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Application of sensitivity analyses to condensed-phase pyrolysis modeling

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ABSTRACT

In this study, sensitivity analyses are performed on a given pyrolysis model. An approach is presented, which involves complex-step differentiation, to compute the normalized first-order local sensitivity coefficients of relevant model outputs with respect to the inputs, i.e. the material properties. This approach is systematic and robust and provides sensitivity coefficients that are dynamic; that is, sensitivity values are given as a function of time for the entire pyrolysis process. In order to demonstrate the proposed methodology, the anaerobic thermal degradation of generic homogeneous materials (a semi-transparent non-charring material, simulating a thermoplastic, and an opaque charring material) exposed to heat flux levels leading to thermally thin and thermally thick material responses is considered. The dynamic sensitivities of mass loss rate and surface temperature are calculated and discussed. The information inferred from the sensitivity analyses presented herein can provide insights into the behavior of a given pyrolysis model and help reduce its complexity for specific applications.

1. Introduction

Recently, considerable advances have been made in the numerical modeling of condensed-phase pyrolysis phenomena [1,2] and pyrolysis models have become an integral part of large-scale fire simulation tools (e.g. [3–5]). These models are considerably complex and can potentially require a large number of input parameters in the form of "material properties" (e.g. [6]). Approaches have been developed in which these parameters, rather than being directly measured, are determined using inverse modeling coupled with evolutionary optimization algorithms [7,8]. Given the complexity of the pyrolysis models as well as the fact that many of their input parameters cannot be known with high accuracy, a question arises as to which of these parameters control the predictions of a given model. In the general context of condensed-phase pyrolysis modeling there exist relatively few studies that explicitly address this question [9–12]. Ramroth et al. [9] performed local as well as global sensitivity analyses of predicted surface temperatures for a fiber-reinforced polymer material exposed to a time-varying thermal load, using a finite-element pyrolysis model. Stoliarov et al. [10] surveyed the literature to determine the variability of physical and chemical properties of synthetic polymers. A pyrolysis model [1] was then used and each property was independently varied between the determined upper and lower bounds and sensitivities were calculated based on the modeled mass loss rate curves. Linteris [11] used two different pyrolysis models [1,5] to study the effect of independently varying thickness, thermal conductivity, heat capacity, radiation absorption, and heat of pyrolysis on the mass loss rate characteristics of poly(methyl methacrylate) (PMMA). Bal [12] performed a detailed study to determine not only parameter sensitivity but also the level of model complexity needed to predict with a given level of accuracy observables of interest; in the case of [12] this observable was the ignition time of PMMA. It is noted that all of these works considered specific applications and, therefore, there is a lack of demonstrated generality of the methodologies used thus far to determine sensitivity in condensed-phase pyrolysis modeling.

In this study, local one-at-a-time sensitivity analyses (wherein each parameter is varied independently) are considered in order to address the challenges identified above. Despite being local methods, simply providing the gradient of the model solution around a nominal set of parameters, such analyses are a powerful and systematic way to quantitatively examine the relationship between an observable of interest, predicted by the model, and the various parameters that define the model. Much of the conceptual background related to sensitivity analyses and their application to dynamic systems can be found in the chemical-kinetic literature (e.g. [13,14]); however, it is noted that sensitivity analyses are used widely in other engineering and scientific fields (e.g. [15]). Rather than reviewing this well-established background (the reader is also referred to [16,17]), focus is placed here on the implementation of sensitivity analyses to pyrolysis modeling as well as on the

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interpretation of results derived from these analyses. This information can provide useful qualitative understanding of the behavior of a given pyrolysis model; in addition, it can help reduce its complexity for specific applications and, by extension, focus the scope of the optimization approaches mentioned above as well as experimental efforts aimed at determining only those properties that have a strong effect on model predictions.

Below, the thermal degradation, in an inert environment, of a non-charring semi-transparent material (simulating a thermoplastic) and a charring material (such as wood) is modeled for two applied heat flux levels typical of bench-scale flammability tests [18,19]. The conditions considered ensure thermally thin and thermally thick material responses. First-order sensitivity coefficients of mass loss rate and surface temperature are calculated with respect to the material properties used as model inputs. These outputs are selected as they represent material responses which are critical to the determination of heat release and radiation exchange between surfaces in a large-scale fire scenario. As opposed to other efforts available in the literature (e.g. [10]) the sensitivity coefficients computed are provided as a function of time. However, it is shown that these coefficients contain all the necessary information to infer the sensitivity of global model responses, such as ignition time and average mass loss rate, to the input parameters.

2. Formulation

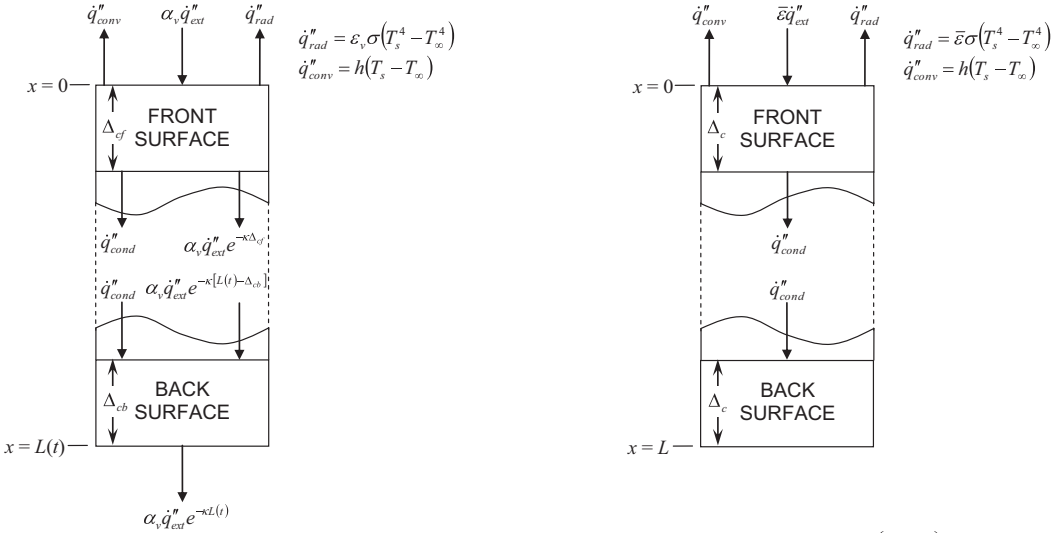
2.1. Pyrolysis model

A pyrolysis model is used here which solves for the heat transfer evolution within a one-dimensional solid, given some boundary and initial conditions, subject to enthalpy and mass gradients due to in-depth reaction. The model is a simplification of that of Ref. [2] and has been described elsewhere [8]; only a brief discussion will be provided highlighting the simplifications made to the model along with assumed boundary conditions. It is noted that such simplifications and assumptions will impact the performance and results of the model within the context of a given application, as described by Bal [12]. However, it is beyond the scope of the present study to determine what those impacts are; furthermore, the model described herein was found appropriate for the simulation of pyrolysis data for some charring as well as non-charring materials [8].

A control volume approach is employed and the governing mass and energy conservation equations are solved numerically using a fully implicit scheme. In the present study only three species are treated: virgin solid, char (where applicable), and pyrolysate. It is assumed that the heterogeneous decomposition of virgin solid to char and/or gas takes place through a single nth-order Arrhenius-type endothermic reaction. Pyrolysis gas is assumed to be in thermal equilibrium with the solid and to escape immediately once it is formed (i.e. no pressure buildup within the solid). All properties in the model are taken to be temperature independent.

A schematic of the boundary heat balances for the two types of materials considered in this study is shown in Fig. 1, which will help interpret the results presented below. For semi-transparent non-charring materials it is assumed that a fraction of the applied external radiation flux, $\dot{q}''_{ext}$, is absorbed and attenuated in-depth (Beer–Lambert law) according to its absorptivity, α_v, and absorption coefficient, κ, i.e. $\alpha_v \dot{q}''_{ext} e^{-\kappa x}$, where x is the depth into the solid from the surface. The front surface loses heat by convection, $\dot{q}''_{conv} = h(T_s - T_\infty)$, where h is the convective heat transfer coefficient, T_s the surface temperature, and T_∞ is the ambient temperature. Surface radiation loss is given by $\dot{q}''_{rad} = \varepsilon_v \sigma (T_s^4 - T_\infty^4)$, where ε_v is the material emissivity and σ is the Stefan–Boltzmann constant. Incoming radiation absorbed in-depth by a given cell is determined by taking the difference between the radiation reaching the top and bottom boundaries of the cell, $\alpha \dot{q}''_{ext} e^{-\kappa x}(1 - e^{-\kappa \Delta_c})$, where Δ_c is the cell thickness (which is a function of time as the surface recedes due to mass loss).

For charring materials the surface is assumed to be completely opaque ($\kappa \to \infty$) so that the external heat flux is absorbed according to $\bar{\varepsilon} \dot{q}''_{ext}$ where $\bar{\varepsilon}$ is an effective emissivity (absorptivity) equal to the average of the virgin material and char emissivities (ε_v and ε_c, respectively) weighted by the volume fractions of virgin material and char present at the surface. This type of weighing is also performed for the charring material in order to obtain an average



$$\rho_v C_{p,v} \frac{\partial T}{\partial t} \Delta_{cf} = \alpha_v \dot{q}''_{ext} \left(1 - e^{-\kappa \Delta_{cf}}\right) - \dot{q}''_{rad} - \dot{q}''_{conv} - \dot{q}''_{cond} + \dot{m}''' \Delta H_p \Delta_{cf} \quad \text{Front Surface} \quad \overline{\rho C}_p \frac{\partial T}{\partial t} \Delta_c = \bar{\varepsilon} \dot{q}''_{ext} - \dot{q}''_{rad} - \dot{q}''_{conv} - \dot{q}''_{cond} + \left(1 - \frac{\rho_c}{\rho_v}\right) \dot{m}''' \Delta H_p \Delta_c$$

$$\rho_v C_{p,v} \frac{\partial T}{\partial t} \Delta_{cb} = \dot{q}''_{cond} + \alpha_v \dot{q}''_{ext} e^{-\kappa L(t)} \left(e^{-\kappa \Delta_{cb}} - 1\right) + \dot{m}''' \Delta H_p \Delta_{cb} \quad \text{Back Surface} \quad \overline{\rho C}_p \frac{\partial T}{\partial t} \Delta_c = \dot{q}''_{cond} + \left(1 - \frac{\rho_c}{\rho_v}\right) \dot{m}''' \Delta H_p \Delta_c$$

Fig. 1. Thermal boundary conditions for non-charring (left) and charring (right) materials. The heat balance equations are written for front and back surfaces subject to the boundary conditions shown.