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# A nonlinear pyrolysis layer model for analyzing thermal behavior of charring ablator

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ABSTRACT

Understanding the pyrolysis phenomena experienced by charring ablators used in thermal protection systems for manned reentry vehicles is crucial for their design. A one-dimension nonlinear pyrolysis layer model without surface recession has been developed to explore the thermal behavior of charring ablator when subjected to an aerodynamic hyper-thermal environment. The charring ablator in this model consists of three distinct zones: char, pyrolysis and virgin material. The heat and mass transfer, the two moving interfaces and the temperature-dependent thermal properties in charring materials undergoing pyrolysis are considered in the formulation of the model. The governing differential equations are derived, and its implicit finite difference formulations are programmed in MATLAB. Examples are given to demonstrate the effectiveness and accuracy of this model. The thermal response of charring material with antioxidants is also predicted under actual service conditions.



## 1. Introduction

The charring ablator normally provides the most efficient thermal protection shield for a manned vehicle during reentry, due to its low thermal conductivity and low density [1]. Charring ablators in the thermal protection system of a vehicle operates by absorbing heat through decomposition and rejecting heat via pyrolysis gas injection back into the boundary layer gas and re-radiation [2]. For example, AVCOAT and PICA materials had been successfully applied to the thermal protection system of the Apollo command module during a lunar-return entry and the Orion multi-purpose crew vehicle during the experimental reentry in 2014, respectively.

Thermal behavior of a charring material exposed to a hyper-thermal environment is an extremely complex phenomenon [3]. The charring ablator can pyrolyze as it is heated, yielding gaseous products and leaving a porous carbonaceous residue, i.e. char. Experimental work in this area focused on the ground tests [4–10]. For example, the thermogravimetric analysis (TGA) technique had been used to determine the kinetic parameters of thermal degradation [4]. The decomposition kinetic parameters and thermal properties were measured in a 4-inch-diameter, high-energy, supersonic, dissociated-gas stream generated by the fully water-cooled arc-jet wind tunnel [5]. Multilayer charring material was successfully tested in a wedge configuration in the NASA Johnson Space Center arcjet wind tunnel for application on the leeward surface of the Orion vehicle [10]. Regrettably, some parameters such as pressure of the arcjet facility exceed the range expected for relevant environments in flight trajectories. Generally, the current ground tests do not allow for exacting duplication of heating rate, enthalpy and flow field associated with the reentry. There are several levels of ground-testing that need to be done before a TPS is flight approved. While flight testing [7,11] is an ultimate proof of the design, it is not commonly sought after because its cost is prohibitively expensive.

With the development of numerical methods a simulation approach can be used to help the design in the thermal protection system. For instance, CMA code, developed by Aerotherm Corporation in the 1960's, was one of the first one-dimensional codes. It solved internal energy balance and decomposition equations coupled with general surface energy balance boundary conditions to simulate the response of pyrolyzing and ablating heatshield in hypersonic flows. FIAT code was developed at NASA Ames Research Center to support the development of lightweight ceramic ablators. TITAN program was developed to perform two-dimensional thermal response and shape change simulations for pyrolyzing ablators. The Navier–Stokes solver, GIANTS, was successfully coupled with TITAN using a loosely coupled method for simulating the fluid/solid interaction. The commercial finite-element code MARC can

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perform thermal and structural analysis of the interior of a space vehicle [12,13]. Their models are all based on the Arrhenius equation $\frac{\partial m}{\partial t} = -\mathrm{A}m_0\left(\frac{m-m_\mathrm{f}}{m_0}\right)^\mathrm{n} e^{(-\mathrm{E}/\mathrm{RT})}$, where $m$, $t$, $T$, A, E, n and R are mass, time and temperature, pre-exponential factor, activation energy, order of reaction, gas constant, respectively. The subscripts 0 and f refer to the initial and final mass of the composite [14–16]. Measuring the kinetic parameters of thermal degradation by thermal analysis tests, the thermal response of charring materials can be obtained on the basis of the Arrhenius equation. It should be mentioned that the accuracy of this method has relied heavily on the assumption where the activation energy in the Arrhenius equation is regarded as a constant independent of temperature. Actually, the heating rate in tests is usually much smaller than the aerodynamic heating rate in the reentry environments, so the results obtained by the Arrhenius equation with the assumption may be inaccurate or uncertain. Because of this, Li et al. [17] developed a modification of the Arrhenius dependent model. They supposed the complex zone between virgin and char as a pyrolysis interface and simplified the rate of mass injection flux of pyrolysis gas by an energy balance equation. Unfortunately, the selection of pyrolysis interface temperature is a controversial topic in the calculation on thermal behaviors.

Notably, the outer surface recession increases turbulence resulting in severely local aerodynamic heating and must be very unfavorable to the thermal protection. The surface recession of charring material is caused by the reaction between carbon and oxygen [11]. To prevent surface recession, antioxidants are added during manufacture of material. It is essential to develop the calculation model for the thermal response of charring material with antioxidants.

On account of the three reasons above, we develop a new pyrolysis layer model, which is also a development of the pyrolysis interface model in Ref. [17], with temperature-dependent properties and moving interfaces. To make the calculation results more closer to the fact, it is essential to consider the rate of mass injection flux of pyrolysis gas between the char zone and the virgin zone. Based on the pyrolysis layer model, we again derive the governing differential equations and their implicit finite difference formulation, and program them in MATLAB. The heat conduction equations with temperature-dependent properties, by the way, are strongly nonlinear [18–21]. Then, the effectiveness and accuracy of this model are proved through examples. Furthermore, the thermal response of charring material with antioxidants under actual service conditions is also predicted.

## 2. Model

### 2.1. Physical model

As the ablator undergoes heating due to incident heat flux, the surface temperature increases to pyrolysis temperature $\mathrm{T_p}$. The surface material undergoes pyrolysis and absorbs heat. Moreover, the main heat starts to be absorbed through the endothermic pyrolysis of the matrix which is called the body-ablation process. In addition, the char produced as a result of reactive processes yields a thermally insulating and protective layer at the material surface. If antioxidants are added into the charring material during manufacture of material or the environmental gases are inert, there is no recession on the outer surface.

Owing to the fact that the temperature gradient vertically to the surface is much larger than those in the other orientations [22], the one-dimensional pyrolysis layer model without surface recession is extended for charring materials with antioxidants (Fig. 1). Along the $x$ direction, the ablator is divided into three layers, namely, the virgin layer, the pyrolysis layer and the char layer. Their physical–chemical phenomena are briefly introduced as follows:

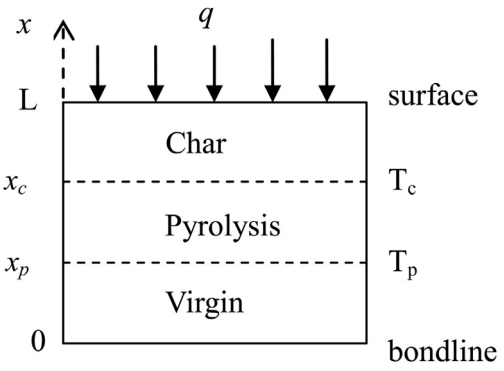


**Fig. 1.** One-dimensional pyrolysis layer model.

(a) The virgin layer ($0 < x < x_p$): the temperature of material is lower than the initial pyrolysis temperature $\mathrm{T_p}$, which is corresponding to $x_p$.
(b) The pyrolysis layer ($x_p < x < x_c$): it is an unsteady and complex reaction zone between the temperature $\mathrm{T_p}$ and the full pyrolysis temperature $\mathrm{T_c}$, which is corresponding to $x_c$, of ablator with two moving interfaces. Charring materials pyrolyze from the virgin state to a porous char layer and simultaneously release mixed gases which mainly consist of methane, ethylene, acetylene and hydrogen.
(c) The char layer ($x_c < x < \mathrm{L}$): it is a foamy solid carbon structure which is higher than the temperature $\mathrm{T_c}$. When the pyrolysis gases flow through this layer to the surface of the ablator, solid carbon and pyrolysis gases continue to absorb heat.

In Fig. 1, $q$ is the heat flux, $x_p$ and $x_c$ are coordinates of two moving interfaces which are functions of time, and L is the thickness of ablator.

### 2.2. Mathematical model for pyrolysis

The following simplifying assumptions are made:

(a) Local thermal equilibrium is maintained between the gas and the porous char;
(b) The gas undergoes no further chemical reaction within the residual material after having been formed;
(c) No gas accumulation and expansion of solid is allowed.

Based on the above assumptions and the physical model (Fig. 1), the transient heat conduction equations in the three layers are respectively written in the forms

$$\rho_1 c_1 \frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[k_1 \frac{\partial T(x,t)}{\partial x}\right] \quad 0 \le x < x_p \tag{1}$$

$$\rho_2 c_2 \frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[k_2 \frac{\partial T(x,t)}{\partial x}\right] + \dot{m}_{g2} c_g \frac{\partial T(x,t)}{\partial x} + \frac{\partial \rho_2}{\partial t}\cdot \mathrm{h} \quad x_p \le x < x_c \tag{2}$$

$$\rho_3 c_3 \frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[k_3 \frac{\partial T(x,t)}{\partial x}\right] + \dot{m}_{g3} c_g \frac{\partial T(x,t)}{\partial x} \quad x_c \le x \le \mathrm{L} \tag{3}$$

where $\rho$, $c$ and $k$ are respectively the density, the specific heat and the thermal conductivity. $\dot{m}$ is the rate of mass injection flux, which