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International Journal of Heat and Mass Transfer 50 (2007) 1196–1201

International Journal of HEAT and MASS TRANSFER

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Technical Note

Quasi-steady solutions for the ablation of charring materials

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Received 7 August 2006; received in revised form 12 October 2006
Available online 16 January 2007

Abstract

The phenomenon of quasi-steady ablation is investigated theoretically for a semi-infinite charring material. The one-dimensional ablation is assumed to proceed under the influence of a steady external heat source. The steady temperature distributions in the virgin and char zones are derived and the associated steady ablation rate is also obtained theoretically. Though the results presented in this study are obtained for the case of steady ablation, they are useful for the verification of transient numerical models of charring ablator, especially those based on a fixed coordinate system.
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Keywords: Ablation; Charring ablator; Steady state; Theoretical solutions

1. Introduction

For hypersonic vehicles subjected to severe aerodynamic heating, charring ablative materials are commonly used in the thermal protection systems (TPS) for the integrity of the structure. They are also used in the nozzle of a solid-propellant rocket motor to protect the nozzle from being over-heated and chemically eroded. The charring ablative materials usually have a matrix of fibers, and the space among these fibers is fulfilled with decomposable resin. The resin, and sometimes the fibers also, will decompose if its temperature rises high enough in a heating process. This causes the release of pyrolysis gases and subsequently the formation of a porous char. If the heating process continues, the pressure of the released pyrolysis gases will build up quickly and then a pressure gradient is formed, which drives the gases moving toward the outer surface and finally being injected into the boundary layer of an external flow field. The surface recession is mainly due to the possible vaporizing, subliming, chemical processes, as well as mechanical erosions on the heated surface.

A great number of researches on charring ablators can be found in the literature. Hurwicz and Rogan [1] presented a very detailed review of this field. Two other reviews were presented recently by Potts [2] and Milos and Rasky [3]. Studies related to the theoretical solutions of quasi-steady ablation are rare in the literature. Only the works of Landau [4], Sunderland and Grosh [5], Quan [6], and Lin [7] can be found. Among these, Quan's research is the only one associated with a charring ablator.

The mechanisms involved in the ablation of charring materials are so complicated that no definitive solutions could be provided so far. A complete numerical model of this problem should consist of three sub-models, namely, (1) an in-depth heat and mass transfer model, (2) a pyrolysis model governing the pyrolysis reaction rates, and (3) a surface recession model governing the surface recession rate. The surface recession and in-depth pyrolysis models involved in one's numerical model may be very complicated. Thus, transient numerical models developed for the detailed simulations of charring ablators can hardly be verified and the validity of the numerical solutions is usually suspected. In view of this, it is worthwhile to seek theoretical solutions for some special cases so as to provide a means for the verification.

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0017-9310/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.ijheatmasstransfer.2006.11.011

Nomenclature

A	frequency factor, 1/s
c_{pc}	specific heat of char, J/(kg K)
c_{pg}	averaged specific heat of pyrolysis gases, J/(kg K)
c_{pv}	specific heat of virgin, J/(kg K)
E	activation energy of pyrolysis reactions, J/mole
H	specific enthalpy of ablative material, J/kg
H_g	average specific enthalpy of pyrolysis gases, J/kg
H_{gw}	average specific enthalpy of pyrolysis gases on the heated surface, J/kg
H_i	initial specific enthalpy of ablative material, J/kg
H_w	specific enthalpy of ablative material on the heated surface, J/kg
k	thermal conductivity of ablative material, W/(m K)
k_c	thermal conductivity of char, W/(m K)
k_v	thermal conductivity of virgin, W/(m K)
$\dot{m}_g$	mass flux of pyrolysis gases, kg/(s m^2)
n	order of reaction for pyrolysis reactions
q_{net}	net heat flux imposed upon the heated surface, W/m^2
R	universal gas constant, 8.3144 J/(mole K)
s_{ab}	accumulative ablated thickness of ablator, m
t	temperature of ablative material, K
t_0	reference temperature at which enthalpy of formation is defined, K
t_{ab}	ablation temperature, K
t_{cut}	cut-off temperature below which the pyrolysis reactions cannot occur, K
t_i	initial temperature, K
t_v	temperature at $y = y_v$, K
t_w	surface temperature at $y = 0$, K
v_{ab}	$v_{ab} \equiv ds_{ab}/d\theta$, ablation rate, m/s
v_s	steady ablation rate, m/s
x	axial distance from the initial position of the heated surface, m
y	axial distance from the heated surface, m
y_c	thickness of char, m
y_v	axial distance where virgin zone starts to appear, m

Greek symbols

α_c	$\alpha_c \equiv k_c/(\rho_c c_{pc})$, thermal diffusivity of char, m^2/s
α_v	$\alpha_v \equiv k_v/(\rho_v c_{pv})$, thermal diffusivity of virgin, m^2/s
ΔH_0	net absorbed heat per unit solid mass loss due to the pyrolysis reactions at reference temperature t_0, J/kg
ΔH_{ab}	effective ablation heat, J/kg
ΔH_{cf0}	enthalpy of formation at temperature t_0 for char, J/kg
ΔH_{gf0}	enthalpy of formation at temperature t_0 for pyrolysis gases, J/kg
ΔH_{vf0}	enthalpy of formation at temperature t_0 for virgin, J/kg
ρ	density of ablative material, kg/m^3
ρ_c	density of char, kg/m^3
ρ_v	density of virgin, kg/m^3
ρ_w	density of ablator on the heated surface, kg/m^3
θ	time, s

Subscripts

0	reference temperature
ab	ablation
c	char
f	formation
g	pyrolysis gases
i	initial condition
net	net effect
s	steady state
v	virgin
w	heated surface

In the present work, the one-dimensional quasi-steady ablation process of a semi-infinite charring ablator is investigated theoretically. The virgin and char are assumed to be homogeneous. In addition, the virgin is assumed to be impermeable. Other general accepted assumptions are adopted as follows:

1. The pyrolysis gases are chemically non-reactive. Thus, deposition (coking) or further chemical reactions of gases are excluded.
2. The density of the pyrolysis gases is small in comparison to that of the condensed phase, i.e., the pyrolysis gases will pass immediately out through the porous char on their formation.
3. The pyrolysis gases are always in thermal equilibrium with the nearby solid.
4. Radiative heat transfer within the porous char is neglected.
5. Volume changes arising from the in-depth pyrolysis reactions and the thermal expansions are neglected. Only the surface recession is taken into consideration.

The purpose of this article is to present some of the exact solutions of quasi-steady ablation for charring materials. The current results are considered to be useful for the verification of numerical models for charring ablators.

2. Governing equations

As depicted in Fig. 1, the left boundary of a semi-infinite charring ablative material is subjected to a steady external heat source which may be provided by means of radiative

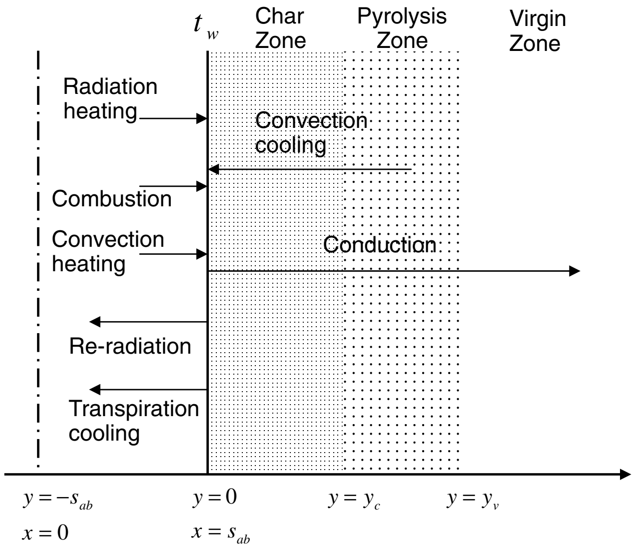

Fig. 1. Schematic of the ablation of a charring ablator.

or aerodynamic heating. The charring ablator can usually be qualitatively separated into three zones, namely, virgin, pyrolysis, and char. In the beginning of a heating process, only the virgin zone exists whereas the other two zones will be produced at a later time during the charring-ablation process. The virgin zone is the region where ablator still remains in its virgin state and no pyrolysis gases exist in this zone. The pyrolysis zone is the region where pyrolysis reactions occur. The solid density and gas mass flux are dependent on the position in this region. The char zone is the region where all the decomposable constituents have already been consumed. No more pyrolysis reactions can occur and hence the solid density and gas mass flux are independent on the position in this region. The transition from virgin to char is basically an asymptotic behavior. Thus, in general, it is impossible to determine distinctively the interfaces between these three zones. Note that the origin of the x coordinate is located at the initial position of the heated surface whereas the origin of y coordinate is fixed on and moves with the receding heated surface.

2.1. Mass conservation equation

According to the aforementioned assumptions in Section 1, the in-depth mass conservation equation of a charring ablator can be derived, in the (y, θ) coordinate, as

$$\frac{\partial \dot{m}_g}{\partial y} = -\frac{\partial \rho}{\partial \theta} + v_{ab}\frac{\partial \rho}{\partial y} \tag{1}$$

Note that the gas mass flux $\dot{m}_g$ should be non-positive due to the flowing direction of pyrolysis gases. At $y = \infty$, the ablator's density is equal to that of virgin and the gas mass flux is zero, i.e., $\rho|_{y=\infty} = \rho_v$ and $\dot{m}_g|_{y=\infty} = 0$. If the steady state has already been achieved, the result of the above equation can thus be obtained as

$$\dot{m}_g = v_s(\rho - \rho_v) \tag{2}$$

where $\dot{m}_g$ and ρ are functions of y. An equation similar to the above was also presented previously by Quan [6]. Thus, the gas mass flux in the char zone can easily be obtained as

$$\dot{m}_g = v_s(\rho_c - \rho_v), \quad \text{for} \quad y \leqslant y_c \tag{3}$$

Note that, in the char zone, the ablator's density ρ_c is constant, and hence the gas mass flux $\dot{m}_g$ should be constant also.

2.2. Energy conservation equation

By Moyer and Rindal [8], the in-depth energy conservation equation for a charring ablator can be derived, in the (y, θ) coordinate, as

$$\left.\frac{\partial(\rho H)}{\partial \theta}\right|_y = \frac{\partial}{\partial y}\left(k\frac{\partial t}{\partial y}\right) + v_{ab}\frac{\partial}{\partial y}(\rho H) - \frac{\partial(\dot{m}_g H_g)}{\partial y} \tag{4}$$

If the steady ablation has already been achieved, the above equation can be reduced to

$$\frac{d}{dy}\left(k\frac{dt}{dy}\right) = \frac{d(\dot{m}_g H_g - v_s\rho H)}{dy} \tag{5}$$

By assuming that the initial temperature of the virgin is uniformly distributed, i.e., $H|_{y=\infty} = H_i$, $\dot{m}_g|_{y=\infty} = 0$, and $(dt/dy)|_{y=\infty} = 0$, the above equation can be integrated to have

$$k\frac{dt}{dy} = v_s\rho_i H_i + \dot{m}_g H_g - v_s\rho H \tag{6}$$

where subscript i represents the initial state and also the position at $y = \infty$. In general, the ablator is in its virgin state in the beginning, i.e., $\rho_i = \rho_v$. So, combining Eq. (6) with Eq. (2) and eliminating $\dot{m}_g$, give the steady temperature gradient in the ablator

$$k\frac{dt}{dy} = v_s[\rho_v H_i + (\rho - \rho_v)H_g - \rho H] \tag{7}$$

where t, k, ρ, H_g, and H are functions of y.

3. Theoretical analyses

3.1. Temperature distribution in virgin zone

In the virgin zone, where no pyrolysis gases exist, if the assumption of constant properties is appropriate, then Eq. (7) can be reduced to

$$\frac{dt}{dy} = -\frac{v_s}{\alpha_v}(t - t_i), \quad \text{for} \quad y \geqslant y_v \tag{8}$$

Integrating the above equation results in the steady temperature distribution in virgin zone:

$$\frac{(t - t_i)}{(t_v - t_i)} = \exp\left(-\frac{v_s(y - y_v)}{\alpha_v}\right), \ \text{for } y \geqslant y_v \tag{9}$$

The form of the above result is consistent with that of Landau [4]. It should be noted that, so far, there is no theoretical ways for determining t_v and y_v and hence these two values can only be estimated with the aid of numerical analyses. This will be demonstrated in Section 4 of this paper.

3.2. Temperature distribution in char zone

In the char zone, there are no more pyrolysis reactions and hence both the solid density and gas mass flux are not functions of position. Therefore, from Eq. (7), we have

$$\left(\frac{k_c}{v_s}\right)\frac{dt}{dy} = \rho_v H_i + (\rho_c - \rho_v)H_g - \rho_c H, \quad \text{for} \quad y \leqslant y_c \tag{10}$$

If the specific heats of char and pyrolysis gases are constant in this zone, i.e., $H = H_w - c_{pc}(t_w - t)$ and $H_g = H_{gw} - c_{pg}(t_w - t)$, then we have

$$\frac{-1}{\rho_c c_{pc} + (\rho_v - \rho_c)c_{pg}}\left(\frac{k_c}{v_s}\right)\frac{dt}{dy} = t - t_w + t^*, \quad \text{for} \quad y \leqslant y_c \tag{11}$$

where

$$t^* \equiv \frac{\rho_v(H_{gw} - H_i) + \rho_c(H_w - H_{gw})}{\rho_c c_{pc} + (\rho_v - \rho_c)c_{pg}} \tag{12}$$

Note that t^* should be a constant while steady ablation is achieved. In general, due to the complicated phenomena that may be involved in the recession process, the ablation rate is a complex function of the surface temperature and vice versa. Nevertheless, the surface temperature must remain a steady value while steady ablation rate is achieved and hence a constant t^* is expected.

If the thermal conductivity of char k_c is also constant, then Eq. (11) can be solved and the steady temperature distribution in the char zone is obtained as

$$\frac{t - t_w}{t^*} + 1 = \exp\left\{-\frac{v_s y}{\alpha_c}\left[1 + \frac{(\rho_v - \rho_c)c_{pg}}{\rho_c c_{pc}}\right]\right\}, \quad \text{for} \quad y \leqslant y_c \tag{13}$$

It should be noted that, though the char zone does usually appear in most of the practical cases, it may not appear in some ablation processes. If the heating environment is very severe and the associated ablation rate is so high that there would not be enough time for the decomposable constituents to fully pyrolyze, therefore, the char zone would not be formed. The appearance of the char zone is more possible for the ablators which have high pyrolyzing and low ablation rates.

3.3. Temperature distribution in pyrolysis zone

In the pyrolysis zone, the solid density is governed by the pyrolysis model which may be very complicated and highly coupled with the temperature of the ablator. Moreover, the thermal conductivity k, specific heat c_p, solid density ρ, gas enthalpy H_g, and solid enthalpy H all vary with position in the pyrolysis zone, thus, no theoretical solution can be obtained and hence the temperature distribution in this zone can only be obtained by numerical methods which are beyond the scope of the current research.

3.4. Steady ablation rate

By considering the energy balance on the heated surface for steady ablation, we have

$$q_{net} = \rho_w v_s \Delta H_{ab} - \left(k\frac{dt}{dy}\right)\bigg|_{y=0} \tag{14}$$

The effects included in q_{net} are radiative heating, re-radiative cooling, convective heating or cooling, transpiration cooling, etc. ΔH_{ab} is called the "effective ablation heat" which represents the net absorbed heat per unit loss of condensed phase on the surface. ΔH_{ab} is defined to include the effects of sublimation, evaporation, combustion or oxidation, mechanical erosion, etc.

The steady temperature gradient on the heated surface can be obtained from Eq. (7) by substituting $y = 0$ into it. Thus, from the above equation, we have

$$v_s = \frac{q_{net}}{\rho_w \Delta H_{ab} + \rho_w H_w - \rho_v H_i + (\rho_v - \rho_w)H_{gw}} \tag{15}$$

This is the theoretical solution of steady ablation rate for a semi-infinite charring ablator.

3.5. More detailed derivations

In Sections 3.2 and 3.4, the results of t^* and v_s are derived in general forms related to the enthalpy of gases and solid. In order to make possible a more detailed treatment and have a deeper physical insight of the current results, some more assumptions should be made here. Therefore, the enthalpy of pyrolysis gases on the heated surface H_{gw} is assumed to be calculated by

$$H_{gw} = \Delta H_{gf0} + c_{pg}(t_w - t_0) \tag{16}$$

whereas the enthalpy of virgin at the initial state is

$$H_i = \Delta H_{vf0} + c_{pv}(t_i - t_0) \tag{17}$$

In addition, if the char zone exists, the solid enthalpy on the heated surface can be assumed as

$$H_w = H_c|_{t=t_w} = \Delta H_{cf0} + c_{pc}(t_w - t_0), \quad \text{for} \quad y_c > 0 \tag{18}$$

In the above three equations, the specific heats of the gases, virgin, and char are all assumed constant. Inserting the above three equations into Eq. (12) gives

$$t^* = t_w - t_0 + \frac{(\rho_v - \rho_c)\Delta H_0 - \rho_v c_{pv}(t_i - t_0)}{\rho_c c_{pc} + (\rho_v - \rho_c)c_{pg}}, \quad \text{for} \quad y_c > 0 \tag{19}$$

where

$$\Delta H_0 \equiv \Delta H_{gf0} + \frac{1}{\rho_v - \rho_c}(\rho_c \Delta H_{cf0} - \rho_v \Delta H_{vf0}). \tag{20}$$

In fact, ΔH_0 represents the net absorbed heat per unit loss of solid due to pyrolysis reactions at the reference temperature t_0.

Similarly, substituting Eqs. (16)–(18) into Eq. (15), and assuming the existence of char, the steady ablation rate can be obtained as

$$v_s = \frac{q_{net}}{\rho_c\Delta H_{ab} + (\rho_v - \rho_c)\Delta H_0 + [\rho_c c_{pc} + (\rho_v - \rho_c)c_{pg}](t_w - t_0) - \rho_v c_{pv}(t_i - t_0)}, \quad \text{for } y_c > 0 \tag{21}$$

In general, the surface temperature t_w in the above equation is coupled with the ablation rate. Thus, the above equation should be combined with one's surface recession model to determine the surface temperature and the associated steady ablation rate.

4. Demonstrations

A transient numerical model called "CAMAC" has been developed for the analyses of charring ablators. This computer code is implemented on a basis of the (x, θ) coordinate system. In order to demonstrate how to use the theoretical results obtained in this research, a typical case of a charring ablator is analyzed by using the CAMAC code. The parameters used for this typical case are shown in Table 1. The given values in Table 1 are not for any specific ablator but just for the purpose of demonstrations, however, they are in a realistic range for general charring ablators. Note that the net heat flux on the heated surface q_{net} is intentionally kept constant to represent a steady external heat source.

In this specific case, a simple surface recession model is used, i.e., the ablation is assumed to proceed at a known fixed temperature t_{ab} (=1000 K) and the effective ablation heat ΔH_{ab} is assumed a known constant also.

As for the in-depth pyrolysis model, a simple one-equation Arrhenius model is adopted for the demonstrations, i.e., the solid density is assumed to be formulated by the following equation [9]:

$$\left.\frac{\partial\rho}{\partial\theta}\right|_x = -A\rho_v\left(\frac{\rho - \rho_c}{\rho_v}\right)^n \exp\left(-\frac{E}{R\cdot t}\right), \quad \text{for} \quad t > t_{cut} \tag{22}$$

where t_{cut} represents a cut-off temperature below which the pyrolysis reactions cannot occur. Since this section is just for a demonstration only, the details of the numerical analysis will not be presented here.

The numerical result of ablation rate for this specific case is shown in Fig. 2. From this figure, it can be seen that the steady ablation rate of 2.149×10^{-4} m/s appears at about time = 25 s. The theoretical result of steady ablation rate, Eq. (21), is also plotted in Fig. 2 for comparisons. Good agreements are shown.

Both the steady solid density and gas mass flux distributions within the ablator, obtained by CAMAC at time = 25 s, are shown in Fig. 3. For convenience, the absolute values of the gas mass flux are used for the plotting. It is observed that, for this specific case, the char zone does exist within a very narrow region near the heated surface($y_c \approx 0.1$ mm) and most of the other space is occupied by a virgin zone. Hence, the use of Eq. (21), which is based on the assumption of the existence of a char layer, in Fig. 2 for comparisons is appropriate. Substituting the numerical results of density distribution and ablation rate into Eq. (3), the theoretical distribution of gas mass flux can be obtained and compared with that from CAMAC. This is shown as a solid line in Fig. 3. Excellent agreement is observed and hence the rule of mass conservation is considered to be preserved adequately in CAMAC.

The temperature distribution within the ablator, obtained by CAMAC at time = 25 s, is shown in Fig. 4. From the numerical results shown in Fig. 3, the value of y_v can be estimated to be about 0.5077 mm. Therefore,

Table 1
Parameters used in the typical case for demonstrations

Parameter	Symbol	Value	Unit
Initial temperature	t_i	303	K
Net heat flux imposed upon the heated surface	q_{net}	0.5×10^6	W/(m^2)
Thermal conductivity of virgin	k_v	0.53	W/(m K)
Density of virgin	ρ_v	1030	kg/m^3
Specific heat of virgin	c_{pv}	1800	J/(kg K)
Thermal conductivity of char	k_c	0.17	W/(m K)
Density of char	ρ_c	800	kg/m^3
Specific heat of char	c_{pc}	2520	J/(kg K)
Specific heat of pyrolysis gases	c_{pg}	1520	J/(kg K)
Ablation temperature	t_{ab}	1000	K
Effective ablation heat	ΔH_{ab}	0.7×10^6	J/kg
Pyrolysis heat at the reference temperature	ΔH_0	0.5×10^6	J/kg
Reference temperature at which the enthalpy of formation is defined	t_0	298	K
Frequency factor	A	2.0×10^{14}	s^{-1}
Order of reaction	n	2.0	–
Activation energy	E	1.6×10^5	J/mole
Cut-off temperature	t_{cut}	400	K

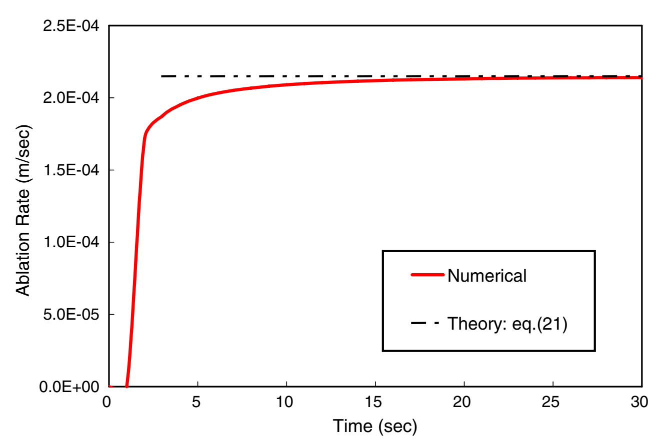

Fig. 2. Variation of ablation rate with time, predicted by CAMAC, and comparisons with the steady theoretical result of Eq. (21).

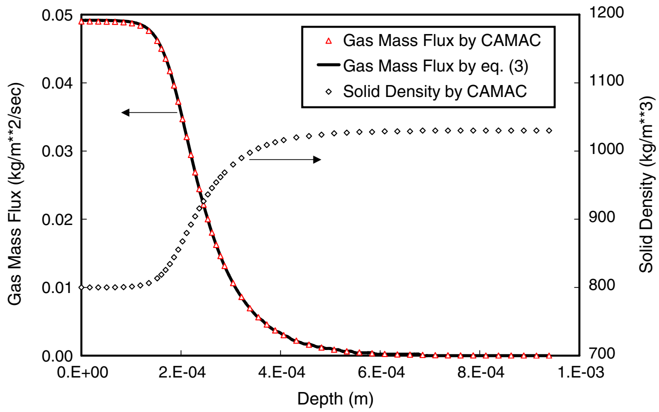

Fig. 3. Steady distributions of gas mass flux and solid density within the ablator, obtained by CAMAC at time = 25 s, comparing with the theoretical gas mass flux from Eq. (3).

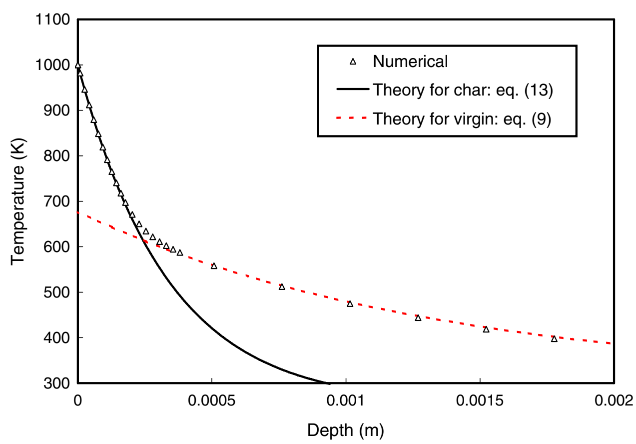

Fig. 4. Steady temperature distribution within the ablator, obtained by CAMAC at time = 25 s, comparing with the theoretical results of Eqs. (9) and (13).

from the numerical result in Fig. 4, we know the corresponding value of t_v to be 558.2 K. Thus, with these two known values, a theoretical temperature distribution in the virgin can be obtained by using Eq. (9). This is also shown in Fig. 4 for comparisons. As expected, the theoretical temperature distribution agrees perfectly with that from CAMAC in the virgin zone. As extrapolated into the regions of char and pyrolysis zones, this theoretical result is observed to be lower than that from the numerical model. This is mainly because the effects of convective cooling of pyrolysis gases and the absorbed heat during pyrolyzing processes have not been taken into account. Also shown in Fig. 4 is the theoretical temperature distribution (Eq. (13)) for the char zone. This theoretical result is almost identical with that from numerical calculations and the deviation between them gradually appears while extrapolating this equation into the pyrolysis zone. Therefore, it is proved that the CAMAC code successfully follows the mass and energy balance equations in the virgin and char zones.

As demonstrated in the above, with the help of one's numerical model, like CAMAC or any others, one can easily judge whether the char layer exists or not and hence the current theoretical results can be used in a proper situation. It should be emphasized that the CAMAC code used here is not for the verification of the theoretical results but just for the demonstrations of the usage. The validity of the current theoretical results has no concern with the pyrolysis or surface recession models used in one's numerical code. Due to the simple mathematics involved in this study, the current theoretical results are considered to be valid and suitable for the verification of one's numerical code.

5. Conclusions

The phenomenon of steady ablation for a semi-infinite charring ablator is investigated theoretically. The steady temperature distributions in the virgin and char zones are derived and the associated steady ablation rate is also obtained theoretically. Though the results obtained in this study are corresponding to the steady ablation in the (y, θ) coordinate system, they are actually transient results from the viewpoint of (x, θ) coordinate system. Hence, it is appropriate to use the current results to verify one's transient numerical models for charring ablators, especially those based on the x coordinate system.

Acknowledgment

The author is grateful to the Tien-Kung Project of Chung Shan Institute of Science and Technology (CSIST) for its sponsorship on this research.

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