially "ends" at 125 sec. In this case, the lower limit of integration should never be less than 50 sec. or the upper limit greater than 125 sec. For a given upper limit of integration, the lower limit should be set 0.8 sec. earlier. Because the devolatilization pulse is so narrow, Simpson's routine with an adjustable step size is used, as it is accurate, precise and simple to apply.
- II. Given the same weighting function, suppose the devolatilization rate is evaluated at a lower final temperature. The devolatilization may therefore proceed very slowly, possibly taking as long as 1×10^5 sec. to be 99 percent complete. In this case, the lower limit will be 50 sec. The upper limit, however, can be as high as the devolatilization time. (Note that the weighting function is not zero after 125 sec., just very small.)

As a final check, the integral of the convolution integral over all relevant times must be unity.

3.1.4 Discussion and Future Work

This work attempts to develop a useful engineering model describing the apparent asymptotic yields and devolatilization rates of major, minor and, in particular, nitrogenous species with as few adjustable parameters as possible. The model uses a distribution of activation energies and properly describes the effect of temperature on apparent ultimate yields. Further, when the heating rate or any adjustable parameter is varied, the model behaves in a predictable, logical fashion. The model may be compared to experimental data through the use of an appropriate weighting function and the convolution integral, which enables interpretation of distorted experimental data.

Ongoing work outside the scope of this contract involves the incorporation of this model into a comprehensive coal combustion model, for which a computer program framework presently exists.

3.2 COAL COMBUSTION MODEL

3.2.1 Background

Development of combustion technology for cleaner, more efficient furnaces can be aided by a better understanding of the basic processes involved in coal combustion. These processes involve both chemical kinetic phenomena and flame aerodynamics and mixing. The current work focuses only on the former, and is concerned with chemical kinetics models describing coal combustion in a plug flow reactor.

The chemical phenomena occurring during combustion may be divided into two major groups: 1) coal pyrolysis/devolatilization, and 2) heterogeneous combustion/gasification of the char. Many researchers are investigating these processes. Essenhigh has written a thorough review of the fundamentals of

coal combustion (Elliot, 1981) in which he references a large number of researchers. Among those studying pyrolysis/devolatilization are Kobayashi, Howard, and Sarofim (1977), Suuberg, Peters, and Howard (1979), and Solomon and Colket (1979). The most comprehensive set of coal and char flame experiments in reactors has been carried out by Smith and co-workers (Smith, 1971; Smith and Tyler, 1974; Smith, 1979).

Experimental studies are continuing, but development of comprehensive mathematical models describing the coal combustion process has lagged behind the experimental research. The models are needed to aid in data analysis, test current theories, and help in planning future work.

Modeling of coal combustion as it occurs in a reactor or furnace presents many problems. The major factors to be considered are:

1. Heat transfer between the particles, gases, and wall.
2. Temperature gradients within the particle.
3. Chemical composition of volatile matter released.
4. Kinetics of devolatilization.
5. Chemical composition and physical structure of char.
6. Heterogeneous reactions and kinetics.
7. Homogeneous gas-phase chemistry.
8. Temperature and concentration gradients within the reactor.
9. Flame aerodynamics and fluid mechanics.
10. Particle trajectories in turbulent flow fields.
11. Mass transfer to and from the particles.
12. Concentration gradients within the particles.

Obviously, not all of the above factors may be modeled in full detail. Knowledge of the processes involved is far from complete, and too detailed of a model would be cumbersome, complex, and difficult to use. One must decide which factors are of most importance to the system of interest and make simplifying assumptions accordingly.

Many models have been developed and each takes a slightly different approach to the treatment of the problems outlined in the previous section. These date back as far as 1924 when Nusselt first presented a film model for the combustion of coal particles. Over the years, the models have become more detailed and diverse. However, they may be classified into two groups: 1) single-particle or cell models, in which the model focuses on the phenomena occurring within a single particle or cell around the particle; and 2) reactor models, in which large-scale processes occurring within the reactor are emphasized.

Single-Particle or Cell Models

A number of these models concentrate on the phenomena occurring in a film or zone surrounding the coal particle. Nusselt (1924) was the first to develop a single film model for the combustion of coal particles. A more recent film model was developed by Caram and Amundson (1977), in which they solved for concentration and temperature profiles around a burning carbon particle. That work was then extended by Mon and Amundson (1978) to include Stefan-Maxwell equations and to account for individual diffusivity and radiation effects. Ubhayakar (1976) used a film model with emphasis on energy balances to study ignition, burning, and extinction of a spherical particle.

A film model developed by Annamalai and Durbetaki (1977) included energy and species mass balances in the reaction zone surrounding the particle. This was used to predict the ignition phase of a reacting coal particle. The film model developed by Shadman and Cavendish (1980) included oxidation and gasification reactions on the particle surface and oxidation of the gasification products in the reaction zone. They used the model to study the burning rates and combustion mechanisms of reacting coal particles. One other cell model, developed by Kansa and Perlee (1980) for coal dust flames, considers such processes as solid pyrolysis, gaseous combustion, solid-gas combustion, radiation transport, mass and thermal diffusion, and convection.

Other cell models have included intraparticle effects in their derivation. Lilley and Wendt (1976) included a single-pore model to describe the heterogeneous char combustion reactions. Arri and Amundson (1978) used a film model with a shell progressive model for the solid structure to study single-particle char gasification. In the model developed by Srinivas and Amundson (1980), the heterogeneous reaction rates were based on the total surface area which was allowed to change with burnout. Hahn and Shadman (in press) used a highly detailed model of the char structure to study NO formation rates during combustion. Their model calculated radial gradients of concentration, surface area, and porosity throughout the char as a function of burnout.

Reactor Models

The earliest models, as well as many of those developed recently, have had a simple plug flow configuration. Hottel and Stewart (1940) developed one of the first, which was used to calculate space requirements in a furnace and used a Rossin-Rammler size distribution for the coal particles. The model of Sprouse (1980) incorporated a detailed treatment of boundary layer phenomena into a plug flow configuration. In the model of Vulis (1961), the focus was on the thermal properties of the system, and some allowance is made for radiation from the flame to the particles.

Other models have included mixing and aerodynamics in their description of the system. Smith and Smoot (1980) considered a plug flow system but included recirculation and mixing terms in the model. The model of Beer and Lee (1965) described the reactor as a well-stirred region followed by a plug flow section. Wen and Chaung (1979) modeled a downfired gasifier as a series

of well-stirred sections for the gas with the solid traveling in plug flow throughout the reactor.

All of the reactor models referenced above are one-dimensional in nature and are for entrained flow reactors. One-dimensional systems may usually be described by a set of coupled ODE's, while multidimensional systems require the use of PDE's, the solution of which involves much more complex numerics. Nevertheless, Gosman et al. (1969) and others are working on multidimensional models for coal combustion. Models of other reactor configurations have also been developed. These must concern themselves with the same processes mentioned previously, but the treatment may be much different due to the conditions under which the coal is reacting. Some of the reactors modeled include fluidized bed (Fan, Tojo, and Chang, 1979) and MHD (Shuck et al., 1979).

Modeling Approach

Many different models have been developed to represent pulverized fuel combustion and gasification systems. Each has its own set of assumptions derived by the investigators with a specific purpose in mind. As a result, the processes involved in coal combustion have received varying degrees of emphasis, depending on the specific goals of the investigator.

In this work, the emphasis is placed on the kinetics of the reactions: devolatilization, heterogeneous char-gas reactions, and homogeneous gas-phase reactions are all modelled in detail. The model is plug flow in nature and does not concern itself with aerodynamics or mixing, nor does it consider resistance to heat and mass transfer to and from the particles or temperature gradients within the particles.

Most reactor models have used simplified kinetics to describe the fate of the volatile material and combustion products released from the coal particles. In many models, the volatiles are assumed to oxidize immediately upon release into the gas phase, and the gas phase is assumed to be in a state of pseudo-equilibrium. While these assumptions have yielded reasonable results when compared to data, for long time scales (> 0.1 sec), they may not be expected to accurately describe the behavior at short times (< 100 μ sec). During devolatilization, the gas phase will be far from equilibrium and these differences may have an influence on the rate of volatile combustion and the final products. Therefore, detailed gas-phase chemistry has been included to more accurately predict the gas-phase composition profiles throughout the reactor. In addition, a devolatilization model is used which predicts both the rates at which the volatiles are released and their composition.

When modeling the heterogeneous oxidation/gasification reactions, it has been shown by many researchers (Smith, 1971; Smith and Tyler, 1974; Srinivas and Amundson, 1980; etc.) that intraparticle and surface area effects are important and may not be neglected. These are particularly important when calculating the rate of NO production from reactions involving fuel nitrogen in the char. To account for intra-particle effects, a detailed model of the char structure is used. From it, surface area, porosity, and effective diffusivity in the char particle are calculated as a function of carbon

conversion. With this information, it is possible to calculate reaction rates based on total internal surface area of the char and the concentration of the gas-phase reactants in the particles.

The bulk of the model is concerned with the calculation of the parameters and reaction rates needed to fully describe the coal combustion reactions. Therefore, most of the other features of the coal combustion process are either modeled in less detail or neglected. These features are considered to be of second-order importance for the system being modeled and many will be treated in more detail in later work. Aerodynamics and mixing are not considered, but extension of this work to include a well-stirred reactor model is planned. Temperature throughout the system is specified, eliminating the need for energy balances. Temperature gradients within the particles and differences between particle and gas velocity are neglected. These simplifications have been shown to be valid for the conditions normally encountered in a plug flow, coal-fired furnace. Resistance to mass transfer between the gas and the particle surface is neglected, but may be included simply as an additional resistance to the heterogeneous reaction rates.

A complete list of the assumptions used in the model and their justifications is presented in Subsection 3.3.

Scope

Experimental work in coal combustion is continuing at a rapid pace. As more is learned about the processes involved and as new data are obtained, there is a need for new models to apply this knowledge to help in describing the operation of real physical systems, and to aid in the interpretation of new data. One useful model is one which describes the fate of coal particles as they travel along a streamline, i.e., a plug flow reactor. This work is concerned with the development of one such model.

Development of any model is a time-consuming process and the model will evolve through a series of changes. Therefore, the final product of this work will not be the complete model, but will be an intermediate product which will be modified and improved upon in future work beyond this contract. This work was performed with two specific goals in mind:

1. To model the char combustion reactions, in full detail and use the results to predict with reasonable accuracy the species concentrations throughout the reactor for both major products (O_2 , CO, and CO_2) and trace species (NO).
2. To set up the basic framework for modeling the devolatilization reactions and use this, combined with the char combustion and gas-phase models, to predict the major species concentration profiles for coal combustion.

The results of this work can be modified in the future to include more detailed and complete devolatilization kinetics. There are also plans to extend this work to model well-stirred reactor configurations. Therefore, this work is the basic framework upon which others will build to obtain the model in its final form.

3.2.2 Model Development

The coal combustion/pyrolysis model was developed as an addition to an existing program (REKINET). REKINET predicts the time-resolved species concentration profiles within a plug flow reactor for homogeneous gas-phase systems, and is designed to consider only homogeneous gas-phase reactions. All reactions are described by the elementary reactions involved in the system. REKINET is also capable of modeling well-stirred reactors and performing heat balances on the reacting systems. However, those two features are not used in this work.

Coal combustion involves a number of complex processes which are not included in the gas-phase model of REKINET, specifically char combustion and devolatilization. This present work is concerned with the development of two new routines, BURNOUT and DEVOL, which are integrated into the existing framework of REKINET, enabling it to model these new processes not previously considered.

Modeling Assumptions

The model is based on the following a priori assumptions:

1. One-dimensional flow of gases and particles.
2. The particle velocity is identically equal to the gas-phase space velocity.
3. Particle numbers are self-preserving (particle attrition and agglomeration processes are neglected).
4. Coal devolatilization is a first-order process in the amount of material yet to be removed.
5. Volatiles consist of CO, CO₂, H₂O, CH₄, and tar (CH_y).
6. Heterogeneous gas-solid reactions are first-order in the concentration of the gas-phase reactant.
7. Axial diffusion of gases is neglected.
8. Perfect radial gas phase mixing.
9. The particles are isothermal.
10. The particle temperature is equal to the temperature of the surrounding gases (heat of reaction and heat transfer to and from the particles are neglected).
11. Microscale gas film diffusion effects are neglected.

Assumption 1 has been found to be satisfactory in cases where good initial mixing has been achieved at long residence times (Sprouse, 1980) and has been demonstrated in the furnace used to collect data used in this model (Glass, 1981).

Assumption 2 is invoked primarily for reasons of practicality. For the small particles used in this type of flow system ($\leq 100 \mu\text{m}$), there should be

little difference in velocity between the gas and the particles. Velocities calculated by Glass (1981) show a 4 percent difference between gas and particle velocities for 60 μm particles at a gas velocity of 122 cm/sec.

Assumption 3 is reasonable for systems with low particle loading. The center-to-center particle distances are large in entrained flow reactors and, therefore, particle interactions are of little importance.

Assumption 4 has been shown to be adequate under these conditions (Anthony and Howard, 1976). A more sophisticated distributed activation energy model will be used in future work.

Assumption 5 is invoked primarily for reasons of convenience with the knowledge that a more detailed description of the volatiles and their composition will be used in the future. CO, CO₂, H₂O, and CH₄ are all species found to be released during devolatilization (Suuberg et al., 1979) and the gas-phase chemistry is reasonably understood for CO and CH₄ combustion.

Assumption 6 allows the use of global intrinsic reactivity expressions. A more detailed description may be obtained using Langmuir-Hinshelwood kinetics; however, this would require simultaneous solution of two or three species equations, adding a degree of complexity not desired.

Assumptions 7 and 8 are required to maintain the one-dimensional nature of the model. Experimental results (Glass, 1981; Wendt et al., 1979) have shown that composition profiles (except in the combustion zone) are relatively flat, leading to small axial diffusion effects. Perfect radial mixing is usually assumed (Field et al., 1967; Smoot and Pratt, 1979) and, indeed, the data of Glass (1981) show little radial variation in gas composition.

Field et al. (1967) have shown that, for small particles (100 μm), the assumption of the particle being isothermal (Assumption 9) is valid even when subjected to heating rates common in flames.

Assumptions 10 and 11 are probably the weakest and are justified largely a posteriori on the grounds that the computed results adequately describe the burning time and char major species experimental results. In addition, Hahn and Shadman (in press) obtained good results when using these assumptions and a very similar model. The small size of the particles plays a key role in allowing the use of these assumptions; they will begin to break down if the size of the particles increases.

Using the above assumptions, two new routines were developed to model the char combustion and devolatilization processes. Detailed explanations of the application of these assumptions and the various models used in the BURNOUT and DEVOL routines are found in subsections 3.2.3 and 3.2.4 respectively.

Pre-Existing Model

A review of REKINET as it existed prior to this work is presented in this section. Knowledge of the operation of the program is vital to the understanding of the present work.

Defining Equations

REKINET is designed to calculate the time-resolved species concentration profiles throughout the reactor. The model operates in units of molar fluxes and concentrations. Temperature is not calculated but is a specified parameter of the system. A simple balance over a slice of the reactor yields the differential equations relating the molar fluxes and residence time:

$$\frac{dFL_I}{dt} = F_I v \quad 3.2.2-1$$

where FL_I = the molar flux of species I, moles I/cm²-sec;
 F_I = the rate of formation of I, moles I/cm³-sec;
 v = the space velocity, cm/sec; and
 t = time (residence time), sec.

There is one equation for each species in the system. This coupled set of differential equations is integrated over the length of the reactor to obtain the species concentration profiles.

Method of Solution

Reacting systems consist of a large number of reactions which may vary by many orders of magnitude in their rates. As a consequence, the systems have widely separated time constants, i.e., the coupled sets of ODE's describing the systems are stiff.

The equations are integrated numerically using a routine developed by Tyson (1964). It is an implicit routine designed specifically for use on stiff systems. It expands the right-hand side of the differential equations around the backward point:

$$F_I v^{h+1} = F_I v^h + \sum_{j=1}^{\delta} \frac{\partial F_I v}{\partial FL_J} (FL_J^{h+1} - FL_J^h) + \frac{\partial F_I v}{\partial t} (t^{h+1} - t^h) \quad 3.2.2-2$$

Then, expanding the function as a Taylor series around the forward point and manipulating the equations yields vector at the a set of linear implicit equations which may be solved to obtain the FL_I vector at the time t^{h+1} . The method consists essentially of linearizing the derivative through a Taylor series expansion, neglecting non-linear terms (second-order and higher) and numerically solving the resulting set of linear, implicit equations.

Examination of equation 3.2.2-2 reveals that the integration routine requires calculation of $F_I v$, the Jacobian or beta matrix

$$\frac{\partial F_I v}{\partial FL_J}$$

and

$$\frac{\partial F_I v}{\partial t}$$

called the alpha vector. When temperature is given as a function of time, $T(t)$, the alpha vector is non-zero since the system is non-autonomous.

Rate Calculations (Homogeneous Kinetics)

Calculation of the reaction rates and the derivatives required for the Jacobian and alpha vector is a straightforward but time-consuming operation. A major portion of the computer code is concerned with performing these calculations. A description of the rate expressions for the gas-phase chemistry and the scheme used in calculating the derivatives are presented in this section.

The species production rates, F_I , are calculated from the rates of the N elementary gas-phase reactions. These reversible reactions have the general form:

with forward and reverse rate constants K_1 and K_{-1} , respectively. The rate constants are functions of temperature of the form:

$$K(T) = aT^b \exp\left(\frac{-c}{RT}\right) \quad 3.2.2-3$$

where a , b , and c are constants. The reactions and the kinetic parameters used in this work are listed in Table 3.2.2-1.

Calculation of the reaction rates is a simple procedure. For the general reaction written above:

$$R = K_1 C_A C_B C_C - K_{-1} C_D C_E C_F \quad 3.2.2-4$$

where C_I is the concentration of species I . From the rates of the reactions and the stoichiometry, the F_I values are easily calculated.

Jacobian and Alpha Calculations

Given the above form of the reaction rate expression and the kinetic parameters, it is a straightforward task to calculate the derivatives needed for the beta matrix, with elements $\beta'_{I,J}$ and the alpha vector, with elements α_I . REKINET calculates the $\beta'_{I,J}$ and α_I elements in two steps. First, it generates a pseudo-beta matrix and pseudo-alpha vector, and these are then adjusted to obtain the true beta and alpha.

The pseudo-beta (beta) matrix has elements $\beta'_{I,J}$ where

$$\beta'_{I,J} = \frac{\partial F_I}{\partial C_J}$$

Table 3.2.2-1 Homogeneous Reaction Set--from Corley (1982)

REACTION		STOICHIOMETRY				FORWARD RATE			REVERSE RATE		
#	NAME					A	B	C	A	B	C
1	CH4	CH4	+H		+CH3	+H2					
2	CH4	CH4	+OH		+CH3	+H2O					
3	CH4	CH4	+O		+CH3	+OH					
4	CH4	CH4	+H		+CH3	+H					
5	CH4	CH4	+O		+CH3	+H					
6	CH4	CH4	+OH		+CH3	+H2O					
7	CH4	CH4	+O2		+CH3	+O					
8	CH4	CH4	+H		+CH3	+H					
9	CH4	CH4	+H		+CH3	+H					
10	CH4	CH4	+OH		+CH3	+H2O					
11	CH4	CH4	+O		+CH3	+OH					
12	CH4	CH4	+O2		+CH3	+O					
13	CH4	CH4	+O		+CH3	+H					
14	CH4	CH4	+OH		+CH3	+H2O					
15	CH4	CH4	+O		+CH3	+H					
16	CH4	CH4	+OH		+CH3	+H2O					
17	CH4	CH4	+O2		+CH3	+O					
18	CH4	CH4	+H		+CH3	+H					
19	CH4	CH4	+OH		+CH3	+H2O					
20	CH4	CH4	+O		+CH3	+OH					
21	CH4	CH4	+O2		+CH3	+O					
22	CH4	CH4	+H		+CH3	+H					
23	CH4	CH4	+OH		+CH3	+H2O					
24	CH4	CH4	+O		+CH3	+OH					
25	CO	CO	+H		+CO	+H					
26	CO	CO	+OH		+CO	+H2O					
27	CO	CO	+O		+CO	+O					
28	CO	CO	+H		+CO	+H					
29	CO	CO	+OH		+CO	+H2O					
30	CO	CO	+O		+CO	+O					
31	CO	CO	+H		+CO	+H					
32	CO	CO	+OH		+CO	+H2O					
33	CO	CO	+O		+CO	+O					
34	CO	CO	+H		+CO	+H					
35	CO	CO	+OH		+CO	+H2O					
36	CO	CO	+O		+CO	+O					
37	CO	CO	+H		+CO	+H					
38	CO	CO	+OH		+CO	+H2O					
39	CO	CO	+O		+CO	+O					
40	CO	CO	+H		+CO	+H					
41	CO	CO	+OH		+CO	+H2O					
42	CO	CO	+O		+CO	+O					
43	CO	CO	+H		+CO	+H					
44	CO	CO	+OH		+CO	+H2O					
45	CO	CO	+O		+CO	+O					
46	CO	CO	+H		+CO	+H					
47	CO	CO	+OH		+CO	+H2O					
48	CO	CO	+O		+CO	+O					
49	CO	CO	+H		+CO	+H					
50	CO	CO	+OH		+CO	+H2O					
51	CO	CO	+O		+CO	+O					
52	CO	CO	+H		+CO	+H					
53	CO	CO	+OH		+CO	+H2O					
54	CO	CO	+O		+CO	+O					
55	CO	CO	+H		+CO	+H					
56	CO	CO	+OH		+CO	+H2O					
57	CO	CO	+O		+CO	+O					
58	CO	CO	+H		+CO	+H					
59	CO	CO	+OH		+CO	+H2O					
60	CO	CO	+O		+CO	+O					
61	CO	CO	+H		+CO	+H					
62	CO	CO	+OH		+CO	+H2O					
63	CO	CO	+O		+CO	+O					
64	CO	CO	+H		+CO	+H					
65	CO	CO	+OH		+CO	+H2O					
66	CO	CO	+O		+CO	+O					
67	CO	CO	+H		+CO	+H					
68	CO	CO	+OH		+CO	+H2O					
69	CO	CO	+O		+CO	+O					
70	CO	CO	+H		+CO	+H					
71	CO	CO	+OH		+CO	+H2O					
72	CO	CO	+O		+CO	+O					
73	CO	CO	+H		+CO	+H					
74	CO	CO	+OH		+CO	+H2O					
75	CO	CO	+O		+CO	+O					
76	CO	CO	+H		+CO	+H					
77	CO	CO	+OH		+CO	+H2O					
78	CO	CO	+O		+CO	+O					
79	CO	CO	+H		+CO	+H					
80	CO	CO	+OH		+CO	+H2O					
81	CO	CO	+O		+CO	+O					
82	CO	CO	+H		+CO	+H					
83	CO	CO	+OH		+CO	+H2O					
84	CO	CO	+O		+CO	+O					
85	CO	CO	+H		+CO	+H					
86	CO	CO	+OH		+CO	+H2O					
87	CO	CO	+O		+CO	+O					
88	CO	CO	+H		+CO	+H					
89	CO	CO	+OH		+CO	+H2O					
90	CO	CO	+O		+CO	+O					
91	CO	CO	+H		+CO	+H					
92	CO	CO	+OH		+CO	+H2O					
93	CO	CO	+O		+CO	+O					
94	CO	CO	+H		+CO	+H					
95	CO	CO	+OH		+CO	+H2O					
96	CO	CO	+O		+CO	+O					
97	CO	CO	+H		+CO	+H					
98	CO	CO	+OH		+CO	+H2O					
99	CO	CO	+O		+CO	+O					

Since the reaction rates are linear functions of concentration, these $\beta'_{I,J}$ are easily calculated.

Once the $\beta'_{I,J}$ elements are known, they are adjusted to obtain beta. The relationship between the two matrices is given below:

$$\beta_{I,J} = \beta'_{I,J} (1 - \omega_J) + R_I / \rho_m \quad 3.2.2-5$$

where

ω_J = the mole fraction of the Jth species; and

ρ_m = the total molar concentration of species in the system.
The pseudo-alpha (alpha) vector has elements α_I' where

$$\alpha_I' = \frac{\partial R_I}{\partial t}$$

The only variable which is an explicit function of time is temperature; therefore:

$$\frac{\partial R_I}{\partial t} = \frac{\partial R_I}{\partial T} \frac{dT}{dt}$$

Both $\partial R_I / \partial T$ and dT/dt are easily calculated, yielding the alpha vector. After the α_I' elements are obtained, they are adjusted to yield desired α_I values. The relationship between the elements of the two vectors is given below:

$$\alpha_I = \alpha_I' v + R_I \left[\frac{R_{I,FL,tot}}{P} \frac{dT}{dt} \right] \quad 3.2.2-6$$

where FL_{tot} = the total molar flux; and
 P = the pressure.

The kinetics of the devolatilization and heterogeneous reactions are significantly different from those described above for the homogeneous gas-phase reactions. Therefore, new routines were needed to adequately describe these additional reactions associated with coal combustion. These routines are required: 1) to calculate the rates of the additional reactions; 2) to generate the new F_I values and elements of the beta matrix and alpha vector for the solid and volatile species in the coal; and 3) to adjust all F_I values, and elements of the beta matrix and alpha vector, for the gas-phase species affected by the devolatilization and char combustion reactions.

Model Structure

The previous section provides a general description of the modeling approach used in REKINET and the modifications required to properly model the processes involved in coal combustion. The model structure, the interrelationships of the routines, and their functions, including those concerned with char combustion and devolatilization, are presented below.

The diagram in Figure 3.2.2-1 illustrates the interrelationship of the subroutines with the main-line program and each other.

There are a number of subroutines in REKINET which are not listed in Figure 3.2.2-1. These were never used in this work and therefore have been omitted. Other subroutines, such as REDATA and TYSON, call subroutines which are not listed. They have been omitted because knowledge of their structure and functions is not necessary to understand the operation of the program in this study. Those subroutines with asterisks beside them were developed for this work, and those marked with a † are previously developed routines which have been modified.

The subroutines BLCALC, BRNOUT, and CALDIF constitute the BURNOUT routine. They calculate all the rates and derivatives associated with the char-gas reactions. The mathematical models and specific calculations used in these routines are presented in section 3.2.2. The DEVOL routine consists of the subroutines COALCMP and VOLRATE. A detailed description of the models and calculations used in these routines is presented in section 3.2.3. A complete program listing and general flow diagrams are included in the Appendix.

Function of Program Components

Table 3.2.2-2 contains the names of the program subroutines, their calling routines, and a brief description of their functions. The remainder of this chapter contains a slightly more detailed description of the various routines and their functions.

Main-Line REKINET

The function of the main-line program is to collect all necessary data, assign the data to the proper variables, and then call the appropriate subroutine, depending on what type of simulation is being executed. Only one type of simulation was used in this work, the plug flow routine. Other options were available, but not used. These include a well-stirred reactor model and both plug flow and well-stirred models with heat balances.

REKINET first sets default values, then calls subroutine REDATA which reads and stores all data to be fed into the program. It then acquires any additional thermochemical data needed for the simulation from internal libraries of data. The thermochemical data are needed only for the heat balance routines. Once all the data have been collected, the program then calls the proper simulation subroutine, in this case PLUGFLO.

Figure 3.2.2-1. REKINET Program Structure. -- * = subroutines developed for this work; † = previously developed routines which have been modified.

Table 3.2.2-2 Subroutine Functions.

Subroutine Name	Calling Routine	Function
PLUGFLO	Main-line	Gather rates and derivatives, feed data to integration routine, and decide when to print data and stop run.
REDATA	Main-line	Read in and store all data.
SORT	Main-line	Sort inputted arrays.
TEMP	PLUGFLO	Calculate temperature at current time.
COALCMP	PLUGFLO	Calculate initial amount of volatile species in coal.
CALRAT	PLUGFLO	Calculate rates of homogeneous gas-phase reactions.
CALBET	PLUGFLO	Calculate elements of Jacobian matrix, alpha vector, and species formation vector using homogeneous reaction rates.
VOLRATE	PLUGFLO	Calculate rate of volatiles released and adjust B, BETA, ALP, AL, and F to include DEVOL rxn's.
BRNOUT	PLUGFLO	Calculate heterogeneous reaction rates and adjust BETA, ALP, AL, B, DCO, and F to include these reactions.
CALDIF	BRNOUT	Calculate all derivatives used in BRNOUT.
RITOUT	PLUGFLO	Write routine.
TYSON	PLUGFLO	Integration routine.

Subroutine PLUGFLO

The function of the PLUGFLO subroutine is 1) to gather all necessary rates and derivatives to be used in the simulation, 2) to feed this information to the integration routine, 3) to determine when to print out the data, and 4) to stop the simulation at the proper time.

Subroutine REDATA

The REDATA subroutine is the data entry routine. This routine reads one line at a time and then stores the data. Each line contains an alpha-numeric "identifier" in the first six spaces which indicates to the read routine the nature of the data and how they are to be stored.

Subroutine SORT

This subroutine sorts any two related vectors passed to it. The vectors are called SIZE and FRACT in the subroutine. The elements of the vectors are sorted into ascending order with respect to the values in SIZE.

Subroutine BLCALC

BLCALC uses the pore size distribution, $\epsilon(r)$, to calculate the probability density function, $\lambda(r)$, which is used in the model of the char structure. It also calculates the zeroth and first moments of the function $\lambda(r)$. These calculations involve some definite integrals which were approximated using the trapezoidal rule.

Function Subprogram TEMP

This subprogram calculates the temperature given the time and initial parameters. The temperature is either specified as an exponential decay or given as a number of data points of temperature versus time.

Subroutine COALCMP

COALCMP calculates the initial FL_I values for the volatiles and solid species when coal is the fuel. The calculations are based on the proximate and ultimate analysis of the coal.

Subroutine CALRAT

In this subroutine, the reaction rates of all the homogeneous gas-phase reactions are calculated. The routine calculates the rate constants at the present temperature and then multiplies these by the appropriate concentrations to obtain the rates.

Subroutine CALBET

CALBET uses the reaction rates calculated in CALRAT to obtain the species production rates and generate the alpha vector and beta matrix.

Subroutine VOLRATE

This subroutine calculates the rates at which the volatiles are being released. It also adjusts the species production rates, alpha vector, and beta matrix to include the contribution of the devolatilization reactions.

Subroutine BRNOUT

BRNOUT calculates the physical properties of the char at each time step. It then uses that information to obtain the heterogeneous reaction rates. The species production rates, alpha vector, and beta matrix are adjusted in BRNOUT to include the contribution of the heterogeneous char reactions.

Subroutine CALDIF

This subroutine calculates all the derivatives used in BRNOUT when adjusting the beta matrix and alpha vector.

Subroutine RITOUT

This is the write routine. It prints out data of the system composition, reaction rates, and physical properties of the char.

Subroutine TYSON

TYSON is the integration routine. It integrates the set of coupled differential equations over one time step given values for F_I , FL_{IV} , R_I , alpha, and beta.

3.2.3 Heterogeneous Reaction Modeling

The kinetics of gas-solid reactions are significantly different from those for homogeneous gas-phase reactions. The rate of reaction is a function of the surface area of the solid, not its concentration. Temperature and concentration gradients between the solid and the gas, as well as within the solid itself, may be present. These differences necessitated the development of a char combustion routine (BRNOUT) which could calculate the reaction rates and the appropriate derivatives to be fed back into the plug flow model.

Solid Species

In the homogeneous model, there are M distinct homogeneous species which give rise to M dependent variables--the species flow rates. The inclusion of solid species in the system adds MH more dependent variables, one for each solid reactant. In addition, if more than one size class of coal or char is

present, the solid carbon is distributed among these classes and each of these fractions of carbon is considered to be a separate species. Each size class behaves differently from the others and the amount of carbon in each class is needed to properly model the reactions as they proceed.

Reaction Kinetics and Species Production Rates

For this model, all gas-solid reactions are assumed to be first-order with respect to the gas-phase reactant. The general form used for the reaction rate is:

$$R_i = K_i S_r P_i \eta_i / M_c \quad 3.2.3-1$$

where R_i = rate of consumption of solid reactant, moles/cm³-sec;
 S_r = total surface area, cm²/cm³;
 P_i = partial pressure of gas-phase reactant, atm; and
 η_i = effectiveness factor, unitless

In this work, only heterogeneous reactions which involved solid carbon or nitrogen are considered. The reactions and the kinetic parameters used are given in Table 3.2.3-1. No kinetic data are given for the reaction of N with O₂. This reaction is closely coupled to the carbon-oxygen reaction, because the solid nitrogen cannot react until it is exposed to the gas. Therefore, the rate of this reaction is simply the rate of the carbon-oxygen reaction multiplied by the mole ratio of nitrogen to carbon in the char.

The species production rates, F_i , have units of mole/cm³-sec. As in the homogeneous model, these F_i values are easily calculated once the reaction rates are known. However, in this case, not only is the concentration or partial pressure of the species needed, but also the surface area and the effectiveness factor must be obtained. Calculation of both the surface area and η requires a detailed knowledge of the structure of the solid char. However, the actual structure of char is quite complex, and detailed information about it is difficult to obtain. In addition, the structure will change as the reactions proceed, adding to the problem. Therefore, some form of mathematical model was needed to provide the necessary information about the structure of the solid.

Char Model

The choice of which model to use for the char structure is based on a number of factors. The model was required to accurately describe the solid structure with a minimum of parameters. From it, the specific surface area (cm²/g) and effective diffusivity within the particles were to be obtained. It should also provide for a way to determine how these properties change with burnout.

Table 3.2.3-1 Heterogeneous Runs and Kinetic Parameters--from Smith (1979), Elliott (1981), and Levy et al. (1981).

			Kinetic Parameter	
Name	Reaction	Stoichiometry	k	E
			$\left(\frac{\text{g C}}{\text{cm}^3 \text{-sec-atm}}\right)$	(cal)
C1 CARBC	$\text{C} + \frac{1}{\alpha} \text{O}_2 + (2 - \frac{2}{\alpha}) \text{CO} + (\frac{2}{\alpha} - 1) \text{CO}_2$		305.	42,850
C2 CO2GAS	$\text{C} + \text{CC}_2 \rightarrow 2\text{CO}$		7.0	60,000
C3 H2OGAS	$\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$		21.0	60,000
N1 NOFORM	$\text{N} + \text{O}_2 \rightarrow \frac{1}{2} \text{NO}$		-	-
N2 NORED	$\text{C} + \text{NC} \rightarrow \frac{1}{2} \text{N}_2 + \text{CO}$		2.7×10^{-2}	34,700

Review of Models

A number of structural models have been developed. One of the simplest is the unreacted shrinking core model, in which the reactions take place on the surface of a non-porous, solid particle. However, coal chars are known to be quite porous with large internal surface areas. Many other models consider the reactions as occurring on internal surfaces of the solid. The models can be classified into two categories: those which consider the solid to consist of a number of nonporous grains, and those which describe the solid as containing numerous pores throughout.

One example of the grain model is that developed by Sohn and Szekely (1972). Use of the model requires determination of two parameters: the size of the grains and their shape. From these, the surface area and a number of other properties of the solid may be calculated.

Petersen (1957) developed a pore model which assumed uniform cylindrical pores which intersect randomly throughout the solid. It also assumes, as do many other pore models, that no new intersections are created as the reactions proceed. Once the parameters describing the number and angles of the pore intersections have been obtained, the desired properties of the solid may be calculated.

Both of the models mentioned above allow for calculation of surface area and porosity as a function of time. However, the grain model predicts a monotonically decreasing surface area for reaction, while measurements of Kawahata and Walker (1962) and Hashimoto et al. (1979) indicate an increase in reacting surface area during early stages of gasification reactions on activated carbons. Petersen's pore model assumes pores of uniform size and no new intersections as reactions proceed. Some more recent pore models of Bhatia and Perlmutter (1980) and Gavalas (1980) allow for a distribution of pore sizes and consider new intersections formed during the reactions. In addition, the parameters of the models are calculated directly from measurable structural properties of the solid and the surface area calculated is not monotonic, but goes through a maximum.

Random Pore Model

The model chosen for this work was one developed by Gavalas (1980). The model as developed describes the structure as being a solid which contains a number of randomly distributed straight cylindrical pores.

These pores are uniform in diameter from end to end, but range in size from a few Angstroms up to a few microns. It is assumed that no new pores form during combustion, and that the reactions proceed at a uniform rate throughout the particles (i.e., kinetically controlled). The model reasonably describes the solid for porosities < 0.7 . For $\epsilon_T > 0.7$, a different model was used.

The details of the derivation of the model will not be presented here. Instead, some of its more important features will be discussed. The assumption of randomly distributed pores allows for overlap and intersections

between them. Therefore, as the pores grow, the surface area per unit volume of the particle initially increases as more of the solid is exposed, and then starts to decrease as the pore walls grow into each other and collapse.

The assumption of a uniform reaction rate throughout the solid allows the solid to be characterized at any time by a single variable, Q . This variable is the distance the pore walls have receded due to the reactions at any given time. This is illustrated in Figure 3.2.3-1. At time $t = 0$, a pore has radius r_0 . Then, at time $t + \Delta t$, the wall has moved distance Q and the new radius $r_1 = r_0 + Q$. The variable Q is easily calculated from the carbon conversion (X_C) by the following expression:

$$Q = \frac{-2B_1 + \sqrt{4B_1^2 - \frac{B_0}{\pi} \ln(1 - X_C)}}{2B_0} \quad 3.2.3-2$$

The only parameter needed for the model is the pore size distribution of the char, $\epsilon(r)$. From it, a probability density function, $\lambda(r)$, is calculated:

$$\lambda(r) = \frac{1}{2\pi r^2} \frac{\epsilon(r)}{1 - \int_r^{\infty} \epsilon(r') dr'} \quad 3.2.3-3$$

It is the probability function describing the number of intersections the axes of pores of radius r have with any unit surface area.

An important result of the random pore model is that, as the char is consumed, the function $\lambda(r)$ preserves its shape and is only shifted with time. In this work, r represents the initial pore radius and the pore radius at any time t is $r + Q(t)$. Therefore,

$$\lambda(r) = \lambda'[r + Q(t)] \quad 3.2.3-4$$

where λ' is the probability function for the pores at time t . Two widely used functions of $\lambda(r)$ are B_0 and B_1 , its zeroth and first moments, respectively.

Using $\epsilon(r)$, $\lambda(r)$, B_0 , and B_1 , the specific surface area and effective diffusivity can be calculated as a function of Q . The equation for $S_g(Q)$ is given below:

$$S_g(Q) = 2.0 \times 10^8 \pi (B_0 Q + B_1) \quad 3.2.3-5$$

This is the surface area per gram of carbon. For the reaction rate calculations, S_r (the surface area per unit volume reactor) is needed. The conversion of S_g to S_r is a simple one, as shown in equation 3.2.3-6;

$$S_r = S_g \frac{C}{c} \frac{M}{c} \quad 3.2.3-6$$

Figure 3.2.3-1 Pore Cross-Section.

Two other important properties of the solid are the porosity as a function of pore radius Q , and the total porosity as a function of Q . These relationships are given in equations 3.7 and 3.8 below:

$$\epsilon(r, Q) = 2\pi(r + Q)^2 \lambda(r) \exp \left[-2\pi \int_r^{r^*} (r' + Q)^2 \lambda(r') dr' \right] \quad 3.2.3-7$$

$$\epsilon_T(Q) = 1 - (1 - \epsilon_{T_0}) \exp [-2\pi(B_0 Q^2 + 2B_1 Q)] \quad 3.2.3-8$$

The effective diffusivity is a function of the pore size distribution and the diffusivity in each pore, $\delta(r)$:

$$\frac{1}{\delta(r)} = \frac{1}{D_{A,B}} + \frac{1}{A_k r} \quad 3.2.3-9$$

where $D_{A,B}$ is the binary diffusivity and $A_k r$ is the Knudsen diffusivity. For r in Angstroms, $A_k = 9.7 \times 10^{-5} \sqrt{T/32}$. To calculate D_e :

$$D_e = \int_{r_*}^{r^*} \epsilon(r, Q) \delta(r + Q) dr \quad 3.2.3-10$$

Effectiveness Factor

Gavalas' model assumes that the char reactions are kinetically controlled. That is often not the case. At temperatures above 1000 K, the speed of the reactions is quite fast, and concentration gradients develop within the particle. Therefore, it was decided to scale the reaction rate with the use of an effectiveness factor, η , the ratio of the actual rate for the whole pellet (R_p) divided by the rate evaluated at surface conditions (R_s).

The existence of a concentration profile and non-uniform reaction rates throughout the particle will mean that the model will not be correct in describing the structure of all of the solid. The pores as described by the model will be too small near the surface of the particle and too large in the center. But the actual solid structure is not of interest. It is only a tool to help calculate the rate of the heterogeneous reactions, and it was hoped that the model, although not totally accurate, would give reasonable results. In addition, the effectiveness factor was used to modify the way in which Q was calculated. This modification will be discussed in more detail later.

Derivation of CO Balance Equation

To demonstrate the development of η , the reaction of carbon with CO_2 will be used as an example:

The reaction is first-order and the pellet is isothermal. Therefore:

$$R_p = \eta K_{C_2} C_{CO_2} R_g T / M_c \quad 3.2.3-12$$

R_g , T and M_c may be absorbed into K , giving a new constant, K_{C_2}' :

$$R_p = \eta K_{C_2}' C_{CO_2} \quad 3.2.3-13$$

To calculate R_g , the concentration of C_{CO_2} throughout the particle must first be obtained. By writing a mass balance over a spherical shell volume of thickness, Δr , the differential equation expression C_{CO_2} as a function of r is obtained. According to the conservation principle:

$$\text{Rate in} - \text{rate out} = - \text{Rate of production} \quad 3.2.3-14$$

The rate of production of CO_2 will be $-K_{C_2}' C_{CO_2} S_v$ per unit volume, where S_v is the surface area per unit volume of the pellet. Therefore, the balance may be written, omitting the subscript CO_2 or C :

$$(-4\pi r^2 D_e \frac{dC}{dr})_r - (-4\pi r^2 D_e \frac{dC}{dr})_{r+\Delta r} = 4\pi r^2 \Delta r S_v K_{C_2}' C \quad 3.2.3-15$$

Rearranging and eliminating common terms:

$$\frac{(r^2 \frac{dC}{dr})_{r+\Delta r} - (r^2 \frac{dC}{dr})_r}{\Delta r} = r^2 \frac{K_{C_2}' S_v}{D_e} C \quad 3.2.3-16$$

Taking the limit as $\Delta r \rightarrow 0$ and rearranging yields:

$$\frac{d^2 C}{dr^2} + \frac{2}{r} \frac{dC}{dr} = \frac{K_{C_2}' S_v}{D_e} C \quad 3.2.3-17$$

This equation may be solved using the following boundary conditions:

1. $\frac{dC}{dr} = 0$ at $r = 0$
2. $C = C_s$ at $r = r_s$

to give

$$\frac{C}{C_s} = \frac{r_s}{r} \frac{\sinh(3\phi \frac{r}{r_s})}{\sinh 3\phi} \quad 3.2.3-18$$

where ϕ is a dimensionless group (the Thiele modulus) defined by

$$\phi = \frac{r_s}{3} \sqrt{\frac{K_{C2}' S_v}{D_e}} \quad 3.2.3-19$$

Since the pellet is at steady state, the rate R_p may be calculated using the concentration profile to calculate the rate of diffusion of reactant into the pellet at r_s :

$$R_p = 4\pi r_s^2 D_e \left(\frac{dC}{dr} \right)_{r=r_s} \quad 3.2.3-20$$

Now

$$\eta = \frac{R_p}{R_s} \quad 3.2.3-21$$

and

$$R_s = \frac{4}{3} \pi r_s^3 S_v K_{C2}' C_s \quad 3.2.3-22$$

Substituting into equation 3.2.3-20 from equations 3.2.3-21 and 3.2.3-22 yields

$$\eta = \frac{3D_e}{r_s S_v K_{C2}' C_s} \left(\frac{dC}{dr} \right)_{r=r_s} \quad 3.2.3-23$$

Differentiating equation 3.2.3-18, evaluating the derivative at $r = r_s$, and substituting into equation 3.2.3-23 gives

$$\eta = \frac{1}{\phi} \left(\frac{1}{\tanh 3\phi} - \frac{1}{3\phi} \right) \quad 3.2.3-24$$

Equation 3.2.3-24 defines η as a function of ϕ and equation 3.2.3-14 gives ϕ in terms of variables which are either parameters of the system or readily calculated. Calculation of η may be simplified for either very small values of ϕ ($\phi < 0.1$) or large ϕ . As $\phi \rightarrow 0$, $\eta \rightarrow 1$, and as ϕ increases, η may be closely approximated as

$$\eta = \frac{1}{\phi} \quad \text{for } \phi > 5 \quad 3.2.3-25$$

The above derivation of η was for one specific reaction. However, the same relationships may be used for the other reactions as well if the proper rate constants and stoichiometric coefficients are used. For example, the reaction of carbon with oxygen is modeled as a first-order, reversible reaction. However, the stoichiometry is

where α is a function of temperature. Therefore, in calculating η for this reaction, the rate R_p becomes

$$R_p = \frac{1}{\alpha} \eta_{Cl} K_{Cl} C_{O_2}^{RT/M_c} \quad 3.2.3-27$$

where K_{Cl} is the rate constant for reaction Cl in units of (g C/cm²-sec-atm O₂). Now the Thiele modulus is

$$\phi_{Cl} = \frac{r_s}{3} \sqrt{\frac{\frac{1}{\alpha} K_{Cl}' S}{D_e}} \quad 3.2.3-28$$

where $K_{Cl}' = K_{Cl}^{RT/M_c}$.

Effectiveness Factor for NO Reduction Reaction

The above method for calculating η was correct for most of the reactions considered. However, the reduction reaction of NO with carbon could not be properly treated with η as it was previously calculated. Not only was NO being reduced within the particle, but it was at the same time being produced by the reactions of the bound nitrogen with oxygen.

Derivation of NO Balance Equations

In this case, the rate of consumption of NO per unit volume in the particle due to reduction is

$$S_v K_{N_2} C_{NO}^{RT/M_c} \quad 3.2.3-29$$

and the rate of production is

$$S_v \gamma \frac{1}{\alpha} K_{Cl} C_{O_2}^{RT/M_c} \quad 3.2.3-30$$

where γ is the ratio of nitrogen to carbon in the particle. Let

$K_{N_2}' = K_{N_2}^{RT/M_c}$, then the balance over a spherical shell volume of thickness Δr for NO gives the following equation:

$$\begin{aligned} (-4\pi r^2 D_e \frac{dC_{NO}}{dr})_r - (-4\pi r^2 D_e \frac{dC_{NO}}{dr})_{r+\Delta r} &= 4\pi r^2 \Delta r S_v K_{N2} C_{NO} \\ &- 4\pi r^2 \Delta r S_v \frac{\gamma}{\alpha} K_{Cl} C_{O_2} \end{aligned}$$

3.2.3-31

C_{O_2} may be substituted for from equation 3.2.3-18, which yields

$$\begin{aligned} \frac{1}{r^2} \frac{d}{dr} r^2 \frac{dC_{NO}}{dr} - \left(\frac{K_{N2} S_v}{D_e} \right) C_{NO} \\ = - \left(\frac{\gamma K_{Cl} S_v}{\alpha D_e} \right) C_{O_{2s}} \frac{r_s}{r} \frac{\sinh(3\phi_{Cl} \frac{r}{r_s})}{\sinh(3\phi_{Cl})} \end{aligned}$$

3.2.3-32

Let

$$\theta = \frac{r}{r_s}$$

and

$$\psi = \frac{C_{NO}}{C_{NO_s}}$$

Then

$$\begin{aligned} \frac{1}{r_s^2} \left(\frac{1}{\theta^2} \frac{d}{d\theta} \theta^2 \frac{d\psi}{d\theta} \right) C_{NO_s} - \left(\frac{K_{N2} S_v}{D_e} \right) \psi C_{NO_s} \\ = \left(\frac{\gamma K_{Cl} S_v}{\alpha D_e} \right) C_{O_{2s}} \frac{1}{\theta} \frac{\sinh(3\phi_{Cl})}{\sinh(3\phi_{Cl})} \end{aligned}$$

3.2.3-33

With BC's:

1. ψ finite at $\theta = 0$.

2. $\psi = 1$ at $\theta = 1$.

Substitute in using equations 3.2.3-19 and 3.2.3-28

$$\phi_{Cl} = \frac{r_s}{3} \sqrt{\frac{K_{Cl} S_v}{\alpha D_e}}$$

3.2.3-34

$$\phi_{N2} = \frac{r_s}{3} \sqrt{\frac{K_{N2} S_v}{D_e}}$$

3.2.3-35

Then, equation 3.2.3-33 becomes

$$\frac{1}{\theta^2} \frac{d}{d\theta} \theta^2 \frac{d\psi}{d\theta} - 9\phi_{N2}^2 \psi = - \frac{\gamma 9\phi_{C1}^2}{\theta} \frac{C_{O2s}}{C_{NOs}} \frac{\sinh(3\phi_{C1})}{\sinh(3\phi_{C1})}$$

3.2.3-36

Let $h_1 = 3\phi_{C1}$ and $h_2 = 3\phi_{N2}$. Then

$$\frac{1}{\theta} \frac{d}{d\theta} \theta^2 \frac{d\psi}{d\theta} - h_2^2 \psi = - \frac{\gamma h_1^2}{\theta} \frac{C_{O2s}}{C_{NOs}} \frac{\sinh(h_1\theta)}{\sinh(h_1)}$$

3.2.3-37

Transforming the equation again, let $v = \psi\theta$. Then

$$\frac{dv}{d\theta} = \psi + \theta \frac{d\psi}{d\theta}$$

and

$$\frac{d^2 v}{d\theta^2} = 2 \frac{d\psi}{d\theta} + \theta \frac{d^2 \psi}{d\theta^2}$$

or

$$\frac{1}{\theta} \frac{d^2 v}{d\theta^2} = \frac{d^2 \psi}{d\theta^2} + \frac{2}{\theta} \frac{d\psi}{d\theta}$$

Substituting into equation 3.2.3-37 above yields

$$\frac{1}{\theta} \frac{d^2 v}{d\theta^2} - h_2^2 \frac{v}{\theta} = - \frac{\gamma h_1^2 C_{O2s}}{C_{NOs}} \frac{1}{\theta} \frac{\sinh(h_1\theta)}{\sinh(h_1)}$$

3.2.3-38

Let

$$B = - \frac{\gamma h_1^2 C_{O2s}}{C_{NOs} \sinh(h_1)}$$

Then equation 3.2.3-38 becomes

$$\frac{d^2 v}{d\theta^2} - h_2^2 v = B \sinh(h_1\theta)$$

3.2.3-39

With BC's:

$$1. \quad v = 0 \quad \text{at} \quad \theta = 0$$

$$2. \quad v = 1 \quad \text{at} \quad \theta = 1$$

Solution of NO Profile

Assume the homogeneous solution (v_H) is of the form

$$v_H = A_1 e^{h_2 \theta} + A_2 e^{-h_2 \theta} \quad 3.2.3-40$$

Now

$$\sinh(h_1 \theta) = \frac{e^{h_1 \theta} - e^{-h_1 \theta}}{2} \quad 3.2.3-41$$

Therefore, the particular solution (v_p) should have the form

$$v_p = C_1 e^{h_1 \theta} + C_2 e^{-h_1 \theta} \quad 3.2.3-42$$

and

$$\frac{d^2 v_p}{d\theta^2} = C_1 h_1^2 e^{h_1 \theta} - C_2 h_1^2 e^{-h_1 \theta} \quad 3.2.3-43$$

Substituting into equation 3.2.3-41 from equations 3.2.3-42 and 3.2.3-43 yields

$$\begin{aligned} C_1 h_1^2 e^{h_1 \theta} + C_2 h_1^2 e^{-h_1 \theta} - C_1 h_2^2 e^{h_1 \theta} - C_2 h_2^2 e^{-h_1 \theta} \\ = B \sinh(h_1 \theta) \end{aligned} \quad 3.2.3-44$$

Substituting in from equation 3.2.3-41 above and rearranging gives

$$C_1 (h_1^2 - h_2^2) e^{h_1 \theta} + C_2 (h_1^2 - h_2^2) e^{-h_1 \theta} = \frac{B}{2} e^{h_1 \theta} - \frac{B}{2} e^{-h_1 \theta}$$

Therefore,

$$C_1 = \frac{B}{2(h_1^2 - h_2^2)} \quad \text{and} \quad C_2 = \frac{-B}{2(h_1^2 - h_2^2)}$$

Substituting into equation 3.2.3-42 for C_1 and C_2 yields

$$\text{or } v_p = \frac{B}{2(h_1^2 - h_2^2)} e^{h_1 \theta} - \frac{B}{2(h_1^2 - h_2^2)} e^{-h_1 \theta}$$

$$v_p = \frac{B}{(h_1^2 - h_2^2)} \sinh(h_1 \theta) \quad 3.2.3-45$$

Now the solution is $v = v_H + v_p$; therefore

$$v = A_1 e^{h_2 \theta} + A_2 e^{-h_2 \theta} + \frac{B}{(h_1^2 - h_2^2)} \sinh(h_1 \theta) \quad 3.2.3-46$$

Applying the boundary conditions and solving for A_1 and A_2 yields

$$A_1 = -A_2$$

and

$$A_1 = \frac{[(h_1^2 - h_2^2) - B \sinh(h_1)]}{2(h_1^2 - h_2^2) \sinh(h_2)}$$

Therefore,

$$v = \frac{[(h_1^2 - h_2^2) - B \sinh(h_1)]}{2(h_1^2 - h_2^2) \sinh(h_2)} (e^{h_2 \theta} - e^{-h_2 \theta})$$

$$+ \frac{B}{(h_1^2 - h_2^2)} \sinh(h_1 \theta) \quad 3.2.3-47$$

Rearranging yields

$$v = \frac{\sinh(h_2 \theta)}{\sinh(h_2)} + \frac{B}{(h_1^2 - h_2^2) \sinh(h_2)} [\sinh(h_2) \sinh(h_1 \theta)$$

$$- \sinh(h_1) \sinh(h_2 \theta)] \quad 3.2.3-48$$

But $v = \psi \theta$; therefore,

$$\psi = \frac{\sinh(h_2)}{\theta \sinh(h_2)} + \frac{B}{\theta (h_1^2 - h_2^2) \sinh(h_2)} [\sinh(h_2) \sinh(h_1 \theta)$$

$$- \sinh (h_1) \sinh (h_2 \theta)] \quad 3.2.3-49$$

Effectiveness Factor Calculation

Defining the effectiveness factor as before,

$$\eta = \frac{R_p}{R_s} \quad 3.2.3-50$$

R_p is calculated by integrating the local reaction rate over the volume of the particle:

$$R_p = \int_0^{r_s} K_{N_2} C_{NO} S_v 4\pi r^2 dr \quad 3.2.3-51$$

Substituting in

$$\theta = \frac{r}{r_s} \quad \text{and} \quad \psi = \frac{C_{NO}}{C_{NO_s}}$$

yields

$$R_p = 4\pi K_{N_2} S_v C_{NO_s} r_s^3 \int_0^1 \psi \theta^2 d\theta \quad 3.2.3-52$$

Evaluating the integral,

$$\int_0^1 \psi \theta^2 d\theta = \int_0^1 \frac{\theta \sinh (h_2 \theta)}{\sinh (h_2)} d\theta + \int_0^1 \frac{B \theta}{(h_1^2 - h_2^2) \sinh (h_2)}$$

$$[\sinh (h_2) \sinh (h_1 \theta) - \sinh (h_1) \sinh (h_2 \theta)] d\theta$$

3.2.3-53

Rearranging yields

$$\begin{aligned} \int_0^1 \psi \theta^2 d\theta &= \frac{1}{\sinh (h_2)} \int_0^1 \theta \sinh (h_2 \theta) d\theta \\ &+ \frac{B}{(h_1^2 - h_2^2)} \int_0^1 \theta \sinh (h_1 \theta) d\theta \\ &- \frac{B \sinh (h_1)}{(h_1^2 - h_2^2) \sinh (h_2)} \int_0^1 \theta \sinh (h_2 \theta) d\theta \end{aligned} \quad 3.2.3-54$$

But,

$$\int_0^1 x \sinh(ax) = \left[\frac{x \cosh(ax)}{a} - \frac{\sinh(ax)}{a^2} \right]_0^1$$

$$\int_0^1 x \sinh(ax) = \frac{\cosh(a)}{a} - \frac{\sinh(a)}{a^2}$$

Therefore, equation 3.2.3-54 above becomes

$$\begin{aligned} \int_0^1 \psi \theta^2 d\theta = & \frac{1}{\sinh(h_2)} \left[1 - \frac{B \sinh(h_1)}{(h_1^2 - h_2^2)} \right] \left[\frac{\cosh(h_2)}{h_2} - \frac{\sinh(h_2)}{h_2^2} \right] \\ & + \frac{B}{(h_1^2 - h_2^2)} \left[\frac{\cosh(h_1)}{h_1} - \frac{\sinh(h_2)}{h_1^2} \right] \end{aligned}$$

3.2.3-55

Rearranging and simplifying yields

$$\begin{aligned} \int_0^1 \psi \theta^2 d\theta = & \left[\frac{1}{h_2 \tanh(h_2)} - \frac{1}{h_2^2} + \frac{B \cosh(h_1)}{h_1(h_1^2 - h_2^2)} \right] \\ & - B \sinh(h_1) \left[\frac{1}{h_2(h_1^2 - h_2^2) \tanh(h_2)} - \frac{1}{h_1^2 h_2^2} \right] \end{aligned}$$

3.2.3-56

which may be substituted into equation 3.2.3-51 to obtain the complete expression for R_p .

Calculation of R_s is much simpler:

$$R_s = K_{N2} 'C_{NO_s} S_v \frac{4}{3} \pi r_s^3$$

3.2.3-57

Substituting into equation 3.2.3-50 for R_p and R_s from equations 3.2.3-51 and 3.2.3-57 yields

$$\eta_{N2} = \frac{4\pi K_{N2} 'S_v r_s^3 C_{NO_s} \int_0^1 \psi \theta^2 d\theta}{\frac{4}{3} \pi K_{N2} 'S_v r_s^3 C_{NO_s}}$$

3.2.3-58

which reduces to

$$\eta_{N2} = 3 \int_0^1 \psi \theta^2 d\theta \quad 3.2.3-59$$

Substituting in for the integral from equation 3.2.3-56 gives

$$\begin{aligned} \eta_{N2} = 3 \left[\frac{1}{h_2 \tanh(h_2)} - \frac{1}{h_2^2} + \frac{B \cosh(h_1)}{h_1(h_1^2 - h_2^2)} \right] \\ - 3 B \sinh(h_1) \left[\frac{1}{h_2(h_1^2 - h_2^2) \tanh(h_2)} - \frac{1}{h_1^2 h_2^2} \right] \end{aligned} \quad 3.2.3-60$$

But

$$h_1 = 3\phi_{C1} \quad \text{and} \quad h_2 = 3\phi_{N2}$$

Therefore,

$$\begin{aligned} \eta_{N2} = 3 \left[\frac{1}{3\phi_{N2} \tanh(3\phi_{N2})} - \frac{1}{(3\phi_{N2})^2} + \frac{B \cosh(3\phi_{C1})}{3\phi_{C1}((3\phi_{C1})^2 - (3\phi_{N2})^2)} \right] \\ - 3 B \sinh(3\phi_{C1}) \left[\frac{1}{27\phi_{N2}(\phi_{C1}^2 - \phi_{N2}^2) \tanh(3\phi_{N2})} \right. \\ \left. - \frac{1}{81\phi_{C1}^2 \phi_{N2}^2} \right] \end{aligned} \quad 3.2.3-61$$

Rearranging and simplifying yields

$$\eta_{N2} = \eta_{N2}' + \frac{B \sinh(3\phi_{C1})}{9(\phi_{C1}^2 - \phi_{N2}^2)} (\eta_{C1} - \eta_{N2}') \quad 3.2.3-62$$

where

$$\eta_{N2}' = \frac{1}{\phi_{N2}} \left[\frac{1}{\tanh(3\phi_{N2})} - \frac{1}{3\phi_{N2}} \right]$$

and

$$\eta_{C1} = \frac{1}{\phi_{C1}} \left[\frac{1}{\tanh(3\phi_{C1})} - \frac{1}{3\phi_{C1}} \right]$$

But

$$B = - \frac{\gamma \phi_{Cl}^2 C_{O_2s}}{C_{NOs} \sinh(3\phi_{Cl})}$$

Therefore

$$\eta_{N_2} = \eta_{N_2'} + \frac{\gamma \phi_{Cl}^2 C_{O_2s}}{(\phi_{Cl}^2 - \phi_{N_2}^2) C_{NOs}} (\eta_{N_2'} - \eta_{Cl'}) \quad 3.2.3-63$$

Substituting in for ϕ_{Cl}^2 and $\phi_{N_2}^2$ from equation 3.2.3-28 and simplifying yields

$$\eta_{N_2} = \eta_{N_2'} + \frac{\gamma K_{Cl}' C_{O_2s}}{(K_{Cl}' - K_{N_2}') C_{NOs}} (\eta_{N_2'} - \eta_{Cl'}) \quad 3.2.3-64$$

Notice that this effectiveness factor may be greater than one. This is possible due to the production of NO in the particle. Some of the NO produced in the particle reacts with the char to form N_2 before it has a chance to diffuse to the surface of the particle. Therefore, the reaction may be proceeding at a faster rate than what would be indicated by surface conditions.

Modifications of Structural Model

As stated earlier, Gavallas' (1980) model was developed for the case of kinetically controlled reactions, while that may not always be the case. To help reduce the error associated with using one variable (Q) to describe the entire solid, it was decided to use η_{Cl} to modify the way in which Q was calculated.

When $\eta = 1$, the concentration of the gas-phase reactant is uniform throughout the char particle and the reactions will be occurring at uniform rates throughout the solid. However, when $\eta < 1$, concentration gradients exist in the particle and the reaction rates are not uniform. In that case, the concentration is higher near the surface and consequently the reaction will be fastest at the surface.

To make use of the difference in reaction rates when $\eta < 1$, the model was modified to allow for carbon to be removed in two ways: 1) it could be removed from the walls of the pores, increasing the diameter and Q; or 2) it could be taken from the outer surface of the particle, reducing its size. The

amount of carbon removed from each source was determined by the value of η_{Cl} . If M_c is the mass of carbon being removed over some time Δt , then ηM_c was removed from the pore wall, while $(1 - \eta)M_c$ was taken from the outer surface of the char particle. In that way, when $\eta^c = 1$, the particle would burn uniformly throughout, and as $\eta \rightarrow 0$ the particle would behave like a shrinking core solid.

With these modifications, it was necessary to develop some expressions which would allow for calculation of r_p and Q as a function of conversion and η_{Cl} . To derive these equations, the following relationship was used:

$$\frac{FL_C}{FL_{C_0}} = \frac{\text{moles of carbon per particle}}{\text{initial moles of carbon per particle}} \quad 3.2.3-65$$

The moles of carbon in a particle are equal to the volume of the particle (cm^3 bulk) times $(1 - \epsilon_T)$ (cm^3 solid/ cm^3 bulk) times the density of carbon (g/cm^3 solid) divided by the molecular weight of the carbon. Therefore,

$$\frac{FL_C}{FL_{C_0}} = \frac{\frac{4}{3} \pi r_p^3 (1 - \epsilon_T) \rho_c (\frac{1}{M_c})}{\frac{4}{3} \pi r_{p_0}^3 (1 - \epsilon_{T_0}) \rho_c (\frac{1}{M_c})} \quad 3.2.3-66$$

which simplifies to give

$$\frac{FL_C}{FL_{C_0}} = \frac{r_p^3 (1 - \epsilon_T)}{r_{p_0}^3 (1 - \epsilon_{T_0})} \quad 3.2.3-67$$

Substituting in for ϵ_T from equation 3.2.3-8, the equation becomes

$$\frac{FL_C}{FL_{C_0}} = \frac{r_p^3}{r_{p_0}^3} \exp [-2\pi (B_0 Q^2 + 2B_1 Q)] \quad 3.2.3-68$$

The above equation may be solved for Q to yield

$$Q = \frac{-2B_1 + \sqrt{4B_1^2 - 2 \frac{B_0}{\pi} \ln \left[\left(\frac{r_{p_0}}{r_p} \right)^3 \frac{FL_C}{FL_{C_0}} \right]}}{2B_0} \quad 3.2.3-69$$

To use the above equation, one needs to know FL_C and r_p . FL_C is calculated directly by the plug flow integration routine. To demonstrate how r_p was calculated, consider the step from time $t = t_1$ to time $t = t_2$. Then,

$$\frac{\text{carbon removed from outer surface}}{\text{carbon initially in particle}} = \frac{(1 - \eta_{Cl}) [FL_C(t_1) - FL_C(t_2)]}{FL_{C_0}}$$

3.2.3-70

and

$$\frac{\text{carbon removed from outer surface}}{\text{carbon initially in particle}}$$

$$= \frac{\frac{4}{3} \pi r_p(t_1)^3 [1 - \epsilon_T(t_1)] \frac{\rho_c}{M_c} - \frac{4}{3} \pi r_p(t_2)^3 [1 - \epsilon_T(t_2)] \frac{\rho_c}{M_c}}{\frac{4}{3} \pi r_{p0}^3 (1 - \epsilon_{T0}) \frac{\rho_c}{M_c}}$$

3.2.3-71

Setting equation 3.2.3-70 equal to equation 3.2.3-71 and simplifying gives

$$\frac{(1 - \eta_c) [FL_C(t_1) - FL_C(t_2)]}{FL_{C_0}}$$

$$= \frac{r_p(t_1)^3 [1 - \epsilon_T(t_1)] - r_p(t_2)^3 [1 - \epsilon_T(t_2)]}{r_{p0}^3 (1 - \epsilon_{T0})}$$

3.2.3-72

If ϵ_T is assumed to be constant over the interval $t_1 \leq t \leq t_2$, then equation 3.2.3-72 above may be solved for $r_p(t_2)$:

$$r_p(t_2) = [r_p(t_1)^3 - \frac{(1 - \eta_{Cl}) (FL_C(t_1) - FL_C(t_2)) r_{p0}^3 (1 - \epsilon_{T0})}{FL_{C_0} (1 - \epsilon_T(t_1))}]^{\frac{1}{3}}$$

3.2.3-73

The total porosity of the particles is calculated at every step and it does change as the reactions progress, but over any time step, Δt , it changes

little and the assumption of constant porosity for the calculation of r_p is valid.

It was also necessary to change to a different model for the case in which $\epsilon_T > 0.7$. For that case, it was assumed that the solid crumbled at $\epsilon_T = 0.7$. After that point, the specific surface area, S_g , was held constant and η was set equal to 1.0 for all reactions. The total surface area in the system would continue to decline as the carbon was consumed, and it would now all be exposed to the same concentration of reactants (i.e., $\eta = 1.0$).

Jacobian

In the homogeneous model, the calculation of the Jacobian elements was a straightforward procedure. The procedure is much the same for the heterogeneous reactions when calculating $\beta_{I,J}$ if species J is a gas-phase reactant. As shown in equation 3.2.3-1, the reaction rates are linear functions of the gas-phase concentrations, with one exception being the reaction of NO with the char. In that case, R_{NO} is also a function of C_{NO} and C_{O_2} , which makes the calculation slightly more complicated, but it is still a simple procedure.

However, when differentiating with respect to the concentration of the solid carbon, the calculations are much more involved. Both the surface area and effectiveness factors are complex functions of the amount of carbon in the system.

Sample Calculations

To demonstrate how the various elements were calculated and adjusted, consider the case of CO_2 . The rate of formation of CO_2 is a function of homogeneous, devolatilization, and heterogeneous reactions:

$$F_{CO_2} = (F_{CO_2})_{homo} + (F_{CO_2})_{het} + (F_{CO_2})_{vol} \quad 3.2.3-74$$

Therefore, the Jacobian may simply be adjusted by adding the appropriate value from the heat reactions to that already calculated from the other reactions:

$$\beta_{CO_2,J} = \left(\frac{\partial F_{CO_2}^v}{\partial FL_J} \right)_{homo} + \left(\frac{\partial F_{CO_2}^v}{\partial FL_J} \right)_{het} + \left(\frac{\partial F_{CO_2}^v}{\partial FL_J} \right)_{vol} \quad 3.2.3-75$$

CO_2 is a reactant in reaction C2 and it is a product in reaction C1; therefore,

$$F_{CO_2} = \left(\frac{2}{\alpha} - 1 \right) R_{C1} - R_{C2} \quad 3.2.3-76$$

and

$$(\beta_{CO_2, J})_{het} = \left(\frac{2}{\alpha} - 1\right) \frac{\partial R_{C1}^v}{\partial FL_J} - \frac{\partial R_{C2}^v}{\partial FL_J} \quad 3.2.3-77$$

Consider the differentials concerning reaction C2:

$$R_{C2} = K_{C2} C_{CO_2} R_g^{TS} r_{C2}^{\eta} / M_c \quad 3.2.3-78$$

Let

$$K_{C2}' = K_{C2} R_g^{T/M_c}$$

Then

$$R_{C2} = K_{C2}' C_{CO_2} S_r^{\eta} r_{C2} \quad 3.2.3-79$$

Expanding the differentials gives

$$\frac{\partial R_{C2}^v}{\partial FL_J} = v \frac{\partial R_{C2}}{\partial FL_J} + R_{C2} \frac{\partial v}{\partial FL_J} \quad 3.2.3-80$$

When calculating the above derivatives, there are three cases to be considered: Case I when J is a gas-phase species, Case II when J is a solid, and Case III when J is a volatile.

Case I: J is a Gas-Phase Specie:

$$\frac{\partial v}{\partial FL_J} = \frac{1}{\rho_m} \quad 3.2.3-81$$

$$v = \frac{\sum_{I=1}^m FL_I}{\rho_m} \quad 3.2.3-82$$

and

$$\frac{\partial R_{C2}}{\partial FL_J} = 0 \quad 3.2.3-83$$

for all J except when J = CO₂. When J = CO₂,

$$\frac{\partial R_{C2}}{\partial FL_{CO_2}} = \frac{\partial R_{C2}}{\partial C_{CO_2}} \frac{\partial C_{CO_2}}{\partial FL_{CO_2}} \quad 3.2.3-84$$

Concentration may be written in terms of FL_I and ρ_m:

$$C_J = \frac{FL_J}{\sum_{I=1}^m FL_I} \rho_m \quad 3.2.3-85$$

Setting J = CO₂ and differentiating with respect to FL_{CO₂} gives

$$\frac{\partial C_{CO_2}}{\partial FL_{CO_2}} = \frac{1}{v} (1 - \omega_{CO_2}) \quad 3.2.3-86$$

$$\omega_{CO_2} = \text{mole of } CO_2$$

Differentiating equation 3.2.3-86 with respect to C_{CO₂} gives

$$\frac{\partial R_{C2}}{\partial C_{CO_2}} = \frac{\partial}{\partial C_{CO_2}} (K_{C2} 'C_{CO_2} S_r \eta_{C2}) \quad 3.2.3-87$$

which reduces to

$$\frac{\partial R_{C2}}{\partial C_{CO_2}} = K_{C2} 'S_r \eta_{C2} \quad 3.2.3-88$$

Substituting equations 3.2.3-81, 3.2.3-86, and 3.2.3-88 into equation 3.2.3-80 gives

$$\frac{\partial R_{C2}^v}{\partial FL_{CO_2}} = K_{C2} 'S_r \eta_{C2} (1 - \omega_{CO_2}) + R_{C2} / \rho_m \quad 3.2.3-89$$

where $J = \text{CO}_2$. For the case when J is any other gas-phase species, substitute equations 3.2.3-81 and 3.2.3-83 into equation 3.2.3-80:

$$\frac{\partial R_{\text{C}_2}^v}{\partial \text{FL}_J} = R_{\text{C}_2} / \rho_m \quad J \neq \text{CO}_2 \quad 3.2.3-90$$

Case II: Species J is a Solid. In equation 3.2.3-82, the summation is overall gas-phase species; v is not a function of FL_J when J is a solid. Therefore,

$$\frac{\partial v}{\partial \text{FL}_J} = 0 \quad 3.2.3-91$$

The heterogeneous reactions are not influenced by the amount of solid nitrogen in the system. Therefore,

$$\frac{\partial R_{\text{C}_2}}{\partial \text{FL}_J} = 0 \quad \text{when } J = \text{N} \quad 3.2.3-92$$

The reactions are, however, functions of FL_C .

Calculation of $\partial R_{\text{C}_2} / \partial \text{FL}_C$ requires the following equations:

$$Q(X_c) = \frac{-2B_1 + \sqrt{4B_1^2 - \frac{2B_0}{\pi} \ln \left[\left(\frac{r_{p0}}{r_p} \right)^3 (1 - X_c) \right]}}{2B_0} \quad 3.2.3-93$$

$$X_c = 1 - \frac{\text{FL}_C}{\text{FL}_{\text{CO}}} \quad 3.2.3-94$$

$$S_r(Q) = 2.0 \times 10^8 \pi (B_0 Q + B_1) C_c M_c \quad 3.2.3-95$$

and the relationships giving η as a function of Q :

$$\eta = \frac{1}{\phi} \left(\frac{1}{\tanh 3\phi} - \frac{1}{3\phi} \right) \quad 3.2.3-96$$

$$\phi = \frac{r_p}{3} \sqrt{\frac{K' S_v}{D_s}} \quad 3.2.3-97$$

$$S_v(Q) = 4.0 \times 10^8 \pi (B_0 Q + B_1) (1 - c_T(Q)) \quad 3.2.3-98$$

$$\epsilon_T(Q) = 1 - (1 - \epsilon_{T_0}) \exp [-2\pi(B_0 Q^2 + 2B_1 Q)] \quad 3.2.3-99$$

$$D_e = \int_{r_*}^{r^*} \epsilon(r, Q) \delta(r, Q) dr \quad 3.2.3-100$$

$$\epsilon(r, Q) = 2\pi(r + Q)^2 \lambda(r) \exp [-2\pi \int_{r_*}^{r^*} (r' + Q)^2 \lambda(r') dr'] \quad 3.2.3-101$$

$$\delta(r, Q) = \left[\frac{1}{D_{A,B}} + \frac{1}{A_k(r + Q)} \right]^{-1} \quad 3.2.3-102$$

Restating the reaction rate for C2:

$$R_{C2} = K_{C2} 'C_{CO_2} S_r \eta_{C2} \quad 3.2.3-103$$

Differentiating with respect to FL_C :

$$\frac{\partial R_{C2}}{\partial FL_C} = K_{C2} 'C_{CO_2} \left(\eta_{C2} \frac{\partial S_r}{\partial FL_C} + S_r \frac{\partial \eta_{C2}}{\partial FL_C} \right) \quad 3.2.3-104$$

The derivative $\partial S_r / \partial FL_C$ may be found by differentiating equation 3.2.3-95 with respect to FL_C :

$$\frac{\partial S_r}{\partial FL_C} = C_c M_c 2 \times 10^8 \pi B_0 \frac{dQ}{dFL_C} + 2 \times 10^8 \pi (B_0 Q + B_1) M_c \frac{\partial C_c}{\partial FL_C} \quad 3.2.3-105$$

dQ/dFL_C is derived by substituting $(1 - FL_C/FL_{CO})$ for X_c in equation 3.2.3-93 and then differentiating:

$$\frac{dQ}{dFL_C} = -\frac{1}{2\pi} \left(\frac{1}{FL_C} - \frac{3}{r_p} \frac{dr_p}{dFL_C} \right) \left[4B_1^2 - \frac{2B_0}{\pi} \ln \left(\left(\frac{r_p}{r_p} \right)^3 \frac{FL_C}{FL_{CO}} \right) \right]^{-\frac{1}{2}} \quad 3.2.3-106$$

Differentiating equation 3.2.3-82 with $J = C$, noting that the summation includes only gas-phase species, yields

$$\frac{\partial C_C}{\partial FL_C} = \frac{1}{v} \quad 3.2.3-107$$

Substitution of equations 3.2.3-106 and 3.2.3-107 into equation 3.2.3-105 gives

$$\begin{aligned} \frac{\partial S_r}{\partial FL_C} = & - C_c M_c \cdot 1 \times 10^8 B_0 \left(\frac{1}{FL_C} - \frac{3}{r_p} \frac{dr_p}{dFL_C} \right) \\ & \cdot \left[4B_1^2 - \frac{2B_0}{\pi} \ln \left(\left(\frac{r_{p0}}{r_p} \right)^3 \frac{FL_C}{FL_{C0}} \right) \right] - \frac{1}{2} \\ & + 2 \times 10^8 \pi (B_0 Q + B_1) M_c / v \end{aligned} \quad 3.2.3-108$$

Calculation of $\partial \eta_{C2} / \partial FL_C$ requires a number of steps. Expanding the derivative gives

$$\frac{\partial \eta_{C2}}{\partial FL_C} = \frac{d\eta_{C2}}{d\phi_{C2}} \frac{\partial \phi_{C2}}{\partial FL_C} \quad 3.2.3-109$$

An analytical solution for $d\eta_{C2}/d\phi_{C2}$ may be obtained by differentiating equation 3.2.3-96 with respect to ϕ_{C2} :

$$\frac{d\eta_{C2}}{d\phi_{C2}} = \frac{1}{\phi_{C2}^2} \left(\frac{1}{3\phi_{C2}} - \frac{1}{\tanh 3\phi_{C2}} \right) + \frac{1}{\phi_{C2}} \left(\frac{1}{3\phi_{C2}^2} - \frac{3}{\sinh^2 3\phi_{C2}} \right) \quad 3.2.3-110$$

Differentiation of equation 3.2.3-97 with respect to FL_C yields

$$\frac{\partial \phi_{C2}}{\partial FL_C} = \frac{dr_p}{dFL_C} \frac{1}{3} \left(\frac{K_{C2} S_v}{D_e} \right)^{\frac{1}{2}} + \frac{r_p}{6} \left(\frac{K_{C2} S_v}{D_e} \right) - \frac{1}{2}$$

$$\cdot \left(\frac{K_{C2}}{D_e} \frac{dS_v}{dFL_C} - \frac{K_{C2} S_v}{D_e^2} \frac{D_e}{FL_C} \right) \quad 3.2.3-111$$

Expanding the derivative dS_v/dFL_C yields

$$\frac{dS_v}{dFL_C} = \frac{dS_v}{dQ} \frac{dQ}{dFL_C} \quad 3.2.3-112$$

dS_v/dQ may be found by differentiating equation 3.2.3-98 with respect to Q (dQ/dFL_C is given in equation 3.2.3-106):

$$\begin{aligned} \frac{dS_v}{dQ} = & 4\pi 10^8 \pi (1 - \epsilon_{T_0}) [B_0 - 4\pi (B_0 Q + B_1)^2] \\ & \exp [-2\pi (B_0 Q^2 + 2B_1 Q)] \end{aligned} \quad 3.2.3-113$$

Calculation of $\epsilon D_e / \partial FL_C$ needed in equation 3.2.3-111 is outlined below. Since n_e is a function of Q , it is convenient to rewrite the derivative as

$$\frac{\partial D_e}{\partial FL_C} = \frac{\partial D_e}{\partial Q} \frac{dQ}{dFL_C} \quad 3.2.3-114$$

dQ/dFL_C is given in equation 3.2.3-106. Differentiating equation 3.2.3-100 with respect to Q gives

$$\frac{\partial D_e}{\partial Q} = \int_{r_*}^{r^*} [\epsilon(r, Q) \frac{\partial \delta(r, Q)}{\partial Q} + \delta(r, Q) \frac{\partial \epsilon(r, Q)}{\partial Q}] dr \quad 3.2.3-115$$

Differentiation of equation 3.2.3-102 with respect to Q yields

$$\frac{\partial \delta(r, Q)}{\partial Q} = \left[\frac{1}{D_{A,B}} + \frac{1}{A_k(r+Q)} \right]^{-2} \frac{1}{A_k(r+Q)^2} \quad 3.2.3-116$$

$\partial \epsilon(r, Q) / \partial Q$ is found by differentiating equation 3.2.3-101 with respect to Q :

$$\frac{\partial \epsilon(r, Q)}{\partial Q} = 4\pi \lambda(r)(r+Q) \exp [-2\pi \int_{r_*}^{r^*} (r'+Q)^2 (r') dr']$$

$$\cdot \left[1 + \frac{1}{2} (r+Q) (-2\pi \int_{r_*}^{r^*} 2(r'+Q)\lambda(r') dr') \right] \quad 3.2.3-117$$

Finally, all necessary derivatives have been obtained to allow the calculation of $\partial R_{C2}/\partial FL_C$. A summary of the calculations is given below.

$$\frac{\partial R_{C2}}{\partial FL_C} = K_{C2}' C_{CO_2} \left(\eta_{C2} \frac{\partial S_r}{\partial FL_C} + S_r \frac{\partial \eta_{C2}}{\partial FL_C} \right) \quad 3.2.3-118$$

where

$$\frac{\partial S_r}{\partial FL_C} = - C_c M_c \cdot 1 \times 10^8 B_0 \left(\frac{1}{FL_C} - \frac{3}{r_p} \frac{dr_p}{dFL_C} \right)$$

$$\left[4B_1^2 - \frac{2B_0}{\pi} \ln \left(\left(\frac{r_{p0}}{r_p} \right)^3 \frac{FL_C}{FL_{CO}} \right) \right]^{-\frac{1}{2}}$$

$$+ 2 \times 10^8 \pi (B_0 Q + B_1) M_c / v \quad 3.2.3-119$$

and

$$\frac{\partial \eta_{C2}}{\partial FL_C} = \frac{d\eta_{C2}}{d\phi_{C2}} \frac{\partial \phi_{C2}}{\partial FL_C}$$

From equation 3.2.3-110,

$$\frac{d\eta_{C2}}{d\phi_{C2}} = \frac{1}{\phi_{C2}^2} \left(\frac{1}{3\phi_{C2}} - \frac{1}{\tanh 3\phi_{C2}} \right) + \frac{1}{\phi_{C2}} \left(\frac{1}{3\phi_{C2}^2} - \frac{3}{\sinh^2 3\phi_{C2}} \right)$$

3.2.3-120

and equation 3.2.3-111,

$$\frac{\partial \phi_{C2}}{\partial FL_C} = \frac{dr_p}{dFL_C} \frac{1}{3} \left(\frac{K_{C2}' S_v}{D_e} \right)^{\frac{1}{2}} + \frac{r_p}{6} \frac{K_{C2}' S_v}{D_e} - \frac{1}{2} \left[\frac{K_{C2}'}{D_e} \frac{dS_v}{dFL_C} \right.$$

$$\left. - \frac{K_{C2}' S_v}{D_e^2} \frac{\partial D_e}{\partial FL_C} \right]$$

3.2.3-121

where

$$\frac{dS_v}{dFL_C} = - 2 \times 10^8 (1 - \epsilon_{T_0}) (B_0 - 4\pi (B_0 Q + B_1)^2)$$

$$\exp \left[-2\pi (B_0 Q^2 + 2B_1 Q) \right] \left(\frac{1}{FL_C} - \frac{3}{r_p} \frac{dr_p}{dFL_C} \right) \cdot \left[4B_1^2 - \frac{2B_0}{\pi} \ln \left(\left(\frac{r_{p0}}{r_p} \right)^3 \frac{FL_C}{FL_{CO}} \right) \right]^{-\frac{1}{2}} \quad 3.2.3-122$$

and

$$\frac{\partial D_e}{\partial FL_C} = -\frac{1}{2\pi} \left(\frac{1}{FL_C} - \frac{3}{r_p} \frac{dr_p}{dFL_C} \right) \left[4B_1^2 - \frac{2B_0}{\pi} \ln \left(\left(\frac{r_{p0}}{r_p} \right)^3 \frac{FL_C}{FL_{CO}} \right) \right]^{-\frac{1}{2}}$$

$$\int_{r_*}^{r^*} \left[\epsilon(r, Q) \left(\frac{1}{D_{A,B}} + \frac{1}{A_k(r+Q)} \right) - 2 \frac{1}{A_k(r+Q)^2} + \delta(r, Q) 4\pi \lambda(r)(r+Q) \exp \left(-2\pi \int_{r_*}^{r^*} (r'+Q)^2 \lambda(r') dr' \right) \right. \\ \left. \cdot \left[1 + \frac{1}{2} (r+Q) \left(-2\pi \int_{r_*}^{r^*} 2(r'+Q) \lambda(r') dr' \right) \right] \right] dr \quad 3.2.3-123$$

The above equations are functions of system variables which are calculated directly, and dr/dFL_C which is approximated for any step as $\Delta r/\Delta FL_C$ from the previous step. So, for Case II when $J = C$,

$$\frac{\partial R_{C2}^v}{\partial FL_J} = v \frac{\partial R_{C2}}{\partial FL_J} \quad 3.2.3-124$$

Case III: Specie J is a Volatile. As in Case II, V is not a function of FL_J . Therefore,

$$\frac{\partial v}{\partial FL_J} = 0 \quad 3.2.3-125$$

The heterogeneous reactions are independent of the volatile concentrations so that

$$\frac{\partial R_{C2}}{\partial FL_J} = 0 \quad 3.2.3-126$$

Substituting equations 3.2.3-125 and 3.2.3-126 into equation 3.2.3-80 yields

$$\frac{\partial R_{C2}^v}{\partial FL_J} = 0 \quad 3.2.3-127$$

The above series of calculations demonstrates the procedures used when calculating the derivatives $\partial R_{C2}^v / \partial FL_J$. Calculation of the derivatives needed for the other Jacobian elements where heterogeneous reactions are involved is the same as in the above example. Only the rate constants and stoichiometry of the reactions may be different, depending on which reaction is involved.

Alpha Vector

When calculating the reaction rates for the homogeneous reactions, the only variables which are a function of time are the Arrhenius rate constants. These are functions of temperature and temperature is a specified function of time in this model. Therefore, calculation of the elements of the alpha vector was quite simple

When heterogeneous reactions are involved, the calculations become slightly more complicated. Now, not only are the rate constants functions of temperature, but so are the effectiveness factors.

Sample Calculations

To demonstrate how the various elements were calculated and adjusted, the case of CO_2 will again be used as an example:

$$F_{CO_2} = (F_{CO_2})_{homo} + (F_{CO_2})_{het} + (F_{CO_2})_{vol} \quad 3.2.3-128$$

Therefore,

$$\alpha_{CO_2} = \frac{\partial F_{CO_2}^v}{\partial t} = \left(\frac{\partial F_{CO_2}^v}{\partial t} \right)_{homo} + \left(\frac{\partial F_{CO_2}^v}{\partial t} \right)_{het} + \left(\frac{\partial F_{CO_2}^v}{\partial t} \right)_{vol} \quad 3.2.3-129$$

$$F_{CO_2} = \left(\frac{2}{\alpha} - 1 \right) R_{C1} - R_{C2} \quad 3.2.3-130$$

and

$$(\alpha_{CO_2})_{het} = \left(\frac{2}{\alpha} - 1 \right) \frac{\partial R_{C1}^v}{\partial t} - \frac{\partial R_{C2}^v}{\partial t} \quad 3.2.3-131$$

Consider the differentials concerning reaction C2:

$$R_{C2} = K_{C2} C_{CO_2}^{S_{rC2}} \quad 3.2.3-132$$

Multiplying R_{C2} by v and differentiating with respect to t :

$$\frac{\partial R_{C2} v}{\partial t} = v \frac{\partial R_{C2}}{\partial t} + R_{C2} \frac{\partial v}{\partial t} \quad 3.2.3-133$$

As stated before, temperature (T) is a specified function of time. Therefore, equation 3.2.3-133 may be rewritten to give

$$\frac{\partial R_{C2} v}{\partial t} = (v \frac{\partial R_{C2}}{\partial T} + R_{C2} \frac{\partial v}{\partial T}) \frac{dT}{dt} \quad 3.2.3-134$$

In the system, temperature is either specified as an exponential decay or given as a number of points of temperature along the length of the reactor. When the temperature is an exponential function, a simple analytical expression giving the derivative as a function of time is used. Given

$$T = T_a \exp \left(\frac{t}{t_b} \log \frac{T_b}{T_a} \right) \quad 3.2.3-135$$

where T_a is the temperature at time $t = 0$ and T_b is the temperature at time $t = t_b$. Then

$$\frac{dT}{dt} = T \left(\frac{1}{t_b} \log \frac{T_b}{T_a} \right) \quad 3.2.3-136$$

If the temperature is given as a number of discrete points, a second-order Langrange's interpolating polynomial is used to obtain the temperature profile in the reactor:

$$T(t) = \frac{(t - t_2)(t - t_3)}{(t_1 - t_2)(t_1 - t_3)} T_1 + \frac{(t - t_1)(t - t_3)}{(t_2 - t_1)(t_2 - t_3)} T_2 + \frac{(t - t_1)(t - t_2)}{(t_3 - t_1)(t_3 - t_2)} T_3 \quad 3.2.3-137$$

Differentiating equation 3.2.3-137 with respect to t gives

$$\begin{aligned} \frac{dT}{dt} = & \frac{2t - t_2 - t_3}{(t_1 - t_2)(t_1 - t_3)} T_1 + \frac{2t - t_1 - t_3}{(t_2 - t_1)(t_2 - t_3)} T_2 \\ & + \frac{2t - t_1 - t_2}{(t_3 - t_1)(t_3 - t_2)} T_3 \end{aligned} \quad 3.2.3-138$$

The derivative $\partial v / \partial T$ is obtained by differentiating equation 3.2.3-80 with respect to T :

$$\frac{\partial v}{\partial T} = \frac{R_g \sum_{I=1}^m FL_I}{P} \quad 3.2.3-139$$

Before calculating $\partial R_{C2} / \partial T$, it is convenient to rewrite R_{C2} by combining equation 3.2.3-134 with equations 3.2.3-78 and 3.2.3-6:

$$R_{C2} = K_{C2} P_{CO_2} S_g C_c \eta_{C2} \quad 3.2.3-140$$

Then, from equation 3.2.3-85,

$$C_c = \frac{FL_C}{\sum_{I=1}^m FL_I} \rho_m \quad 3.2.3-141$$

and

$$\rho_m = \frac{P}{R_g T} \quad 3.2.3-142$$

Therefore,

$$R_{C2} = P_{CO_2} S_g \frac{FL_C}{\sum_{I=1}^m FL_I} \frac{P}{R_g} \frac{K_{C2} \eta_{C2}}{T} \quad 3.2.3-143$$

Of the variables in equation 3.2.3-143 above, K_{C2} , η_{C2} , and T are the only ones which are functions of T (pressure is constant). Let

$$B = P_{CO_2} S_g \frac{FL_C}{\sum_{I=1}^m FL_I} \frac{P}{R_g} \quad 3.2.3-144$$

Then

$$\frac{\partial R_{C2}}{\partial T} = B \left(\frac{\eta_{C2}}{T} \frac{dK_{C2}}{dT} + \frac{K_{C2}}{T} \frac{\partial \eta_{C2}}{\partial T} + K_{C2} \eta_{C2} \frac{d}{dT} \frac{1}{T} \right) \quad 3.2.3-145$$

Now, calculating the derivatives in equation 3.2.3-145 above,

$$\frac{d}{dT} \frac{1}{T} = -\frac{1}{T^2} \quad 3.2.3-146$$

By definition,

$$K_{C2} = k_{C2} \exp \left(\frac{-E_{C2}}{R_g T} \right) \quad 3.2.3-147$$

Differentiating gives

$$\frac{dK_{C2}}{dT} = K_{C2} \frac{E_{C2}}{R_g T^2} \quad 3.2.3-148$$

Calculation of the derivative of η_{C2} requires that it first be rewritten as

$$\frac{\partial \eta_{C2}}{\partial T} = \frac{d\eta_{C2}}{d\phi_{C2}} \frac{\partial \phi_{C2}}{\partial T} \quad 3.2.3-149$$

$d\eta_{C2}/d\phi_{C2}$ is given in equation 3.2.3-120. Differentiation of equation 3.2.3-97 with respect to T yields

$$\frac{\partial \phi_{C2}}{\partial T} = \frac{r_p}{3} \left(\frac{K_{C2} S_v}{D_e} \right) - \frac{1}{2} \left(\frac{S_v}{D_e} \frac{dK_{C2}}{dT} - \frac{K_2 S_v}{D_e^2} \frac{\partial D_e}{\partial T} \right) \quad 3.2.3-150$$

However, since K_2 is a much stronger function of T than D_e , the above equation reduced to

$$\frac{\partial \phi_{C2}}{\partial T} = \frac{r_p}{3} \left(\frac{S_v}{K_{C2} D_e} \right) - \frac{1}{2} \frac{dK_{C2}}{dT} \quad 3.2.3-151$$

dK_{C2}/dT is given in equation 3.2.3-148 above. Substituting the appropriate values back into equation 3.2.3-145 gives

$$\begin{aligned} \frac{\partial R_{C2}}{\partial T} = & P_{CO_2} S_g \frac{FL_C}{\sum_{I=1}^m FL_I} \frac{PK_{C2}}{R_g T^2} \left(\frac{\eta_{C2} E_{C2}}{R_g T} \right. \\ & \left. + \frac{E_{C2}}{R_g} \frac{r_p}{3} \left(\frac{K_{C2} S_v}{D_e} \right) \frac{1}{2} \frac{d\eta_{C2}}{d\phi_{C2}} - \eta_{C2} \right) \end{aligned} \quad 3.2.3-152$$

where

$$\frac{d\eta_{C2}}{d\phi_{C2}} = \frac{1}{\phi_{C2}^2} \left(\frac{1}{3\phi_{C2}} - \frac{1}{\tanh 3\phi_{C2}} \right) + \frac{1}{\phi_{C2}} \left(\frac{1}{3\phi_{C2}^2} - \frac{3}{\sinh^2 3\phi_{C2}} \right) \quad 3.2.3-153$$

Now that dT/dt , $\partial v/\partial T$, and $\partial R_{C2}/\partial T$ have all been calculated, they may be used in equation 3.2.3-134 to obtain $\partial R_{C2} v/\partial t$. Calculation of $\partial R_J v/\partial t$, where J represents any heterogeneous reaction, involves the same procedure as that outlined above. These derivatives may then be used to calculate or adjust the α_I elements.

3.2.4 Devolatilization Modeling

As with the heterogeneous reactions, the devolatilization reaction kinetics are significantly different from those for the homogeneous gas-phase reactions. The rate of the devolatilization is a function of the amount of volatilizable material remaining rather than the concentration of one or more species. Therefore, it was necessary to develop a separate routine for the devolatilization reactions.

The devolatilization routine calculates all the rates for the devolatilization reactions and uses them to find the new F_I values and modify any others which are affected. It calculates all necessary derivatives and then adjusts the alpha vector and beta matrix to include any new elements and modify those affected by the devolatilization reactions. It also calculates the amount of volatilizable material present in the coal, given the proximate and ultimate analysis.

Volatile Species

The addition of the volatiles to the system adds MV dependent variables to the set, one for each volatile species. If more than one size class is present, the volatiles are evenly distributed among the classes, but there is still only one dependent variable for each volatile species. Therefore, at any time, the FL vector will contain information on how many moles of volatile

species I are flowing through the system, but it will not say how it is distributed among the various size classes.

To determine how much of each species is in each size fraction, the initial amount is simply found by multiplying the weight fraction of each size class by the total initial amount of each volatile species. Then, after each step, the amount of species I devolatilized from size fraction J is calculated and then subtracted from the previous value to give the present amount of species I in size fraction J. The amount of I devolatilized from fraction J cannot be calculated exactly, but may be approximated as the total amount of I devolatilized multiplied by the ratio of the rate of I devolatilized from fraction J over the total rate of devolatilization of species I from all fractions.

Volatile Composition and Reactions

It is assumed that the gases produced during devolatilization consist of the following species: CO, CO₂, H₂O, CH₄, tar (CH_Y), and moisture. A distinction is made between water present in the coal before combustion (called moisture) and that formed during devolatilization (called H₂O). These products evolve from pockets of volatilizable material in the coal.

For the purpose of modeling, the coal may be described by a pie chart with the sections representing the type and amount of volatile and solid material present in the coal (Figure 3.2.4-1).

The volatile material is superscripted with an * to differentiate them from the gas-phase species. The devolatilization reactions are, then, simply

The tar reaction is more complex. Tar is a chemically complex substance which consumes oxygen as it is released into the gas phase. However, the homogeneous model is unable to handle the case of CH_Y reacting with O₂ due to the fact that Y is not an integer and no reaction path or kinetic data is available for such a reaction. Therefore, it is assumed that the tar reacts with oxygen instantaneously upon being evolved into the gas phase to form CO and CH₄.

Figure 3.2.4-1. Coal Composition (Schematic).

Reaction Kinetics

For this model, it is assumed that the rate of the devolatilization reactions is directly proportional to the amount of volatilizable material remaining. The reaction rates may be written in the form

$$R_v = K_v C_v \quad 3.2.4-1$$

where K_v is an Arrhenius rate constant, C_v is the concentration of the volatilizable material, and R_v is the rate at which the volatile material is being evolved. A listing of the kinetic parameters used is given in Table 3.2.4-1.

Table 3.2.4-1. Devolatilization Kinetic Parameters.

Volatile Specie	k (sec^{-1})	E (cal)	Reference
CO*	2.63×10^{12}	59,000	Suuburg et al. (1979)
CO ₂ *	2.14×10^{11}	36,200	Suuburg et al. (1979)
H ₂ O*	7.93×10^{13}	51,400	Suuburg et al. (1979)
CH ₄ *	6.6×10^4	25,000	Kobayashi et al. (1977)
Tar	6.6×10^5	25,000	Kobayashi et al. (1977)

The rates are easily calculated and are then used to modify the F_I values. The rate of formation of any specie is a function of the rates of all the reactions in which it is involved. For example, F_{O_2} would have to be modified to include the contribution of the tar reaction²

$$(F_{O_2})_{\text{total}} = (F_{O_2})_{\text{hom}+\text{het}} - \frac{1}{2} \left(1 - \frac{Y}{4}\right) R_{v6} \quad 3.2.4-2$$

Jacobian

As with the heterogeneous reactions, the Jacobian elements may simply be adjusted by adding in the appropriate values for each species (see equation 3.2.3-75). Again using the case of CO₂ as an example, the partial derivative of $(F_{CO_2})_{\text{vol}}$ with respect to the various species may be found.

F_{CO_2} is only a function of one devolatilization reaction. Therefore,

$$(F_{CO_2})_{\text{vol}} = R_{v_2} \quad 3.2.4-3$$

Substituting in for R_{v_2} from Table 3.2.4-1,

$$(F_{CO_2})_{vol} = K_{v_2} C_{CO_2*} \quad 3.2.4-4$$

Multiplying by v and differentiating with respect to species J gives

$$\frac{\partial (F_{CO_2})_{vol} v}{\partial FL_J} = v K_{v_2} \frac{\partial C_{CO_2*}}{\partial FL_J} + K_{v_2} C_{CO_2*} \frac{\partial v}{\partial FL_J} \quad 3.2.4-5$$

When calculating the above derivative, there are three cases to be considered: Case I when species J is a gas, Case II when species J is a solid, and Case III when species J is a volatile.

First, consider the derivative of v with respect to FL_J . The answers for cases I and II were calculated previously and are given below. For Case I, species J as a gas:

$$\frac{\partial v}{\partial FL_J} = \frac{1}{\rho_m} \quad 3.2.4-6$$

For Case II, species J as a solid:

$$\frac{\partial v}{\partial FL_J} = 0 \quad 3.2.4-7$$

For Case III, the derivative may be found by substituting in for v :

$$v = \frac{\sum_{I=1}^m FL_J}{\rho_m} \quad 3.2.4-8$$

and noting that the summation is only over the gas-phase species. Therefore, for Case III, species J as a volatile:

$$\frac{\partial v}{\partial FL_J} = 0 \quad 3.2.4-9$$

Next, the partial derivative of C_{CO_2} with respect to FL_J may be found by first expanding the derivative

$$\frac{\partial C_{CO_2^*}}{\partial FL_J} = \frac{\partial C_{CO_2^*}}{\partial C_J} \frac{\partial C_J}{\partial FL_J} \quad 3.2.4-10$$

$\partial C_{CO_2^*}/\partial C_J$ is zero for all $J \neq CO_2^*$. Therefore,

Case I:

$$\frac{\partial C_{CO_2^*}}{\partial C_J} = 0 \quad 3.2.4-11$$

Case II:

$$\frac{\partial C_{CO_2^*}}{\partial C_J} = 0 \quad 3.2.4-12$$

Case III:

$$\frac{\partial C_{CO_2^*}}{\partial C_J} = 0 \quad \text{for all } J \neq CO_2^* \quad 3.2.4-13$$

$$\frac{\partial C_{CO_2^*}}{\partial C_J} = 1 \quad \text{for } J = CO_2^* \quad 3.2.4-14$$

Equation 3.2.3-85 gives C_J in terms of FL_J and ρ_m :

$$C_J = \frac{FL_J}{\sum_{I=1}^m FL_I} \rho_m \quad 3.2.4-15$$

If $J = CO_2^*$, then differentiating with respect to $FL_{CO_2^*}$ gives

$$\frac{\partial C_{CO_2^*}}{\partial FL_{CO_2^*}} = \frac{\rho_m}{\sum_{I=1}^m FL_I} = \frac{1}{v} \quad 3.2.4-16$$

Therefore, substituting into equation 3.2.4-5 from equations 3.2.4-6 through 3.2.4-16 gives the following:

Case I:

$$(\beta_{\text{CO}_2, \text{J}})_{\text{col}} = K_{\text{v2}} C_{\text{CO}_2^*} / \rho_{\text{m}} \quad 3.2.4-17$$

Case II:

$$(\beta_{\text{CO}_2, \text{J}})_{\text{vol}} = 0 \quad 3.2.4-18$$

Case III:

$$(\beta_{\text{CO}_2, \text{J}})_{\text{vol}} = K_{\text{v2}} \quad 3.2.4-19$$

Calculation of the other Jacobian elements would be carried out in the same manner using the appropriate rate constants and coefficients for each species.

Alpha Vector

The elements of the alpha vector are of the form

$$\alpha_{\text{I}} = \frac{\partial F_{\text{I}}^{\text{v}}}{\partial t} \quad 3.2.4-20$$

Recognizing again that F_{I} has a homogeneous, heterogeneous, and volatile component,

$$\alpha_{\text{I}} = \left(\frac{\partial F_{\text{I}}^{\text{v}}}{\partial t} \right)_{\text{homo}} + \left(\frac{\partial F_{\text{I}}^{\text{v}}}{\partial t} \right)_{\text{het}} + \left(\frac{\partial F_{\text{I}}^{\text{v}}}{\partial t} \right)_{\text{vol}} \quad 3.2.4-21$$

The homogeneous and heterogeneous components have been discussed previously. To demonstrate calculation of the volatile component, CO_2 will again be used as an example:

$$(\alpha_{\text{CO}_2})_{\text{vol}} = \frac{\partial}{\partial t} (K_{\text{v2}} C_{\text{CO}_2^*}^{\text{v}}) \quad 3.2.4-22$$

Substituting in for $C_{CO_2^*}$ from equation 3.2.3-85,

$$(\alpha_{CO_2})_{vol} = \frac{\partial}{\partial t} (K_{v2} \frac{FL_{CO_2^*}}{\sum_{I=1}^m FL_I} \frac{P}{R_g T} v) \quad 3.2.4-23$$

Recalling equation 3.2.3-82,

$$v = \frac{\sum_{I=1}^m FL_I}{(\frac{P}{R_g T})} \quad 3.2.4-24$$

Equation 3.2.4-23 above reduces to

$$(\alpha_{CO_2})_{vol} = \frac{\partial}{\partial t} (K_{v2} FL_{CO_2^*}) \quad 3.2.4-25$$

Since $FL_{CO_2^*}$ is not an explicit function of time,

$$(\alpha_{CO_2})_{vol} = FL_{CO_2^*} \frac{\partial K_{v2}}{\partial t} \quad 3.2.4-26$$

Substituting in for K_{v2} from Table 3.2.4-1 and differentiating gives

$$(\alpha_{CO_2})_{vol} = FL_{CO_2^*} k_{v2} \exp\left(\frac{-E_{v2}}{R_g T}\right) \frac{E_{v2}}{R_g T^2} \quad 3.2.4-27$$

or

$$(\alpha_{CO_2})_{vol} = K_{v2} FL_{CO_2^*} \frac{E_{v2}}{R_g T^2} \quad 3.2.4-28$$

The elements of the alpha vector for the other volatile species would be the same as in equation 3.2.4-28 above except for rate constants and coefficients. Some of the species are affected by more than one devolatilization reaction and would, therefore, require summing the contributions from each reaction.

Calculation of Volatiles Composition

As mentioned previously, the rate of volatile evolution is a function of the amount of volatile material present. It is difficult to measure the amount of these materials present in the raw coal. Therefore, a scheme was

devised to calculate the initial amounts from the proximate and ultimate analysis of the coal.

The volatile materials assumed to be present in the coal are CO, CO₂, H₂O, CH₄, tar (CH_y), and moisture. In performing the calculations, four other assumptions are invoked: 1) all the oxygen and hydrogen come off with the volatiles; 2) the ratio oxygen is N₂O, CO, and CO₂ is the same as that reported by Suuberg et al. (1979); 3) all nitrogen and sulfur remain in the char; and 4) the carbon-to-hydrogen ratio in the tar is equal to the carbon-hydrogen ratio in the coal after removal of the CO, CO₂, and H₂O from the coal.

Since the initial mass flow rate of the coal is known, the initial flow rates of the species in the coal were calculated directly from the coal flow rate. The flow area in the model is held constant throughout the reactor, therefore balancing mass or molar fluxes is identical to balancing total flow. Table 3.2.4-2 contains some characteristic values for the coal flow, and proximate and ultimate analysis used in this work. It also shows the species molar flow rates and coal composition in weight % as calculated using the following procedure.

The initial amounts of volatiles are calculated as follows. FL_{coal}' is the initial mass flux of coal in the system, FR_I is the mass fraction of element I in the coal, and FRO_J is the fraction of the oxygen in the coal contained in species J. Then

$$FL_{CO*} = FL_{coal} 'FR_O FRO_{CO} / M_O \quad 3.2.4-29$$

$$FL_{CO_2*} = FL_{coal} 'FR_O FRO_{CO_2} / (M_O \times 2) \quad 3.2.4-30$$

$$FL_{H_2O*} = FL_{coal} 'FL_O FRO_{H_2O} / M_O \quad 3.2.4-31$$

Calculation of the amount of tar in the coal required a few more calculations. Making a balance on the moles of volatile carbon in the coal,

$$FL_{C_{vol}} = FL_{CO*} + FL_{CO_2*} + FL_{CH_4*} + FL_{tar} \quad 3.2.4-32$$

Balancing the hydrogen gives

$$FL_H = 2FL_{H_2O} + 4FL_{CH_4} + YFL_{tar} \quad 3.2.4-33$$

Table 3.2.4-2. Coal Composition: Bituminous coal SR = 0.4; coal flow rate ($\text{g}/\text{cm}^2\text{-sec}$) = 8.28.

Proximate Analysis (wt %)	Ultimate Analysis (wt %)	Oxygen Distribution (wt %)	Species Flow Rates ($\text{mol}/\text{cm}^2\text{-sec}$)	Coal Composition (wt %)
			<u>Volatiles</u>	
$\text{FR}_{\text{vol}} = 47.2$	$\text{FR}_{\text{C}} = 66.0$	$\text{FR}_{\text{CO}} = 21.3$	$\text{FL}_{\text{moisture}} = 0.02576$	$\text{CO}_2 = 1.18$
$\text{FR}_{\text{C solid}} = 37.7$	$\text{FR}_{\text{H}} = 4.86$	$\text{FR}_{\text{CO}_2} = 7.1$	$\text{FL}_{\text{CO}_2} = 0.00223$	$\text{CO} = 4.52$
$\text{FR}_{\text{moisture}} = 5.6$	$\text{FR}_{\text{N}} = 1.15$	$\text{FR}_{\text{H}_2\text{O}} = 71.6$	$\text{FL}_{\text{CO}} = 0.01337$	$\text{CH}_4 = 10.89$
$\text{FR}_{\text{ash}} = 9.4$	$\text{FR}_{\text{O}} = 12.01$		$\text{FL}_{\text{CH}_4} = 0.05636$	$\text{H}_2\text{O} = 9.77$
			$\text{FL}_{\text{H}_2\text{O}} = 0.04494$	$\text{Tar} = 19.62$
			$\text{FL}_{\text{tar}} = 0.12782$	$\text{Moisture} = 5.60$
			<u>Solids</u>	
			$\text{FL}_{\text{C}} = 0.26034$	$\text{C} = 37.70$
			$\text{FL}_{\text{N}} = 0.00687$	$\text{N} = 1.16$
				$\text{Ash} = 9.40$

$FL_{C_{vol}}$ and FR_H may be calculated directly as follows:

$$FL_{C_{vol}} = FL_{coal} (FR_C - FR_{C_{solid}}) / M_C$$

$$FL_H = FL_{coal} FR_H / M_H$$

Solving equations 3.2.4-32 above for FL_{CH_4} and substituting the result into equation 3.2.4-33 gives

$$FL_H = 2FL_{H_2O^*} + 4 (FL_{C_{vol}} - FL_{CO^*} - FL_{CO_2^*} - FL_{tar}) + YFL_{tar} \quad 3.2.4-34$$

Solving the equation for FL_{tar} yields

$$FL_{tar} = \frac{FL_H - 2FL_{H_2O^*} - 4 (FL_{C_{vol}} - FL_{CO^*} - FL_{CO_2^*})}{Y - 4} \quad 3.2.4-35$$

Y, the ratio of hydrogen to carbon in the tar, is calculated as

$$Y = \frac{(FR_H FL_{coal} / M_H) - 2FL_{H_2O^*}}{(FR_C FL_{coal} / M_C) - FL_{CO^*} - FL_{CO_2^*}} \quad 3.2.4-36$$

Once FL_{tar} has been obtained, FL_{CH_4} is easily found by rearranging equation 3.2.4-32 and substituting in the proper values for FL_{CO^*} , $FL_{CO_2^*}$, $FL_{C_{vol}}$, AND FL_{tar} :

$$FL_{CH_4} = FL_{C_{vol}} - FL_{CO^*} - FL_{CO_2^*} - FL_{tar} \quad 3.2.4-37$$

The initial fluxes of the solid species are also easily calculated:

$$FL_{C_{solid}} = FL_{coal} FR_{C_{solid}} / M_C \quad 3.2.4-38$$

$$FL_{N_{solid}} = FL_{coal} FR_N / M_N \quad 3.2.4-39$$

$$FL_{S_{solid}} = FL_{coal} \cdot FR_S / M_S$$

3.2.4-40

3.2.5 Model Results

Having developed the model as outlined in the previous sections, the results of a number of simulations are presented in this section and compared with data from the literature in an effort to assess the accuracy of the model. It is hoped that the model may be used in the future to aid with experimental work on combustion of pulverized fuel in plug flow configurations. Therefore, data from such a furnace are used for comparison with the model. Data on burning times are compared with those predicted by the model, and values calculated for surface area, porosity, effective diffusivity, and effectiveness factors are also presented.

The results are presented in two sections: first, those related to char modeling alone and, second, the results of the coal modeling including char combustion and devolatilization modeling.

Char Combustion

Use of the model requires a full reaction set of both the homogeneous and heterogeneous reactions. The complete set of heterogeneous reactions listed in Table 3.2.3-1 are used in both the char and coal runs. When modeling the coal data, all the reactions listed in Table 3.2.2-1 are used, but in the char runs the methane combustion set is not used.

The particle size distributions used are given in Table 3.2.5-1. They are taken directly from the particle size distributions reported by Glass (1981).

Measurements of the pore size distribution of the char used in Glass's work were made using adsorption-desorption experiments (Hamilton, 1981). This distribution is given in Figure 3.2.5-1 and was used for all coal and char runs. The distribution when used in Gavalas' (1980) model yielded an initial specific surface area of 207 m²/g and an initial porosity of 0.486.

Table 3.2.5-1 Particle Size Distributions.

Char		Coal	
Diameter (μm)	Weight Fraction	Diameter (μm)	Weight Fraction
12	0.21	30	0.317
32	0.32	49	0.194
51	0.23	76	0.350
77	0.21	98	0.064
120	0.03	133	0.076

The temperature profiles used are those reported by Glass for char at stoichiometric ratios of 0.4 and 0.8. These profiles are plotted in Figure 3.2.5-2.

All runs contained an initial gas composition of 0.21 mole fraction oxygen and 0.79 mole fraction nitrogen. In addition, the char runs included a trace amount of H_2O , CO_2 , and H_2 .

Two simulations were run for char combustion, one at a stoichiometric ratio (SR) of 0.8 and one at 0.4. The concentration profiles are presented in four plots, two of the major species and two of NO.

Major Species Profiles

The predicted major species profiles for SR = 0.8 are plotted in Figure 3.2.5-3, along with the data of Glass. The final composition is in good agreement with the data except that the model over-predicts the CO concentration. Also, the oxygen is consumed more rapidly than is indicated by the data.

The results of the SR = 0.4 simulation are in Figure 3.2.5-4. As with the SR = 0.8 case, the model predicts a more rapid oxygen consumption than what is indicated by the data. The predicted CO and CO_2 mole fractions are in good agreement with the data for times greater than one second.

NO Profiles

The NO profiles for the SR = 0.8 and SR = 0.4 cases are in Figures 3.2.5-5 and 3.2.5-6, respectively. In both cases, the predicted NO concentration increases and comes to a peak more rapidly than the data due to the rapid consumption of the oxygen noted in Figures 3.2.5-3 and 3.2.5-4. The peak predicted NO concentration is also significantly greater than the data; approximately a factor of three greater in both cases. While the predicted and measured values do not agree, the general shape of the profiles closely corresponds to the shape suggested by the data.

Burning Time

The burning time for five different size particles in 21% O_2 at 1500 K was calculated using the model. The burning time for the particles is defined here as the time it takes to reach a conversion of carbon in the particles of 0.995. The burning time results are given in Table 3.2.5-2.

Smith (1979) reported the burning times of a large number of carbonaceous particles in 21% v/v O_2 at 1500 K. When compared to the data, the model results are within a factor of 2 of the range reported. However, the model predicts burning times longer than those reported for the smaller particles and shorter than those reported for the larger particles. The relationship of the burning time as a function of radius is linear for the model, while the data suggest that the time varies as the square of the radius.

Figure 3.2.5-1 Pore Size Distribution

Figure 3.2.5-2 Char Temperature Profiles.

Figure 3.2.5-3 Char Major Species Profiles, SR = 0.8

Figure 3.2.5-4 Char: Major Species Profiles, SR = 0.4.

Figure 3.2.5-5 Char NO Profile, SR = 0.8.

Figure 2.5-6 Char NO Profile, SR = 0.4.

Table 3.2.5-2 Burning Time.

Initial Diameter (μm)	Model	Burning Time (sec)	
		Data Range	
50	0.365	-	
100	0.620	0.1	0.37
200	1.174	0.2	1.0
500	3.735	1.0	6.3
1,000	6.414	6.8	19

Surface Area

For the pore size distribution used in this study, the value of the initial specific surface area is $207 \text{ m}^2/\text{g}$ and the surface area per unit volume of char is $213 \text{ m}^2/\text{cm}^3$. This is in good agreement with values reported in the literature which range from 100 to $1,000 \text{ m}^2/\text{g}$. Smith (1979) reported values of $300 \text{ m}^2/\text{g}$ for a semi-anthracite and $430 \text{ m}^2/\text{g}$ for a brown coal char.

The behavior of the surface area as a function of burnout is presented in Figure 3.2.5-7. The specific surface area shows a linear, monotonic increase with burnout, while the surface area per unit volume goes through a maximum at a burnout of 0.1. The values calculated from the model are a function of the pore size distribution; however, the general behavior of the surface area with burnout is a characteristic of the model, not the pore size distribution.

Surface area predictions as a function of time for the $\text{SR} = 0.8$ char combustion are presented in Figures 3.2.5-8 and 3.2.5-9. The surface area changes much more rapidly for the smaller size fractions due to the more rapid reaction rates.

Effective Diffusivity

Calculated values for the effective diffusivity at 1700 K ranged from $0.027 \text{ cm}^2/\text{sec}$ at time zero to $0.037 \text{ cm}^2/\text{sec}$ at a porosity of 0.69 (just prior to "crumbling"). These values are 0.97% and 1.33% of the bulk diffusivity of the oxygen in the system. This agrees well with a reported value of 3.5% of the bulk diffusivity for a brown coal char with a porosity of 0.7 (Smith and Tyler, 1974).

Calculations show that, for the pore size distribution used, Knudsen diffusion is dominant. The pore density function, $\epsilon(r)$, has a peak value at approximately $20 \text{ \AA}$. Calculation of the diffusivity in the pore at 1700 K yields a Knudsen diffusivity of 0.0226 and an overall diffusivity in the pore of 0.0224.

The behavior of the effective diffusivity as a function of residence time in the reactor for the char run at $\text{SR} = 0.8$ is plotted in Figure 3.2.5-10.

Figure 3.2.5-7 Surface Area as a Function of Burnout.

Figure 3.2.5-8 Surface Area versus Residence Time for Three Size Classes (Char SR = 0.8).

Figure 3.2.5-9 Specific Surface Area versus Residence Time for Three Size Fractions (Char SR = 0.8).

Figure 3.2.5-10 Effective Diffusivity versus Residence Time for Three Size Fractions (Char SR = 0.8).

The values increase by 130% from 0.0135 to 0.314 cm^2/sec as the temperature increases and the reactions proceed. The results of the isothermal run show an increase of 32 percent from 0.027 to 0.037 cm^2/sec , indicating that the increase in diffusivity in the $\text{SR} = 0.8$ case is attributed to both an increase in temperature and an enlarging of the pores.

Conversion ($\text{SR} = 0.8$)

The carbon conversion within the system is a strong function of the initial particle size (Figure 3.2.5-11). Under these fuel-rich conditions, the smaller particles are totally converted, while the largest particles only reached a conversion of 42%. Therefore, the combustion products of the small particles will be exposed to a much more fuel-lean gas phase than most of the products from the larger particles.

Effectiveness Factor ($\text{SR} = 0.8$)

The only effectiveness factors which show any significant variation during char combustion are those for the char oxidation reaction and the NO reduction reaction (Figure 3.2.5-12). The CO_2 and H_2O gasification reactions are essentially chemically controlled under the conditions in the reactor. The effectiveness factors reach minimum values of 0.96 and 0.89 for the CO_2 and H_2O reactions, respectively.

The effectiveness factor for the NO reduction reaction is near 100 at early times, but falls rapidly to less than 5.0 at 0.21 seconds residence time. For the remainder of the run, it remains close to 1.0. The char oxidation effectiveness factor decreases rapidly from 1.0 at 0.9 seconds to less than 0.1 at 0.4 seconds, remaining near 0.1 for times > 0.4 seconds.

Examination of an isothermal run reveals an increase in the char oxidation effectiveness factor with burnout. However, in the $\text{SR} = 0.8$ simulation, it decreased dramatically throughout most of the run, indicating, as expected, that the effectiveness factor is a much stronger function of the temperature than the char structure and effective diffusivity.

Coal Combustion

The same reaction sets used in the char combustion modeling are used in the coal simulations, the only difference being the inclusion of a reaction set for the homogeneous combustion of methane (Table 3.2.2-1). The kinetic parameters used for the devolatilization reactions are given in Table 3.2.4-1.

The particle size distribution used is given in Table 3.2.5-1. As in the char modeling, the measured pore size distribution presented in Figure 3.2.5-1 is used to calculate the structural properties of the solid.

All the runs contained an initial gas composition of 21 mole percent oxygen and 79 mole percent nitrogen. The temperature profiles used are those reported by Glass (1981) for coal at stoichiometric ratios of 0.4 and 0.8. These profiles are plotted in Figure 3.2.5-13.

Figure 3.2.5-11 Percent Conversion versus Residence Time for Three Size Classes (Char SR = 0.8).

Figure 3.2.5-12 Effectiveness Factors versus Residence Time for 51 μm Particles (Char SR = 0.8).

Figure 3.2.5-13. Temperature Profiles for Coal Runs.

The proximate and ultimate analysis of the two coals modeled in this study are given in Table 3.2.5-3, along with the data on how the oxygen is distributed among the volatile species. Data on the amount of volatile material in a bituminous and lignite coal are reported by Suuberg et al. (1979) and are used to calculate the distribution of oxygen in the coal.

It has been noted by Kobayashi et al. (1977) that the total volatile yields from coal is a function of temperature. A simple linear relationship for volatile yield as a function of temperature was obtained from data reported by Blair and Wendt (1981). For every 100 K increase in temperature, the total weight fraction of volatile material increased by 0.0184. Using this relationship, and the peak temperature of each run, adjusted proximate analyses were obtained for the test runs (Table 3.2.5-4).

Concentration Profiles

The results of four different coal runs are presented here, two using the compositions of a bituminous coal and two on a lignite. Each coal was run at two different stoichiometric ratios: 0.4 and 0.8. The bituminous runs are compared to the data of Glass (1981) collected using Utah bituminous coal at SR = 0.4 and 0.8. The lignite runs are included to show the influence of coal composition on the specie profiles.

Figure 3.2.5-14 contains the profiles for the bituminous coal run at SR = 0.8. As can be seen from the graph, the predicted values of CO₂ are higher than the data, and the CO and H₂ are much lower than the data.

The modeled hydrogen profile is not plotted due to the low values predicted. The hydrogen concentration increased slightly from a mole fraction of 8×10^{-4} at 0.1 second to 11×10^{-4} at 1.3 seconds; these values are roughly a factor of 10 to 20 less than the data. Also, the model predicts an oxygen concentration of 0.04 mole fraction at 0.1 second, but the data at that time show no measurable O₂ present.

The profiles of the bituminous run at SR = 0.4 are in Figure 3.2.5-15. As with the previous case, CO₂ is over-predicted and CO is under-predicted. Here again, the predicted H₂ values are approximately a factor of 10 lower than the data.

The results of the lignite runs for SR = 0.8 and 0.4 are plotted along with Glass' data in Figures 3.2.5-16, and 3.2.5-17, respectively. When compared with the data, these predicted values show the same general behavior as noted for the bituminous runs. However, there are some slight differences.

For both the SR = 0.8 and 0.4 cases, three differences were noted for the lignite runs when compared with the bituminous:

1. Higher CO₂ concentrations.
2. Lower CO concentrations.
3. Slower consumption of the oxygen.

Table 3.2.5-3. Coal Analysis.

	Bituminous (wt %)	Lignite (wt %)
Proximate Analysis		
Volatile matter	40.6	35
Fixed carbon	44.3	35
Moisture	5.6	11.8
Ash	9.4	18.2
Ultimate Analysis (Dry Basis)		
Carbon	70.0	53.2
Hydrogen	5.15	3.7
Nitrogen	1.22	0.92
Sulphur	6.96	3.18
Oxygen	12.7	20.8
Ash	9.96	18.2

Table 3.2.5-4. Proximate Analysis (Adjusted for Peak Temperature).*

	Bituminous (wt %)	Lignite (wt %)
SR = 0.4		
Volatile matter	47.2	41.6
Fixed carbon	37.7	28.4
SR = 0.8		
Volatile matter	52.1	46.5
Fixed carbon	32.8	23.5

*Ash and moisture unchanged.

Figure 3.2.5-14. Major Species Profiles, Bituminous Coal, 5R = 0.8.

Figure 3.2.5-15. Major Species Profiles, Bituminous Coal, SR = 0.4.

Figure 3.2.5-16. Major Species Profiles, Lignite Coal, SR = 0.8.

Figure 3.2.5-17. Major Species Profiles, Lignite Coal, SR = 0.4.

Examination of the $SR = 0.8$ runs when compared with those at $SR = 0.4$ revealed some differences which are described in Table 3.2.5-5.

Devolatilization Rates

A check of the rates of devolatilization was provided by comparison of the time needed to achieve total ($> 99\%$) devolatilization as calculated by the model and the reported values of Kobayashi et al. (1977). The model predicts total devolatilization at 37 milliseconds residence time when the reactor temperature is 1750 K. The data of Kobayashi et al. indicate total devolatilization is achieved between 30 and 50 milliseconds.

Fixed Carbon Conversion

In fuel-rich coal combustion, the oxygen is consumed by both the volatiles and the char. Measurements taken by Glass (1981) show all of the oxygen consumed by the first sampling port, indicating that the majority of the oxygen is consumed at early times by the volatiles. The results of the coal runs allow for direct calculation of the amount of oxygen consumed by each fuel.

For the slightly fuel-rich case ($SR = 0.8$), the final char conversion is 51.6%; therefore, the maximum amount of oxygen consumed by the char is 28.7% of the O_2 fed to the furnace. A residence time of 0.1 second corresponds to the position of the first sampling port in the furnace used by Glass. The conversion at 0.1 second is 23.1%, corresponding to a maximum O_2 consumption of 12.5%. At total devolatilization, the conversion has progressed to 34.7%, accounting for a maximum O_2 consumption of 18.7%.

Carbon conversion in the extremely fuel-rich case ($SR = 0.4$) is considerably less than for the $SR = 0.8$ case. The final conversion is only 3.6% which corresponds to a maximum O_2 consumption of 4.4%. At the time corresponding to the position of the first port (0.27 sec), the carbon conversion is 2.4 and the maximum O_2 consumed by the char is 2.9%. By the time of total devolatilization, the conversion has increased to 3.4%, which indicates a maximum O_2 consumption of 4.2%.

As indicated by Glass' (1981) data, and confirmed by the above calculations, the majority of the oxygen is consumed by the volatiles; for these cases, $> 70\%$. In the char modeling cases, the char was consumed more rapidly than shown by the data. Therefore, the actual amount of oxygen consumed by the volatiles at early times may be less than the above-calculated values.

3.2.6 Discussion

The results of the modeling runs have been presented in the previous section. In this section, those results will be examined and the model's performance discussed. Two other models have been applied to the data of Glass (1981) and their results are used to aid in explaining the model's results.

Table 3.2.5-5. Concentration Profile Comparison: SR = 0.4, SR = 0.8.

Specie	SR = 0.4	SR = 0.8
CO ₂	Reaching a peak concentration between 0.1 and 0.2 second and then leveling off at a value slightly lower than for SR = 0.8	Monotonically increasing for all times > 0.1 second to a final value greater than for SR = 0.4
CO	Greater than for SR = 0.8 and increasing with time	Less than for the 0.4 case and decreasing with time
H ₂	Greater than for SR = 0.8 and gradually increasing with time	Much less than for SR = 0.4 and remaining constant or slowly decreasing with time
O ₂	More rapidly consumed; time of consumption less than 0.2 second	Slower consumption; not totally consumed until after 0.5 second

Burning Time

The predicted burning times of the particles at 1500 K varied linearly with the diameter. The reason for this may be easily explained by examining the rate equation for the major heterogeneous reaction of solid carbon with oxygen. For that reaction, the initial reaction rate of any given particle is

$$R_p = K_{Cl}' C_{O_2} \eta_{Cl} S_g V_p \rho_p \quad 3.2.6-1$$

where R_p is in g/sec; K_{Cl}' is a function of temperature only; and the oxygen concentration was in excess so that both K_{Cl}' and C_{O_2} are constant. ρ_p and S_g are the same for each particle, so that only η_{Cl} and V_p are functions of the initial particle radius:

$$V_p = \frac{4}{3} \pi r_p^3 \quad 3.2.6-2$$

For the carbon-oxygen reaction, even for the smallest particle, at 1500 K the Thiele modulus was > 7 ; therefore, η_{Cl} may be approximated as

$$\eta_{Cl} = \frac{1}{\phi_{Cl}} \quad 3.2.6-3$$

where

$$\phi_{Cl} = \frac{r_p}{3} \sqrt{\frac{K_{Cl}' S_v}{D_e}} \quad 3.2.6-4$$

The burning time (τ) of any particle, based on the initial rate, is given by

$$\tau = \frac{V_p \rho_p}{R_p} \quad 3.2.6-5$$

Substituting into equation 3.2.6-1 from equations 3.2.6-2, 3.2.6-3, and 3.2.6-4 yields

$$R_p = K_{Cl}' C_{O_2} \frac{3}{r_p} \left(\frac{K_{Cl}' S_v}{D_e} \right)^{-\frac{1}{2}} S_g \frac{4}{3} \pi r_p^3 \rho_p \quad 3.2.6-6$$

Collecting all variables which are not functions of r_p into one constant (B) yields

$$R_p = B r_p^2 \quad 3.2.6-7$$

Substituting into equation 3.2.6-5 from equations 3.2.6-2 and 3.2.6-7

gives

$$\tau = \frac{\frac{4}{3} \pi r_p^3 \rho_p}{Br_p} \quad 3.2.6-8$$

which reduces to

$$\tau = \frac{4\pi\rho_p}{3B} r_p \quad 3.2.6-9$$

Therefore, τ is a linear function of particle radius. Admittedly, the particle radius and other properties change during combustion, but the relationship is preserved as is indicated by the model results.

The data at 1500 K suggest a relationship with the burning time varying as the square of the radius. Smith (1979) has suggested that for these high temperatures the char combustion reaction is so rapid that the rate is controlled by rate of diffusion of oxygen to the surface of the particles. His calculations of burning time based on diffusion controlling give a relationship which varies as the square of the radius and fits the data well.

In spite of the differences in reaction rate calculations, the predicted burning times are in reasonable agreement with the data, indicating that the reaction rate calculations give reasonable results.

Char Combustion--Major Species

The predicted major species profiles in Figures 3.2.5-4 and 3.2.5-5 show good agreement with the data except for one major point--the oxygen is consumed too quickly. This may be due to a number of factors: 1) the non-ideality of the experimental furnace, 2) differences in temperature between the gas and the particles, 3) concentration gradients between the bulk gas and the particle surface, and 4) use of kinetic parameters which give too high a reaction rate.

No experimental furnace is capable of true plug flow operation. Recirculation and imperfect radial mixing are just two factors which could contribute to a delay in the consumption of the oxygen. These factors could create zones within the reactor which are leaner in fuel than the average and thereby delay O_2 consumption.

It was assumed that the particles are the same temperature as the gas, neglecting any temperature gradients between gas and particles. This is not the case and may account for some of the discrepancy. In the beginning section of the furnace, there is rapid heating and the particles, though small, will lag behind the gas temperature. Once the peak temperature is reached, the temperature may still vary due to radiation and heat released during the char combustion. Measurements of the particle temperature made by Glass (1981) in the region of the peak temperature show that their temperature is approximately 100 K less than the gas. A rise in temperature from 1700 K

to 1800 K increases the rate constant for the char oxidation reaction by a factor of 2.

The reaction rate at elevated temperatures could be fast enough to be influenced by diffusion of oxygen to the surface of the particle. If that were the case, the rate would not be as fast as that calculated in the program.

The rate constant used for the char oxidation reaction was obtained by Smith (1979) from the analysis of reaction rate data on many chars. It is the best estimate available; however, chars vary greatly in their reactivity due to their varied physical and chemical properties and no single rate constant can be expected to fit them all.

Char Combustion--NO

While the major species profiles matched the data fairly well, the NO profiles were significantly greater. During char combustion under these conditions, only two reactions are significant in the formation of NO. They are the heterogeneous reactions oxidizing the fuel N to NO, and the reaction of NO with char to produce N_2 . The NO production reaction is fixed by the char oxidation reaction. The solid nitrogen cannot react until exposed to oxygen. The NO reduction reaction, on the other hand, is a function of the surface area available for reaction, temperature, and the local NO concentration in the char particle.

As mentioned earlier, the particles are assumed to be isothermal, at the same temperature as the gas, and the surface area is calculated from the conversion and Cavalas' (1980) model. Since the properties of the char are considered to be constant throughout the particle, the local concentration of NO in the char is not needed, but an average value. This average value is the NO concentration at the surface times the effectiveness factor for the NO reduction reaction.

The effectiveness factor was developed specifically to try to overcome the problem of over-predicting the NO peak. It takes into account both production and consumption of NO within the particle and may, therefore, be greater than one, as NO is produced within the particle. The effectiveness factor was used in the char runs, but it did not significantly decrease the NO peak.

Examination of the rates of the two competing reactions reveals the reason for the large NO peak. Table 3.2.6-1 gives values for the O_2 and NO concentration as well as the rates of the two reactions, their difference (net NO production), and the effectiveness factor for the 51 μm size fraction. In the region of the greatest NO production, the NO reduction reaction is always at least one order of magnitude less than the NO production reaction, even though the effectiveness factor for NO reduction is greater than one. Only when the oxygen is almost completely consumed does the NO reduction reaction begin to make a significant contribution.

At the peak NO concentration, 75% of the fuel nitrogen in the char has been converted to NO and only 5.6% has been converted to N_2 , while Glass

Table 3.2.6-1. NO Reaction Rates.

O_2 (mol fr)	NO (ppm)	R_{NO}^P	R_{NO}^R	R_{NO}^N	η_{NO}
0.209	11	2.36×10^{-9}	1.58×10^{-12}	2.36×10^{-9}	47.8
0.199	174	1.48×10^{-8}	6.2×10^{-11}	1.48×10^{-8}	17.2
0.148	986	2.77×10^{-8}	3.27×10^{-10}	2.74×10^{-8}	4.39
*0.112	1,600	2.98×10^{-8}	4.92×10^{-10}	2.93×10^{-8}	2.65
0.059	2,510	2.15×10^{-8}	7.93×10^{-10}	2.07×10^{-8}	1.53
0.034	2,890	1.40×10^{-8}	8.92×10^{-10}	1.31×10^{-8}	1.21
0.028	2,980	1.15×10^{-8}	8.92×10^{-10}	1.06×10^{-8}	1.14
0.019	3,110	7.89×10^{-9}	8.75×10^{-10}	7.02×10^{-9}	1.05
0.010	3,220	4.71×10^{-9}	1.06×10^{-9}	3.65×10^{-9}	0.93
*0.005	3,250	2.55×10^{-9}	1.13×10^{-9}	1.42×10^{-9}	0.86
0.001	3,220	2.58×10^{-10}	9.23×10^{-10}	-6.65×10^{-10}	0.85

*Indicates location of maximum R_{NO}^P and C_{NO} .

(1981) reports 26% conversion to NO and 64% conversion to N_2 . All of this indicates that, even with the use of the modified effectiveness factor for the NO reduction reaction, the rate of that reaction during the times of greatest NO production was under-predicted.

It is tempting to say that the kinetic parameters used for the NO reduction reaction are at fault. However, two factors indicate that this is not the case. First, the rate of decay of the NO concentration in the region after the oxygen has been consumed closely agrees with the data. One simulation was run in which the peak NO concentration in the model was set to the value measured by Glass. The results of that run are presented in Figure 3.2.6-1. The data and the model are in good agreement in this case.

Secondly, Hahn and Shadman (in press) obtained good results when modeling the same data using these kinetic parameters and a very similar model. There are two major differences between their model and this one: 1) the gas-phase reactions are not modeled in full detail, and 2) the physical structure of the char is allowed to change non-uniformly throughout the particle due to concentration and reaction rate gradients within the particle. They applied Gavalas' (1980) model locally throughout the particle, giving rise to a structure whose physical properties may vary with the distance from the center of the particle instead of a particle with constant properties throughout. They modeled the physical properties, concentration gradients, and reaction rates in detail throughout the particles using the same kinetic parameters and a modified version of Gavalas' model, and obtained results which match the data remarkably well.

The difference in the results of the two models is difficult to explain. The homogeneous kinetics did not play a significant role in the NO profile of this model and, therefore, cannot account for the difference. It appears that something is lost by going to a model which uses average values for physical properties and concentrations instead of a detailed evaluation. The combination of surface area and porosity differences with the concentration profiles within the particle work together to give a faster consumption of NO during the critical time of rapid oxygen consumption and NO production.

Therefore, it appears that an even more detailed model of the solid structure is required if the NO profile is to be modeled with reasonable accuracy. Work is currently in progress on a two zone model to account for differences in effective diffusivity between regions where carbon is oxidized and NO is being heterogeneously reduced.

The assumptions of particle and gas temperature being equal and no film resistance to mass transfer may have introduced some error which affects the NO profile. If these were accounted for in the model, they would reduce the rate of the carbon oxidation and, therefore, the NO production as well. However, comparison of the $SR = 0.8$ run with one under identical conditions except for lower temperatures (approximately 100 K) shows that the NO peak was not reduced, only delayed.

It is difficult to determine what effect film resistance to mass transfer could have on the NO profile. It is conceivable that with a decrease in the

Figure 3.2.6-1. NO Decay (Char SR = 0.4).

char oxidation reaction due to mass transfer resistance the NO peak could be reduced. However, it is quite unlikely that it would be able to decrease the peak by a factor of three.

Although the NO peak was not accurate when compared to the data, the results of the model may be used to identify the sensitivity of the model to various parameters used in the simulations.

The effect of particle size on reaction rates and concentration profiles is of interest. It has already been shown that the char oxidation reaction is a linear function of the particle radius at temperatures around 1500 K. The effect of particle size on the NO profile was also investigated.

The results of three isothermal runs using monosize particles at 1700 K and $SR = 0.8$ are shown in Figure 3.2.6-2. The greatest influence of particle size on the profile is that the peak was delayed for the larger particles. Secondly, the smaller the particle, the larger the peak concentration. However, an increase in particle size from 12 to 120 μm only decreased the peak by 13%, from 3490 ppm to 3040 ppm. As the time increases, the difference in NO concentration also decreases, until the final value for the 51 μm and 120 μm particles are almost equal.

Coal Combustion

The coal results presented previously have dealt only with the major species profiles. No attempt was made to model the fuel nitrogen conversion in the fuel runs. The purpose of the coal modeling was to establish the framework for future modeling studies and to determine if reasonable results could be obtained for the major species profiles using a simple devolatilization scheme.

From the results, it is evident that the model as it exists does not reasonably predict the major species concentrations. The predominance of CO_2 in the system and low concentrations of CO and H_2 predicted by the model indicate that, while the overall system was fuel-rich, the volatiles were being oxidized in the gas phase under fuel-lean conditions.

Using the system parameters for the proximate and ultimate analysis of the coal and the assumptions concerning volatile composition, the total amount of volatile carbon, hydrogen, and oxygen may be calculated. Then, assuming final combustion products of H_2O and CO_2 , the maximum amount of oxygen consumed by the volatiles may be obtained.

The maximum amount of O_2 consumed by the volatiles in the case of bituminous coal at $SR = 0.8$ is 0.15 moles. This leaves 0.06 moles or 29% of the oxygen to be consumed by the char. Therefore, for the gas phase to be fuel-rich in the volatile combustion phase, there must be either 1) a significant increase in the amount of volatile material, or 2) an increase in the char-oxidation reaction rate yielding a more rapid depletion of the oxygen.

The results of the char modeling indicate good agreement with the data for the rate of the char-oxidation. Therefore, it is most likely that the

Figure 3.2.6-2. NO Profile versus Time for Three Size Classes (Char SR = 0.8).

volatile matter released at early times in the experiments of Glass (1981) is significantly greater than the proximate analysis value or the adjusted number used in the model.

While the major problem in the $SR = 0.8$ case appears to be an underestimation of the volatile matter, the same is not true of the extremely fuel-rich case ($SR = 0.4$). The maximum amount of O_2 which may be consumed by the volatiles is 0.264 moles--more than the total amount of O_2 fed to the reactor. In this case, the discrepancy appears to be caused by an underprediction of the amount of volatiles which are released at early times. Much better agreement with the data was obtained if the volatile matter was instantaneously evolved at time zero in the form of CH_4 and CO (Figure 3.2.6-3). The devolatilization rate compared well with the data of Kobayashi et al. (1977), but there still could be substantial error involved at early times and lower temperatures.

At present, the model does not predict the volatile rates of evolution and ultimate yields with sufficient accuracy to reasonably describe the major species concentrations. Modification of the model to include a more complete description of the types and amounts of volatiles released at early times should give results which agree more closely with the data.

3.2.7 Conclusions and Recommendations from Coal Combustion Modeling Work

This work has succeeded in developing the basic framework of a kinetic model of coal combustion. The detailed description of the coal structure incorporated into the model yielded results for surface area, porosity, and effective diffusivity which are in good agreement with the data.

The detailed treatment of the kinetics of the heterogeneous reactions and simplified treatment of heat and mass transfer between gas and solid phases has produced results which are in good agreement with data for fuel-rich char combustion. This demonstrates that resistance to diffusion within the particles has a significant effect on the rate of the reactions.

The model, in its present form, is not capable of accurately describing the NO production/reduction process as it occurs within the particles. A more detailed description of the char structure with burnout is required to accurately model the NO production/reduction scheme in char combustion (radial gradients of surface area and porosity are important and may not be neglected).

The major species profiles predicted by the model for fuel-rich coal combustion indicate that the devolatilization model underestimates the amount of volatile species released at early times; the gas phase must be fuel-rich to produce the high values of H_2 and CO measured by Glass (1981).

Previous models have assumed that the gas phase is in a state of pseudo-equilibrium throughout the reactor. The influence of the use of detailed gas-phase chemistry in the place of equilibrium values is difficult to determine from the work completed to date. It most likely has a minimal effect on the heterogeneous modeling results. However, with the inclusion of a more detailed

Figure 3.2.6-3. Major Species Profiles, Bituminous Coal, SR = 0.4, Infinite Devolatilization Rate.

devolatilization model, the contribution of the detailed treatment of the gas-phase chemistry should become more significant.

Modification of the char model to include the radial variations in porosity, effective diffusivity, and surface area should be attempted. Preferably, this would involve minor modifications to the existing model using parameters and properties which may be calculated directly from system properties. Use of a detailed model on the scale of that incorporated in the work of Hahn and Shadman (in press) is not practical in this context.

The inclusion of heat transfer effects in the model is desirable. Under the conditions considered in this work, the effect of differences in temperature between the solid and gas phases has proved to be negligible. However, when considering devolatilization and char combustion under fuel-lean conditions, the temperature effects will be much more pronounced.

At high temperatures and for larger particles, the film resistance to mass diffusion around the particles is no longer negligible. A more comprehensive description of the heterogeneous reaction rates should include film resistances. The treatment of Glass in his modeling work may be applicable.

The results of the coal simulations have clearly demonstrated the need for a more comprehensive model of coal devolatilization. The model should include: 1) a more accurate description of the composition of the volatile products; and 2) a more detailed treatment of the volatile production rates, in particular at low temperatures and early times.

3.2.8 Nomenclature for Section 3.2: Coal Combustion Model

a	Pre-exponential for homogeneous rate constants.
A_1, A_2	Constants used in η_{NO} derivation.
A_k	Knudsen diffusivity constant ($\text{cm}^2/\text{sec-A}^\circ$).
b	Exponent on T for homogeneous rate constants.
B	Constant used in η_{NO} derivation.
B_0	Zeroth moment of λ .
B_1	First moment of λ .
c	Activation energy for homogeneous rate constants (kcal).
C_1, C_2	Constants used in η_{NO} derivation.
C_I	Concentration of species I (moles/cm^3).
C_s	Concentration at the outer surface of the particle (moles/cm^3).
D_e	Effective diffusivity in char (cm^2/sec).
$D_{A,B}$	Binary diffusivity (cm^2/sec).
E_i	Activation energy for heterogeneous and devolatilization rate constants (cal).
F_I	Rate of formation of species I ($\text{moles I}/\text{cm}^3\text{-sec}$).
FL_I	Flow rate or flux of species I ($\text{moles I}/\text{cm}^2\text{-sec}$).
FR_I	Weight fraction of species I in the coal.
FRO_I	Fraction of oxygen in coal in species I.
h	Step size (sec).
h_1, h_2	Dimensionless groups in η_{NO} derivation.

k	Pre-exponential for heterogeneous and devolatilization reaction rate constants.
K	Reaction rate constant.
K'	Adjusted rate constant for heterogeneous reactions.
M_I	Molecular weight of species I (g/mole).
P	Pressure (atm).
P_i	Partial pressure of gas-phase reactant for reaction i (atm).
Q	Distance moved by pore wall ($\text{\AA}$).
r	Pore radius ($\text{\AA}$).
r^*, r_*	Initial radius of largest and smallest pore, respectively ($\text{\AA}$).
r_s	Distance from center of particle to outer surface (cm).
r_p	Particle radius (cm).
R_g	Gas constant.
R_i	Rate of reaction i (moles/cm ³ -sec).
R_p	Reaction rate for entire particle (moles/sec).
R_s	Reaction rate for particle based on surface conditions (moles/sec).
S_g	Specific surface area of char (cm ² /g).
S_r	Surface area of char per unit volume reactor (cm ² /cm ³).
S_v	Surface area of char per unit volume particle (cm ² /cm ³).
t	Time (sec).
t_1, t_2, t_3	Time at the three data points used for temperature profile (sec).
T	Temperature (K).

T_1, T_2, T_3	Temperature at the three data points used for temperature profile (K).
T_a, T_b	Temperature parameters for exponential T decay (K).
v	Linear space velocity (cm/sec).
V_p	Volume of particle.
X_c	Carbon conversion.
Y	Carbon/hydrogen ratio in tar.

Greek Symbols

α	Parameter defining the CO/CO_2 ratio for the char oxidation reaction.
α_I	Element of true alpha vector.
α_I'	Element of pseudo-alpha vector.
$\beta_{I,J}$	Element of the beta matrix.
$\beta_{I,J}'$	Element of pseudo-beta matrix.
δ	Diffusivity in individual pores (cm^2/sec).
ϵ	Void fraction occupied by individual pores.
ϵ_T	Total porosity of char.
λ	Probability density function for char structural model.
ω_J	Mole fraction of species J in the reactor (moles J/total moles gas).
ρ_m	Total molar gas density (moles/ cm^3).
γ	Ratio of nitrogen to carbon in the char.
θ	Dimensionless distance used in η_{NO} derivation.
ψ	Dimensionless concentration.

- v Variable used in transformation of equations in η_{NO} derivation.
- ϕ_i Thiele modulus for reaction i .
- η_i Effectiveness factor for reaction i .

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APPENDIX

SAMPLE OUTPUT

NUMBER OF SPECIES 18				NUMBER OF REACTIONS 35				
INITIAL	HOLE	FRACTIONS	OF SPECIS	H FORM	KCAL/MOLE	SPECIFIC HEAT	ACP+BCP+ALOG(T)+CCP+T+OCP+T**2	CAL/MOLE DEG K
1	CH4	0.	0.	0.	0.	0.	0.	0.
2	H	0.	0.	0.	0.	0.	0.	0.
3	CH3	0.	0.	0.	0.	0.	0.	0.
4	H2	0.	0.	0.	0.	0.	0.	0.
5	OH	0.	0.	0.	0.	0.	0.	0.
6	H2O	0.	0.	0.	0.	0.	0.	0.
7	O	0.	0.	0.	0.	0.	0.	0.
8	CH2O	0.	0.	0.	0.	0.	0.	0.
9	CH2	0.	0.	0.	0.	0.	0.	0.
10	O2	.210E+00	0.	0.	0.	0.	0.	0.
11	CH3O	0.	0.	0.	0.	0.	0.	0.
12	HCO	0.	0.	0.	0.	0.	0.	0.
13	CH	0.	0.	0.	0.	0.	0.	0.
14	CO	0.	0.	0.	0.	0.	0.	0.
15	CO2	0.	0.	0.	0.	0.	0.	0.
16	N2	.790E+00	0.	0.	0.	0.	0.	0.
17	N	0.	0.	0.	0.	0.	0.	0.
18	NO	0.	0.	0.	0.	0.	0.	0.
MOLE FRACTION OF MET. SPECIES								
1	C	0.						
2	NH	0.						

FORWARD RATE COEFF.,AF,TEF,EF										REVERSE RATE COEFFICIENT,AR,TER,ER									
1	CH4	CH4	+H	+	+CH3	+H2	+	.1410E+08	.2000E+01	.8840E+01	.5850E+05	.2259E+01	.7476E+01						
2	CH4	CH4	+OH	+	+CH3	+H2O	+	.1590E+07	.2130E+01	.2430E+01	.6004E+05	.2300E+01	.1655E+02						
3	CH4	CH4	+O	+	+CH3	+OH	+	.1170E+04	.2080E+01	.7630E+01	.2711E+05	.2310E+01	.4263E+01						
4	CH4	CH4	+H	+	+CH3	+H	+H	.1260E+18	0.	.8840E+02	.1302E+16	-.1670E+01	-.1654E+02						
5	CH4	CH3	+O	+	+CH2O	+H	+	.9000E+14	0.	.2000E+01	.6874E+16	-.2060E+00	.7232E+02						
6	CH4	CH3	+OH	+	+CH2	+H2O	+	.6300E+11	.7000E+00	.2000E+01	.3906E+11	.1014E+01	.1151E+02						
7	CH4	CH3	+O2	+	+CH3O	+O	+	.6000E+10	.1000E+01	.2860E+02	.7474E+12	.5528E+00	.6180E+01						
8	CH4	CH3O	+H	+	+CH2O	+H	+H	.5000E+14	0.	.2100E+02	.4300E+12	.3744E+00	.3530E+00						
9	CH4	CH3O	+H	+	+CH2O	+H2	+	.1000E+15	0.	0.	.3453E+12	.6502E+00	.6293E+02						
10	CH4	CH3O	+OH	+	+CH2O	+H2O	+	.1000E+14	0.	0.	.9671E+12	.5610E+00	.9639E+02						
11	CH4	CH3O	+O	+	+CH2O	+OH	+	.1000E+15	0.	0.	.1924E+12	.6220E+00	.8693E+02						
12	CH4	CH2	+O2	+	+CH2O	+O	+	.7700E+10	.1000E+01	.5400E+00	.4988E+12	.7946E+00	.6150E+02						
13	CH4	CH2	+O	+	+HCO	+H	+	.6500E+14	0.	0.	.1577E+16	-.1816E+00	.8997E+02						
14	CH4	CH2	+OH	+	+CH	+H2O	+	.5000E+12	.5000E+00	.6000E+01	.2962E+12	.6940E+00	.2356E+02						
15	CH4	CH2	+OH	+	+CH3	+O	+	.5000E+12	.5000E+00	.6000E+01	.1348E+15	.1244E+00	.1395E+02						
16	CH4	CH2	+OH	+	+CH2O	+H	+	.1000E+14	0.	.5000E+01	.2059E+18	-.5812E+00	.4327E+04						
17	CH4	CH2	+H2	+	+CH3	+H	+	.1000E+12	.5000E+00	.5730E+01	.1506E+14	.9606E+01	.1168E+02						
18	CH4	CH	+O	+	+CO	+H	+	.5600E+14	0.	0.	.1642E+16	.5990E+01	.1753E+03						
19	CH4	CH	+OH	+	+HCO	+H	+	.5000E+12	.5000E+00	.5620E+01	.3442E+15	.6343E+01	.9597E+02						
20	CH4	CH	+H2	+	+CH2	+H	+	.1600E+14	0.	0.	.3152E+15	-.2832E+00	-.2120E+01						
21	CH4	CH	+O2	+	+HCO	+O	+	.2000E+14	0.	0.	.4306E+14	-.5580E+00	.7214E+02						
22	CH4	CH	+CH4	+	+CH2	+CH3	+	.2500E+12	.7000E+00	.6000E+01	.1634E+11	.6751E+00	.2516E+01						
23	CH4	CH2	+CH2	+	+CH3	+CH	+	.5000E+12	.5000E+00	.6000E+01	.4777E+13	.3798E+00	.1437E+02						
24	CH4	CH2	+CH4	+	+CH3	+CH3	+	.1260E+13	.7000E+00	.2000E+02	.7872E+12	.5553E+00	.2459E+04						
25	CO	CH2O	+H	+	+HCO	+H	+H	.3310E+17	0.	.8102E+02	.1734E+15	.1524E+00	-.4250E+01						
26	CO	HCO	+HCO	+	+CH2O	+CO	+	.4000E+14	0.	0.	.1455E+16	.9692E+01	.7506E+02						
27	CO	CH2O	+H	+	+HCO	+H2	+	.2500E+11	.1000E+01	.3200E+01	.5273E+08	.1425E+01	.1650E+02						
28	CO	CH2O	+OH	+	+HCO	+H2O	+	.7530E+13	0.	.1750E+00	.1483E+12	.3386E+00	.2893E+02						
29	CO	CH2O	+O	+	+HCO	+OH	+	.1300E+11	.1000E+01	.2050E+01	.1531E+08	.1430E+01	.1334E+02						
30	CO	CO	+O	+	+CO2	+H	+	.3800E+25	.5000E+01	.6170E+01	.2293E+31	-.3944E+01	.1188E+03						
31	CO	HCO	+H	+	+CO	+H	+H	.1890E+15	0.	.1468E+02	.2962E+14	.2493E+00	-.560E+00						
32	CO	CO	+OH	+	+CO2	+H	+	.1513E+08	.1300E+01	.7650E+03	.3992E+14	.1090E+00	.2679E+02						
33	CO	CO	+O2	+	+CO2	+O	+	.6900E+08	.1000E+01	.3481E+02	.5739E+12	.1896E+00	.4553E+02						
34	CO	HCO	+H	+	+CO	+H2	+	.2000E+19	0.	0.	.1535E+14	.5247E+00	.3836E+02						
35	CO	HCO	+O	+	+CO	+OH	+	.5500E+13	.5000E+00	0.	.2357E+12	.9965E+00	.8635E+02						
36	CO	HCO	+O	+	+CO2	+H	+	.5500E+13	.5000E+00	0.	.6232E+18	-.1947E+00	.1124E+03						
37	CO	CH3	+OH	+	+CO	+H2O	+	.5000E+11	.1000E+01	0.	.2149E+11	.1436E+01	.1038E+03						
38	H2	H	+O2	+	+OH	+O	+	.1488E+18	-.9799E+00	.4731E+02	.4613E+15	-.5491E+00	0.						
39	H2	H	+O	+	+OH	+H	+	.7997E+06	.2250E+01	.6677E+01	.4467E+06	.2221E+01	.4674E+01						
40	H2	H2	+OH	+	+H2O	+H	+	.5734E+07	.2000E+01	.2868E+01	.5353E+08	.1911E+01	.1433E+02						
41	H2	OH	+OH	+	+H2O	+O	+	.5960E+09	.1260E+01	0.	.9962E+10	.1199E+01	.1747E+02						
42	H2	H2	+O2	+	+OH	+OH	+	.2510E+13	0.	.3900E+02	.4411E+10	.3526E+00	.1969E+02						
43	H2	H	+OH	+	+H2O	+H2	+	.4900E+22	-.1760E+01	0.	.1837E+23	-.1574E+01	.1190E+03						
44	H2	H	+OH	+	+H2O	+H2O	+	.1920E+24	-.2040E+01	0.	.7138E+24	-.1854E+01	.1190E+03						
45	H2	H	+OH	+	+H2O	+CO2	+	.3500E+24	-.2440E+01	0.	.1312E+25	-.2254E+01	.1190E+03						
46	H2	H	+OH	+	+H2O	+H	+	.4900E+22	-.1760E+01	0.	.1837E+23	-.1574E+01	.1190E+03						
47	H2	H	+H	+	+H2	+H2	+	.6580E+19	-.1320E+01	0.	.2842E+19	-.1045E+01	.1336E+03						
48	H2	H	+H	+	+H2O	+H2O	+	.1570E+20	-.1110E+01	0.	.7509E+20	-.4346E+00	.1336E+03						
49	H2	H	+H	+	+CH4	+H2	+	.4030E+19	-.1140E+01	0.	.1618E+19	-.8646E+00	.1036E+03						
50	H2	H	+H	+	+CO2	+H2	+	.2460E+22	-.2290E+01	0.	.9879E+21	-.2015E+01	.1036E+03						
51	H2	H	+H	+	+H2	+H2	+	.5370E+17	-.4930E+00	0.	.2144E+17	-.2175E+00	.1036E+03						
52	H2	H	+H	+	+H2	+H	+	.6580E+19	-.1320E+01	0.	.2842E+19	-.1045E+01	.1036E+03						
53	LANG	H	+OH	+	+NO	+H	+	.5300E+12	.5000E+00	.5620E+01	.9530E+14	0.	.5500E+02						
54	CO	NO	+H	+	+H2	+O	+	.3100E+14	0.	.3340E+00	.1360E+15	0.	.7540E+02						
55	CO	NO	+H	+	+NO	+O	+	.6430E+10	.1000E+01	.6250E+01	.1550E+10	.1000E+01	.3864E+02						

HETEROGENEOUS REACTIONS WITH COEFFICIENTS										K	EACT
1	CARBON	C	+O2	*	-CO	+CO2	*			.3050E+03	.4295E+03
			-1.00	-.50	0.00	1.00	0.00	0.00			
2	NOFQRM	NH	+O2	*	-NO	*				.3050E+03	.4285E+03
			-1.00	-.50	0.00	1.00	0.00	0.00			
3	NORED	C	+NO	*	-CO	+N2	*			.2250E-02	.3470E+03
			-1.00	-1.00	0.00	1.00	.50	0.00			

1	CH41	1	2	0	3	4	0
2	CH42	1	5	0	3	6	0
3	CH43	1	7	0	3	5	0
4	CH44	1	99	0	3	2	99
5	CH45	1	7	0	8	7	0
6	CH46	1	5	0	9	7	0
7	CH47	1	18	0	11	7	0
8	CH48	11	99	0	8	2	99
9	CH49	11	2	0	8	4	0
10	CH410	11	5	0	8	6	0
11	CH411	11	7	0	8	3	0
12	CH412	9	10	0	8	7	0
13	CH413	9	7	0	12	2	0
14	CH414	9	5	0	13	6	0
15	CH415	9	5	0	3	7	0
16	CH416	9	5	0	8	2	0
17	CH417	9	4	0	3	2	0
18	CH418	13	7	0	14	2	0
19	CH419	13	5	0	12	2	0
20	CH420	13	4	0	9	2	0
21	CH421	13	10	0	12	7	0
22	CH422	13	1	0	9	3	0
23	CH423	9	9	0	3	13	0
24	CH424	9	1	0	3	3	0
25	CO1	8	99	0	12	2	99
26	CO2	12	12	0	8	14	0
27	CO3	8	2	0	12	4	0
28	CO4	8	5	0	12	6	0
29	CO5	8	7	0	12	5	0
30	CO6	14	7	99	15	99	0
31	CO7	12	99	0	14	2	99
32	CO8	14	5	0	15	2	0
33	CO9	14	10	0	15	7	0
34	CO10	12	2	0	14	4	0
35	CO11	12	7	0	14	5	0
36	CO12	12	7	0	15	2	0
37	CO13	12	5	0	14	6	0
38	H21	2	10	0	5	7	0
39	H22	4	7	0	5	2	0
40	H23	4	5	0	4	2	0
41	H24	4	8	0	4	7	0
42	H25	4	10	0	5	5	0
43	H26	2	5	16	6	16	0
44	H27	2	5	6	6	6	0
45	H210	2	5	15	6	15	0
46	H211	2	5	99	6	99	0
47	H214	2	2	16	4	16	0
48	H215	2	2	6	4	6	0
49	H216	2	2	1	4	1	0
50	H217	2	2	15	4	15	0
51	H218	2	2	4	4	4	0
52	H219	2	2	99	4	99	0
53	LAMG8	17	5	0	18	2	0
54	LOSU1	18	17	0	18	7	0
55	LOSU3	10	17	0	18	7	0

TEMPERATURE DECAY FROM 1730.0000EG KEL INITIALLY, FALLING TO 1700.0000EG KEL IN 1.0000SECONDS
 START AT 0.0000 AND END AT 1.900
 INTEGRATION PARAMETERS- STEP SIZE, M= .100E+04 STEP SIZE CONTROL= .500E-01
 PRINT PARAMETER= 50ESUGPARAMETERS, BU01, BU02 0 1000

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1) .....
2) THE FOLLOWING IS A PLUGFLOW REACTOR CALCULATION FOR THE ABOVE INPUT REACTIONS AND INITIAL CONDITIONS.
3) .....

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EPSTO = .4858E+00 HZERO = .1048E-03 BONE = .3241E-02 SAREA = .2126E+07

COAL COMPOSITION:

VOLATILES	WEIGHT FR.
1 CO ₂	.0118
2 CO	.0452
3 CH ₄	.1089
4 H ₂ O	.0477
5 TAR	.1962
6 WATER	.0560

SOLIDS	
1 C	.3770
2 HH	.0116
3 ASH	.0940

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ITERATION 0
TIME 0.
STEP SIZE .100J0E+04
TEMPERATURE 1700.000 PRESSURE 1.000 MOLAR DENSITY .71675E-05 MOLAR FLOW OUT 1.026

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SPECIE	MOLE FRACT	FLOW OUT	FFED IN	CONCENTRATION	RATE FURNED	WMS UP DIFF EQ
1 CH4	.0	.0	.0	.0	.800E-04	.114E+02
2 H2	.0	.0	.0	.0	.190E-04	.272E-04
3 CH4	.0	.0	.0	.0	.0	.0
4 H2	.0	.0	.0	.0	.0	.0
5 OH	.0	.0	.0	.0	.190E-04	.272E-04
6 H2O	.250E-01	.250E-01	.2576000E-01	.185E-06	.614E+01	.879E+06
7 O	.0	.0	.0	.0	.0	.0
8 CH2O	.0	.0	.0	.0	.0	.0
9 CO2	.0	.0	.0	.0	.0	.0
10 O2	.210E+00	.210E+00	.2100000E+00	.151E-05	-.148E-03	-.212E+02
11 CH3O	.0	.0	.0	.0	.0	.0
12 HCO	.0	.0	.0	.0	.0	.0
13 CH	.0	.0	.0	.0	.0	.0
14 CO	.0	.0	.0	.0	.580E-02	.830E+03
15 CO2	.0	.0	.0	.0	.739E-01	.106E+05
16 H2	.790E+00	.790E+00	.7900000E+00	.566E-05	.0	.0
17 H	.0	.0	.0	.0	.0	.0
18 H2O	.0	.0	.0	.0	.0	.0
VOLATILES						
1 CO2	.0	.223E-02	.2226224E-02	.0	-.739E-01	-.106E+05
2 CO	.0	.114E-01	.1336934E-01	.0	-.550E-02	-.787E+03
3 CH4	.0	.564E-01	.5636454E-01	.0	-.154E-04	-.227E+01
4 H2O	.0	.449E-01	.4494108E-01	.0	-.614E+01	-.879E+06
5 FAR	.0	.1278150E+00	.0	.0	-.360E-03	-.512E+02

REACTION						FORWARD	REVERSE	NET FWD	FWD RATIO	REV RATIO
1 CH61	CH4	+H	+	+CH3	+H2	+	0.	0.	.298E+13	.127E+12
2 CH62	CH4	+OH	+	+CH3	+H2O	+	0.	0.	.370E+13	.120E+11
3 CH63	CH4	+O	+	+CH3	+OH	+	0.	0.	.641E+13	.223E+12
4 CH64	CH4	+H	+	+CH3	+	+H	0.	0.	.543E+06	.154E+18
5 CH65	CH3	+O	+	+CH2O	+H	+	0.	0.	.478E+14	.748E+06
6 CH66	CH3	+OH	+	+CH2	+H2O	+	0.	0.	.630E+13	.244E+13
7 CH67	CH3	+O2	+	+CH3O	+O	+	0.	0.	.256E+10	.445E+14
8 CH68	CH3O	+H	+	+CH2O	+H	+H	0.	0.	.998E+11	.622E+13
9 CH69	CH3O	+H	+	+CH2O	+H2	+	0.	0.	.100E+15	.947E+03
10 CH610	CH3O	+OH	+	+CH2O	+H2O	+	0.	0.	.300E+14	.140E+03
11 CH611	CH3O	+O	+	+CH2O	+OH	+	0.	0.	.100E+15	.776E+03
12 CH612	CH2	+O2	+	+CH2O	+O	+	0.	0.	.112E+14	.236E+07
13 CH613	CH2	+U	+	+HCO	+H	+	0.	0.	.650E+14	.125E+04
14 CH614	CH2	+OH	+	+CH	+H2O	+	0.	0.	.349E+13	.480E+11
15 CH615	CH2	+OH	+	+CH3	+O	+	0.	0.	.347E+13	.544E+13
16 CH616	CH2	+OH	+	+CH2O	+H	+	0.	0.	.228E+13	.537E+05
17 CH617	CH2	+H2	+	+CH3	+H	+	0.	0.	.756E+12	.973E+12
18 CH618	CH	+O	+	+CO	+H	+	0.	0.	.560E+14	.640E+07
19 CH619	CH	+OH	+	+HCO	+H	+	0.	0.	.331E+13	.330E+03
20 CH620	CH	+H2	+	+CH2	+H	+	0.	0.	.163E+15	.718E+14
21 CH621	CH	+O2	+	+HCO	+O	+	0.	0.	.200E+14	.366E+03
22 CH622	CH	+CH4	+	+CH2	+CH3	+	0.	0.	.772E+13	.118E+13
23 CH623	CH2	+CH2	+	+CH3	+CH	+	0.	0.	.344E+13	.125E+13
24 CH624	CH2	+CH4	+	+CH3	+CH3	+	0.	0.	.617E+12	.338E+11
25 CO1	CH2O	+H	+	+HCO	+H	+H	0.	0.	.127E+07	.938E+16
26 CO2	HCO	+HCO	+	+CH2O	+CO	+	0.	0.	.400E+14	.667E+06
27 CO3	CH2O	+H	+	+HCO	+H2	+	0.	0.	.165E+14	.164E+14
28 CO4	CH2O	+OH	+	+HCO	+H2O	+	0.	0.	.715E+13	.351E+09
29 CO5	CH2O	+O	+	+HCO	+OH	+	0.	0.	.120E+10	.982E+10
30 CO6	CO	+U	+H	+CO2	+H	+	0.	0.	.124E+15	.259E+01
31 CO7	HCO	+H	+	+CO	+H	+H	0.	0.	.201E+13	.217E+15
32 CO8	CO	+OH	+	+CO2	+H	+	0.	0.	.191E+12	.323E+11
33 CO9	CH	+H2	+	+CO2	+H	+	0.	0.	.342E+07	.596E+07
34 CO10	HCO	+H	+	+CO	+H2	+	0.	0.	.200E+15	.332E+04
35 CO11	HCO	+U	+	+CO	+OH	+	0.	0.	.227E+15	.109E+04
36 CO12	HCO	+U	+	+CO2	+H	+	0.	0.	.227E+15	.522E+03
37 CO13	HCO	+OH	+	+CO	+H2O	+	0.	0.	.510E+14	.420E+02
38 H21	H	+O2	+	+OH	+O	+	0.	0.	.864E+12	.777E+13
39 H22	H2	+U	+	+OH	+H	+	0.	0.	.206E+13	.167E+13
40 H23	H2	+OH	+	+H2O	+H	+	0.	0.	.709E+13	.191E+17
41 H24	OH	+OH	+	+H2O	+U	+	0.	0.	.701E+13	.423E+12
42 H25	H2	+O2	+	+OH	+OH	+	0.	0.	.243E+09	.179E+09
43 H27	H	+OH	+H2	+H2O	+H2	+	.783E-10	-.783E-10	.101E+17	.744E+02
44 H28	H	+OH	+H2O	+H2O	+H2O	+	.125E-10	-.125E-10	.493E+17	.366E+03
45 H210	H	+OH	+CO2	+H2O	+CO2	+	0.	0.	.454E+16	.340E+02
46 H211	H	+OH	+H	+H2O						

ITERATION 1
 TIME .25503E-10 STEP SIZE .25503E-10
 TEMPERATURE 1700.000 PRESSURE 1.000 MOLAR DENSITY .71675E-05 MOLAR FLOW OUT 1.026

SPECIE	MOLE FRACT	FLOW OUT	FEED IN	CONCENTRATION	RATE FORMED	RHS OF DIFF EQ
1 CH4	.285E-09	.293E-09	.2925756E-09	.204E-14	.800E-04	.114E+02
2 H2	.678E-15	.696E-15	.6955397E-15	.486E-20	.183E-09	.262E-04
3 CH3	.284E-19	.291E-19	.2911105E-19	.203E-24	.796E-14	.114E-08
4 H2O	.112E-20	.115E-20	.1151939E-20	.805E-26	.307E-15	.440E-10
5 OH	.678E-15	.696E-15	.6955392E-15	.486E-20	.183E-09	.262E-04
6 H2O	.251E-01	.258E-01	.2574245E-01	.180E-08	.614E+01	.879E+06
7 O	.315E-17	.323E-17	.3226251E-17	.225E-22	.880E-12	.123E-06
8 CH2O	.579E-31	.594E-31	.5942603E-31	.415E-36	.162E-25	.232E-20
9 CH2	0.	0.	0.	0.	.725E-32	.104E-26
10 O2	.205E+00	.210E+00	.2100000E+00	.147E-05	-.202E-03	-.289E+02
11 CH3O	.280E-26	.287E-26	.2870178E-26	.201E-31	.765E-21	.109E-15
12 HCO	.410E-23	.420E-23	.4202832E-23	.294E-28	.112E-17	.160E-12
13 CH	0.	0.	0.	0.	.461E-40	.663E-35
14 CO	.207E-07	.212E-07	.2121080E-07	.148E-12	.590E-02	.844E+03
15 CO2	.263E-06	.270E-06	.2701972E-06	.189E-11	.739E-01	.106E+05
16 H2	.770E+00	.790E+00	.7900000E+00	.552E-05	-.342E-23	-.440E-18
17 N	.125E-28	.128E-28	.1284360E-28	.897E-34	.342E-23	.490E-18
18 NO	.125E-28	.128E-28	.1284350E-28	.898E-34	.273E-05	.350E+00
VOLATILES						
1 CO2	.127E+00	.130E+00	.1300650E+00	.907E-06	-.970E-04	-.133E+02
2 CO	.130E+00	.134E+00	.1330932E+00	.934E-07	-.550E-02	-.787E+03
3 CH4	.549E-01	.564E-01	.5636454E-01	.394E-06	-.159E-04	-.227E+01
4 H2O	.438E-01	.447E-01	.4441803E-01	.314E-06	-.614E+01	-.879E+06
5 TAN	.125E+00	.128E+00	.1270150E+00	.893E-06	-.360E-03	-.512E+02
SOLID SPECIES						
1 C	.127E+00	.130E+00	.1300650E+00	.907E-06	-.970E-04	-.133E+02
2 C	.127E+00	.130E+00	.1300650E+00	.905E-06	-.103E-04	-.147E+01
2 HM	.670E-02	.687E-02	.6868742E-02	.480E-07	-.273E-05	-.390E+00

SIZE (CM)	FRACTION	Q	POROSITY	SAREA	SPAREA	EFULFF
1 .001000	.500	0.	.4058E+00	.2126E+07	.2068E+07	.2698E-01
2 .010000	.500	.127E-11	.4658E+00	.2126E+07	.2068E+07	.2698E-01

REACTION	FORWARD	REVERSE	NET FWD	FWD RATCO	REV RATCO
1 CH4 + H	.296E-22	.208E-39	.296E-22	.298E-13	.127E+12
2 CH4 + OH	.567E-22	.441E-21	-.385E-21	.570E+13	.120E+11
3 CH4 + H2O	.295E-24	.220E-33	.295E-24	.641E+13	.223E+12
4 CH4 + CH3	.796E-14	.109E-32	.796E-14	.543E+06	.154E+18
5 CH4 + CH3O	.228E-33	.151E-40	.228E-33	.498E+14	.748E+06
6 CH4 + CH2O	.629E-32	0.	.629E-32	.638E+13	.244E+13
7 CH4 + CH2	.765E-21	.201E-40	.765E-21	.256E+10	.445E+14
8 CH4 + CH	.143E-25	.910E-49	.143E-25	.948E+11	.629E+13
9 CH4 + CO	.975E-38	.317E-59	.975E-38	.100E+15	.747E+03
10 CH4 + CO2	.292E-38	.105E-41	.292E-38	.300E+14	.140E+02
11 CH4 + HCO	.452E-40	.157E-53	.452E-40	.100E+15	.776E+03
12 CH4 + CH2O	0.	.221E-52	-.221E-52	.112E+14	.238E+07
13 CH4 + CH2	0.	.178E-45	-.178E-45	.650E+14	.125E+04
14 CH4 + CH	0.	0.	0.	.349E+13	.480E+11
15 CH4 + CO	0.	.251E-34	-.251E-34	.349E+13	.568E+13
16 CH4 + CO2	0.	.108E-51	-.108E-51	.228E+13	.537E+05
17 CH4 + HCO	0.	.962E-33	-.962E-33	.756E+12	.973E+12
18 CH4 + CH3	0.	.461E-40	-.461E-40	.560E+14	.840E+07
19 CH4 + CH3O	0.	.471E-46	-.471E-46	.391E+13	.330E+03
20 CH4 + CH2O	0.	0.	0.	.180E+14	.713E+14
21 CH4 + CH	0.	.238E-48	-.238E-48	.200E+14	.340E+03
22 CH4 + CH2	0.	0.	0.	.772E+13	.118E+12
23 CH4 + CH3	0.	0.	0.	.349E+13	.125E+13
24 CH4 + CH2O	0.	.140E-38	-.140E-38	.617E+12	.338E+11
25 CH4 + CH2	.377E-35	.857E-38	.377E-35	.127E+07	.433E+10
26 CH4 + HCO	.145E-43	.412E-43	-.267E-43	.460E+14	.667E+06
27 CH4 + CO	.333E-43	.387E-44	-.544E-44	.183E+14	.104E+11
28 CH4 + CO2	.144E-43	.186E-26	.186E-26	.715E+13	.351E+09
29 CH4 + CH2O	.113E-45	.140E-38	-.140E-38	.120E+14	.982E+10
30 CH4 + CO	.298E-26	.351E-16	-.351E-16	.124E+15	.259E+01
31 CH4 + HCO	.423E-21	.112E-23	.422E-21	.201E+13	.217E+15
32 CH4 + CH2	.137E-21	.246E-21	-.199E-21	.141E+12	.123E+11
33 CH4 + CO	.853E-12	.254E-27	.853E-12	.392E+07	.596E+07
34 CH4 + HCO	.285E-34	.396E-35	.246E-34	.240E+15	.332E+04
35 CH4 + CO2	.150E-36	.222E-29	-.222E-29	.227E+15	.309E+04
36 CH4 + CH2O	.150E-36	.479E-29	-.479E-29	.227E+15	.522E+03
37 CH4 + CH3	.728E-35	.112E-17	-.112E-17	.513E+14	.420E+02
38 CH4 + CH2	.616E-14	.851E-30	.851E-30	.664E+12	.777E+13
39 CH4 + CH	.373E-36	.346E-20	-.346E-20	.206E+13	.167E+13
40 CH4 + CO	.277E-33	.307E-15	-.307E-15	.709E+13	.351E+12
41 CH4 + HCO	.166E-27	.172E-17	-.172E-17	.701E+13	.423E+12
42 CH4 + CH2	.267E-24	-.22E-32	.287E-24	.243E+08	.179E+09
43 CH4 + CH3O	.132E-24	.745E-10	-.745E-10	.161E+17	.749E+02
44 CH4 + CH2O	.210E-30	.119E-10	-.119E-10	.443E+17	.366E+03
45 CH4 + CO	.205E-36	.116E-16	-.116E-16	.459E+16	.340E+02
46 CH4 + CH2	.171E-29	.967E-10	-.967E-10	.101E+17	.749E+02
47 CH4 + CH	.467E-31	.234E-24	-.234E-24	.350E+15	.553E+02
48 CH4 + CO2	.207E-31	.106E-28	-.106E-28	.480E+16	.729E+04
49 CH4 + HCO	.404E-40	.207E-38	-.207E-38	.837E+15	.126E+03
50 CH4 + CH2O	.439E-38	.224E-36	-.224E-36	.988E+14	.147E+02
51 CH4 + CH3	.261E-51	.133E-44	-.133E-44	.137E+16	.205E+05
52 CH4 + CH2	.666E-31	.510E-29	-.510E-29	.358E+15	.538E+02
53 CH4 + CO	.131E-41	.353E-47	.181E-41	.414E+13	.809E+07
54 CH4 + CH2O	.226E-54	.342E-23	-.342E-23	.281E+14	.275E+05
55 CH4 + CH3O	.226E-27	.374E-49	.226E-27	.172E+13	.284E+04

HETEROGENEOUS RNS	RATE CONST	MIN RATE	KO	THIELE	ETA
1 CARBC C + O2	.634E+02	.930E+04	.122E+08	.354E+01	.256E+00
2 NOFORM NH + O2	.700E+01	.103E+04	.122E+08	.354E+02	.283E-01
3 NURED C + NO	.167E+01	.246E+05	.120E+08	.351E+01	.256E+00
	.185E+00	.271E+06	.120E+08	.351E+02	.256E-01
	.204E-01	.183E-35	.192E+04	.445E+01	.999E+00
	.183E-01	.184E-35	.192E+04	.445E+00	.898E+00

COEFFICIENTS	1.000	-.501	0.000	.980	.020	0.000
1 CARBC	1.000	-.500	0.000	1.000	0.000	0.000
2 NOFORM	1.000	-.500	0.000	1.000	.500	0.000

SIZE (CM)	FRACTION	Q	PURSITY	SAREA	SPANEA	FFDIFF
1	.001000	.500	.1622E-08	.4858E+00	.2126E+07	.2698E-01
2	.010000	.500	.2281E-10	.4858E+00	.2126E+07	.2698E-01

REACTION					FORWARD	REVERSE	NET FWD	FWD RATIO	REV RATIO		
1 CH41	CH4	+M	+	+CH3	+M2	+	.357E-22	.255E-39	.357E-22	.249E+13	.127E+12
2 CH42	CH4	+OH	+	+CH3	+M20	+	.683E-22	.490E-21	-.422E-21	.570E+13	.120E+11
3 CH43	CH4	+O	+	+CH3	+OH	+	.360E-24	.268E-33	.360E-24	.641E+13	.223E+12
4 CH44	CH4	+M	+	+CH3	+	+	.133E-32	.875E-14	.343E-14	.343E+06	.154E+18
5 CH45	CH3	+O	+	+CH20	+	+	.281E-33	.184E-30	.281E-33	.498E+14	.748E+06
6 CH46	CH3	+OH	+	+CH2	+M20	+	.765E-32	.785E-38	.765E-32	.638E+13	.244E+13
7 CH47	CH3	+O2	+	+CH30	+O	+	.849E-21	.247E-30	.849E-21	.259E+10	.444E+11
8 CH48	CH30	+	+	+CH20	+	+	.159E-25	.159E-25	.159E-25	.998E+11	.998E+11
9 CH49	CH30	+M	+	+CH20	+M2	+	.118E-37	.389E-59	.118E-37	.100E+15	.947E+03
10 CH410	CH30	+OH	+	+CH20	+M20	+	.355E-38	.117E-41	.355E-38	.300E+14	.140E+07
11 CH411	CH30	+O	+	+CH20	+OH	+	.555E-40	.191E-53	.555E-40	.100E+15	.776E+03
12 CH412	CH2	+O2	+	+CH20	+O	+	.367E-36	.272E-52	.367E-36	.112E+14	.236E+07
13 CH413	CH2	+O	+	+HC0	+	+	.364E-52	.216E-45	-.216E-45	.650E+14	.125E+04
14 CH414	CH2	+OH	+	+CH	+M20	+	.417E-51	.122E-47	-.122E-47	.349E+13	.440E+11
15 CH415	CH2	+OH	+	+CH3	+O	+	.417E-51	.309E-51	-.309E-51	.349E+13	.348E+13
16 CH416	CH2	+OH	+	+CH20	+	+	.272E-51	.132E-51	-.146E-51	.228E+13	.537E+05
17 CH417	CH2	+H2	+	+CH3	+	+	.151E-57	.117E-32	-.117E-32	.756E+12	.973E+12
18 CH418	CH	+O	+	+CO	+	+	.197E-60	.557E-44	-.557E-44	.560E+14	.640E+07
19 CH419	CH	+OH	+	+HC0	+	+	.294E-59	.572E-46	-.572E-46	.391E+13	.330E+03
20 CH420	CH	+H2	+	+CH2	+	+	.201E-66	.859E-50	-.859E-50	.160E+14	.718E+14
21 CH421	CH	+O2	+	+CO	+O	+	.414E-64	.293E-48	.414E-64	.200E+14	.380E+03
22 CH422	CH	+CH4	+	+CH2	+CH3	+	.245E-53	.595E-36	.245E-53	.772E+13	.118E+13
23 CH423	CH2	+CH2	+	+CH3	+CH	+	.176E-77	.399E-64	.399E-64	.349E+13	.125E+13
24 CH424	CH2	+CH4	+	+CH3	+CH3	+	.311E-46	.172E-38	.172E-38	.617E+12	.338E+11
25 CO1	CH20	+M	+	+HC0	+	+	.419E-35	.104E-35	.418E-35	.127E+07	.838E+14
26 CO2	HC0	+HC0	+	+CH20	+CO	+	.423E-43	.504E-43	-.808E-44	.400E+14	.689E+06
27 CO3	CH20	+	+	+HC0	+H2	+	.405E-43	.474E-44	.357E-43	.185E+14	.164E+11
28 CO4	CH20	+OH	+	+HC0	+M20	+	.176E-43	.206E-26	-.206E-26	.715E+13	.351E+09
29 CO5	CH20	+O	+	+HC0	+OH	+	.139E-45	.170E-38	-.170E-38	.120E+14	.982E+10
30 CO6	CO	+O	+	+CO2	+	+	.364E-26	.386E-16	-.386E-16	.124E+15	.259E+01
31 CO7	HC0	+M	+	+CO	+	+	.469E-21	.135E-23	.468E-21	.201E+13	.217E+15
32 CO8	CO	+OH	+	+CO2	+	+	.166E-21	.357E-21	-.191E-21	.141E+12	.323E+11
33 CO9	CO	+O2	+	+CO2	+O	+	.940E-12	.309E-27	.940E-12	.392E+07	.596E+07
34 CO10	HC0	+H	+	+CO	+H2	+	.347E-34	.483E-35	.298E-34	.200E+15	.332E+04
35 CO11	HC0	+O	+	+CO	+OH	+	.184E-36	.268E-29	.268E-29	.227E+15	.309E+04
36 CO12	HC0	+O	+	+CO2	+	+	.184E-36	.577E-29	.577E-29	.227E+15	.522E+03
37 CO13	HC0	+OH	+	+CO	+H20	+	.884E-35	.124E-17	.124E-17	.510E+14	.420E+02
38 CO14	H	+O2	+	+OH	+O	+	.676E-14	.103E-29	.676E-14	.684E+12	.777E+13
39 CO15	H2	+O	+	+OH	+	+	.457E-36	.475E-28	.475E-28	.206E+13	.167E+13
40 CO16	H2	+OH	+	+H20	+	+	.337E-33	.337E-15	-.337E-15	.709E+13	.351E+12
41 CO17	OH	+OH	+	+H20	+O	+	.199E-27	.190E-17	.190E-17	.701E+13	.423E+12
42 CO18	H2	+O2	+	+OH	+OH	+	.318E-24	.508E-32	.318E-24	.243E+08	.177E+09
43 CO19	H	+	+	+H2	+H20	+	.158E-29	.745E-10	.745E-10	.101E+17	.749E+02
44 CO20	H	+OH	+	+H20	+H20	+	.292E-30	.119E-10	.119E-10	.493E+17	.366E+03
45 CO21	H	+OH	+	+CO2	+CO2	+	.271E-36	.127E-16	.127E-16	.459E+16	.340E+02
46 CO22	H	+OH	+	+H20	+	+	.206E-29	.968E-10	.968E-10	.101E+17	.747E+02
47 CO23	H	+H2	+	+H2	+H2	+	.501E-31	.264E-49	.259E-49	.338E+15	.538E+02
48 CO24	H	+H20	+	+H2	+H20	+	.248E-31	.117E-28	.117E-28	.485E+16	.729E+04
49 CO25	H	+H	+	+CH4	+	+	.534E-40	.252E-38	.246E-38	.837E+15	.126E+03
50 CO26	H	+	+	+CO2	+	+	.500E-38	.227E-36	.267E-36	.984E+14	.147E+02
51 CO27	H	+H2	+	+H2	+H2	+	.347E-51	.163E-49	.159E-49	.137E+16	.205E+03
52 CO28	H	+H	+	+H2	+	+	.729E-31	.343E-29	.336E-29	.338E+15	.538E+02
53 CO29	N	+OH	+	+NO	+	+	.219E-41	.300E-30	.300E-30	.414E+13	.809E+07
54 CO30	N	+	+	+N2	+	+	.195E-37	.379E-23	.379E-23	.281E+14	.275E+05
55 CO31	N2	+	+	+NO	+O	+	.251E-27	.494E-32	.251E-27	.127E+13	.284E+08

HETEROGENEOUS RXNS							RATE CONST		RAM RATE		KO		THIELE		ETA	
1	CAROC	C	*U2	+	*CU	+CO2	+	.634E+02	.430F-C4	.122E+04	.337E+01	.256E+00				
								.700E+01	.103E-04	.122E+08	.154E+02	.281E-01				
2	YUFORM	NH	*U2	+	*NU	+	+	.167E+01	.246E-05	.120E+08	.351E+01	.256E+00				
								.185E+00	.271E-06	.120E+08	.351E+02	.283E-01				
3	NORCU	C	*NO	+	*CO	+N2	+	.162E+09	.113E-08	.192E+04	.445E+01	.793E+10				
								.189E+09	.132E-08	.192E+04	.445E+00	.929E+10				

COEFFICIENTS							
1	CARD	-1.00+	-.51+	0.00=	.98+	.52+	0.00
2	WQFM	-1.00+	-.50+	0.00=	1.00+	0.00+	0.50
3	YURE	-1.00+	-1.00+	0.00=	1.00+	.50+	0.00

LISTING OF PROGRAM REKINET

REKINET

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C3  DEBUG
C3  ARRAYS
PROGRAM REKINET (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)

C
C *****
C
C  VERSION 6/14/73 JOLW KINETCS PROGRAM
C  VERSION 11/29/73 JOLW HEAT BALANCED OPTION ADDED
C  MAIN PROGRAM CALLS REDATA TO READ AND INTERPRET DATA AND THEN
C  CALLS PLUGFLOW OR CONST. STIRRED REACTOR PROGRAM.
C  IF LSTIR IS TRUE CSTR IS USED, LSTR IS TRUE IF A WELLSTIRRED
C  CARD APPEARS IN DATA DECK
C  IF LPLUG IS TRUE PLUGFLO IS USED, LPLUG IS TRUE IF A PLUGFLOW
C  CARD IS USED.
C  IF BOTH LSTIR AND LPLUG ARE TRUE, A CSTR IS FOLLOWED BY PLUGFLOW
C  USING OUTPUT VARIABLES FROM CSTR AS INPUT TO PLUGFLOW.
C  STACKED RUNS ARE POSSIBLE, SEPARATED BY EXECUTE CARDS IN DATA DECK.
C  FOR STACKED RUNS CSTR RUNS, FEEDS ARE KEPT CONSTANT UNLESS CHANGED
C  IN NEW DATA INPUT.
C  FOR STACKED PLUGFLOW RUNS OR CSTR AND PLUGFLO RUNS ALL INITIAL
C  CONDITIONS ARE SET EQUAL 0 FOR CONCS.
C  STACKED RUNS ALL KEEP ORIGINAL REACTIONS AND RATE COEFFS.,
C  ALTHOUGH ADDITIONS AND CHANGES MAY BE MADE.
C  REACTION NAMES OR SPECIES NAMES CANNOT BE
C  DELETED IN STACKED RUNS.
C  LAST STEP FOR CSTR GIVES STEADY STATE SOLUTION.
C  IF A NON-REACTING DILUENT IS PRESENT LDIL IS TRUE.
C  LDIL SET EQUAL TO TRUE BY INSERTING A DILUENT CARD IN DATA.
C  IF HEAT BALANCED SPLUTON DESIRED LHEAT SET EQ TO TRUE
C  LHEAT SET EQ TO TRUE BY INSERTING HEATBALANCE CARD IN DATA
C  ENTHALPY CARDS MUST COME AFTER ALL USED SPECIES HAVE BEEN INTRODUCES
C  ENTHALPY CARDS DO NOT ADD A SPECIES ON TO SPECIES SLATE
C *****
C
C  COMMON BLOCK CONTAINING DERIVED QUANTITIES USED TO SAVE STORAGE
COMMON/B1/ F(35),FL(35),DCO(35),BETA(35,35),B(35,35),
1  AL(35),ALP(35)
COMMON/B2/ RATE(150),RKf(150),RKr(150),RF0(150),RRE(150),
1  CP(35),CPDQT(35),ENTH(35)
COMMON/B3/ SIZEPRT(5),SIZEFR(5),ISMH(10,6),COEFF(10,6),
1  IDHREA(10),NMISMH(10,6)
COMMON/B4/ CO(35),CM(35),PORRAD(50),PORFR(50),DKNUD(50,5),
1  EPS(50,5),DIFF(50,5)
COMMON/B5/DRHOC(10,35,5),IS(5),EFDIFF(5),KO(10,5),
1  HRATE(10,5),CONC(10),EACT(10),KZERO(10),THIELE(10,5),
2  ETA(10,5),DRHOT(10,5),RATEK(10,5)
COMMON/REDATA/RHOSLO,DOZREF,IPOR,MINRIT,
1HREAC,NH,MH,LCOAL,LMONSZ,ISIZE,LTMP,HSTART
COMMON/V1/FRVOL,FRFXC,FRWAT,FRASH,FRC,FRN,FRO,FRS,FRH,FROCO
1 ,FRQCO2,FRQW30,IVOL,VSPG(5),KSTAR(10),ESTAR(10),COALIN,LCHAR
COMMON/T1/ICOUNT,X1,X2,X3,C1,C2,C3,C4,C5,TMP(20),TIM(20),ITEMP
REAL AF(150),TEF(150),EF(150),AR(150),TER(150),ER(150)
REAL FD(35),KZERO,Q(5),KSTAR,REACIN(35)
INTEGER IDREAC(150),ISM(150,6),NAMISM(150,6),BUG1,BUG2
1 ,HREAC(10)
INTEGER PRITE
REAL DH(35),ACP(35),BCP(35),CCP(35),DCP(35)
LOGICAL LPLUG,LSTIR
LOGICAL LDIL
LOGICAL LHEAT

```

LOGICAL LFLAME
LOGICAL LCOAL,LCHAR,LTMP
LOGICAL LMONSZ

C
C
C
C

THESE STATEMENTS INITIALIZE AND SET ALL DEFAULT VALUES

LPLUG=.FALSE.
LSTIR=.FALSE.
LDIL=.FALSE.
LHEAT=.FALSE.
LFLAME=.FALSE.
LCOAL=.FALSE.
LMONSZ=.TRUE.
LTMP=.FALSE.
LEVEL = 1
P=1.
N=0
M=0
NH=0
MH=0
BUG1=0
BUG2=1000
DELTA=0.05
TIMEIN=0.
TIMEOUT=1.0
NRITE=5
PRITE=5
ITMX=500
VOLT=1000.0
WTFAC=1000.
COMIN=1.0E-12
TDELET=1.0E-06
FDTEMP=298.00
TEMPST=2000.0
FROCO=0.328
FROCO2=0.332
FROMH2O=0.34
DO2REF=2.30
RHOSLD=2.0
DO 11 K=1,70
IF (K.GT.5) GO TO 2
Q(K)=0.0
SIZPRT(K)=0.0
SIZEFR(K)=0.0
2 IF (K.GT.50) GO TO 3
PORRAD(K)=0.0
PORFR(K)=0.0
3 AF(K)=0.
TEF(K)=0.
EF(K)=0.
AR(K)=0.
TER(K)=0.
ER(K)=0.
IDREAC(K)=6H
DO 11 L=1,6
ISM(K,L)=0
NAMISM(K,L)=6H

C
C
C

```

11 CONTINUE
  DO 13 I=1,10
    IDHREA(I)=6H
    DO 13 J=1,6
      ISMH(I,J)=0
13 NMISMH(I,J)=6H
  DO 30 I=1,35
    REACIN(I)=6H
    OH(I)=0.
    ACP(I)=0.
    BCP(I)=0.
    CCP(I)=0.
    DCP(I)=0.
30 CONTINUE
19 CONTINUE
  ISIZE=0
  IPOR=0
  ITEMP=0
  H=1000.
  DO 26 I=1,35
    CM(I)=0.
    FD(I)=0.0
26 CONTINUE

C
C   FOR SERIES OF WELLSTIRRED STAGES LOOP STARTS HERE
C
35 CONTINUE
  WRITE(6,201)

C
C   *****
C   READ IN DATA IN FREE FORMAT, COMMAS MUST SEPARATE NAMES AND NUMBERS.
C   *****
C
      CALL REDATA(CM,AF,TEF,EF,AR,TER,ER,ISM,NAMISM,KEACIN,IDREAC,
1DELTA,TIMEIN,TIMOUT,TO,TFIN,TIMF,BUG1,BUG2,NRITE,M,N,H,P,LPLUG,
2LSTIR,FD,VOL,LDIL,LEVEL,DH,ACP,BCP,CCP,DCP,LHEAT,POTEMP,TEMPST,
3BOLTZ,HTRAN,TWALL,LFLAME,IFUEL,CHI,WTFAC,T,VLTM,COMIN,TOLET,PRITE
4 ,ITMX,IDHREA,NMISMH,ISMH,COEFF,PORRAD,PORFR,SIZPRT,SIZEFR)
  IF (LCOAL.OR.LCHAR) CALL SORT(PORRAD,PORFR,IPOR)
  IF (.NOT.LMONSZ) CALL SORT(SIZPRT,SIZEFR,ISIZE)
  IF (LTMF) CALL SORT (TIM,TMP,ITEMP)
C
C   SET THERMOCHEMICAL DATA FROM INTERNAL LIBRARY
C   DATA READ IN FROM INPUT WILL HAVE PRECEDENCE
C
C   THE CALL THERMO STATEMENT WAS DELETEDFROM THIS POINT
C
C   PRINT OUT TRANSLATED DATA
C   WRITE(6,101) M,N
101 FORMAT(1H1,10X,"NUMBER OF SPECIES",I3,10X,"NUMBER OF REACTIONS",
1I3)
  WRITE(6,117)
117 FORMAT(/10X,"INITIAL MOLE FRACTIONS OF SPECIS H FORM KCAL/MOLE
1SPECIFIC HEAT ACP+BCP*ALOG(T)+CCP*T+DCP*T**2 CAL/MOLE DEG K")
  DO 5 I=1,M
    WRITE(6,103) I,REACIN(I),CM(I),OH(I),ACP(I),BCP(I),CCP(I),DCP(I)
103 FORMAT(10X,I3,5X,A6,5X,E12.3,5X,E12.6,10X,E12.6,3X,E12.6,3X,
1E12.6,3X,E12.6)

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```

5 CONTINUE
  IF (.NOT.LCOAL) GO TO 6
  WRITE (6,303)
  DO 8 J=1,MH
    K=J+M
    8 WRITE (6,103) J,HREAC(J),CM(K)
303 FORMAT (/,10X,"MOLE FRACTION OF NET. SPECIES")
    6 WRITE(6,205)
    WRITE(6,107)
    WRITE(6,203)
107 FORMAT(T54,"FORWARD RATE COEFF,AF,TEF,EF",T93,
1"REVERSE RATE COEFFICIENT,AR,TER,ER" )
    DO 10 I=1,N
      WRITE(6,105) I,IDREAC(I),(NAMISM(I,L),L=1,6),AF(I),TEF(I),EF(I),
      1AR(I),TER(I),ER(I)
105 FORMAT(1X,I3,1X,A6,1X,A6,1H+,A6,1H+,A6,1H-,A6,1H+,A6,1H-,A6,
13(1X,E12.4),4X,3(1X,E12.4))
    10 CONTINUE
    IF (.NOT.LCOAL) GO TO 12
    WRITE (6,304)
304 FORMAT (/,T10,"HETEROGENEOUS REACTIONS WITH COEFFICIENTS",
1 T60, "K",T73,"EACT",/)
    DO 7 J=1,NH
      WRITE (6,105) J,IDHREA(J),(NMISM(J,K),K=1,6),KZERO(J),EACT(J)
    7 WRITE (6,305) (COEFF(J,K),K=1,6)
305 FORMAT (10X,6F7.2)
    12 WRITE (6,205)
    WRITE(6,205)
    DO 15 KR=1,N
      WRITE(6,109) KR,IDREAC(KR),(ISM(KR,L),L=1,6)
109 FORMAT(10X,I3,10X,A6,6(3X,I3))
    15 CONTINUE
    WRITE(6,205)
    WRITE(6,111)TO,TFIN,TIMF
111 FORMAT(10X,"TEMPERATURE DECAY FROM",F10.3,"DEG KEL INITIALLY,FALLI
ING TO",F10.3,"DEG KEL IN",F10.3,"SECONDS")
    WRITE(6,113) TIMEIN,TIMOUT
113 FORMAT(10X,"START AT",F10.3,"AND END AT",F10.3)
    WRITE(6,115)H,DELTA,NRITE,BUG1,BUG2
115 FORMAT(20X,"INTEGRATION PARAMETERS- STEP SIZE,H=",E10.3,"STEP SIZE
1CONTROL=",E10.3/,20X,"PRINT PARAMETER=",I6,"DEBUGPARAMETERS,BUG1,
2BUG2",I6,I6/)
    IF(.NOT. LSTIR) GO TO 20
    WRITE (6,205)
    WRITE (6,121) VOL
121 FORMAT( 10X," WELL STIRRED STAGE CALCULATION HAS VOLUME = ",F10.3,
1 " CC /MOLE/SEC FEED "/)
    DO 25 I=1,M
      WRITE(6,123) REACIN(I),FD(I)
123 FORMAT(10X," FEED ",A6,E10.3," MOLE FRACTION ")
    25 CONTINUE
    20 CONTINUE
201 FORMAT(1H1)
203 FFORMAT(/)
205 FORMAT(/////)
    IF ( .NOT. LPLUG ) GO TO 35
    IF (LPLUG.AND..NOT.LHEAT)
      1 CALL PLUGFLO ( M,N,REACIN,ISM,AF,TEF,EF,AR,TER,ER,P,DELTA,
      2H,BUG1,BUG2,PRITE,NAMISM,TIMEIN,TIMOUT,TO,TFIN,TIMF,IDREAC,LDIL,
      3LEVEL,ITMX,COMIN,TDELET,RHOSLO,MINRIT,HSTART,
      4 DDZREF,IPOR,ISIZE,Q,LCOAL,HREAC,NH,MH)
    GO TO 19
  END

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```

SUBROUTINE REDATA(CM,AF,TEF,EF,AR,TER,ER,ISM,NAMISM,REACIN,IDREAC,
1DELTA,TIMEIN,TIMOUT,TO,TFIN,TIMF,BUG1,BUG2,NRITE,M,N,H,P,LPLUG,
2LSTIR,FD,VOL,LDIL,LEVEL,OH,ACP,BCP,CCP,DCP,LHEAT,FDTEMP,TEMPST,
3BOLTZ,HTRAN,TWALL,LFLAME,IFUEL,CHI,WTFAC,VOLTM,COMIN,TOLEET,PRITE
4,ITMX,IOHREA,NMISMH,ISMH,COEFF,PORRAD,PORFR,SIZPRT,SIZEFR)

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COMMON/D/ ISKIP

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*****
VERSION AUGUST 2,1973 JDLW
VERSION 29/11/73 JDLW HEAT BALANCED OPTION ADDED
READS IN FREE FORMAT DATA AND TRANSLATES.
SEE NOTES FOR VARIABLE LIST.

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*****
COMMON/REDATA/RHOSLD,DD2REF,IPOR,MINRIT,
1HREAC,NH,MH,LCOAL,LMONSZ,ISIZE,LTMP,HSTART
COMMON/B5/DRHOC(10,35,5),IS(5),EFOFF(5),K0(10,5),
1 HRATE(10,5),CONC(10),EACT(10),KZERO(10),THIELE(10,5),
2 ETA(10,5),DRHOTT(10,5),RATEK(10,5)
COMMON/V1/FRVOL,FRFIXC,FRWAT,FRASH,FRC,FRN,FRO,FRS,FRM,FROCD
1,FRJCO2,FROH2O,IVOL,VSPEC(5),KSTAR(10),ESTAR(10),COALIN,LCHAR
COMMON/T1/ICJUNT,X1,X2,X3,C1,C2,C3,C4,C5,IMP(20),TIM(20),ITEMP
INTEGER IWRD(80),ISPEC(6),REACIN(35),IDREAC(150),ISM(150,6)
DIMENSION NAMISM(150,6),NISM(6)
DIMENSION IOHREA(10),NMISMH(10,6),ISMH(10,6),HREAC(10)
1,COEFF(10,6),X(6)
INTEGER BUG1,BUG2
DIMENSION CM(35),AF(150),TEF(150),EF(150),AR(150),TER(150),ER(150)
DIMENSION FD(35)
DIMENSION OH(35),ACP(35),BCP(35),CCP(35),DCP(35)
DIMENSION PORRAD(50),PORFR(50),SIZPRT(5),SIZEFR(5)
REAL KZERO,KSTAR
LOGICAL LPLUG,LSTIR
LOGICAL LDIL
LOGICAL LHEAT
LOGICAL LFLAME
LOGICAL LCOAL
LOGICAL LCHAR,LTMP
LOGICAL LMONSZ
INTEGER PRITE
DO 15 L=1,6
NISM(L)=0
ISPEC(L)=611
IDIST=6H
15 CONTINUE
ISKIP=0
1 CONTINUE
READ( 5,100) INAM,(IWRD(K),K=1,74)
IF(EOF(5))40,55
100 FORMAT(A5,1X,74A1)
55 WRITE(6,101) INAM,(IWRD(K),K=1,74)
101 FORMAT(1H-,9X,A6,74A1)
50 IF(INAM.EQ.5HNRITD) ISKIP=1
IF(INAM.EQ.5HNRIT) ISKIP=0
IF(INAM.EQ.5HSTOIC) GO TO 500
IF(INAM.EQ.5HSTOI) GO TO 525
IF(INAM.EQ.5HCOEFF) GO TO 550
IF(INAM.EQ.5HFRATC) GO TO 575
IF(INAM.EQ.5HRRATC) GO TO 600

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IF (INAM.EQ.5HSPECI) GO TO 650
IF (INAM.EQ.5HHSPEC) GO TO 675
IF (INAM.EQ.5HENTHA) GO TO 700
IF (INAM.EQ.5HHRATE) GO TO 750
IF (INAM.EQ.5HPORDA) GO TO 800
IF (INAM.EQ.5HTDATA) GO TO 850
IF (INAM.EQ.5HSIZPR) GO TO 900
IF (INAM.EQ.5HPRXAN) GO TO 925
IF (INAM.EQ.5HULTAN) GO TO 950
IF (INAM.EQ.5HQ2DIS) GO TO 975
IF (INAM.EQ.5HVSPEC) GO TO 1000
IF (INAM.EQ.5HTARSP) GO TO 1025
IF (INAM.EQ.5HEXECU) GO TO 1100
IF (INAM.EQ.5HPLUGF) LPLUG = .TRUE.
IF (INAM.EQ.5HNOPLU) LPLUG = .FALSE.
IF (INAM.EQ.5HWELLS) LSTIR = .TRUE.
IF (INAM.EQ.5HNOVEL) LSTIR = .FALSE.
IF (INAM.EQ.5HDILUE) LDIL = .TRUE.
IF (INAM.EQ.5HNODIL) LDIL = .FALSE.
IF (INAM.EQ.5HHEATB) LHEAT = .TRUE.
IF (INAM.EQ.5HNOHEA) LHEAT = .FALSE.
IF (INAM.EQ.5HFLAME) LFLAME = .TRUE.
IF (INAM.EQ.5HNOFLA) LFLAME = .FALSE.
IF (INAM.EQ.5HCOAL) LCOAL = .TRUE.
IF (INAM.EQ.5HNOCOA) LCOAL = .FALSE.
IF (INAM.EQ.5HCHAR) LCHAR = .TRUE.
IF (INAM.EQ.5HMONSI) LMONSZ = .TRUE.
IF (INAM.EQ.5HSIZDS) LMONSZ = .FALSE.
CALL DECIP (INAM,IWRD,5HSTEPI,IDIOT,H,D,O,O,O,O,1D,1D,1D,1D,1D,1D,
12)
CALL DECIP (INAM,IWRD,5HSSCON,IDIOT,DELTA,O,O,O,O,O,O,1D,1D,1D,1D,1D,
1D,2)
CALL DECIP (INAM,IWRD,5HTIMEI,IDIOT,TIMEIN,O,O,O,O,O,O,1D,1D,1D,1D,
1D,1D,2)
CALL DECIP (INAM,IWRD,5HTIMQU,IDIOT,TIMOUT,O,O,O,O,O,O,1D,1D,1D,1D,
1D,1D,2)
CALL DECIP (INAM,IWRD,5HTDECA,IDIOT,TO,TFIN,TIMF,TIM2,O,O,1D,1D,1D,
1D,1D,1D,2)
CALL DECIP (INAM,IWRD,5HTY0BU,IDIOT,O,O,O,O,O,O,BUG1,BUG2,1D,1D,1D,
1D,3)
CALL DECIP (INAM,IWRD,5HNPRIN,IDIOT,O,O,O,O,O,O,NRITE,1D,1D,1D,1D,
1D,3)
CALL DECIP (INAM,IWRD,5HPPRIN,IDIOT,O,O,O,O,O,O,PRITE,1D,1D,1D,
1D,1D,3)
CALL DECIP (INAM,IWRD,5HVOLUM,IDIOT,VOL,O,O,O,O,O,O,1D,1D,1D,1D,1D,
1D,2)
CALL DECIP (INAM,IWRD,5HLEVEL,IDIOT,O,O,O,O,O,O,LEVEL,1D,1D,1D,
2ID,1D,3)
CALL DECIP (INAM,IWRD,5HPDECA,IDIOT,P,O,O,O,O,O,1D,1D,1D,1D,1D,
2ID,2)
CALL DECIP (INAM,IWRD,5HFDTEM,IDIOT,FDTEMP,O,O,O,O,O,O,
1D,1D,1D,1D,1D,1D,2)
CALL DECIP (INAM,IWRD,5HTEMPS,IDIOT,TEMPST,O,O,O,O,O,O,
1D,1D,1D,1D,1D,1D,2)
CALL DECIP (INAM,IWRD,5HFLAME,IFUEL,CHI,O,O,O,O,O,1D,1D,1D,1D,
1D,1D,1)
CALL DECIP (INAM,IWRD,5HMTLQS,IDIOT,BOLTZ,MTRAN,TWALL,O,O,O,O,
1D,1D,1D,1D,1D,1D,2)
CALL DECIP (INAM,IWRD,5HWTFAC,IDIOT,WTFAC,O,O,O,O,O,O,1D,1D,1D,1D,
1D,1D,2)
CALL DECIP (INAM,IWRD,5HDELET,IDIOT,COMIN,TDELET,O,O,O,O,O,O,1D,1D,1D,
1D,1D,2)

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```

1 ID, ID, ID, 2)
  CALL DECIP (INAM, IWRD, 5HVOLWT, IDIOT, VOLTH, 0, 0, 0, 0, 0, ID, ID, ID, ID,
1 ID, ID, 2)
  CALL DECIP (INAM, IWRD, 5HMAXIT, IDIOT, 0, 0, 0, 0, 0, 0, ITMX, ID, ID, ID, ID,
1 ID, 3)
  CALL DECIP (INAM, IWRD, 5HMINRI, IDIOT, 0, 0, 0, 0, 0, 0, 0,
1 MINRI, ID, ID, ID, ID, ID, 3)
  CALL DECIP (INAM, IWRD, 5HDIFFQ, IDIOT, 0, 0, 0, 0, 0, 0, 0,
1 ID, ID, ID, ID, ID, ID, 2)
  CALL DECIP (INAM, IWRD, 5HCOALI, IDIOT, COALIN, 0, 0, 0, 0, 0, 0,
1 ID, ID, ID, ID, ID, ID, 2)
  CALL DECIP (INAM, IWRD, 5HCAKBU, IDIOT, RHOSLD, 0, 0, 0, 0, 0, 0,
1 ID, ID, ID, ID, ID, ID, 2)
  CALL DECIP (INAM, IWRD, 5HHSTAR, IDIOT, HSTAR, U, U, 0, 0, 0, 0,
1 ID, ID, ID, ID, ID, ID, 2)
  GO TO 1
500 CONTINUE

C
C   DECIPHER STOICH CARDS, PUT REACTIONS AND SPECIES
C   ON RESPECTIVE SLATES
C
  CALL OESTOIC (INAM, IWRD, IDIOT, ISPEC)
  DO 505 L=1, 6

C
C   ***** SPECIES SLATE JSPEC *****
C
  CALL SSLATE (ISPEC(L), M, REACIN, JSPEC)
  NISM(L)=JSPEC
505 CONTINUE

C
C   ***** REACTION SLATE JREAC *****
C
  CALL SSLATE (IDIOT, N, IDREAC, JREAC)
  DO 510 L=1, 6
    ISM(JREAC, L)=NISM(L)
    NAMISM(JREAC, L)=ISPEC(L)
510 CONTINUE

C
C   *****
C
  DEBUG WRTIEOUT, BUG1 CONTROLS HOW MANY IN SUCCESSION YOU WRITE
  AND BUG2 HOW MANY STEPS BETWEEN EACH GROUP OF BUG1 OUTPUTS
  *****

  IF (ISKIP.EQ.0) GO TO 9000
  WRITE (6, 103) IDIOT, (ISPEC(K), K=1, 6)
103 FORMAT(10X, A6, 6(10X, A6))
  DO 523 I=1, M
    WRITE(6, 105) I, REACIN(I)
105 FORMAT(10X, I3, 5X, A6)
  DO 521 L=1, N
    WRITE(6, 107) IDREAC(L), (NAMISM(L, K), K=1, 6)
107 FORMAT(10X, A6, 5X, A6, 1H+, A6, 1H+, A6, 1H+, A6, 1H+, A6, 1H+, A6)
521 CONTINUE
  DO 522 L=1, N
    WRITE(6, 109) L, (ISM(L, K), K=1, 6)
109 FORMAT(10X, I6, 5X, 6(I6, 1X))
522 CONTINUE
9000 CONTINUE
  GO TO 1

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```

525 CONTINUE
    CALL DESTOIC (INAM,IWRD,IDIOT,ISPEC)

    DO 540 L=1,6
    DO 530 I=1,M
    IF (ISPEC(L).EQ.REACIN(I)) GO TO 535
530 CONTINUE
    CALL SSLATE (ISPEC(L),MH,HREAC,JSPEC)
    IF (JSPEC.EQ.J) GO TO 532
    NISM(L)=JSPEC*M
    GO TO 540
532 NISM(L)=0
    GO TO 540
535 NISM(L)=I
540 CONTINUE
    CALL SSLATE(IDIOT,NH,IDHREA,JREAC)
    DO 545 L=1,6
    ISMH(JREAC,L)=NISM(L)
545 NMISMH(JREAC,L)=ISPEC(L)
    GO TO 1
550 CONTINUE
    CALL DECIP(INAM,IWRD,5HCoeff,IDIOT,X(1),X(2),X(3),X(4),
    1 X(5),X(6),ID,ID,ID,ID,ID,1)
    DO 560 I=1,NH
    IF (IDIOT.EQ.IDHREA(I)) GO TO 565
560 CONTINUE
    GO TO 1
565 DO 570 J=1,6
570 COEFF(I,J)=X(J)
    GO TO 1
575 CONTINUE
C
C *****
C
C DECIPHERS FRATCO CARDS AND MATCHES WITH REACTIONS ON
C SLATE OR ADDS TO SLATE IF NEW REACTION
C *****
C
    CALL DECIP(INAM,IWRD,5HFRATC ,IDIOT,A,B,C,D,E,F,ID,ID,ID,ID,ID,
    11)
    CALL SSLATE (IDIOT,N,IDREAC,JREAC)
    AF(JREAC)=A
    TEF(JREAC)=B
    EF(JREAC)=C
    GO TO 1
C
C 600 CONTINUE
C
C *****
C
C DOES THE SAME AS ABOVE BUT WITH THE RRATCO CARDS
C *****
C
    CALL DECIP(INAM,IWRD,5HRRATC ,IDIOT,A,B,C,D,E,F,ID,ID,ID,ID,ID,
    11)
    CALL SSLATE (IDIOT,N,IDREAC,JREAC)
    AR(JREAC)=A
    TER(JREAC)=B
    ER(JREAC)=C

```

```

      GO TO 1
650 CONTINUE
C
C *****
C
C   DECIPHERS SPECIES INITIAL MOLE FRACTION AND/OR FEED AND
C   MATCHES OR ADDS TO SLATE
C
C *****
C
      CALL DECIP(INAM,IWRD,SHSPECI,NAMSPE,A,B,C,D,E,F,10,10,10,10,10,10
1,1)
      CALL SSLATE(NAMSPE,M,REACIN,JSPEC)
      CM(JSPEC)=A
      FO(JSPEC)=B
      GO TO 1
-575-CONTINUE
      CALL DECIP(INAM,IWRD,SHMSPEC,NAMSPE,A,B,C,D,E,F,10,10,10,10,10,10
1,10,1)
      CALL SSLATE(NAMSPE,MH,HREAC,JSPEC)
      JSPEC=JSPEC+M
      CM(JSPEC)=A
      FO(JSPEC)=B
      GO TO 1
700 CONTINUE
C
C   DECIPHERS ENTHALPY AND SPECIFIC HEAT CARDS
C   ENTHALPY IN KCAL/MOLE-DEG K      SP HEAT IN CAL/MOLE-DEG K
C   ENTHALPY CARDS MUST COME AFTER ALL THE SPECIES HAVE BEEN INTRODUCED
C   THROUGH THE STOICH OR SPECIE CARDS
C   ENTHALPY CARDS WILL NOT ADD SPECIES TO SPECIES SLATE
      CALL DECIP(INAM,IWRD,SHENTHA,NAMSPE,A,B,C,D,E,F,10,10,10,10,10,10
1,10,1)
      MM=M
      CALL SSLATE(NAMSPE,MH,REACIN,JSPEC)
      IF (MM.GT.M) GO TO 1
      OM(JSPEC)=A
      ACP(JSPEC)=B
      BCP(JSPEC)=C
      CCP(JSPEC)=D
      OCP(JSPEC)=E
      GO TO 1
C
C   DECIPHERS RATE CARDS AND MATCHES WITH REACTIONS ON SLATE OR
C   ADDS TO SLATE IF NEW REACTION.
C
750 CALL DECIP(INAM,IWRD,SHMRATE,IDIQT,A,B,C,D,E,F,10,10,10,10,10,10
1,10,10,10,1)
      CALL SSLATE(IDIQT,NH,1DHREA,JREAC)
      KZERO(JREAC)=A
      EACT(JREAC)=B
      GO TO 1
C
C   DECIPHERS PORDAT CARDS AND STORES VALUES IN PORRAD AND
C   PORFR.
C
800 CONTINUE
      CALL DECIP(INAM,IWRD,SHPORDA,IDIQT,A,B,C,D,E,F,10,10,10,10,10,10
1,10,10,10,2)
      PORRAD(IPOR+1)=A
      PORFR(IPOR+1)=B

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      PORRAD(IPOR+2)=C
      PORFR(IPOR+2)=O
      PORRAD(IPOR+3)=E
      PORFR(IPOR+3)=F
      IPOR=IPOR+3
      GO TO 1
850 CONTINUE
C
C      DECIPHERS TDATA CARDS AND STORES DATA IN TIM AND TMP.
C
      CALL DECIP (INAM,IWRD,5HTDATA,IDIOT,A,B,C,D,E,F,IO,IO,IO,
1  IO,IO,IO,2)
      ITEMP=ITEMP+1
      TIM(ITEMP)=A
      TMP(ITEMP)=B
      IF (D.LE.O.O) GO TO 1
      ITEMP=ITEMP+1
      TIM(ITEMP)=C
      TMP(ITEMP)=D
      IF (F.LE.O.O) GO TO 1
      ITEMP=ITEMP+1
      TIM(ITEMP)=E
      TMP(ITEMP)=F
      GO TO 1
900 CONTINUE
C
C      DECIPHERS SIZPRT CARDS AND STORES DATA IN SIZPRT AND
C      SIZEFR.
C
      CALL DECIP(INAM,IWRD,5HSIZPR ,IDIOT,A,B,C,D,E,F,IO,IO,IO,
1  IO,IO,IO,2)
      ISIZE=ISIZE+1
      SIZPRT(ISIZE)=A
      SIZEFR(ISIZE)=B
      IF (C.LE.O.O)GO TO 1
      ISIZE=ISIZE+1
      SIZPRT(ISIZE)=C
      SIZEFR(ISIZE)=D
      IF (E.LE.O.O) GO TO 1
      ISIZE=ISIZE+1
      SIZPRT(ISIZE)=E
      SIZEFR(ISIZE)=F
      GO TO 1
925 CONTINUE
C
C      DECIPHERS PRXANL CARDS.
C
      CALL DECIP (INAM,IWRD,5HPRXAN,IDIOT,A,B,C,D,E,F,IO,IO,IO,IO,
1  IO,IO,1)
      IF (IDIOT.EQ.5HFRVOL) FRVOL=A
      IF (IDIOT.EQ.5HFRFIXC) FRFIXC=A
      IF (IDIOT.EQ.5HFRWAT) FRWAT=A
      IF (IDIOT.EQ.5HFRASH) FRASH=A
      GO TO 1
950 CONTINUE
C
C      DECIPHERS ULTANL CARDS.
C
      CALL DECIP (INAM,IWRD,5HULTAN,IDIOT,A,B,C,D,E,F,IO,IO,IO,IO,
1  IO,IO,1)
      IF (IDIOT.EQ.3HFRFC) FRC=A

```

```
      IF (IDIOT.EQ.3HFRH) FRH=A
      IF (IDIOT.EQ.3HFRS) FRS=A
      IF (IDIOT.EQ.3HFRN) FRN=A
      IF (IDIOT.EQ.3HFRO) FRO=A
      IF (IDIOT.EQ.5HFRWAT) FRWAT=A
      IF (IDIOT.EQ.5HFRASH) FRASH=A
      GO TO 1
975 CONTINUE
C
C   DECIPHERS OZDIST CARDS.
C
      CALL DECIP (INAM,IWRD,5HOZDIS,IDIOT,A,B,C,D,E,F,ID,ID,ID,ID,
1 ID,ID,1)
      IF (IDIOT.EQ.5HFRCO ) PROCO=A
      IF (IDIOT.EQ.5HFRCO2) PROCO2=A
      IF (IDIOT.EQ.5HFRH2O) FROMH2O=A
      GO TO 1
1000 CONTINUE
C
C   DECIPHERS VSPEC CARDS.
C
      CALL DECIP (INAM,IWRD,5HVSPEC,NAMSPE,A,B,C,D,E,F,ID,ID,ID,ID,
1 ID,ID,1)
      CALL SSLATE (NAMSPE,IVOL,VSPEC,JSPEC)
      KSTAR(JSPEC)=A
      ESTAR(JSPEC)=B
      GO TO 1
1025 CONTINUE
C
C   DECIPHERS TARSP CARDS.
C
      CALL DECIP (INAM,IWRD,5HTARSP,NAMSPE,A,B,C,D,E,F,ID,ID,ID,ID,
1 ID,ID,2)
      KSTAR(IVOL+1)=A
      ESTAR(IVOL+1)=B
      GO TO 1
1100 RETURN
40 CONTINUE
CALL EXIT
END
```

SUBROUTINE DECIP (INAM,IWRD,ANAME,IDIOT,A,B,C,D,E,F,IA,IB,IC,ID,IE
1,IF,ITYPE)

```

C
C      COMMON/O/ ISKIP
C      *****
C
C      VERSION AUGUST 2,1973 JOLW
C      DECIPHERS IWRD ACCORDING TO THREE TYPES
C      ITYPE=1 IWRD CONTAINS AN ALPHA WORD,IDIOT, FOLLOWED BY NOT MORE
C      THAN 6 FLOATING PT. VARIABLES
C      ITYPE=2 IWRD CONTAINS NOT MORE THAN 6 FLOAT, VARIABLES
C      ITYPE=3 IWRD CONTAINS NOT MORE THAN 6 INTEGER VARIABLES
C      RETURNS WITH ALPHA WORD IN IDIOT(ITYPE=1), E FORMAT
C      VARIABLES IN A,B,C,D,E,F (ITYPE=1 OR 2), I FORMAT VARIABLES
C      IN IA,IB,IC,ID,IE,IF( ITYPE=3)
C      PROGRAM ALSO CHECKS WHETHER INAM=ANAME
C      THIS SUBROUTINE CONTAINS ENCODE AND DECODE STATEMENTS
C      AND IL THE NUMBER OF BLANKS TO BE FILLED INTO THE NUMBER
C      BEING RIGHT HAND JUSTIFIED. THESE MAY HAVE TO BE CHANGED
C      FOR MACHINES WITH WORD LENGTHS OTHER THAN TEN.
C      IS AND IE ARE THE STARTING AND ENDING POSITIONS
C      OF THE NUMBERS WHICH ARE FOUND BY DETECTING THE COMMAS
C      IN THE SUPPRESSED DATA.
C
C      *****
C
C      REAL VAR(10)
C      INTEGER IVAR(10),IWRD(80),INUM(3),IBLANK(20),IWS(10),IWE(10),COMMA
C      INTEGER ANAME
C      DATA COMMA/1H, /
C      DATA IBLANK/20*1H /
C
C      *****
C      DATA INUM/3*10H /
C      *****
C
C      IF (INAM.NE.ANAME) RETURN
C      IF(ISKIP.EQ.0) GO TO 9001
C      WRITE(6,2001) (IWRD(K),K=1,74)
2001 FORMAT(10X,74A1)
9001 CONTINUE
C      CALL SUPPRE(IWRD)
C      IF(ISKIP.EQ.0) GO TO 9002
C      WRITE(6,2001) (IWRD(K),K=1,74)
9002 CONTINUE
C      LC=0
C      IDIOT=6H
C      DO 1 I=1,10
C      IWS(I)=0
C      IWE(I)=0
C      IVAR(I)=0
C      VAR(I)=0.
1 CONTINUE
C      DO 5 I=1,74
C      IF (IWRD(I).NE.COMMA) GO TO 5
C      LC=LC+1
C      IWS(LC)=I+1
C      IF (IWRD(I+1).EQ.1H ) IWS(LC)=0
C      IF (LC.EQ.1) GO TO 5
C      IWE(LC-1)=I-1
5 CONTINUE

```

```
C *****
C
      K=K+1
      IVAR(K)=KNUM
      IF(ISKIP.EQ.0) GO TO 9006
      WRITE(6,2009) K,IVAR(K)
2009  FORMAT(10X,"K=",I3,"IVAR(K)=",I10)
9006  CONTINUE
      15 CONTINUE
      25 CONTINUE
      A=VAR(1)
      B=VAR(2)
      C=VAR(3)
      D=VAR(4)
      E=VAR(5)
      F=VAR(6)
      IA=IVAR(1)
      IB=IVAR(2)
      IC=IVAR(3)
      ID=IVAR(4)
      IE=IVAR(5)
      IF=IVAR(6)
      RETURN
      END
```



```
      ENCODE(10,100,LSPEC) (IWRD(K),K=IS,IE)
C
C *****
      ISPEC(LC-1) =LSPEC
20  CONTINUE
C  NOW MUST FILL IN BLANKS SO THAT RHS AND LHS OF REACTION ARE PROPERLY STORE
      DO 30 I=1,3
30  IF(I.LE.IEQ) NSPEC(I)=ISPEC(I)
      ICOUNT=IEQ
      DO 40 I=4,6
      ICOUNT=1+ICOUNT
      NSPEC(I)=ISPEC(ICOUNT)
40  CONTINUE
      RETURN
      END
```

SUBROUTINE SUPPRE (IWRD)

VERSION AUGUST 2,1973 JOLW
SUPPRESSES BLANKS FROM THE FREE FORMAT DATA INPUT

```

      INTEGER IWRD(80)
      DATA IBLANK/1H /
      K=0
      DO 5 I=1,74
      IF (IWRD(I).NE.IBLANK) GO TO 10
      GO TO 5
10    K=K+1
      IWRD(K)=IWRD(I)
      5 CONTINUE
      KK=K+1
      DO 20 I=KK,74
      IWRD(I)=IBLANK
20    CONTINUE
      RETURN
      END

```

SUBROUTINE SSLATE (NAMSP,NUMBS,REACIN,JSPEC)

VERSION AUGUST 2, 1973 JOLW
CHECKS IF NAMSP IS ALREADY LISTED IN REACIN
IF SO RETURNS NUMBER IN JSPEC
IF NOT, ADDS ON SLATE, REACIN, AND ADVANCES
NUMBS, TOTAL NUMBER LISTED.
JSPEC THEN EQUAL NUMBS.

```

INTEGER REACIN(150)
DATA IBLANK/6H      /
DATA MBLANK/6HHM    /
JS=0
IF(NAMSP.EQ.IBLANK) GO TO 10
IF (NAMSP.EQ.MBLANK) JS=99
IF (NAMSP.EQ.MBLANK) GO TO 10
IF (NUMBS.LE.0) NUMBS=0
IF (NUMBS.EQ.0) GO TO 60
DO 5 J=1,NUMBS
IF (NAMSP.NE.REACIN(J)) GO TO 5
JS=J
GO TO 10
5 CONTINUE
60 CONTINUE
NUMBS=NUMBS+1
REACIN(NUMBS)=NAMSP
JS=NUMBS
10 CONTINUE
JSPEC=JS
RETURN
END

```

```
      SUBROUTINE SORT(SIZE,FRACT,N)
C
C   THIS SUBROUTINE SORTS THE ARRAYS SIZE AND FRACT,
C   AND PUTS THEM IN ACENDING ORDER WITH RESPECT TO THE VALUES
C   IN SIZE.
C
      DIMENSION SIZE(50),FRACT(50)
      M = N
10  M = M-1
      MPLUS=M+1
      DO 100 I=1,M
        IF (SIZE(I).GT.SIZE(MPLUS)) GO TO 50
      GO TO 100
50  SIZSAV=SIZE(MPLUS)
      SIZE(MPLUS)=SIZE(I)
      SIZE(I)=SIZSAV
      SFRACT=FRACT(MPLUS)
      FRACT(MPLUS)=FRACT(I)
      FRACT(I)=SFRACT
100 CONTINUE
      IF (M.GE.2) GO TO 10
      RETURN
      END
```

Subroutine PLUGFLOW

Subroutine PLUGFLOW Variable List

AL	the true alpha vector.
ALP	the pseudo-alpha vector.
AF, AR	the pre-exponential for the rate constant for the forward and reverse reaction rates.
B	the true beta matrix (the Jacobian).
BETA	the pseudo-beta matrix.
BUG1, BUG2	parameters used when debug output is wanted.
CM	mole fraction vector.
CMCIN	the initial mole fraction of solid carbon in the feed; moles carbon/total moles of gas.
CMN	the initial mole fraction of solid nitrogen in the feed.
DCO	the vector containing the species production rates; moles/(cm**3*sec).
DELTA	the value below which a species is no longer considered.
EF, ER	the activation energy for the homogeneous reaction rate constants; cal.
F	the vector containing the species production rates times the velocity; the right-hand side of differential equation; moles/(cm**2*sec**2).
FL	the species flow rate vector; moles/(cm**2*sec).
H	the step size; sec.
HSTART	the fraction of the tar remaining when char combustion begins.
IDREAC	homogeneous reaction name vector.
IN	the flag used in the integration routine to know which integration scheme to use; a different one is used for the first two steps.
IPLOT	the iteration counter.
ISIZE	the number of size fractions.

ISM	the homogeneous reaction species number matrix.
LCHAR	the logical variable which is true if the char is reacting.
LCOAL	the logical variable which is true as long as volatiles are present in the coal.
LDIL	logical variable which is true if a diluent is present.
LEVEL	print parameter.
M	the number of homogeneous gas phase species.
MINRIT	the first iteration where data will be printed.
N	the number of homogeneous reactions.
NRITE	the data are printed out every NRITE steps.
NAMISM	the homogeneous reaction species name matrix.
MPLUS	the number of dependent variables including devolatilized and heterogeneous reactants.
P	the pressure, atm.
RATE	the vector of homogeneous reaction rates; moles/(cm**3*sec).
REACIN	the species name vector.
RFO	the vector of forward reaction rates; moles/(cm**3*sec).
RHO	the total molar gas density; moles/(cm**3).
RKF	the vector of forward rate constants.
RKR	the vector of reverse rate constants.
RRE	the vector of reverse reaction rates; moles/(cm**3*sec).
S	the total molar flow; moles/(cm**2*sec).
SIZPRT	the particle size vector; cm.
SIZEFR	the vector containing the weight fraction of the size classes.
T	temperature, K.

TEF, TER	the exponents on T for the homogeneous reaction rate constants.
TIMEIN	the time at the start of the run.
TDELET	the maximum time for the run.
X	the current time.

```
C
C
C CDC VERSION OF PLUGFLOW SUBROUTINE
C
C   SUBROUTINE PLUGFLO ( M,N,REACIN,ISM,AF,TEF,EF,AR,TER,ER,P,DELTA,
C   2H,BUG1,BUG2,NRITE,NAMISM,TIMEIN,TIMOUT,TO,TFIN,TIMF,IDREAC,LOIL,
C   3LEVEL,ITMX,COMIN,TDELET,RHOSLD,MINRIT,HSTART,
C   4 DOZREF,IPOR,ISIZE,Q,LCOAL,HREAC,NH,MH)
C
C *****
C
C   VERSION 2 JULY 24,1973 JDLW
C   CONSTRUCTS AND SOLVES EQUATIONS FOR A PLUGFLOW REACTOR,
C   WITH SPECIFIED TEMPERATURE AND PRESSURE
C   VERSION ALLOWING CONSISTENT MOLAR CONCENTRATIONS, MOLE FRACTIONS
C   AND CHANGES IN VELOCITY AND TOTAL MOLAR FLUXES, FOR SPECIFIED
C   TEMPERATURE AND PRESSURE
C
C *****
C
C   MODIFIED JAN '82 G. KYLE
C   INCLUDES CHAR COMBUSTION ROUTINE AND DEVOLATILIZATION FOR
C   COAL COMBUSTION.
C
```

```

C
C COMMON BLOCK CONTAINING DERIVED QUANTITIES USED TO SAVE STORAGE
COMMON/81/ F(35),FL(35),DCQ(35),BETA(35,35),B(35,35),
1 AL(35),ALP(35)
COMMON/82/ RATE(150),RKF(150),RKR(150),RFO(150),RRE(150),
1 CP(35),CPOOT(35),ENTH(35)
COMMON/83/ SIZPRT(5),SIZEFR(5),ISMH(10,6),COEFF(10,6),
1 IDHREA(10),NMISMH(10,6)
COMMON/84/CO(35),CM(35),PORRAD(50),PORFR(50),DKNUD(50,5),
1 EPS(50,5),DIFF(50,5)
COMMON/85/DRHOC(10,35,5),IS(5),EFDIFF(5),KO(10,5),
1 HRATE(10,5),CONC(10),EACT(10),KZERO(10),THIELE(10,5),
2 ETA(10,5),DRHDTT(10,5),RATEK(10,5)
COMMON/T1/ICOUNT,X1,X2,X3,C1,C2,C3,C4,C5,TMP(20),TIM(20),ITEMP
COMMON/V1/FRVOL,FRFIXC,FRWAT,FRASH,FRC,FRN,FRQ,FRS,FRH,FRUCJ
1 ,FROCO2,FROH2O,IVOL,VSPEC(5),KSTAR(10),ESTAR(10),COALIN,LCHAR
COMMON/V2/DCOV(10,5),IBURN
1 ,VOLSTR(5),DCOVOL(10),TAR,WATER,TARSTP(5)
COMMON/BRN1/CSHKNK(5),FLCSAV(5),SIZSAV(5)
REAL AF(150),TEF(150),EF(150),AR(150),TER(150),ER(150)
1 DIMENSION ISM(150,6),HREAC(10),EPST(5),SAREA(5),
1 SPAREA(5),Q(5),VSTAR(5,5),TARSTR(5),
2 TARCHK(5),VOLIN(5),REACIN(35)
REAL LAMDA(50),OLAMDQ(50),KZERO,KSTAR
INTEGER BUG1,BUG2
LOGICAL LOIL
LOGICAL LCOAL,LCHAR
WRITE(6,199)
199 FORMAT(1H0,"*****")
1 *****")
WRITE(6,198)
198 FORMAT(1H0," THE FOLLOWING IS A PLUGFLOW REACTOR CALCULATION FOR
1 THE ABOVE INPUT REACTIONS AND INITIAL CONDITIONS. " )
WRITE(6,199)
C SET INITIAL VALUES OUTSIDE TYSON LOOP
IF (LCOAL.OR.LCHAR) CALL BLCALC (EPSTO,BZERO,BONE,LAMDA,IPOR,
1 OLAMDQ)
IF (LCOAL) CALL COALCMP (VSTAR,TARSTR,HREAC,MH,ISIZE,
1 SIZEFR,CM,Y,M,VOLIN,TARIN,REACIN)
IF (LCHAR) IBURN=ISIZE
INIT=0
INO=0
IBSAVE=0
ICOUNT=1
C SET INITIAL VALUES OUTSIDE TYSON LOOP
X=TIMEIN
IN=0
IPLOT=0

```

```

T=TEMP(X,TDASH,TO,TFIN,TIME,TIM2)
TAR=1.0
WATER=1.0
DO 2 I=1,5
2 VOLSTR(I)=1.0
DO 3 L=1,ISIZE
TARCHK(L)=TARSTR(L)*HSTART
TARSTP(L)=TARSTR(L)*0.01
IS(L)=0
SIZSAV(L)=SIZPRT(L)
CSHRNK(L)=0.0
EPST(L)=EPSTO
3 CONTINUE
C ENTER WITH INITIAL MOLE FRACTIONS- MUST INCLUDE DILUENT
RHO=P/(82.07*T)
S=0.
C IN CASE SUM OF INITIAL MOLE FRACTIONS DO NOT EQUAL 1
DO 5 I=1,M
FL(I)=CM(I)
S=S+FL(I)
CO(I)=CM(I)*RHO
5 CONTINUE
C
C CO, CM, AND FL ARE CALCULATED FOR THE MET SPECIES.
C
C IF (.NOT.LCOAL.AND..NOT.LCHAR) GO TO 9
C
C THE SOLID CARBON IS DISTRIBUTED AMONG THE SIZE FRACTIONS.
C
DO 8 I=1,MH
J=I+M
IF (HREAC(I).NE.2HC ) GO TO 6
CMCIN=CM(J)
FLCSAV(I)=CMCIN
GO TO 7
6 IF (HREAC(I).NE.2HMH) GO TO 7
CMH=CM(J)
7 CO(J)=CM(J)*RHO
FL(J)=CM(J)
8 CONTINUE
9 DIL = 0.0
IF (.NOT.LCOAL.AND..NOT.LCHAR) GO TO 14
IF (ISIZE.LE.1) GO TO 14
ISUM1=ISIZE+M+MH
ISUM2=M+MH+1
DO 12 I=1,MH
J=ISUM1-I
K=ISUM2-I
FL(J)=FL(K)
12 CONTINUE
DO 13 I=1,ISIZE
J=M+I
FL(J)=CMCIN*SIZEFR(I)
FLCSAV(I)=FL(J)
CO(J)=FL(J)*RHO
13 CONTINUE
14 CONTINUE
IF ( LDIL ) OIL = 1.0 -S
S = OIL + S
VEL=S/RHO
C BEGIN TYSON LOOP

```

```

30 CONTINUE
C
C SUBROUTINES CALRAT,CALBET, VOLRAT, AND BRNOUT ARE CALLED
C TO CALCULATE RATES AND DERIVATIVES.
C
      CALL CALRAT(P,T,M,N,CM,AF,TEF,EF,AR,TER,ER,      ISM,RHO,
1 CO,RFO,RRE,RATE,RKF,RKR)
      CALL CALBET (M,N,ISM,RHO,RATE,RKF,RKR,CO,REACIN,BETA,OCO,T,TDASH,
1 ALP,RFO,RRE,TEF,TER,EF,ER)
      IF(LCOAL) CALL VOLRAT(VSTAR,TARSTR,LCOAL,
1 LCHAR,ISIZE,M,KSTAR,ESTAR,VSPEC,T,X,Y,IVOL,RHO,S,MH,
2 TDASH,VOLIN,TARIN,REACIN,IN,TARCHK)
      IF (LCHAR) CALL BRNOUT(RHOSLO,SPAREA,T,OO2REF,IPOR,
1 REACIN,IPLT,IBURN,Q,M,N,RHO,MHET,MH,NH,BONE,BZERO,EPSTO,
2 EPST,LAMDA,COMIN,INIT,TDASH,VEL,SAREA,S,P,IN,CMCIN,CMN,
3 OLAMDO,INO,ISAVE)
C
C NEXT, F(I), AND AL(I) ARE CALCULATED FOR THE GAS PHASE
C SPECIES.
C
      DO 10 I=1,M
      F(I)=OCO(I)*VEL
      AL(I)=ALP(I)*VEL+OCO(I)*S*82.07*TDASH/P
10 CONTINUE
C
C BETA IS ADJUSTED TO GIVE B.
C
      DO 15 I=1,M
      DO 15 J=1,M
      B(I,J)=BETA(I,J)*(1.-CM(J))+OCO(I)/RHO
15 CONTINUE
      MPLUS=M
      IF (LCHAR) MPLUS=M+MHET
      IF (X.LT.TDELET) GO TO 310
      DO 320 I=1,MPLUS
      IF (FL(I).LT.COMIN.AND.F(I).LT.0.0) F(I)=0.0
320 CONTINUE
310 CONTINUE
C
C IF THE CURRENT STEP IS A PRINT STEP, THE DATA ARE PRINTED OUT.
C
      IF (IPLT.NE.0.AND.IPLT.LT.MINRIT)GO TO 16
      IF (IPLT.EQ.0.OR.MOD(IPLT,NRITE).EQ.0 .OR. X .GT. TIMOUT )
1 CALL RITOUT (M,N,CM,FL,FL,CO,OCO,F,REACIN,IDREAC,NAMISM,
1 RFO,RRE,RATE,RKF,RKR,IPLT,X,H,BETA,ALP,S,RHO,T,P,LEVEL,B,AL,
2 LCOAL,HREAC,CMCIN,Q,ETA,IDHREA,NMISMH,HRATE,CDEFF,EPST,SAREA,
3 NH,MH,EFDIFF,SPAREA,KO,RATEK,THIELE,ISIZE,SIZPRT,SIZEFR,
4 IVOL,VSPEC,LCHAR,VOLSTR,OCOVOL,TAR)
C
C IF IT IS TIME TO STOP, OR IF THE MAX ITERATION HAS BEEN
C REACHED, THE RUN IS STOPPED.
C
16 IF(X.GT.TIMOUT) GO TO 40
   IF (IPLT.GE.ITMX) RETURN
   IF (LCOAL) MPLUS=M+MH+ISIZE-1+IVOL+1
C
C THE INTEGRATION ROUTINE IS CALLED.
C
350 CALL TYSON (MPLUS,FL,F,X,H,AL,B,BUG1,BUG2,DELTA,IN)
C
C T, RHO, S, CO, CM, AND VEL ARE CALCULATED AT THE NEW TIME.

```

```
C      T=TEMP(X,TDASH,TO,TFIN,TIME,TIM2)
      RHO=P/(82.07*T)
      S=0.
C
C      THIS DO LOOP SUMS OVER ALL GAS PHASE SPECIES.  S IS THE
C      TOTAL MOLAR FLOW OF THE GAS.
C
      DO 25 I=1,M
      S=S+FL(I)
25  CONTINUE
      S = OIL + S
      DO 35 I=1,MPLUS
      CM(I)=FL(I)/S
      CO(I)=CM(I)*RHO
35  CONTINUE
38  VEL=S/RHO
      IPLOT=IPLOT+1
C      VALUES NOW SET FOR NEXT ITERATION
      GO TO 30
40  CONTINUE
      RETURN
      END
```

Subroutine BLCALC Variable List

BONE	the first moment of lambda.
BZERO	the zeroth moment of lambda.
DELTAR	the change in pore radius from on point in the pore size distribution to the next.
EPSTO	the initial total porosity of the char.
IPOR	the number of data points in the pore size distribution.
LAMDA(K)	the probability density function for the char structural model.
PORFR(K)	the void volume occupied by the pores of radius PORRAD(K).
PORRAD(K)	the pore radii; Angstroms.
SAREA	the surface area of the char per unit volume of the particle; cm^2/cm^3 .

```

      SUBROUTINE BLCALC(EPSTO,BZERO,BONE,LAMDA,IPOR,DLAMDO)
C
C   THIS SUBROUTINE CALCULATES THE PARAMETERS LAMDA, BZERO,
C   BONE AND EPSTO WHICH ARE USED IN THE BRNOUT SUBROUTINE
C   TO CALCULATE THE SURFACE AREA OF THE CHAR.
C
      COMMON/84/ CD(35),CM(35),PORRAD(50),PORFR(50),DKNUD(50,5),
      1 EPS(50,5),DIFF(50,5)
      REAL LAMDA(50),DLAMDO(50)
      BZERO = 0.0
      BONE = 0.0
      LAMDA(IPOR)=0.0
      J=IPOR-1
      EPSTO = 0.0
C
C   THE CALCULATIONS INVOLVE NUMERICAL INTEGRATION USING THE
C   TRAPIZOIDAL RULE.
C
      DO 100 K =1,J
      I=IPOR-K
      IF (PORRAD(I).EQ.0.0) GO TO 100
      GO TO 60
      IF (I.LE.21)GO TO 50
      PORFR(I)=PORFR(I)/10.
      GO TO 60
50 PORFR(I)=PORFR(I)*35.
60 DELTA=PORRAD(I+1)-PORRAD(I)
   EPSTO=EPSTO+((PORFR(I+1)+PORFR(I))/2.)*DELTA
   LAMDA(I) = PORFR(I) / (6.283*PORRAD(I)**2.*(1.-EPSTO))
   DLAMDO(I)=(LAMDA(I+1)-LAMDA(I))/DELTA
   BZERO=BZERO+((LAMDA(I+1)+LAMDA(I))/2.)*DELTA
   BONE=BONE+((LAMDA(I+1)*PORRAD(I+1)+LAMDA(I)*PORRAD(I))/2.)
   1 *DELTA
100 CONTINUE
   SAREA=12.566*(1.-EPSTO)*BONE*1.E+8
   WRITE (6,101) EPSTO,BZERO,BONE,SAREA
101 FORMAT (1X,/,T10,"EPSTO = ",E10.4,5X,"BZERO = ",E10.4,5X,
   1 "BONE = ",E10.4,5X,"SAREA = ",E10.4,/)
      RETURN
      END

```


Subroutine COALCMP

Subroutine COALCMP Variable List

B, C	variables used in calculation of TARSTR and CH4STR.
CH4STR	initial moles of volatile CH ₄ .
CLEFT	moles carbon remaining in the coal after CO, CO ₂ , and H ₂ O removed.
COALIN	initial mass flow rate of coal; grams C/total moles gas.
COSTAR	initial moles of volatile CO.
CO2STR	initial moles of volatile CO ₂ .
ESTAR(I)	activation energy for devolatilization reactions.
FRASH	weight fraction of ash in the coal.
FRC	weight fraction of carbon in the coal.
FRCH ₄	weight fraction of CH ₄ in the coal.
FRCO	weight fraction of CO in the coal.
FRCO ₂	weight fraction of CO ₂ in the coal.
FRFIXC	weight fraction of solid carbon in the coal.
FRH	weight fraction of hydrogen in the coal.
FRH ₂ O	weight fraction of water in the coal.
FRN	weight fraction of nitrogen in the coal.
FR _O	weight fraction of oxygen in the coal.
FR _{OCO}	mole fraction of oxygen in the coal in CO.
FR _{OCO2}	mole fraction of oxygen in the coal in CO ₂ .
FR _{OH2O}	mole fraction of oxygen in the coal in H ₂ O.
FRS	weight fraction of sulfur in the coal.
FRSLD(J)	weight fraction of solid species in the coal; used for writing out the data.
FRTAR	weight fraction of tar in the coal.

FRV(I)	weight fraction of volatiles in the coal; used for writing out the data.
FRVOL	weight fraction of volatiles in the coal.
FRWAT	weight fraction of moisture in the coal.
GVOLC	grams of volatile carbon.
GVOLH	grams of volatile hydrogen.
GVOLO	grams of volatile oxygen.
HLEFT	moles hydrogen remaining in the coal after CO, CO ₂ , and H ₂ O removed.
H2OSTR	initial moles of volatile H ₂ O.
IVOL	number of volatile species not including tar and moisture.
KSTAR(I)	pre-exponential for devolatilization reactions.
LCHAR	logical variable; true if char reacting.
LCOAL	logical variable; true if volatiles still present in coal.
MVOLC	moles of volatile carbon in coal.
MVOLH	moles of volatile hydrogen in coal.
MVELO	moles of volatile oxygen in coal.
TARIN	total tar molar flow.
TARSTR(K)	molar flow rates of tar.
TOTAL	total of ultimate analysis including moisture and ash.
VOLIN(I)	molar flow rates for volatiles; it is the summation of VSTAR over all size fractions.
VSPEC(I)	volatile species vector.
VSTAR(I,K)	molar flow rates of volatiles.
WATIN	initial moles of volatile water.
Y	H/C ratio in tar.

```

      SUBROUTINE COALCMP(VSTAR,TARSTR,HREAC,MH,ISIZE,SIZEFR,CM,Y,
      1 M,VOLIN,TARIN,REACIN)
C     THIS SUBROUTINE CALCULATES THE INITIAL AMOUNTS OF VOLATILIZABLE
C     MATERIAL PRESENT IN THE COAL USING THE PROXIMATE AND ULTIMATE
C     ANALYSIS OF THE COAL.
      COMMON/81/ F(35),FL(35),DCO(35),BETA(35,35),B(35,35),
      1 AL(35),ALP(35)
      COMMON/V1/FRVOL,FRFIXC,FRWAT,FRASH,FRC,FKN,FRQ,FRS,FRH,FRCD
      1 ,FRCD2,FRH2O,IVOL,VSPEC(5),KSTAR(10),ESTAR(10),COALIN,LCHAR
      DIMENSION VSTAR(5,5),TARSTR(5),HREAC(10),SIZEFR(5),CM(35)
      1 ,REACIN(35),FRV(5),FRSLD(5)
      REAL KSTAR,MVOLC,MVOLD,MVOLH,VOLIN(5)
      LOGICAL LCHAR
C
C     CHECK AND ADJUST ULTIMATE ANALYSIS IF NECESSARY.
      TOTAL=FRC+FRH+FRS+FRN+FRQ+FRASH+FRWAT
      IF (TOTAL.EQ.1.0) GO TO 100
      FRC = FRC/TOTAL
      FRS = FRS/TOTAL
      FRH = FRH/TOTAL
      FRN = FRN/TOTAL
      FRQ = FRQ/TOTAL
100 CONTINUE
C
C     CALCULATE GRAMS AND THEN MOLES OF VOLATIZABLE CARBON,
C     OXYGEN, AND HYDROGEN IN THE COAL.
      GVOLC = (FRC-FRFIXC)*COALIN
      GVOLD = FRQ*COALIN
      GVOLH = FRH*COALIN
      MVOLC = GVOLC/12.
      MVOLD = GVOLD/16.
      MVOLH = GVOLH
C
C     CALCULATE MOLES OF VOLATILE SPECIES PRESENT IN THE COAL AT
C     TIME ZERO.
      COSTAR = FRCD*MVOLD
      CO2STR = FRCD2*MVOLD*0.5
      H2OSTR = FRH2O*MVOLD
      CLEFT = (FRC*COALIN)/12.-COSTAR-CO2STR
      HLEFT = FRH*COALIN-2.*H2OSTR
      Y = HLEFT/CLEFT
      B = MVOLC-(COSTAR+CO2STR)
      C = MVOLH-2.*H2OSTR
      TARIN = (4.*B-C)/(4.-Y)
      CH4STR = B-TARIN
C
C     CALCULATE THE WT. FRACTION COMPOSITION OF THE COAL.
      FRCD=COSTAR*28./COALIN
      FRCD2=CO2STR*44./COALIN
      FRH2O=H2OSTR*18./COALIN
      FRCH4=CH4STR*16./COALIN
      FRTAR=TARIN*(12.+Y)/COALIN
      FRTIN = FRWAT*COALIN/16.
C
C     THE STATEMENTS THRU 290 STORE THE CALCULATED VALUES IN THE
C     PROPER VARIABLES FOR THE VOLATILES.

```

```

C
DO 200 I=1,IVOL
  IF (VSPEC(I).NE.3HCO ) GO TO 110
  VOLIN(I) = COSTAR
  FRV(I) = FRCO
  GO TO 150
110 IF (VSPEC(I).NE.3HCO2) GO TO 120
  VOLIN(I) = CO2STR
  FRV(I)=FRCO2
  GO TO 150
120 IF (VSPEC(I).NE.3HH2O) GO TO 130
  VOLIN(I) = H2OSTR
  FRV(I)=FRH2O
  GO TO 150
130 IF (VSPEC(I).NE.3HCH4) GO TO 200
  VOLIN(I) = CH4STR
  FRV(I)=FRCH4
150 K=M+MH+ISIZE-1+I
  FL(K)=VOLIN(I)
  DO 190 J=1,ISIZE
    VSTAR(I,J) = VOLIN(I)*SIZEFR(J)
190 CONTINUE
200 CONTINUE
  K=M+MH+ISIZE+IVOL
  FL(K)=TARIN
  DO 230 J=1,M
230 IF (REACIN(J).EQ.3HH2O) CM(J)=CM(J)+WATIN
  DO 250 J=1,ISIZE
    TARSTR(J) = TARIN*SIZEFR(J)
250 CONTINUE
C
C   THE STATEMENTS THRU 300 STORE THE VALUES FOR THE SOLID SPECIES
C   AND ADD SPECIES NAMES TO SPECIES SLATE.
C
  NAMSPE = 2HC
  CALL SSLATE(NAMSPE,MH,HREAC,JSPEC)
  FRSLD(JSPEC)=FRFIXC
  JSPEC = JSPEC+M
  CM(JSPEC) = FRFIXC*COALIN/12.
  IF (FRS.EQ.0.0) GO TO 275
  NAMSPE = 2HS
  CALL SSLATE(NAMSPE,MH,HREAC,JSPEC)
  FRSLD(JSPEC)=FRS
  JSPEC = JSPEC+M
  CM(JSPEC) = FRS*COALIN/32.
275 IF (FRN.EQ.0.0) GO TO 300
  NAMSPE = 2HNNH
  CALL SSLATE(NAMSPE,MH,HREAC,JSPEC)
  FRSLD(JSPEC)=FRN
  JSPEC = JSPEC+M
  CM(JSPEC) = FRN*COALIN/14.
300 CONTINUE
C
C   THE FINAL PORTION OF CODE WRITES OUT THE COAL COMPOSITION IN WT.
C   FR. OF VOLATILES, MOISTURE, ASH, AND SOLID SPECIES.
C
  WRITE (6,101)
101 FORMAT (T10,"COAL COMPOSITION:",//,T10,"VOLATILES",T25,
1 "WEIGHT FR.")
  DO 310 I=1,IVOL
310 WRITE (6,102) I,VSPEC(I),FRV(I)

```

```
102 FORMAT (T10,I2,2X,A5,T27,F6.4)
    ANAME=3HTAR
    I=IVOL+1
    WRITE (6,102) I,ANAME,FRTAR
    ANAME=5HWATER
    I=I+1
    WRITE (6,102) I,ANAME,FRWAT
    WRITE (6,103)
103 FORMAT (T10,"SOLIDS")
    DO 320 I=1,MH
320 WRITE (6,102) I,HREAC(I),FRSLD(I)
    ANAME=3HASH
    I=MH+1
    WRITE (6,102) I,ANAME,FRASH
    RETURN
    END
```

```

C      FUNCTION TEMP(X,TDASH,TA,TB,TC,TD)
C
C      *****
C
C      VERSION AUGUST 2,1973 JOLW
C      USER CAN SUPPLY THIS FUNCTION PROVIDED HE CAN ALSO SUPPLY
C      THE DERIVATIVE
C      TDASH IS THE DERIVATIVE, TA= BEGIN TEMP, TB= END TEMP
C      EXAMPLE HERE IS EXPONENTIAL DECAY FROM TA TO TB IN TC SECONDS
C
C      *****
C
C      MODIFIED JAN '82 G. KYLE. INCLUDES THE OPTION OF SPECIFYING
C      THE TEMPERATURE AS A NUMBER OF DATA POINTS. THE ROUTINE
C      FITS A CURVE TO THE DATA AND CALCULATES TEMP AND THE TIME
C      DERIVATIVE OF TEMP.
C
C      *****
C
C      DIMENSION TIM(20),TMP(20)
C      COMMON/T1/ICOUNT,X1,X2,X3,C1,C2,C3,C4,C5,TMP(20),TIM(20),ITEMP
C
C      TEMPERATURE FROM EXPONENTIAL DECAY.
C
C      IF (TC.EQ.0.0) GO TO 50
C      TEX=ALOG(TB/TA)/TC
C      IF (X.GT.0.0)GO TO 10
C      T=TA
C      GO TO 20
C 10 T=TA*EXP(TEX*X)
C 20 TDASH=TEX*T
C      IF(T.LE.TB) TDASH=0.
C      IF(T.LE.TB)T=TB
C      TEMP=T
C      RETURN
C 50 IF (X.EQ.0.0.OR.X.GT.X3) GO TO 100
C
C      TEMPERATURE FROM SPECIFIED DATA. AN INTERPOLATION POLYNOMIAL
C      IS USED FOR POINTS BETWEEN GIVEN DATA AND TO OBTAIN THE
C      DERIVATIVE.
C
C 70 TEMP=(X-X2)*(X-X3)*C1+(X-X1)*(X-X3)*C2+(X-X1)*(X-X2)*C3
C      TDASH=2.*X*C4-C5
C      RETURN
C
C      THE LAST SECTION GENERATES THE CONSTANTS FOR THE INTERPOLATION
C      POLYNOMIAL WHEN X > X3 OR X = 0.
C
C 100 I1=ICOUNT
C      I2=I1+1
C      I3=I2+1
C      X1=TIM(I1)
C      X2=TIM(I2)
C      X3=TIM(I3)
C      C1=TMP(I1)/((X1-X2)*(X1-X3))
C      C2=TMP(I2)/((X2-X1)*(X2-X3))
C      C3=TMP(I3)/((X3-X1)*(X3-X2))
C      C4=C1+C2+C3
C      C5=C1*(X3+X2)+C2*(X1+X3)+C3*(X1+X2)
C      ICOUNT=ICOUNT+2
C      GO TO 70
C      END

```

[illegible]

FUNCTION RATECO(A,TE,E,T)

VERSION AUGUST 2,1973 JOLW

EVALUATES RATECOEFF=AT**N EXP(-E/RT)

E IS ACTIVATION ENERGY IN KILOCALORIES, T DEGREES KELVIN

RATE=0.0

IF(A.LT.1.0E-80) GO TO 10

ARG=ALOG(A)+TE*ALOG(T)-E/(0.001987*T)

IF(ARG.LT.-80)ARG=-80.0

IF(ARG.GT.80) ARG=80.0

RATE=EXP(ARG)

10 CONTINUE

RATECO=RATE

RETURN

END

SUBROUTINE CALBET (M,N,ISM,RHO,RATE,RKF,RKR,CO,REACIN,BETA,DCO
1,T,TDASH,ALP,RFO,RRE,TEF,TER,EF,ER)

VERSION AUGUST 2,1973 JOLW
CALCULATES R(I) =RATE OF FORMATION OF SPECIES I
ALSO CALCULATES THE MATRIX D(R(I))/D(C(J))
DCO(I) = R(I) RATE OF FORMATION, BETA(I(J)) = MATRIX

LOGICAL MFLAG
REAL DCO(35),BETA(35,35),RKF(150),RKR(150),RATE(150),CO(35)
REAL RFO(150),RRE(150),TEF(150),TER(150),EF(150),ER(150),ALP(35)
INTEGER ISM(150,6),REACIN(35)
DO 5 I=1,35
DCO(I)=0.
ALP(I)=0.
DO 5 J=1,35
BETA(I,J)=0.
5 CONTINUE

SCANS REACTIONS

DO 10 K=1,N
MFLAG=.FALSE.

IS REACTION 3 BODY
MFLAG IS SET EQ TRUE IF REACTION IS THREE BODY

DO 20 L=1,6
IF (ISM(K,L).GT.M) MFLAG=.TRUE.
20 CONTINUE
DO 30 L=1,6

FINDS SPECIES IN REACTION AND CONSTRUCTS SPECIES FORMATION DUE TO REACTION

IF (ISM(K,L).EQ.0) GO TO 30
IF (ISM(K,L).GT.M) GO TO 30
LSN=ISM(K,L)
IF (L.LE.3) DCO(LSN)=DCO(LSN)-RATE(K)
IF (L.GT.3) DCO(LSN)=DCO(LSN)+RATE(K)
RDT=RFO(K)*(TEF(K)/T+EF(K)/(0.001987*T*T))
1 -RRE(K)*(TER(K)/T+ER(K)/(0.001987*T*T))
RDTT=RDT*TDASH
IF (L.LE.3) ALP(LSN)=ALP(LSN)-RDTT
IF (L.GT.3) ALP(LSN)=ALP(LSN)+RDTT
CQ=-RKF(K)

```
      IF (L.GE.4) CQ=RKR(K)
      IF (MFLAG) CQ=CQ*RHO
      MMS=1
      MML=3
      IF (L.GE.4) MMS=4
      IF (L.GE.4) MML=6
      DO 40 MM=MMS,MML
      IF (ISM(K,MM).EQ.0) GO TO 40
      IF (ISM(K,MM).GT.M) GO TO 40
      IF (MM.EQ.L) GO TO 40
      LSN=ISM(K,MM)
      CQ=CQ*CO(LSN)
40    CONTINUE
      SG=1.0
      DO 50 LP=1,6
      IF (ISM(K,LP).EQ.0) GO TO 50
      IF (ISM(K,LP).GT.M) GO TO 50
      IF (LP.GE.4) SG=-1.0
      LTP=ISM(K,LP)
      LTQ=ISM(K,L)
      BETA(LTP,LTQ)=BETA(LTP,LTQ)+SG*CQ
50    CONTINUE
30    CONTINUE
10    CONTINUE
C      AUGMENT DCO AND BETA FOR GLOBAL REACTION
      RETURN
      END
```

Subroutine VOLRATE

Subroutine VOLRATE Variable List

AL(J)	true alpha vector.
ALP(J)	pseudo-alpha vector.
ALPHA	constant used in calculation of ALP elements.
B(I,J)	true Jacobian matrix.
BET(J)	pseudo-Jacobian elements for volatile species.
BETA(I,J)	pseudo-Jacobian matrix.
DCO(J)	species production rates; moles/(cm**3*sec).
DCOV(J,K)	rate of evolution of volatile species for each size fraction; moles/(cm**3*sec).
DCOVOL(J)	total devolatization rate for each species; summation of DCOV(J,K) over all size fractions; moles/(cm**3*sec).
DELTA	the total amount of a volatile species evolved over the most recent time step; moles/cm**2.
ESTAR(I)	the activation energy for the devolatization rxn's; cal.
F(J)	the species production rates times the velocity; the right-hand side of the differential equations.
FRVLFT	the fraction of the original volatile material remaining in the coal.
IBURN	the number of size fractions currently reacting.
ICH4	number assigned to the gas phase CH4.
ICO	number assigned to CO in the gas phase.
IO2	number assigned to O2 in the gas phase.
ISIZE	number of size fractions.
IVOL	number of volatile species, not including tar and moisture.
KSTAR(I)	the pre-exponential for the devolatization rxn's; sec**-1.
KV	subscript used for the volatile species.

LCHAR	logical variable; true if char is reacting.
LCOAL	logical variable; true if volatiles still present in coal.
TAR	total flow rate of tar in the coal at any time; moles/(cm**3*sec).
TARCHK(K)	the flow rate of tar in the coal below which the char will begin to react; moles/(cm**2*sec).
TARSTR(K)	the flow rate of tar in each size fraction of coal at any time; moles/(cm**2*sec).
TPART(K)	the temperature of the particles; equal to T in this case; K.
VOLSTR(J)	the total flow rate of volatile species J present in the coal; moles/(cm**2*sec).
VSPEC(J)	array containing names of volatile species.
VSTAR(J,K)	the flow rate of volatile material present in each size fraction of coal; moles/(cm**2*sec).

Subscripts

I	reaction number.
J	species number.
K	size fraction.

```

      SUBROUTINE VOLRATE(VSTAR,TARSTR,LCOAL,
1    LCHAR,ISIZE,M,KSTAR,ESTAR,VSPEC,T,X,Y,IVOL,RHO,S,MH,
2    TDASH,VOLIN,TARIN,REACIN,IN,TARCHK)

C
C   THIS SUBROUTINE CALCULATES THE RATE OF DEVOLITIZATION OF THE
C   COAL PRODUCTS AND ADJUSTS THE DCO, ALP AND BETA VECTORS AND
C   MATRIX.
C
      COMMON/V2/DCOV(10,5),IBURN
2    ,VOLSTR(5),DCOVOL(10),TAR,WATER,TARSTP(5)
      COMMON/81/ F(35),FL(35),OCO(35),BETA(35,35),B(35,35),
1    AL(35),ALP(35)
      DIMENSION VSTAR(5,5),TARSTR(5),TARCHK(5),BET(35),
1    REACIN(35),ESTAR(10),VSPEC(5),TPART(5),VOLIN(5)
      LOGICAL LCHAR,LCOAL
      REAL KSTAR(10)

C
C   THE VARIABLES ARE INITIALIZED.
C
      LCOAL=.FALSE.
      ISTART=M+MH+ISIZE
      ISTOP=M+MH+ISIZE+IVOL
      DO 15 I=ISTART,ISTOP
        BET(I)=0.0
        DO 10 J=1,M
          B(J,I)=0.0
10    CONTINUE
15    CONTINUE

C
C   THE DO LOOP THRU STATEMENT 100 CALCULATES NEW VSTAR AND VOLSTR
C   VALUES. IT ALSO CALCULATES DCOV, BET, AND ALPHA FOR
C   ALL VOLATILE SPECIES EXCEPT THE TAR. DCO, B, AND ALP ARE ALSO
C   ADJUSTED TO INCLUDE THE CONTRIBUTION OF THE DEVOL REACTIONS.
C
      DO 100 I=1,IVOL
        KV=M+MH+ISIZE-1+I
        IF (FL(KV).GT.0.0) LCOAL=.TRUE.

C
C   FIRST DELTA IS CALCULATED FOR SPECIES KV.
C
      DELTA=FL(KV)-VOLSTR(I)
      IF (VOLSTR(I).LE.1.0E-12) GO TO 100

C
C   NEXT THE GAS PHASE SPECIES BEING EVOLVED IS FOUND.
C
      DO 20 K=1,M
        IF (REACIN(K).NE.VSPEC(I)) GO TO 20
        GO TO 30
20    CONTINUE
30    VOLSTR(I)=0.0

C
C   THE AMOUNT OF VOLATILES REMAINING IS CHECKED. IF IT IS
C   < 1% OF THE ORIGINAL AMOUNT, THE REMAINING AMOUNT IS IM-
C   MEDIATELY ADDED TO THE GAS PHASE.
C
      FRVLFT=FL(KV)/VOLIN(I)
      IF (FRVLFT.GT.0.01) GO TO 40
31    FL(K)=FL(K)+FL(KV)
      FL(KV)=0.0
      DELTA=0.0
      IN=U

```

```

      DO 35 J=1,ISIZE
35  VSTAR(I,J)=0.0
      GO TO 100
C
C   THE DO LOOP ENDING AT 90 IS EXECUTED ONCE FOR EACH SIZE
C   FRACTION.
C
40  DO 90 J=1,ISIZE
      TPART(J)=T
      IF (DCOVOL(I).EQ.0.0) GO TO 60
C
C   THE AMOUNT DEVOLATILIZED (DELTA) IS DISTRIBUTED AMONG THE
C   SIZE FRACTIONS USING THE RATIO DCOV/DCOVOL.
C
      VSTAR(I,J)=VSTAR(I,J)+(DCOV(I,J)/DCOVOL(I))*DELTA
      IF (VSTAR(I,J).LT.0.0) GO TO 31
60  VOLSTR(I)=VOLSTR(I)+VSTAR(I,J)
C
C   THE RATES AND DERIVATIVES ARE NEXT CALCULATED FOR EACH SIZE
C   FRACTION AND SUMMED FOR THE TOTAL FOR EACH SPECIES.
C
      CONST=VSTAR(I,J)*KSTAR(I)*EXP(-ESTAR(I)/(1.987*TPART(J)))*(RHO/S)
      UCOV(I,J)=-CONST
      OCO(K)=OCO(K)+CONST
      OCO(KV)=OCO(KV)-CONST
      BET(KV)=BET(KV)-CONST/(VSTAR(I,J)*RHO/S)
      B(K,KV)=B(K,KV)+CONST/(VSTAR(I,J)*RHO/S)
      ALPHA=CONST*((ESTAR(I)/(1.987*TPART(J)**2))-1./TPART(J))*TDASH
      ALP(K)=ALP(K)+ALPHA
      ALP(KV)=ALP(KV)-ALPHA
90  CONTINUE
100 CONTINUE
C
C   THIS NEXT DO LOOP PICKS OUT SPECIES NUMBERS FOR USE IN THE
C   TAR DEVOL ROUTINE.
C
      DO 150 K=1,M
      IF (REACIN(K).NE.3HCO ) GO TO 110
      ICO=K
      GO TO 150
110 IF (REACIN(K).NE.3HCH4) GO TO 130
      ICH4=K
      GO TO 150
130 IF (REACIN(K).NE.3HO2 ) GO TO 150
      IO2=K
150 CONTINUE
C
C   THE NEXT SERIES OF STATEMENTS (THRU 160) PERFORM THE SAME
C   CALCULATIONS FOR THE TAR AS THOSE FOR THE OTHER VOLATILES. A
C   SEPERATE ROUTINE IS NEEDED FOR THE TAR DUE TO THE STOICHEMETRY
C   OF IT'S DEVOL REACTION.
C
      ITAR=IVOL+1
      IF (TAR.LE.1.0E-12) GO TO 200
      KV=M+MM+ISIZE+IVOL
      IF (FL(KV).GT.0.0) LCOAL=.TRUE.
      DELTA=FL(KV)-TAR
      TAR=0.0
      FRVLFT=FL(KV)/TARIN
      GO TO 154
151 FL(ICO)=FL(ICO)+(1.-Y/4.)*FL(KV)

```



```

      FL(ICH4)=FL(ICH4)+(Y/4.)*FL(KV)
      FL(IO2)=FL(IO2)-(0.5*(1.-Y/4.))*FL(KV)
      FL(KV)=0.0
      DELTA=0.0
      IN=0
      DO 152 I=1,ISIZE
152  TARSTR(I)=0.0
      GO TO 200
154  DO 160 I=1,ISIZE
      IF (DCOVOL(ITAR).EQ.0.0) GO TO 158
      TARSTR(I)=TARSTR(I)+(DCOV(ITAR,I)/DCOVOL(ITAR))*DELTA
      IF (TARSTR(I).GE.TARSTP(I)) GO TO 156
      IBURN=ISIZE
      GO TO 151
156  IF (TARSTR(I).LT.TARCHK(I)) IBURN=I
158  TAR=TAR+TARSTR(I)
      CONST=(1.-Y/4.)*TARSTR(I)*KSTAR(ITAR)*EXP(-ESTAR(ITAR)/
1    (1.987*TPART(I)))*(RHO/S)
      DCOV(ITAR,I)=-(4./(4.-Y))*CONST
      DCO(ICD)=DCO(ICD)+CONST
      DCO(KV)=DCO(KV)-(4./(4.-Y))*CONST
      BET(KV)=BET(KV)-(4./(4.-Y))*CONST/(TARSTR(I)*RHO/S)
      B(ICD,KV)=B(ICD,KV)+CONST/(TARSTR(I)*RHO/S)
      ALPHA=CONST*((ESTAR(ITAR)/(1.987*TPART(I)**2))-1./TPART(I))*TDASH
      ALP(ICD)=ALP(ICD)+ALPHA
      ALP(KV)=ALP(KV)-(4./(4.-Y))*ALPHA
      CONST=(Y/4.)*TARSTR(I)*KSTAR(ITAR)*EXP(-ESTAR(ITAR)/
1    (1.987*TPART(I)))*(RHO/S)
      DCO(ICH4)=DCO(ICH4)+CONST
      B(ICH4,KV)=B(ICH4,KV)+CONST/(TARSTR(I)*RHO/S)
      ALP(ICH4)=ALP(ICH4)+CONST*((ESTAR(ITAR)/(1.987*TPART(I)**2))
1    -1./TPART(I))*TDASH
      CONST=-(0.5*(1.-Y/4.))*TARSTR(I)*KSTAR(ITAR)*EXP(-ESTAR(ITAR)/
1    (1.987*TPART(I)))*(RHO/S)
      DCO(IO2)=DCO(IO2)+CONST
      B(IO2,KV)=B(IO2,KV)+CONST/(TARSTR(I)*RHO/S)
      ALP(IO2)=ALP(IO2)+CONST*((ESTAR(ITAR)/(1.987*TPART(I)**2))
1    -1./TPART(I))*TDASH
160  CONTINUE
200  IF (IBURN.NE.0) LCHAR=.TRUE.
      IVP=IVOL+1
      DO 250 I=1,IVP
      DCOVOL(I)=0.0
250  CONTINUE
C
C    F, B, AND AL VALUES ARE CALCULATED FOR THE VOLATILE SPECIES
C    FROM DCO, BET AND ALP CALCULATED ABOVE.
C
      DO 300 I=1,IVP
      KV=M+MH+ISIZE-1+I
      VEL=S/RHO
      F(KV)=DCO(KV)*VEL
      B(KV,KV)=BET(KV)
      AL(KV)=ALP(KV)*VEL+DCO(KV)*S*62.07*TDASH
      DO 280 J=1,M
      B(KV,J)=DCO(KV)/RHO
280  CONTINUE
      DO 290 J=1,ISIZE
      DCOVOL(I)=DCOVOL(I)+DCOV(I,J)
290  CONTINUE
300  CONTINUE
      RETURN
      ENH

```

Subroutine BRNOUT

Subroutine BRNOUT Variable List

AL(J)	true alpha vector.
ALP(J)	pseudo-alpha vector.
B(I,J)	true beta matrix.
BETA(I,J)	pseudo-beta matrix.
BONE	first moment of lambda.
BZERO	zeroth moment of lambda.
CM(J)	species mole fractions.
CMCIN	initial molar flow rate of solid carbon; moles/(cm**2*sec).
CMN	initial molar flow rate of solid nitrogen.
CO(J)	species molar concentrations; moles/cm**3.
COEFF(I,J)	coefficient matrix for heterogeneous reactions.
COMIN	species concentration cut-off value.
CONC(I)	concentration of gas phase reactant for heterogeneous reactions.
DCO(J)	species production rates; moles/(cm**3*sec).
DIFF(L,K)	the diffusivity in each individual pore; cm**2/sec.
DKNUD(L,K)	the Knudsen diffusivity of oxygen in each individual pore; cm**2/sec.
DO2REF	binary diffusivity of O2 in N2 at 1500 K; cm**2/sec.
DRDFLC(K)	approximation of the derivative of the particle radius with the solid carbon.
DRHDC(I,J,K)	the derivative of the heterogeneous reaction rates with respect to concentration.
DRHDTT(I,K)	the derivative of the heterogeneous reaction rates with respect to time.
EACT(I)	activation energy for the heterogeneous reaction rate constants; cal.

EFDIFF(K)	the effective diffusivity within the char particles; cm**2/sec.
EINT	variable used in numerical integration for calculation of EFDIFF.
EPS(L,K)	the pore size distribution for each particle size class at any time.
EPST(L)	total porosity of the char.
EPSTO	total porosity of char at time zero.
ETA(I,K)	effectiveness factors for heterogeneous reactions.
ETANO(K)	effectiveness factor for NO reduction reaction before modification.
F(J)	species flow rates; moles/(cm**2*sec).
FLCSAV(K)	FL(K) for the previous time step for the solid carbon.
HRATE(I,K)	rate of heterogeneous reactions; moles/(cm**3*sec).
IBSAVE	number of char fractions reacting at previous time step.
IBURN	number of char fractions currently reacting.
ICH	number assigned to char oxidation reaction.
IDHREA(I)	vector containing heterogeneous reaction names.
IN	integration routine flag.
INH	number assigned to nitrogen oxidation rxn.
INO	number assigned to NO.
INR	number assigned to NO reduction reaction.
INUMB(J)	numbers of gas species affected by heterogeneous reactions.
IO2	number assigned to O2.
IPOR	number of data points in the pore size distribution.
IS(K)	flag for char model.
ISMH(I,J)	species number reaction matrix for heterogeneous reactions.

KO(I,K)	heterogeneous reaction rate constants; sec^{-1} .
KZERO(I)	pre-exponential for heterogeneous rate constants; $\text{grams C}/(\text{cm}^2 \cdot \text{sec} \cdot \text{atm})$.
LAMDA(L)	probability density function for char model.
M	number of gas phase species.
MHET	number of additional dependent variables due to heterogeneous reactions.
N	number of homogeneous gas phase reactions.
NH	number of heterogeneous reactions.
NMISMH(I,J)	species name reaction matrix for heterogeneous reactions.
P	pressure; atm.
PORFR(L)	the initial void fraction occupied by the pores.
PORRAD(L)	the initial pore radii; Angstroms.
Q(K)	distance moved by pore walls; Angstroms.
RATEK(I,J)	the heterogeneous reaction rates divided by the concentration of the gas phase reactant; sec^{-1} .
RCOEFF(I)	the coefficients of the gas phase reactants for the heterogeneous reactions.
REACIN(J)	gas phase species vector; contains alpha-numeric names of gas phase species.
RHO	total molar gas density; moles/cm^3 .
RHOSLD	the density of solid carbon; grams/cm^3 .
RSAVE(K)	rate of NO reduction reaction calculated using ETANO(K); $\text{moles}/(\text{cm}^3 \cdot \text{sec})$.
S	total molar gas flux; $\text{moles}/(\text{cm}^2 \cdot \text{sec})$.
SAREA(K)	surface area of char per unit volume of particle; cm^2/cm^3 .
SIZEFR(K)	weight fraction of coal in particle size class.
SIZPRT(K)	diameter of particles; cm.

SIZSAV(K) size of the particles at the previous time step; cm.
SPAREA(K) the specific surface area of each size class; cm**2/gram.
T temperature; K.
TDASH time derivative of temperature; K/sec.
THIELE(I,K) Thiele modulus for the heterogeneous reactions.
VEL linear space velocity; cm/sec.
Z variable used when calculating the coefficients of the
 char oxidation reaction.

Variable Subscripts

I species or heterogeneous reaction number.
J species number.
K particle size class.
L pore number.

```

      SUBROUTINE BRNOUT (RHOSLD,SPAREA,T,DO2REF,IPOR,REACIN,IPLJT,
1  IBURN,Q,M,N,RHO,MHET,MH,NH,BONE,BZERO,EPSTO,EPST,LAMDA,
2  COMIN,INIT,TDASH,VEL,SAREA,S,P,IN,CMCIN,CMN,DLAMDQ,INO,IBSAVE)
C
C  THIS SUBROUTINE AUGMENTS THE BETA(I,J) AND ALP(I) VALUES
C  WHICH ARE AFFECTED BY THE ADDITION OF THE HETEROGENECUS
C  REACTIONS. IT ALSO CALCULATES THE NEW VALUES FOR B(I,J)
C  AND AL(I) WHICH ARISE DUE TO THESE REACTIONS.
C
      COMMON/81/F(35),FL(35),DCQ(35),BETA(35,35),B(35,35),
1  AL(35),ALP(35)
      COMMON/83/SIZPRT(5),SIZEFR(5),ISMH(10,6),COEFF(10,6),
1  IDHREA(10),NMISMH(10,6)
      COMMON/84/CO(35),CM(35),PORRAD(50),PORFR(50),DKNUD(50,5),
1  EPS(50,5),DIFF(50,5)
      COMMON/85/DRHDC(10,35,5),IS(5),EFDIFF(5),KO(10,5),
1  HRATE(10,5),CDNC(10),EACT(10),KZERO(10),THIELE(10,5),
2  ETA(10,5),DRHDTT(10,5),RATEK(10,5)
      COMMON/BRN1/CS+RNK(5),FLCSAV(5),SIZSAV(5)
      REAL LAMDA(50),KO,KZERO
      DIMENSION INUMB(35),DLAMDQ(50),EPST(5),SAREA(5),ETANQ(5),
1  SPAREA(5),Q(5),CMCARB(5),REACIN(35),RCOEFF(10),RSAVE(5)
2  ,ORDFLC(5)
C
C  THE VARIABLES ARE INITIALIZED
C
      IBURN AND IBSAVE ARE COMPARED TO SEE IF THE NUMBER OF
      CHAR SIZE FRACTIONS RREACTING HAS CHANGED.
C
      IF (IBURN.EQ.IBSAVE) GO TO 2
      IBSAVE=IBURN
      IN=0
2  CONTINUE
      DO 5 LQ=1,IBURN
      EFDIFF(LQ) = 0.0
      DO 3 I=1,50
      IF (I.GT.10) GO TO 3
      RATEK(I,LQ)=0.0
3  DIFF(I,LQ)=0.0
5  CONTINUE
      MSTOP=M+MH+IBURN-1
      DO 8 I=1,MSTOP
      IF (REACIN(I).EQ.2H02) I02=I
      IF (I.LE.M) GO TO 6
      F(I)=0.0
      AL(I)=0.0
      DCQ(I)=0.0
6  DO 7 J=1,MSTOP
      IF (I.LE.M.AND.J.LE.M) GO TO 7
      B(I,J)=0.0
7  CONTINUE
8  CONTINUE
      EINT = 0.0
      DO 9 I=1,IBURN
9  CMCARB(I)=SIZEFR(I)*CMCIN
C
C  NEXT LL IS SET AND CHECKED AGAINST IBURN.
C
      LL=1
      DO 10 I=1,IBURN
      IF (FL(M+I).EQ.0.0) LL=I+1

```

```

10 CONTINUE
   IF (LL.LE.IBURN) GO TO 15
   MHET=0
   RETURN
C
C   THE NEXT SECTION OF THE PROGRAM (THRU 60) CALCULATES THE
C   COEFFICIENTS FOR THE REACTIONS OF CARBON AND NITROGEN
C   WITH OXYGEN.
C
15 Z=2500.*EXP(-6249./T)
   FI=(2.*Z+2.)/(Z+2.)
   INH=0
   INR=0
   DO 60 I=1,NH
     IF (IDHREA(I).NE.6HNOFORM) GO TO 50
     INH=I
     GU IU 60
50 IF (IDHREA(I).NE.5HNOREO) GO TO 55
   INR=I
   GO TO 60
55 IF (IDHREA(I).NE.5HCARBC) GO TO 60
   ICH=I
   COEFF(I,1)=-1.0
   COEFF(I,2)=-1./FI
   COEFF(I,4)=2.-2./FI
   COEFF(I,5)=2./FI-1.
60 CONTINUE
C
C   THE DO LOOP THRU 80 PICKS OUT THE PROPER REACTANT
C   CONCENTRATION FOR EACH REACTION.
C
   DO 80 I=1,NH
     DO 75 J=1,3
       NISM=ISMH(I,J)
       IF (NISM.LE.0.OR.NISM.GT.M) GO TO 75
       CONC(I)=CO(NISM)
       RCOEFF(I)=-COEFF(I,J)
       IF (NISM.EQ.102) RCOEFF(I)=RCOEFF(I)+0.5*CMN/CMCIN
75 CONTINUE
80 CONTINUE
C
C   THE NEXT DO LOOP, ENDING AT STATEMENT 268, IS EXECUTED ONCE FOR
C   EACH SIZE FRACTION CURRENTLY REACTING.
C
   DO 268 LQ=LL,IBURN
C
C   IF THE TOTAL POROSITY IS GREATER THAN 0.7 (IS>0) THEN
C   GAVALAS'S MODEL IS NOT USED. INSTEAD, THE PROGRAM SKIPS
C   DOWN TO 170 WHERE THE SPECIFIC SURFACE AREA REMAINS CONSTANT.
C
     IF (IS(LQ).GE.1) GO TO 170
C
C   THE NEW SIZE OF THE PARTICLES IS CALCULATED AND THEN USED
C   WITH FL(M+LQ) TO CALCULATE Q(LQ).
C
     SZPRT=SZPRT(LQ)
     SZPRT(LQ)=2.*((SZPRT(LQ)/2.)**3-(1.-ETA(ICH,LQ))*(FLCSAV(LQ)-
1   FL(M+LQ))*(SZSAV(LQ)/2.)**3*(1.-EPSTD)/(CMCARB(LQ)*
2   (1.-EPSTD(LQ))))*(1./3.)
     FLDIF=FL(M+LQ)-FLCSAV(LQ)
     IF (FLDIF.NE.0.0) GO TO 90

```



```

      DRDFLC(LQ)=0.0
      GO TO 95
90  DRDFLC(LQ)=(SIZPRT(LQ)-SZPRT)/FLDIF*2
95  Q(LQ)=(-2.0*8ONE+(4.*8ONE**2-0.6366*8ZERO*ALOG((FL(M+LQ)/
      1  CMCARB(LQ))*(SIZSAV(LQ)/SIZPRT(LQ)**3))**0.5)/(2.*8ZERO)
      IF (Q(LQ).LT.0.0) Q(LQ)=0.0
C
C  Q IS NOW USED TO CALCULATE EPST, SAREA, AND SPAREA.
C
      EPST(LQ) = 1.-(1.-EPST0)*EXP(-6.283*(8ZERO*Q(LQ)**2+2.*8ONE*
      1  Q(LQ)))
      SAREA(LQ) = 12.566E+08*(1.-EPST(LQ))*(8ZERO*Q(LQ)+8ONE)
      SPAREA(LQ) = SAREA(LQ)/(2.*(1.-EPST(LQ)))
      FLCSAV(LQ)=FL(M+LQ)
      IF (EPST(LQ).GE.0.7) GO TO 160
C
C  IN THE FOLLOWING SECTION, THE EFFECTIVE DIFFUSIVITY IS
C  IS CALCULATED. THIS INVOLVES A NUMERICAL INTEGRATION OF
C  DIFFUSIVITY IN THE PORES OVER THE ENTIRE PORE SIZE DISTRIBUTION
C  USING THE TRAPIZOIDAL RULE.
C
      DQ2AB = DQ2REF*(T/1500.）**1.5
      NIPOR=IPOR-1
      EINT = 0.0
      DO 150 J=1,NIPOR
      I= IPOR-J
      IF (PORRAD(I).EQ.0.0) GO TO 150
      DKNUD(I,LQ) = (PORRAD(I)+Q(LQ))*9.7E-05*(T/32.0)**0.5
      DELTAR=PORRAD(I+1)-PORRAD(I)
      AVEINT=((PORRAD(I)+Q(LQ))**2*LAMDA(I)+(PORRAD(I+1)+Q(LQ))**2
      1  *LAMDA(I+1))/2.
      EINT=EINT+AVEINT*DELTAR
      EPS(I,LQ) = 6.283*(PORRAD(I)+Q(LQ))**2*LAMDA(I)*EXP(-6.283*EINT)
      DIFF(I,LQ) = 1./((1./DQ2AB)+(1./DKNUD(I,LQ)))
      AVEINT=(EPS(I,LQ)*DIFF(I,LQ)+EPS(I+1,LQ)*DIFF(I+1,LQ))/2.
      EFDIFF(LQ)=EFDIFF(LQ)+AVEINT*DELTAR
150  CONTINUE
      GO TO 210
C
C  THESE STATEMENTS ARE ONLY EXECUTED THE FIRST TIME EPST > 0.7
C  FOR A SIZE FRACTION. THEY SET THE VALUE OF SPAREA AND SET IS=1.
C  SPAREA IS ADJUSTED BY ETA(1,LQ) TO AVOID A JUMP IN THE CHAR
C  OXIDATION RATE.
C
160  IN=0
      IF (IS(LQ).GT.0) GO TO 170
      SPAREA(LQ)=SPAREA(LQ)*ETA(1,LQ)
      IS(LQ)=1
170  CONTINUE
      DO 180 I=1,NH
180  ETA(I,LQ)=1.0
C
C  NEXT, THE RATE OF EACH HETEROGENEOUS REACTION IS
C  CALCULATED. THE RATES ARE SCALED BY AN EFFECTIVENESS FACTOR
C  WHICH IS CALCULATED FROM THE RATE CONSTANT AND THE EFFECTIVE
C  DIFFUSIVITY.
C
210  DO 265 I=1,NH
      IF (IS(LQ).GE.1) GO TO 255
      KO(I,LQ)=KZERO(I)*EXP(-EACT(I)/(1.987*T))*SAREA(LQ)*82.07*T
      1  *RCDEFF(I)/12.

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      THIELE(I,LQ) = SIZPRT(LQ)/6.*(KO(I,LQ)/EFDIFF(LQ))*0.5
C
C   THREE DIFFERENT STATEMENTS CALCULATE ETA DEPENDING ON THE SIZE
C   OF THIELE.  IF THIELE < 0.001, THEN ETA=1.0.  IF THIELE > 4,
C   THEN ETA = 1/THIELE.  IF 0.001 < THIELE < 4, THEN THE EQUATION
C   IN STATEMENT 240 IS USED.
C
      IF (THIELE(I,LQ).LT.0.001) GO TO 250
      IF (THIELE(I,LQ).LT.4.0) GO TO 240
      ETA(I,LQ)=1./THIELE(I,LQ)
      GO TO 255
240  ETA(I,LQ) = (1./THIELE(I,LQ))*(1./TANH(3.*THIELE(I,LQ))-1./(3.*
      1  THIELE(I,LQ)))
      GO TO 255
250  ETA(I,LQ) = 1.
C
C   IF ETA FOR THE NO REDUCTION REACTION IS BEING CALCULATED A
C   SPECIAL RELATIONSHIP IS USED.
C
255  IF (I.NE.INR) GO TO 263
      ETANO(LQ)=ETA(I,LQ)
      IF (CONC(I).LT.1.E-28) GO TO 263
      ETA(I,LQ)=ETA(I,LQ)+KO(ICH,LQ)*CMN*CONC(ICH)*(ETA(I,LQ)-
      1  ETA(ICH,LQ))/(RCOEFF(ICH)*(KO(ICH,LQ)-
      2  KO(I,LQ))*CMCIN*CONC(I))
263  RATEK(I,LQ) = KZERO(I)*EXP(-EACT(I)/(1.987*T))*SPAREA(LQ)
      1  *82.07*T*ETA(I,LQ)*CO(M+LQ)
      HRATE(I,LQ)=RATEK(I,LQ)*CONC(I)
265  CONTINUE
C
C   THE RATE OF THE REACTION BETWEEN SOLID NITROGEN AND OXYGEN
C   IS EQUAL TO THE RATE OF THE CARBON OXYGEN REACTION
C   MULTIPLIED BY THE RATIO OF SOLID NITROGEN TO SOLID
C   CARBON.
C
      IF (INH.EQ.0) GO TO 268
      HRATE(INH,LQ)=HRATE(ICH,LQ)*(CMN/CMCIN)
      RSAVE(LQ)=HRATE(INH,LQ)
      RATEK(INH,LQ)=RATEK(ICH,LQ)*(CMN/CMCIN)
      ETA(INH,LQ)=ETA(ICH,LQ)
268  CONTINUE
C
C   SUBROUTINE CALDIF IS NOW CALLED TO CALCULATE ALL
C   THE NECESSARY DIFFERENTIALS.
C
270  CALL CALDIF (R40,IPOR,IBURN,TDASH,T,VEL,MHUSLO,BONE,
      1  BZERO,Q,JOZAB,LAMDA,SPAREA,EPSTO,EPST,LL,CMCIN,CMN,ETANO,
      2  NH,MM,M,S,P,ICH,INR,INH,IQ,OLAMDO,CMCARB,RCOEFF,IQ2,DROFLC,
      3  SAREA)
C
C   THE REMAINDER OF THE SUBROUTINE, THRU 300, IS EXECUTED
C   ONCE FOR EACH SIZE FRACTION OF CHAR CURRENTLY REACTING.
C
      DO 300 LQ=LL,IBURN
C
C   THE FOLLOWING DO LOOPS WHICH END WITH LINE 300 ADJUST THE
C   ALP AND DCO VECTORS.
C
      DO 300 I=1,NM
      DO 300 J=1,6
      INUM = ISMH(I,J)

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      IF (INUM.EQ.0.OR.INUM.GT.M) GO TO 300
      DCO(INUM) = DCO(INUM)+COEFF(I,J)*HRATE(I,LQ)
      ALP(INUM) = ALP(INUM)+COEFF(I,J)*DRHOTT(I,LQ)
300 CONTINUE
C
C   THE NEXT DO LOOP END AT LINE 350. IN IT THE BETA MATRIX
C   IS ADJUSTED FOR ALL HOMOGENEOUS SPECIES AFFECTED BY THE
C   HETEROGENEOUS REACTIONS. ALSO, THE NEW ELEMENTS OF THE
C   B MATRIX AND AL AND F VECTORS WHICH ARISE DUE TO THE
C   HETEROGENEOUS REACTIONS ARE CALCULATED.
C
      DO 350 I=1,NH
C
C   THE SUBSCRIPT I INDICATES WHICH HET. REACTION IS
C   BEING USED NOW. THE NEXT SET OF DO LOOPS WHICH END AT
C   LINE 311 PICK OUT WHICH HOMOGENEOUS SPECIES ARE AFFECTED
C   BY THE I' TH HET. REACTION.
C
      DO 311 J=1,M
      DO 310 K=1,6
      IF (J.NE.ISMH(I,K)) GO TO 308
      INUM8(J)=J
      GO TO 311
308 INUM8(J)=0
310 CONTINUE
311 CONTINUE
C
C   THE NEXT SECTION OF CODE, THROUGH LINE 320, ADJUSTS
C   THE BETA MATRIX.
C
      DO 320 K=1,M
      IF (INUM8(K).NE.K) GO TO 320
      IT=0
      DO 315 J=1,M
      IF (INUM8(J).NE.J) GO TO 315
      DO 313 L=1,6
      IF (INUM8(K).NE.ISMH(I,L)) GO TO 313
      BETA(K,J)=BETA(K,J)+COEFF(I,L)*DRHDC(I,J,LQ)
      IF (IT.GT.0) GO TO 313
      B(K,M+LQ)=B(K,M+LQ)+COEFF(I,L)*DRHDC(I,M+LQ,LQ)
      IT=1
313 CONTINUE
315 CONTINUE
320 CONTINUE
C
C   IN THIS SECTION, THE B MATRIX AND AL AND F VECTOR ELEMENTS
C   FOR THE HETEROGENEOUS SPECIES ARE CALCULATED.
C
      IO=M+MH+LQ
      IL=M+1
      IU=M+MH
      DO 325 K=1,6
      DO 323 L=IL,IU
      IF (ISMH(I,K).NE.L) GO TO 323
      J=L
      IF (J.NE.M+1) GO TO 322
      J=J+LQ-1
      GO TO 326
322 J=J+IBURN-1
      GO TO 326
323 CONTINUE

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```
325 CONTINUE
326 DO 330 K=1,M
    B(J,K)=B(J,K)-DRHDC(I,K,LQ)*(1.-CM(K))-HRATE(I,LQ)/RHO
330 CONTINUE
    B(J,M+LQ)=B(J,M+LQ)-DRHDC(I,M+LQ,LQ)
    AL(J)=AL(J)-DRHDT(I,LQ)*VEL-HRATE(I,LQ)*S*82.07*TDASH/P
    F(J)=F(J)-HRATE(I,LQ)*VEL
    DCO(J)=DCO(J)-HRATE(I,LQ)
350 CONTINUE
500 CONTINUE
    MHET = MH + ISURN - 1
    RETURN
    END
```

Subroutine CALDIF

Subroutine CALDIF Variable List

Variables common to both BRNOUT and CALDIF are listed in BRNOUT only. All derivatives are partial derivatives.

ACONST	constant used in calculation of DRHDC.
AVEINT	variable used in numerical integration calculation of DIFEDQ.
CH	constant used in calculation of DRHDT.
CONST	constant used in calculation of DETADC for the NO reduction reaction.
DDIFDC	the derivative of the effective diffusivity with respect to the carbon concentration.
DDIFDQ	the derivative of the effective diffusivity with respect to Q.
DEPSDQ(L)	the derivative of EPS(L) with respect to Q.
DETADC	the derivative of ETA(I,LQ) with respect to the carbon concentration.
DETADP	the derivative of ETA with respect to Thiele.
DETADT	the derivative of ETA with respect to temperature.
DIFLST	variable used in calculation of DIFEDQ.
DINT1,2,3	variables used in numerical integration of DEPSDQ.
DPHIDC	the derivative of Thiele with respect to the carbon concentration.
DPHIDT	the derivative of Thiele with respect to temperature.
DQDCC	the derivative of Q with respect to the carbon concentration.
DRHDT	the derivative of the heterogeneous reaction rate with respect to temperature.
DRHODT	the derivative of RHO with respect to temperature.
DSAVE(K)	variable used when calculating DETADC for the NO reduction reaction.

DSDCC	the derivative of specific surface area with respect to the carbon concentration.
DSVDCC	same as DSDCC but for surface area per unit volume of the char.
DVELDT	the derivative of velocity with respect to time.
EXP2	exponential portion of heterogeneous rate constant.

```

SUBROUTINE CALDIF (RHO,IPOR,IBURN,TDASH,T,VEL,RHOSLD,BONE,
1  BZERO,Q,DJ2AB,LAMDA,SPAREA,EPSTO,EPST,LL,CMCIN,CMN,ETANO,
2  NH,MH,M,S,P,ICH,INR,INH,IQ,OLAMDQ,CMCARB,RCOEFF,IQZ,ORDFLC,
3  SAREA)
COMMON/81/F(35),FL(35),OCO(35),BETA(35,35),B(35,35),
1  AL(35),ALP(35)
COMMON/83/SIZPRT(5),SIZEFR(5),ISMH(10,6),COEFF(10,6),
1  IDHREA(10),NMISMH(10,6)
COMMON/84/CO(35),CM(35),PORRAD(50),PORFR(50),DKNUO(50,5),
1  EPS(50,5),DIFF(50,5)
COMMON/85/DRHOC(10,35,5),IS(5),EFDIFF(5),KO(10,5),
1  HRATE(10,5),CONC(10),EACT(10),KZERO(10),THIELE(10,5),
2  ETA(10,5),DRHOTT(10,5),RATEK(10,5)
COMMON/88N1/CSHRNK(5),FLCSAV(5),SIZSAV(5)
REAL LAMDA(50),KO,K1,KZERO
DIMENSION DEPSDQ(50),OLAMDQ(50),EPST(5),SPAREA(5),Q(5),SAREA(5)
1  ,CMCARB(5),ETANO(5),OSAVE(5),RCOEFF(10),ORDFLC(5)

C THIS SUBROUTINE CALCULATES THE DERIVATIVES NEEDED TO
C CALCULATE THE NEW AL(I) AND B(I,J) VALUES FOR THE HETERO-
C GENEQUS REACTIONS
C
C THE VARIABLES ARE FIRST INITIALIZED.
C
      ISKIP=0
      DO 10 I=1,10
      DO 9 J=1,35
      IF (J.GT.5) GO TO 6
      DRHOTT(I,J)=0.0
6 CONTINUE
      DO 7 K=1,5
      DRHOC(I,J,K)=0.0
7 CONTINUE
9 CONTINUE
10 CONTINUE
      DRHOTT=-P/(82.07*T**2)
      OVELDT=S*82.07*TDASH/P

C THE ENTIRE SUBROUTINE, THRU 400, IS EXECUTED ONCE FOR EACH
C SIZE FRACTION.
C
      DO 400 LQ=LL,IBURN
C IF IS > 0 (EPST > 0.7) THEN THE PROGRAM SKIPS DOWN TO 200
C
      IF (IS(LQ).GE.1) GO TO 200

C THE DERIVATIVES WHICH ARE ONLY FUNCTIONS OF THE CHAR STRUCTURE
C ARE CALCULATED FIRST. THE MOST INVOLVED CALCULATION IS
C CONCERNED WITH THE DERIVATIVE OF THE EFFECTIVE DIFF WITH
C RESPECT TO Q OR CONVERSION. THIS CALCULATION INVOLVES TWO
C NUMERICAL INTEGRATIONS; EACH USING THE TRAPIZOIDAL RULE.
C THE INTEGRATIONS ARE PERFORMED IN THE DO LOOPS WHICH END AT
C STATEMENTS 50 AND 100.
C
      DINT1=0.0
      DINT2=0.0
      DINT3=0.0
45 NIPOR=IPOR-1
      DO 50 J=1,NIPOR
      I1=IPOR-J
      DELTAR=PORRAD(I1+1)-PORRAD(I1)

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      AVINT1= (PORRAD(I1)+Q(LQ))*LAMDA(I1)+(PORRAD(I1+1)+Q(LQ))
1      *LAMDA(I1+1)
      AVINT2=((PORRAD(I1)+Q(LQ))*2*LAMDA(I1)+(PORRAD(I1+1)+Q(LQ))*2*
1      LAMDA(I1+1))/2.
      OINT1=OINT1+AVINT1*DELTAR
      OINT2=OINT2+AVINT2*DELTAR
50  DEPSDQ(LQ)=12.566*LAMDA(I1)*(PORRAD(I1)+Q(LQ))*EXP(-6.283*
1      OINT2)*(1.+0.5*(PORRAD(I1)+Q(LQ))*(-6.283*OINT1))
      OIFLST=0.0
      OIFEDQ=0.0
      DO 100 J =1,NIPOR
      I1=IPOR-J
      IF (DKNUD(I1,LQ).LE.0.0001.OR.PORRAD(I1).LE.1.0) GO TO 100
      DDIFDQ = (1./DJ2AB+1./DKNUD(I1,LQ))*(-2.)*(1./((PORRAD(I1)
1      +Q(LQ))*2*9.7E-05*(T/32.))*0.5))
      DELTAR=PORRAD(I1+1)-PORRAD(I1)
      AVEINT=((DEPSDQ(I1+1)*DIFF(I1+1,LQ)+EPS(I1+1,LQ)*OIFLST)
1      +(DEPSDQ(I1)*DIFF(I1,LQ)+EPS(I1,LQ)*DDIFDQ))/2.
      OIFLST=DDIFDQ
      OIFEDQ=OIFEDQ+AVEINT*DELTAR
100  CONTINUE
      QQDCC=-(VEL/6.283)*(1./FL(M+LQ)-6.*DRDFLC(LQ)/SIZPRT(LQ))
1      *(4.*BONE**2-0.6366*BZERO*ALOG((SIZSAV(LQ)/SIZPRT(LQ))*3
2      *(FL(M+LQ)/CMCARB(LQ))))*(-0.5)
      DSQCC=QQDCC*(6.283E+8*BZERO)
      DSVDQ=12.566E+8*(1.-EPSTO)*(BZERO-12.566*(BZERO*Q(LQ)+BONE)
1      **2)*EXP(-6.283*(BZERO*Q(LQ)**2+2.*BONE*Q(LQ)))
      DSVDCC=DSVDQ*QQDCC
      DDIFDC=OIFEDQ*QQDCC
      DO 140 I=1,NH
      EXP2=EXP(-EACT(I)/(1.987*T))
C
C   THE DO LOOP WHICH END AT 200 CALCULATES THE PARTIAL DERIVATIVE
C   OF THE REACTION RATES WITH RESPECT TO CONCENTRATION FOR THE
C   GAS PHASE SPECIES.
C
      DO 20 J=1,3
      NISM=ISMH(I,J)
      IF (NISM.LE.0.OR.NISM.GT.M) GO TO 20
      IF (NISM.NE.2*HNQ) GO TO 15
      DRHOC(I,NISM,LQ)=DRHOC(I,NISM,LQ)+RATEK(I,LQ)*ETANO(LQ)/ETA(I,LQ)
      DRHOC(I,I02,LQ)=DRHOC(I,I02,LQ)+(RATEK(I,LQ)*KO(ICH,LQ)*
1      ETA(ICH,LQ)*CMN*RCOEFF(ICH)/(ETA(I,LQ)*KO(INR,LQ)*CMCIN))*
2      (1.-ETANO(LQ))
      GO TO 20
15  DRHOC(I,NISM,LQ)=DRHOC(I,NISM,LQ)+RATEK(I,LQ)
20  CONTINUE
      EXP1 = EXP(-6.283*(BZERO*Q(LQ)**2+2.*BONE*Q(LQ)))
      IF (ETA(I,LQ).LT.0.999.OR.ETA(I,LQ).GT.1.0) GO TO 45
      DETADC=0.0
      DETADP=0.0
      GO TO 100
      IF (THIELE(I,LQ).LT.4.0) GO TO 105
      DETADP=-1./THIELE(I,LQ)**2
      GO TO 100
105  DETADP=(1./THIELE(I,LQ)**2)*(1./(3.*THIELE(I,LQ))-1./TANH(3.
1      *THIELE(I,LQ)))+(1./THIELE(I,LQ))*(1./(3.*THIELE(I,LQ)**2)-3./
2      (SINH(3.*THIELE(I,LQ))))**2)
C
C   THE FOLLOWING STATEMENTS, ENDING AT 117, CALCULATE DRHOC FOR
C   THE CASE WHERE THE SPECIES BEING CONSIDERED IN SOLID CARBON.

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C
106 IF (ETA(ICH,LQ).EQ.1.0) GO TO 112
    OPHIDC=VEL*ORDFLC(LQ)*THIELE(I,LQ)*2./SIZPRT(LQ)+
    1 (THIELE(I,LQ)/SAREA(LQ))*(OSVOC-SAREA(LQ)*DDIFDC/
    2 EFDIFF(LQ))
    DETADC=OPHIDC*DETAOP
112 IF (I.NE.ICH) GO TO 114
C
C   DETADC IS ADJUSTED FOR THE NO REDUCTION REACTION.
C
    OSAVE(LQ)=DETAJC
    GO TO 116
114 IF (I.NE.INR) GO TO 116
    IF (CONC(I).LT.1E-28) GO TO 116
    CONST=(KO(ICH,LQ)*CMN*CONC(ICH)*RCOEFF(ICH))/
    1 (RCUEFF(INR)*(KO(ICH,LQ)-KO(INR,LQ))*CMCIN*CONC(INR))
    DEIAUC=-CONST*OSAVE(LQ)*(1.+CONST)*DETAJC
116 ACONST=HRATE(I,LQ)/(SPAREA(LQ)*CO(M+LQ)*ETA(I,LQ))
117 DRHOC(I,M+LQ,LQ)=ACONST*(SPAREA(LQ)*ETA(I,LQ)+CO(M+LQ)*OSVOC*
    1 ETA(I,LQ)+CO(M+LQ)*SPAREA(LQ)*DETAJC)
C
C   THE STATEMENTS THRU 140 CALCULATE THE DERIVATIVE OF THE
C   REACTION RATE WITH RESPECT TO TIME (DRHOTT).
C
    EOVERT = EACT(I)/(1.987*T**2)
    IF (ETA(I,LQ).LT.1.0) GO TO 120
    DETADT=0.0
    GO TO 130
120 OPHIDT = SIZPRT(LQ)/12.*(KO(I,LQ)/EFDIFF(LQ))*0.3*EOVERT*EXP
    1 (-EACT(I)/(1.987*2.*T))
    DETADT = OETAOP*OPHIDT
130 CH = HRATE(I,LQ)/(EXP2*ETA(I,LQ)*RHO)
    IF (CH.EQ.0.0) GO TO 140
    DRHDT = CH*((ETA(I,LQ)*EOVERT*EXP2*RHO)+(EXP2*RHO*DETAJC)+
    1 (ETA(I,LQ)*EXP2*DRHDT))
    DRHOTT(I,LQ) = DRHDT*TDASH
140 CONTINUE
150 GO TO 400
C
C   THESE LAST STATEMENTS CALCULATE DRHOC AND DRHOTT FOR THE CASE
C   WHEN EPST > 0.7. SPAREA AND ETA ARE CONSTANT,
C   THEREFORE, THE REACTIONS ARE ONLY FUNCTIONS OF CONCENTRATIONS AND
C   TEMP; THE CHAR STRUCTURE NO LONGER ENTERS THE CALCULATIONS.
C
200 EXP3=EXP(17.644-30260./(1.8*T))
    DO 300 I=1,NH
        EOVERT = EACT(I)/(1.987*T**2)
        EXP2 = EXP(-EACT(I)/(1.987*T))
        CH = HRATE(I,LQ)/(EXP2*RHO)
        DRHDT = CH*(EOVERT*EXP2*RHO+EXP2*DRHDT)
        DRHOTT(I,LQ) = DRHDT*TDASH
    DO 290 J=1,M
        DO 200 K=1,3
            IF (J.NE.ISMH(I,K)) GO TO 280
            DRHOC(I,J,LQ)=RATEK(I,LQ)
            GO TO 290
280 CONTINUE
290 CONTINUE
    DRHOC(I,M+LQ,LQ)=HRATE(I,LQ)/CO(M+LQ)
300 CONTINUE
400 CONTINUE
    RETURN
    END

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SUBROUTINE TYSON (N,Y,F,X,H,ALP,B,BUG1,BUG2,DELTA,IN)
DIMENSION Y(35),F(35),HREAC(10)
DIMENSION ALP(35),B(35,35),A(40,41),ASTORE(35,36)
LOGICAL LCOAL
REAL K(35),K1(35),KBYY(35)
REAL ADASH(35,36)
REAL KIDASH(35)
INTEGER BUG1,BUG2
DIMENSION OLDY(35),OLDP(35),OLDALP(35),OLDB(35,35),OLDK1(35),BIGK(
135)
IF(IN.NE.0) GO TO 1
FACT=-1.0E-28
IF (H.GT.1.) FACT=H
IF (FACT.GT.0.) CALL STEPIN (N,H,B,FACT)
C
C
C----- THE INITIAL STEP SIZE HAS NOW BEEN SET
C----- INITIALIZE INDICES
C
      IDEBUG=1
      ISTEP=0
      ICOUNT=0
      ITYSON=0
      IN=1
      1 IF(IN.NE.1) GO TO 2
      10 ITYSON=1+ITYSON
C
C----- ITYSON COUNTS ITERATIONS
C----- ISTEP COUNTS SUCCESSFUL STEPS
C----- EULER INTEGRATION (IMPLICIT) FOR FIRST STEP ONLY
C
      CALL EULIMP (N,Y,F,X,H,ALP,B,ASTORE,K,A)
C
C----- EVALUATES DELTA Y-S BUT DOES NOT ADVANCE Y-S OR X
C
      CALL EULSTP (N,Y,K,H,KBYY,IFLAG,DELTA)
C
C----- CHECKS STEP SIZE BUT DOES NOT ADVANCE Y-S OR X
C----- IF IFLAG =1 STEP IS DIVIDED BY TEN AND LOOP IS REPEATED
C
C----- FIRST STEP INFO IS STORED FOR USE IN TYSTEP
C
      CALL STORE (N,Y,F,X,H,ALP,B,K1,HP,IFLAG,
      1,OLDY,OLDP,OLDALP,OLDB,OLDK1,OLDHP,OLDX)
C
C----- DO WE WANT DEBUG OUTPUT? NOT IF BUG1 EQ 0
C
      IF (BUG1.EQ.0) GO TO 11
      IF (MOD(IDEBUG,BUG1).NE.0)
      1CALL TYDBUG(N,Y,F,X,H,ALP,B,BUG1,BUG2,DELTA,IN,ITYSON,IDEBUG,
      1ASTORE,K,K1,KBYY,HP,IFLAG,FACT,A,ISTEP,BIGK,OLDP,OLDALP,OLDB,OLDK1
      1,OLDHP,ADASH,KIDASH,BIGH)
C
      IF (MOD(ITYSON,BUG2).EQ.0)
      IF (ISTEP.GT.BUG2)
      1CALL TYDBUG(N,Y,F,X,H,ALP,B,BUG1,BUG2,DELTA,IN,ITYSON,IDEBUG,
      1ASTORE,K,K1,KBYY,HP,IFLAG,FACT,A,ISTEP,BIGK,OLDP,OLDALP,OLDB,OLDK1
      1,OLDHP,ADASH,KIDASH,BIGH)
      11 IF (IFLAG.EQ.1) GO TO 10
C
C----- NOW ADVANCE Y-S AND X AND STORE OLD K-S AND OLD H
C----- IF IFLAG EQ 2 H STAYS SAME( IF IFLAG EQ 3 H IS DOUBLED

```

```

C
C      ISTEP = ISTEP + 1
C      CALL FORWARD (N, Y, F, X, H, K, K1, HP, IFLAG, K1DASH)
C      IN = 2
C      RETURN
2 CONTINUE

C      ----- INITIALLY IFLAG EQ 2 OR WE ASSUME STEP DOES NOT CHANGE
C      ----- IFLAG IS SET TO ITS CORRECT VALUE IN TYSTEP
C
C      IFLAG = 2
C      ITYSON = ITYSON + 1
C
C      ----- THREE POINT TYSON IMPLICIT INTEGRATION
C
C      CALL TYSINT(N, Y, F, X, H, ALP, B, K, K1, HP, ASTORF, A)
C
C      ----- EVALUATES DELTA Y-S BUT DOES NOT ADVANCE THEM OR X
C
C      CALL CHECKY(N, Y, H, K, IFLAG)
C
C      ----- AT THIS POINT IFLAG IS EQ 1 ONLY IF SOME Y IS NEG
C      ----- AND IN THIS CASE WE DO NOT WANT TO CALL TYSTEP OR STORE
C
C      IF (IFLAG.EQ.1) GO TO 3
C      NSTEP = ISTEP + 1
C
C      ----- TYSTEP IS CALLED EVERY ODD STEP
C      ----- STORE IS CALLED EVERY EVEN STEP
C
C      IF (MOD(NSTEP, 2).EQ.0)
C      1CALL TYSTEP (N, Y, K, H, HP, X, K1, OLDY, OLDF, OLDALP, OLDB, OLDK1, OLDHP,
C      1BIGK, IFLAG, NSTEP, KBYY, DELTA, ADASH, A, BIGH, K1DASH)
C
C      ----- CHECKS STEP SIZE DOES NOT ADVANCE Y-S AND X
C      ----- IF IFLAG=1 H HAS BEEN HALVED IF NOT H HAS NOT CHANGED
C      ----- IFLAG HAS BEEN SET EQ 2 IF STEP STAYS SAME
C      ----- IFLAG HAS BEEN SET EQ 3 IF STEP IS TO BE DOUBLED
C      ----- NOTE THAT MATRIX A NOW CONTAINS ELEMENTS FROM TYSTEP
C
C      IF (MOD(ISTEP, 2).NE.0) GO TO 3
C      IF (IFLAG.EQ.1) GO TO 3
C      CALL STORE (N, Y, F, X, H, ALP, B, K1, HP, IFLAG,
C      1OLDY, OLDF, OLDALP, OLDB, OLDK1, OLDHP, OLDY)
C      3 CONTINUE
C      IF (BUG1.EQ.0) GO TO 12
C      IF (MOD(IDEBUG, BUG1).NE.0)
C      1CALL TYDBUG(N, Y, F, X, H, ALP, B, BUG1, BUG2, DELTA, IN, ITYSON, IDEBUG,
C      1ASTORE, K, K1, KBYY, HP, IFLAG, FACT, A, ISTEP, BIGK, OLDF, OLDALP, OLDB, OLDK1,
C      1, OLDHP, ADASH, K1DASH, BIGH)
C      IF (MOD(ITYSON, BUG2).EQ.0)
C      IF (ISTEP.GT.BUG2)
C      1CALL TYDBUG(N, Y, F, X, H, ALP, B, BUG1, BUG2, DELTA, IN, ITYSON, IDEBUG,
C      1ASTORE, K, K1, KBYY, HP, IFLAG, FACT, A, ISTEP, BIGK, OLDF, OLDALP, OLDB, OLDK1,
C      1, OLDHP, ADASH, K1DASH, BIGH)
C      12 IF (IFLAG.EQ.1) GO TO 2
C
C      ----- ADVANCE Y-S ETC STORE K-S IN K1-S AND H IN HP
C      ----- ADJUST H IF STEP SIZE IS TO BE INCREASED
C
C      ISTEP = ISTEP + 1

```

```
CALL FORWAD (N,Y,F,X,H,K,K1,HP,IFLAG,K1DASH)
RETURN
END
```

```
      SUBROUTINE STEPIN (N,H,B,FACT)
C
C-----ESTIMATES INITIAL STEP SIZE
C
      DIMENSION B(35,35)
C----- FIND LARGEST ELEMENT IN BETA MATRIX
      B11=ABS(B(1,1))
      B12=ABS(B(1,2))
      BMAX=AMAX1(B11,B12)
      DO 1 I=1,N
      DO 1 J=1,N
      BIJ=ABS(B(I,J))
      BMAX=AMAX1(BMAX,BIJ)
1 CONTINUE
      CHATIM=1./BMAX
      H=CHATIM/FACT
C*****
      IF (H.GT.0.001)H=0.001
C*****
      RETURN
      END
```

```

SUBROUTINE EULIMP(N,Y,F,X,H,ALP,B,ASTORE,K,A)
C
  DIMENSION Y(35),F(35)
  INTEGER DDL
  REAL K(35)
  REAL K1(35)
  DIMENSION ALP(35),B(35,35),A(40,41),ASTORE(35,36)
  DIMENSION JC(35),V(2)
C
C----- EULER IMPLICIT INTEGRATION
C----- SET UP MATRIX
C
  1 DO 2 I=1,N
    DO 2 J=1,N
      A(I,J)=-H*B(I,J)
  2 CONTINUE
    DO 3 I=1,N
      A(I,I)=1.-H*B(I,I)
      A(I,N+1)=H*(F(I)+H*ALP(I))
  3 CONTINUE
    DO 4 I=1,N
      DO 5 J=1,N
        ASTORE(I,J)=A(I,J)
      4 ASTORE(I,N+1)=A(I,N+1)
      V(1)=4.
      L=N+1
      CALL GJR (A,41,40,N,L,DDL,JC,V)
      IF (DDL.EQ.6) GO TO 6
      DO 7 I=1,N
        K(I)=A(I,N+1)
  7 CONTINUE
      RETURN
  6 CALL GJBOMB (N,Y,F,X,H,ALP,B,K,K1,HP,ASTORE,A)
      CALL EXIT
      END

```

```

SUBROUTINE GJR(A,NC,NR,N,MC,DOL,JC,V)
INTEGER DOL
DIMENSION A(NR,NC),JC(1),V(2)
DOL=0
L=N+1
DETER=1.
DO 9 K=1,N
  DETER=DETER*A(K,K)
  KP1=K+1
  DO 5 J=KP1,L
6    A(K,J)=A(K,J)/A(K,K)
    A(K,K)=1.
    DO 9 I=1,N
      IF(I.EQ.K.OR.A(I,K).EQ.0.) GO TO 9
      DO 8 J=KP1,L
6      A(I,J)=A(I,J)-A(I,K)*A(K,J)
      A(I,K)=0.
9    CONTINUE
    IF(ABS(DETER).LT.1.E-20) DOL=6
  RETURN
END

```

```

SUBROUTINE GJBOMB (N,Y,F,X,H,ALP,B,K,K1,HP,ASTORE,A)
DIMENSION Y(35),F(35)
DIMENSION ALP(35),B(35,35),A(40,41),ASTORE(35,36)
REAL K(35),K1(35),KBY(35)
WRITE (6,1000)
1000 FORMAT(120H -----GJR BOMBED OUT MATRIX IS
1SINGULAR,TRY REDUCUNG STEP-----)

```

C
C
C
C
C
C
C

```

-----IN ORDER TO SAVE STORAGE THERE ARE UNDIMENSIONED DUMMY VARIA
-----BLES IN THE ARGUMENT LIST FOR TYDEBUG.
-----THEREFORE PROGRAM MUST CALL EXIT AFTER GJBOMB IS CALLED

```

```

CALL TYDEBUG(N,Y,F,X,H,ALP,B,BUG1,BUG2,DELTA,IN,ITYSON,IDEBUG,
1ASTORE,K,K1,KBY,HP,IFLAG,FACT,A,ISTEP,BIGK,OLUF,OLDALP,OLD8,OLDK1
1,OLDHP,ADASH)
RETURN
END

```

```

      SUBROUTINE EULSTP (N,Y,K,H,KBY,Y,IFLAG,DELTA)
C-----
C----- CHECKS EULER STEP SIZE IF IFLAG =1 STEP DIVIDED BY TEN
C-----
      DIMENSION Y(35)
      REAL K(35),KBY(35)
      IFLAG =2
      DO 2 I=1,N
      YNEW=Y(I)+K(I)
      IF(YNEW.LT.0.) IFLAG=1
2  CONTINUE
      IF(IFLAG.NE.1) GO TO 3
      H=H/10.
      RETURN
      3 DO 5 I=1,N
      YNEW=Y(I)+K(I)
      IF (Y(I).LT.1.0E-14) GO TO 5
      KBY(I)=ABS(K(I)/YNEW)
      IF (KBY(I).GT.DELTA*10.) IFLAG=1
5  CONTINUE
      IF (IFLAG.EQ.1) H=H/10.
      RETURN
      END

```

```

      SUBROUTINE STORE (N,Y,F,X,H,ALP,B,K1,HP,IFLAG,
1OLDY,OLDF,OLDALP,OLDB,OLDK1,OLDHP,OLDX)
C-----
C----- STORES OLD VALUES FOR USE IN TYSTEP
C-----
      REAL Y(35),F(35),ALP(35),B(35,35),K1(35)
      REAL OLDY(35),OLDF(35),OLDALP(35),OLDB(35,35),OLDK1(35)
C-----
      DO 1 I=1,N
      OLDY(I)=Y(I)
      OLDF(I)=F(I)
      OLDALP(I)=ALP(I)
      OLDK1(I)=K1(I)
      DO 1 J=1,N
      OLDB(I,J)=B(I,J)
1  CONTINUE
      OLDHP=HP
      OLDX=X
      RETURN
      END

```



```

SUBROUTINE TYDBUG (N,Y,F,X,H,ALP,B,BUG1,BUG2,DELTA,IN,ITYSON,IDEBU
IG,ASTORE,K,K1,KBY,Y,P,IFLAG,FACT,A,ISTEP,BIGK,OLDF,OLDALP,OLDB,
1OLDK1,OLDHP,ADASH,KIDASH,BIGH)

```

----- TYSON DEBUG SUBROUTINE -----

```

DIMENSION Y(35),F(35)
DIMENSION ALP(35),B(35,35),A(40,41),ASTORE(35,36)
REAL K(35),K1(35),KBY(35)
REAL KIDASH(35)
DIMENSION BIGK(35)
REAL OLDF(35),OLDALP(35),OLDB(35,35),OLDK1(35),ADASH(35,36)
INTEGER ROW,COLUMN,BUG1,BUG2
IDEBUG=IDEBUG+1
WRITE(6,1000)
1000 FORMAT (1H0,10X,20HTYSON DEBUG PRINTOUT)
CALL DBSNGI (6H 1STEP,ISTEP)
CALL DBSNGI (6HITYSON,ITYSON)
CALL DBSNGI (6HIDEBUG,IDEBUG)
CALL DBSNGI (6H IFLAG,IFLAG)
CALL DBSNGI (6H IN,IN)
CALL DBSNGE (6H FACT,FACT)
CALL DBSNGE (6H DELTA,DELTA)
CALL DBSNGE (6H H,H)
CALL DBSNGE (6H HP,HP)
CALL DBSNGE (6H X,X)
CALL DBSNGI (6H BUG1,BUG1)
CALL DBSNGI (6H N,N)
CALL DBSNGI (6H BUG2,BUG2)
COLUMN=N
CALL VECTOR (6H Y,Y,COLUMN)
CALL VECTOR (6H F,F,COLUMN)
CALL VECTOR (6H ALP,ALP,COLUMN)
CALL VECTOR (6H K,K,COLUMN)
CALL VECTOR (6H K1,K1,COLUMN)
CALL VECTOR (6H KBY,KBY,COLUMN)
CALL VECTOR (6H BIGK ,BIGK,COLUMN)
ROW=N
NROW=35
CALL MATRIX (6H BETA,B,ROW,COLUMN,NROW)
COLUMN=N+1
CALL MATRIX (6HASTORE,ASTORE,ROW,COLUMN,NROW)
NROW=40
CALL MATRIX (6H A,A,ROW,COLUMN,NROW)
CALL DBSNGE (6H BIG H,BIGH)
CALL DBSNGE (6HOLD HP,OLDHP)
COLUMN=N
CALL VECTOR (6HKIDASH,KIDASH,COLUMN)
CALL VECTOR (6H OLD F,OLDF,COLUMN)
CALL VECTOR (6HOLD K1,OLDK1,COLUMN)
CALL VECTOR (6HOLDALP,OLDALP,COLUMN)
ROW=N
NROW=35
CALL MATRIX (6H OLD B,OLDB,ROW,COLUMN,NROW)
COLUMN=N+1
CALL MATRIX (6H ADASH ,ADASH,ROW,COLUMN,NROW)
RETURN
END

```

```

SUBROUTINE FORWAD(N,Y,F,X,H,K,K1,HP,IFLAG,K1DASH)
REAL K1DASH(35)
DIMENSION Y(35),F(35)
REAL K(35),K1(35)
C----- ADVANCES Y-S AND STORES K-S. ALSO ADVANCES X
C
DO 2 I=1,N
Y(I)=Y(I)+K(I)
K1DASH(I)=K1(I)
K1(I)=K(I)
2 CONTINUE
X=X+H
HP=H
IF (IFLAG.GE.3) GO TO 1
C
C ADJUST INCREASED STEP SIZE DEPENDING ON IFLAG
C
C
RETURN
1 CONTINUE
C
C
IF (IFLAG.GE.3) H=2.*H
C IF (IFLAG.EQ.4) H=4.*H
C IF (IFLAG.EQ.5) H=10.*H
C IF (IFLAG.EQ.6) H= 100.*H
RETURN
END

```

```

SUBROUTINE TYSINT (N,Y,F,X,H,ALP,B,K,K1,HP,ASTORE,A)
C-----THREE POINT IMPLICIT INTEGRATION
C-----SET UP MATRIX A AND INVERT USING GJR
C-----UNEQUAL STEPS HP AND H, OLD DELTA Y IS K1.
C-----PROGRAM CALCULATES NEW DELTA Y-S=K-S
C-----Y-S AND X ARE NOT ADVANCED IN THIS SUBPROGRAM

DIMENSION Y(35),F(35)
DIMENSION ALP(35),B(35,35),A(40,41),ASTORE(35,36)
REAL K(35),K1(35)
INTEGER DOL
DIMENSION JC(35),V(2)
DO 1 I=1,N
DO 1 J=1,N
A(I,J)=-H*B(I,J)
1 CONTINUE
DO 2 I=1,N
A(I,I)=(HP+2.*4)/(H+HP)-H*B(I,I)
A(I,N+1)=H*(F(I)+H*ALP(I))+K1(I)*H**2/(HP*(HP+H))
2 CONTINUE
DO 3 I=1,N
DO 4 J=1,N
4 ASTORE(I,J)=A(I,J)
3 ASTORE(I,N+1)=A(I,N+1)
V(1)=4.
L=N+1
CALL GJR(A,41,40,N,L,DOL,JC,V)
IF(DOL.EQ.6) GO TO 6
DO 24 I=1,N
K(I)=A(I,N+1)
24 CONTINUE
RETURN
6 CALL GJBOMB (N,Y,F,X,H,ALP,B,K,K1,HP,ASTORE,A)
CALL EXIT
END

```

SUBROUTINE TYSTEP (N,Y,K,H,HP,X,K1,OLDY,OLDF,OLDALP,OLDB,OLDK1,
1,OLDHP,BIGK,IFLAG,ISTEP,KBY,DELTA,ASTORE,A,BIGH,K1DASH)

C
C
C----- CALCULATES DELTA Y-S FOR STEP AS LARGE AS SUM AS LAST TWO
C

REAL Y(35),K(35),K1(35)
REAL KBY(35)
REAL K1DASH(35)
REAL OLDY(35),OLDF(35),OLDALP(35),OLDB(35,35),OLDK1(35),BIGK(35)
REAL ASTORE(35,36), A(40,41)
IFLAG=2
I1=0
I2=0
I3=0
I4=0
I5=0
BIGH=H+HP

C
C
C-----SET LARGER STEP AND SEE WHETHER NEW Y-S ARE CLOSE TO OLD Y-S
C

IF (ISTEP.EQ.2)
1CALL EULIMP (N,OLDY,OLDF,OLDX,BIGH,OLDALP,OLDB,ASTORE,BIGK,A)
IF (ISTEP.GE.4)
1CALL TYSINT(N,OLDY,OLDF,OLDX,BIGH,OLDALP,OLDB,BIGK,OLDK1,OLDHP
1,ASTORE,A)

C
C
C----- COMPARE Y-S WITH LARGE STEP TO Y-S WITH SMALL STEP
C

DO 1 I=1,N
IF (ABS(OLDY(I)+BIGK(I)).LT.1.00E-6) GO TO 1
DIFF=1.-ABS((OLDY(I)+BIGK(I))/(Y(I)+K(I)))
KBY(I)=ABS(DIFF)
IF (KBY(I).GE.0.001*DELTA) I5=1
IF (KBY(I).GE.0.01*DELTA) I4=1
IF (KBY(I).GE.0.1*DELTA) I3=1
IF (KBY(I).GE.DELTA) I1=1
IF (KBY(I).GE.10.*DELTA) I2=1
1 CONTINUE
IF (I2.EQ.1) IFLAG=1
IF (I2.NE.1.AND.I1.EQ.1) IFLAG=2
IF (I1.NE.1) IFLAG=3
IF (I3.NE.1) IFLAG=4
IF (I4.NE.1) IFLAG=5
IF (I5.NE.1) IFLAG=6

C
C
C-----H UNCHANGED UNLESS IFLAG EQ 1, IN WHICH CASE H IS HALVED
C

IF (IFLAG.EQ.1) H=H/2.
RETURN
END

```
SUBROUTINE CHECKY(N,Y,H,K,IFLAG)  
  DIMENSION Y(35)  
  REAL K(35)
```

```
C  
C  -----CHECKS TO SEE IF Y-S ARE NEGATIVE   IF SO, SETS H=0.1*H  
C  
  IFLAG=2  
  DO 1 I=1,N  
    YNEW= Y(I) +K(I)  
    IF (YNEW.LT.0.) IFLAG=1  
1  CONTINUE  
  IF(IFLAG.EQ.1) H=0.1*H  
  RETURN  
  END
```

```
SUBROUTINE OVERFL(IFL)  
  IFL = IABS(LEGVAR(IFL))  
  RETURN  
  END
```

```

SUBROUTINE RITOUT (M,N,CF,FL,FD,CO,DCO,F,REACIN,IDREAC,NAMISM,
1 RFO,RRE,RATE,RKF,RKR,IPLT,TIM,H,BETA,ALP,S,RHO,T,P,LEVEL,B,AL,
2 LCOAL,HREAC,CMCIN,Q,ETA,IDHREA,NMISM,HRATE,COEFF,EPST,SAREA,
3 NM,MH,EFDIFF,SPAREA,KO,RATEK,THIELE,ISIZE,SIZPRT,SIZEFR,
4 IVOL,VSPEC,LCHAR,VOLSTR,DCOVOL,TAR)

C
C *****
C
C VERSION AUGUST 2,1973 JOLW
C WRITES OUT VARIABLES IN ARGUMENT
C LEVEL 1 - LOWER LEVEL WRITEOUT
C LEVEL 2 - ALSO WRITES OUT JACOBIAN AND ADJUSTED
C JACOBIAN, ALPHA AND ADJUSTED ALPHA.
C *****
C
C MODIFIED JAN '82 G. KYLE
C INCLUDES WRITE STATEMENTS FOR DATA FOR DEVOLATILIZATION
C AND HETEROGENEOUS REACTIONS INVOLVED IN COAL COMBUSTION.
C ALSO PRINTS DATA ON VOLATILE AND SOLID SPECIES IN THE
C SYSTEM IN COAL COMBUSTION.
C

REAL CF(35),FL(35),FD(35),CO(35),DCO(35),F(35),RFO(150),RRE(150),
1 RATE(150),RKF(150),RKR(150),BETA(35,35),ALP(35),B(35,35),AL(35)
INTEGER REACIN(35),IDREAC(35),NAMISM(150,6)
DIMENSION ISMH(10,6),COEFF(10,6),HREAC(10),IDHREA(10),Q(5),
1 NMISM(10,6),ETA(10,5),HRATE(10,5),KO(10,5),RATEK(10,5),
2 THIELE(10,5),EPST(5),SAREA(5),SPAREA(5),SIZPRT(5),SIZEFR(5)
3 ,EFDIFF(5),VOLSTR(5),DCOVOL(10),VSPEC(5),FV(10),COV(10),CFV(10)
LOGICAL LCOAL,LCHAR
WRITE(6,97)
WRITE(6,101) IPLT
WRITE(6,103) TIM,H
WRITE(6,105) T,P,RHO,S
WRITE(6,99)
WRITE(6,111)
DO 1 I=1,M
WRITE(6,107) I,REACIN(I),CF(I),FL(I),FD(I),CO(I),DCO(I),F(I)
1 CONTINUE

C
C WRITE STATEMENTS FOR VOLATILE SPECIES (THRU STATEMENT 4).
C
IF(.NOT.LCOAL) GO TO 4
WRITE(6,301)
301 FORMAT(T10,"VOLATILES")
DO 3 I=1,IVOL
KV=M+MH+ISIZE-1+I
WRITE (6,107) I,VSPEC(I),CF(KV),FL(KV),FD(KV),CO(KV),DCO(KV),F(KV)
3 CONTINUE
VNAME=3HTAR
ITAR=IVOL+1
KV=M+MH+ISIZE+IVOL
WRITE (6,107) ITAR,VNAME,CF(KV),FL(KV),FD(KV),CO(KV),DCO(KV),F(KV)
4 IF(.NOT.LCHAR) GO TO 9

C
C WRITE STATEMENTS FOR SOLID SPECIES (THRU STATEMENT 6).
C
WRITE (6,401)
401 FORMAT(T10,"SOLID SPECIES")
K=M+1
J=1

```

```

WRITE (6,107) J, HREAC(1), CF(K), FL(K), FL(K), CO(K), DCO(K), F(K)
IF (ISIZE.EQ.1) GO TO 1010
L=1
DO 1005 K=2, ISIZE
J=M+K
WRITE (6,107) L, HREAC(1), CF(J), FL(J), FL(J), CO(J), DCO(J), F(J)
1005 CONTINUE
1010 CONTINUE
IF (MH.LE.1) GO TO 6
DO 5 I=2, MH
K=I+M+ISIZE-1
J=I
WRITE (6,107) J, HREAC(I), CF(K), FL(K), FL(K), CO(K), DCO(K), F(K)
5 CONTINUE
6 CONTINUE

C
C WRITE STATEMENTS FOR CHAR STRUCTURE PARAMETERS (THRU
C STATEMENT 8).
C
WRITE (6,201)
DO 8 J=1, ISIZE
IF (EPST(J).LT.0.7) GO TO 7
WRITE (6,202) J, SPAREA(J)
GO TO 8
7 WRITE (6,203) J, SIZPRT(J), SIZEFR(J), Q(J), EPST(J),
1 SPAREA(J), SPAREA(J), EFDIFF(J)
8 CONTINUE
201 FORMAT (/ , T10, "SIZE (CM)", T25, "FRACTION", T44 "Q", T55,
1 "POROSITY", T70, "SAREA", T85, "SPAREA", T100, "EFDIFF")
202 FORMAT (7X, I3, T13, "TOTAL POROSITY IS GREATER THAN 0.7, ",
1 "THEREFORE Q IS NO LONGER USED.", 2X, "SURFACE AREA = ", E10.4)
203 FORMAT (7X, I3, X, F9.6, 2X, F8.3, 7X, 6(E10.4, 5X))
9 WRITE (6,99)
WRITE (6,113)
DO 10 I=1, N
WRITE (6,109) I, IDREAC(I), (NAMISM(I, J), J=1, 6), RFO(I), RRE(I), RATE(I)
1, RKF(I), RKR(I)
10 CONTINUE

C
C WRITE STATEMENTS FOR HETEROGENEOUS REACTIONS (THRU
C STATEMENT 20).
C
IF (.NOT.LCHAR) GO TO 20
WRITE (6,99)
WRITE (6,210)
210 FORMAT (T10, "HETEROGENEOUS RXNS", T70, "RATE CONST", T81,
1 "RXN RATE", T95, "KO", T104, "THIELE", T116, "ETA")
DO 206 J=1, NH
WRITE (6,109) J, IDHREA(J), (NHISMH(J, K), K=1, 6), RATEK(J, 1),
1 HRATE(J, 1), KO(J, 1), THIELE(J, 1), ETA(J, 1)
IF (ISIZE.EQ.1) GO TO 206
DO 205 K=2, ISIZE
205 WRITE (6,212) RATEK(J, K), HRATE(J, K), KO(J, K), THIELE(J, K), ETA(J, K)
212 FORMAT (1X, T63, 5(E10.3, 1X))
206 CONTINUE
WRITE (6,211)
211 FORMAT (/ , T10, "COEFF.
DO 208 J=1, NH
208 WRITE (6,209) J, IDHREA(J), COEFF(J, K), K=1, 6)
209 FORMAT (1X, 6X, I3, 2X, A6, 4X, F6.2, 1H+, F6.2, 1H+, F6.2, 1H+,
1 2(F6.2, 1H+), F6.2)

```

```
20      IF (LEVEL.NE.2) GO TO 50
      MHET=M+MH+ISIZE-1+IVOL+2
      CALL MATRIX (6HB      ,B,MHET,MHET,35)
      CALL VECTOR (6HALPHA ,AL,MHET)
      CALL VECTOR (6HF      ,F,MHET)
      97 FORMAT(//////)
      99 FORMAT(/)
101  FORMAT(8X,"ITERATION",I5)
103  FORMAT(10X,"TIME",E12.5,5X,"STEP SIZE",E12.5)
105  FORMAT(10X,"TEMPERATURE",F10.3,5X,"PRESSURE",F10.3,5X,"MOLAR DENSIT
      Y",E12.5,5X,"MOLAR FLOW OUT",F10.3)
107  FORMAT ( 7X,I3,2X,A6,4X,2(E10.3,5X),E15.7,2X,3(E10.3,5X))
109  FORMAT ( 7X,I3,2X,A6,4X,A6,1H+,A6,1H+,A6,1H+,A6,1H+,A6,1H+,A6,4X,
      15(E10.3,1X))
111  FORMAT (T10,"SPECIE",T25,"MOLE FRACT",T40,"FLOW OUT",T55,"FEED IN"
      1,T70,"CONCENTRATION",T85,"RATE FORMED",T100,"RHS OF DIFF EQ")
113  FORMAT (T10,"REACTION",T70,"FORWARD",T81,"REVERSE",T92,"NET FWD",
      1T103,"FWD RATCO",T114,"REV RATCO")
50  RETURN
      END
```



```
      SUBROUTINE VECTOR (NAME,ARRAY,COLUMN)
C
C
C
      SUBROUTINE PRINTS OUT ARRAYS WITH THEIR NAMES
      INTEGER COLUMN
      DIMENSION ARRAY(COLUMN)
      IF (COLUMN.NE.0) GO TO 9000
      WRITE (6,8000) NAME
      GO TO 1
3000  FORMAT (1H0,10X,A6)
9000  CONTINUE
      WRITE (6,1000) NAME
1000  FORMAT (1H0,10X,A6,1X,6HVECTOR)
3000  FORMAT (1H ,5X,10(2X,E10.4))
      WRITE (6,3000) (ARRAY(J),J=1,COLUMN)
1     CONTINUE
      RETURN
      END
```

```
      SUBROUTINE MATRIX (NAME,ARRAY,ROW,COLUMN,NROW)
C
C
C
      SUBROUTINE PRINTS OUTS ARRAYS WITH THEIR NAMES
      INTEGER ROW,COLUMN
      DIMENSION ARRAY(NROW,COLUMN)
1000  FORMAT (1H0,10X,A6,1X,6HMATRIX)
3000  FORMAT (1H ,5X,10(2X,E10.3))
      IF (NROW.EQ.0.OR.ROW.EQ.0.OR.COLUMN.EQ.0) GO TO 9999
      WRITE (6,1000) NAME
      DO 2000 I=1,ROW
2000  WRITE (6,3000) (ARRAY(I,J), J=1,COLUMN)
      GO TO 8000
9999  CONTINUE
      WRITE (6,9876) NAME
9876  FORMAT (1H0, 10X, A6)
8000  CONTINUE
      RETURN
      END
```

```
      SUBROUTINE DBSNGE (NAME,VALUE)
C
C
C      SUBROUTINE PRINTS OUT NAME AND VALUE IN EXPONENTIAL FORM
      WRITE (6,1000) NAME ,VALUE
1000  FORMAT (1H0,5X,A6,2X,1H=,E13.6)
      RETURN
      END
```

```
      SUBROUTINE DBSNGI (NAME,IVALUE)
C
C
C      SUBROUTINE PRINTS OUT VALUE AND NAME IN INTEGER FORM
      WRITE (6,1000) NAME,IVALUE
1000  FORMAT (1H0,5X,A6,1H=,I7)
      RETURN
      END
```