Modeling Reacting Gas Flow in the Char Layer of an Ablator

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The solution of the general equations of change applied to the nonequilibrium flow of pyrolysis gas products through the char layer of an ablative heat shield is presented. Comparisons of the calculated exit gas compositions with experimentally determined compositions between 1550°F and 2300°F are used to demonstrate the reliability of the model and illustrate the shortcomings of the frozen and equilibrium flow calculations. Typical results indicating the effectiveness of the nonequilibrium flow analysis are presented for the flow of pyrolysis gases through a $\frac{1}{4}$-in. nylon-phenolic resin char at a mass flux of 0.05 lb/ft²-sec over a temperature range of 1500°F–3000°F.

Nomenclature

A = area, ft^2
C_p = heat capacity of a pure component at constant pressure, Btu/lb-°F
$\bar{C}_p$ = heat capacity of a mixture at constant pressure, Btu/lb-°F
c = concentration of a component in the system, lb-moles/ft^3
E = energy of activation of a chemical reaction, Btu/lb-mole
H = enthalpy of a component or mixture, Btu/lb-mole
K = total number of gas species in the system, no units
k = thermal conductivity of a pure component, Btu/ft-hr-°F; reaction rate constant for a chemical reaction, see Table 1
k° = frequency factor for a chemical reaction, see Table 1
L = char thickness, ft
M_w = molecular weight of a component in the system, lb/lb-mole
m = total number of chemical reactions in the system, no units
n = moles of a species in the system, lb-moles
P = pressure, lb/ft^2
p = stoichiometric coefficient of the products in a chemical reaction, no units
p' = power on the product concentration term for a chemical reaction, no units
Q = conductive, convective and radiative energy transfer, Btu/hr-ft^2
R = ideal gas constant, Btu/lb-mole-°F; chemical reaction rate, lb-mole/ft^3-hr
$\bar{R}$ = effective chemical reaction rate for gas and solid species, lb-mole/ft^3-hr
r = chemical reaction rate of a chemical species, lb-mole/ft^3-hr
r' = power on the reactant concentration term for a chemical reaction, no units
s = power on the temperature in the rate equation, no units
T = temperature, °F
u,v = velocity of gas species in the system, ft/hr
W = mass flux based on the superficial velocity, lb/ft^2-hr
W_P = mass flux based on the velocity within the pore spaces, lb/ft$^2_{\text{voids}}$-hr
x = mass fraction of the species, lb of species/lb total
z = distance in the axial direction, ft
β = inertial coefficient in the modified Darcy's equation, ft^{-1}
γ = permeability of a porous medium, ft^2
Δ = difference between two parameters, units of parameters
ϵ = porosity of a porous medium, ft^3 voids/ft^3 total
$\bar{\epsilon}$ = emissivity of a porous medium, no units
μ = viscosity of a pure component, lb/ft-hr
ρ = density of a pure component, lb/ft^3
π = product operator, no units

Subscripts

c = conductive or convective
e = effective or over-all value
f = fluid or gas phase
g = gas phase
L = front surface of the char
0 = initial or inlet condition
P = pyrolysis or pores or pressure
r = radiation
rr = reradiation
T = temperature or total
z = distance from the back surface of the char

1. Introduction

THE charring ablator has proven to be one of the most successful heat shields for re-entry heat protection. These heat shields are a combination of plastics that decompose to a char or porous carbon and low molecular weight gases. Protection of the vehicle is achieved by conductive and convective heat transfer, plastic decomposition, transpiration, endothermic chemical reactions of the pyrolysis products, reradiation from the char front surface, and thickening of the boundary layer. The charring ablator is conveniently divided into three separate zones which include the plastic decomposition layer, the char layer and the boundary layer as shown in Fig. 1.

Each of the aforementioned regions has been the subject of a sizeable research effort, and various types of mathematical models to describe the charring ablator have been developed.[1–3]

In this research a better description of the phenomena taking place in the char zone is presented. An accurate description is needed of the energy transfer in the char and the species compositions and fluxes entering the boundary layer. At present these variables are evaluated by considering the flow to be either frozen (no chemical reactions) or in chemical equilibrium.

For a more accurate description of the reacting flow in the char layer the kinetics of the chemical reactions must be included in solving the energy equation. The solution is more complex than the limiting cases because compositions of the pyrolysis products must be calculated from the reaction rate expressions which are differential equations. Of all the possible reactions that could occur within the char over the temperature range encountered, those that actually occur must be selected and included in the analysis.

In addition, experiments must be conducted to assure the theoretical model accurately predicts the energy transfer in the char layer. This can be achieved by flowing a mixture of compounds typical of the actual pyrolysis gases through chars formed in arcjet heaters. The chars can be radiantly heated to simulate the surface heating during re-entry. Gases entering and leaving the char layer can be analyzed to determine

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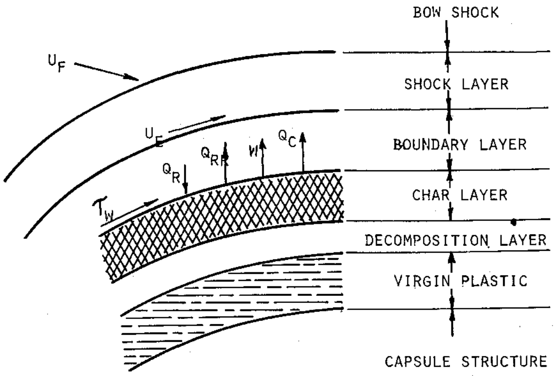

Fig. 1 Diagram of the zones developed during re-entry of a capsule protected by a char-forming ablative heat shield.

the extent of the reactions taking place. Thus the accuracy of the mathematical computations can be assessed. Furthermore, the results of the analysis, referred to as the nonequilibrium model, can be compared with the limiting cases. In this way the shortcomings that result by assuming equilibrium or frozen flow are evaluated.

2. Mathematical Model

2.1 General Description

The momentum, energy, and mass transfer associated with the flow of pyrolysis products through the char layer of a char-forming ablative plastic is considered. The pyrolysis products, formed by the thermal degradation of the plastic heat shield, enter the char zone at the decomposition temperature of the plastic. The products experience a temperature increase as they flow through the char and undergo thermal cracking to lower molecular weight species which react with each other and with the carbonaceous char layer. These predominantly endothermic reactions are important modes of energy absorption and must be included in any realistic analysis of the energy transfer in the char layer.

The mathematical model describing the transport phenomena taking place has the form of a one-dimensional and steady flow. The pyrolysis gas products are considered to be ideal with physical and thermodynamic properties a function of temperature. Thermal equilibrium between the gases and the char is likewise assumed. Char porosity and permeability are considered constant, while the char thermal conductivity can vary with temperature. A schematic diagram indicating pyrolysis gas flow through a porous char zone is depicted in Fig. 2. As shown, the pyrolysis products enter the char at the decomposition temperature T_0, and exit at a higher front surface temperature T_L. Changes in the mass flux of the various species within the char occur as a result of chemical reactions at finite reaction rates R_i.

Because of the relatively high mass flux values experienced during re-entry, a modified form of Darcy's equation including inertial contributions is used to calculate the pressure gradient $(P_0 - P_L)$ across the char. Energy transport by viscous dissipation, P-V work, diffusion and gravity are small and are not included in the model.

2.2 Equations of Change

To compute the energy transferred and the pressure distribution within a porous char, it is necessary to solve the energy and momentum equations with appropriate boundary conditions. For the restrictions just stated, the energy equation has the following form:

$$W_p\bar{C}_p\epsilon \frac{dT}{dz} = \frac{d}{dz}\left[k_e \frac{dT}{dz}\right] + \epsilon \sum_{i=1}^{K+1} H_iR_i + (1-\epsilon)H_cR_c \quad (1)$$

To describe the pressure distribution, a modified form of Darcy's equation is used which accounts for inertial effects that are important due to relatively high mass fluxes of the degradation products. The following equation solves for the pressure at any point z within the char:

$$P = \left\{P_L{}^2 + 2R\left[\int_z^L \left(\frac{\mu}{\gamma}\right)(W)\left(\frac{T}{M_w}\right)dz + \int_z^L \beta\left(\frac{T}{M_w}\right)(W)^2dz\right]\right\}^{1/2} \quad (2)$$

The energy absorbed in the char zone is equal to the difference between the heat flux at the high temperature surface and the heat flux at the back surface. Thus the net energy absorbed for nonequilibrium flow is calculated by the following heat flux equation:

$$Q_{c_z} = (Q_L - Q_0) = \sum_{i=1}^{K+1}\int_{T_0}^{T_L} \epsilon W_pC_{pi}x_idT + \sum_{i=1}^{K+1}\int_{T_0}^{T_L} (H_iR_i)\left(\frac{dz}{dT}\right)dT \quad (3)$$

A detailed derivation of the above equations is presented in Ref. 4.

2.3 Boundary Conditions

There are two sets of boundary conditions that are used to solve the equations of change for flow of reacting gases within the char layer. The first set specifies the pressure and temperature at the front surface,

$$T = T_L, P = P_L \qquad \text{at} \qquad z = L \quad (4)$$

and, the temperature and pyrolysis gas composition entering the back surface of the char

$$T = T_0, x_i = x_{i0} \qquad \text{at} \qquad z = 0 \quad (5)$$

These conditions for mass flux W as a parameter make the solution of the energy equation a two point boundary value problem. This requires an iterative solution. Because P-V work is negligible, the momentum equation is solved using an average pressure within the char. The heat flux at the char front surface is calculated using Eq. (3).

The second set of boundary conditions specifies the temperature, initial pyrolysis gas composition and the sum of the heat of pyrolysis and the heat conducted in the virgin plastic (Q_p) at the back surface.

$$T = T_0, x_i = x_{i0}, Q_p = -(k_edT/dz)_0 \qquad \text{at} \qquad z = 0 \quad (6)$$

For mass flux W, and Q_p as parameters, the solution of the energy equation as an initial value problem is obtained. This

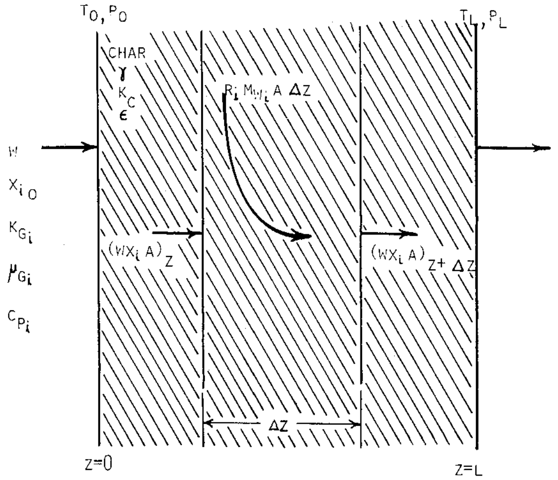

Fig. 2 Diagram of the char layer model.

does not require an iterative solution as did the first case. However, to be useful, a parametric study of W and Q_p is needed over the range of values expected during re-entry.

2.4 Application of the Equations to Nonequilibrium Flow

The application of the simplified equations of change to nonequilibrium flow is different from the frozen and equilibrium flow models in the manner by which the term H_iR_i is calculated in Eq. (1) and Eq. (3). For frozen flow H_iR_i is zero since there are no chemical reactions taking place. For the equilibrium flow case, the term H_iR_i is not zero, and R_i, the reaction rate of species i, is calculated as a function of temperature and pressure by the method of free energy minimization.[5] In the case of nonequilibrium flow of gases within the char, H_iR_i is again nonzero with R_i calculated from finite reaction rate data describing the important chemical reactions occurring.

For the general reaction below,

$$aA + bB + \ldots + \underset{\mathrm{k}_r}{\overset{\mathrm{k}_f}{\rightleftarrows}} rR + sS + \ldots + \tag{7}$$

the reaction rate, R_i, has the form of Eq. (8)

$$R_i = \sum_{j=1}^{m} (p_{ij} - r_{ij}) \left[k_{fj} \prod_{i=1}^{q} (c_i)^{p_{ij}'} - kr_j \prod_{i=1}^{q} (c_i)^{r_{ij}'} \right] \tag{8}$$

The ten chemical reactions which accurately describe the energy transfer associated with reacting gas flow through the char between 500°F and 3000°F are listed in Table 1. A detailed discussion of the criteria used in arriving at these reactions is presented in Ref. 6.

In addition to the important chemical reactions, the initial pyrolysis gas composition must be specified as a boundary condition. The composition used in this research is based on the recent results reported by Sykes[7,8] and are shown in Table 2. These data represent the identification of approximately 90% of the total products released when a nylon-phenolic resin is thermally degraded. The simulated pyrolysis gas composition used in the experimental portion of this research is also listed in Table 2.

2.5 Physical and Thermodynamic Properties

In any problem where the temperature gradient varies over a wide range, changes in the physical and thermodynamic properties as a function of temperature occur. For the multicomponent flow of a reacting gas within a porous char, composition change by chemical reactions is also important. The equations used in this investigation for calculating the variations in thermodynamic properties with temperature and composition are of the usual polynomial form found in the literature. Equations for the viscosity and thermal conductivity of gases are of the form presented by the Chapman-Enskog and Chapman-Cowling treatments, respectively.

Table 1 Important reactions and associated kinetic data for the pyrolysis product species in the char layer between 500°F and 3000°F

General rate constant equation: $k = k^\circ T^{-s} \exp(-E/RT)$

Reaction formula	Rate law	Activation energy kcal/g-mole, E	Frequency factor	s
$CH_4 \rightarrow 1/2H_2 + 1/2C_2H_6$	k_fA	95.0	7.6×10^{14a}	0
$C_2H_6 \rightarrow C_2H_4 + H_2$	k_fA	70.0	3.1×10^{14a}	0
$C_2H_4 \rightarrow C_2H_2 + H_2$	k_fA	40.0	2.6×10^{8a}	0
$C_2H_2 \rightarrow 2C + H_2$	k_fA^2	10.0	2.1×10^{10b}	0
$C + 2H_2 \rightarrow CH_4$	k_f	17.0	2.0×10^{9c}	0
$C_6H_6O + H_2 \rightarrow H_2O + C_6H_6$	k_fA	45.0	2.0×10^{13a}	0
$C_6H_6 \rightarrow 3C_2H_2$	k_fA	35.0	1.4×10^{9a}	0
$C + H_2O \rightarrow CO + H_2$	k_fAB	82.0	1.2×10^{12b}	−1
$CO + H_2O \rightarrow H_2 + CO_2$	k_fAB	30.0	1.0×10^{12b}	0
$C + CO_2 \rightleftarrows 2CO$	$k_fA - k_rR^2$	50.0	1.0×10^{6a}	−1
		61.0	1.0×10^{-9b}	0

[a] First-order reaction (sec^{-1}).
[b] Second-order reaction (cm^3/g-mole-sec).
[c] Zeroth-order reaction (g-mole/cm^3-sec).

Table 2 Pyrolysis products from the thermal decomposition of a nylon-phenolic resin composite heat shield

Component identification	Composition, mole-% Analysis of Sykes	Simulated pyrolysis products
Dimethylphenol	1.2	0.0
Phenol	4.7	6.2
Benzene	0.1	0.0
Toluene	0.2	0.0
Water	48.9	48.9
Carbon dioxide	1.1	1.1
Carbon monoxide	3.7	3.7
Methane	6.7	6.7
Hydrogen	33.4	33.4
Total	100.0	100.0

2.6 Numerical Solution of the Equations of Change

The solution of the equations of change applied to the nonequilibrium flow of pyrolysis products within a porous char was obtained by numerical techniques on an IBM 360/75 computer. The specific techniques used were a fourth-order Runge-Kutta formula for the solution of the differential energy and species continuity equations, and Simpson's Rule for the solution of the differential momentum and heat flux equations. In the case of nonequilibrium flow, the energy and species continuity equations were solved simultaneously because of the interdependence of the temperature and species concentrations.

3. Char Zone Thermal Environment Simulator

The experimental data presented in this study were obtained using an apparatus that simulated the flow of pyrolysis gases through the char layer. Low-density nylon-phenolic resin chars were obtained from NASA's Entry Structures Branch at the Langley Research Center. These specimens were placed in a metal holder with the front surface exposed to a bank of infrared quartz lamps used to simulate the high temperatures experienced by a re-entering vehicle. Simulated pyrolysis gases were passed through the char from the rear surface to the heated front surface. The exit gases were sampled and analyzed for comparison with the inlet gas composition to determine the extent of chemical reaction within the char. These results were also compared with the calculated exit gas compositions for frozen, equilibrium, and nonequilibrium flow conditions. Thus this method determined the accuracy of the nonequilibrium model for predicting the flow of reacting pyrolysis gases in the char layer. A schematic diagram of the Char Zone Thermal Environment Simulator is shown in Fig. 3. A detailed description of the equipment, including dimensions, materials of construction and assembly diagrams are given in Ref. 4.

4. Results of the Nonequilibrium Analysis

4.1 Comparison of the Nonequilibrium Analysis with Experimental Data

The basis for evaluating the nonequilibrium flow model as an accurate and realistic analysis of energy transfer in the char layer is the comparison of the experimentally determined exit product compositions from the Char Zone Thermal Environment Simulator with the calculated compositions in the nonequilibrium flow model. This was done for seventeen

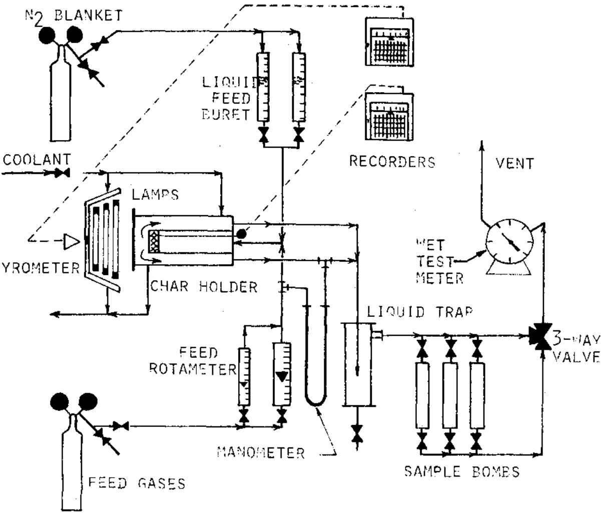

Fig. 3 Schematic diagram of the char zone thermal environment simulator.

experiments using low-density nylon-phenolic resin chars in which front surface temperatures of 1550°F to 2300°F and pyrolysis gas mass flux values of 0.00003–0.108 lb/ft²-sec were investigated.

In order to obtain significant conversion of the pyrolysis gases over the temperature range studied, the residence time within the porous char was increased by decreasing the mass flux. Thus the combination of the highest temperature and lowest mass flux produced the largest conversion resulting from chemical reactions.

Typical experimental results for the entire range of parameters studied are presented in Table 3. Also listed are the exit gas compositions resulting from the frozen (or initial composition), equilibrium, and nonequilibrium flow analyses. The excellent agreement of the calculated nonequilibrium compositions with the experimentally determined exit gas composition obtained in the Char Zone Thermal Environment Simulator proves the analysis to be realistic and accurate over the range of temperature and mass flux values investigated. In addition, a definite transition from the frozen condition, corresponding to relatively low temperatures and high mass fluxes, to a nonequilibrium condition, corresponding to higher temperatures and lower mass fluxes, is noted. Also, in all cases except those in which the mass flux values were extremely small (less than 0.00003 lb/ft²-sec), the compositions predicted by the equilibrium flow model were inaccurate and unrealistic. A more direct comparison of the three models will be discussed in the following section with emphasis on the shortcomings of the two ideal flow cases (frozen and equilibrium analyses).

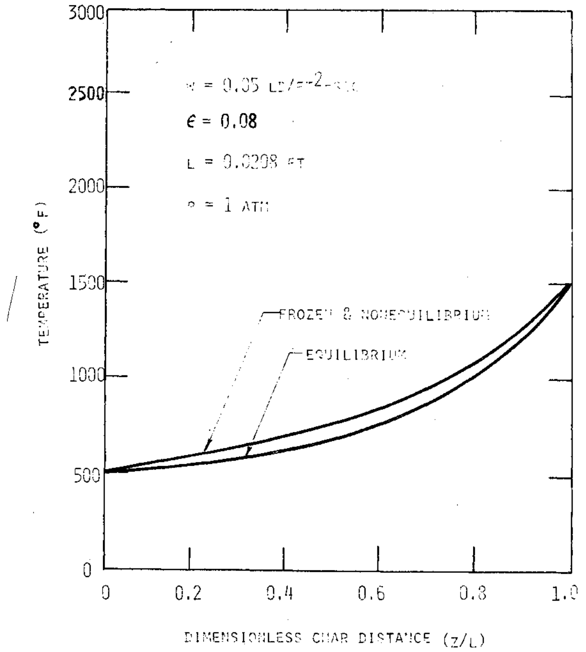

Fig. 4 Temperature profiles in the char layer (T_L = 1500°F).

4.2 Comparison of the Nonequilibrium Analysis with the Ideal Models

The frozen and equilibrium flow models bracket the nonequilibrium case. Frozen flow corresponds to a system in which no chemical reactions occur, while equilibrium flow refers to a system of species undergoing chemical reactions which are at equilibrium. Since the nonequilibrium flow model predicts the actual behavior, comparison of the exit gas compositions, temperature and pressure distributions, and surface heat flux for each model will determine the accuracy of the two limited flow analyses in predicting the energy transfer within the char layer.

These results are presented in Fig. 4 and Table 4 for a mass flux of 0.05 lb/ft²-sec, a front surface temperature of 1500°F and a back surface temperature of 500°F. The char porosity is 0.8 and the char thickness is 0.25 in. As seen, the tempera-

Table 3 Comparison of calculated and experimental exit gas compositions for pyrolysis gas flow through a $\frac{1}{4}$-in., low-density, nylon-phenolic resin char at mass fluxes between 0.00003–0.108 lb/ft²-sec and front surface temperatures between 1550°F and 2300°F

Run number:	V-11				XVIII-58				XIX-60				XX-64				XVI-48			
Mass flux:	0.0014				0.1080				0.00248				0.00103				0.00003			
Front surface temperature:	1550°F				1680°F				2030°F				2300°F				2055°F			
Back surface temperature:	730°F				690°F				1375°F				1190°F				1260°F			
Flow model:	a	b	c		a	b	c	d	a	b	c	d	a	b	c	d	a	b	c	d
Exit gas composition, mole %:																				
Hydrogen	37.2	71.6	37.2	37.0	30.6	59.5	30.6	30.8	29.3	62.7	38.2	41.3	28.4	65.9	25.2	26.7	31.7	83.1	84.7	84.5
Methane	32.5	1.4	32.5	32.0	6.2	3.5	6.2	6.1	6.0	0.8	17.2	18.2	5.4	0.3	25.6	26.4	46.3	0.4	8.2	7.7
Carbon monoxide	8.2	14.9	8.2	8.5	3.5	26.0	3.5	3.4	3.3	35.2	25.2	23.4	3.4	33.6	38.5	40.3	5.5	7.0	2.9	3.0
Carbon dioxide	6.6	0.1	6.6	6.4	1.0	4.4	1.0	1.1	0.9	1.5	8.8	7.6	1.0	0.0	0.9	0.6	2.5	0.0	0.0	0.6
Nitrogen	15.5	11.4	15.5	15.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	14.0	9.4	3.8	4.2
Water	0.0	0.6	0.0	0.0	51.9	6.5	51.9	50.8	53.7	0.9	4.9	5.0	46.0	0.2	0.0	0.0	0.0	0.1	0.0	0.0
Phenol	0.0	0.0	0.0	0.0	6.8	0.0	6.8	5.8	6.8	0.0	5.1	4.6	15.8	0.0	7.9	7.1	0.0	0.0	0.0	0.0
Ethylene	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.4	0.0	0.0	0.1	0.0
Acetylene	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.0	0.0	0.0	1.3	1.0	0.0	0.0	0.3	0.4
Pressure drop across char, lb/ft²:	0.5	0.5	0.5	0.7	22.0	18.8	22.0	17.5	0.7	0.6	0.6	0.7	0.2	0.3	0.2	0.2	0.0	0.0	0.1	0.1
Calculated heat flux, Btu/ft²-sec:	0.9	13.1	0.9	...	69.8	735.2	69.8	...	1.2	13.0	2.4	...	1.1	32.5	1.2	...	0.01	0.3	0.03	...

[a] Frozen flow model. [b] Equilibrium flow model. [c] Nonequilibrium flow model. [d] Experimental data—Char zone thermal environment simulator.

Table 4 Results of the frozen, equilibrium and nonequilibrium flow analyses for pyrolysis gas flow through a ¼-in. low-density nylon-phenolic resin char at 1500°F (T_L)

Conditions: $W = 0.05$ lb/ft²-sec, $\epsilon = 0.8$, $L = 0.0208$ ft, $T_0 = 500$°F

Char position:	Inlet	Exit $(z/L) = 1$		
Flow model:	(All)	Frozen	Equilibrium	Nonequilibrium
Mass flux, lb/ft$^2_{\text{voids}}$-sec:	0.063	0.063	0.063	0.063
Temperature, °F:	500.0	1500.0	1500.0	1500.0
Composition, mole %:				
Hydrogen	33.4	33.4	12.6	33.4
Methane	6.7	6.7	31.8	6.7
Phenol	6.2	6.2	0.0	6.2
Water	48.9	48.9	45.8	48.9
Carbon monoxide	3.7	3.7	0.2	3.7
Carbon dioxide	1.1	1.1	9.6	1.1
Pressure drop, lb/ft²:	...	5.8	5.3	5.9
Heat flux, Btu/ft²-sec:	...	31.8	46.3	31.9

ture profile of the nonequilibrium flow analysis is identical to the frozen flow temperature profile. The relative closeness of these two models at these conditions is likewise seen by comparing the exit gas compositions, pressure drop across the char and the surface heat flux in Table 4. There is little evidence of chemical reactions in the char and the energy transfer is closely predicted by the frozen flow model.

In Fig. 5 and Table 5, the same results are presented for a front surface temperature of 2000°F. Although the reported nonequilibrium values are again nearly equal to the frozen flow results, a noticeable change, especially in the concentration profiles and surface heat flux, is observed. This indicates chemical reactions among species within the char layer.

A continuation of the analysis to front surface temperatures of 2500°F (Fig. 6 and Table 6) and 3000°F (Fig. 7 and Table 7) shows a more dramatic change which is reflected by a downward shift of the nonequilibrium temperature profile toward the equilibrium curve and corresponding rapid changes in the concentration profiles and heat fluxes. Chemical reactions are obviously a very important mode of energy absorption under these last two sets of conditions.

Table 5 Results of the frozen, equilibrium and nonequilibrium flow analyses for pyrolysis gas flow through a ¼-in. low-density nylon-phenolic resin char at 2000°F (T_L)

Conditions: $W = 0.05$ lb/ft²-sec, $\epsilon = 0.8$, $L = 0.0208$, ft, $T_0 = 500$°F

Char position:	Inlet	Exit $(z/L) = 1$		
Flow model:	(All)	Frozen	Equilibrium	Nonequilibrium
Mass flux, lb/ft$^2_{\text{voids}}$-sec:	0.063	0.063	0.063	0.063
Temperature, °F:	500.0	2000.0	2000.0	2000.0
Composition, mole %:				
Hydrogen	33.4	33.4	28.3	34.7
Methane	6.7	6.7	23.4	6.7
Phenol	6.2	6.2	0.0	6.2
Water	48.9	48.9	36.2	47.4
Carbon monoxide	3.7	3.7	1.0	3.2
Carbon dioxide	1.1	1.1	11.1	2.0
Pressure drop, lb/ft²:	...	7.2	6.0	7.2
Heat flux, Btu/ft²-sec:	...	50.1	98.3	50.5

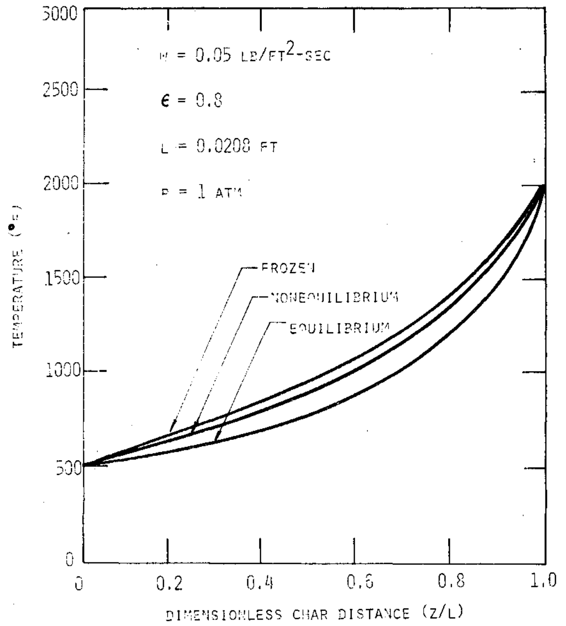

Fig. 5 Temperature profiles in the char layer (T_L = 2000°F).

It is not possible to extend the nonequilibrium analysis to temperatures above 3000°F since the chemical behavior within the char will not be predicted by the chemical reactions in Table 1. In this event additional reactions must be included to accurately describe the energy transfer within the char layer.

4.3 Parametric Study of Reacting Gas Flow in the Char Layer

A comparison of the nonequilibrium flow results with the experimental data was important in determining the accuracy of the flow model. However, very little quantitative information, beyond the discrete sets of data for each experiment,

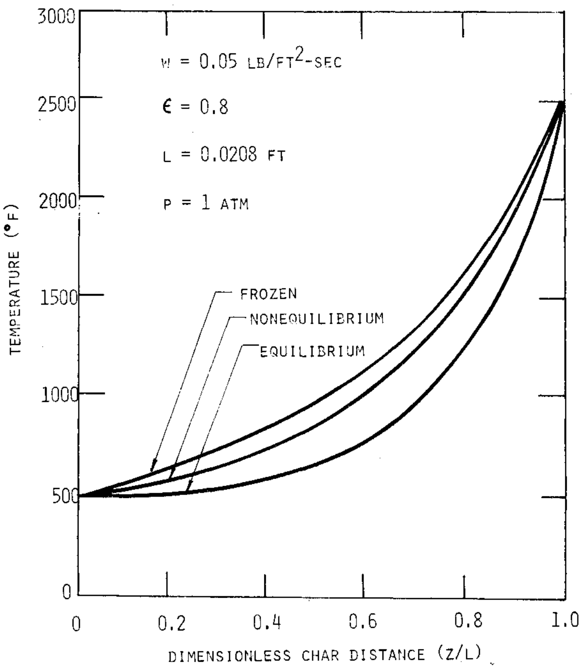

Fig. 6 Temperature profiles in the char layer (T_L = 2500°F).

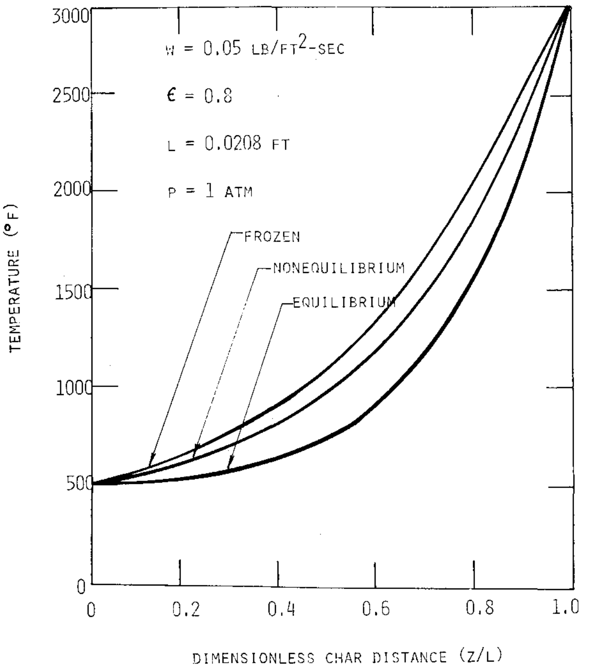

Fig. 7 Temperature profiles in the char layer (T_L = 3000°F).

was assembled regarding the effect of changing mass flux and/or temperature. As a result, a parametric study was undertaken to accurately relate the changes in these variables with variations in energy absorption within the char. To do this the initial value problem was solved in which the back surface temperature and temperature gradient were specified as boundary conditions for various values of the mass flux.

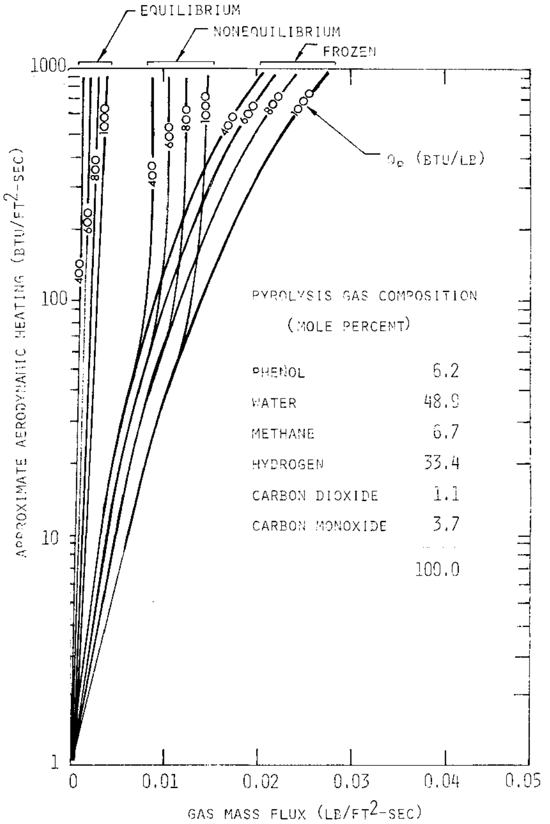

Fig. 8 Approximate aerodynamic heating vs gas mass flux for pyrolysis gas flow in the char layer.

The results of the calculations were in the form of the net heat transfer at the surface, called the approximate aerodynamic heating, which was the sum of the surface heat flux and radiant heat flux resulting from the calculated front surface temperature:

$$Q_a = -k_e(dT/dz)|_{z=L} + \bar{\epsilon}\sigma T_L^4 \tag{9}$$

where a value of 0.95 was used for the emissivity, $\bar{\epsilon}$. This information is summarized in Fig. 8 in which the mass flux is plotted against the approximate aerodynamic heating for various heats of pyrolysis, Q_p. The heat of pyrolysis is a function of the composition of the heat shield and is calculated by making an energy balance at the back surface of the char:

$$Q_p = -k_e(dT/dz)|_{z=0} \tag{10}$$

where Q_p is the sum of the energy absorbed by the decomposition of the plastic heat shield and the energy conducted through the virgin plastic. Results for the frozen, equilibrium and nonequilibrium flow models are presented. This form of presenting the results is a very convenient and informative method as will be seen.

In heat shield design one of the important questions asked is, "What is the required heat shield weight necessary for the protection of a vehicle for a specific mission?" Specification of the type of heat shield material to be used (e.g., nylon-phenolic resin) brackets the heat of pyrolysis value, while the trajectory calculations determine the amount of aerodynamic heating that can be expected. For example, an approximate aerodynamic heating rate of 500 Btu/ft²-sec and a heat of pyrolysis of 400 Btu/lb locates three distinctive points on Fig. 8; one for each of the frozen, equilibrium and nonequilibrium flow models. This corresponds to three values of the mass flux; 0.017 lb/ft²-sec for frozen, 0.002 lb/ft²-sec for equilibrium and 0.009 lb/ft²-sec for nonequilibrium flow. The nonequilibrium flow analysis accurately predicts the behavior and would specify the exact heat shield weight (which is a function of the mass flux) required. The frozen flow model shows an overprediction because important endothermic chemical reactions are omitted, and the equilibrium flow model shows an underprediction because chemical reactions are assumed to occur at a greater extent than the actual behavior.

The results presented in Fig. 8 also provide a method of determining at what point the nonequilibrium flow changes from frozen flow behavior. This figure very graphically

Table 6 Results of the frozen, equilibrium and nonequilibrium flow analyses for pyrolysis gas flow through a ¼-in. low-density nylon-phenolic resin char at 2500°F (T_L)

Conditions: W = 0.05 lb/ft²-sec, ϵ = 0.8, L = 0.0208 ft, T_0 = 500°F

Char position:	Inlet	Exit (z/L) = 1		
Flow model:	(All)	Frozen	Equilibrium	Nonequilibrium
Mass flux, lb/ft$^2_{\text{voids}}$-sec:	0.063	0.063	0.061	0.075
Temperature, °F:	500.0	2500.0	2500.0	2500.0
Composition, mole %:				
Hydrogen	33.4	33.4	55.7	53.8
Methane	6.7	6.7	7.8	5.1
Phenol	6.2	6.2	0.0	4.7
Water	48.9	48.9	19.2	9.0
Carbon monoxide	3.7	3.7	5.5	21.7
Carbon dioxide	1.1	1.1	11.8	5.6
Pressure drop, lb/ft²	. . .	9.1	6.7	9.0
Heat flux, Btu/ft²-sec:	. . .	70.2	192.6	110.7

Table 7 Results of the frozen, equilibrium and nonequilibrium flow analyses for pyrolysis gas flow through a $\frac{1}{4}$-in. low-density nylon-phenolic resin char at 3000°F (T_L)

Conditions: $W = 0.05$ lb/ft²-sec, $\epsilon = 0.8$, $L = 0.0208$ ft, $T_0 = 500$°F

Char position:	Inlet	Exit (z/L) = 1		
Flow model:	(All)	Frozen	Equilibrium	Nonequilibrium
Mass flux, lb/ft$^2_{\text{voids}}$-sec:	0.063	0.063	0.071	0.233
Temperature, °F	500.0	3000.0	3000.0	3000.0
Composition, mole %:				
Hydrogen	33.4	33.4	80.0	0.0[a]
Methane	6.7	6.7	0.0	54.0
Phenol	6.2	6.2	0.0	2.4
Water	48.9	48.9	0.2	0.0
Carbon monoxide	3.7	3.7	10.4	28.9
Carbon dioxide	1.1	1.1	9.4	17.4
Pressure drop, lb/ft²:	...	11.3	7.3	11.0
Heat flux, Btu/ft²-sec:	...	92.5	335.5	193.4

[a] Nonequilibrium flow model requires additional important reactions and associated kinetic data to accurately describe the energy transport above ~3000°F.

illustrates the differences in each model and allows the presentation of a large volume of information in a clear and readily accessible manner.

4.4 Calculation of the Reacting Gas Heat Capacity

In addition to the preceding information, the reacting gas heat capacity for the nonequilibrium flow of pyrolysis products through a porous char layer has been determined. This term is very useful in the calculations of the one-dimensional, transient response of an ablative composite structure. The energy equation for the transient case can be put in the following form for the char zone:

$$-\frac{\partial}{\partial z}\left(k\frac{\partial T}{\partial z}\right) + \left[\left(\frac{W}{W_0}\right)\bar{C}_p + \sum_{i=1}^{K+1} H_iR_i \Big/ W_0\left(\frac{\partial T}{\partial z}\right)\right] \times W_0\frac{\partial T}{\partial z} = -C_p\frac{\partial T}{\partial z} \qquad (11)$$

where W is the mass flux of pyrolysis products at z and W_0 is the mass flux of pyrolysis products entering the char. The term in brackets [ ] is referred to as the effective reacting gas heat capacity. For example, the flow within the char zone can be considered frozen (H_iR_i is zero) by introducing the reacting gas heat capacity as an input function to the transient calculations. In Fig. 9 a plot of the reacting gas heat capacity as a function of temperature is shown for frozen, equilibrium and nonequilibrium flow within the char layer up to 3000°F. These curves were calculated for a mass flux of 0.05 lb/ft²-sec, a back surface temperature of 500°F, and, char porosity and thickness of 0.8 and 0.25 in., respectively. The differences in the manner used to calculate the energy transfer by chemical reaction (H_iR_i) for equilibrium and nonequilibrium flow causes the curves to separate as shown.

5. Conclusions

The reacting flow of pyrolysis products from nylon-phenolic resin composites in the char layer is accurately described by a nonequilibrium model employing reaction kinetic data of the important reactions occurring in the system. For the simulated pyrolysis product compositions in Table 2, mass flux values between 0.00003–0.108 lb/ft²-sec and a front surface temperature range of 1550°–2300°F, the reactions and associated kinetic data in Table 1 accurately describe the energy transfer in the char layer. These reactions are valid to approximately 3000°F. Above this temperature, additional reactions must be specified to accurately describe the reacting flow system.

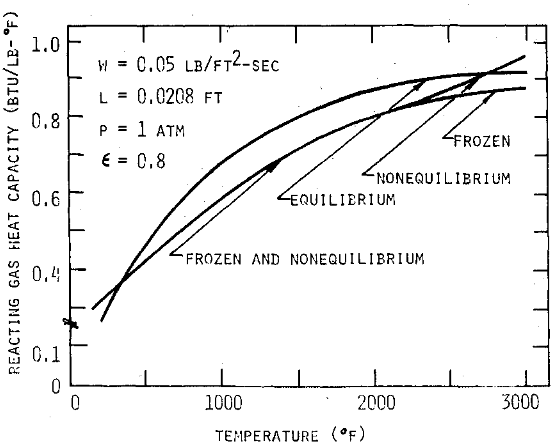

Fig. 9 Reacting gas heat capacity as a function of temperature.

Under conditions of high mass flux (greater than 0.01 lb/ft²-sec) and/or low temperatures (less than 2000°F), the flow of pyrolysis products through the char layer is essentially frozen. These conditions define the upper limit of the frozen flow model.

The equilibrium flow model erroneously predicts the behavior in the char for all conditions except those in which the mass flux is smaller than 0.00003 lb/ft²-sec. Mass fluxes greater than this value require the use of a nonequilibrium flow analysis to describe chemical reactions occurring at finite rates.

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