Modeling of the pyrolysis of a composite material made of randomly distributed short fibers.

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Abstract - A 2D axisymmetrical model is developed to analyze the 3D behavior of materials during pyrolysis. To develop the model, changes of scale are done on the fibrous structure (Darcy's law, pyrolysis effective kinetic). The results are compared to experiments and the coupling between physico-chemical phenomena is analyzed.

Nomenclature

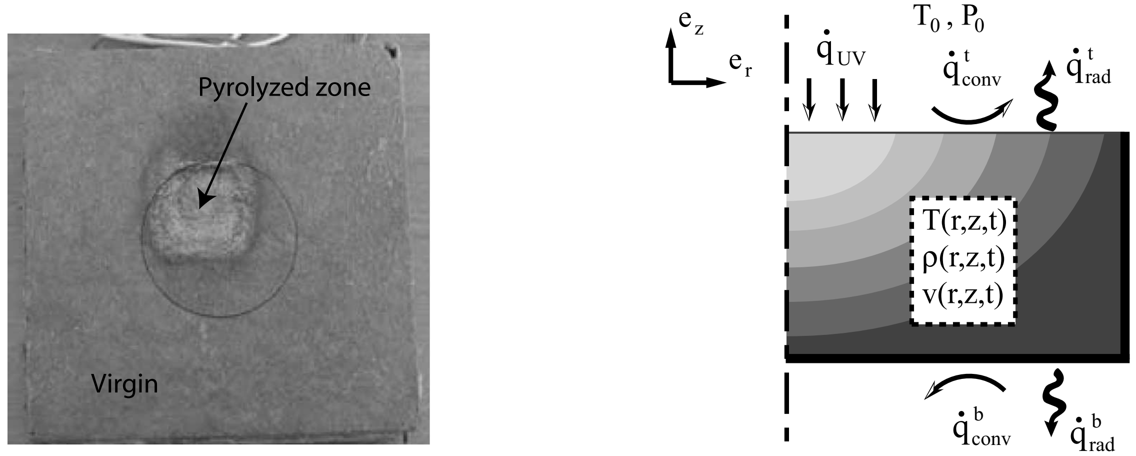
A	pre-exponential factor, $kg \cdot m^{-3} \cdot s^{-1}$	*Greek letters*	
c	specific heat, $J \cdot K^{-1} \cdot kg^{-1}$	δ	variations
Ea	activation energy, J	ϵ_i	volume fraction of i
h	specific enthalpy, $J \cdot kg^{-1}$	ρ	density, $kg \cdot m^{-3}$
$\mathbf{k}$	conductivity tensor, $W \cdot m^{-1} \cdot K^{-1}$	*Subscripts*	
$\mathbf{K}$	permeability tensor, m^2	c	pyrolyzed resin
P	pressure, Pa	g	gas phase
$\dot{q}$	flux per surface unit, $W \cdot m^{-2}$	p	pyrolyzable phase (resin)
r, z	cylindrical coordinates, m	s	solid phase (fiber and resin)
R_g	perfect gas constant, $J \cdot mol^{-1} \cdot K^{-1}$	v	virgin material
T	temperature, K	$conv$	convection
t	time, s	rad	radiation
$\mathbf{v}$	velocity, $m \cdot s^{-1}$	UV	ultraviolet

1. Introduction

During atmospheric entry of space vehicles, the wall temperature of thermal protection systems may reach several thousand degrees leading to ablation by gasification on the surface [1] (possibly preceded by fusion for silica-based materials), and to heat flux inside the structure. Ablative materials made of randomly distributed short silica fibers partially impregnated by a polymer resin are leading candidates for thermal protection (AQ60 : Huygens, Aleastrasil : ARD). For these materials, a pyrolysis front coupled to the heat flux penetrates the structure. Depending on the material permeability, pyrolysis gases can either freely escape to the surface or lead to a significant local overpressure that can affect the local thermodynamical equilibrium of pyrolysis, or increase the effective thermal transfer. This study aims to improve the understanding of the intrinsic behavior of materials being pyrolyzed, and to analyze the coupling between physico-chemical phenomena.

2. Studied problem

In order to reproduce radiative heat flux entry conditions into Titan's atmosphere, Laub, White, and Bouilly [2] submitted an ablative material sample to a radiative heat flux (UV lamp) under a nitrogen flow (see figure 1). Modeling the experiment using 1D models, only a homogeneous heating can be modeled [2], while a 2D axisymmetric model enable modeling the radiative heating as a gaussian beam.



a) Top view of the sample after a test (1,5 MW/m² at the peak intensity point)

b) 2D axisymmetric cell (cross-section)

Figure 1 : *Picture and scheme of the studied problem*

AQ60, which is a porous composite material (porosity : 84%), is used as model material for this study. It consists of short silica fibers (diameter : $9\,\mu m$, length : $0.5\,mm$) randomly distributed, but parallel to the surface [3] (see figure 2-a). The fibers are covered by a $1.2\mu m$ phenolic resin coat. The volume fraction of silica and resin are respectively 10% and 6% [3].

3. Macroscopic pyrolysis model

The local Péclet number being low in the studied case (high porosity, low gas velocity), local thermodynamical equilibrium between the different phases (fibers, matrix, gaz) can be assumed [4]. Inside this porous material, heat transfer is conductive (material and gas), radiative (material), and convective (pyrolysis gaz of velocity $\mathbf{v_g}$). The radiative transfer can be locally linearized using Rosseland hypothesis (optically dense material) [5]. Conduction and radiation can be locally modeled by an equivalent effective conductivity $\mathbf{k}$. Pyrolysis being endothermic, the heat balance has to account for a sink term. Under these hypotheses, the heat balance equation writes :

$$(\epsilon_g \rho_g c_g + \epsilon_s \rho_s c_s)\frac{\partial T}{\partial t} = \nabla \cdot (\mathbf{k} \cdot \nabla T) - \epsilon_g \rho_g c_g \mathbf{v_g} \cdot \nabla T + \delta h_p \frac{\partial \epsilon_p \rho_p}{\partial t} \tag{1}$$

In the solid phase reference frame (fibers/matrix, assumed immovable), the mass balance equation writes :

$$\frac{\partial \epsilon_g\, \rho_g}{\partial t} + \nabla \cdot (\epsilon_g\, \rho_g\, \mathbf{v_g}) = -\frac{\partial \epsilon_p \rho_p}{\partial t} \tag{2}$$

with $\rho_g = PM_g/RT$, according to perfect gas law (chemical equilibrium is assumed inside the material).

The momentum balance equation can be homogenized into Darcy's Law [4] :

$$\epsilon_g\, \mathbf{v_g} = -\frac{\mathbf{K_g}}{\mu_g} \cdot \nabla p_g \tag{3}$$

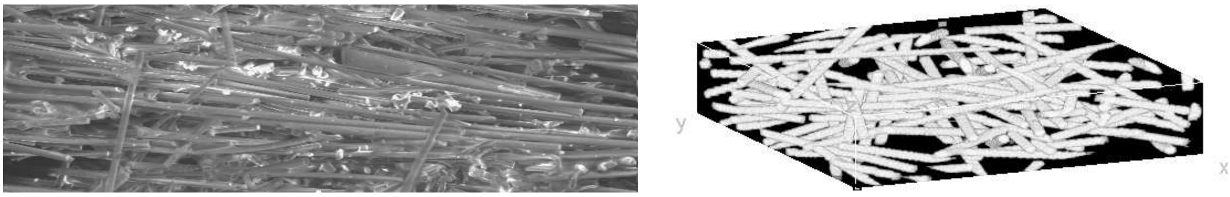
Pyrolysis is modeled using an Arrhenius law [6] :

$$\frac{\partial \rho_p}{\partial t} = -(\rho_p - \rho_c)\, AT \exp\left(-\frac{Ea}{RT}\right) \tag{4}$$

Boundary conditions in temperature are obtained by solving the heat balance at the wall (gaussian UV beam, nitrogen convection, conduction to the sample, radiation of the sample). The pressure is equal to atmospheric pressure on the top face. The sample has been covered by an impermeable coating on the sides and on the bottom (null pressure gradient).

4. Multiscale analysis

The macroscopic equations have to be guided by experimental observations. To date, three data are particularly difficult to assess with accuracy : the pyrolysis law, the effective permeability, and the effective conductivity.



a) Micrograph (Scanning electron microscopy)

b) Reproduction by fiber draws (Monte-Carlo method) and resine coating (fiber dilatation)

Figure 2 : *AQ60 fibrous architecture*

4.1. Using TGA analysis to model pyrolysis

The way to determine the pyrolysis law is the object of many discussions. The pyrolysis law is currently obtained by thermogravimetric analysis (TGA) using pure resin samples, the characteristic size of which ranges from millimeters to centimeters. In the case of the UV test, the local heating rate reaches $1000\, K/min$. Experiments on samples of pure resin show that the pyrolysis kinetic may decrease as the heating rate increases for heating rates above $10\, K/min$ [6]. The explanation to this limitation is argued to be : heat transfer limitation inside the sample (creating temperature gradients), mass transport limitation (creating a local overpressure leading to a modification of the thermochemical equilibrium). This problem has been modeled in 1D (equations (1), (2) et (3)) considering as boundary conditions : null gradients at the bottom of the line, and an imposed heating rate at the top. The solution (obtained by finite element modeling ; www.pdesolutions.com) for a pure resin sample of $1\, cm$ shows that the thermal time response is non-negligible for heating rates higher than $10\, K/min$. For millimetric samples, thermal time response is important for heating rates higher than $100\, K/min$, the local pressure also increases significantly. The fact that the pyrolysis is endothermic plays a great role. With the pyrolysis front moving at a velocity v_{pyr}, a thermal gradient takes place in any sample whose thickness e is not small enough to ensure that the dimensionless number $P = v_{pyr}\, e\, \delta h_p\, \rho_p / k$ is small. In the case of AQ60, at microscopic scale, the resin thickness is of the order of microns. In this case the thermal response is instantaneous, even for heating rates as high as $1000\, K/min$. To conclude, from a physics point of view, this study recommend the use of TGA experimental laws obtained at very low heating rates (equilibrium) for modeling of th AQ60 materials for which the fiber coating is micrometric, even for local heating rates of $1000\,K/min$.

4.2. Modeling the flow inside porous media

Measurement of the effective permeability is difficult and expensive, because the permeability in a function of the degree of pyrolysis of the material. It would then be useful to prepare many samples, pyrolyzed at temperatures spanning between $20^{\circ}C$ and $1200^{\circ}C$ (end of pyrolysis reactions). Moreover, the pyrolyzed material displays low mechanical properties that make permeability experiments difficult. The alternative is to compute the permeability, knowing the microscopic structure of the material. The semi-empirical equation of Kozeny-Carman enable evaluation of the permeability for fibrous media. However, only an order of magnitude is accessible because the accurate assessment of the Kozeny constant, which depends on the actual structure of the media, is not possible [7]. Today, computational tools enable to solve straightforwardly Navier-Stokes equations in 3D in an elementary representative volume of one thousands of fibers. The first step is the 3D numerical reproduction of a model material at microscopic scale using as a reference scanning electron microscopy (SEM) micrographs (cf. figure 2). Computations in 3D are under process. In the mean time, the same approach has been applied in 2D and solved by finite elements (see figure 3). Taking into account a volume reduction of 50% of the resin after pyrolysis, the effective permeability was computed to lie in the range from $1.6 \cdot 10^{-11}\,m^2$ (virgin material) to $2 \cdot 10^{-11}\,m^2$ (pyrolyzed material). Therefore, the Kozeny constant is found to lie around 10, which is a value in accordance with literature data [7].

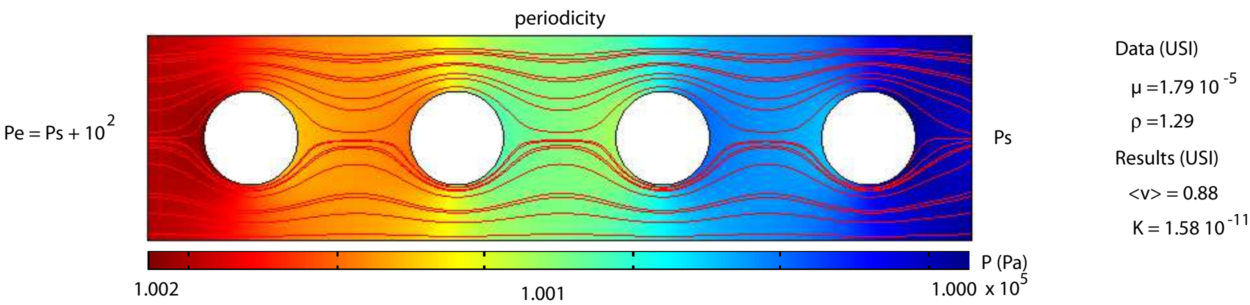


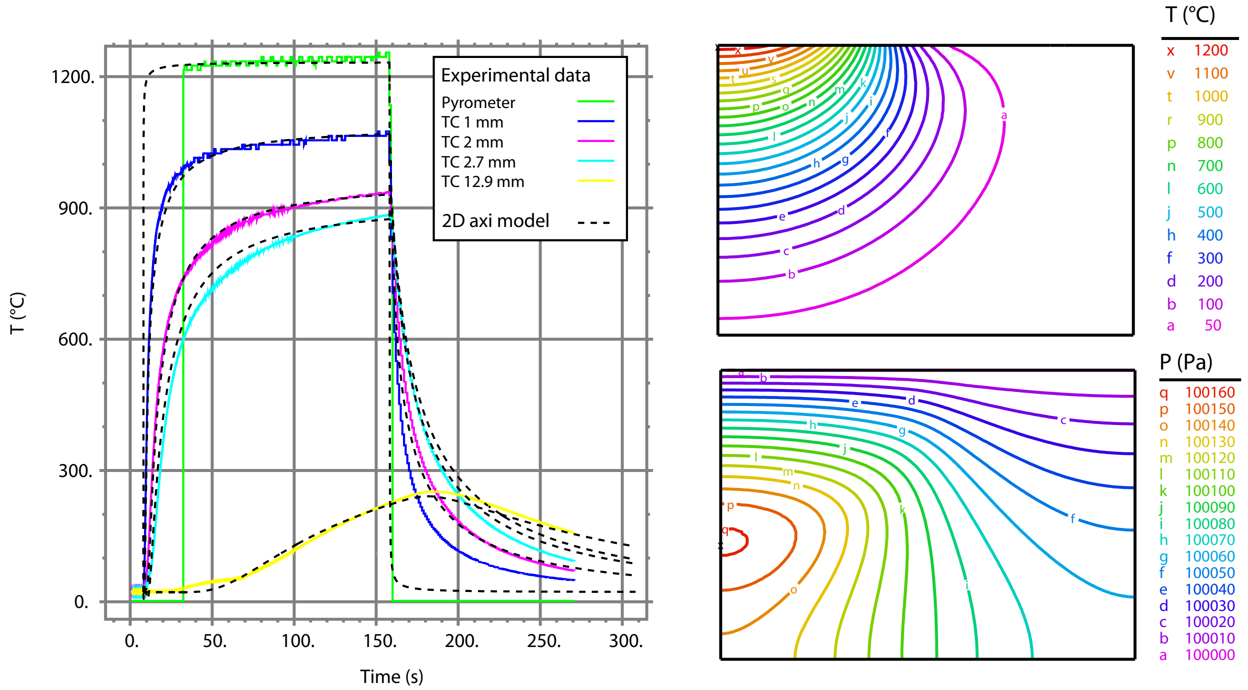
Figure 3 : *Computation of the effective reactivity of AQ60 by finite elements*

4.3. Modeling the effective conductivity

The determination of the effective conductivity by a change of scale approach is difficult when radiative transfer cannot be neglected (*i.e.* for temperatures higher than $500^{\circ}C$). In the case of pure conduction, the change of scale has already been addressed and shows correct accuracy [8]. The problem of coupling with radiation is not resolved in the general case. One solution is to linearize the radiative transfer under Rosseland hypothesis [5]. The accuracy of this method decreases with porosity and thermal gradients inside the material. However, it enables the assumption that a local effective reactivity exists. At this point, to determine the effective reactivity, an experimental measurement at macroscopic scale is the only reliable method. Consequently, in this work, the effective conductivity has been determined by an inverse method. The dynamical response of a thermocouple placed deeply in the material (TC $12.9\,mm$ of figure 4-a) is used. The response is representative of the development of the thermal flux in the material, which is in itself an image of the thermal conductivity as a function of temperature. We propose this approach as a method to determine the conductivity as a function of temperature , knowing the specific heat (determined by calorimetry). To our knowledge, the implementation of the method in 2D dynamic at high temperature is original. It enables, using a simple and economic test, to obtain a data that is today determined at the cost of difficult and expensive experiments.

5. Comparison between model and experiments

Four thermocouples have been positioned in the sample shown in figure 1-a. Their axial position, verified by X-ray, is reported figure 4-a. The macroscopic model, described in section 3, has been solved by finite elements (FlexPDE ; www.pdesolutions.com) in the 2D axisymmetric domain shown in figure 1-b. Figure 4-a shows that good agrement with experiment is obtained. As represented on the contour map of temperature (figure 4-b), 3D effects play the role of a sink term on the axis : part of the flux being diverted to heat the sample transversally. The increase of pressure inside the material is negligible for experiments carried out at atmospheric pressure (figure 4-b), because the permeability is high and the mass fraction of resin is quite low. However, pressure effects can be important in actual entry conditions, because the static pressure may be low for atmospheric entry. In particular, the evolution of pressure has a strong effect on the mass transport of oxidizing gas at the surface (ablation). For AQ60, the endothermic effect of the pyrolysis on the thermal response is negligible due to the low resin proportion.



a) Thermocouple response : comparaison experience/model

b) Temperature and pressure contours

Figure 4 : *Simulation results and comparison to an experiment*

6. Conclusion

A macroscopic pyrolysis model has been solved in cylindrical coordinates to model an experiment simulating radiation for an entry into Titan's atmosphere (UV radiation, nitrogen). The macroscopic model has been partly developed with data from an analysis of the microscopic architecture of the material. It has been shown that the local pyrolysis of a micrometric coating of resin at a heating rate of $1000\,K/min$ was thermodynamically equivalent to the pyrolysis of a sample of order cm^3 of pure resin at $10\,K/min$ in a thermogravimetric analysis test. The effective permeability has been determined by numerical simulation using 2D modeling of the fibrous architecture (Darcy's law). An analogue 3D approach is in process. At macroscopic scale, an inverse method for determining thermal conductivity at high temperature has been developed. It enables us to obtain the thermal conductivity as a function of temperature using the dynamic response of a thermocouple placed in the middle of a sample, while the sample is submitted to a heat flux on one of its faces. The results of the macroscopic model, obtained using these data, are in agreement with the experiments.

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Références

[1] J. Lachaud, Y. Aspa, G. L. Vignoles, and J.-M. Goyhénèche. Modélisation 3D de l'ablation thermochimique des composites C/C. In *Congrès Français de Thermique*, volume 1, pages 125–130, Île de Ré, France, 16-19 May 2006. SFT.

[2] B. Laub, S.M. White, and J.-M. Bouilly. Uv radiation testing of the Huygens probe thermal protection material. In *4th International Symposium on Atmospheric Reentry Vehicles and Systems*, Arcachon, France, March 2005.

[3] C. Loupias, J.M. Sibeaud, and P.L. Hereil. Hypervelocity impacts of orbital debris on an advanced heat shielding material : comparison of ouranos computations to experimental results. *Int. J. Impact Engng*, 20 :545–556, 1997.

[4] N. Puiroux, M. Prat, M. Quintard, and F. Laturelle. Macro-scale non-equilibrium heat transfer in ablative composite layers. In *Proceedings of 8th Joint Thermophysics and Heat Transfer Conference*, number 3336, page 11, St. Louis, Missouri, 24-26 June 2002.

[5] S. Bories and M. Prat. Transferts de chaleur dans les milieux poreux. *Techniques de l'ingénieur*, B(8250) :1–33, 1996.

[6] K. A. Trick, T. E. Saliba, and S. S. Sandhu. A kinetic model of the pyrolysis of phenolic resin in a carbon/phenolic composite. *Carbon*, 35(3) :1509–1515, 1996.

[7] X. Chen and T. D. Papathanasiou. On the variability of the kozeny constant for saturated flow across unidirectional disordered fiber arrays. *Composites : Part A*, 37 :836–846, 2006.

[8] C. Lorrette. *Outils de caractérisation thermophysique et modèles numériques pour les composites thermostructuraux à haute température*. PhD thesis n°3364, Université Bordeaux I, 2007.