A COMPUTER STUDY OF THE PYROLYSIS

OF POROUS SOLIDS

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PREFACE

This work could not have been completed without the love and sacrifice of my wife, Mary Jo, and my children, Cheri, Evan, Brian, and Jeaniece. Together with my parents, George and Gladys Rittmann, they gave this work a personal purpose and meaning and it is to them that this is dedicated.

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NOMENCLATURE

Symbol	Description
A_i	time-dependent, polynomial coefficient i, for the temperature approximation
a_i	frequency factor for reaction i, sec^{-1}
B	x-temperature derivative at heated surface
b_i	mole fraction for species i in reaction expression, moles of species i/mole of reactant
C	constant pressure specific heat, cal/gm-°K
c_1	mass fraction of solid converted in reaction 1, gm $Solid_2$/gm $Solid_1$
c_2	mass fraction of solid converted in reaction 3, gm $Solid_6$/gm $Solid_2$
E_i^*	activation energy for reaction i, cal/mole
F_i	frequency factor parameter for reaction i (see Table VI)
f_m	weighting function m
G	heat flux parameter (see Table VI)
G_i	Gas species i
$\bar{H}_i$	non-dimensional heat generation term i
$H_{i,n}$	time-dependent polynomial coefficient n for heat generation approximation term i
h	heat transfer coefficient, cal/cm^2-sec-°K
$J_{i,n}$	time-dependent polynomial coefficient n for approximation term i

Note: For symbols having both a dimensional and non-dimensional representation, an asterisk (*) is used to denote the dimensional value. Table IV defines the non-dimensional quantity.

Symbol	Description

K — effective thermal conductivity based on constant unit area

$\bar{K}$ — thermal conductivity of solid based on solid area

k_i — rate constant for reaction i, $\sec^{-1}$

$\bar{k}_i$ — exponential part of the rate constant

$\bar{k}_{i,j}$ — exponential part of the rate constant at the approximating strip j

L — slab thickness, between insulated and heated surfaces, cm

M_i — molecular weight of species i

$\dot{m}'_i$ — rate of generation of species i per unit volume from all reactions

$\dot{m}'_{i,j}$ — rate of generation of species i per unit volume from reaction j

N — number of approximating strips

Ne — number of ordinary differential equations, $4N + 2$

Nu — Nusselt number (see Table VI)

Q_i — heat of reaction i, cal/gm of reactant

$\dot{Q}'_i$ — rate of generation of heat in reaction i per unit volume

$\dot{Q}'$ — rate of generation of heat from all reactions per unit volume

q — heat flux, cal/cm^2-sec

R° — universal gas constant, 1.986 cal/mole-°K

R_i — heat of reaction i parameter (see Table VI)

S_i — Solid species i

T^* — temperature, °K

T^*_∞ — convective heat source temperature

t^* — time, sec

Symbol	Description
w^*	mass flux, gm/cm^2-sec
x^*	slab distance from insulated surface, cm
ρ^*	effective density of total solid, mass of solid/constant unit volume
$\bar{\rho}^*$	actual density of total solid, mass of solid/volume of solid

Subscripts	Description
0	initial value, time = 0
$1, 2, \ldots, 6$	species number
R	Radiant heating boundary condition
C	Convective heating boundary condition

CHAPTER I

INTRODUCTION

When a porous solid such as wood, cellulose or a polymer foam is heated, its temperature rises at a rate dependent on the rate of surface heating and upon the rate of heat conduction into the solid. The solid continues to absorb heat until the temperature is high enough for chemical reactions to be important. These reactions cause changes in local temperature and solid composition thus affecting future reactions. If it were possible to specify all reactions and their rates, one could, in principle, predict the behavior of the solid, given the boundary conditions and physical properties.

For many years, experimental studies have been made of thermal decomposition of porous solids. Industries have been concerned with improving fuels such as coke and charcoal. The Forest Service has undertaken extensive investigations to understand the spread of forest fires and the effectivness of flame retardants. Insurance companies and agencies concerned with Building Codes are interested in fire spread in buildings, structural damage to supporting members and effects of different methods of fireproofing. Problems of self-heating and ignition also arise when materials are stored for long periods of time in ships and warehouses. Airlines are concerned with fire spread in the interiors of planes when cloth or plastic materials ignite. The Armed Forces study effects of flame weapons on combustible targets such as buildings,

wooden ships and fuel soaked earth. The study of nuclear weapon
effects presents problems involving ignition and sustained combustion.
Recently, the aerospace industry has been interested in heating ef-
fects on solids because of the use of char-forming ablative heat
shields on re-entry spacecraft. Another area of interest is the
study of effects of in-depth reactions on solid propellant combustion.
All industries are involved with the use of polymer foams. These
foams are used for electrical, thermal and acoustical insulation as
well as lightweight structural applications. Finally, cellulose
products used in the textile and paper industries are subject to
pyrolysis reactions. These few examples demonstrate the usefulness
of improving the mathematical analysis of pyrolysis of porous solids.

There are two main obstacles in performing an analysis; extreme
complexity in the physical processes and mathematical difficulties in
solving the resulting equations. In the present field, more is known
about the qualitative physical events than has been previously in-
corporated in the mathematical solution. However, large digital com-
puters have enabled more complex problems to be solved and, therefore,
more physically realistic models to be studied. Thus, the purpose of
the present work is to incorporate more of the known physical events
into the mathematical analysis of porous solid pyrolysis.

This report is composed of four major sections. The first sec-
tion presents background information as to the experimental results
that indicate the important physical events. Also included is a dis-
cussion of previous mathematical analyses. The second section out-
lines the development of the mathematical equations and boundary con-
ditions. The third section describes the method used in solving the

equations and the fourth section presents the results and interpretations of the computer solutions.

Background

Wood has been in use since the beginning of time and is still the widest used porous solid today. As a result, a great deal of experimental work has been done on wood and its components.

The three major components of wood are hemicellulose, cellulose, and lignin with approximately half being cellulose. The thermal decomposition rate of wood closely follows that of cellulose whereas hemicellulose decomposes faster, and lignin, slower. Thus, many experiments are done with cellulose to better understand the pyrolysis of wood and other materials. Also, cellulose can be made into homogeneous samples having a wide choice of closely controlled densities and physical constants.

Browne (5)[1] reviews the theories of the combustion of wood up to 1963 while MacKay (13) gives a review of information on the thermal degradation of cellulose up to 1967. Shafizadeh (17) presented, in 1968, a complete review of the experimental information on the pyrolysis and combustion of cellulosic materials and includes effects of flame-retarding chemicals.

In one type of experiment, a slab of cellulose is placed into a constant temperature furnace that is being flushed with an inert gas. Usually, the temperature at certain points is recorded as well as the

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[1]Throughout the report, numbers in parenthesis after a proper name refer to an entry in the Bibliography.

weight of the slab. As heat enters the cellulose, its temperature rises and causes pyrolysis reactions which produce a different solid and evolve gases. Since some solid has been changed to a gas the solid becomes more porous. The reactions proceed into the solid while the gases flow through the pores and out the surface. Higher temperatures increase the reaction rate, producing more gases and increasing the porosity. Thus, at a given instant, the solid is in various stages of decomposition ranging from the virgin material deep within the solid, through the more porous reacting solid, to the inert highly porous hot char next to the surface. Of course, continued heating to higher temperatures would eventually decompose the char. However, in most practical situations one is concerned with the events from the initial heating to the production of char.

The gases evolved from the reactions are very important in ignition and combustion studies since these gases may ignite and burn. The first gases that are formed are primarily non-combustible water vapor and carbon dioxide. Next, more combustible carbon monoxide, hydrogen and the highly inflammable levoglucosan, sometimes called tar, are evolved. Also produced are methane, formaldehyde, methanol and acids. Efforts in flame-proofing materials are directed toward producing less tar and more non-combustible gases. Thus, before a complete understanding of ignition and combustion stages can be obtained, a thorough investigation of the initial pyrolysis events must be made.

The first comprehensive analytical model of initial pyrolysis was formulated by Bamford, et al (1), in conjuction with their experiments on wood. Slabs of wood of various thicknesses were heated either on

both sides by flames from a burner or on one side by a radiant heater. Measurements were made of the central slab temperature, depth of char, and time required to achieve sustained burning for the flame heated slabs and piloted ignition[2] for the radiantly heated slabs.

In the analysis, the slabs were considered to behave as a one-dimensional solid heated by a surface-temperature-dependent convective heat flux. The unsteady heat conduction equation included a term for heat generation within the slab. Heat generation was considered to be from a single exothermic reaction and was expressed as a constant heat of reaction times a reaction rate. The reaction rate was expressed as a first-order, Arrhenius-type reaction.[3] In addition to the heat of reaction, Bamford assumed constant thermal conductivity, specific heat, surface heat transfer coefficient, activation energy and pre-exponential factor. The latter two constants were chosen by matching the calculated central slab temperature with the experimentally measured one. The temperature was found from the energy equation by a finite-difference method and the mass loss was determined by a finite-difference approximation to the species conservation equation. The calculations for the central temperature, based on a single overall reaction, did not agree with measured values when different slab thicknesses were used. This indicates that more than one reaction needs to be considered.

Weatherford (21) used the same constants and equations as Bamford

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[2]Piloted ignition occurs when a small flame placed near a heated surface acts as an ignition source for the evolving gases.

[3]An Arrhenius-type reaction is one that expresses the reaction rate constant as $k = a \exp(-E*/R°T*)$. See Nomenclature for the definition of the symbols.

and calculated the surface temperature and vapor-generation rate. Source temperatures considered for the convective boundary condition varied between 667°K and 767°K. Calculations were continued until the vapor generation rate reached 10^{-4} gm/cm^2-sec, became constant, or reached a maximum. He used a finite-difference technique and showed that undulations which Bamford found in the gas-generation rate curves were caused by too large a step size in the finite-difference approximations. Weatherford proposed that a criterion for wood to sustain stable burning would be the departure of its surface temperature or vapor-generation rate from the solution for the infinite thickness case.

Experiments were performed by Weatherford and Sheppard (22) on convectively heated slabs to determine piloted ignition times. Various slab thicknesses, bulk densities, and heat source temperatures were used. The data showed that small changes in density or slab thickness exerted significant influence on the ignition time. For the range of variables considered, the surface temperature calculated with the heat generation term included was within 10% of the solution for an inert slab.

Lawson and Simms (11) considered piloted and spontaneous ignition[4] of wood slabs heated on one side by radiation. Times to ignition were recorded for various radiation intensities and different species of wood. By extrapolating graphs of radiation intensity vs. ignition-time out to infinite time, a minimum intensity necessary for ignition was determined for slabs thick enough to be considered

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[4]Spontaneous ignition relies on the conditions of the heated material for ignition.

a semi-infinite solid. For most species, a constant minimum intensity was found for each of the two types of ignition.

Martin (14) heated thin cellulose slabs by radiation and measured (not all simultaneously) the spontaneous ignition time, temperatures within the slab, weight loss and composition of the gaseous products for various radiation intensities. The temperature profiles differed considerably from the theoretical ones for a semi-infinite, inert solid having constant thermal properties. A maximum in the rate of evolution of volatile products occurred near the ignition time but no evidence was found for an ignition criterion based on a threshold rate of volatile evolution. Evidence of competing reactions was seen by observing a different final weight of char for different heating rates. Char formed from the levoglucosan reaction was found to be negligible.

In the preceding ignition work, the two types of boundary conditions considered were a constant radiative heat flux and a convective heat flux. The combination of radiation heating with Newtonian cooling at the surface, considered by Lawson and Simms, can be considered as a psuedo-convective case. The factors which seem to be the most important in ignition are the gas composition and generation rate and surface temperature, all of which depend on the nature of the pyrolysis reactions. These factors were considered in developing the results of this study.

To obtain more information on the kinetics of reactions, techniques were developed by the physical chemists. Some of these techniques are Thermogravimetric analysis (TGA) and Differential Thermal analysis (DTA). A better understanding of the nature of the reactions helps to explain the causes of differing experimental results as well

as determining the effects of adding fire retardant chemicals.

Broido and Kilzer (4) presented a critique on the knowledge of the mechanism of cellulose pyrolysis to 1961 and indicated that more detail was needed in interpreting the reaction mechanism as well as in experimental studies. They pointed out that previous considerations of the reaction products as only gas, tar, and char failed to explain many of the observed experimental results. The important effects of trace impurities on the internal reactions caused many earlier experimental results to be questioned.

Kilzer and Broido (9) present data from a number of cellulose pyrolysis observations made by TGA, DTA, mass spectrometric thermal analysis (MTA) and gas and paper chromatographic analysis of the products. The results show that as a cellulose sample is heated, a slightly endothermic reaction starts at about 220°C causing the pure cellulose to lose water and form a "dehydrocellulose." (This is after vaporization of any extra-cellulosic moisture). Next, a strongly endothermic reaction becomes evident at about 280°C in which the remaining pure cellulose depolymerizes and volatilizes as tar, thus competing with the first reaction for the original cellulose. The third major reaction is strongly exothermic and results in the "dehydrocellulose" decomposing into a number of gaseous products and residual char. Each of the three processes actually involve a number of reactions. They concluded that the pyrolysis of cellulose must be described by at least two competing endothermic reactions and a consecutive exothermic reaction.

Broido (3) presents TGA and DTA results of cellulose containing practically no contamination (<.01%) and containing as much as 1.5%

$KHCO_3$. The results showed that as little as 0.15% contamination can significantly affect the pyrolysis reactions. The addition of 1.5% $KHCO_3$ lowered by 80°C the temperature at which significant decomposition began but eliminated the flame-producing reactions in favor of those leading to glowing combustion.

Tang and Neill (18), in their experiments on the effects of salts on wood and its components, supported the reaction stages described by Broido. They showed that the effect of the salts was to lower the overall activation energy, stimulating the dehydration reaction.

Further effects of multiple reactions were seen when Murty and Blackshear (15) showed that the overall activation energy decreased with radius for heated cylinders of cellulose. The frequency factor varied unsystematically while incubation of the interior caused the amount of solid that occurred at a given temperature to decrease toward the center. This also suggests that the reaction rate decreased toward the center.

Tinney (20) heated small wooden dowels in a constant temperature furnace and measured the center temperature and rate of weight loss. During his calculations for temperature and weight loss, he changed the overall activation energy, frequency factor and heat of reaction to a new value in an attempt to simulate the apparent changes during wood pyrolysis. He obtained fair agreement between experimental and calculated values for the surface temperature and weight loss but poor agreement for the center temperature. He concluded that more than one change in the parameters would be necessary to match the center temperatures for exothermic reactions.

Thus, investigations into the reaction mechanisms of cellulose

have shown the existence of and provided information on multiple reactions while pyrolysis experiments have shown the need for consideration of more than one overall reaction.

The same pattern of three major reactions in porous cellulose is found in the study of the pyrolysis of polymer foams. Hilado (8) describes the combustion process of urethane foams which parallels similar events seen in cellulose and other organic polymers. Tilley, et al (19), include DTA and TGA analysis of the pyrolysis of urethane foams and find three major regions of weight loss as a function of temperature. They associate the weight loss regions with three major reactions whose rates were fitted to the Arrhenius equation. Learmonth and Osborn (12) present the results of the pyrolysis of phenolic resins and describe three main types of products; gases, tars, and carbon residue. As with cellulose, the above references indicate that the nature of the products and the rate of decomposition of polymer foams vary with temperature, rate of temperature rise, and endothermic and exothermic reactions. Thus, learning how different factors influence the pyrolysis of cellulose will contribute to the understanding of the pyrolysis of many organic polymers as well as cellulose and wood.

In summary, the mathematical analysis of the pyrolysis of cellulose or wood has been limited to consideration of the unsteady heat conduction equation with heat generation from one exothermic reaction. Experiments have shown that more than one reaction needs to be considered and should include competing and consecutive, endothermic and exothermic reactions. The effect of a density-dependent effective thermal conductivity also needs to be studied. Also, since previous

mathematical studies involved specific ignition events with limited parameter values, a general analysis is needed to establish the relevant parameters and present results of the influence of parameter variations on the pyrolysis events. The development and solution of the equations as given in the remaining sections will be pointed toward these objectives.

CHAPTER II

THE MATHEMATICAL ANALYSIS

Geometry

As shown in Figure 1, the porous solid is considered to be an
infinite slab of finite thickness, L. The slab is heated at the front
surface and insulated against heat or mass transfer at the back sur-
face. These conditions also apply to one-half of a slab of thickness
2L that is symmetrically heated.

Two types of heating conditions will be considered for depositing
energy at the front surface. The first is a time-dependent, radiative
heat flux and the second is a convective heat flux.

Energy Equation

Heat is transferred into the slab from the surface by conduction
and causes chemical reactions which either absorb or generate heat.
Gaseous products that are formed from the reactions flow out of the
solid. It is assumed that any heat transferred between the flowing
gases and the solid does not significantly change the solid tempera-
ture. This is approximately true since the increasing porosity and
cracks allow the gas to flow out with little solid area contact and
short residence time.

Specific heat and thermal conductivity of the solid material are
considered constant for the ranges in temperatures to be encountered.

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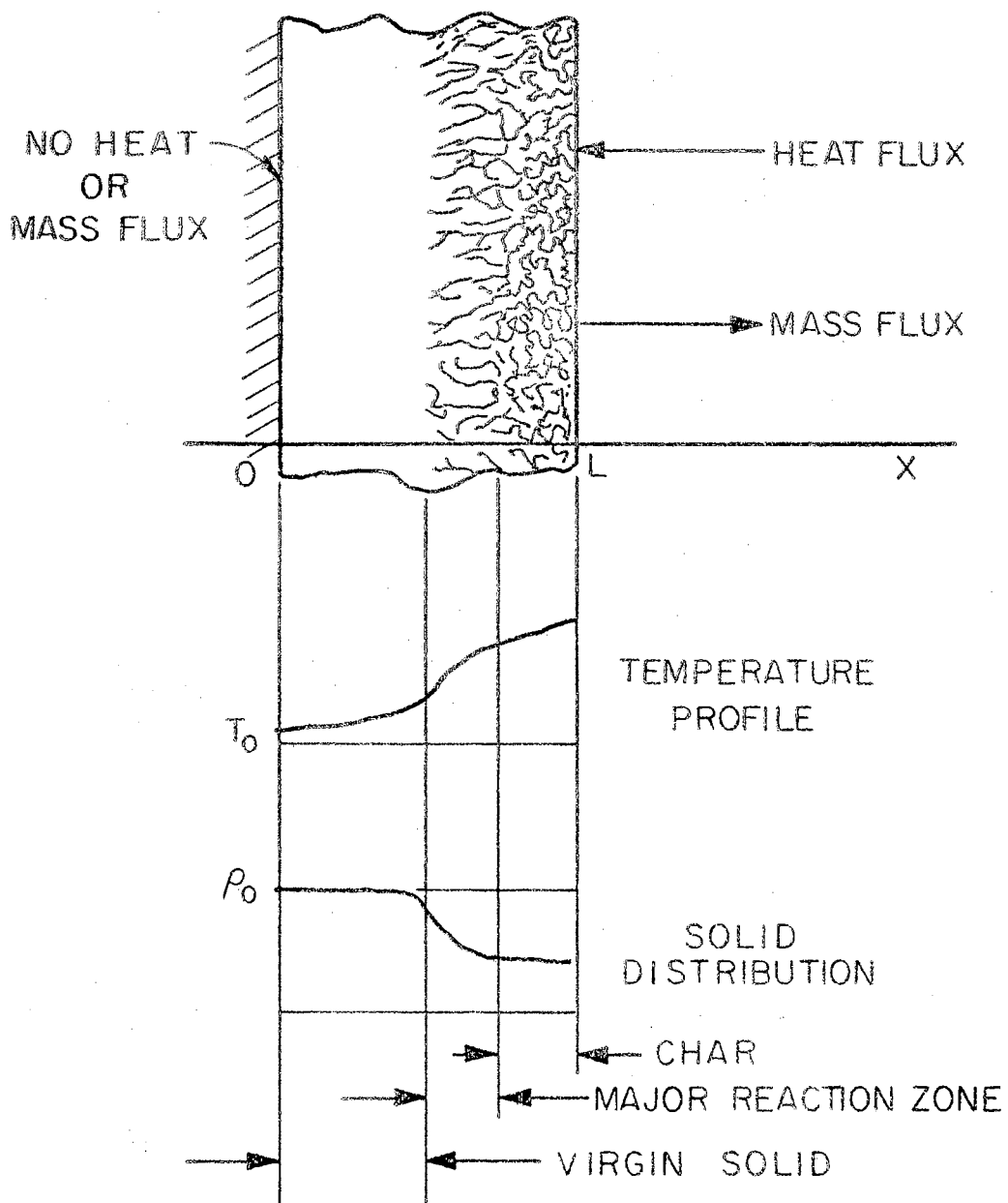
Figure 1. Porous Solid Being Heated

Also, the heats of reaction per mass of reactant are constant. Finally, the dimensions of the slab are assumed constant and a psuedo-density ρ^*, based on a constant unit volume, will be used.

With these considerations, the energy equation for the solid can be written by applying the conservation of energy to a differential volume and taking the limit as the thickness goes to zero. The result is valid at every x-position within the solid and is given by

$$\rho^* c \frac{\partial T^*}{\partial t^*} = \frac{\partial}{\partial x^*}(K \frac{\partial T^*}{\partial x^*}) + \dot{Q}' \qquad (2.1)$$

$$\underset{I}{} \qquad \underset{II}{} \qquad \underset{III}{}$$

Term I   = Rate of accumulation of thermal energy per unit volume

Term II = Net rate of conduction of thermal energy per unit volume

Term III = Rate of heat generation by chemical reaction per unit volume

Effective Thermal Conductivity

The cross section of a porous solid can be divided into two areas; the area occupied by solid material, A_{solid}, and the void area occupied by gas (see Figure 2).
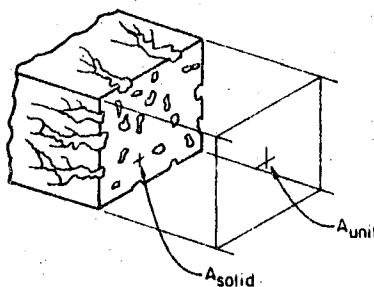
Figure 2.   Representation of Unit
and Solid Areas

Heat conduction in the slab occurs only through the solid area, A_{solid}. Since the solid area changes, it is more convenient to base the equations on the total unit area, A_{unit}, which is constant because of the assumption that the slab dimensions are constant. Thus, an effective conductivity, K, based on the total unit area is defined by

$$K \, A_{unit} = \overline{K} \, A_{solid}$$

where $\overline{K}$ is the thermal conductivity of the solid material and is considered constant. The ratio of the areas can be expressed as a density ratio by considering a unit thickness. Then,

$$\frac{A_{solid}}{A_{unit}} = \frac{\rho*}{\overline{\rho*}}$$

where $\overline{\rho*}$ is the density of the solid material (i.e., no porosity) and is considered constant.

With the above equations, an expression for the effective thermal conductivity becomes

$$K = K_0 \, \frac{\rho*}{\rho_0^*} \tag{2.2}$$

where K_0 and ρ_0^* are the effective conductivity and density at time 0.

Substituting Equation (2.2) into term II of Equation (2.1), expanding and dividing by $\rho* C$ gives

$$\frac{\partial T*}{\partial t*} = \frac{K_0}{\rho_0^* C} \frac{\partial^2 T}{\partial x*^2} + \frac{K_0}{\rho_0^* C \rho*} \frac{\partial \rho*}{\partial x*} \frac{\partial T*}{\partial x*} + \frac{\dot{Q}'}{\rho* C} \tag{2.3}$$

$$\text{I} \qquad \text{IIa} \qquad \text{IIb} \qquad \text{III}$$

Previous investigators did not consider that the changing effective

thermal conductivity affected the energy equation. They argued in-correctly that since the thermal diffusivity, K/ρ*C, remained constant, then term IIa was the only conduction contribution. This approximation can only be true if term IIb is negligible. From another viewpoint, we might consider that previous workers have unintentionally combined terms IIb and III into a new, equivalent, heat generation term. Term IIb will always be negative or zero and thus introduces an equivalent endothermic heat generation term that will vary throughout the slab as well as time. As a result, heat generation calculations based on an energy equation that considers the effective thermal conductivity to be a constant may calculate values that largely include a distance and time dependency from the conductivity change. This investigation will include calculations to determine how a density-dependent thermal conductivity may affect the results.

<div align="center">Boundary Conditions</div>

Consideration of a surface with changing porosity introduces several possibilities for the surface heating conditions. For the radiant heat flux[1] condition, all the energy strikes the solid either at the surface or at some small depth due to the pores (see Figure 3).

It is assumed that the depth at which the energy is deposited is small enough to consider it all at the surface. Therefore, the amount of radiant energy striking the surface is not dependent on the amount of solid present. The rate at which the energy is conducted into the solid, however, is dependent on the porosity through the effective

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[1]Heat flux refers to the total energy per constant unit area per unit time.
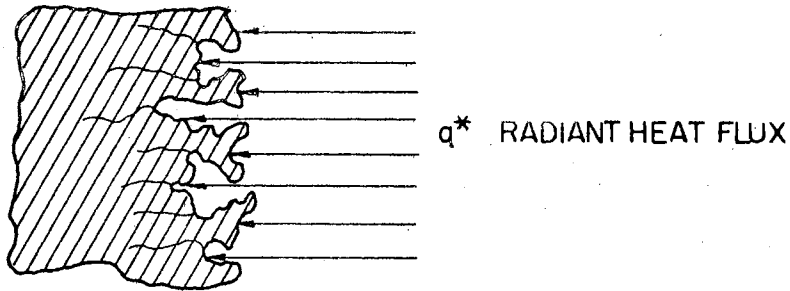
Figure 3. Radiant Heat Flux Deposited at the
Surface

thermal conductivity. Thus, the first possibility is a time-dependent

heat flux at the surface with a density-dependent, effective thermal

conductivity. This condition will be called Case 1. For comparison

purposes, Case 0 will denote problems with the heat flux treated as in

Case 1 but with the effective thermal conductivity considered constant.

Another possibility is when the energy deposited at the surface

decreases in proportion to the amount of solid at the surface. This

is difficult to justify physically but might approximate a radiative

heat flux reduced by opaque gases flowing from the solid or, if energy

was lost from the surface by re-radiation and conduction to the gases

at an equivalent rate. The resulting condition is the same as Case 0

but with term IIb included in the energy equation (2.3). Thus, the

contribution of the change in the effective thermal conductivity to the

energy equation can be found. This condition will be called Case 2.

For the convective heat flux condition, three cases also are de-

veloped. Case 0 considers no change in the effective thermal conduc-

tivity and a constant convective heat transfer coefficient. Case 1

considers a density-dependent, effective thermal conductivity and a
constant convective heat transfer coefficient. This is equivalent to
saying that the convective fluid at the surface is always in contact
with the solid as the surface becomes more porous. Case 2 considers
that the convective heat transfer coefficient and the effective ther-
mal conductivity decrease as the solid at the surface decreases. This
would mean that the convective gases were in contact with the solid
that was present only at the surface (see Figure 4).
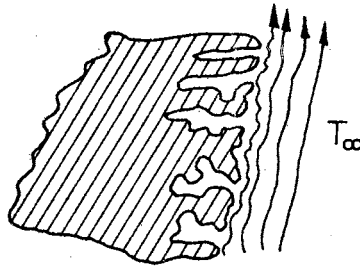
Figure 4. Convective Heat
Flux at the
Surface

Cases 1 and 2 represent an upper and lower bound on the physical
events for the convective case with the intermediate Case 0 probably
being a good assumption.

At the instant heat is applied, the slab, $solid_1$, is at a constant
temperature and density. With the insulated boundary at $x^* = 0$ and the
heated surface at $x^* = L$, the boundary conditions for radiant and con-
vective heating become

For time = 0

$$T*(x*, 0) = T_0^*$$
(2.4a)

$$\rho*(x*, 0) = \rho_1^*(x*, 0)$$
(2.4b)

$$\rho_i^*(x*, 0) = 0, \quad i = 2, 3, \ldots, 6$$
(2.4c)

At $x* = 0$

$$\frac{\partial T*}{\partial x*} = 0$$
(2.4d)

$$\frac{\partial \rho*}{\partial x*} = 0$$
(2.4e)

At $x* = L$: Type I (Radiative)

Case 0
$$K_0 \frac{\partial T*}{\partial x*} = q*(t*)$$
(2.4f)

Case 1
$$K_0 \frac{\rho*}{\rho_0^*} \frac{\partial T*}{\partial x*} = q*(t*)$$
(2.4g)

Case 2
$$K_0 \frac{\partial T*}{\partial x*} = q*(t*)$$
(2.4h)[2]

At $x* = L$: Type II (Convective)

Case 0
$$K_0 \frac{\partial T*}{\partial x*} = h(T_\infty^* - T*)$$
(2.4i)

Case 1
$$K_0 \frac{\rho*}{\rho_0^*} \frac{\partial T*}{\partial x*} = h(T_\infty^* - T*)$$
(2.4j)

Case 2
$$K_0 \frac{\partial T*}{\partial x*} = h(T_\infty^* - T*)$$
(2.4k)[2]

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[2]Equations (2.4h, k) would normally have the term $\rho*/\rho_0^*$ multiplying the terms on both sides of the equal sign but is shown already canceled.

Equation (2.4) represents the boundary conditions that will be used with the energy and species equations for completely specifying the problem. Equation (2.4e) can be determined by taking the x-derivative of the species equations (see Appendix F).

Chemical Reactions

The reactions that will be considered are shown in Figure 5 with identification of each species for the case of cellulose. Of course, the same reaction scheme or any combination of the reactions may be used for many other materials.

Even though these reactions represent only the overall effects of a number of reactions, they include the major pyrolysis events in most porous solids. Also, three competitive and consecutive reactions are just enough to enable a large number of possible effects to be studied.

Steps leading to expressions for the heat generated by the reactions and the rate of species production begin with writing the reactions on a mole basis:

$$S_1 \xrightarrow{k_1} b_2 S_2 + b_3 G_3$$

$$S_1 \xrightarrow{k_2} b_4 G_4$$

$$S_2 \xrightarrow{k_3} b_6 S_6 + b_5 G_5$$
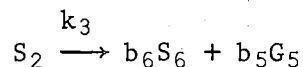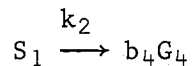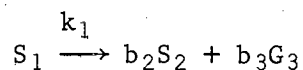
where S = Solid, G = Gas, k_i = rate of reaction i, $b_i = \dfrac{\text{moles of Species } i}{\text{mole of reactant}}$. Let M_i = Molecular weight of Species i. Then, mass is conserved if

$$M_1 = b_2 M_2 + b_3 M_3 \qquad \text{for reaction 1}$$
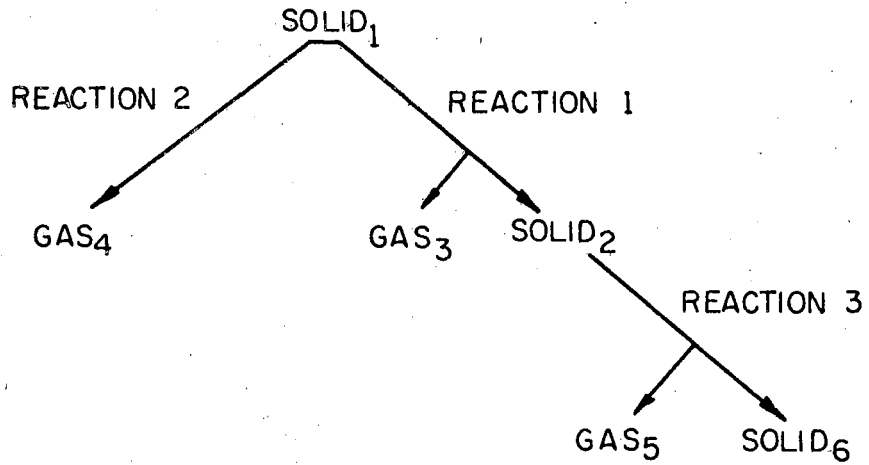
REACTIONS 1 and 2 are COMPETITIVE

REACTIONS 1 and 3 are CONSECUTIVE

For Cellulose:

$Solid_1$ = original cellulose

$Solid_2$ = "dehydrocellulose"

Gas_3 = water vapor

Gas_4 = "tar" (levoglucosan)

Gas_5 = CO, CO_2, H_2O, etc.

$Solid_6$ = char

Figure 5. Reactions in the Slab

$$M_1 = b_4M_4 \qquad \text{for reaction 2}$$

$$M_2 = b_6M_6 + b_5M_5 \qquad \text{for reaction 3.}$$

Letting $\qquad c_1 = b_2M_2/M_1 = \text{gm } S_2/\text{gm } S_1 \qquad 0 \leq c_1 \leq 1$

$$c_2 = b_6M_6/M_2 = \text{gm } S_6/\text{gm } S_2 \qquad 0 \leq c_2 \leq 1$$

the reactions may then be written on a gram basis noting that

$1 = b_4M_4/M_1$

$$S_1 \xrightarrow{k_1} c_1S_2 + (1 - c_1) \, G_3 \qquad\qquad (2.5a)$$

$$S_1 \xrightarrow{k_2} G_4 \qquad\qquad (2.5b)$$

$$S_2 \xrightarrow{k_3} c_2S_6 + (1 - c_2) \, G_5 \qquad\qquad (2.5c)$$
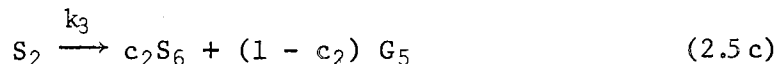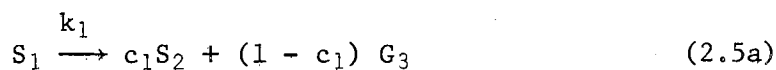
It is assumed that all reactions are first-order[3] homogeneous reactions, i.e., the rate of decrease of reactant is proportional to the amount of reactant present. The proportionality constant is given by the reaction rate constant. It is expected that basic homogeneous reactions will be first order. However, when several reactions are occurring simultaneously, the resulting overall effect may be of zero order or some intermediate value. Shafizadeh (17) discusses experimental results that determine the order of cellulose reactions, most of which indicate the reactions to be first order with some reports of zero order depending on the experiment. Most analyses also consider the reactions to be first order.

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[3]Order refers to the exponent on the mass term in the reaction rate equation, $(d\rho_1^*)/(dt^*) = -\rho_1^* k_1$.

With the reaction order specified, the rate of species production can be expressed.

Let $\overset{\circ}{m}'_{i,j}$ = rate of generation of species i per unit volume as a result of reaction j. Then,

$$\dot{m}'_{1,1} = -\rho_1^* k_1 \; ; \qquad \dot{m}'_{2,1} = c_1 \rho_1^* k_1 \; ; \qquad \dot{m}'_{3,1} = (1 - c_1) \, \rho_1^* k_1$$

$$\dot{m}'_{1,2} = -\rho_1^* k_2 \; ; \qquad \dot{m}'_{4,2} = \rho_1^* k_2$$

$$\dot{m}'_{2,3} = -\rho_2^* k_3 \; ; \qquad \dot{m}'_{6,3} = c_2 \rho_2^* k_3 \; ; \qquad \dot{m}'_{5,3} = (1 - c_2) \, \rho_2^* k_3$$

Now, the total rate of generation of species i is found by summing over all reactions.

$$\dot{m}'_i = \sum_j \dot{m}'_{i,j}$$

$$\dot{m}'_1 = -\rho_1^* k_1 - \rho_1^* k_2 \tag{2.6a}$$

$$\dot{m}'_2 = c_1 \rho_1^* k_1 - \rho_2^* k_3 \tag{2.6b}$$

$$\dot{m}'_3 = (1 - c_1) \, \rho_1^* k_1 \tag{2.6c}$$

$$\dot{m}'_4 = \rho_1^* k_2 \tag{2.6d}$$

$$\dot{m}'_5 = (1 - c_2) \, \rho_2^* k_3 \tag{2.6e}$$

$$\dot{m}'_6 = c_2 \rho_2^* k_3 \tag{2.6f}$$

For the heat of reaction given as Q_i = heat generated in reaction i per unit mass reacted and for $\dot{Q}'_i$ = rate of generation of heat per unit volume in reaction i, then,

$$\dot{Q}'_1 = Q_1 \dot{m}'_{1,1} \; ; \qquad \dot{Q}'_2 = Q_2 \dot{m}'_{1,2} \; ; \qquad \dot{Q}'_3 = Q_3 \dot{m}'_{2,3} \; .$$

Summing over all reactions, $\sum\limits_{i} \dot{Q}'_i$, gives the total rate of generation of heat per unit volume, $\dot{Q}'$, or also

$$\dot{Q}' = -Q_1 \rho_1^* k_1 - Q_2 \rho_1^* k_2 - Q_3 \rho_2^* k_3 \qquad (2.7)$$

For the reaction rate constant, k_i, the usual assumption is made that the dependency of the rate of reaction i on the temperature is given by the Arrhenius expression, $k_i = a_i \exp(-E_i^*/R^\circ T^*)$.

Species Equations

The conservation of a solid species within a unit volume requires that the rate of accumulation of a species within the volume equals the rate of production of the species from chemical reactions. Taking the limit as the volume thickness goes to zero gives an equation that is valid at any x-position,

$$\frac{\partial \rho_1^*}{\partial t^*} = \dot{m}'_i \; .$$

Since the species production equations are given by Equation (2.6), the rate of change of each solid species at any position within the slab is

$$\frac{\partial \rho_1^*}{\partial t^*} = -\rho_1^* k_1 - \rho_1^* k_2 \qquad (2.8a)$$

$$\frac{\partial \rho_2^*}{\partial t^*} = c_1 \rho_1^* k_1 - \rho_2^* k_3 \qquad (2.8b)$$

$$\frac{\partial \rho_6^*}{\partial t^*} = c_2 \rho_2^* k_3 \qquad (2.8c)$$

Non-Dimensional Equations

The equations and boundary conditions are non-dimensionalized in order to determine relevant parameter groupings and minimize the number of parameters which affect the calculations. Reference values used to non-dimensionalize the variables are selected as being a characteristic dimension of the problem. Usually, the reference value will enable the non-dimensional quantity to have an order of magnitude of unity. For the slab, the independent variables, x^* and t^*, are non-dimensionalized by the slab thickness and the characteristic conduction time, the Fourier number. The dependent variables ρ_i^* are non-dimensionalized by the initial density, ρ_0^*. The temperature is non-dimensionalized by consideration of the boundary conditions. The resultant non-dimensional variables are given in Table I (see Nomenclature for symbol identification).

TABLE I

NON-DIMENSIONAL VARIABLES

<u>Dependent Variables</u>

$$T_R = \frac{T^* - T_0^*}{q_0^* L / K_0}$$

$$T_C = \frac{T^* - T_0^*}{T_\infty^* - T_0^*}$$

$$q = \frac{q^*}{q_0^*}$$

$$\rho_i = \frac{\rho_i^*}{\rho_0^*}$$

$$w = \frac{w^* C L}{K_0}$$

<u>Independent Variables</u>

$$x = \frac{x^*}{L}$$

$$t = \frac{K_0 t^*}{\rho_0^* C L^2}$$

When the non-dimensional variables are substituted into the energy equation (2.3), the species equation (2.8), and the boundary conditions (2.4), the reference quantities become grouped into non-dimensional parameters. It is the value of the particular combination of reference quantities as given in the new parameters that determine the character of the solutions rather than the values of the reference quantities themselves. The resulting new parameters are given in Table II.

TABLE II

NON-DIMENSIONAL PARAMETERS

Definition	Description
$E_i = \dfrac{E_i^*}{R^\circ T_0^*}$	Activation Energy Parameter
$F_i = \dfrac{K_0(1/a_i)}{\rho_0^* C L^2}$	Frequency Factor Parameter
$R_i = \dfrac{Q_i}{C T_0^*}$	Heat of Reaction Parameter
$G = \begin{cases} \dfrac{q_0^* L}{K_0 T_0^*} & \text{(Radiative)} \\[2ex] \dfrac{T_\infty^* - T_0^*}{T_0^*} & \text{(Convective)} \end{cases}$	Heat Flux Parameter
$Nu = \dfrac{hL}{K_0}$	Nusselt Number

The resulting non-dimensional energy equation is

$$\frac{\partial T}{\partial t} = \frac{\partial^2 T_2}{\partial x^2} + \frac{1}{\rho}\frac{\partial \rho}{\partial x}\frac{\partial T}{\partial x} - \frac{R_1}{F_1 G}\left(\frac{\rho_1}{\rho}\right)\bar{k}_1 - \frac{R_2}{F_2 G}\left(\frac{\rho_1}{\rho}\right)\bar{k}_2 - \frac{R_3}{F_3 G}\left(\frac{\rho_2}{\rho}\right)\bar{k}_3 \quad (2.9)$$

The non-dimensional species equations are

$$\frac{\partial \rho_1}{\partial t} = -\rho_1\left(\frac{\bar{k}_1}{F_1} + \frac{\bar{k}_2}{F_2}\right) \tag{2.10a}$$

$$\frac{\partial \rho_2}{\partial t} = c_1\rho_1\frac{\bar{k}_1}{F_1} - \rho_2\frac{\bar{k}_3}{F_3} \tag{2.10b}$$

$$\frac{\partial \rho_6}{\partial t} = c_2\rho_2\frac{\bar{k}_3}{F_3} \tag{2.10c}$$

where $\bar{k}_i = \exp[-E_i/(1 + GT)]$. Finally, the non-dimensional boundary conditions are

$t = 0$:

$$T(x, 0) = 0 \tag{2.11a}$$

$$\rho(x, 0) = 1 = \rho_1(x, 0) \tag{2.11b}$$

$$\rho_i(x, 0) = 0 , \quad i = 2, 3, \ldots, 6 \tag{2.11c}$$

$x = 0$:

$$\frac{\partial T}{\partial x} = 0 \tag{2.11d}$$

$$\frac{\partial \rho_i}{\partial x} = 0 , \quad i = 1, 2, \ldots, 6 \tag{2.11e}$$

$x = 1$: Type I (Radiative)

Case 0 $$\frac{\partial T}{\partial x} = q(t) \tag{2.11f}$$

Case 1 $$\frac{\partial T}{\partial x} = \frac{q(t)}{\rho(1, t)} \tag{2.11g}$$

Case 2 $\qquad \dfrac{\partial T}{\partial x} = q(t)$ $\qquad\qquad$ (2.11h)

x = 1: Type II (Convective)

$\qquad$ Case 0 $\qquad \dfrac{\partial T}{\partial x} = Nu\ (1 - T)$ $\qquad\qquad$ (2.11i)

$\qquad$ Case 1 $\qquad \dfrac{\partial T}{\partial x} = \dfrac{Nu\ (1 - T)}{\rho(1,\ t)}$ $\qquad\qquad$ (2.11j)

$\qquad$ Case 2 $\qquad \dfrac{\partial T}{\partial x} = Nu\ (1 - T)$ $\qquad\qquad$ (2.11k)

Therefore, the problem to be solved consists of Equations (2.9), (2.10), and (2.11).

CHAPTER III

SOLUTION OF THE EQUATIONS

Background

There are basically two approaches available for the computer

solution of non-linear partial differential equations. The first is

the finite-difference method where the derivatives are replaced by

finite differences. At each step, a system of linear algebraic equa-

tions must be solved. Computer programs are usually complex and re-

quire large core storage. The second approach is the integral method.

Basically, it reduces the partial differential equations to a system

of ordinary differential equations by integrating over one variable.

The ordinary differential equations can then be solved by any one of

a number of highly developed techniques.

There have been a number of different integral approaches used

to reduce the partial differential equations. The simplest approach

is to divide the region of integration into strips and replace the

derivatives across the strips by finite differences. However, a large

number of strips are required to obtain good accuracy. Other simple

techniques have been discussed by Goodman (7).

Method of Integral Relations

Berlotserkovskii and Chushkin (2) present the essential features

of the method of Integral Relations, as generalized by Dorodnitsyn, and

discuss a number of sample problems in the field of Gas Dynamics. This method offers the best accuracy and the fewest number of necessary approximating strips of any of the integral techniques.

The basic approach is to multiply the partial differential equation by a "weighting" function, $f(x)$, and then integrate with respect to its independent variable. Functions within the integrals are then approximated by an interpolation formula. This enables the integrals to be evaluated and results in a system of ordinary differential equations in the remaining independent variable. The final system of equations can then be solved by such standard techniques as Runga-Kutta or an Adams method. The accuracy of the method is improved by increasing the number of strips in the region.

In contrast to a finite difference technique, this method approximates an integral instead of a derivative. Thus, the approximated function is smoother than the integrand and can be represented by a smaller number of interpolation strips. Also, the integral can be continuous even when the integrand is discontinuous. Another consideration is that computer storage requirements are small.

The weighting functions used to multiply the partial differential equations are arbitrarily chosen except for some general restrictions. They must generate as many independent partial differential equations as there are interpolating points and thus must be linearly independent. They are also used to insure convergence of an integrand at any point within the region. Finally, they should enable the approximating functions to be more accurate in regions of greater importance.

Application of the Method of Integral Relations

The energy equation (2.9) along with the boundary conditions (2.11) will be reduced by applying the method of Integral Relations to the x-variable. The Integral method will not need to be applied to the species equations (2.10) since they do not contain derivatives with respect to x.

The first step is to multiply the energy equation (2.9) by a weighting function $f_m(x)$ and then integrate between the slab bound-aries. The result is

$$\int_0^1 f_m(x) \frac{\partial T}{\partial t} \, dx = \int_0^1 f_m(x) \frac{\partial^2 T}{\partial x^2} \, dx + \int_0^1 f_m(x) \frac{1}{\rho} \frac{\partial \rho}{\partial x} \frac{\partial T}{\partial x} \, dx$$

$$- \frac{1}{G} \sum_{i=1}^3 \int_0^1 f_m(x) \, \overline{H}_i \, dx \qquad (3.1)$$

where $\qquad \overline{H}_1 = \frac{R_1}{F_1} \left(\frac{\rho_1}{\rho}\right) \overline{k}_1 \qquad (3.2a)$

$$\overline{H}_2 = \frac{R_2}{F_2} \left(\frac{\rho_1}{\rho}\right) \overline{k}_2 \qquad (3.2b)$$

$$\overline{H}_3 = \frac{R_3}{F_3} \left(\frac{\rho_2}{\rho}\right) \overline{k}_3 \qquad (3.2c)$$

Next, the slab is divided into (N - 1) strips by (N - 2) equally spaced planes parallel to the boundaries x = 0 and x = 1. With the boundaries, this gives N points where the equations and boundary con-ditions will be applied, (N ≥ 2). Therefore, there must be N inde-pendent equations like equation (3.1). This is obtained by choosing a system of linearly independent weighting functions, $f_m(x)$, with m = 1, 2, . . ., N. Since the temperatures increase toward the heated surface, x = 1, this region will have a greater importance in the

problem than the back surface, x = 0. Therefore, the weighting func-
tions will be selected to give more "weight" to this region and enable
the approximations to be more accurate. The linearly independent
functions are chosen as

$$f_m(x) = [1, x, x^2, \ldots, x^{(N-1)}]$$

i.e., $\qquad f_m(x) = x^{(m-1)}, \qquad (m = 1, 2, \ldots, N) \qquad (3.3)$

With this set of f_m's, Equation (3.1) becomes[1]

$$\frac{d}{dt} \int_0^1 x^{(m-1)} T\, dx = \left.\frac{\partial T}{\partial x}\right|_{x=1} - (m-1)\, T\Big|_{x=1} + \left\{ \begin{array}{ll} T\big|_{x=0} & ; \ m = 2 \\ 0 & ; \ m \neq 2 \end{array} \right\}$$

$$+ (m-1)(m-2) \int_0^1 x^{(m-3)}\, T\, dx + \left(\ell n\, \rho \cdot \frac{\partial T}{\partial x}\right)_{x=1}$$

$$- \int_0^1 x^{(m-1)}\, \ell n\, \rho \cdot \frac{\partial^2 T}{\partial x^2}\, dx$$

$$- (m-1) \int_0^1 \ell n\, \rho \cdot x^{(m-2)}\, \frac{\partial T}{\partial x}\, dx$$

$$- \frac{1}{G} \sum_{i=1}^{3} \int_0^1 x^{(m-1)}\, \overline{H}_i\, dx, \qquad (m = 1, 2, \ldots, N)$$

$$(3.4)$$

In the next step, the integrands are approximated by polynomials
in x with time-dependent coefficients. The number of terms will equal
the number of interpolation points, N, plus any additional terms that
can be determined from applying the boundary conditions. Thus, the

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[1]See Appendix A.

temperature can be approximated with a polynomial having (N + 2) terms since two boundary conditions for the temperature derivative are known. The approximations will then be

$$T(x, t) = \sum_{n=1}^{N+2} A_{(n)}(t) \cdot x^{(n-1)} \qquad (3.5a)$$

$$\ln \rho \cdot \frac{\partial^2 T}{\partial x^2} = \sum_{n=1}^{N} J_{1(n)}(t) \cdot x^{(n-1)} \qquad (3.5b)$$

$$\ln \rho \cdot \frac{\partial T}{\partial x} = \sum_{n=1}^{N} J_{2(n)}(t) \cdot x^{(n-1)} \qquad (3.5c)$$

$$\overline{H}_i = \frac{R_i}{F_i} \sum_{n=1}^{N+1} H_{i(n)}(t) \cdot x^{(n-1)} \qquad (3.5d)$$

The problem now centers around finding the polynomial coefficients, and thus, the temperature as given by Equation (3.5a). Substituting the approximations (3.5) into Equation (3.4) and integrating[2] gives N equations for the temperature coefficients, $A_{(n)}(t)$:

$$\frac{1}{m} \frac{dA_{(1)}}{dt} + \sum_{n=1}^{N} \left(\frac{1}{m+n+1}\right) \frac{dA_{(n+2)}}{dt} = (1 + \ln \rho) \left. B \right|_{x=1}$$

$$- (m - 1) \sum_{n=1}^{N} \left(\frac{n+1}{m+n-1}\right) A_{(n+2)}$$

$$- \sum_{n=1}^{N} \left(\frac{1}{m+n-1}\right) J_{1(n)}$$

$$- (m - 1) \sum_{n=1}^{N-1} \left(\frac{1}{m+n-1}\right) J_{2(n+1)}$$

$$- \frac{1}{G} \sum_{i=1}^{3} \frac{R_i}{F_i} \sum_{n=1}^{N+1} \left(\frac{1}{m+n-1}\right) H_{i(n)}$$

$$(m = 1, 2, \ldots, N) \qquad (3.6)$$

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[2]See Appendix B.

Another equation must be included with Equation (3.6) in order to solve

for the (N + 1) unknowns. This equation is formed by using the temper-

ature approximation (3.5a) in one of the boundary conditions (2.11f-k),

depending on the Type and Case, and then differentiating with respect

to time. The results for Case 1 are

$$\sum_{n=1}^{N+2} (n - 1) \frac{dA_{(n)}}{dt} = (q)(\frac{-1}{\rho^2(1, t)}) \frac{d\rho(1, t)}{dt} + \frac{1}{\rho} \frac{dq}{dt} , \text{ Type I} \quad (3.7a)$$

$$\sum_{n=1}^{N+2} (\frac{N}{\rho} + n - 1) \frac{dA_{(n)}}{dt} = [\frac{-N(1 - T)}{\rho^2} \frac{d\rho}{dt}]_{x=1} , \text{ Type II} \quad (3.7b)$$

Equations (3.6) and (3.7) form a set of (N + 1) equations each contain-

ing (N + 1) ordinary first-order derivatives of the temperature coeffi-

cients on the left side. The derivatives are equated to terms composed

only of the temperature coefficients and species densities. Thus, this

system of equations can be solved simultaneously to give an explicit

equation in canonical form for each of the derivatives of the tempera-

ture coefficients.

The time-dependent coefficients in Equations (3.5b, c, d) are

determined by evaluating the approximations at each of the N strips,

$x = x_j$. For example, Equation (3.5b) would become

$$\sum_{n=1}^{N} J_{1(n)}(t) \cdot x_j^{(n-1)} = \ell n \rho (x_j, t) \cdot \sum_{n=1}^{N+2} (n - 1) A_{(n)}(t) \cdot x_j^{(n-2)}$$

$$(j = 1, 2, \ldots , N)$$

A set of algebraic equations are thus formed for each approximation

and can be solved simultaneously for the coefficients. The additional

term in Equation (3.5d) is found by taking the x-derivatives of the

approximation and the approximated function, Equation (3.2), and apply-ing the boundary conditions (2.11d and e).

The remaining unknowns are the solid species 1, 2, and 6. As stated previously, the equations defining the time derivatives of the species, Equation (2.10), do not contain x-derivatives and thus do not need to be integrated with respect to x. By treating x as a parameter, the species equations are applied at each x_j to obtain a set of N first order ordinary differential equations already in canonical form for each solid species. Thus, at $x = x_j$, $j = 1, 2, \ldots, N$

$$\frac{d\rho_{1,j}}{dt} = -\rho_{1,j} \left(\frac{\overline{k}_{1,j}}{F_1} + \frac{\overline{k}_{2,j}}{F_2} \right) \tag{3.8a}$$

$$\frac{d\rho_{2,j}}{dt} = c_1 \rho_{1,j} \frac{\overline{k}_{1,j}}{F_1} - \rho_{2,j} \frac{\overline{k}_{3,j}}{F_3} \tag{3.8b}$$

$$\frac{d\rho_{6,j}}{dt} = c_2 \rho_{2,j} \frac{\overline{k}_{3,j}}{F_3} \tag{3.8c}$$

where

$$\overline{k}_{i,j} = \exp\left[\frac{-E_i}{1 + G \sum_{n=1}^{N+2} A_{(n)} x_j^{(n-1)}} \right]$$

In summary, there are $(4N + 2)$ first-order differential equations of the form

$$\frac{df_j}{dt} = F_j(f_1, f_2, \ldots, f_{Ne}, t) \qquad Ne = 4N + 2$$

resulting from $(N + 2)$ equations for the temperature coefficients and N equations for each of the three solid species. The system of equa-tions was then solved by a general integration subroutine which

employed an Adams-Moulton technique (10).

Initial Conditions

In order to start the solution for the $(4N + 2)$ unknowns, their initial values must be given. The temperature approximation (3.5) is used in the boundary conditions (2.11) to obtain equations for the initial values of the coefficients.[3]

The initial temperature coefficients are

$$A_{(1)}(0) = 0 \tag{3.9a}$$

$$A_{(2)}(0) = 0 \tag{3.9b}$$

$$\sum_{n=3}^{N+2} A_{(n)}(0) \, x_j^{(n-1)} = 0 \qquad j=2,3,\ldots,N \tag{3.9c}$$

$$\sum_{n=3}^{N+2} (n-1) \, A_{(n)}(0) = 1 \tag{3.9d}$$

Using the values of x_j at each of the interpolation points in Equation (3.9c) produces $(N - 1)$ equations which can be solved simultaneously with Equation (3.9d) for the N coefficients. The result, shown in Figure 6, is an $(N + 1)$-order polynomial for the initial temperature $T = 0$ that passes through zero at N points and has a slope of 1.0 at $x = 1$ and a slope of 0.0 at $x = 0$.

The initial species values are obtained directly by applying the boundary conditions (2.11b, c) at each x_j:

$$\rho_1(x_j, 0) = 1 \tag{3.10a}$$

$$\rho_2(x_j, 0) = \rho_6(x_j, 0) = 0 \qquad (j=1,2,\ldots,N) \tag{3.10b}$$

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[3]See Appendix C.
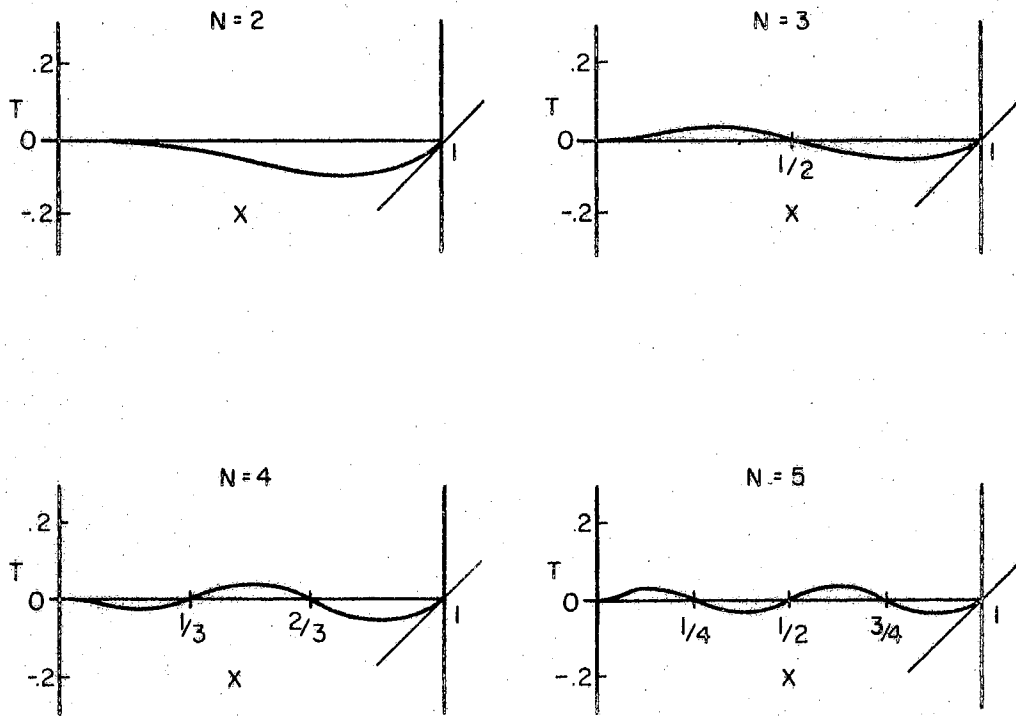
Figure 6. Temperature Profiles at Time = 0 for
Various N Interpolation Strips

Equations (3.5) through (3.10) constitute the complete problem
to be solved on a digital computer to obtain temperature and species
histories within the slab.

Summary of the Integral Technique

The purpose of the integral technique is to reduce the second-
order partial differential energy equation to a system of first-order
ordinary differential equations that are then solved by an Adams-
Moulton technique. The preceding discussion has described in detail
the steps necessary to accomplish this and is now summarized.

First, divide the slab by N equally spaced planes parallel to
the boundaries. Then, multiply the energy equation by a system of
N linearly independent weighting functions that "weight" the heated
boundary of the slab. Integrate the weighted equations over the slab
to obtain N independent integral relations. Approximate the functions
remaining under the integrals with polynomials in x having time-
dependent coefficients. Complete the integration to obtain a system of
(N + 2) first-order ordinary differential equations for the time-
dependent temperature coefficients. Apply the solid species equations
at the N strips to obtain 3N first-order ordinary differential equa-
tions. Use the boundary conditions to evaluate the initial values of
the temperature coefficients and local solid species. Solve the sys-
tem of (4N + 2) differential equations by an Adams-Moulton technique
for the temperature coefficients (and thus the slab temperature dis-
tribution) and N local densities of each solid species at a given time.

Computer Programming

The computer programs were developed to solve Equations (3.5) through (3.10) for the temperature profiles and local solid species concentration. From the calculated local solid species concentrations and their time derivatives, additional variables were calculated; the local amounts of each gas species produced from the N strips, the total amount of each gas species produced from the slab, the local rate of mass loss, the mass flux from the slab, and the average solid density for the slab.

The total amount of each gas species that was produced from each of the N strips was found from the solid species densities by[4]

$$Gas_3 = (1 - c_1)\left(\frac{\rho_6}{c_1 c_2} + \frac{\rho_6}{c_1}\right) \tag{3.11a}$$

$$Gas_4 = 1 - \rho_1 - \frac{\rho_6}{c_1 c_2} - \frac{\rho_2}{c_1} \tag{3.11b}$$

$$Gas_5 = (1 - c_2)\frac{\rho_6}{c_2} \tag{3.11c}$$

An Nth order polynomial in x having $(N + 1)$ time-dependent coefficients was then used to approximate the average slab production of each gas species. The coefficients were evaluated by simultaneously solving the $(N + 1)$ equations that are formed from applying Equation (3.11) at the N strips and the zero x-derivative of the solid species at $x = 0$. Integrating the approximations over the slab gives the total amount of each gas species produced from the slab. Likewise, the local values

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[4]See Appendix E.

of the total solid species were used to obtain the average solid for the slab (called the Total Weight in the computer output).

The local gas generation rate was calculated by taking the negative of the sum of the local solid generation rates

$$-(\frac{d\rho_1}{dt} + \frac{d\rho_2}{dt} + \frac{d\rho_6}{dt}) \ .$$

In the program, this value is called the Mass Loss Rate and is proportional to the reaction rate.

Finally, to find the mass flux out of the slab, a polynomial of (N + 1) terms was formed based on the local gas generation rates and the zero x-derivative of the generation rate at x = 0. Integrating the polynomial over the slab then gives the mass flux at the surface.

The programs that were written for the Integral technique solution are the MAIN program and subroutine DERFUN. A variable listing is given in Appendix G. Programs already in existence were used for the simultaneous solutions of the algebraic equations (subroutine SIMQ (16)) and the solution of the ordinary differential equations (subroutines START AND KAMSUB (10)). A description of the use of the latter three subroutines is given in Appendix H as well as a complete program listing of all routines in Appendix I. The basic steps followed in the computer programs are given in Table III with an expanded description given in Appendix J.

TABLE III

BASIC COMPUTING STEPS

1. Read the number of approximation strips, N.

2. Read the parameter values and the program control constants.

3. Calculate the initial values of the unknowns (Equations 3.9 and 3.10).

4. Calculate the 3N time derivatives of the local solid species (Equation 3.8).

5. Calculate the coefficients for the interpolation formulas (Equation 3.5).

6. Calculate the (N + 2) time derivatives of the temperature co-efficients (Equations 3.6 and 3.7).

7. Integrate the (4N + 2) time derivatives to obtain values of the unknowns at the new time step.

8. Calculate the local values for the gas species, gas generation rate, temperature, and total solid.

9. Calculate the average slab values for the gas species, mass flux, and total solid.

CHAPTER IV

COMPUTER RESULTS

Introduction

Most of the computer work involved the development of both the
integral technique and the computer technique as well as checking the
accuracy of the results. However, this section will consider only
some of the final results of the computer calculations.

Since a large number of parameters and possible parameter values
were involved in addition to the various boundary conditions and reac-
tions, a study was first made of the influence of individual parameters
and events and then of the effects of combinations of events. The
investigation of the influence of individual events was also necessary
to the development of the computer technique since the selection of
the program constants was highly dependent on the values of the prob-
lem parameters.

These results are not able to cover in depth all possible effects
and combinations of the parameters but will show some of the major
effects and trends for all the boundary condition cases and reaction
combinations.

Parameter Values

Since the reaction scheme used in the program is based on organic
solids such as cellulose and wood, the parameter values were chosen

from published data on these substances. As discussed earlier,
Weatherford used the same physical and kinetic constants as Bamford,
which represents values for one overall reaction in wood; their cal-
culations were based on an activation energy of 33 kcal per mole and
a frequency factor of 5×10^8 per second. Tang gives typical acti-
vation energies and frequency factors for cellulose in two tempera-
ture ranges; 23 and 54 kcal per mole for the activation energy and
0.3×10^6 and 0.6×10^7 per second for the frequency factor for tem-
peratures from 280°C to 350°C. Murty and Blackshear also present
kinetic constants which varied throughout cellulose from 13.6 to
22.6 kcal per mole for the activation energy and from 2×10^4 to
4×10^6 per second for the frequency factor. Similar values also
apply to polymer foams as Tilley, et al, mention an activation energy
of 50 kcal per mole and a frequency factor of 10^{13} per second for one
of the major reactions in urethane foams. For three reactions, basic
activation energies and frequency factors were chosen which were in
the range of the reported values and which gave maximum reaction rates
in the temperature ranges reported by Broido.

The overall heats of reaction for wood and cellulose are of the
same magnitude with wood being exothermic and cellulose, endothermic.
Weatherford used -86 cal per gm for wood while Tang reported +88 cal
per gm for cellulose. Broido describes the three major reactions of
cellulose as slightly endothermic, highly endothermic and highly exo-
thermic. For the three reaction cases, basic heats of reaction were
chosen which demonstrated Broido's findings and had an overall heat
of reaction similar to the published values.

A basic value for the radiant heat flux was chosen as the maximum

initial heat flux in Weatherford's experiments. While experimental

radiant heat fluxes are normally much higher than Weatherford's ini-

tial convective value, the slab thicknesses used are much smaller.

Therefore, the numerator, qL, of the heat flux parameter, G, would

be of the same magnitude in either case.

The dimensional values used in computing the basic parameters

are given in Table IV, with the resulting non-dimensional parameters

given in Table V. The particular parameter values used in each com-

puter run given in the results are presented in Table VI.

The Inert Slab

Inert slab calculations were made and compared with known solu-

tions. Carslaw and Jaeger (6) give the exact solution for an inert

slab heated by a constant heat flux. As shown in Figure 7, increas-

ing the number of approximating strips gives a more accurate answer,

and, a good approximation for the inert case was obtained with only

three approximating strips. Increasing the number of approximating

strips results in curves which lie midway between the exact solution

and the previous approximation.

For the convective boundary condition, Weatherford (23) graphs

the solution for the surface temperature of an inert slab. Figure 8

shows that three approximating points again give the exact solution

except for the early times. Higher approximations are practically

indistinguishable from the exact solution for all times and for the

chosen parameters.

Thus, the exact solutions show that the integral technique can

accurately represent the linear portion of the problem. However,

TABLE IV

BASIC DIMENSIONAL CONSTANTS

a_1 . . . . 8.2 x 10^4 sec^{-1}

a_2 . . . . 8.2 x 10^6 sec^{-1}

a_3 . . . . 8.2 x 10^9 sec^{-1}

c_1 (one reaction) . . . . 0.5 gm/gm

c_1 (three reactions) . . . . 0.9 gm/gm

c_2 . . . . 0.833 gm/gm

C . . . . 0.55 cal/gm-°K

E_1 . . . . 23,844 cal/mole

E_2 . . . . 31,000 cal/mole

E_3 . . . . 35,748 cal/mole

h . . . . 4.4 x 10^{-4} cal/cm^2-sec-°K

K_0 . . . . 2.7 x 10^{-4} cal-cm/cm^2-sec-°K

L . . . . 1.0 cm

Q_1 . . . . +16.5 cal/gm

Q_2 . . . . +165 cal/gm

Q_3 . . . . -94.2 cal/gm

q_0 . . . . 0.081 cal/cm^2-sec

R° . . . . 1.986 cal/mole-°K

T_0 . . . . 300°K

ρ_0 . . . . 0.6 gm/cm^3

TABLE V

BASIC NON-DIMENSIONAL PARAMETERS

Nu 2.0

E_1 . . . . 40.0

E_2 . . . . 52.0

E_3 . . . . 60.0

F_1 . . . . 0.1×10^{-7}

F_2 . . . . 0.1×10^{-9}

F_3 . . . . 0.1×10^{-12}

G (Type I) 1.0

G (Type II). 1.535

R_1 . . . . +0.1

R_2 . . . . +1.0

R_3 . . . . -0.571

TABLE VI

PARAMETER VALUES USED IN COMPUTED RESULTS

Run Number	B.C.	Case	E_1	E_2	E_3	F_1	F_2	F_3	R_1	R_2	R_3	c_1	c_2	G	Nu
210	0	1	40	--	--	10^{-8}	--	--	0	--	--	.5	--	1.0	--
211	0	1	40	--	--	10^{-8}	--	--	0	--	--	.8	--	1.0	--
213	1	2	40	--	--	10^{-8}	--	--	0	--	--	.5	--	1.535	2.0
220	1	1	40	--	--	10^{-8}	--	--	0	--	--	.5	--	1.535	2.0
222	0	1	40	--	--	10^{-8}	--	--	+.3	--	--	.5	--	1.0	--
223	0	0	40	--	--	10^{-8}	--	--	+.3	--	--	.5	--	1.0	--
226	0	0	40	--	--	10^{-8}	--	--	-.3	--	--	.5	--	1.0	--
228	0	0	40	--	--	10^{-8}	--	--	0	--	--	.5	--	1.0	--
229	0	0	40	--	--	10^{-8}	--	--	0	--	--	.5	--	2.0	--
243	0	0	40	--	--	10^{-8}	--	--	+.3	--	--	.5	--	1.0	--
261	0	1	40	52	60	10^{-9}	10^{-11}	10^{-13}	+.1	+1.0	-.571	.9	.833	1.0	--
262	1	0	40	52	60	10^{-8}	10^{-10}	10^{-12}	+.1	+1.0	-.571	.9	.833	1.5	2.0
263	1	0	40	52	60	10^{-8}	10^{-10}	10^{-12}	+.1	+1.0	-.571	.9	.833	1.75	2.0
264	1	0	40	52	60	10^{-8}	10^{-10}	10^{-12}	+.1	+1.0	-.571	.9	.833	1.45	2.0
265	1	2	40	52	60	10^{-8}	10^{-10}	10^{-12}	+.1	+1.0	-.571	.9	.833	1.75	2.0
080	1	0	50	55.66	60	10^{-10}	10^{-11}	10^{-12}	0	0	0	.9	.833	1.535	2.0
081	1	0	50	55.66	60	10^{-10}	10^{-11}	10^{-12}	0	0	0	.9	.833	2.0	2.0
082	1	0	48	55.66	60	10^{-10}	10^{-11}	10^{-12}	0	0	0	.9	.833	1.535	2.0
083	1	0	50	55.66	60	5×10^{-10}	10^{-11}	10^{-12}	0	0	0	.9	.833	1.535	2.0
125	0	0	50	55.66	--	10^{-10}	10^{-11}	--	0	0	0	.5	--	1.0	--
131	0	0	50	55.66	--	10^{-10}	10^{-11}	--	0	0	0	.5	--	1.5	--
143	0	2	55.66	--	--	10^{-10}	--	--	0	0	0	.5	--	1.0	--

Note: For the constant heat flux boundary condition, B.C. = 0. For the convective heated boundary condition, B.C. = 1. Exothermic reactions denoted by (-) and endothermic reactions by (+).
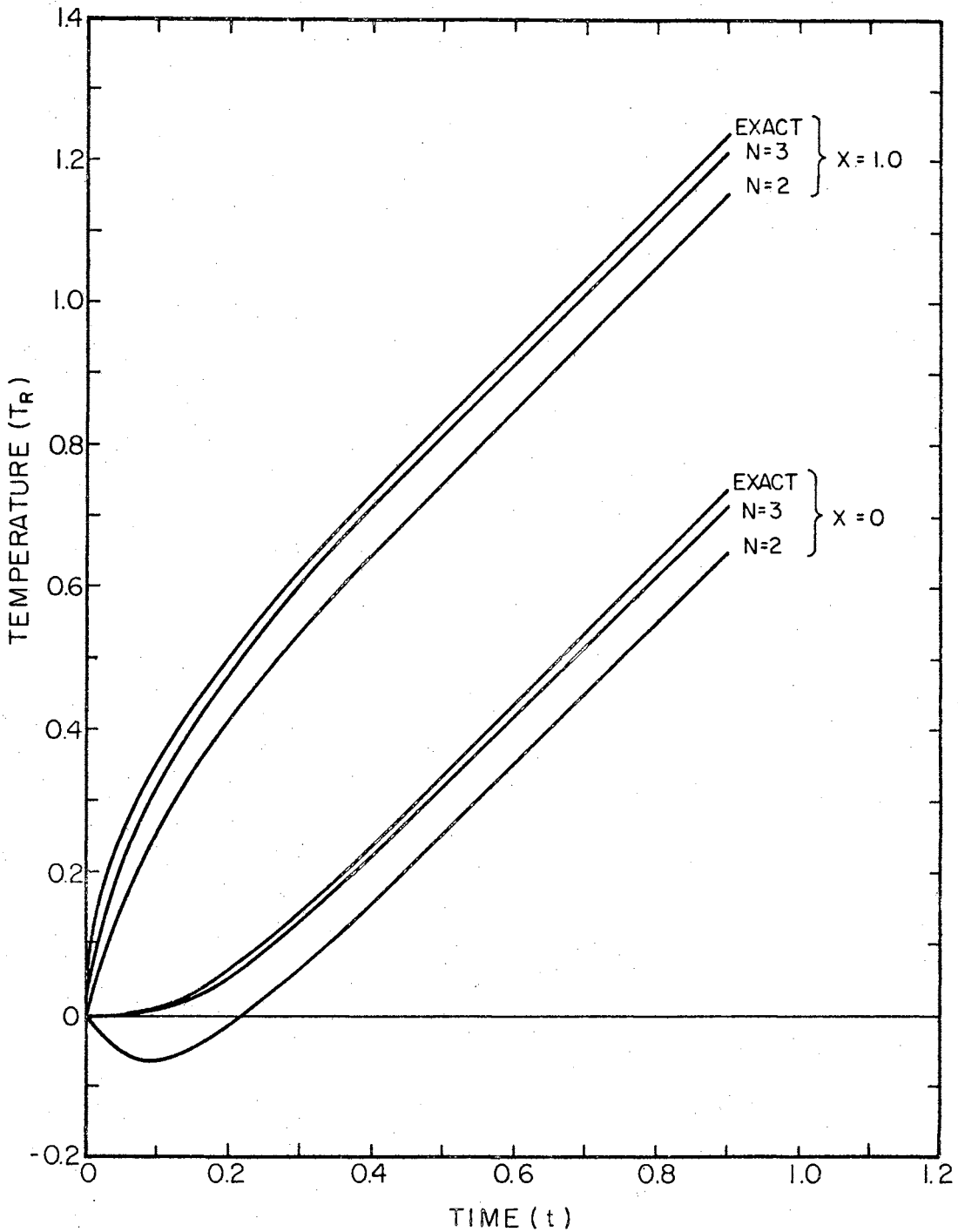
Figure 7. Comparison of Approximate Solutions
With Exact Solution for Constant
Heat Flux Case
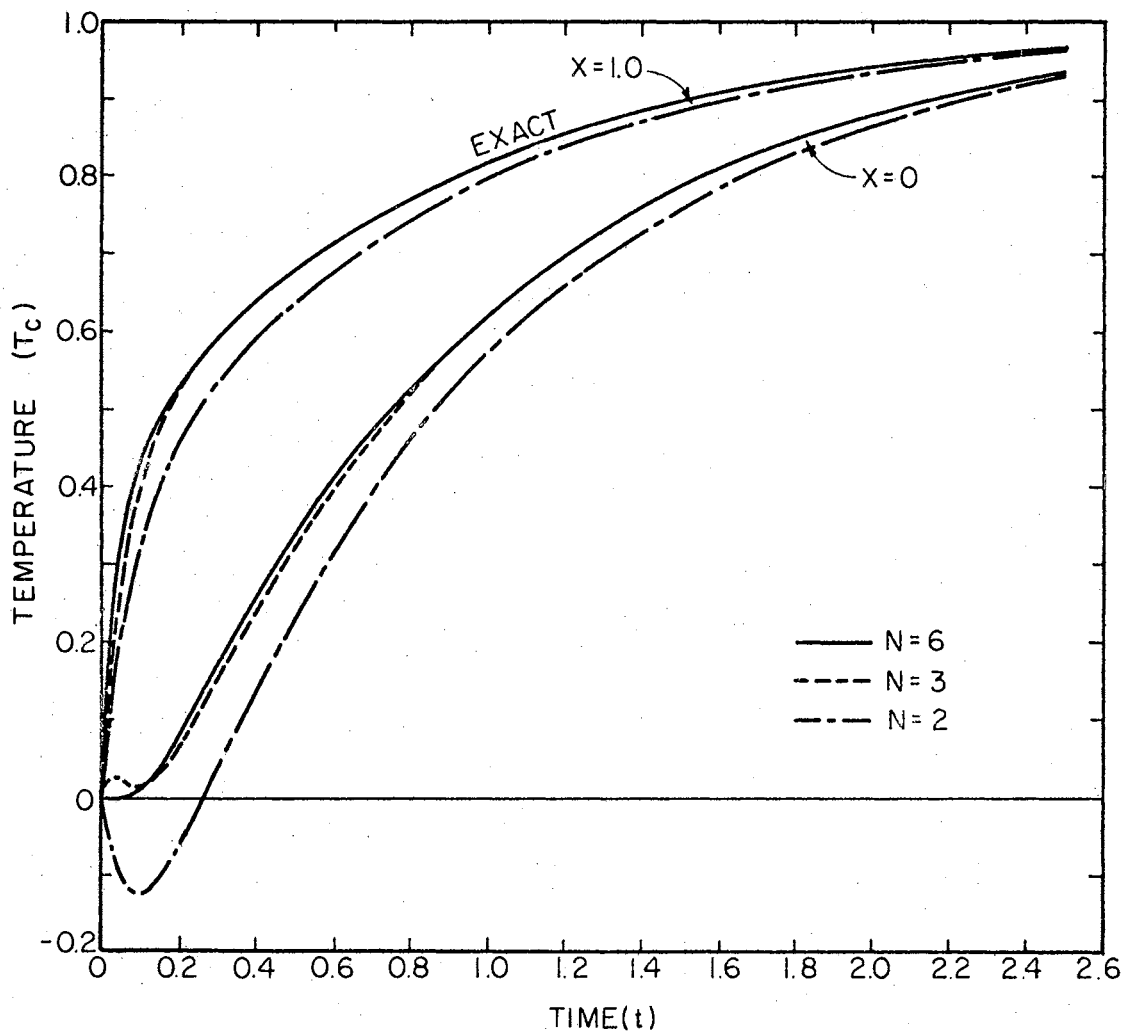
Figure 8. Comparison of Approximate and Exact
Solutions for Convective Heating,
Nu = 2

there are no exact solutions for checking the validity of the technique when including the non-linear terms for the generated heat and the change in effective thermal conductivity. For this reason, the method of computation was made to allow any order of approximation to be used, enabling the results to be generally checked by comparing with a higher approximation.

One Reaction--Case 0

In order to interpret the results with multiple reactions, the single reaction cases were studied first. Initially, a constant effective thermal conductivity was assumed.

In Figure 9 the temperature history of the front and back surfaces are shown for a slab heated by a constant heat flux and an exothermic reaction. The front surface temperature follows the inert value until the reaction begins to generate heat, causing the temperature to increase at a higher rate. As the reaction proceeds into the slab, the amount of generated heat increases, thereby increasing the amount of conducted heat. This has two major effects: temperatures within the slab begin to deviate from the "inert" value even before a reaction starts at that particular location, and the temperature rise becomes increasingly steeper at greater depths.

As the reaction ends at the heated surface, the temperature increases at a constant rate that is higher than the inert value, showing that the rate of heat conduction into the slab is less due to the increased internal temperatures. A result of the accumulation of generated and conducted heat is that the temperature at the back surface (adiabatic surface) becomes higher than the slab just ahead of it for
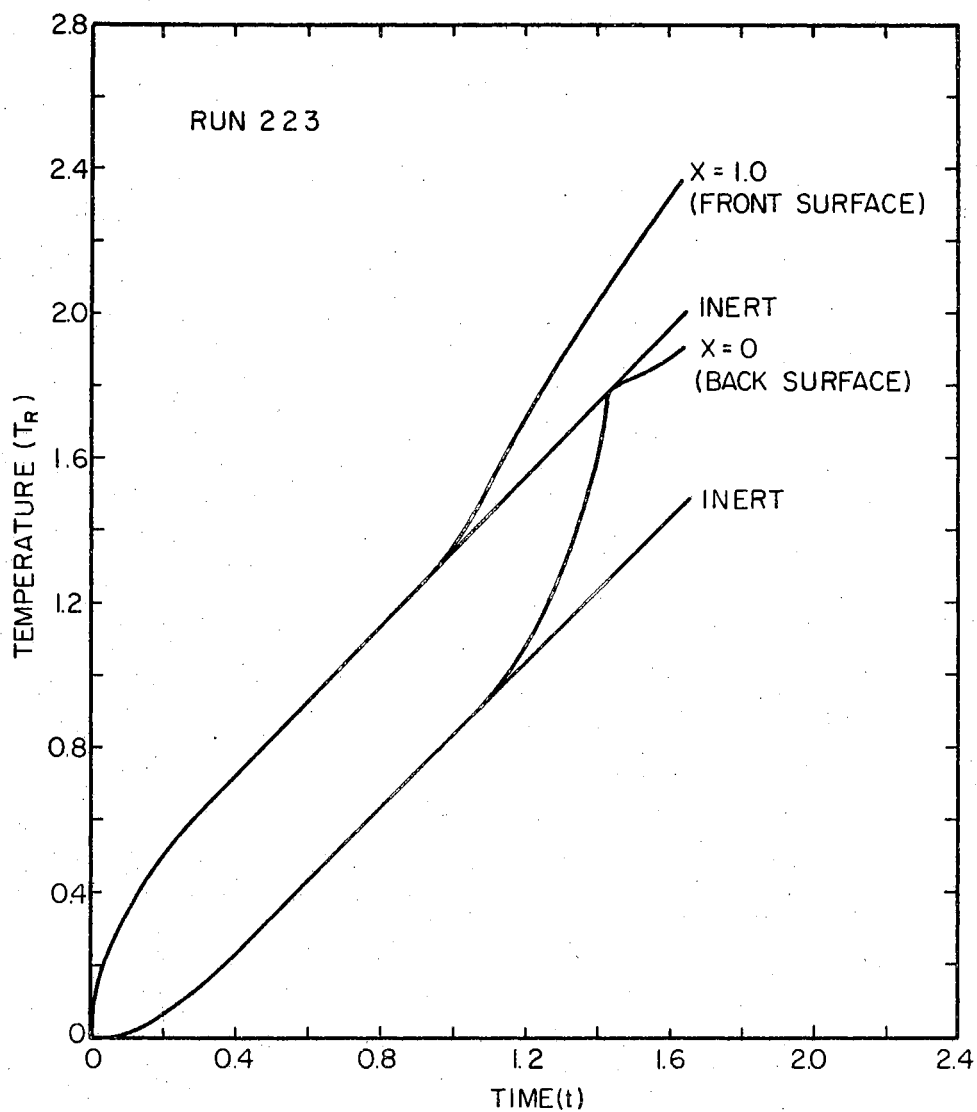
Figure 9. Effect of Heat of Reaction: Temperature
History of Front and Back Surfaces--
Constant Heat Flux, One Exothermic Re-
action, Case 0

a short time, up until the reaction reaches its maximum. An abrupt drop in the rate of temperature rise then follows as the reaction in the slab ends. When the reaction ceases, the rate of temperature rise, compared to the inert solution, ranges from higher at the front surface to lower at the back surface. Of course, after this transient period, the temperatures throughout the slab would become parallel to the inert solution with an offset from the inert values.

Results for an endothermic reaction are shown in Figure 10. Effects are similar to the exothermic reaction except with an opposite sign. Note that the reaction events are spread over a longer time period, and the temperature rise becomes parallel to the inert solution very quickly after the slab is through reacting.

Another basic difference in the character of endothermic and exothermic reactions can be seen in Figures 11 and 12 where temperature profiles are given as the reaction proceeds through the slab. This time the endothermic reaction is discussed first. The profiles all have a slope of 1.0 at the front surface and zero at the back surface. The earliest profile shows the temperature distribution when the front surface reaction starts. The next profile (t = 1.33) was taken when the surface reaction rate is at its maximum. The effect of the energy absorbed by the reaction is to depress the temperature rise, i.e., the front temperature rise is less than the back surface. Likewise, as the reaction proceeds through the slab, the profiles show the same effect with the last profile showing that the reaction is at the back surface.

For the exothermic reaction, however, the profiles are warped because of the reaction, as seen in Figure 12. The increasing times
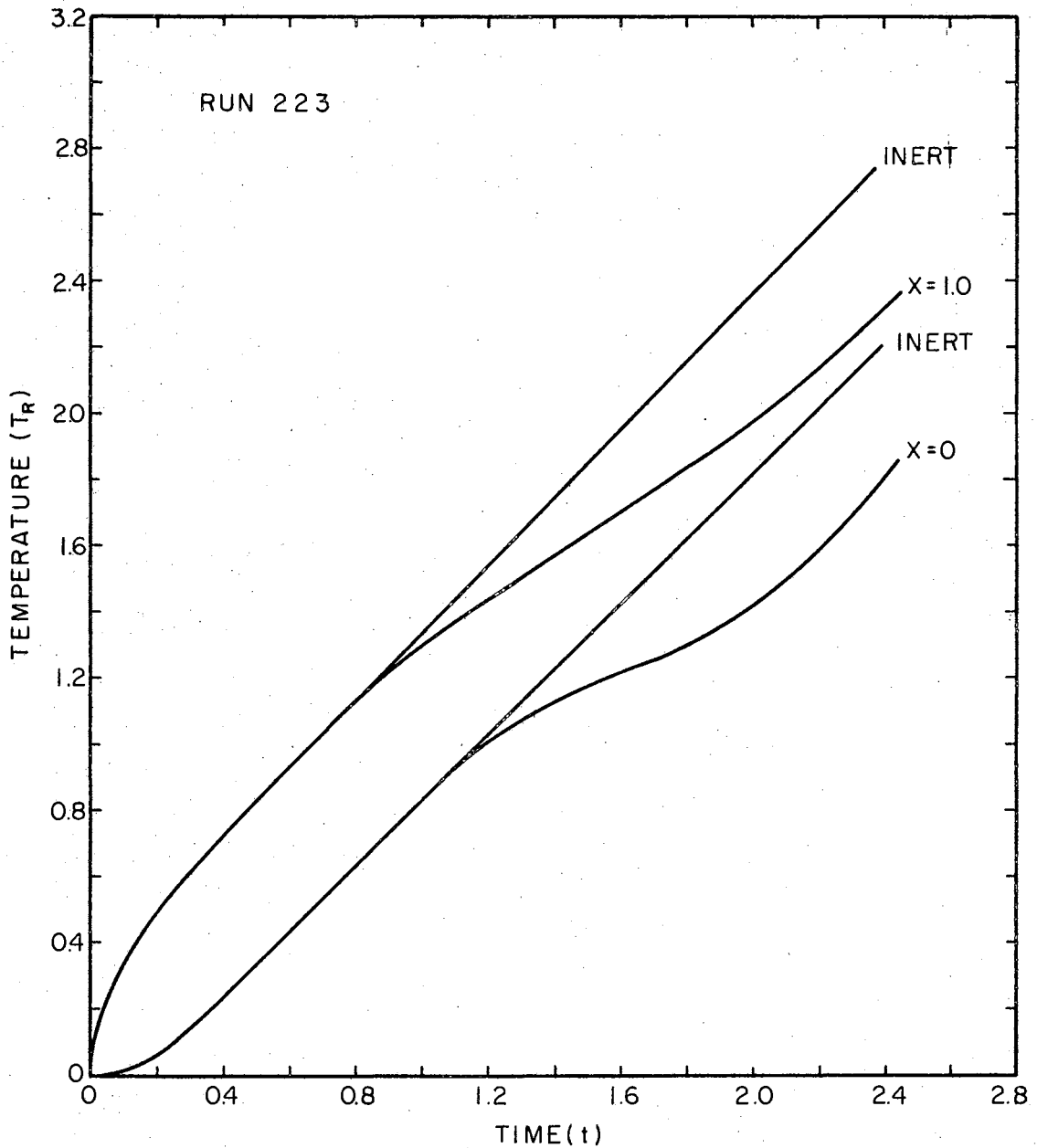
Figure 10. Effect of Heat of Reaction: Temperature History of Front and Back Surfaces-- One Endothermic Reaction, Constant Heat Flux, Case 0
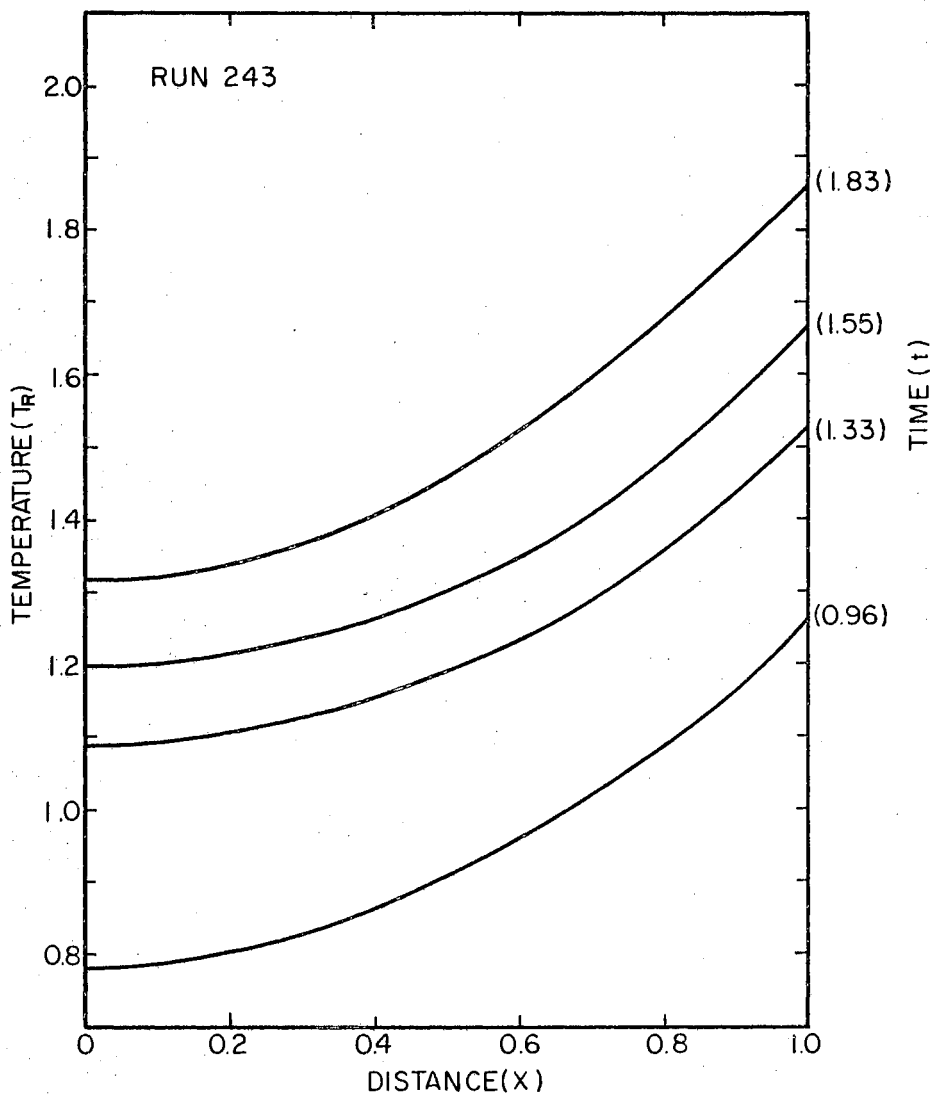
Figure 11. Effect of Heat of Reaction: Temperature Profiles for One Endothermic Reaction--Constant Heat Flux, Case 0
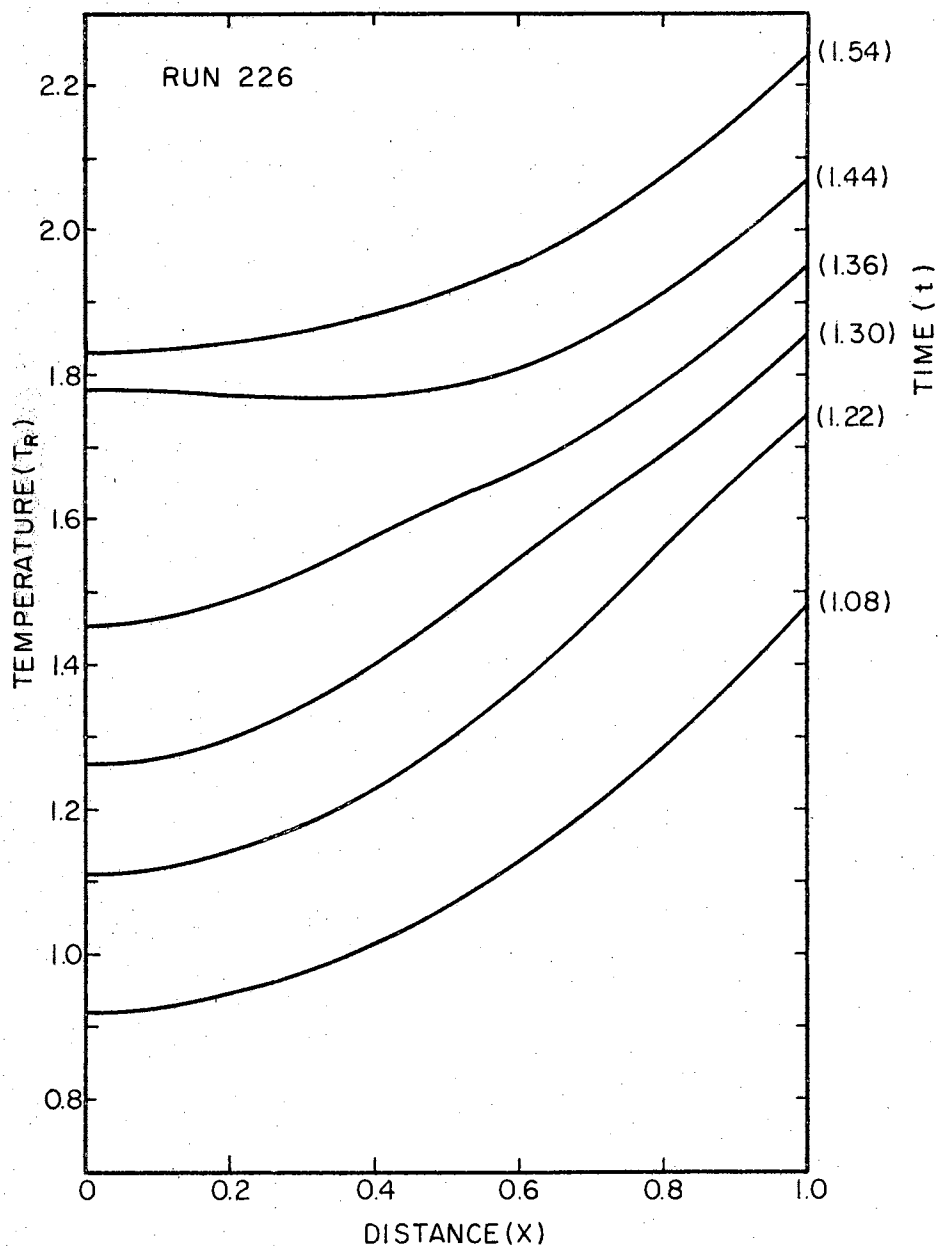
Figure 12. Effect of Heat of Reaction: Temper-
ature Profile for One Exothermic
Reaction, Constant Heat Flux, Case 0

trace the reaction through the slab with the back part briefly achiev-
ing a higher temperature than the middle as described earlier. Because
of the profiles warping, a larger number of approximating strips is
needed for exothermic reactions than for an equivalent endothermic
reaction.

The reaction rate shows another striking difference between endo-
thermic and exothermic processes. Figure 13 demonstrates that the
maximum reaction rate increases for exothermic reactions at distances
farther into the slab. The curves show the progression of the reaction
through the slab and show the reaction rate distribution at six times.
These are the times when the reaction rate reached a maximum at each
of the six interpolation strips. The maximum reaction rate at the back
surface is more than two and one-half times the rate at the front sur-
face. This is a result of the higher temperature rise from the in-
creasing amount of heat conducted ahead of the reaction. Since the
rate of reaction is dependent on the product of the amount of reactant
and the temperature-dependent rate constant, the additional conducted
heat causes the temperature to be slightly higher for a given amount
of reactant, thus increasing the reaction rate. This is shown in
Figure 14 where the back surface always has a higher temperature than
the front surface for a given amount of reactant.

Of course, the increase in the reaction rate through the slab
also means that the heat generation rate increases. For reactions
having higher heats of reaction, more heat would be generated causing
the difference in the reaction rates to be greater. Finally, by com-
paring the times at which the maximum rate occurred at each x-position,
it is seen that the velocity of the "reaction zone" increased as it
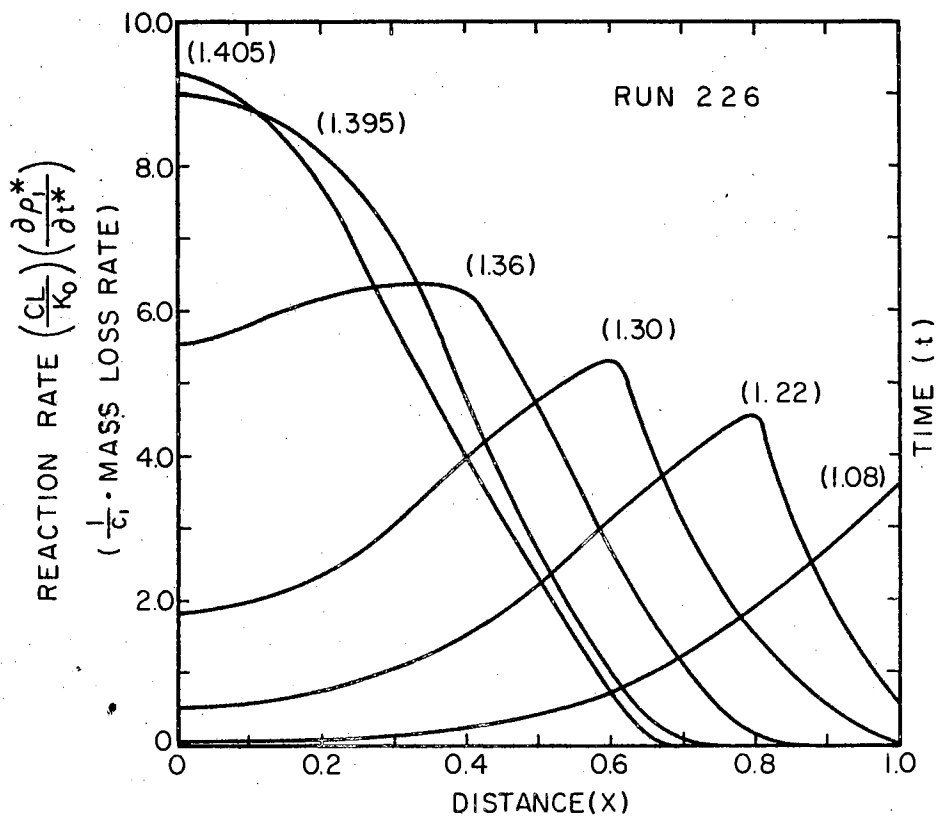
Figure 13. Effect of Heat of Reaction: Reaction Rate in Slab for One Exothermic Reaction--Constant Heat Flux, Case 0
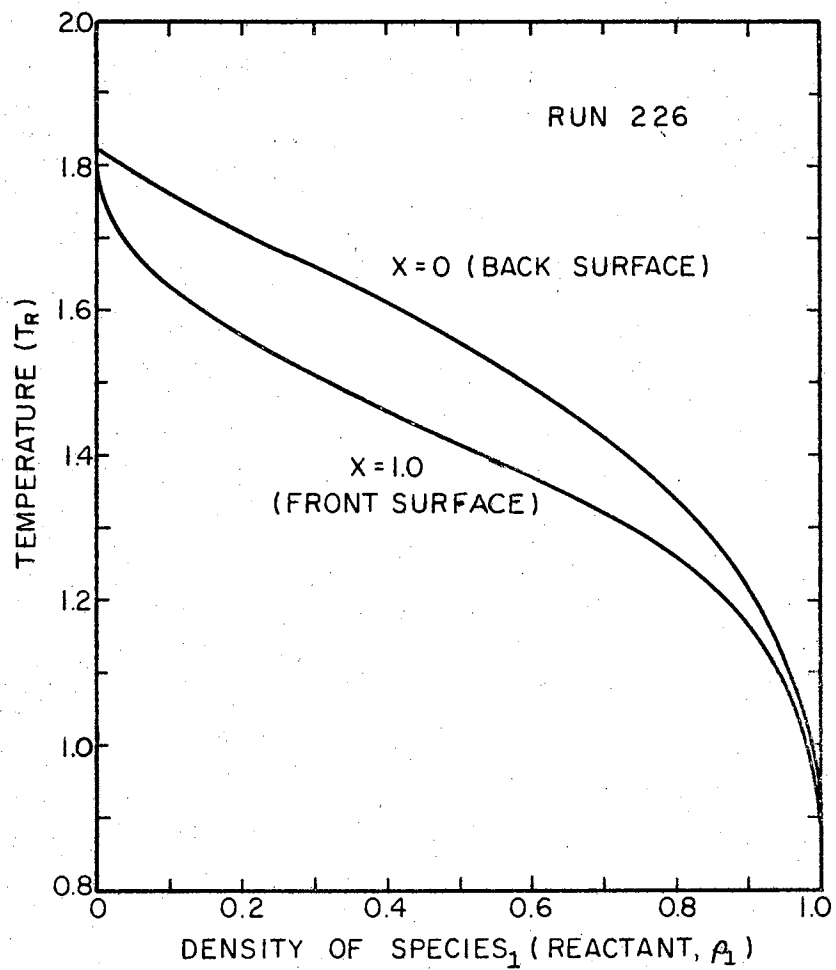
Figure 14. Effect of Heat of Reaction: Temperature
vs. Reactant Density Front and Back
Surfaces—Constant Heat Flux, One Exo-
thermic Reaction, Case 0

proceeded into the slab. Two factors contribute to this: the increasing rate of reaction and the longer residence times at greater depths resulting in less solid remaining for the reaction.

For the endothermic reaction, Figure 15 shows that the maximum reaction rate decreases from the front to the back surface. This indicates that a result of the energy absorption is a lower temperature for a given reactant density. The difference in times at which the maximum reaction rate occurred again shows that the "reaction wave" accelerated as it traveled farther into the slab. Thus, the longer reacting times for the interior solid contributed more to increasing the velocity of the "reaction wave" than the decreasing reaction rate did to retard it.

A difference of major importance in the effects of the endothermic and exothermic reactions is shown by the mass flux curves in Figure 16. The area under the mass flux curves equals the total mass of solid lost from the slab and is the same in both cases. The exothermic reaction was completed in half the time of the endothermic reaction, and the maximum mass flux was increased by three times. The "lump" on the side of the endothermic curve near the end of the reaction is apparently due to the increasing reaction rate near the insulated surface.

Figure 17 gives the solid distribution for both reaction cases as points in the slab reached a given density. The solid distribution profiles were steeper for the exothermic reaction than for the endothermic reaction up until the reaction was nearly completed. This is a result of the longer residence times of the solid interior for the endothermic reaction.
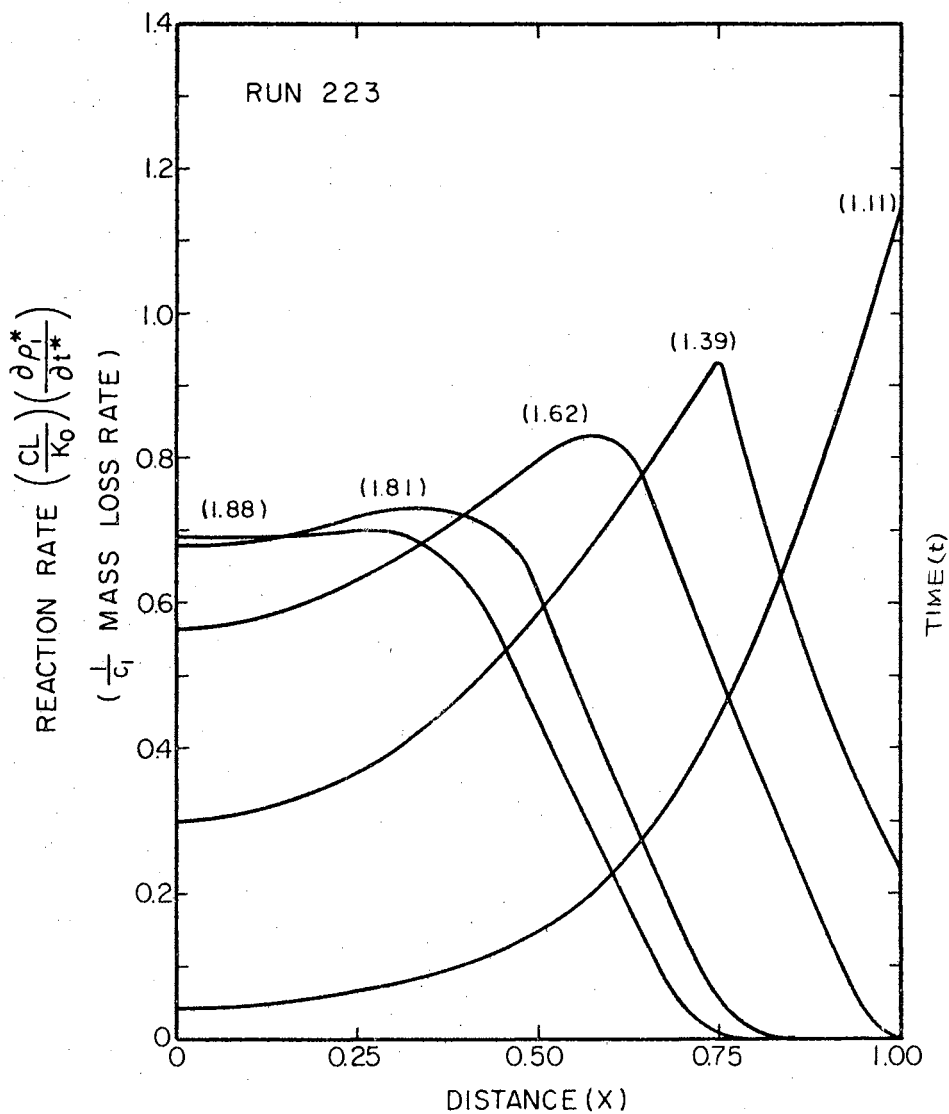
Figure 15. Effect of Heat of Reaction: Reaction
Rate in the Slab--Constant Heat Flux--
One Endothermic Reaction, Case 0
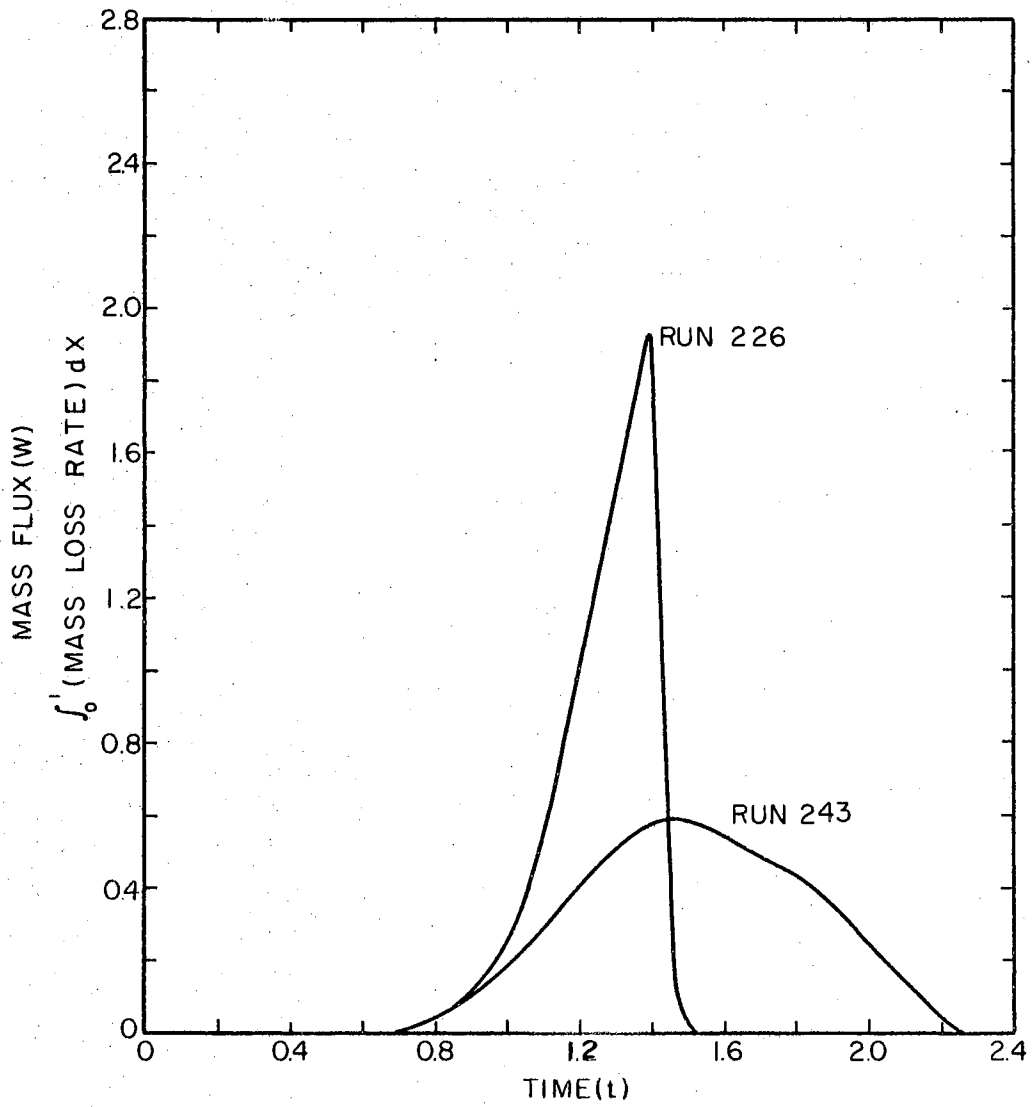
Figure 16. Effect of Heat of Reaction: Mass Flux
From Slab for Exothermic and Endothermic
Reactions—Constant Heat Flux, Case 0
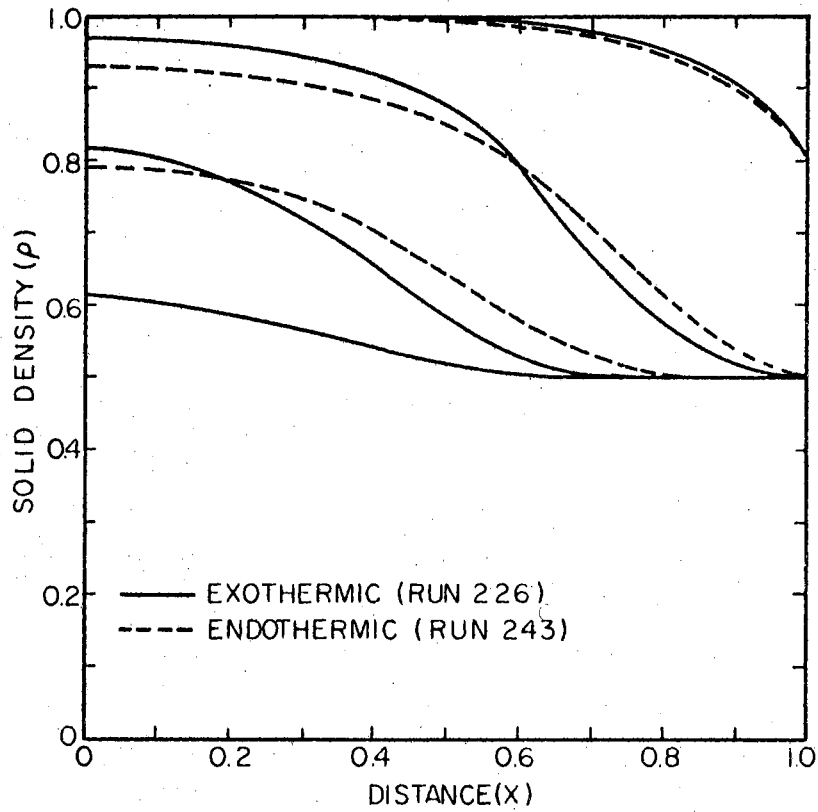
Figure 17. Effect of Heat of Reaction: Comparison of Solid Density Profiles for Exothermic and Endothermic Reactions—Constant Heat Flux, Case 0

The previous discussion has been concerned with the differences in endothermic and exothermic reactions under the same heating conditions. The effect of a change in the heat flux parameter alone can be seen by making the heat of reaction parameter zero. Figure 18 gives the reaction rate vs. surface temperature for two difference values of G. Not only does increasing the heat flux cause an increase in the reaction rate but it also causes the maximum reaction rate to occur at a higher temperature. Since a given temperature fixes the reaction rate constant, the increase comes from a larger value for the density of reactant (see Equation 2.10a). This is verified by Figure 19 which shows the increase in the reactant present at a given temperature. This effect is a result of a higher rate of increase in the reaction temperature with increasing G, giving the solid less time to react, thus making more solid available at a given temperature.

In summary, the computations have given temperature profiles and histories for exothermic and endothermic reactions with constant parameters. The heat generated or absorbed from the reactions have been shown to have a great effect on the solid ahead of and behind the reactions, not only with respect to temperatures, but also reaction rates and mass flux. Increasing the heat flux parameter was shown to increase the maximum reaction rate and also the temperature at which it occurs.

One Reaction--Cases 1 and 2

Temperature histores were calculated to show the effect of a variable effective thermal conductivity. A density-dependent, effective thermal conductivity affects both the front surface boundary condition
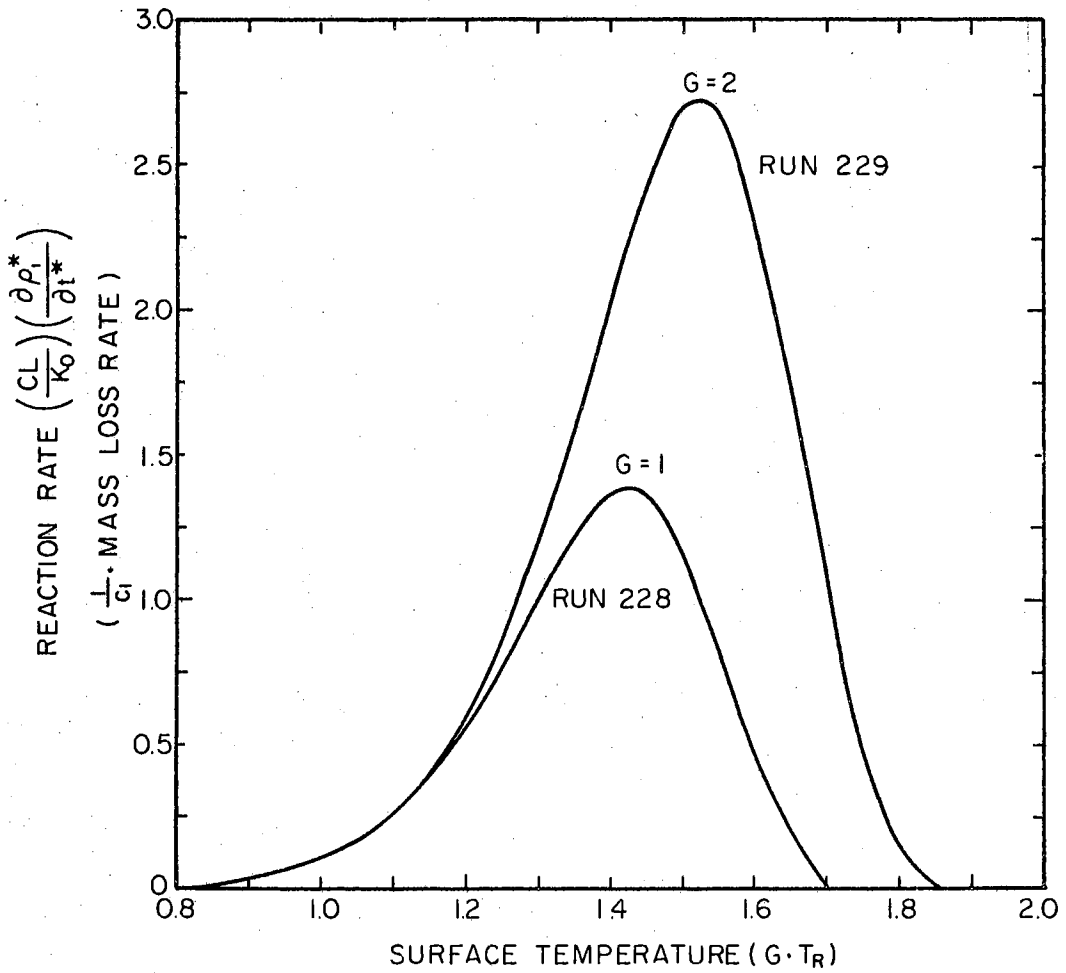
Figure 18. Effect of Heat Flux Parameter: Surface
Reaction Rate vs. Temperature--Constant
Heat Flux, Case 0
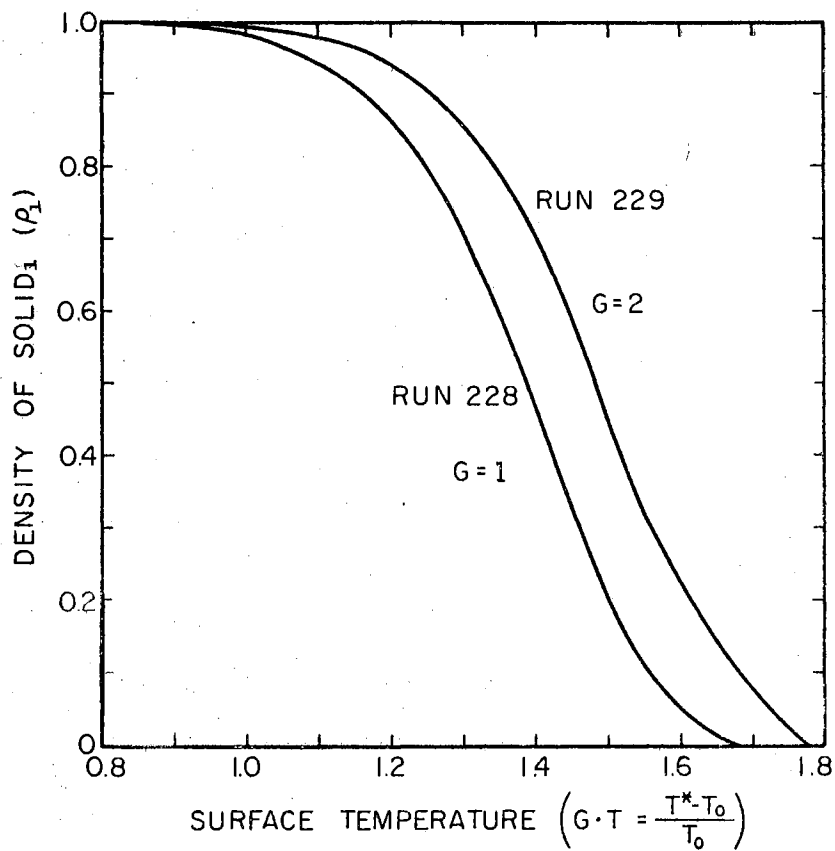
Figure 19. Effect of Heat Flux Parameter: Surface
Reactant Density vs. Temperature--
Constant Heat Flux, Case 0

and the energy equation for Case 1 or just the energy equation for Case 2.

Figure 20 shows, for the convective heating case, the surface temperature history for Cases 1 and 2 and also the constant effective thermal conductivity Case 0. The heat of reaction parameter is zero so the temperature deviations from the constant conductivity case occur only from the changes in the effective thermal conductivity and the heat transfer coefficient. For Case 1 the heat transfer coefficient is constant while the effective thermal conductivity decreases as solid is lost. The result is that the rate of heat conducted from the surface is less, causing the temperature to increase.

For Case 2 the heat transfer coefficient and the effective thermal conductivity both decrease as solid is lost, with the result that the surface boundary condition is the same as the constant effective conductivity case while the decreasing effective conductivity appears as an equivalent endothermic contribution in the energy equation. Neither case causes the temperature to deviate much from the constant effective conductivity solution for the parameters that were used. The primary reason is that the temperature dependency in the surface boundary condition causes a compensating effect in both cases. For Case 1, as the surface temperature tends to rise, the difference in the source and surface temperatures becomes less, decreasing the heat flux to the surface and partially decreasing the rate of increase of the surface temperature. Likewise, for Case 2, as the surface temperature tries to rise at a slower rate, the temperature difference is greater causing a higher heat flux. As higher source temperatures are used, the trend would be for a greater effect of the changing effective thermal
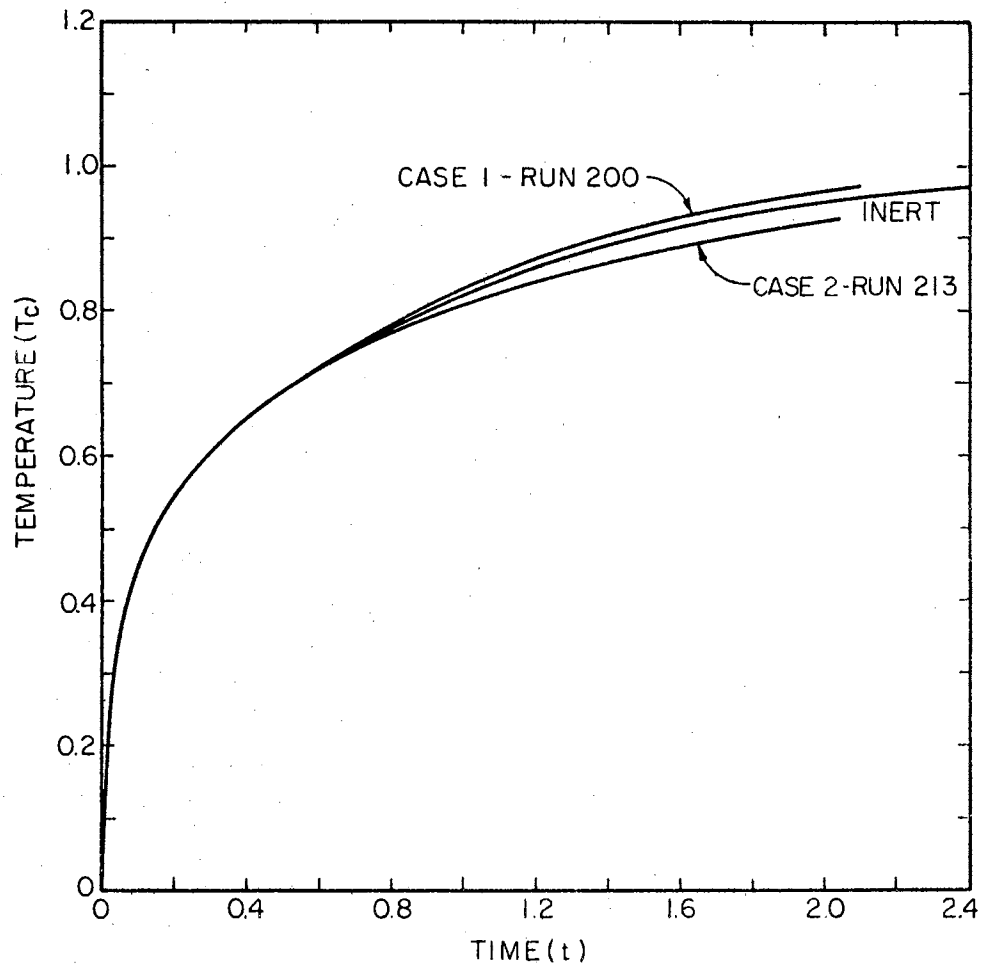
Figure 20. Effect of Variable Effective Thermal
Conductivity and Heat Transfer Coef-
ficient: Temperature History of
Front Surface, Convective Boundary
Condition, Cases 1 and 2

conductivity on the temperature since the surface and source temperature difference would increase, thus decreasing the influence of a changing surface temperature.

When the radiation boundary condition is used, the effects are more pronounced. For no heat of reaction and a constant heat flux input, Figure 21 shows how the decreasing effective thermal conductivity affects the surface temperature history (Case 1). Since the effective conductivity depends on the amount of solid present, calculations were made for two final solid densities, 50% and 80% of the original density. The temperature increases faster as the amount of final solid decreases. The slope of the temperature rise after the reaction has been completed is the inverse of the final density. As the solid drops from its original density to 50%, the surface boundary condition shows that the slope of the temperature profile increases from 1 to 2. For 80% of the original solid density, the slope increases from 1 to 1.25. Thus, for Case 1, low final solid densities will greatly affect the slab temperatures.

Case 2 for the constant heat flux condition has essentially the same boundary conditions as the constant effective thermal conductivity case but includes the effect of the change in the effective conductivity in the energy equation. Figure 22 gives the temperature history for the front and back surfaces with no heat of reaction. The result shows that the changing effective thermal conductivity appears in the energy equation as an endothermic reaction if the heat input decreases so as to hold constant the slope of the surface temperature profile. This contribution does not occur at exactly the same time as a true endothermic reaction because the heat generated from a reaction depends
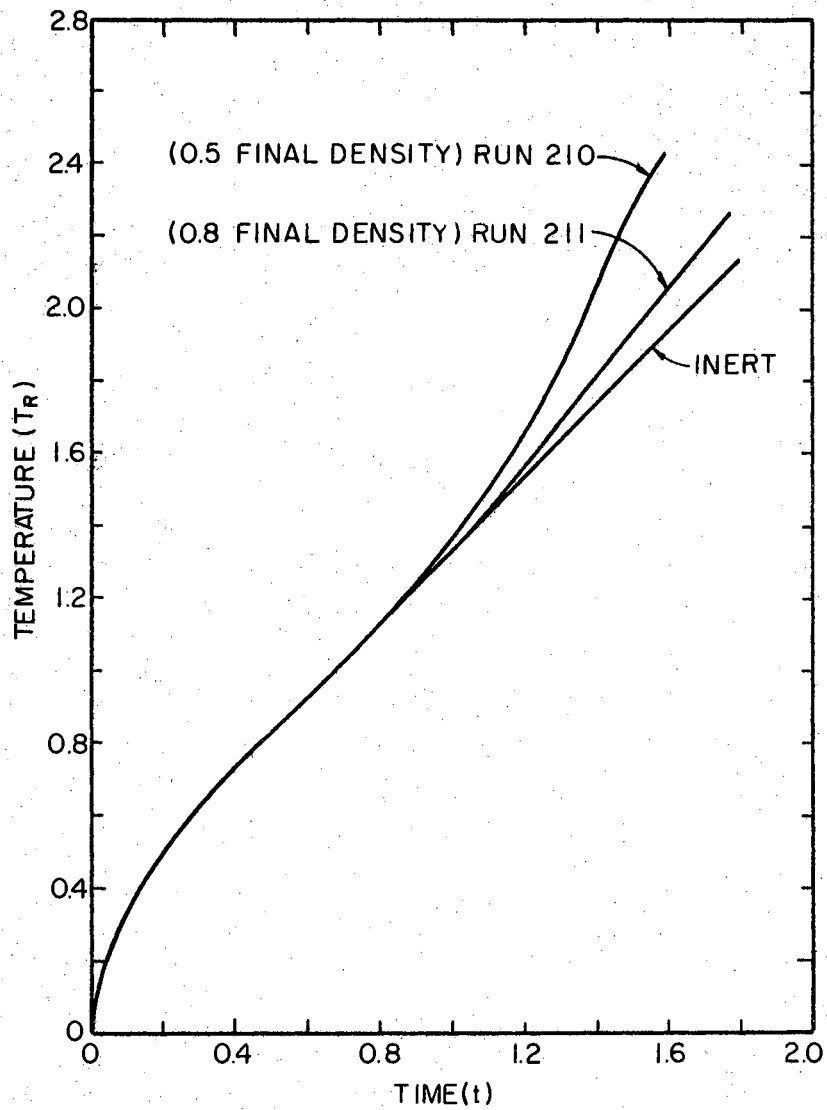
Figure 21. Effect of Solid Density on
Effective Thermal Conductiv-
ity: Temperature History of
Front Surface for Final Solid
Densities of 0.5 and 0.8--
Constant Heat Flux, Case 1
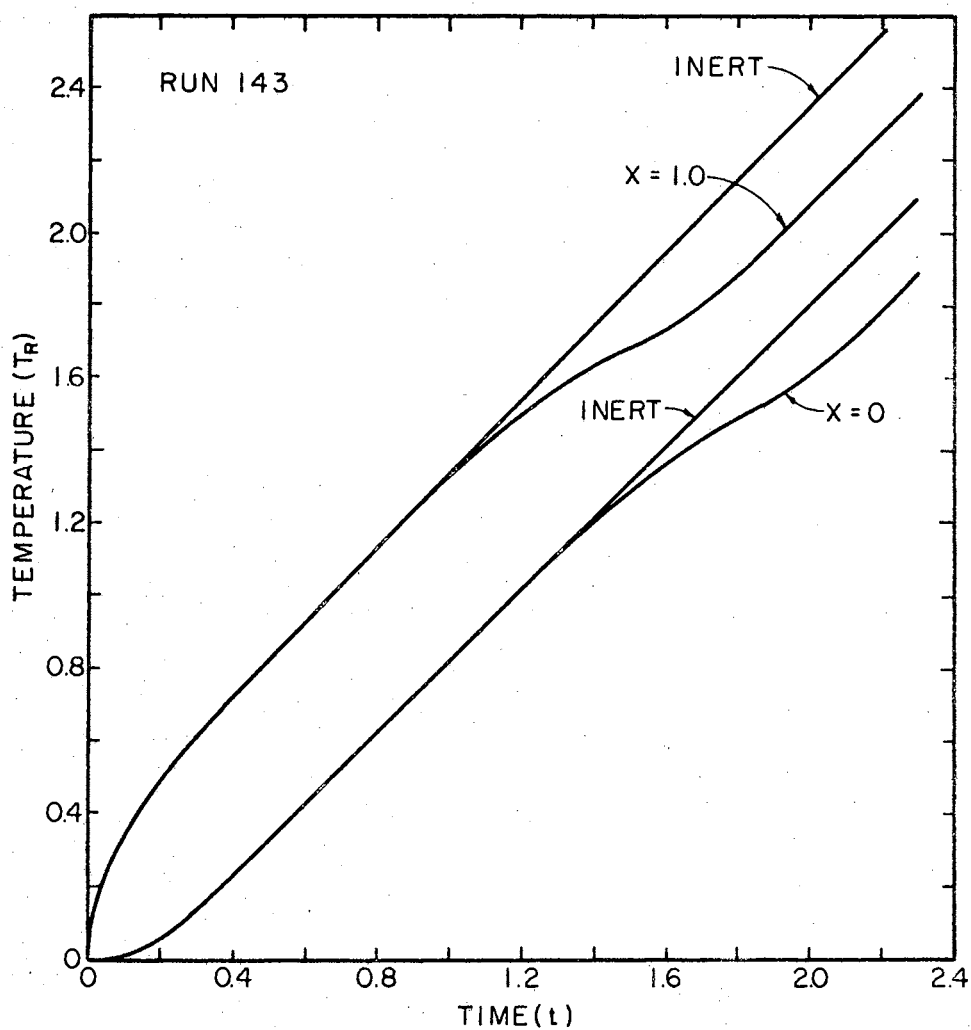
Figure 22. Effect of Conductivity Change on Energy
Equation: Temperature History of
Front and Back Surfaces for Constant
Heat Flux--Case 2

on the time rate-of-change of the solid, while the contribution from

the variable conductivity depends on the product of the rates of change

of density and temperature with respect to x (see Equations 2.3, 2.7,

and 2.8).

The combination of an endothermic reaction and a changing effec-

tive thermal conductivity is given in Figure 23. This figure shows

the surface temperature history for Cases 1 and 0 together with Case 1

having an endothermic reaction. For Case 1 with the reaction, the rate

of temperature rise first begins to decrease from the constant effec-

tive conductivity case, indicating that the endothermic reaction is

affecting the temperature more than the changing effective conductivity.

As the reaction proceeds, the high rate of increase of the temperature

from the changing conductivity eventually causes the temperature to in-

crease at a greater rate until the surface reaction ends and the rate

of temperature rise is parallel to the Case 1 value. The overall ef-

fect of the changing effective conductivity cannot be represented by

a single equivalent reaction.

The effect of a density-dependent, effective thermal conductivity

and heat transfer coefficient is negligible for convective heating

when source temperatures are low. For radiant heating and high source

temperature convective heating, the change in effective thermal con-

ductivity can greatly affect the temperature history of the slab.

This is especially true as the final densities become smaller. These

effects must be carefully considered when interpreting temperature

histories.
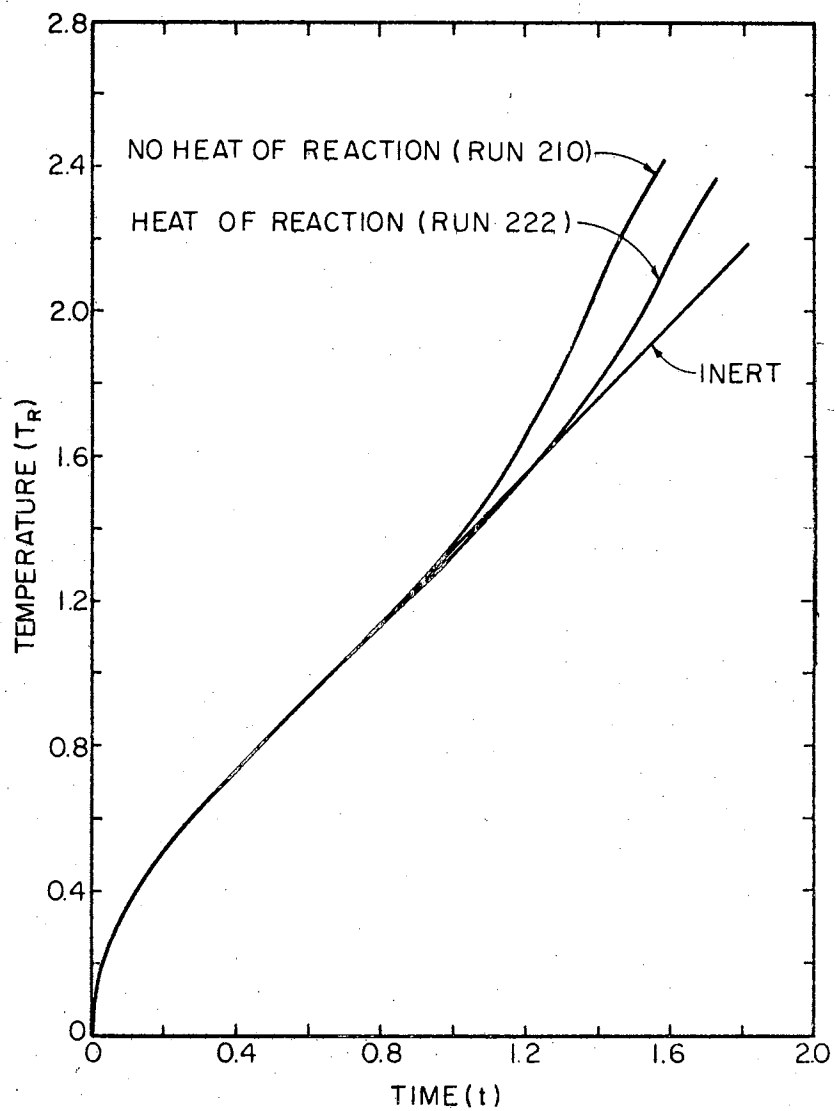
Figure 23. Effect of Heat of Reaction:
Temperature History of Front
Surface for Constant Heat
Flux--Case 1, With and With-
out Heat of Reaction

Three Reactions--Case O

The effects of parameter changes on the competing reactions were studied with zero heats of reaction and a constant effective thermal conductivity. Figure 24 shows typical density curves for the three solid species and Gas_4. Gas_3 and Gas_5 are not shown since they are similar to Gas_4. As $Solid_1$ reacts, it gives off Gas_3 and forms $Solid_2$. At higher temperatures the competing reaction tends to form more Gas_4 from $Solid_1$. As the temperature rises, $Solid_2$ begins to give off Gas_5 and form $Solid_6$. When the rate of reaction of $Solid_2$ equals its rate of formation, it species curve reaches a maximum. The final species present is $Solid_6$ with Gas_4 indicating the total amount produced from the slab.

For cellulose, Gas_4 is the flammable species that competes for $Solid_1$. Its importance in ignition and combustion occurs in several ways; ignition may occur if the surface temperature and the quantity of Gas_4 evolving is high, while sustained combustion depends on the rate as well as the quantity of Gas_4 evolving. Figure 25 indicates that a change in the heat flux parameter does not have as much effect on the total amount of Gas_4 produced as it does on the rate of evolution and the time when it is evolved. The maximum rate of production of Gas_4 (indicated by the slope of the curves) is not much greater for the higher heat flux parameter case but the maximum is attained quicker and held throughout most of the reaction.

The amount of $Solid_1$ that does not form Gas_4 has gone to produce the other species. Since a higher heat flux produces more Gas_4, less $Solid_1$ is available for the other species. Figure 26 shows that the amount of char formed is less for the higher heat flux but like Gas_4,
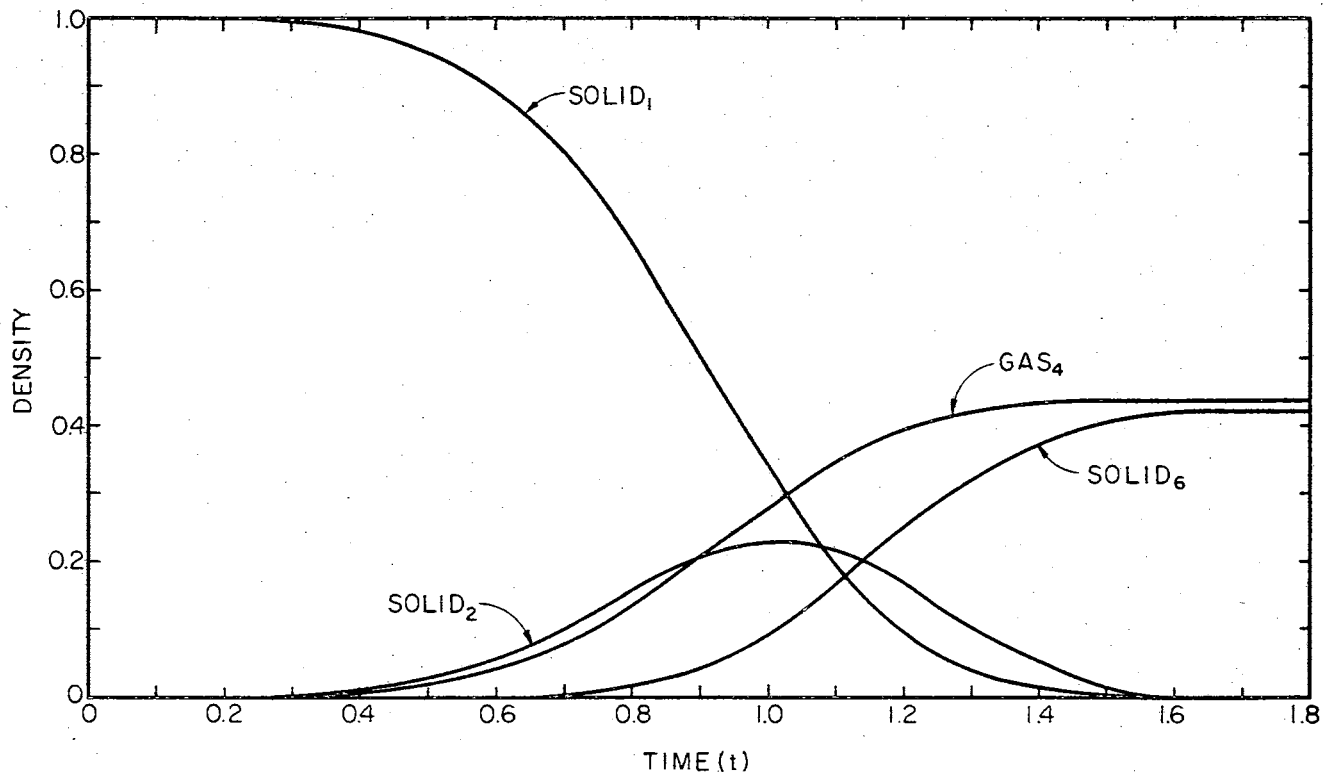
Figure 24.   Selected Species Histories for Three Reactions--
Convective Heating, Case 0
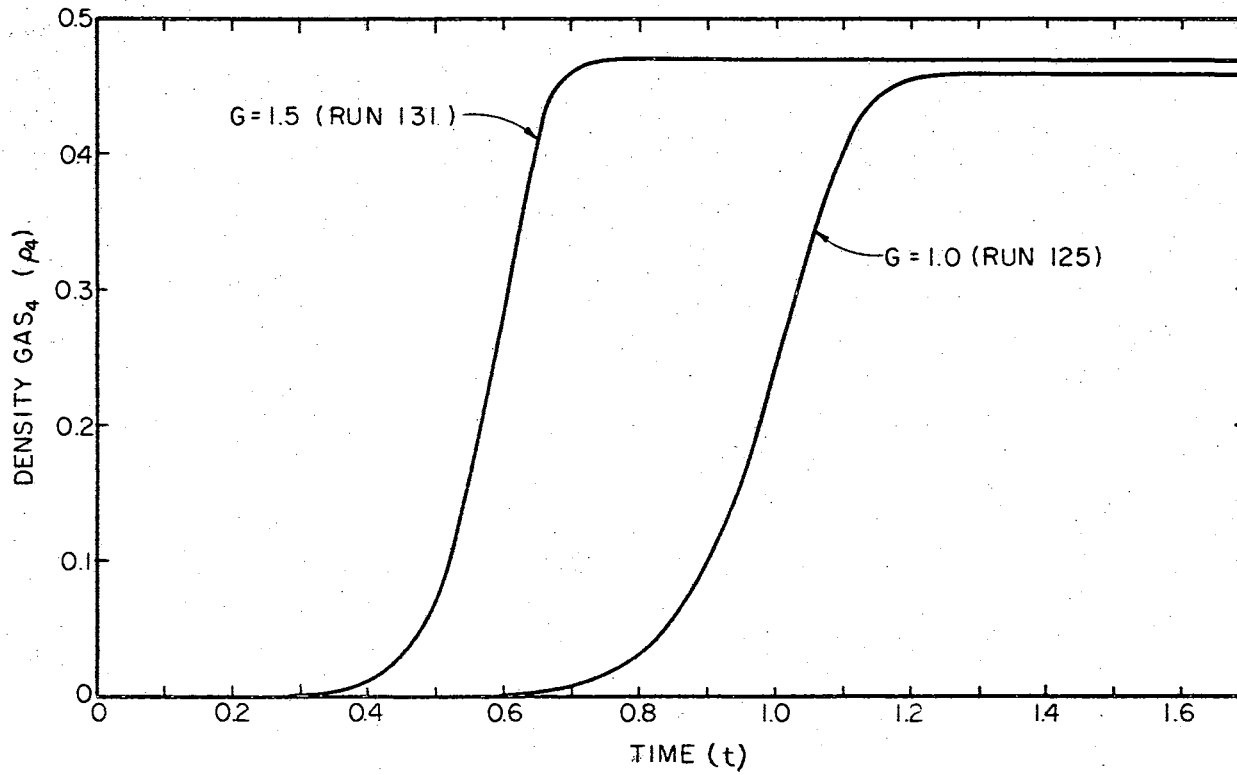
Figure 25. Effect of Heat Flux Parameter: Production of Gas$_4$ from $x = 1.0$--Constant Heat Flux, Three Reactions, Case 0
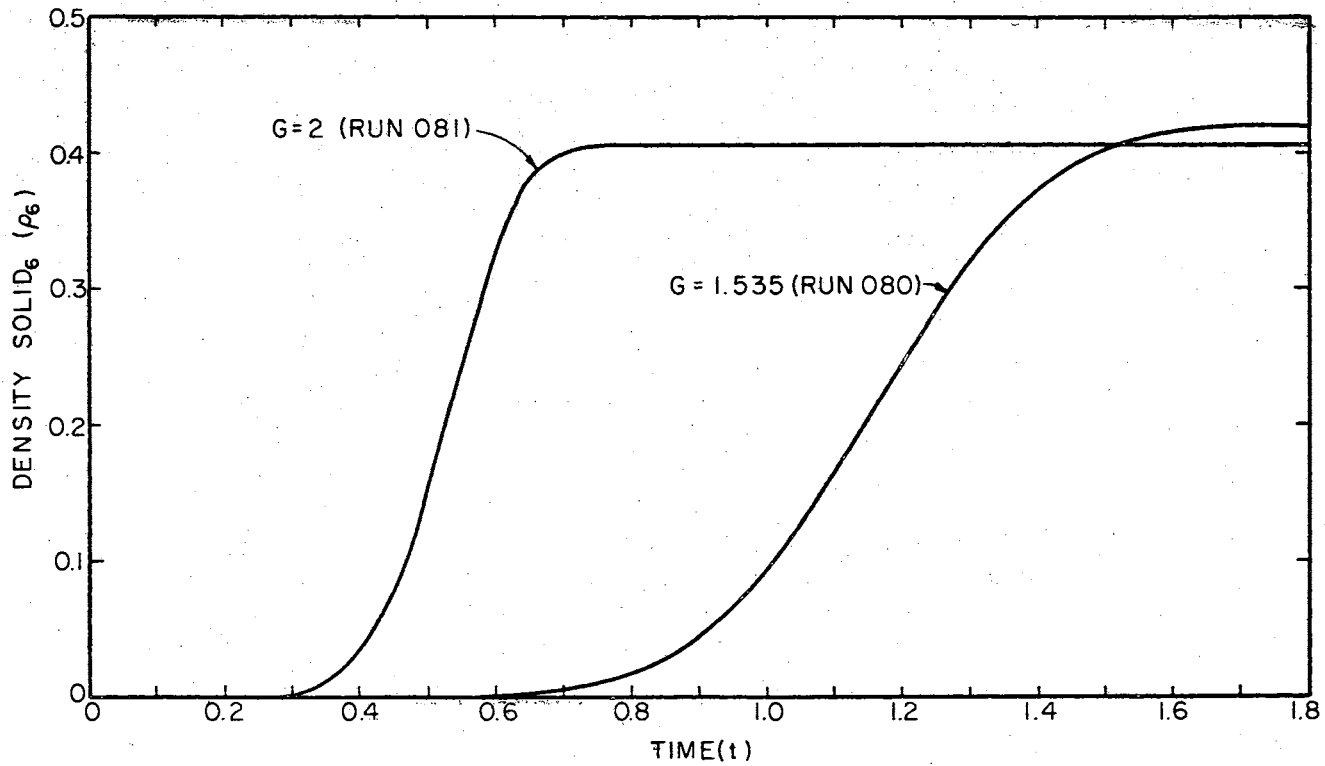
Figure 26. Effect of Heat Flux Parameter: Production of $Solid_6$
at $x = 1.0$--Convective Heating, Three Reactions,
Case 0

its rate of formation is higher and time of formation is much sooner than for the lower heat flux case.

One theory for the addition of chemicals to the solid for fire retardant purposes is that it tends to lower the activation energy for the first reaction thus producing more char and less Gas_4. Figure 27 shows that lowering the activation energy for reaction 1 by 4% increased the amount of char by 30%, which also greatly reduced the amount of Gas_4 produced. The reaction times were about the same with the rate of production then depending on the amount of $Solid_6$ produced.

The largest experimental error in the kinetic constants occurs in the determination of the frequency factor since the actual mass of reactant is difficult to determine for multiple reactions. Figure 28 shows the effect of a change in the frequency factor for reaction 1 on the amount of $Solid_6$ produced. Increasing the frequency factor by a factor of 5 increased the amount of char by a factor of 3.

The amount of solid present may be important to slab strength considerations as well as for thermal conductivity effects. Figure 29 shows the total solid history for changes in the activation energy of reaction 1. The early times of the reaction show less solid present for the lower activation energy case and the latter times show more solid present. The higher activation energy case delays the reaction of $Solid_1$, causing more total solid to be available in the early times. In fact, combinations of the kinetic constants could produce a crossover point of equal amount of solid for high and low activation energies that was less than some value for strength requirements. This would mean that addition of fire retardant chemicals could produce a solid that burned slower but failed quicker than an untreated solid.
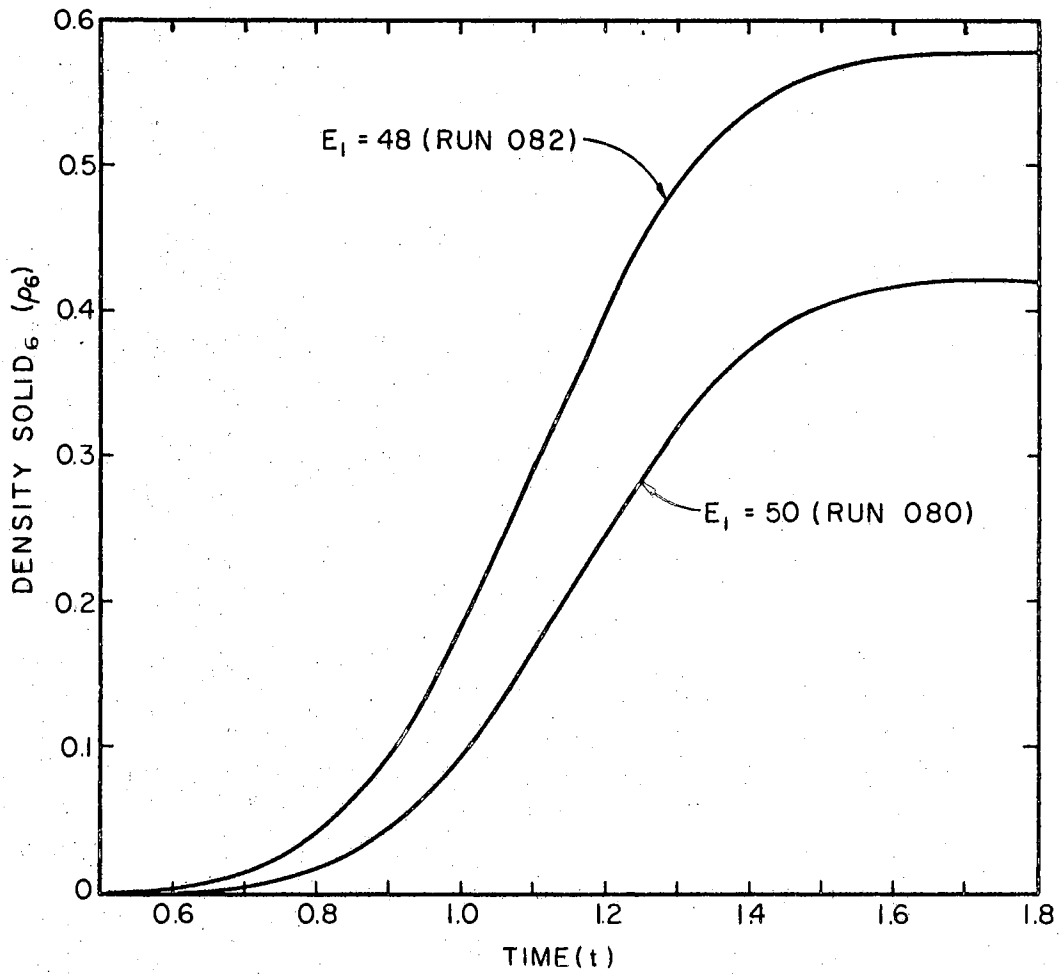
Figure 27. Effect of Change of Activation Energy
Parameter for Reaction 1: Production
of $Solid_6$ at x = 1.0--Convective Heat-
ing, Three Reactions, Case 0
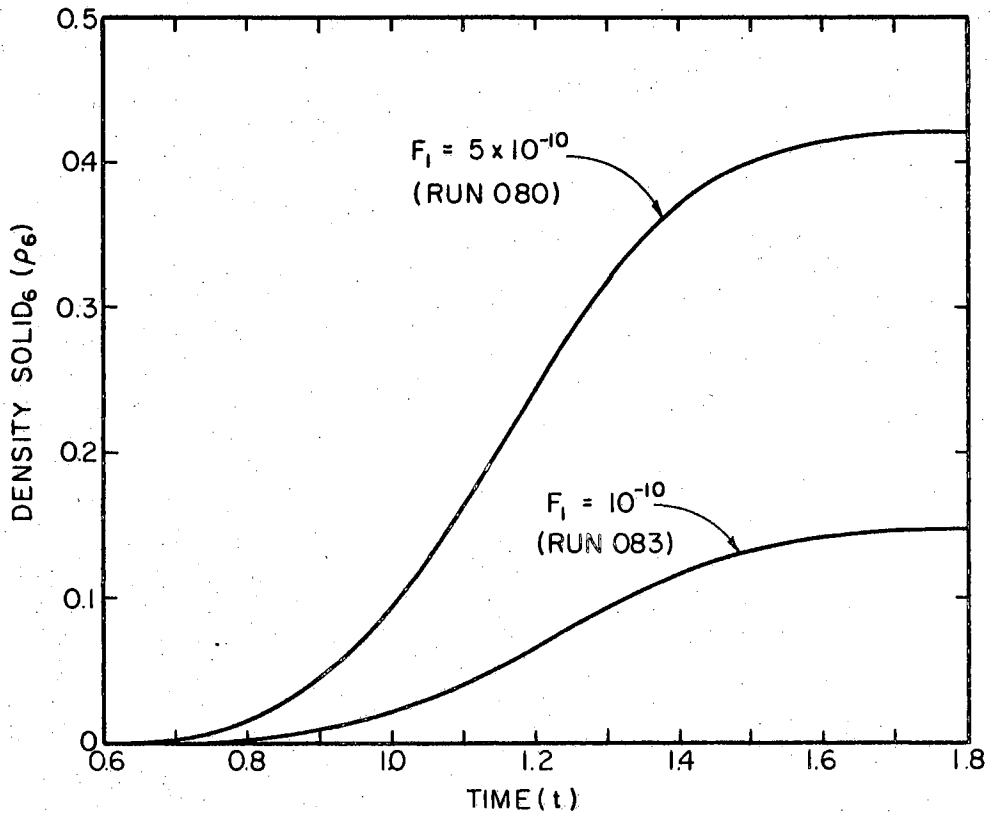
Figure 28. Effect of Change of Frequency Factor Parameter for Reaction 1: Production of $Solid_6$ at $x = 1.0$--Convective Heating, Three Reactions, Case 0
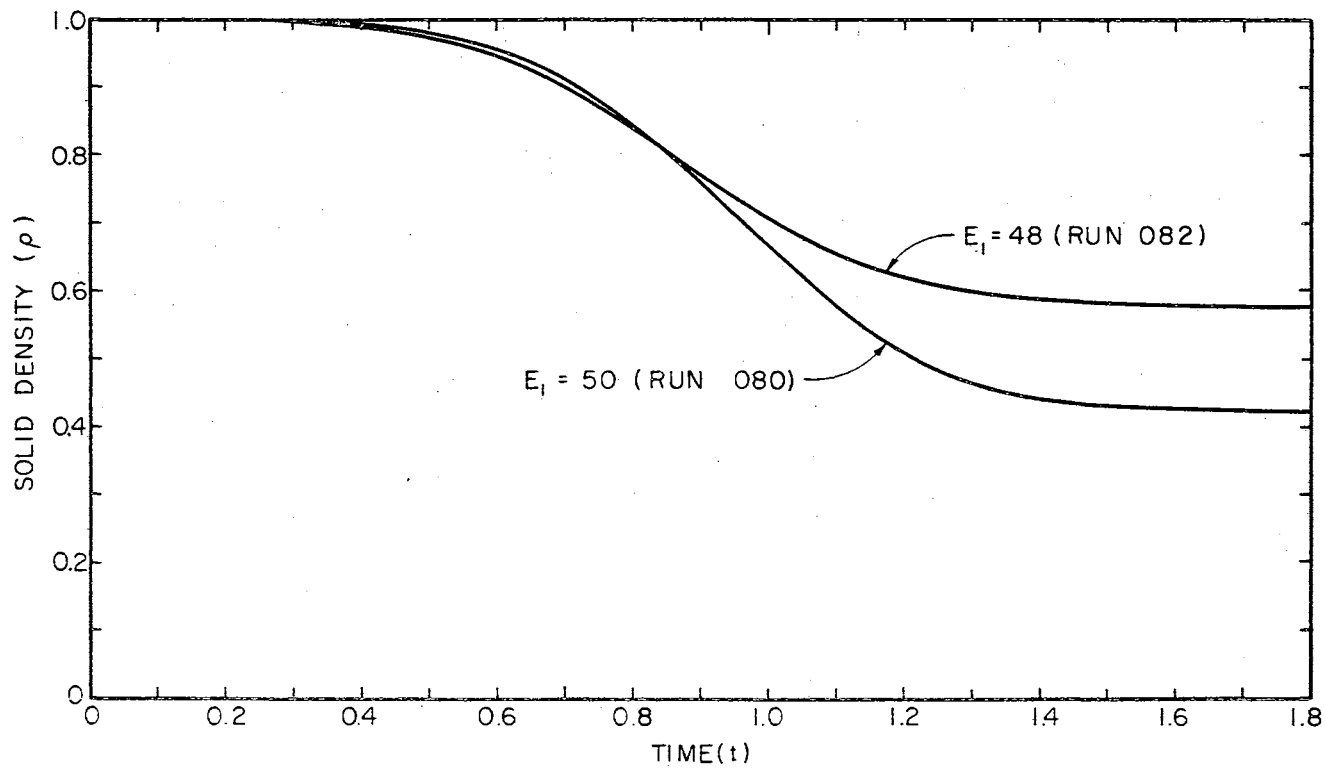
Figure 29. Effect of Change of Activation Energy of
          Reaction 1: Production of Total Solid
          at x = 1.0--Convective Heating, Three
          Reactions, Case 0

In conclusion, this section showed how the competing reactions affected the production of $Solid_6$ and Gas_4 when changes were made in the kinetic constants and heat flux parameter.

Three Reactions with Heats of Reaction

After investigating the influence of separate events, the problem was calculated with all the reactions and heats of reaction included. For the radiantly heated boundary condition, the density-dependent, effective thermal conductivity case was used with a constant heat flux at the surface and no heat losses (Case 1). Cases 0 and 2 are not presented since Case 1 is closer to the actual physical situation, and similar effects of the two cases are shown by the convective heated boundary conditions.

Figure 30 gives the temperature history for the radiantly heated slab with endothermic, competing reactions producing Gas_3, $Solid_2$, and Gas_4, and an exothermic reaction producing Gas_5 and $Solid_6$. At the surface, the endothermic reactions and the decreasing effective thermal conductivity tend to cancel the heat production effects while the endothermic reactions and the decreasing conducted heat effects the temperatures farther into the slab. Eventually, the exothermic reaction at the surface combines with the decreasing effective thermal conductivity to increase the temperature from the inert solution. An effect due to the approximation technique is seen next as the surface temperature tends to level off when the exothermic reaction ends and the interior endothermic reactions continue. When the exothermic reaction starts at the next approximation point ($x = 0.8$), the temperatures all increase at a steep rate as the combined effects of heat
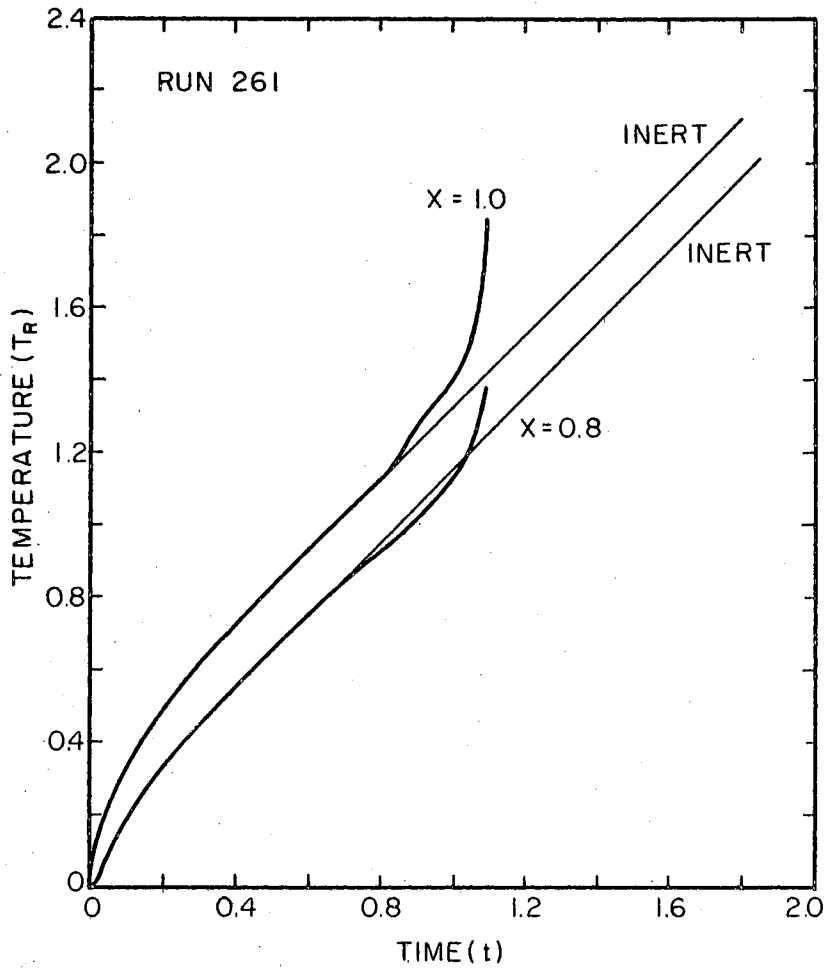
Figure 30. Effect of Heat of Reaction: Tempera-
ture History at x = 1.0 and x = 0.8
for Constant Heat Flux--Three Rea-
tions with Heats of Reactions, Case 1

generated and the decreasing effective thermal conductivity force the
temperature up. In reality, the surface temperature would continue
increasing when its exothermic reaction ended for the reaction would
be continuing into the slab, decreasing the heat conducted from the
surface. Figure 31 shows the production of $Solid_6$ and Gas_4 at x = 1.0
and x = 0.8 (the next approximating strip). The slopes of the species
curve is proportional to the rate of the reaction producing that spe-
cies. The rate of reaction 2 (producing Gas_4) begins increasing at
x = 0.8 before it starts decreasing at x = 1.0. Thus, the finite dis-
tance between the approximating strips does not visibly affect the
temperature history. The rate of reaction 3 (producing $Solid_6$) however,
is almost zero at x = 1.0 before it becomes significant at x = 0.8.
Therefore, the effect of the finite distance is as though the reaction
was turned off and then on. This shows how the width of the reaction
zone can affect any approximation technique that uses a finite number
of points to represent the slab. Without changing the parameters or
kinetic constants, this error can be reduced by increasing the number
of approximating strips and thus decreasing the distance between the
strips. This also illustrates the difficulty in calculating the tem-
peratures for this type of boundary condition with exothermic reactions
because, as the reaction proceeds into the solid, the reaction rate
increases, the temperatures increase, and the higher temperature reac-
tions (here, the exothermic reaction) dominate, causing the tempera-
tures to increase more, increasing the mass loss and decreasing the
effective thermal conductivity. This quickly becomes a runaway situ-
ation with the slab probably following different boundary conditions
after a short period of time due to re-radiation or ignition. Of
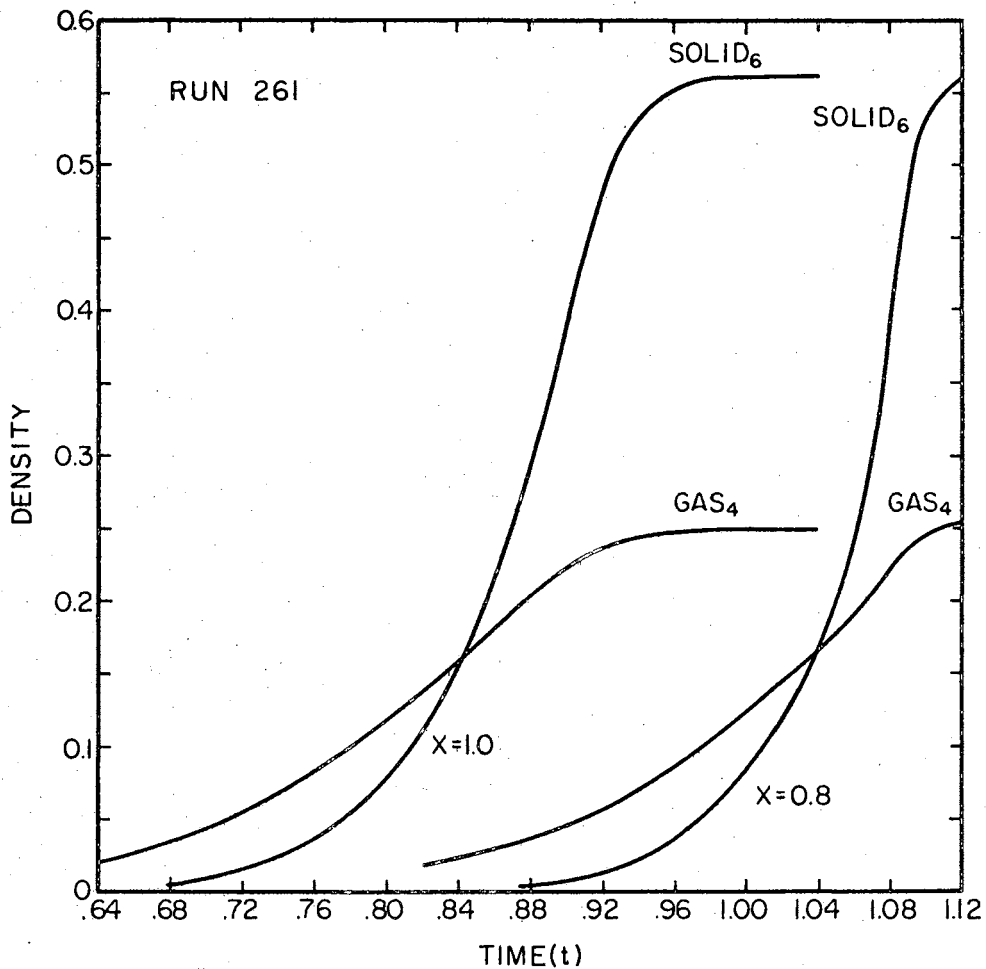
Figure 31. Effect of Heat of Reaction: Production of $Solid_6$ and Gas_4 at $x = 1.0$ and $x = 0.8$--Constant Heat Flux, Three Reactions, Case 1

course, selected values of the reaction constants are possible that would enable this case to be calculated accurately but would probably not be physically realistic.

For the convectively heated boundary condition, three reactions are used, first with a constant effective thermal conductivity and then with the Case 2 conditions. Figure 32 gives the temperature history of the front and back surfaces. The initial endothermic reactions cause the surface temperature to fall below the inert solution until the exothermic reaction increases the temperature above the inert value. At the back surface, the decreasing conducted heat and the endothermic reactions cause the rate of temperature rise to become less than the inert solution. However, as the exothermic reaction begins generating heat from the front surface, the heat begins to accumulate and increases the reaction rate within the solid and finally causes the back surface temperature to exceed the front surface temperature. The initial endothermic character of the reactions caused the competing reactions to produce more $Solid_2$, and thus more $Solid_6$, part of the way into the solid. As the exothermic reaction began to dominate, the competing reactions began producing more Gas_4, and thus, less $Solid_6$. Table VII shows the final slab distribution of $Solid_6$.

If the heat flux parameter is decreased slightly from 1.5 to 1.45, then the first competing reaction will produce more $Solid_2$, and thus $Solid_6$, by being held longer at the lower temperatures. Figure 33 shows the difference in the temperature histories of the front and back surfaces for the two heat flux cases. The smaller heat flux delays the heating events and, by producing more $Solid_6$, causes the exothermic reaction to produce more heat and increase the slab temperatures
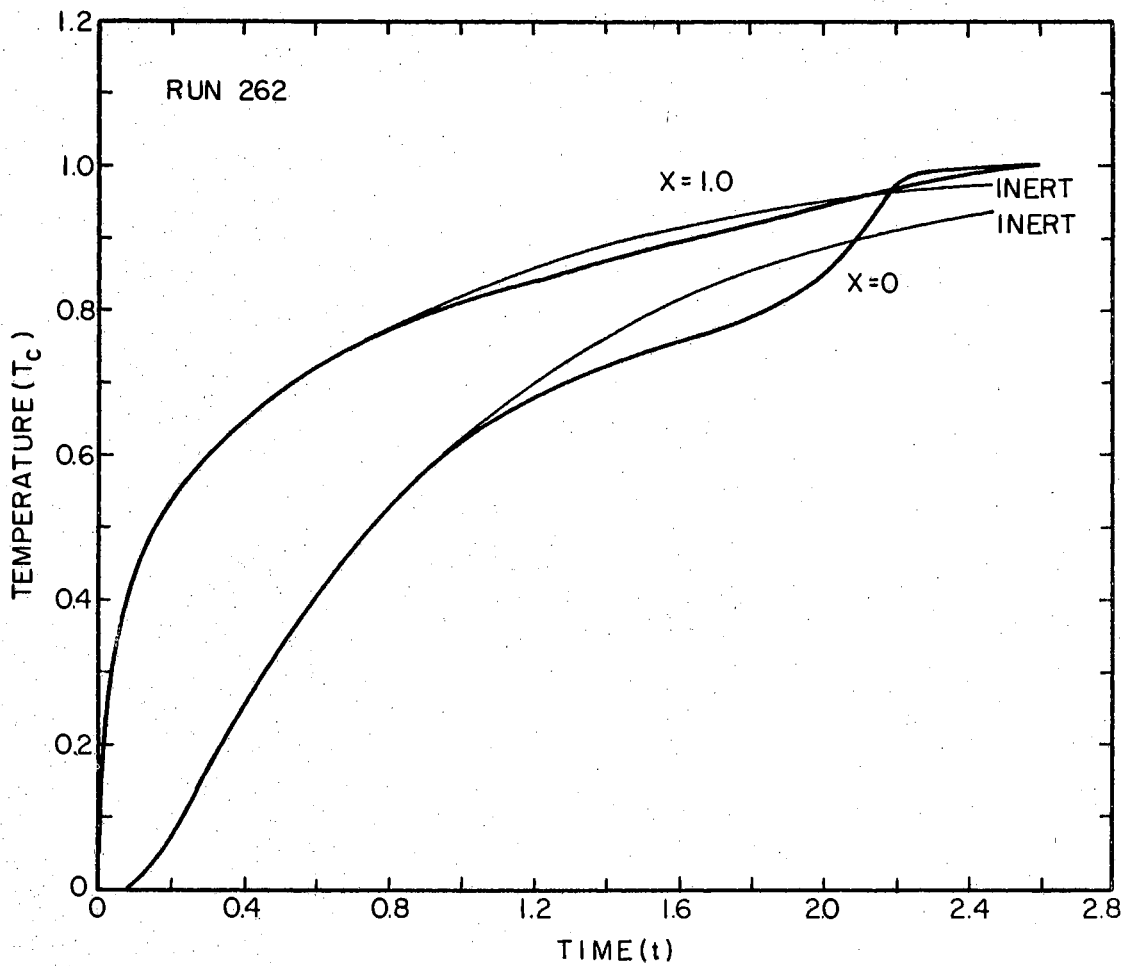
Figure 32. Effect of Heat of Reaction: Temperature Histories
of Front and Back Surfaces for Convective Heating,
Three Reactions with Heats of Reaction, Case 0,
$G = 1.5$
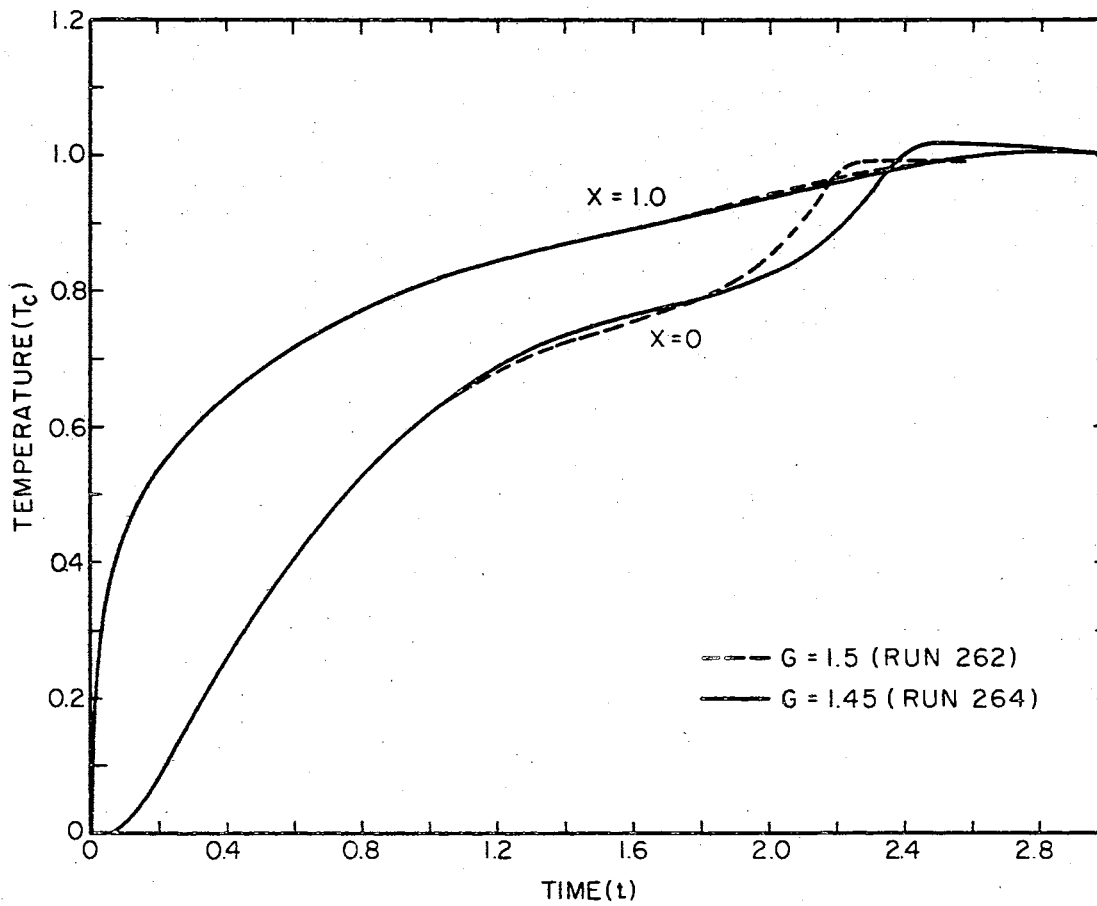
Figure 33.   Effect of Heat Flux Parameter: Temperature
Histories of Front and Back Surfaces--
Convective Heating--Three Reactions with
Heats of Reaction, Case 0

TABLE VII

SLAB DISTRIBUTION OF $SOLID_6$

x	Density of $Solid_6$		
	G = 1.45	G = 1.5	G = 1.75
1.00	.5248	.5195	.4975
0.75	.5260	.5209	.5005
0.50	.5241	.5193	.5008
0.25	.5209	.5161	.4984
0.00	.5192	.5143	.4965

at the later times.

The mass flux also reflects the change in the heat flux parameter. Figure 34 shows that the higher heat flux not only causes the mass flux to increase and occur sooner, but also tends to separate the two main gas producing events which occur as a result of the overall reaction rate increasing in the slab after initially decreasing.

The higher heat flux was then used with the Case 2 boundary condition that considers a density-dependent, effective thermal conductivity and heat transfer coefficient. Figure 35 gives the temperature histories for the two surfaces compared with the Case 0 solution. The resulting effect is that of an endothermic reaction that occurs over the entire temperature range but occurs slightly "out-of-phase" with the other reactions (as described earlier). Also the exothermic reaction tends to be dampened since the trend to increase the change in density and temperature in the x-direction would give a higher endothermic
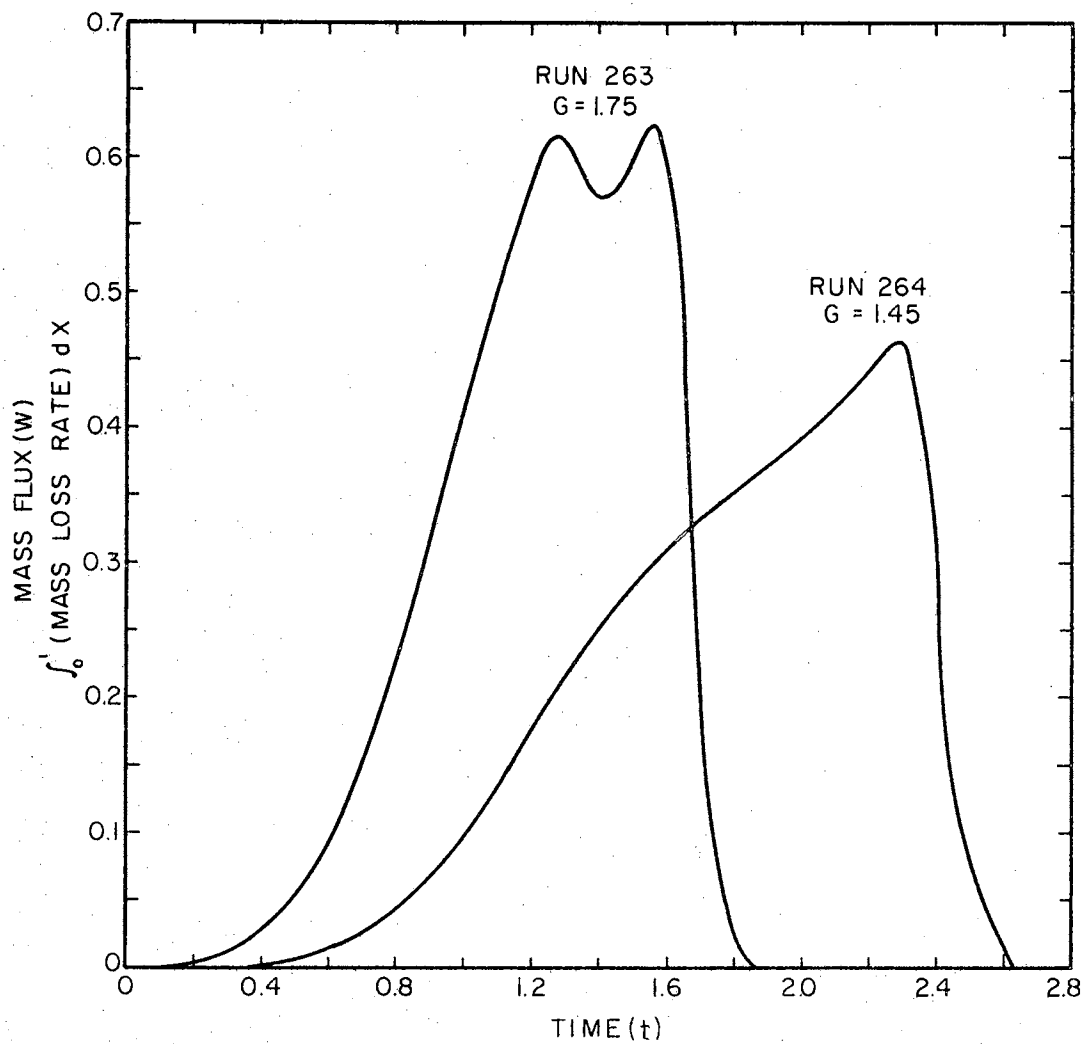
Figure 34. Effect of Heat Flux Parameter: Mass Flux.
from Slab--Convective Heating, Three
Reactions, Case 0
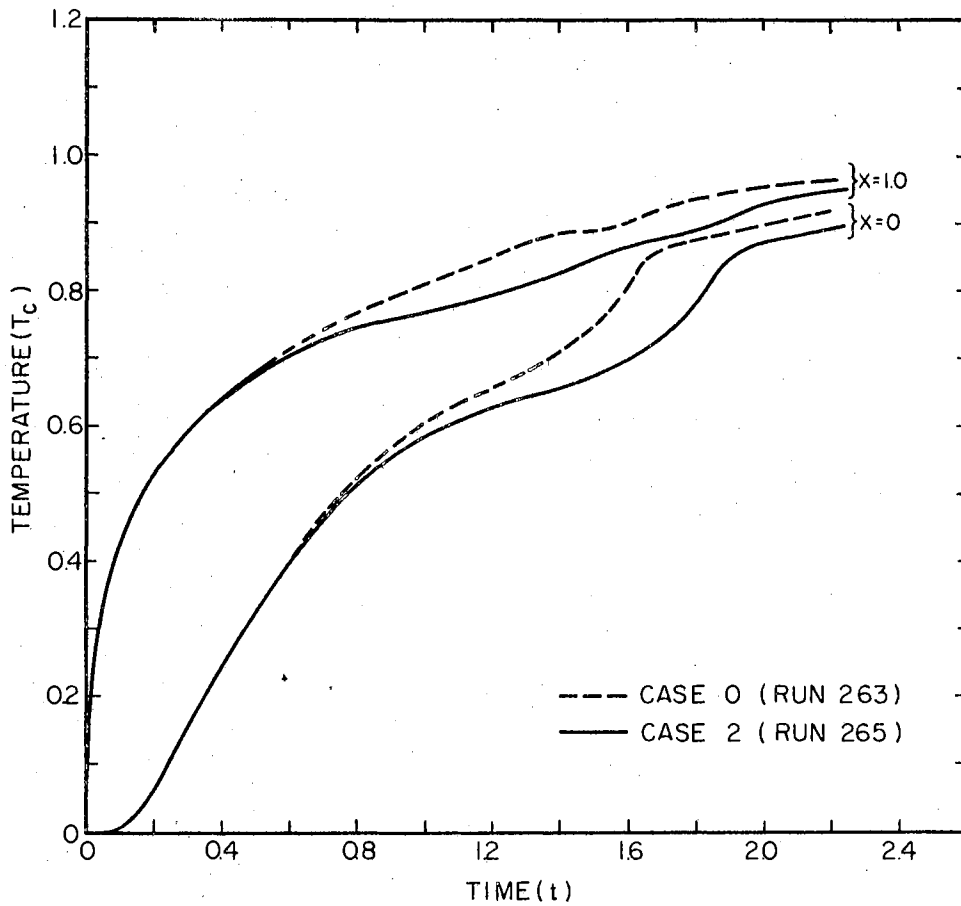
Figure 35. Effect of Variable Conductivity and Heat
            Transfer Coefficients: Temperature
            History of Front and Back Surfaces for
            Convective Heating--Three Reactions
            with Heats of Reaction, Cases 0 and 2

contribution from the conductivity term. Figure 36 shows that the mass flux is modified from the resulting lower surface heat flux.

This section presented the results of three competitive and consecutive reactions with endothermic and exothermic heats of reaction. It was found that a small change in the heat flux parameter greatly affects the temperature history, mass flux, and final char distributions. Higher heat flux values also make heat transfer coefficients and effective thermal conductivity effects more important. A major effect of the competing reaction is to cause a change in the character of the reactions throughout the slab.
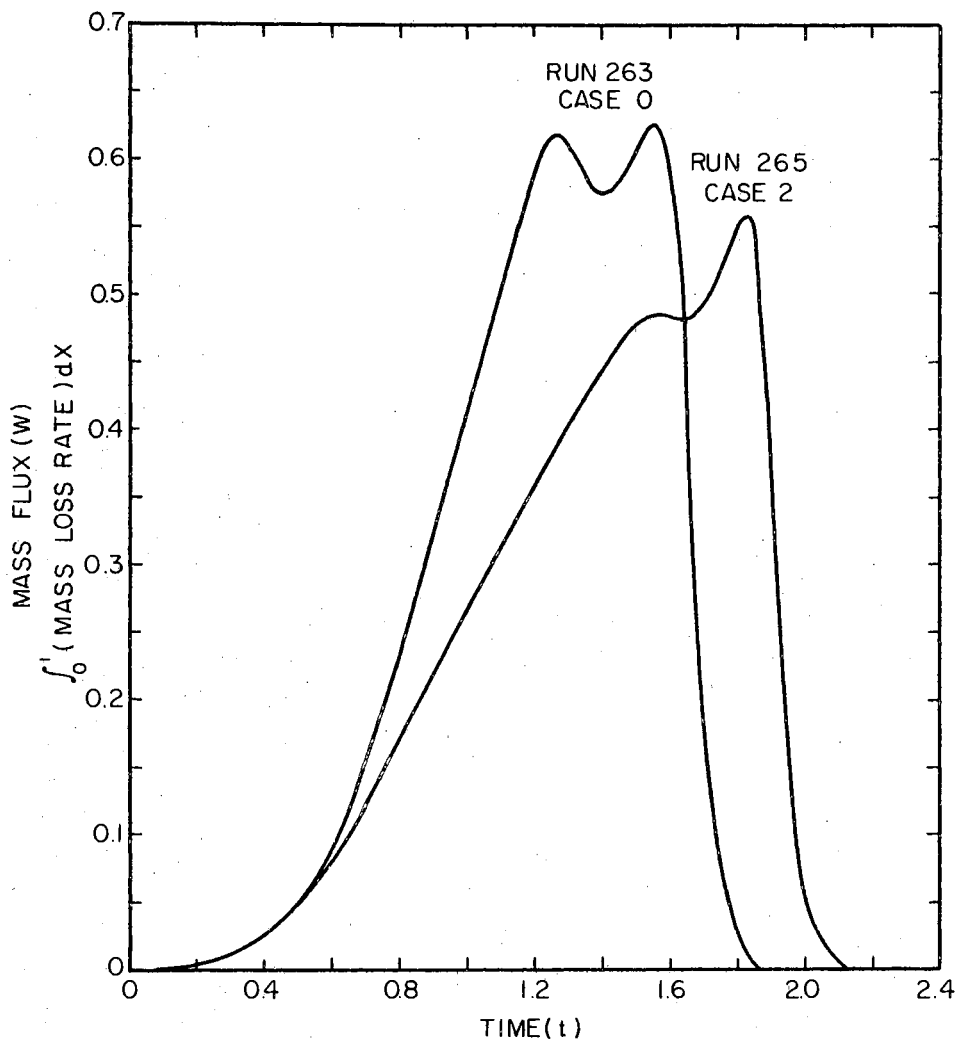
Figure 36. Effect of Changing Conductivity:
Mass Flux from Slab for Convec-
tive Heating--Three Reactions
with Heats of Reaction, Cases 0
and 2

CHAPTER V

SUMMARY

The literature pertaining to the pyrolysis of porous solids was reviewed for information regarding the extent of previous mathematical analyses and experimental determination of the important physical events. As a result, the mathematical analysis was extended to include competitive and consecutive, homogeneous reactions with reactant depletion and consideration of both a constant and density-dependent, effective thermal conductivity. Two types of surface heating for a finite thickness, infinite slab were considered: a constant heat flux, radiative type, and a constant source temperature, convective type. A density-dependent, as well as a constant, heat transfer coefficient for convective heating was included in the various cases that were studied. The characteristic non-dimensional parameters were also developed for both types of boundary conditions.

In order to solve the resulting unsteady, non-linear, second-order, partial differential equation, a numerical technique was developed, based on the method of Integral Relations. The technique requires only a small amount of computer storage and can obtain accurate results for most cases with three to six approximating strips. The ability to obtain better approximations by increasing the number of approximating strips is limited only by the longer computer times required.

The computed results presented temperature and species histories

and slab profiles as well as mass flux, reaction rates, and weight loss information. It was shown that the heat generated or absorbed from the reactions has a great effect on the solid ahead of and behind the reactions as well as in the reaction zone, not only with respect to temperature, but also reaction rates and mass flux. An increasing surface heat flux increases the maximum reaction rate and the temperature at which it occurs.

The effect of a density-dependent, effective thermal conductivity and heat transfer coefficient is negligible for convective heating when source temperatures are low. For radiant heating and high source temperature convective heating, the change in effective thermal conductivity can greatly affect the temperature history of the slab. This is especially true as the final densities become smaller. These effects must be carefully considered when interpreting temperature histories.

Small changes in the activation energies, frequency factors, and surface heat flux, greatly affect the time and rate of production of species for competing reactions while only slightly affecting the quantity produced.

The competing reactions cause a change in the character of the overall reaction throughout the slab and enable small changes in the surface heat flux to greatly affect the temperature history, mass flux, and final char distributions.

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APPENDIX A

INTEGRATION OF EQUATION (3.1)

Starting with Equation (3.1), each term can be integrated as shown.

$$\int_0^1 f_m(x) \frac{\partial T}{\partial t} = \int_0^1 f_m(x) \frac{\partial^2 T}{\partial x^2}\, dx + \int_0^1 f_m(x) \frac{1}{\rho} \frac{\partial \rho}{\partial x} \frac{\partial T}{\partial x}\, dx$$

$$\underset{\text{I}}{} \qquad\qquad \underset{\text{II}}{} \qquad\qquad \underset{\text{III}}{}$$

$$- \frac{1}{G} \sum_{i=1}^3 \int_0^1 f_m(x)\, \overline{H}_i\, dx \qquad\qquad (3.1)$$

$$\underset{\text{IV}}{}$$

Term I:

Using Leibnitz's rule

$$\frac{d}{dt} \int_0^1 f_m(x)\, T\, dx = \int_0^1 f_m(x) \frac{\partial T}{\partial t}\, dx$$

$$\underset{\text{I}}{}$$

Term II:

Integrating by parts

$$\int_0^1 f_m(x) \frac{\partial^2 T}{\partial x^2}\, dx = f_m \left.\frac{\partial T}{\partial x}\right|_0^1 - \left.\frac{df_m}{dx} T\right|_0^1 + \int_0^1 \frac{d^2 f_m}{dx^2}\, T\, dx \qquad (A.1)$$

$$\underset{\text{II}}{}$$

Since

$$f_m(x) = 1,\ x,\ x^2,\ \ldots\ ,\ x^{(N-1)} = x^{(m-1)},\ (m = 1,\ 2,\ \ldots\ ,\ N)$$

$$(A.2a)$$

then

$$\frac{df_m}{dx} = (m - 1) \, x^{(m-2)}, \, \frac{df_1}{dx} = 0, \, \frac{df_2}{dx} = 1 \qquad (A.2b)$$

and

$$\frac{d^2 f_m}{dx^2} = (m - 1)(m - 2) \, x^{(m-3)} \qquad (A.2c)$$

Therefore, Equation (A.1) is

$$\int_0^1 f_m \frac{\partial^2 T}{\partial x^2} \, dx = \left. \frac{\partial T}{\partial x} \right|_{x=1} - \left. \frac{\partial T}{\partial x} \right|_{x=0} \nearrow^{0 \text{ (boundary condition)}} - (m - 1) \, \left. T \right|_{x=1} + \left\{ \left. \begin{matrix} T \end{matrix} \right|_{x=0} \begin{matrix} ; & m = 2 \\ 0 & ; & m \neq 2 \end{matrix} \right\}$$

$$\underset{\text{II}}{}$$

$$+ (m - 1)(m - 2) \int_0^1 x^{(m-3)} \, T \, dx \; .$$

Term III:

Write $\frac{1}{\rho} \frac{\partial \rho}{\partial x}$ as $\frac{\partial (\ln \rho)}{\partial x}$ then, integrate Term III by parts.

$$\int_0^1 f_m \frac{\partial (\ln \rho)}{\partial x} \frac{\partial T}{\partial x} \, dx = f_m \cdot \ln \rho \cdot \left. \frac{\partial T}{\partial x} \right|_0^1 - \int_0^1 f_m \cdot \ln \rho \cdot \frac{\partial^2 T}{\partial x^2} \, dx$$

$$\underset{\text{III}}{}$$

$$- \int_0^1 \ln \rho \cdot \frac{df_m}{dx} \cdot \frac{\partial T}{\partial x} \, dx$$

Using Equation (A.2)

$$\int_0^1 f_m \frac{\partial (\ln \rho)}{\partial x} \frac{\partial T}{\partial x} \, dx = \ln \rho \cdot \left. \frac{\partial T}{\partial x} \right|_{x=1} - \int_0^1 x^{(m-1)} \ln \rho \cdot \frac{\partial^2 T}{\partial x^2} \, dx$$

$$\underset{\text{III}}{}$$

$$- (m - 1) \int_0^1 \ln \rho \cdot x^{(m-2)} \cdot \frac{\partial T}{\partial x} \, dx$$

Term IV:

Substitute for $f_m(x)$ from Equation (A.2a)

$$\frac{1}{G} \sum_{i=1}^{3} \int_0^1 f_m \, \overline{H}_i \, dx = \frac{1}{G} \sum_{i=1}^{3} \int_0^1 x^{(m-1)} \, \overline{H}_i \, dx$$

Putting the equivalent expression for each term back into Equation (3.1) yields Equation (3.4).

INTEGRATION OF EQUATION (3.4)

Substituting the approximations (3.5) into Equation (3.4) and multiplying the x-polynomials result in

$$\frac{d}{dt} \int_0^1 \sum_{n=1}^{N+2} A_{(n)} x^{(m+n-2)} \, dx = \left. \frac{\partial T}{\partial x} \right|_{x=1} - (m-1) \sum_{n=1}^{N+2} A_{(n)} + A_{(1)} \Big|_{m=2}$$

$$+ (m-1)(m-2) \int_0^1 \sum_{n=1}^{N+2} A_{(n)} x^{(m+n-4)} \, dx$$

$$+ \ln \rho \cdot \left. \frac{\partial T}{\partial x} \right|_{x=1} - \int_0^1 \sum_{n=1}^{N} J_{1(n)} x^{(m+n-2)} \, dx$$

$$- (m-1) \int_0^1 \sum_{n=1}^{N} J_{2(n)} x^{(m+n-3)} \, dx$$

$$- \frac{1}{G} \sum_{i=1}^{3} \frac{R_i}{F_i} \int_0^1 \sum_{n=1}^{N+1} H_{i(n)} x^{(m+n-2)} \, dx \qquad (B.1)$$

Integrate Equation (B.1) and obtain

$$\sum_{n=1}^{N+2} \left(\frac{1}{m+n-1}\right) \frac{dA_{(n)}}{dt} = [(1 + \ln \rho) B|_{x=1} - (m-1) \sum_{n=1}^{N+2} A_{(n)} + A_{(1)}]_{m=2}$$

$$+ (m-1)(m-2) \sum_{n=1}^{N+2} \left(\frac{1}{m+n-3}\right) A_{(n)} - \sum_{n=1}^{N} \left(\frac{1}{m+n-1}\right) J_{1(n)}$$

$$- (m-1) \sum_{n=1}^{N} \left(\frac{1}{m+n-2}\right) J_{2(n)} - \frac{1}{G} \sum_{i=1}^{3} \frac{R_i}{F_i} \sum_{n=1}^{N+1} \left(\frac{1}{m+n-1}\right) H_{i(n)}$$

$$(B.2)$$

Where $B = \left.\dfrac{\partial T}{\partial x}\right|_{x=1}$ and depends on the type and case of boundary condition being considered. Terms 2, 3, and 4 to the right of the equal sign in Equation (B.2) can be combined in the following way: First, rewrite as

$$- (m - 1) A_{(1)} - (m - 1) \sum_{n=2}^{N+2} A_{(n)} + A_{(1)}\Big|_{m=2} + (m - 1) A_{(1)}\Big|_{m \geq 3}$$

$$+ (m - 1)(m - 2) \sum_{n=2}^{N+2} \left(\frac{1}{m + n - 3}\right) A_{(n)}$$

then, the $A_{(1)}$ terms will cancel for all values of m and the remaining terms will combine to give

$$\sum_{n=2}^{N+2} \left[\frac{(m - 1)(m - 2)}{(m + n - 3)} - (m - 1)\right] A_{(n)} = -(m - 1) \sum_{n=2}^{N+2} \frac{(n - 1)}{(m + n - 3)} A_{(n)}$$

When the temperature approximation (3.5a) is used in the boundary condition (2.11d), the result is that $A_{(2)}(t) = 0$. Therefore, the summation index on the above term can be changed to

$$- (m - 1) \sum_{n=1}^{N} \frac{(n + 1)}{(m + n - 1)} A_{(n+2)} \tag{B.3}$$

Likewise, the first term of Equation (B.2) can be written as

$$\frac{1}{m} \frac{dA_{(1)}}{dt} + \sum_{n=1}^{N} \left(\frac{1}{m + n + 1}\right) \frac{dA_{(n+2)}}{dt} \tag{B.4}$$

Substituting expressions (B.3) and (B.4) into Equation (B.2) gives Equation (3.6).

APPENDIX C

EVALUATION OF INITIAL TEMPERATURE COEFFICIENTS

The temperature approximation (3.5a) is used in the boundary conditions (2.11a, d) to evaluate the initial values for the coefficients in the following way.

Since

$$T(x, 0) = 0$$

then

$$\sum_{n=1}^{N+2} A_{(n)}(0) \ x^{(n-1)} = 0 \qquad (C.1)$$

giving

$$A_{(1)}(0) = 0 \ . \qquad (C.2)$$

Since

$$\left. \frac{\partial T}{\partial x} \right|_{x=0} = 0$$

then

$$A_{(2)}(0) = 0 \qquad (C.3)$$

At $x = 1$, $t = 0$; $\frac{\partial T}{\partial x} = \frac{q(0)}{\rho(1, 0)} = \frac{1}{1}$, all cases

Therefore,

$$\sum_{n=3}^{N+2} (n - 1) \ A_{(n)}(0) = 1 \qquad (C.4)$$

Equations (C.1) to (C.4) are also Equations (3.9).

APPENDIX D

CALCULATION OF THE TEMPERATURE IN

AN INERT SLAB BY THE

INTEGRAL METHOD

For the inert slab only the first two terms of Equation (2.9) are
needed:

$$\frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2} \tag{D.1}$$

The boundary conditions will be Equation (2.11a, d, f):

$$T(x, 0) = 0 \tag{D.2}$$

$$\left.\frac{\partial T}{\partial x}\right|_{x=0} = 0 \tag{D.3}$$

$$\left.\frac{\partial T}{\partial x}\right|_{x=1} = 1 \quad \text{(constant heat flux)} \tag{D.4}$$

Following the steps outlined in Chapter III, "Summary of the Inte-
gral Technique," the slab is divided by two planes (N = 2), the sur-
faces $x = 0$ and $x = 1$. Equation (D.1) is multiplied by the weighting
functions, $f_m(x) = 1$, x, and integrated over the slab:

$$\frac{d}{dt} \int_0^1 1 \cdot T \, dx = 1 \cdot \left.\frac{\partial T}{\partial x}\right|_{x=1} - 1 \cdot \left.\frac{\partial T}{\partial x}\right|_{x=0} - T(1, t) \cdot 0 + T(0, t) \cdot 0$$

$$\tag{D.5a}$$

$$\frac{d}{dt} \int_0^1 x \cdot T \, dx = (1) \cdot \frac{\partial T}{\partial x}\Big|_{x=1} - (0) \frac{\partial T}{\partial x}\Big|_{x=0} - T(1, t) \cdot 1 + T(0, t) \cdot 1$$

$$(D.5b)$$

Using the temperature approximation, Equation (3.5a),

$$T(x, t) = \sum_{n=1}^{N+2} A_{(n)}(t) \, x^{(n-1)} = A_{(1)} + A_{(2)}x + A_{(3)}x^2 + A_{(4)}x^3$$

$$(D.6)$$

Equation (D.3) gives

$$A_{(2)} = 0 \qquad\qquad (D.7)$$

while Equation (D.4) gives

$$2A_{(3)} + 3A_{(4)} = 1 \qquad\qquad (D.8)$$

Using Equation (D.6) and (D.7) in (D.5) gives

$$\frac{d}{dt} \int_0^1 (A_{(1)} + A_{(3)}x^2 + A_{(4)}x^3) \, dx = 1 \qquad (D.9a)$$

$$\frac{d}{dt} \int_0^1 (A_{(1)}x + A_{(3)}x^3 + A_{(4)}x^4) \, dx = 1 - A_{(3)} - A_{(4)} \qquad (D.9b)$$

Integrating

$$\frac{dA_{(1)}}{dt} + \frac{1}{3}\frac{dA_{(3)}}{dt} + \frac{1}{4}\frac{dA_{(4)}}{dt} = 1 \qquad\qquad (D.10a)$$

$$\frac{1}{2}\frac{dA_{(1)}}{dt} + \frac{1}{4}\frac{dA_{(3)}}{dt} + \frac{1}{5}\frac{dA_{(4)}}{dt} = 1 - A_{(3)} - A_{(4)} \qquad (D.10b)$$

Taking the derivative of Equation (D.8) and using Equation (D.10) elim-

inates $\frac{dA_{(4)}}{dt}$:

$$\frac{dA_{(4)}}{dt} = \frac{1}{3} - \frac{2}{3}\frac{dA_{(3)}}{dt}$$

$$\frac{dA_{(1)}}{dt} + \frac{1}{6}\frac{dA_{(3)}}{dt} = 1 \qquad (D.11a)$$

$$3\frac{dA_{(1)}}{dt} + \frac{7}{10}\frac{dA_{(3)}}{dt} = 4 - 2A_{(3)} \qquad (D.11b)$$

Solving Equation (D.11) simultaneously gives explicit equations for each coefficient:

$$\frac{dA_{(1)}}{dt} = \frac{1}{6} + \frac{5}{3}A_{(3)} \qquad (D.12a)$$

$$\frac{dA_{(3)}}{dt} = 5 - 10A_{(3)} \qquad (D.12b)$$

Integrating (D.12b)

$$A_{(3)} = \frac{1}{2} + c_1 e^{-10t} \qquad (D.13)$$

Substituting Equation (D.13) into (D.12a) and integrating

$$A_{(1)} = t - \frac{1}{6} c_1 e^{-10t} + c_2 \qquad (D.14)$$

Using the initial conditions (D.2) at both N strips together with Equations (D.8), (D.13), and (D.14) evaluates the two constants. The coefficients then become

$$A_{(1)} = t + \frac{1}{4}(e^{-10t} - 1)$$

$$A_{(3)} = \frac{1}{2}(1 - 3e^{-10t})$$

$$A_{(4)} = e^{-10t}$$

$$A_{(2)} = 0$$

Equation (D.6) then becomes

$$T(x, t) = t + \frac{1}{2} x^2 - \frac{1}{4} + \frac{1}{4} (1 - 6x^2 + 4x^3) e^{-10t}$$

Compare with the exact solution from Carslaw and Jaeger (6):

$$T(x, t) = t + \frac{1}{2} x^2 - \frac{1}{6} + \frac{2}{\pi^2} (1 - \frac{\pi^2}{2} x^2 + \frac{\pi^4}{24} x^4 - \ldots) e^{-\pi^2 t} - \ldots$$

APPENDIX E

CALCULATION OF GAS SPECIES

By identifying the fraction of each solid species that is consumed or produced in the various reactions, the mass balance equations (2.5) can be used to calculate the gas species.

$\rho_{1,1}$ = mass of $solid_1$ converted to product in reaction 1

$\rho_{1,2}$ = mass of $solid_1$ converted to product in reaction 2

$\rho_{2,1}$ = mass of $solid_2$ produced in reaction 1

$\rho_{2,3}$ = mass of $solid_2$ converted to product in reaction 3

ρ_1, ρ_2, and ρ_6 are the calculated solid species that are present at a given instant. ρ_3, ρ_4, and ρ_5 are the gas species that have been produced up to a given point in time.

Then,

$$1 = \rho_1 + \rho_{1,1} + \rho_{1,2}$$

$$c_1\rho_{1,1} = \rho_{2,1} = \rho_2 + \rho_{2,3} ; \quad (1 - c_1)\, \rho_{1,1} = \rho_3$$

$$\rho_{1,2} = \rho_4$$

$$c_2\rho_{2,3} = \rho_6 ; \quad (1 - c_2)\rho_{2,3} = \rho_5$$

Using these relations, the amount of each gas species can be found from the solid species:

$$\rho_{2,1} = \rho_2 + \frac{\rho_6}{c_2} \; ; \qquad \rho_{1,1} = \frac{\rho_2}{c_1} + \frac{\rho_6}{c_1 c_2}$$

$$\rho_3 = (1 - c_1)(\frac{\rho_2}{c_1} + \frac{\rho_6}{c_1 c_2}) = Gas_3 \qquad\qquad (E.1a)$$

$$\rho_4 = 1 - \rho_1 - (\frac{\rho_2}{c_1} + \frac{\rho_6}{c_1 c_2}) = Gas_4 \qquad\qquad (E.1b)$$

$$\rho_5 = \frac{(1 - c_2)}{c_2} \rho_6 = Gas_5 \qquad\qquad (E.1c)$$

Equations (E.1) then become Equations (3.11).

APPENDIX F

DERIVATION OF EQUATION (2.4e)

Start with the species equation for Solid$_1$ (2.8a)

$$\frac{\partial \rho_1^*}{\partial t^*} = -\rho_1^*(k_1 + k_2) \ ,$$

divide by ρ_1^* ,

$$\frac{\partial(\ln \rho_1^*)}{\partial t^*} = -(k_1 + k_2) \ ,$$

and take the x-derivative

$$\frac{\partial}{\partial x^*}\left(\frac{\partial \ln \rho_1^*}{\partial t^*}\right) = -\left(\frac{\partial k_1}{\partial x^*} + \frac{\partial k_2}{\partial x^*}\right) \ . \tag{F.1}$$

Since $k_i = a_i \exp[(-E_i^*)/(R°T^*)]$, then

$$\frac{\partial k_i}{\partial x^*} = \frac{a_i E_i^*}{R°T^{*2}} \frac{\partial T^*}{\partial x^*} \exp\left(\frac{-E_i^*}{R°T^*}\right)$$

at x = 0, Equation (2.4d) gives

$$\frac{\partial T^*}{\partial x^*} = 0$$

thus, at x = 0

$$\frac{\partial k_i}{\partial x^*} = 0$$

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Equation (F.1) then becomes

$$\frac{\partial}{\partial x^*} \left(\frac{\partial \ln \rho_1^*}{\partial t^*}\right) = 0$$

Reverse the order of differentiation,

$$\frac{\partial}{\partial t^*} \left(\frac{\partial \ln \rho_1^*}{\partial x^*}\right) = 0$$

integrating,

$$\frac{\partial \ln \rho_1^*}{\partial x^*} = f(x) + c_1$$

or also,

$$\frac{1}{\rho_1^*} \frac{\partial \rho_1^*}{\partial x^*} = f(x) + c_1$$

Since $\frac{1}{\rho_1^*} \frac{\partial \rho_1^*}{\partial x^*}$ is not a function of time, it can be determined by evaluating it at any one value of time. At $t = 0$, $\rho_1^* = \rho_0^*$, a constant. Therefore, $\frac{\partial \rho_1^*}{\partial x^*} = 0$ for all time at $x = 0$. The same approach is taken for other solid species so that Equation (2.4e) can be shown for the total solid by

$$\frac{\partial \rho^*}{\partial x^*} = \frac{\partial \rho_1^*}{\partial x^*} + \frac{\partial \rho_2^*}{\partial x^*} + \frac{\partial \rho_6^*}{\partial x^*} = 0$$

at $x = 0$ for all time.

APPENDIX G

LISTING OF COMPUTER PROGRAM VARIABLES

Main Program

Computer Variable with Maximum Dimension	Mathematical Variable	Description
A(N+2)	$A_{(n)}$	Polynomial temperature coefficient
B(N*N)		Matrix coefficients for columnwise input to SIMQ--destroyed in computation
E(3)	E_i	Activation energy parameter for reaction i
G	G	Surface heat flux parameter
N	N	Number of interpolation strips
R(3)	R_i	Heat of reaction parameter
T	t	Time variable
X(N)	x_j	x-value of jth interpolation strip
Y(202)		Variables used in START and KAMSUB to store unknowns and derivatives
AB(N)		Vector of original constants for input to SIMQ--Returns solution values
BO	Nu	Nusselt number
CS(N+1)		Polynomial coefficients for average solid (weight)
C1(N)	$\rho_{1,j}$	Local density of Solid$_1$
C2(N)	$\rho_{2,j}$	Local density of Solid$_2$

Computer Variable with Maximum Dimension	Mathematical Variable	Description
C3(N)	$\rho_{3,j}$	Local total mass of Gas$_3$ produced from strip j
C4(N)	$\rho_{4,j}$	Local total mass of Gas$_4$ produced from strip j
C5(N)	$\rho_{5,j}$	Local total mass of Gas$_5$ produced from strip j
C6(N)	$\rho_{6,j}$	Local density of Solid$_6$
DI	n	Summation dummy index
F1	F_1	Frequency factor parameter for reaction 1
F2	F_2	Frequency factor parameter for reaction 2
F3	F_3	Frequency factor parameter for reaction 3
KS		Flag in SIMQ: 0 = normal solution, 1 = singular solution (see Appendix H)
LN	(N-1)	Program constant
NE	(4N+2)	Number of unknowns--for START and KAMSUB
S3(N+1)		Polynomial coefficients for total mass of Gas$_3$ produced from slab
S4(N+1)		Polynomial coefficients for total mass of Gas$_4$ produced from slab
S5(N+1)		Polynomial coefficients for total mass of Gas$_5$ produced from slab
XJ		Intermediate computational value
XP		Intermediate computational value
AP1	(N+1)	Program constant
AP2	(n+2)	Summation dummy index + 2
BCS((N-1)^2)		Matrix coefficients for total solid polynomial--input to SIMQ

Computer Variable with Maximum Dimension	Mathematical Variable	Description
BDC$((N-1)^2)$		Matrix coefficients for gas generation polynomial--input to SIMQ
BS3$((N-1)^2)$		Matrix coefficients for total Gas_3 polynomial--input to SIMQ
BS4$((N-1)^2)$		Matrix coefficients for total Gas_4 polynomial--input to SIMQ
BS5$((N-1)^2)$		Matrix coefficients for total Gas_5 polynomial--input to SIMQ
CS1	c_1	Mass fraction of $Solid_1$ converted to $Solid_2$
CS2	c_2	Mass fraction of $Solid_2$ converted to $Solid_6$
DCT$(N+1)$		Polynomial coefficients for gas generation rate
DEL		Initial time step-size
DLP		Fraction used to reduce time step-size
DSM(N)		Local solid density time-derivative
IBC		Boundary condition type: $0 =$ Type I, $1 =$ Type II (see Chapter II)
IM1	$(n-1)$	Summation dummy index $- 1$
IP1	$(n+1)$	Summation dummy index $+ 1$
IP2	$(n+2)$	Summation dummy index $+ 2$
JM1	$(m-1)$	Summation dummy index $- 1$
MER		Error calculation option in KAMSUB: $1 =$ relative error, $2 =$ absolute error
MOP		Integration option for KAMSUB: $1 =$ Runga-Kutta, $2 =$ Adams fixed step size, $3 =$ Adams variable step size
NP1	$(N+1)$	Program constant

Computer Variable with Maximum Dimension	Mathematical Variable	Description
NP2	$(N+2)$	Program constant
NSQ	N^2	Program constant
RCS(N)	ρ_j	Local total solid density at strip j
WGT		Slab weight--average solid density
XJI		Intermediate computational value
ASUM		Intermediate computational value
BBCS(N-1)		Vector of original constants for input to SIMQ
BBDC(N-1)		Vector of original constants for input to SIMQ
BBS3(N-1)		Vector of original constants for input to SIMQ
BBS4(N-1)		Vector of original constants for input to SIMQ
BBS5(N-1)		Vector of original constants for input to SIMQ
CSUM		Intermediate computational value
DELT		Difference in present and previously printed time-step
DLMN		Minimum allowable time-step in KAMSUB
DLMX		Maximum allowable time-step in KAMSUB
ERMN		Minimum allowable error for KAMSUB
ERMX		Maximum allowable error for KAMSUB
FLUX		Mass flux from slab
FSUM		Intermediate computational value
SPC3		Total mass of Gas_3 produced from slab

Computer Variable with Maximum Dimension	Mathematical Variable	Description
SPC4		Total mass of Gas$_4$ produced from slab
SPC5		Total mass of Gas$_5$ produced from slab
SSFX(N)		Local gas generation rate
TEND		Time value to end calculation
TMIN		Minimum value of DELT for printing all values
TPRT		Value of time when values are printed
XPTH		Intermediate computational value
ICOND		Effective thermal conductivity case: 0 = Case 0, 1 = Case 1, 2 = Case 2 (see Chapter II)
NPRNT		Value of i for printing every i^{th} time step
TMPTR(N)		Local temperature
MCOUNT		Punch and/or print option: 0 = print only, 1 = print and punch
NCOUNT		Number of time-steps computed since the last printed step

Subroutine DERFUN

Variables already described in the Main Program will not be listed as they are either in common or perform the same function.

Computer Variable with Maximum Dimension	Mathematical Variable	Description
M	m	Summation dummy index
Q(3)		Intermediate computational value

Computer Variable with Maximum Dimension	Mathematical Variable	Description
AN	N	Number of interpolation strips
$BG((N-1)^2)$		Matrix coefficients for input to SIMQ
BI	$(n+1)$	Summation dummy index + 1
BN	$(m+n-1)$	Summation dummy indices - 1
$BT((N-1)^2)$		Matrix coefficients for input to SIMQ
DA(N+2)	$\dfrac{dA}{dt}(n)$	Derivative of polynomial temperature coefficients
GS(N)	$J_{1(n)}(t)$	Polynomial coefficients for effective conductivity integral approximation
GT(N)	$J_{2(n)}(t)$	Polynomial coefficients for effective conductivity integral approximation
HS(3, N+1)	$H_{i,(n)}(t)$	Polynomial coefficients for heat generation from reaction i integral approximation
QS	$q(t)$	Time dependent surface heat flux function
BBG(N-1)		Vector of original constants for input to SIMQ
BBT(N-1)		Vector of original constants for input to SIMQ
$BH1((N+1)^2)$		Matrix coefficients for input to SIMQ
$BH2((N-1)^2)$		Matrix coefficients for input to SIMQ
$BH3((N-1)^2)$		Matrix coefficients for input to SIMQ
BII	$n(n+1)$	Summation dummy index term
BMN	$(m+n+1)$	Summation dummy indices + 1
BM1	m	Summation dummy index

Computer Variable with Maximum Dimension	Mathematical Variable	Description
BM2	$(m-1)$	Summation dummy index $-$ 1
BM3	$(n+1)$	Summation dummy index $+$ 1
CK1		Intermediate computational value
CK2		Intermediate computational value
CK3		Intermediate computational value
DC1(N)	$\dfrac{dC_{1(n)}}{dt}$	Local time derivative of Solid$_1$ density
DC2(N)	$\dfrac{dC_{2(n)}}{dt}$	Local time derivative of Solid$_2$ density
DC6(N)	$\dfrac{dC_{6(n)}}{dt}$	Local time derivative of Solid$_6$ density
DQS	$\dfrac{dq}{dt}$	Derivative of time dependent surface heat flux function
DRG		Intermediate computational value
TP1		Intermediate computational value
TP2		Intermediate computational value
TP3		Intermediate computational value
XX1	$(m+1)$	Summation dummy index
ANP2		Intermediate computational value
ASRF		Intermediate computational value
BBH1(N+1)		Vector of original constants for input to SIMQ
BBH2(N+1)		Vector of original constants for input to SIMQ
BBH3(N+1)		Vector of original constants for input to SIMQ
BRCS		Intermediate computational value
BSUM		Intermediate computational value
CNDX		Intermediate computational value

Computer Variable with Maximum Dimension	Mathematical Variable	Description
DNDX		Intermediate computational value
DSUM		Intermediate computational value
SUBK(3, N)	$\overline{k}_{i,(n)}$	Exponential term of local reaction rate constant for reaction i
TSLP		Intermediate computational value
XJII		Intermediate computational value
XJP1		Intermediate computational value

APPENDIX H

DESCRIPTION OF THE SUBROUTINES SIMQ, START, AND KAMSUB

Description of the Subroutine SIMQ

```
C                                                                          SIMQ 001
C     ooooooooooooooooooooooooooooooooooooooooooooooooooooooooooooooooooo SIMQ 002
C                                                                          SIMQ 003
C          SUBROUTINE SIMQ                                                 SIMQ 004
C                                                                          SIMQ 005
C          PURPOSE                                                         SIMQ 006
C             OBTAIN SOLUTION OF A SET OF SIMULTANEOUS LINEAR EQUATIONS,   SIMQ 007
C             AX=B                                                         SIMQ 008
C                                                                          SIMQ 009
C          USAGE                                                           SIMQ 010
C             CALL SIMQ(A,B,N,KS)                                          SIMQ 011
C                                                                          SIMQ 012
C          DESCRIPTION OF PARAMETERS                                       SIMQ 013
C             A - MATRIX OF COEFFICIENTS STORED COLUMNWISE.   THESE ARE    SIMQ 014
C                 DESTROYED IN THE COMPUTATION.   THE SIZE OF MATRIX A IS  SIMQ 015
C                 N BY N.                                                  SIMQ 016
C             B - VECTOR OF ORIGINAL CONSTANTS (LENGTH N). THESE ARE       SIMQ 017
C                 REPLACED BY FINAL SOLUTION VALUES, VECTOR X.             SIMQ 018
C             N - NUMBER OF EQUATIONS AND VARIABLES. N MUST BE .GT. ONE.   SIMQ M01
C             KS - OUTPUT DIGIT                                            SIMQ 020
C                  0 FOR A NORMAL SOLUTION                                 SIMQ 021
C                  1 FOR A SINGULAR SET OF EQUATIONS                       SIMQ 022
C                                                                          SIMQ 023
C          REMARKS                                                         SIMQ 024
C             MATRIX A MUST BE GENERAL.                                    SIMQ 025
C             IF MATRIX IS SINGULAR , SOLUTION VALUES ARE MEANINGLESS.     SIMQ 026
C             AN ALTERNATIVE SOLUTION MAY BE OBTAINED BY USING MATRIX      SIMQ 027
C             INVERSION (MINV) AND MATRIX PRODUCT (GMPRD).                 SIMQ 028
C                                                                          SIMQ 029
C          SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                   SIMQ 030
C             NONE                                                         SIMQ 031
C                                                                          SIMQ 032
C          METHOD                                                          SIMQ 033
C             METHOD OF SOLUTION IS BY ELIMINATION USING LARGEST PIVOTAL   SIMQ 034
C             DIVISOR. EACH STAGE OF ELIMINATION CONSISTS OF INTERCHANGINGSIMQ 035
C             ROWS WHEN NECESSARY TO AVOID DIVISION BY ZERO OR SMALL       SIMQ 036
C             ELEMENTS.                                                    SIMQ 037
C             THE FORWARD SOLUTION TO OBTAIN VARIABLE N IS DONE IN         SIMQ 038
C             N STAGES. THE BACK SOLUTION FOR THE OTHER VARIABLES IS       SIMQ 039
C             CALCULATED BY SUCCESSIVE SUBSTITUTIONS. FINAL SOLUTION       SIMQ 040
C             VALUES ARE DEVELOPED IN VECTOR B, WITH VARIABLE 1 IN B(1),   SIMQ 041
C             VARIABLE 2 IN B(2),.........., VARIABLE N IN B(N).           SIMQ 042
C             IF NO PIVOT CAN BE FOUND EXCEEDING A TOLERANCE OF 0.0,       SIMQ 043
C             THE MATRIX IS CONSIDERED SINGULAR AND KS IS SET TO 1. THIS   SIMQ 044
C             TOLERANCE CAN BE MODIFIED BY REPLACING THE FIRST STATEMENT.  SIMQ 045
C                                                                          SIMQ 046
C     ooooooooooooooooooooooooooooooooooooooooooooooooooooooooooooooooooo SIMQ 047
C                                                                          SIMQ 048
```

Description of the Subroutines START and KAMSUB

Solution of Ordinary Differential Equations

Purpose. Numerical solution of Ne simultaneous first-order ordinary differential equations.

Type. FORTRAN IV.

Mode of Operation. Real, single, and double precision arithmetic.

General Description. The available subroutine package performs numerical integration of Ne (Ne ≤ 100) simultaneous first-order ordinary differential equations. The integration may be carried forward or backward from a specified Ne-set of one-point boundary conditions. The user has the option of selecting the Runge-Kutta or the Adams-Moulton method of numerical integration. When using the Adams-Moulton technique, the user may try a fixed step size or he may let the routine calculate its own step size based on minimum and maximum limits on the integration errors.

In addition to the user's main or calling program, three subroutines are used. Two of these are SUBROUTINE KAMSUB (NSTART) and SUBROUTINE START (M1, M2, M3, A1, A2, A3, A4, A5, A6). The third, entitled SUBROUTINE DERFUN, is prepared by the user to define the functional forms of his differential equations.

The internal operation of the integration is carried out in double-precision arithmetic in order to improve the accuracy. The solutions available externally are in single precision numbers.

Instructions for Usage.

1) The user provides in his main program the following sequence of instructions:

a) Declare a common block: COMMON Y(202)

b) Define the boundary conditions:

$$Y(1), Y(2), \ldots, Y(Ne), Y(Ne + 1)$$

where Y(Ne + 1) is the initial value of the independent

variable.

c) Call the subroutine START to begin the integration process.

The subroutine requires that nine arguments be provided.

The function of each of these parameters is described below.

CALL START (M1, M2, M3, A1, A2, A3, A4, A5, A6)

where M1, M2, M3 are fixed-point numbers and A1, A2, . . . ,

A6 are floating-point numbers.

M1 – The number of equations (M1 ≤ 100)

M2 – Option Parameter

M2 = 1   Integrates by Runge-Kutta Method

M2 = 2   Integrates by Adams-Moulton Method

with fixed step size

M2 = 3   Integrates by Adams-Moulton Method

with the step size internally calcu-

lated based on specified error limits.

M3 – Option parameter for error determination.

M3 = 1   Error calculated as relative error.

M3 = 2   Error calculated as absolute error.

A1 – The step size. (If M2 = 3, this is used as a

first trial value and then adjusted so that the

error conforms to the limits.) A negative value

causes backward integration.

A2 – Maximum value of integration error at each step.

A3 - Minimum value of integration error at each step.

A4 - Largest permitted step size.

A5 - Smallest permitted step size.

A6 - The factor used to reduce the step size when $M2 = 3$ and the integration error is too large.

      Notes: (1) M3, A2 through A6 are applicable only if $M2 = 3$.

           (2) If $A3 = 0$, the routine sets $A3 = A2/55$.

           (3) A6 is specified normally as $0 < A6 < 1$; however, an initial value of zero will cause the routine to set $A6 = 1/2$.

d) Call the subroutine KAMSUB (1) for each step of the independent variable. The call is repeated until the integration has been carried to the desired final value of the independent variable. To preserve the solution for later calculations or printing, it is necessary to store the values after each call of KAMSUB. The block Y(202) only holds the current values of the solution.

2) The user defines the specific functional forms of the differential equation to be integrated in a subroutine DERFUN. The equations must be expressed as first-order equations. The common block Y is utilized as follows:

Y(1), Y(2), . . . , Y(Ne) - The values of the dependent variables.

Y(Ne + 1)   - The corresponding value of the independent variable.

Y(Ne + 2)   - The current step size.

Y(Ne + 3), . . . , Y(2Ne + 2) - The current values of the

derivatives.

where Y(Ne + 3) is the derivative of Y(1) and Y(Ne + 4) is the

derivative of Y(2), etc.

Caution to User

A labeled common block SHARE is used to transfer data internally.
The user should not use a common area with this name.

APPENDIX I

COMPUTER LISTING OF ALL PROGRAMS

80/80 LIST

```
          00000000011111111112222222222333333333344444444445555555555666666666677777
          1234567890123456789012345678901234567890123456789012345678901234567890123456789012345
CARD
0001    C*******************************************************************************
0002    C**  MAIN program                                                            **
0003    C**THIS PROGRAM IS THE ENTRY POINT TO THE INTEGRAL METHOD SOLUTION OF         **
0004    C**THE PARTIAL DIFFERENTIAL EQUATIONS.                                        **
0005    C**                                                                           **
0006    C**ALL ARRAYS ARE DIMENSIONED AND EQUIVALENCED ACCORDING TO THE ORDER         **
0007    C**OF THE APPROXIMATION AND CAN BE INSERTED AS A GROUP BETWEEN THE            **
0008    C**COMMON Y(202) AND THE FIRST FORMAT STATEMENT.                              **
0009    C**                                                                           **
0010    C**ALL INPUT DATA IS READ IN AT THE BEGINNING OF THE PROGRAM.                 **
0011    C**                                                                           **
0012    C**THE FUNCTION OF THIS BEGINNING ROUTINE IS TO CALCULATE THE INITIAL         **
0013    C**VALUES FOR THE POLYNIMIAL TEMPERATURE COEFFICIENTS AND THE INITIAL         **
0014    C**SOLID SPECIES VALUES, SEND THE NECESSARY INFORMATION TO THE ENTRY          **
0015    C**POINT OF THE ORDINARY DIFFERENTIAL EQUATIONS INTEGRATION ROUTINE,          **
0016    C**RECEIVE THE NEW INTEGRATED VALUES AT THE NEXT TIME STEP, MAKE              **
0017    C**NECESSARY CALCULATIONS BASED ON THE NEW VALUES, PUNCH AND/OR PRINT         **
0018    C**THE DESIRED INFORMATION AND RETURN TO THE INTEGRATION FOR ANOTHER          **
0019    C**TIME STEP.                                                                 **
0020    C**                                                                           **
0021    C**THE CALCULATION OF THE ORDINARY DIFFERENTIAL EQUATIONS BY THE              **
0022    C**INTEGRAL METHOD IS DONE IN ROUTINE 'DERFUN' WHICH IS CALLED ONLY           **
0023    C**BY THE ORDINARY DIFF. EQ. ROUTINE.                                         **
0024    C**                                                                           **
0025    C**THE ROUTINE 'SIMQ' SOLVES A SET OF SIMULTANEOUS ALGEBRAIC EQUATIONS**
0026    C**AND WILL PRINT AN S.S. MESSAGE IF THE MATRIX IS SINGULAR.                  **
0027    C**                                                                           **
0028    C*******************************************************************************
0029          COMMON Y(202)
0030          DOUBLE PRECISION B(36),AB(6),X(6),G,BS3(25),BS4(25),BS5(25),BBS3(5
0031         1),BBS4(5),BBS5(5),DCT(7),BCS(25),BBCS(5),BDC(25),BBDC(5)
0032          COMMON/CUMA/X,G,E(3),R(3),FLUX,LN,NSQ,N,     NE,F1,F2,F3,CS1,CS2
0033         1,NP2,NP1,WGT,ICOND,IBC,BO,DSM(6),API
0034          DIMENSION C1(06),C2(06),C3(6),C5(6),C6( 6),A(8),TMPTR( 6),C4(6),
0035         1RCS(6),S3(7),S4(7),S5(7),SSFX(6),CS(7)
0036          EQUIVALENCE (Y(1),C1(1)),(Y( 7),C2(1)),(Y(13),C6(1)),(Y(19),A(1)),
0037         1(Y(27),T)
0038    1000  FORMAT(I3)
0039    1001  FORMAT(D16.8)
0040    1010  FORMAT(5H X(J), 4X,11HTEMPERATURE, 3X,11HTOTAL SOLID, 4X,9HSPECIES
0041         1 1, 5X,9HSPECIES 2, 5X,9HSPECIES 6, 5X,9HSPECIES 3,5X,9HSPECIES 4,
0042         25X,9HSPECIES 5,15H MASS LOSS RATE)
0043    1111  FORMAT(3H J=,I2,1X,9E14.5)
0044    1500  FORMAT(23H MASS FLUX AT SURFACE =,E16.6,5X,14HTOTAL WEIGHT =,E16.6
0045         1)
0046    2000  FORMAT(E16.8)
0047    2010  FORMAT(5H1DATA)
0048    2020  FORMAT(6H EI  =,E16.6,6H  E2 =,E16.6,6H  E3 =,E16.6,6H  R1 =,
0049         1E16.6,6H  R2 =,E16.6,6H  R3 =,E16.6)
0050    2030  FORMAT(6H F1  =,E16.6,6H  F2 =,E16.6,6H  F3 =,E16.6,
0051         1      6H  CS1=,E16.6,6H  CS2=,E16.6)
0052    2040  FORMAT(6H TEND=,E16.6,6H  DEL=,E16.6,6H  BO =,E16.6)
0053    2050  FORMAT(6(2H X,I2,2H =,D16.6))
0054    2055  FORMAT(5H G = ,D14.6)
0055    2070  FORMAT(3H N=,I3, 5X,             3HNE=,I3, 5X,4HMOP=,I3, 5X,4HMER=
```

124

80/80 LIST

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        000000000111111111122222222223333333333444444444455555555556666666666777777
        1234567890123456789012345678901234567890123456789012345678901234567890123456
CARD
0056       1,I3, 5X,7HMCOUNT=,I3, 5X,6HNPRNT=,I3,5X,6HICOND=,I3,5X,4HIBC=,I3)
0057  2222 FORMAT(6I5)
0058  3000 FORMAT(11HOFOR TIME =,E13.5,5X,13HTOTAL GAS 3 =,E13.5,4X,13HTOTAL
0059       1GAS 4 =,E13.5,4X,13HTOTAL GAS 5 =,E13.5)
0060  3001 FORMAT(13H S.S. FOR   S3)
0061  3002 FORMAT(13H S.S. FOR   S4)
0062  3003 FORMAT(13H S.S. FOR   S5)
0063  3333 FORMAT(6H ERMX=,E16.6,1X,5HERMN=,E16.6,1X,5HDLMX=,E16.6,1X,5HDLMN=
0064       1,E16.6,1X,5HDLP =,E16.6,1X,5HTMIN=,E16.6)
0065  4000 FORMAT(11H S.S. FOR A)
0066  4444 FORMAT(4F20.6)
0067  5555 FORMAT(6D13.5)
0068  6666 FORMAT(6E13.5)
0069  7000 FORMAT(13H S.S. FOR CS )
0070  7777 FORMAT(I5,5E15.6)
0071  8000 FORMAT(13H S.S. FOR BDC)
0072  C************READ ALL INPUT DATA************************************
0073       READ (5,1000) N,   NE,MOP,MER,MCOUNT,NPRNT,ICOND,IBC
0074       READ (5,2000)E,R,F1,F2,F3,CS1,CS2,TEND,DEL,BO,ERMX,ERMN,DLMX,DLMN,
0075       1DLP,TMIN
0076       READ(5,1001)(X(I),I=1,N ),G
0077  C************PRINT ALL INPUT DATA************************************
0078       WRITE(6,2010)
0079       WRITE(6,2070)N,   NE,MOP,MER,MCOUNT,NPRNT,ICOND,IBC
0080       WRITE(6,2020)E,R
0081       WRITE(6,2030)F1,F2,F3,   CS1,CS2
0082       WRITE(6,2040)TEND,DEL,BO
0083       WRITE(6,3333)ERMX,ERMN,DLMX,DLMN,DLP,TMIN
0084       WRITE(6,2050)(I,X(I),I=1,N )
0085       WRITE(6,2055)G
0086       IF(MCOUNT.EQ.0)GO TO 5
0087  C************IF DESIRED, PUNCH ALL INPUT DATA***********************
0088       WRITE(7,2222)N,   NE,MOP,MER,MCOUNT,NPRNT
0089       WRITE(7,4444)E,R,F1,F2,F3,   CS1,CS2,TEND,DEL,ERMX,ERMN,DLMX,DLMN,
0090       1DLP,TMIN
0091       WRITE(7,5555)X,G
0092  C************INITIALIZE TIME TO ZERO********************************
0093  5    T=0.
0094  C************SET PROGRAM CONSTANTS**********************************
0095       LN=N-1
0096       NP2=N+2
0097       NSQ=N*N
0098       NP1=N+1
0099       AP1=NP1
0100  C************CALCULATE INITIAL POLYNOMIAL TEMPERATURE COEFFICIENTS*****
0101       A(1)=0.
0102       A(2)=0.
0103       DO 20  J=1,LN
0104       DO 15 I=1,N
0105       K=J+(I-1)* N
0106       B(K)=X(J+1)**(I+1)
0107  15   CONTINUE
0108       L=J*N
0109       B(L)=J+1
0110       AB( J )=0.
```

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                0000000001111111111222222222233333333334444444444555555555566666666667777777
                1234567890123456789012345678901234567890123456789012345678901234567890123456789012345
CARD
0111      20  CONTINUE
0112          B(NSQ)=NP1
0113          AB( N)=1.
0114          CALL SIMQ(B,AB, N,KS)
0115          IF(KS.NE.0)WRITE(6,4000)
0116          DO 25 I=1, N
0117          A(I+2)=AB(I)
0118  C***************SET INITIAL LOCAL SOLID SPECIES VALUES********************
0119          C1(1)=1.
0120          C2(1)=0.
0121          C6(1)=0.
0122      25  CONTINUE
0123  C**************ENTER ORDINARY DIFFERENTIAL EQUATIONS INTEGRATION START
0124  C             ROUTINE*****************************************************
0125          CALL START(NF,MOP,MER,DEL,ERMX,ERMN,DLMX,DLMN,DLP)
0126          TPRT=0.
0127          NCOUNT=0
0128  C**************INTEGRATE ORDINARY DIFFERENTIAL EQUATIONS FOR VALUES OF
0129  C             THE VARIABLES AT THE NEXT TIME STEP*************************
0130      31  CALL KAMSUB(1)
0131          DELT=T-TPRT
0132          NCOUNT=NCOUNT+1
0133  C**************IF THE TOTAL NUMBER OF TIME STEPS OR THE TOTAL LENGTH OF
0134  C             TIME SINCE THE LAST PRINTED STEP IS THE DESIRED VALUE,
0135  C             THEN THE CALCULATIONS WILL PROCEED, OTHERWISE THE PROGRAM
0136  C             WILL RETURN TO INTEGRATE FOR THE NEXT TIME STEP.**********
0137          IF(NCOUNT.GE.NPRNT.OR.DELT.GE.TMIN)GO TO 32
0138          GO TO 31
0139      32  TPRT=T
0140  C**************USING THE NEW SOLID SPECIES VALUES, CALCULATE THE LOCAL
0141  C             VALUES FOR EACH GAS SPECIES, MASS FLUX AND TOTAL SOLID AS
0142  C             WELL AS THE POLYNOMIAL COEFFICIENTS FOR THE OVERALL
0143  C             AVERAGE GAS SPECIES, MASS FLUX AND SOLID WEIGHT.**********
0144          CS(1)=C1(1)+C2(1)+C6(1)
0145          CS(2)=0.
0146          NCOUNT=0
0147          XP=C6(1)/CS1/CS2+C2(1)/CS1
0148          C3(1)=(1.-CS1)*XP
0149          C4(1)=1.-C1(1)-XP
0150          C5(1)=(1.-CS2)*C6(1)/CS2
0151          RCS(1)=C1(1)+C2(1)+C6(1)
0152          SSFX(1)=-DSM(1)
0153          DO 140 J=2,N
0154          SSFX(J)=-DSM(J)
0155          XPTH=C6(J)/CS1/CS2+C2(J)/CS1
0156          C3(J)=(1.-CS1)*XPTH
0157          C4(J)=1.-C1(J)-XPTH
0158          C5(J)=(1.-CS2)*C6(J)/CS2
0159          XJ=X(J)
0160          ASUM=0.
0161          DO 135 I=1,NP2
0162          IM1=I-1
0163  C**************CALCULATE THE LOCAL TEMPERATURE USING THE NEW TEMPERATURE
0164  C             COEFFICIENTS.*********************************************
0165          ASUM=ASUM+A(I)*X(J)**IM1
```

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                              80/80  LIST

            0000000001111111111222222222233333333334444444444555555555566666666667777777
            12345678901234567890123456789012345678901234567890123456789012345678901234567890123456
CARD
0166          IF(I.GT.LN)GO TO 135
0167          IP1=I+1
0168          K=(J-1)+IM1*LN
0169          XJI=XJ**IP1
0170          BCS(K)=XJI
0171          BDC(K)=XJI
0172          BS3(K)=XJI
0173          BS4(K)=XJI
0174          BS5(K)=XJI
0175      135 CONTINUE
0176          JM1=J-1
0177          RCS(J)= C1(J)+ C2(J)+ C6(J)
0178          BBS3(JM1)=C3(J)-C3(1)
0179          BBS4(JM1)=C4(J)-C4(1)
0180          BBS5(JM1)=C5(J)-C5(1)
0181          BBCS(JM1)=RCS(J)-RCS(1)
0182          BBDC(JM1)=DSM(J)-DSM(1)
0183          TMPTR(J  )=ASUM
0184      140 CONTINUE
0185          FSUM=0.
0186          CSUM=0.
0187          IF(LN.EQ.1)GO TO 142
0188          CALL  SIMQ(BS3,BBS3,LN,KS)
0189          IF(KS.NE.0)WRITE(6,3001)
0190          CALL  SIMQ(BS4,BBS4,LN,KS)
0191          IF(KS.NE.0)WRITE(6,3002)
0192          CALL  SIMQ(BS5,BBS5,LN,KS)
0193          IF(KS.NE.0)WRITE(6,3003)
0194          CALL  SIMQ(BCS,BBCS,LN,KS)
0195          IF(KS.NE.0)WRITE(6,7000)
0196          CALL  SIMQ(BDC,BBDC,LN,KS)
0197          IF(KS.NE.0)WRITE(6,8000)
0198      142 DO 143 I=1,LN
0199          IP2=I+2
0200          AP2=I+2
0201          CS(IP2)=BBCS(I)
0202          CSUM=CSUM+CS(IP2)/AP2
0203          DCT(IP2)=BBDC(I)
0204          S3(IP2)=BBS3(I)
0205          S4(IP2)=BBS4(I)
0206          S5(IP2)=BBS5(I)
0207          FSUM=FSUM+DCT(IP2)/AP2
0208      143 CONTINUE
0209          DCT(1)=DSM(1)
0210          DCT(2)=0.
0211          FLUX=-FSUM-DCT(1)
0212          WGT=CSUM+CS(1)
0213          S3(1)=C3(1)
0214          S4(1)=C4(1)
0215          S5(1)=C5(1)
0216          S3(2)=0.
0217          S4(2)=0.
0218          S5(2)=0.
0219          TMPTR(1)= A(1)
0220          SPC3=0.
```

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          0000000001111111111222222222233333333334444444444555555555566666666667777777
          1234567890123456789012345678901234567890123456789012345678901234567890123456
CARD
0221          SPC4=0.
0222          SPC5=0.
0223          DO 141 I=1,NPL
0224          DI=I
0225          SPC3=SPC3+ S3(I)/DI
0226          SPC4=SPC4+ S4(I)/DI
0227          SPC5=SPC5+ S5(I)/DI
0228    141   CONTINUE
0229          IF(MCOUNT.EQ.0)GO TO 33
0230    C*************IF DESIRED, PUNCH OUTPUT***********************************
0231          WRITE(7,6666)T,SPC3,SPC4,SPC5,FLUX,WGT
0232          WRITE(7,7777)(J,TMPTR(J),RCS(J),C1(J),C2(J),C6(J),C3(J),C4(J),C5(J
0233         1),SSEX(J),J=1,N)
0234    C*************PRINT OUTPUT**********************************************
0235    33    WRITE(6,3000) T,SPC3,SPC4,SPC5
0236          WRITE(6,1010)
0237          WRITE(6,1111)(J,TMPTR(J),RCS(J),C1(J),C2(J),C6(J),C3(J),C4(J),C5(J
0238         1),SSEX(J),J=1,N)
0239          WRITE(6,1500)FLUX,WGT
0240    C*************IF TIME LIMIT IS NOT REACHED, RETURN TO INTEGRATION
0241    C              ROUTINE.*********************************************
0242          IF(T.GE.TEND)STOP
0243          GO TO 31
0244          END
```

80/80 LIST

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        00000000011111111112222222222333333333344444444445555555555666666666677777777
        12345678901234567890123456789012345678901234567890123456789012345678901234567
CARD
0001         SUBROUTINE DERFUN
0002    C******************************************************************************
0003    C**                                                                         **
0004    C**THIS ROUTINE IS THE COMPANION PROGRAM FOR THE INTEGRAL METHOD            **
0005    C**SOLUTION OF THE PARTIAL DIFFERENTIAL EQUATIONS.                          **
0006    C**                                                                         **
0007    C**THE SIMULTANEOUS ORDINARY DIFFERENTIAL EQUATIONS ARE FORMED AND          **
0008    C**SOLVED TO GIVE A SYSTEM OF EXPLICIT FIRST ORDER ORDINARY                 **
0009    C**DIFFERENTIAL EQUATIONS.                                                  **
0010    C**                                                                         **
0011    C**INPUT IS THE VARIABLES AT THE NEW TIME STEP AND COMES FROM THE           **
0012    C**INTEGRATION ROUTINE.                                                     **
0013    C**                                                                         **
0014    C**OUTPUT IS THE DERIVATIVES OF THE VARIABLES AT THE SAME TIME STEP         **
0015    C**AND RETURNS THEM TO THE INTEGRATION ROUTINE                              **
0016    C**                                                                         **
0017    C**DIMENSIONED AND EQUIVALENCED VARIABLES CHANGE WITH THE ORDER OF THE      **
0018    C**APPROXIMATION AND CAN BE INSERTED AS A GROUP BETWEEN THE FIRST           **
0019    C**DOUBLE PRECISION STATEMENT AND THE SECOND CONTINUATION CARD OF THE       **
0020    C**EQUIVALENCE STATEMENT.                                                   **
0021    C**                                                                         **
0022    C**THE ROUTINE 'SIMQ' SOLVES A SET OF SIMULTANEOUS ALGEBRAIC EQUATIONS      **
0023    C**AND WILL PRINT AN S.S. MESSAGE IF THE MATRIX IS SINGULAR.                **
0024    C**                                                                         **
0025    C******************************************************************************
0026         COMMON Y(202)
0027         DOUBLE PRECISION DEXP,DLOG
0028         DOUBLE PRECISION G,BMN,ASUM,BSUM,CSUM,TSLP,DRG,HS(3, 7),CNDX,
0029        1BN,BG(25),BH1(49),BH2(25),BH3(25),BBG(5),BBH1(7),BBH2(5),
0030        2BBH3(5),BM1,GS(6),RCS(6),SUBK(3,6),Q(3),X(6),CK1(6),CK2(6),CK3(6),
0031        3GT(6),BT(25),BBT(5)
0032         COMMON/COMA/X,G,E(3),R(3),FLUX,LN,NSQ,N,    NE,F1,F2,F3,CS1,CS2
0033        1,NP2,NP1,WGT,ICOND,IBC,BO,DSM(6),APL
0034         DIMENSION DC1(6),DC2(6),DC6(6),A(8),DA(8),C1(6),C2(6),C6(6)
0035         EQUIVALENCE (Y(1),C1(1)),(Y( 7),C2(1)),(Y(13),C6(1)),(Y(19),A(1)),
0036        1(Y(27),T),(Y(29),DC1(1)),(Y(35),DC2(1)),(Y(41),DC6(1)),(Y(47),DA(1
0037        2))
0038    5500 FORMAT(12H S.S. FOR GS)
0039    6000 FORMAT(12H S.S. FOR GT)
0040    6500 FORMAT(13H S.S. FOR HS1)
0041    6501 FORMAT(13H S.S. FOR HS2)
0042    6502 FORMAT(13H S.S. FOR HS3)
0043    9500 FORMAT(12H S.S. FOR DA)
0044    C*************CALCULATE THE RATIO OF THE HEAT FLUX PARAMETER TO THE
0045    C             PRE-EXPONENTIAL PARAMETER**********************************
0046         Q(1)=R(1)/F1
0047         Q(2)=R(2)/F2
0048         Q(3)=R(3)/F3
0049         AN=N
0050         GS(1)=0.
0051    C*************CALCULATE THE REACTION RATE CONSTANTS AND THE POLYNOMIAL
0052    C             COEFFICIENTS FOR HEAT GENERATION INTEGRAL*****************
0053         RCS(1)=C1(1)+C2(1)+C6(1)
0054         DO 40 I=1,2
0055         SUBK(I,1)=DEXP(-E(I)/(1.+G*A(1)))
```

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                  00000000011111111112222222222333333333344444444445555555555666666666677777771
                  12345678901234567890123456789012345678901234567890123456789012345678901234567890123456
CARD
0056          HS(1,1)=C1(1)*SUBK(1,1)/RCS(1)
0057          HS(1,2)=0.
0058      40  CONTINUE
0059          SUBK(3,1)=DEXP(-E(3)/(1.+G*A(1)))
0060          HS(3,1)=C2(1)*SUBK(3,1)/RCS(1)
0061          HS(3,2)=0.
0062          CK1(1)=C1(1)*SUBK(1,1)/F1
0063          CK2(1)=C1(1)*SUBK(2,1)/F2
0064          CK3(1)=C2(1)*SUBK(3,1)/F3
0065          DC1(1)=-CK1(1)-CK2(1)
0066          DC2(1)=CS1*CK1(1)-CK3(1)
0067          DC6(1)=CS2*CK3(1)
0068          DSM(1)=DC1(1)+DC2(1)+DC6(1)
0069          GS(1)=DLOG(RCS(1))*2.*A(3)
0070          GT(1)=0.
0071          ANP2=A(NP2)
0072          DO 60 J=2,N
0073          ASUM=0.
0074          BSUM=0.
0075          CSUM=0.
0076          XJ=X(J)
0077          DO 45 I=1,NP2
0078          IM1=I-1
0079          XJII=XJ**IM1
0080          CSUM=CSUM+A(I)*XJII
0081          IF(I.GT.LN)GO TO 45
0082          IP2=I+2
0083          BI=I+1
0084          BII=I*(I+1)
0085          XJI=XJ**I
0086          XJP1=XJ**(I+1)
0087          ASUM=ASUM+BI*A(IP2)*XJI
0088          BSUM=BSUM+BII*A(IP2)*XJII
0089          K=(J-1)+IM1*LN
0090  C*************CALCULATE POLYNOMIAL COEFFICIENTS FOR INTEGRALS
0091  C              REPRESENTING A CHANGE IN THERMAL CONDUCTIVITY*************
0092          BG(K)=XJI
0093          BT(K)=XJI
0094          BH1(K)=XJP1
0095          BH2(K)=XJP1
0096          BH3(K)=XJP1
0097      45  CONTINUE
0098          ASUM=ASUM+AP1*ANP2*XJ**N
0099          BSUM=BSUM+AN*AP1*ANP2*XJ**(N-1)
0100          JM1=J-1
0101          RCS(J)=C1(J)+C2(J)+C6(J)
0102          DRG=DLOG(RCS(J))
0103          BBG(JM1)=DRG*BSUM-GS(1)
0104          BBT(JM1)=DRG*ASUM
0105          DO 50 L=1,3
0106          SUBK(L,J)=DEXP(-E(L)/(1.+G*CSUM))
0107      50  CONTINUE
0108          BBH1(JM1)=C1(J)*SUBK(1,J)/RCS(J)-HS(1,1)
0109          BBH2(JM1)=C1(J)*SUBK(2,J)/RCS(J)-HS(2,1)
0110          BBH3(JM1)=C2(J)*SUBK(3,J)/RCS(J)-HS(3,1)
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                            80/80  LIST

         0000000001111111111222222222233333333334444444444555555555566666666667777777
         1234567890123456789012345678901234567890123456789012345678901234567890123456
CARD
0111          CK1(J)=C1(J)*SUBK(1,J)/F1
0112          CK2(J)=C1(J)*SUBK(2,J)/F2
0113          CK3(J)=C2(J)*SUBK(3,J)/F3
0114    C************CALCULATE LOCAL SOLID SPECIES DERIVATIVES***************
0115          DC1(J)=-CK1(J)-CK2(J)
0116          DC2(J)=CS1*CK1(J)-CK3(J)
0117          DC6(J)=CS2*CK3(J)
0118          DSM(J)=DC1(J)+DC2(J)+DC6(J)
0119     60   CONTINUE
0120          IF(LN.EQ.1)GO TO 90
0121          CALL SIMQ(BG,BBG,LN,KS)
0122          IF(KS.NE.0)WRITE(6,5500)
0123          CALL SIMQ(BT,BBT,LN,KS)
0124          IF(KS.NE.0)WRITE(6,6000)
0125          CALL SIMQ(BH1,BBH1,LN ,KS)
0126          IF(KS.NE.0)WRITE(6,6500)
0127          CALL SIMQ(BH2,BBH2,LN ,KS)
0128          IF(KS.NE.0)WRITE(6,6501)
0129          CALL SIMQ(BH3,BBH3,LN ,KS)
0130          IF(KS.NE.0)WRITE(6,6502)
0131     90   CONTINUE
0132          ASRF=0.
0133          DO 95 I=1,LN
0134          IP1=I+1
0135          IP2=I+2
0136          GS(IP1)=BBG(I)
0137          GT(IP1)=BBT(I)
0138          HS(1,IP2)=BBH1(I)
0139          HS(2,IP2)=BBH2(I)
0140          HS(3,IP2)=BBH3(I)
0141          ASRF=ASRF+A(IP2)
0142     95   CONTINUE
0143          ASRF=ASRF+A(1)+A(NP2)
0144    C************CALCULATE POLYNOMIAL COEFFICIENTS FOR THE TEMPERATURE
0145    C             DERIVATIVE WITH CHOICE OF BOUNDARY CONDITIONS AND THERMAL
0146    C             CONDUCTIVITY EFFECTS***********************************
0147          DNDX=DSM(N)
0148          CNDX=RCS(N)
0149          IF(ICOND.EQ.1)GO TO 96
0150          RCS(N)=1.
0151          DNDX=0.
0152          IF(ICOND.EQ.0)CNDX=1.
0153     96   IP2=QS(I)
0154          IF(IBC.EQ.1)TP2=(1.-B0*ASRF)
0155          TSLP=(1.+DLOG(CNDX))*IP2/RCS(N)
0156          BRCS=B0/RCS(N)
0157          DO 110 M=1, N
0158          ASUM=0.
0159          BSUM=0.
0160          CSUM=0.
0161          DSUM=0.
0162          BM1=M
0163          DO 105 I=1,NP1
0164          BN=M+I-1
0165          DO 100 J=1,3
```

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                                     80/80  LIST

            )00)00000011111111112222222222333333333344444444445555555555666666666677777777
            1234567890123456789012345678901234567890123456789012345678901234567890123456
 CARD
 0166            CSUM=CSUM+Q(J)*HS(J,I)/BN
 0167     100    CONTINUE
 0168            IF(I.GT.N)GO TO 105
 0169            BM4=M+I+1
 0170            BM3=I+1
 0171            BSUM=BSUM+BM3*A(I+2)/BN
 0172            K=M+I*NP1
 0173            BHI(K)=1./BMN
 0174            IF(ICOND.EQ.0)GO TO 105
 0175            ASUM=ASUM+GS(I)/BN
 0176            IF(I.GT.LN)GO TO 105
 0177            DSUM=DSUM+GT(I+1)/BN
 0178     105    CONTINUE
 0179            BHI(M)=1./BM1
 0180            I=(M+1)*NP1
 0181            XX1=M+1
 0182            IF(IBC.EQ.1)XX1=XX1+BRCS
 0183            BHI(L)=XX1
 0184            BM2=M-1
 0185            BBHI(M)=TSLP-BM2*BSUM-ASUM-BM2*DSUM-CSUM/G
 0186     110    CONTINUE
 0187            TP1=0.
 0188            TP3=DQS(1)
 0189            IF(IBC.EQ.0)GO TO 111
 0190            TP3=0.
 0191            TP1=BRCS
 0192     111    BHI(NP1)=TP1
 0193            BBHI(NP1)=-TP2*DNDX   /RCS(N))/RCS(N)+TP3/RCS(N)
 0194            CALL  SIMQ(BHI,BBHI,NP1,KS)
 0195            IF(KS.NE.0)WRITE(6,9500)
 0196            DO 115 I=2,NP1
 0197            DA(I+1)=BBHI(I)
 0198     115    CONTINUE
 0199            DA(1)=BBHI(1)
 0200            DA(2)=0.
 0201            RETURN
 0202            END
 0203            FUNCTION QS(T)
 0204            QS=1.
 0205            RETURN
 0206            END
 0207            FUNCTION DQS(T)
 0208            DQS=0.
 0209            RETURN
 0210            END
```

80/80 LIST

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                 0000000)0)11111111111222222222233333333334444444444555555555566666666667777777
                 12345678901234567890123456789012345678901234567890123456789012345678901234567890123456

CARD
0001          SUBROUTINE SIMQ(A,B,N,KS)                                          SIM
0002          DOUBLE PRECISION DABS                                              SIM
0003          DOUBLE PRECISION BIGA,SAVE,A(1),B(1)                               SIM
0004   C                                                                         SIM
0005   C          FORWARD SOLUTION                                               SIM
0006   C                                                                         SIM
0007          TOL=0.0                                                            SIM
0008          KS=0                                                               SIM
0009          JJ=-N                                                              SIM
0010          DO 65 J=1,N                                                        SIM
0011          JY=J+1                                                             SIM
0012          JJ=JJ+N+1                                                          SIM
0013          BIGA=0                                                             SIM
0014          IT=JJ-J                                                            SIM
0015          DO 30 I=J,N                                                        SIM
0016   C                                                                         SIM
0017   C          SEARCH FOR MAXIMUM COEFFICIENT IN COLUMN                       SIM
0018   C                                                                         SIM
0019          IJ=IT+I                                                            SIM
0020          IF((DABS(BIGA)-DABS(A(IJ))).GE.0.)GO TO 30                         SIM
0021          BIGA=A(IJ)                                                         SIM
0022          IMAX=I                                                             SIM
0023   30     CONTINUE                                                           SIM
0024   C                                                                         SIM
0025   C          TEST FOR PIVOT LESS THAN TOLERANCE (SINGULAR MATRIX)           SIM
0026   C                                                                         SIM
0027          IF((DABS(BIGA)-TOL).GT.0.)GO TO 40                                 SIM
0028          KS=1                                                               SIM
0029          RETURN                                                             SIM
0030   C                                                                         SIM
0031   C          INTERCHANGE ROWS IF NECESSARY                                  SIM
0032   C                                                                         SIM
0033   40     I1=J+N*(J-2)                                                       SIM
0034          IT=IMAX-J                                                          SIM
0035          DO 50 K=J,N                                                        SIM
0036          I1=I1+N                                                            SIM
0037          I2=I1+IT                                                           SIM
0038          SAVE=A(I1)                                                         SIM
0039          A(I1)=A(I2)                                                        SIM
0040          A(I2)=SAVE                                                         SIM
0041   C                                                                         SIM
0042   C          DIVIDE EQUATION BY LEADING COEFFICIENT                         SIM
0043   C                                                                         SIM
0044   50     A(I1)=A(I1)/BIGA                                                   SIM
0045          SAVE=B(IMAX)                                                       SIM
0046          B(IMAX)=B(J)                                                       SIM
0047          B(J)=SAVE/BIGA                                                     SIM
0048   C                                                                         SIM
0049   C          ELIMINATE NEXT VARIABLE                                        SIM
0050   C                                                                         SIM
0051          IF((J-N).EQ.0)GO TO 70                                            SIM
0052          IQS=N*(J-1)                                                        SIM
0053          DO 65 IX=JY,N                                                      SIM
0054          IXJ=IQS+IX                                                         SIM
0055          IT=J-IX                                                            SIM
```

80/80 LIST

```
          000000000111111111122222222223333333333444444444455555555556666666666777777
          12345678901234567890123456789012345678901234567890123456789012345678901234 5(
CARD
0056            DO 60  JX=JY,N                                                          SIM(
0057            IXJX=N*(JX-1)+IX                                                        SIM(
0058            JJX=IXJX+IT                                                             SIM(
0059      60  A(IXJX)=A(IXJX)-(A(IXJ)*A(JJX))                                           SIM(
0060      65  B(IX)=B(IX)-(B(J)*A(IXJ))                                                 SIM(
0061  C                                                                                 SIM
0062  C         BACK SOLUTION                                                           SIM
0063  C                                                                                 SIM
0064      70  NY=N-1                                                                    SIM
0065            IT=N*N                                                                  SIM
0066            DO 30  J=1,NY                                                           SIM
0067            IA=IT-J                                                                 SIM
0068            IB=N-J                                                                  SIM
0069            IC=N                                                                    SIM
0070            DO 80 K=1,J                                                             SIM
0071            B(IB)=B(IB)-A(IA)*B(IC)                                                 SIM
0072            IA=IA-N                                                                 SIM
0073      80  IC=IC-1                                                                   SIM
0074            RETURN                                                                  SIM
0075            END                                                                     SIM
```

```
                              80/80  LIST


            0000000001111111111222222222233333333334444444444555555555566666666667777777
            1234567890123456789012345678901234567890123456789012345678901234567890123451
CARD
0001          SUBROUTINE KAMSUB(NSTART)
0002          COMMON Y(202)
0003          COMMON /SHARE/NN,SPACE,MODE,KKA,E1MAX,E1MIN,E2MAX,E2MIN,FACT
0004          DIMENSION DELY(4,100),BET(4),XV(5),FV(4,100)
0005          COMMON/INTDAT/Z(5,202),IERR
0006          DOUBLE PRECISION YU(5,100)
0007   C
0008   C      NO INFORMATION IS REQUIRED IN THIS SUBROUTINE
0009   C
0010          IF(NSTART.LE.0)GO TO 9977
0011          IF(MODE.EQ.1)GO TO 1001
0012          GO TO 2000
0013   C      RUNGE-KUTTA
0014   1000  LL=1
0015   1001  XTM2=Y(N2)
0016          XTM3=XV(MM)
0017          DO 1034 K=1,4
0018          XTM1=BET(K)
0019          DO 1350 I=1,NN
0020          DELY(K,I)=XTM2 *FV(MM,I)
0021          Q=YU(MM,1)
0022   1350  Y(I)=Q+XTM1  *DELY(K,I)
0023          Y(NP1)=XTM1*XTM2+XTM3
0024          CALL DERFUN
0025          DO 1100 I=1,NN
0026          IPN2=I+N2
0027   1100  FV(MM,I)=Y(IPN2)
0028   1034  CONTINUE
0029          MMP1=MM+1
0030          DO 1039 I=1,NN
0031          DEL=(DELY(1,I)+2.0*DELY(2,I)+2.0*DELY(3,I)+DELY(4,I))/6.0
0032          YU(MMP1,I)=YU(MM,I)+DEL
0033          Y(I)=YU(MMP1,I)
0034   1039  CONTINUE
0035          MM=MMP1
0036          XV(MM)=XV(MM-1)+Y(N2)
0037          Y(NP1)=XV(MM)
0038          CALL DERFUN
0039          IF(MODE.EQ.1)GO TO 42
0040          DO 150 I=1,NN
0041          IPN2=I+N2
0042   150   FV(MM,I)=Y(IPN2)
0043          IF(MM.NE.4)GO TO 1001
0044   C      ADAMS-MOULTON
0045   2000  XTM2=Y(N2)
0046          DO 2048 I=1,NN
0047          DEL=XTM2 *(55.0*FV(4,I)-59.0*FV(3,I)
0048         1+37.0*FV(2,I)-9.0*FV(1,I))/24.0
0049          Y(I)=YU(4,I)+DEL
0050   2048  DELY(1,I)=Y(I)
0051          Y(NP1)=XV(4)+XTM2
0052          CALL DERFUN
0053          XV(5)=Y(NP1)
0054          DO 2051 I=1,NN
0055          IPN2=I+N2
```

```
                                    80/80  LIST


          0000000001111111111222222222233333333334444444444555555555566666666667777777
          1234567890123456789012345678901234567890123456789012345678901234567890123456
 CARD
 0056           DEL=XTM2 *(9.0*Y(IPN2)+19.0*FV(4,I)
 0057          1-5.0*FV(3,I)+FV(2,I))/24.0
 0058           YU(5,I)=YU(4,I)+DEL
 0059  2051     Y(I)=YU(5,I)
 0060           CALL DERFUN
 0061           IF(MODE.NE.3)GO TO 42
 0062  C        ERROR ANALYSIS
 0063           SSE=0.0
 0064           DO 3033 I=1,NN
 0065           EPSIL=R*ABS(Y(I)-DELY(1,I))
 0066           IF(KKA.EQ.2)GO TO 3307
 0067           IF(Y(I).EQ.0.)GO TO 3307
 0068           EPSIL=EPSIL/ABS(Y(I))
 0069  3307     IF((SSE-EPSIL).LT.0.)SSE=EPSIL
 0070  3033     CONTINUE
 0071           IF((E1MAX-SSE).GT.0.)GO TO 3035
 0072           IF((ABS(Y(N2))-E2MIN).GT.0.)GO TO 4340
 0073           GO TO 42
 0074  3035     IF((SSE-E1MIN).GE.0.)GO TO 42
 0075           IF((E2MAX-ABS(Y(N2))).GT.0.)GO TO 5360
 0076           GO TO 42
 0077  4340     LL=1
 0078           IERR = 1
 0079           MM=1
 0080           Y(N2)=Y(N2)*FACT
 0081           GO TO 1001
 0082  5360     IF(LL.EQ.1)GO TO 42
 0083           XV(2)=XV(3)
 0084           XV(3)=XV(5)
 0085           DO 5363 I=1,NN
 0086           FV(2,I)=FV(3,I)
 0087           IPN2=I+N2
 0088           FV(3,I)=Y(IPN2)
 0089           YU(2,I)=YU(3,I)
 0090  5363     YU(3,I)=YU(5,I)
 0091           Y(N2)=2.0*Y(N2)
 0092           IERR = 2
 0093           LL=2
 0094           MM=3
 0095           GO TO 1001
 0096  C        EXIT ROUTINE
 0097    42     IF(MODE.EQ.1)GO TO 43
 0098           DO 707 K=1,4
 0099           Z(K,NP1)= XV(K)
 0100           Z(K,N2)=XV(K+1)-XV(K)
 0101           DO 707 I=1,NN
 0102           Z(K,I)= YU(K,I)
 0103           IPN2 = N2 + I
 0104    707    Z(K,IPN2)= FV(K,I)
 0105    43     Z(5,NP1) = XV(5)
 0106           DO 708 I= 1,NN
 0107           Z(5,I)= YU(5,I)
 0108           IPN2  = N2 + I
 0109    708    Z(5,IPN2)= Y(IPN2)
 0110           Z(5,N2)= Y(N2)
```

```
                                        80/80   LIST

            0000000001111111111222222222233333333334444444444555555555566666666667777777
            1234567890123456789012345678901234567890123456789012345678901234567890123456
   CARD
   0111          DO 12 K=1,3
   0112          XV(K)=XV(K+1)
   0113          DO 12 I=1,NN
   0114          FV(K,I)=FV(K+1,I)
   0115   12     YU(K,I)=YU(K+1,I)
   0116          LL=2
   0117          MM=4
   0118          XV(4)=XV(5)
   0119          DO 52 I=1,NN
   0120          IPN2=I+N2
   0121          FV(4,I)=Y(IPN2)
   0122   52     YU(4,I)=YU(5,I)
   0123          IF(MODE.EQ.3)GO TO 73
   0124          RETURN
   0125   9977   CONTINUE
   0126          XV(2)=0.
   0127          XV(3)=0.
   0128          IERR = 3
   0129          ALPHA=Y(NN+1)
   0130          EPM=0.0
   0131          MM=1
   0132          IF(MODE.EQ.1)MM=4
   0133          BET(1)=0.5
   0134          BET(2)=0.5
   0135          BET(3)=1.0
   0136          BET(4)=0.0
   0137          N2=NN+2
   0138          Y(N2)=SPACE
   0139          NP1=NN+1
   0140          R=19.0/270.0
   0141          XV(MM)=Y(NP1)
   0142          IF(ELMIN.LE.0.)ELMIN=ELMAX/55.0
   0143          IF(FACT.LE.0.)FACT=0.5
   0144          CALL DEPFUN
   0145          DO 320 I=1,NN
   0146          IPN2=I+N2
   0147          FV(2,I)=0.
   0148          FV(3,I)=0.
   0149          FV(MM,I)=Y(IPN2)
   0150          YU(2,I)=0.
   0151          YU(3,I)=0.
   0152   320    YU(MM,I)=Y(I)
   0153          GO TO 1000
   0154   73     E=ABS(XV(4)-ALPHA)
   0155          IF((E-EPM).LE.0.)GO TO 2000
   0156          EPM=E
   0157          RETURN
   0158          END
```

```
                              80/80  LIST
```

```
              000000000111111111122222222223333333333444444444455555555556666666666777777
              1234567890123456789012345678901234567890123456789012345678901234567890123456
 CARD
 0001          SUBROUTINE START(M1,M2,M3,A1,A2,A3,A4,A5,A6)
 0002          COMMON/SHARE/NN,SPACE,MODE,KKA,E1MAX,E1MIN,E2MAX,E2MIN,FACT
 0003     C
 0004     C    NO INFORMATION IS REQUIRED IN THIS SUBROUTINE
 0005          NN=M1
 0006          MODE=M2
 0007          KKA=M3
 0008          E1MAX=A2
 0009          E1MIN=A3
 0010          E2MAX=A4
 0011          E2MIN=A5
 0012          FACT=A6
 0013          SPACE=A1
 0014          CALL KAMSUB(0)
 0015          RETURN
 0016          END
```

APPENDIX J

COMPUTER PROGRAM STEPS

Card Numbers		Step Description

MAIN

73-76   (1)   Enter MAIN program and read the number of approximation strips, N, and the program control constants.

78-85   (2)   Print all the input data.

86   (3)   Decide whether to punch the input data.

88-91   (4)   If desired, punch the input data.

93   (5)   Initialize time to zero.

95-99   (6)   Set internal program constants.

101-117   (7)   Calculate the initial polynomial temperature coefficients (Equation 3.9).

119-122   (8)   Set the initial solid species densities (Equation 3.10).

125   (9)   Enter the ordinary differential equations integration START program with its program control constants. Return to MAIN.

126-127   (10)   Initialize program constants.

130   (11)   Enter the ordinary differential equations integration program KAMSUB to calculate the unknowns at the next time step. Enter subroutine DERFUN from KAMSUB to calculate the ordinary differential equations.

DERFUN

46-50   (12)   Calculate program constants.

53-142   (13)   Calculate the reaction rate constants, the polynomial coefficients for the heat generation integral (Equation 3.5d), the polynomial coefficients for the

Card Numbers		Step Description
		integrals representing a change in the effective thermal conductivity (Equation 3.5b, c), and the local solid species derivatives.
143-200	(14)	Calculate the polynomial coefficients for the temperature derivative (Equation 3.6) including the surface boundary condition (Equation 3.7a or b) with terms depending on the type of boundary condition (Radiative or Convective) and case (0, 1, or 2) being considered.
203-210	(15)	Give functions for time-dependent radiative heat flux and its derivative (constant flux considered).
201	(16)	Return derivatives of the variables to KAMSUB to be integrated for values at the new time step. Return values to MAIN.
MAIN		
137	(17)	If the total number of time steps or the total length of time since the last printed step is not the desired value, go back to KAMSUB and integrate for the next time step; otherwise continue with the values of variables at this time step.
144-228	(18)	Calculate the local values for each gas species, temperature, mass loss rate, and total solid; including the polynomial coefficients for the overall average values of each gas species, mass flux, and total weight.
229	(19)	Decide whether to punch the output.
231-233	(20)	If desired, punch the output.
235-239	(21)	Print the output.
242-243	(22)	If the desired total length of time has not been reached, go back to KAMSUB and integrate for the next time step; otherwise stop.

Note: Card numbers refer to the program listings given in Appendix I.

VITA

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