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PRESSURE DISTRIBUTION IN THE CHAR LAYER OF A POLIMERIC COMPOSITE ABLATOR

Pamela Bartolomeu Torsani, pamelabtorsani@usp.br

Escola de Engenharia de Lorena – EEL, Universidade de São Paulo – USP, Estrada Municipal do Campinho s/n, Lorena, SP, 12602-810, Brazil.

Humberto Araujo Machado, humbertoham@fab.mil.br

Instituto de Aeronáutica e Espaço - IAE, Pç Mal. Eduardo Gomes 50, São José dos Campos, SP, 12228-904, Brazil
Faculdade de Tecnologia – FAT/UERJ, Rod. Pres. Dutra km 298, Resende, RJ, 27537-000, Brazil

Abstract. *Polymeric composites are extensively used in thermal protection systems for space vehicles. In this kind of material, the aerodynamic warming causes a pyrolysis reaction that absorbs heat and results in a char layer, which acts as a thermal insulator against heat conduction and oxygen penetration into the reaction zone. In order to assure the structural integrity of such layer, the pressure distribution of the gas flow from the chemical decomposition of the polymeric material must be estimated. In this work, a reliable model for such estimation is presented and compared with the structural strength of the char layer, which allows determining if the pressure drop is capable to break up that layer.*

Keywords: *TPS, ablation, polymeric composite, pyrolysis, char layer*

1. INTRODUCTION

Space and sub-orbital vehicles reach hypersonic velocities in atmospheric flight, which leads to a warming over their external surfaces. The resulting high temperatures and heat fluxes demand a thermal protection system (TPS) in order to assure the integrity of vehicle structure and payload.

The most common type of thermal protection in use is the ablative shield. Ablation is a thermo-physical process that absorbs and eliminates heat through material loss. The ablation can be a simple phase change process, like evaporation or sublimation, or involve a complex endothermic chemical reaction. The last is the case for polymeric composites.

Composite materials are vastly employed in launching vehicles due its stiffness, mechanical strength, low weight and heat resistance. The high temperature exposition of the polymeric composite structure results in a pyrolysis reaction, an endothermic processes that absorbs the heat. This phenomenon is given the name of composite ablation (Duffa, 2013).

The most important property of composites used as TPS are high capacity of heat absorption per mass unit that is well provided by carbon fiber/phenolic resin composites. The matrix structure of this composite produces content when subject to pyrolysis and the resulting char (porous carbon residue) yields a protective layer over the structure (Silva, 2015).

Char layer plays an important role in thermal protection. This layer acts as a thermal insulator, since its thermal conductivity is lower than that of the virgin material. Most important, the char layer avoids the contact of atmospheric oxygen with the pyrolysis zone, which would turn the endothermic reaction of decomposition into an exothermic reaction of oxidation, adding a heat input to the external heat load. Because of this protective effect, this is very important to assure the integrity of the char layer during the composite ablation.

The main causes of mechanical char break up are the shearing stress due the aerodynamic friction and dynamic pressure, the thermal stresses due high temperature gradients between external surface and pyrolysis zone where char is formed and the internal pressure gradient due the gases yielded by resin decomposition. The first two effects were previously studied in the work of Santos and Machado (2018). In that work it was verified that the char strength was higher than both, internal and external loads.

The estimation of pressure distribution within the char layer is quite complex, since it involves the full modeling and simulation of resin pyrolysis. In this work, a simple but reliable model for estimating the gas pressure in every point of the char layer was proposed, in order to evaluate pressure distribution in a char layer resulting from carbon-phenolic ablation. Results allow comparing pressure gradients with the char strength and verify the possibility of char break up due the internal gas flow.

2. PHYSICAL PROBLEM AND MATHEMATICAL MODEL

The ablation in a polymeric composite is a complex phenomenon, with many simultaneously physical and chemical processes, as shown in Fig. 1. The diverse gases are produced within the pyrolysis zone and flow to the external surface through the char porous. During the flowing these gases continue reacting, transforming in different products of resin decomposition, according with the temperature distribution in the char layer. The estimation of pressure gradient must account such transformations and consequently the temperature distribution.

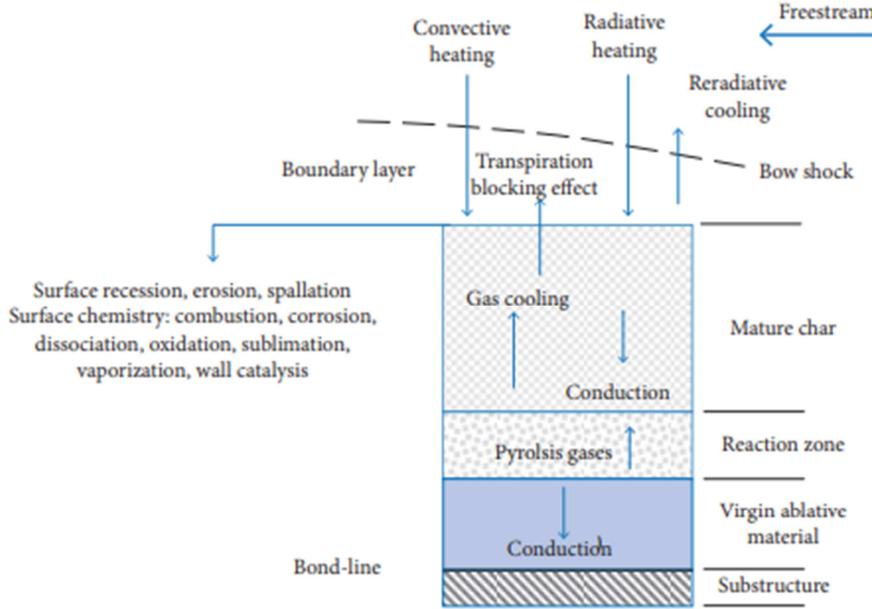


Figure 1. Physical and chemical processes during polymeric composite ablation

In this work, the temperature profile in the char layer thickness is obtained from the previous simulation performed by Pesci et al (2018), where a simple model for ablation was employed. In that model, pyrolysis zone was approached as a front where the decomposition occurs. All the mathematical treatment is detailed in the work of Machado (2014).

With the known temperature distribution, the gas chemical composition is evaluated at each temperature, in order to estimate the gas mixing properties. The decomposition of the phenolic resin generates diverse gas species, one of the major molecules is the phenol (C_6H_5OH). These gases also decompose and react with each other in a chain reaction. The full mechanism of phenolic resin decomposition includes 48 species and 135 reversible reactions. The reaction rate is represented by a simplified form of Arrhenius equation:

$$k_{f,i} = A_i T^{\beta_i} \exp\left(-\frac{E_{a,i}}{RT}\right) \quad (1)$$

where A_i is the pre-exponential factor of Arrhenius, β_i is constant and $E_{a,i}$ is the activation energy of a species i . These three constants have to be provided for every reaction to represent the proposed kinetic mechanics. These constants were extracted from *NIST Chemical Kinetics Web Version* data bank. The constant R is calculated with the gas molecular weight.

The sequence of chemical reactions and specie decomposition of phenolic resin was supposed to begin with phenol and then follow a sequence where all new species are added to the group, until all paths of reaction were included. A reduced but representative form was reached, and presented in Tab. 1.

A numerical code was built in **Matlab R2018b**® to evaluate $k_{f,i}$ with temperature, where the Arrhenius Law, Eq. (1) was used for many temperature steps from an initial value of 800 K, when the decomposition is supposed to begin, until 1800 K., when it is assumed to be completed. The gas composition according with the temperature for carbon-phenolic resin decomposition is showed in Fig. 2, where it is compared with some literature data (Scoggins, 2011), presenting excellent agreement.

Once the gas flow composition is established as a function of temperature, its properties and the local pressure is estimated. The local value of R (the gas constant) for the gas mixing is calculated. Figure 3 shows the dependence of R concerned to gas temperature. The local gas density is then obtained through the ideal gas equation:

$$\rho = P/RT \quad (2)$$

Table 1. Simplified model for the sequence of reactions adopted for phenolic resin decomposition.

#	Reaction	A_i	E_i
1.	$H + C_6H_5O \leftrightarrow C_6H_5OH$	$2,50 \times 10^8$	
2.	$C_6H_5OH \leftrightarrow C_5H_6 + CO$	$1,50 \times 10^{11}$	254,00
3.	$C_6H_5OH + H \leftrightarrow C_6H_5O + H_2$	$1,15 \times 10^8$	51,90
4.	$C_6H_5OH + H \leftrightarrow C_6H_6 + OH$	$2,21 \times 10^7$	33,10
5.	$C_6H_5OH + OH \leftrightarrow C_6H_5O + H_2O$	$6,00 \times 10^6$	
6.	$C_6H_5O \leftrightarrow CO + C_5H_5$	$2,50 \times 10^{11}$	183,90
7.	$C_6H_5OH + C_5H_5 \leftrightarrow C_5H_6 + C_6H_5O$	$2,67 \times 10^8$	105,60

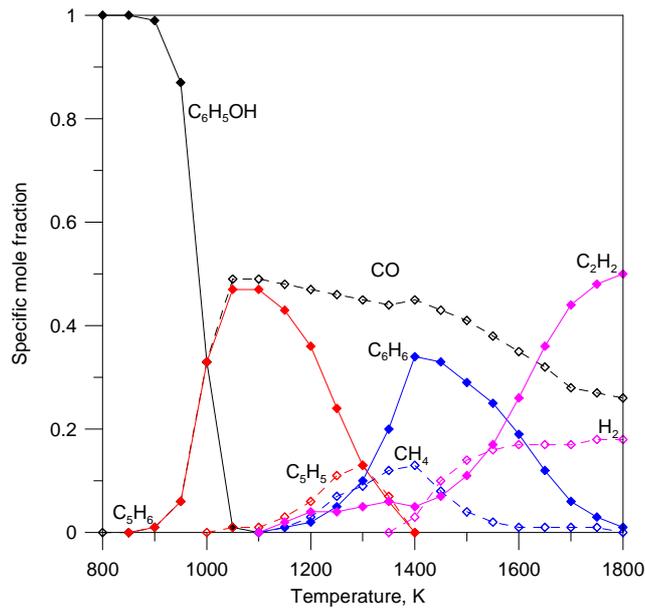


Figure 2. Resulting specie fractions in the resin pyrolysis, according with temperature. The symbols in the curves correspond to the results extracted from Scoggins (2011).

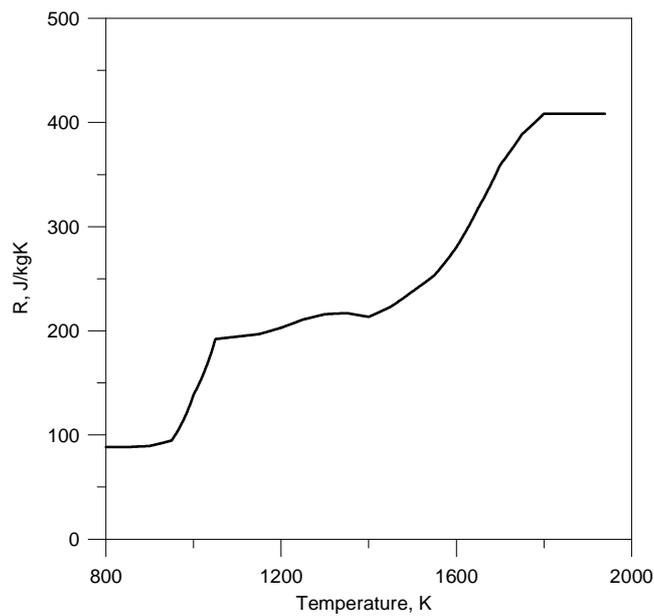


Figure 3. Gas constant R as function of temperature.

For a specific instant during ablation, the pressure distribution can be estimated through a modified form of the Equation of Ergun (Martin and Boyd, 2010) for a fluidized bed:

$$\frac{dP}{dx} = 150 \frac{\dot{m}}{D_p^2} \mu \frac{(1-\varepsilon)^2}{\varepsilon^3} + 1.75 \frac{\dot{m}^2 (1-\varepsilon)}{D_p \varepsilon^3} RT \quad (3)$$

where x is the coordinate normal to the char surface, \dot{m} is the gas flow rate (in mass per second per surface unit), μ is the gas viscosity, D_p is the average porous diameter and ε is the void fraction or porosity of char. The integrations of Eq.(3) allow obtaining the pressure distribution in the char layer:

$$\int_{P_1}^{P_2} P dP = \int_0^x \left[150 \frac{\dot{m}}{D_p^2} \mu \frac{(1-\varepsilon)^2}{\varepsilon^3} + 1.75 \frac{\dot{m}^2 (1-\varepsilon)}{D_p \varepsilon^3} \right] RT dx \quad (4)$$

The local gas viscosity is estimated though the formula proposed by Lee et al. (1966) for natural gases over a temperature range of 560-800 °R, up to 8000 psia, extrapolated to 1000 K-2000 K interval:

$$\mu = 10^{-4} a \exp [b (\rho_g/62.43)^c] \quad (5)$$

where

$$\begin{aligned} a &= (9.379 + 0.0160M) T^{1.5} / (209.2 + 19.26M + T) \\ b &= 3.448 + 0.01009M + (986.4/T) \\ c &= 2.4 - 0.2b \end{aligned}$$

μ_g is the gas viscosity (cp) at the absolute temperature of T (°R), M is the gas molecular weight, and ρ_g is the gas density at prevailing pressure and temperature, in lbm/ft³. Figure 4 shows viscosity variation according with temperature, accounting the gas composition. Since the variation is discreet and the equation has been already extrapolated, an average value of 0.5 kg/m.s was assumed.

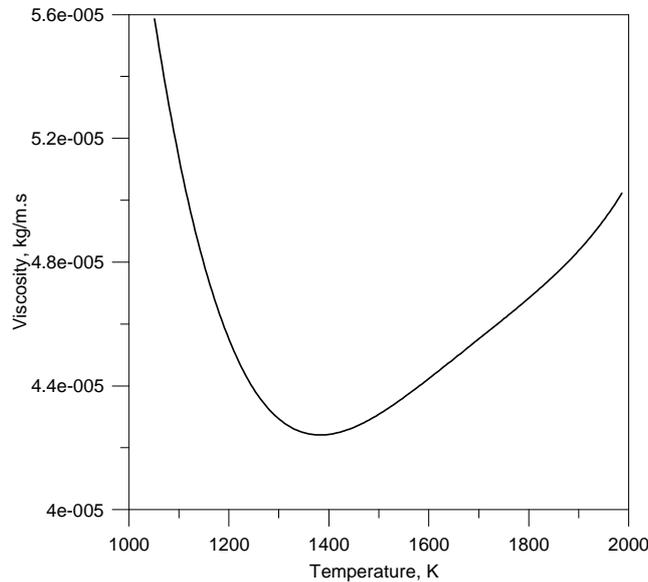


Figure 5. Gas viscosity as a function of temperature, according with Eq. (5) and accounting gas composition.

3. RESULTS

The proposed model was applied in one of the results presented by Bittencourt et al (2018) for Carbon-Phenolic resin ablation in a plasma torch. The process was one dimensional, since it was performed in a cylindrical sample with the lateral side thermal insulated. In the case studied, a layer of char was considered after 55 seconds of exposure to a plasma torch, when the whole layer of virgin material has been consumed and the char layer have reached the assumed char melting temperature of 1939 K and a thickness of 7.5 mm. The pyrolysis zone was stabilized in 973 K.

Temperature distribution in the coordinate x , extracted from the numerical simulation results, is presented in Fig. 5. At that point, the mass rate \dot{m} obtained by numerical simulation was 0.018 kg/m²s.

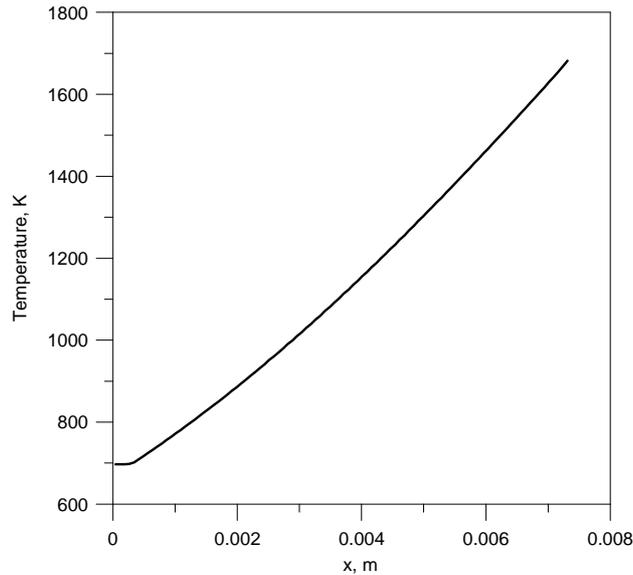


Figure 5. Temperature distribution in coordinate x .

The micrographic analysis performed in the work of Pesci et al. (2108) allowed supposing that the diameter has an order near or smaller than the fiber diameter. Because of this uncertainty, a sensibility analysis for the porous diameter is done, in order to verify its influence in the pressure distribution within the char layer. The void fraction is obtained from the relationship:

$$\varepsilon = 1 - \rho_{char}/\rho_C \quad (6)$$

where ρ_{char} is the char density and ρ_C is the amorphous carbon density, which are 1135 kg/m^3 (Pesci, 2018) and 2100 kg/m^3 (Manocha, 2003), respectively. These values result in a void fraction of 0.540.

Once all parameters of Eq. (4) are known, the pressure distribution can be obtained. The results for diverse porous diameters are presented in Fig. 6, which shows the total pressure variation in char layer, from the pyrolysis front, where the gas is generated, to the char surface, with the coordinate x . This graphics was generated considering an environment pressure of 95 kPa (Pesci, 2018). Pressure distribution is qualitative and quantitative coherent with the results presented by Martin and Boyd (2010). According with Silva (2010), the char strength is about 4 MPa at 1181°C . From a straight comparison, it seems that porous diameter should be greater than $1 \mu\text{m}$ (10^{-6} m). However, the structural analysis is not linear, and should be performed considering the whole pressure distribution, not only the maximum value.

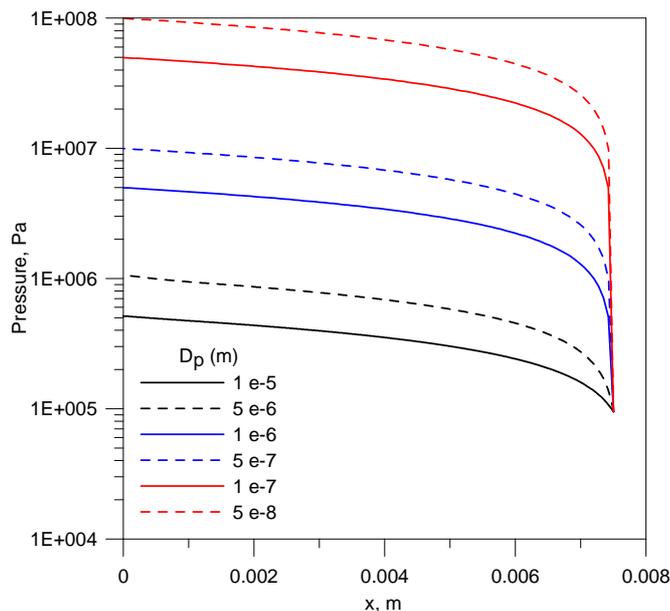


Figure 6. Pressure distribution in coordinate x for diverse values of porous diameter.

It should be mentioned that the environment pressure should decrease during the flight. According with the equations, the pressure gradient is quite sensitive to temperature and less sensitive to absolute pressure. However, in future works, this aspect should be included in a more detailed analysis.

4. CONCLUSION

In this work, a simple but reliable method to estimate the pressure distribution of the resulting pyrolysis gas in a char layer of a composite ablator was presented. According with the results, the maximum pressure occurs in the pyrolysis zone, and the values are compatible with the gas pressure drop until the char surface.

Comparing directly the maximum pressures with the char strength, a minimum porous diameter was found. Since the porous diameter appears to be of the same order of the fiber used in the composite and the fiber roles much of the char strength, this is mandatory to consider this parameter during the ablator selection. However, in order to assure that the char layer will effectively resist to ablation process, the total combined stresses should be accounted, including the thermal stress and the shear and normal surface stresses, which are to be included in future works.

5. ACKNOWLEDGEMENTS

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