Critical Evaluation of Parameter Estimation Techniques for Pyrolysis of Charring Materials

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Pyrolysis models proposed to describe the thermal degradation of solid fuel sources and the associated rate of production of flammable vapors represent one of the major bottlenecks in fire modeling. Current pyrolysis models may be categorized into fully empirical, semi-empirical or comprehensive formulations. Fully empirical formulations prescribe the evolution of the fuel mass loss rate based on data obtained in representative experiments. In contrast, comprehensive models consider detailed descriptions of the processes that occur inside solid fuel sources in response to the heat loading. Comprehensive models require a fundamental understanding of the processes involved, as well as suitable experimental and/or theoretical methods to evaluate material properties and chemical parameters. Semi-empirical models correspond to an intermediate approach based on simplified descriptions of in-solid heat transfer and chemical processes. Semi-empirical models differ from comprehensive models, in particular because they consider material properties and chemical parameters as model parameters rather than “true” properties of the material. The present study examines the predictive capability of pyrolysis models developed via a calibrated semi-empirical approach. The study first introduces six different semi-empirical models developed to simulate pyrolysis of polyvinyl chloride (PVC). All of the models are similar and use a global one-step Arrhenius-type pyrolysis reaction. They differ because of different modeling assumptions made that impact the number of unknown model parameters and/or because of the optimization technique used to determine the unknown parameters (a genetic algorithm or a stochastic hill-climber algorithm). The six PVC pyrolysis models are calibrated by comparisons with experimental data corresponding to cone calorimeter tests performed at high values of the radiation intensity; by design, the six models provide similar results under conditions that are close to those of the reference cone calorimeter experiments. The study then considers an evaluation of the predictive capability of the six pyrolysis models through a series of numerical experiments, including several cone calorimeter tests and one vertical upward flame spread problem. These configurations feature conditions that are significantly different from the reference conditions used in the model calibration phase. It is found that predictions from the PVC pyrolysis models start to diverge for conditions that lie outside of the calibration range. Most notably, the models lead to conflicting results when applied to the flame spread problem. These results suggest that the domain of validity of semi-empirical pyrolysis models is limited and that extrapolation to non-calibrated conditions may result in a significant loss of accuracy.

1. Introduction
The advent of computer simulation provides an excellent tool in predicting flame spread and fire growth in real-world geometries. Now, there is a significant interest in fire community to use CFD-based fire simulator as it not only provides a cost-effective alternative to expensive full-scale fire tests but also can be used to provide a fundamental understanding of material flammability and fire growth. Nonetheless, accurate prediction of solid fuel mass loss rate is essential for CFD-based fire growth modeling because it determines the amount of gaseous fuel generated by the solid for the flames. In fire applications, solid pyrolysis corresponds to the transformation of carbon and hydrogen matter from solid to gas phase and thereby controls the rate of formation of flammable vapors that fuels the combustion process. Pyrolysis is driven by the gas-to-solid heat transfer process — also called the thermal feedback — which includes convection and
thermal radiation components. A significant amount of experimental and theoretical studies have been conducted over the past few decades for the analysis and prediction of pyrolysis process of both charring and non-charring materials [1-10]. It is not the intent of the present study to give a thorough review on pyrolysis modeling, but a brief overview will be presented.

Pyrolysis models feature a variety of approaches and may be categorized as: 1) fully empirical models in which the evolution of the fuel mass loss rate is prescribed based on data obtained in reference bench-scale or furniture calorimeter experiments; 2) semi-empirical or comprehensive models that are based on detailed descriptions of the many physical and chemical processes that occur inside solid fuel sources in response to the gas-to-solid thermal loading [1-7].

Semi-empirical models correspond to an intermediate approach based on simplified descriptions of in-solid heat transfer and chemical processes [9-13]. These cost-effective models rely on a number of simplifications, e.g. infinitely fast or global single-step pyrolysis chemistry, the assumption of a single-phase homogeneous medium, etc. Semi-empirical pyrolysis models require a large number of input parameters, including chemical kinetic parameters (pre-exponential factor, activation energy, heat of reaction) for each pyrolysis reaction, thermal diffusion properties (thermal conductivity, mass density and specific heat capacity) for each chemical species (virgin, char and intermediate species), and thermal radiation properties of the solid (surface emissivity, in-depth radiation absorption coefficient). In general, there are two different approaches to the problem of determining pyrolysis model parameters: a first approach aimed at measuring “true” properties in specialized micro-scale experiments (e.g., thermo-gravimetric analysis, differential scanning calorimetry, etc.); and a second approach adopted in semi-empirical pyrolysis models and aimed at evaluating “apparent” properties from bench-scale experiments (i.e., cone calorimeter tests or fire propagation apparatus tests) combined with model simulations and error minimization algorithms based on advanced optimization techniques [10]. While the first approach has the ability to produce general-purpose, accurate, comprehensive models, its domain of application is limited to a small list of materials (primarily wood and plastic materials) for which precise micro- and bench-scale measurements have been performed; the second approach is currently the dominant approach used to treat pyrolysis in CFD applications. Note that the accuracy of the semi-empirical approach depends strongly on the scope and quality of the calibration data used to determine the pyrolysis model parameters.

While semi-empirical formulations provide an attractive solution to the problem of treating pyrolysis in CFD-based fire simulations, it is worth emphasizing that their domain of validity remains typically unspecified. First, while by construction, semi-empirical pyrolysis models are expected to be accurate for conditions close to those used during model calibration, there is no guarantee that they will remain accurate for conditions that lie outside of the calibration range. This guarantee exists in comprehensive models but is lost in semi-empirical models because of the built-in simplifications and use of apparent properties. In addition, despite the importance of these choices, there is no established guideline on the nature, quality and completeness of the reference experimental data that are used during calibration. In fact, the literature features a wide variety of choices for calibration data, ranging from relying exclusively on data obtained in bench-scale experiments (e.g., cone calorimeter or fire propagation apparatus tests) to using data obtained in both bench-scale and micro-scale experiments (thermo-gravimetric analysis, differential scanning calorimetry, etc.). Additional choices for calibration data range from using data obtained in a limited set of bench-scale experiments, for instance experiments performed with high values of the radiant panel intensity (greater than 50 kW/m² - a typical value used to represent post-flashover compartment fires) to using data obtained in a larger set of bench-scale experiments featuring high and low values of the radiant panel intensity (including intensities below 25 kW/m² - a typical value used to represent flame spread). Choices also includes relying exclusively on fuel mass loss rate data from bench-scale tests versus using both mass loss rate and in-solid temperature data.

The general objective of the present study is to evaluate the predictive capability of semi-empirical pyrolysis models. We choose to examine polyvinyl chloride (PVC) as a representative charring material. The paper is organized as follows: the next section presents the modeling framework and parameter estimation techniques that leads to the development of two semi-empirical models to simulate PVC pyrolysis; the discussion then turns to an evaluation of the performance of the two PVC pyrolysis models in CFD simulations of a laboratory-scale test corresponding to an upward flame spread problem; lessons learned are summarized in the conclusion section.

2. Material property estimation

This section presents the development of two models to describe PVC pyrolysis. Test data were obtained from Ref. [6]. The configuration is a classical air-supplied cone calorimeter set-up in which the top surface of horizontal samples of PVC were exposed to controlled levels of radiation intensity as provided by a calibrated radiant panel. The samples were 6 mm thick; the bottom surface of the samples was lined with a 20 mm thick dense Kaowool blanket which rested on top of a 13 mm thick Kaowool M board; the bottom and sides of each sample were wrapped with aluminum foil. The experimental matrix included several tests corresponding to different levels of radiation intensity at 50, 75 and 92 kW/m² [6].
2.1 Pyrolysis Model
The pyrolysis model is formulated as a classical one-dimensional problem in the direction normal to the exposed solid surface. The model formulation is based on simple conservation statements for heat and mass, coupled with a global one-step finite-rate decomposition chemistry model proposed for char materials [13]. The reader is referred to Ref. [13] for model development and numerical solution details; only the simplifications made to the model along with assumed boundary conditions are described here for brevity. The solid material is treated as optically opaque. The heat flux at the exposed surface of the solid material (at \( x = 0 \)) is:

\[
q_n^*(t) = \frac{\varepsilon G - \varepsilon \sigma(T_{s,w}^4 - T_x^4) - h(T_{s,w} - T_x)}{\varepsilon + \varepsilon_{\infty} - \varepsilon_{\infty}}
\]

where \( \varepsilon \) is the surface emissivity, \( G \) the irradiation from the radiant panel, \( \sigma \) the Stefan-Boltzmann constant, \( T_{s,w} \) the solid surface temperature (at \( x = 0 \)), \( T_x \) the ambient gas temperature, and \( h \) the convective heat transfer coefficient (\( h = 10 \) W/m²/K). Also, in one of the models considered below, a flame heat flux is added to the RHS of Eq. (1) in order to represent the additional contribution of the flame to heat transfer once flaming is established. The back PVC surface (at \( x = L \)) is either assumed to be adiabatic or is treated using a more realistic two-layer model that simulates the experimental conditions in which the back surface of the PVC sample is in contact with a 20 mm thick Kaowool blanket.

The complete list of model parameters for the single-step finite-rate-chemistry char-producing pyrolysis model is presented in Table 1. The model features 13 parameters to describe material properties and chemical reaction coefficients; unless specified otherwise, these parameters are considered as unknown. Note that the material properties for the virgin solid and char residue are assumed to be constant (i.e., temperature-independent). Note also that for a single-step char-producing reaction, the char yield (also called the residue yield) is equal to 1 minus the volatile yield (also called fuel yield).

2.2 Optimization Algorithms
The present study considers two optimization techniques for parameter estimation: a genetic algorithm (GA) and a stochastic hill-climber algorithm (HCA). It is not the intent of this paper to describe the GA and HCA optimization algorithms. Detailed descriptions of these algorithms can be found in Refs. [10, 12-13]. In general, the pyrolysis model parameters are determined by finding the best agreement between simulation results and experimental data in terms of variations of the mass loss rate, front surface temperature and back wall surface temperature. The genetic and stochastic hill-climber algorithms have been written to automatically and iteratively adapt the values of the unknown model parameters in order to minimize the error between model predictions and experimental data.

The number of unknown model parameters may be reduced by considering that some of the solid properties are known from experimental measurements or that some simplifying assumptions can be made. The present study considers different parameter estimation methodologies corresponding to different weights given to the random mathematical search. In the GA-based model (also called GA hereafter), the PVC surface emissivities are assumed equal to 0.9; also, the virgin solid mass density, char mass density and char yield are treated as unknown (independent) parameters. The number of degrees of freedom in GA is therefore 11. In the HCA-based model (also called HCA hereafter), the chemical kinetic parameters \( A \) and \( E \) are assumed to be known from TGA test data (the values of \( A \) and \( E \) are extracted from analysis of TGA data from Ref. [6]). The analysis assumes that only 47% of the initial virgin solid mass is transformed into fuel volatiles or char, the remaining 53% being transformed into inert volatiles; also, the concept of a threshold temperature is removed from the model formulation; and the char yield is estimated as the ratio of char mass density divided by virgin solid mass density (constant volume is assumed). The number of degrees of freedom in HCA is therefore 9. Finally, GA assumes \( q_{\text{flame}}^* = 10 \) W/m² (see Ref. [6]) and treat the back PVC surface as adiabatic, whereas HCA neglects flame heat flux but adopts a more realistic model in which the back surface of the PVC sample is in contact with a Kaowool layer.

<table>
<thead>
<tr>
<th>Virgin Material Properties</th>
<th>GA</th>
<th>HCA</th>
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</thead>
<tbody>
<tr>
<td>( \rho ) (kg/m³)</td>
<td>1673.05</td>
<td>2700</td>
</tr>
<tr>
<td>( c ) (kJ/kg/K)</td>
<td>0.72</td>
<td>0.99</td>
</tr>
<tr>
<td>( k ) (W/m/K)</td>
<td>0.078</td>
<td>0.2</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>0.90</td>
<td>1</td>
</tr>
<tr>
<td>( \eta )</td>
<td>0.81</td>
<td>0.976</td>
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<table>
<thead>
<tr>
<th>Residue Material Properties</th>
<th>GA</th>
<th>HCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho ) (kg/m³)</td>
<td>0.035</td>
<td>65</td>
</tr>
<tr>
<td>( c ) (kJ/kg/K)</td>
<td>3.984</td>
<td>1</td>
</tr>
<tr>
<td>( k ) (W/m/K)</td>
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<td>0.1</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>0.90</td>
<td>0.95</td>
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<tr>
<th>Reaction Parameters</th>
<th>GA</th>
<th>HCA</th>
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<tr>
<td>( \Delta H_p ) (kJ/kg)</td>
<td>366.3</td>
<td>380</td>
</tr>
<tr>
<td>( A ) (s⁻¹)</td>
<td>9.95E+14</td>
<td>5.98E+03</td>
</tr>
<tr>
<td>( E ) (kJ/mol)</td>
<td>251.6</td>
<td>71.6</td>
</tr>
<tr>
<td>( T_{\text{thr}} ) (°C)</td>
<td>317.89</td>
<td>20</td>
</tr>
</tbody>
</table>

| Table 1. Input parameters for the two pyrolysis models (called GA and HCA). |
Table 1 presents the values of the model parameters after GA-based and HCA-based optimization. Parameters shaded in grey have been assumed. Note that some of the values of the model parameters reported in Table 1 are clearly unrealistic, for instance the very low value for the mass density of the char in GA. This may be explained by the underdetermined nature of the optimization problem, which results in the existence of multiple solutions. The values of the model parameters in Table 1 correspond to one of several valid solutions of the mathematical optimization problem but should not be considered as the (presumably unique) physical solution. The values of the model parameters in Table 1 correspond to one of several valid solutions of the mathematical optimization problem but should not be considered as the (presumably unique) physical solution.

The GA-based algorithm uses both mass loss rate and solid temperature data, for two levels of radiation intensity, $G = 75 \text{ kW/m}^2$ and $G = 92 \text{ kW/m}^2$, while the HCA-based algorithm uses similar data for only one level of radiation intensity, $G = 75 \text{ kW/m}^2$. Note that temperature measurements in Ref. [6] are limited to the back surface location (at $x = L = 6 \text{ mm}$) and to temperature values below 135 °C.

Figures 1a and b present a comparison of the time variations of the fuel mass loss rate (MLR) between cone calorimeter data and model predictions. The figures show that both models are successful at reproducing the global features of the time variations MLR observed in the experimental study, in particular the (short) ignition delay, the timing of the first peak (within 20%), the magnitude of the first peak (within 10%), the timing of the second peak (within 30%), the magnitude of the second peak (within 15%), the total burn out time (within 10%), and the total mass loss (within 5%). Figures 1c and 1d present the corresponding time variations of the back surface temperature. The figure shows that all models are successful at reproducing the early variation of the back surface temperature (up to 100 degrees Celsius). Subsequent measured variations are considered unreliable and are not used, nor plotted. Model GA in particular features the smallest value of thermal inertia and predicts back surface temperatures that are approximately 100 degrees higher than those predicted by model HCA.

![Figures 1](image1.png)

**Figure 1.** Cone calorimeter test for a PVC sample: time variations of: (a) fuel mass loss rate subjected to 75 kW/m², (b) fuel mass loss rate subjected to 92 kW/m², (c) back wall temperature subjected to 75 kW/m², and (d) back wall temperature subjected 92 kW/m².

### 3. Upward flame spread Over PVC wall

The spread of a flame over the surface of a combustible solid is an important ingredient in compartment fire dynamics [11]. We present below results from large eddy simulations (LES) of a representative flame spread configuration. The LES simulations are performed using the Fire Dynamics Simulator (FDS); FDS is a fire modeling software developed by the U.S. National Institute of Standards and Technology. Details of FDS physical modeling capabilities may be found in Refs. [14-15]. The numerical configuration corresponds to a turbulent flame spreading upward along a vertically-oriented PVC sheet; the numerical and modeling choices made in each simulation are identical except for the treatment of pyrolysis; pyrolysis is treated using the semi-empirical models GA and HCA presented above. In the present study, we use FDS version 5.5.1.
3.1. Numerical Configuration
The numerical configuration, shown in Fig. 2a, is inspired from the experimental set-up used in Ref. [16]. The vertical PVC sheet is 55 cm high (z-direction), 30 cm wide (x-direction) and 6 mm thick (y-direction); the PVC sheet is extended with two lateral Marinite panels and one top piece of sheet metal; the PVC/Marinite/sheet-metal assembly (referred to as the PVC panel hereafter) is 60 cm high and 40 cm wide. The PVC sheet is ignited using a high temperature solid device: the ignition device is rectangular-shaped (5 cm high, 30 cm wide and 5 cm deep) and is located at a y-distance of 5 cm from the bottom of the PVC sheet, and features one hot surface (facing the PVC sheet) with a constant uniform temperature equal to 800 degrees Celsius. The irradiation produced by the ignition device is approximately 30 kW/m² at the bottom of the plate. The PVC panel is also equipped with vertical side panels made of metal sheet; the side panels are located at x = 0 and x = 40 cm and act as flow barriers.

![Figure 2](image)

**Figure 2.** (a) Numerical configuration corresponding to bottom ignition of a vertical PVC sheet. (dimensions are given in meters). (b) and (c): Snapshots showing the instantaneous spatial distribution of the fuel mass loss rate on the PVC sheet surface at time t = 15 min, and for the GA and HCA models, respectively.

The computational domain is 60 cm high, 40 cm wide and 50 cm deep. The y-size (50 cm) of the domain is chosen large enough so that air entrainment is not affected by inaccuracies associated with open flow boundary conditions. The PVC panel is located at y = 0; the floor (at z = 0) is a solid boundary (and is treated as isothermal at ambient temperature); the y = 50 cm and z = 60 cm boundaries are open boundaries and play the role of inflow and outflow boundaries, respectively. The computational grid corresponds to a near-wall block (0 ≤ y ≤ 15 cm) with the highest resolution and an outer layer block (15 ≤ y ≤ 50 cm) with a coarser resolution. The near-wall resolution corresponds to Δy = 0.5 cm and Δx = Δz = 1 cm; the outer layer resolution is twice coarser, Δy = 1 cm and Δx = Δz = 2 cm. The choice of a relatively small near-wall grid spacing comes from the intent to perform wall-resolved LES simulations, i.e. simulations in which the near-wall region of the boundary layer flame is grid-resolved and wall gradients are described with suitable accuracy. Note that the boundary layer flame has a thickness on the order of 1 cm and wall-resolved simulations are expected to require near-wall grid spacing on the order of 1 mm. The value of Δy adopted in the present study came from a separate grid convergence study in which the grid was systematically refined and the solution was carefully monitored for changes; the choice of Δy = 0.5 cm near the wall was found to be a suitable trade-off between the conflicting goals of achieving grid convergence and reducing computational cost. The total size of the computational grid is 92,000 cells. The simulations are performed using the Eddy Dissipation Concept combustion model and assuming single-step global combustion chemistry. The PVC fuel vapors are described as C2H3Cl with chlorine treated as an inert chemical species; the soot yield is 17.2%, the CO yield is 7.2% and the heat of combustion is 14.4 MJ/kg [6]. Thermal radiation is treated assuming a grey medium. Furthermore, the simulations are performed using either the GA or HCA pyrolysis model; the thickness of the PVC sheet is L = 6 mm; the back surface is treated as adiabatic.

3.2 Discussion of results and physical observations
Figure 3a presents a comparison of the simulated time variations of MLR as predicted using GA and HCA. It is seen that the models present high levels of disagreement: peak values of MLR vary by a factor of approximately 5 (HCA predicts a peak value of approximately 0.72 g/s while GA predicts 0.15 g/s); the times to peak MLR value vary by a factor of more than 2; and burn out times vary by a factor 1.5. Assuming that all the fuel released from the PVC sheet burns in the wall flame, it is seen that model HCA corresponds to a peak value of the heat release rate (HRR) of approximately 10 kW while model GA corresponds to a peak value of HRR of approximately 2 kW. Note that the simulated combustion intensities are relatively low and that fire conditions remain close to critical conditions required for sustained burning and flame spread.
Figure 3. (a) Time variations of the total fuel mass loss rate. (b) Centerline variations of the local burning efficiency with respect to elevation \( z \). (c) Time variations of the pyrolysis front height.

In order to better quantify the difference between the burning behaviors of each model the burning efficiency of the models is compared. Figure 3b presents the spatial variations of the local burning efficiency measured on the vertical centerline of the PVC sheet and as a function of elevation \( z \). The local burning efficiency is defined as:

\[
\zeta(x_{\text{PVC}}, z_{\text{PVC}}) = \frac{\int_{t_{\text{ign}}}^{t} m_f(t) \, dt}{\rho_f \omega_t L}
\]

where \( x_{\text{PVC}} \) and \( z_{\text{PVC}} \) designate spatial coordinates on the exposed surface of the PVC sheet. The burning efficiency \( \zeta \) compares the total release of flammable PVC vapors (measured from ignition to burn out) to the value that is obtained when pyrolysis processes go to completion (as was the case in the cone calorimeter tests presented above): \( \zeta \) takes values between 0 and 1 (\( \zeta = 0 \) when pyrolysis is not active; and \( \zeta = 1 \) when pyrolysis is active and sustained up to total fuel depletion); \( \zeta \) provides a convenient measure of deviations from complete pyrolysis. The global burning efficiency (integral of \( \zeta \) over the entire surface of the PVC sheet) is 12% for GA and 83% for HCA. Figure 3b shows that model HCA predicts a successful flame spread fueled by a nearly complete pyrolysis process (83% of the initial virgin solid PVC mass is transformed into pyrolysis products, i.e. flammable volatiles and char); in contrast, model GA predicts no flame spread and a pyrolysis process limited to the vicinity of the ignition device (only 12% of the initial virgin solid PVC mass is transformed into flammable volatiles and char).

Figure 3c presents the time variations of the pyrolysis front height \( x_p \), defined as the highest location along the vertical centerline of the PVC sheet at which the local fuel mass loss rate reaches the critical value of 1 g/m²/s. The upward rate of spread of the vertical flame may be defined as the time derivative of \( x_p \). Flame spread, as seen from the HCA data presented in Fig. 3c, may be characterized by the following sequence of events: an initial induction phase (\( x_p \leq 5 \) cm) during which the ignition device thermally loads the bottom of the PVC sheet and establishes a small base flame; a flame spread phase (\( x_p \) increases from 5 to 55 cm) during which the pyrolysis region extends (both vertically and horizontally) and the wall flame intensifies; a burn out phase (\( x_p = 55 \) cm) during which pyrolysis and combustion are sustained for a certain time. However, in the GA-based simulation, the induction phase lasts for approximately 3 minutes, PVC temperatures remain sub-critical and transition to a flame spread phase is not observed. Figures 2b and 2c provide a graphical representation of the extent and speed of flame spread, in the form of an instantaneous distribution of the fuel mass loss rate (per unit surface area) along the PVC sheet. Consistent with results of Fig. 3a, at \( t = 15 \) min (900 s), the HCA-based simulation reaches the burn out phase, whereas the GA-based simulation is still in the induction phase.

One of the important parameter driving the rate of upward flame spread is the flame height and the heat transferred to the unburned surface. The values of the intensity of the thermal loading measured on the vertical centerline of the PVC sheet are relatively low: peak values of the gauge heat flux range between 10 and 20 kW/m²; these values are significantly lower than those used in the cone calorimeter tests of the model calibration phase (where \( G = 75 \) kW/m² and 92 kW/m²).

In order to further examine the predictions of the pyrolysis models for conditions that are significantly different from those used during calibration we perform two new cone calorimeter test simulations, for \( G = 12.5 \) kW/m² and 17.5 kW/m². These levels of \( G \) correspond to representative average values of the gauge heat flux at \( z = 10 \) and 40 cm in the flame spread problem. Figure 4 shows that at these low levels of the thermal loading, model HCA predicts moderate values of MLR (i.e., peak MLR values between 5 and 10 g/s/m²) while model GA predicts critically low values (i.e., peak MLR values below 5 g/s/m²). The low values predicted by GA are unlikely to be large enough for sustained
burning and flame spread. Combined together, these results are consistent with the conflicting flame spread predictions observed in Figs. 2 and 3. If one uses peak MLR values obtained in the cone calorimeter tests of Fig. 4 in order to establish a ranking between GA and HCA in terms of flame spread propensity, one may easily conclude that the propensity of the HCA model is much higher than that of the GA model. This ranking is consistent with the flame spread results presented in Fig. 2. Note also that these results support the usual assumption made in fire research that bench scale data can be extrapolated to full scale fire problems (provided that the intensity of the thermal feedback is similar in both configurations).

A sensitivity analysis was carried out with the intent to understand the source of discrepancy between the two pyrolysis models at low values of \( G \) through a better understanding of the relative importance of the different pyrolysis model parameters on the PVC response to thermal loading. The thermal properties \( (k, \rho, c) \) of the virgin solid and char, the chemical kinetic parameters \( (A \) and \( E) \), and the heat of pyrolysis \( (\Delta H_p) \) were systematically varied around the values given in Table 1, and for values of \( G \) between 5 and 200 kw/m². It was found that for \( G \leq 25 \) kw/m², the response of PVC is strongly influenced by the values of \( A \) and \( E \), whereas at higher values of \( G \), the response is approximately insensitive to the choice of chemical kinetic parameters (under high \( G \) conditions, the pyrolysis chemistry may be considered as infinitely fast). In other words, the increasing discrepancy between the predictions of the two PVC pyrolysis models as one goes to low values of \( G \) may be explained by the large variations in the values of \( A \) and \( E \) adopted by these models. This analysis suggests that a correct calibration of the chemical reaction coefficients \( A \) and \( E \) requires including experimental data at low irradiation levels and that the limited calibration (using cone calorimeter data obtained at \( G = 75 \) kw/m² and/or \( G = 92 \) kw/m²) does not allow an application of the pyrolysis models to low \( G \) conditions.

4. Conclusion
The general objective of the present study is to evaluate the predictive capability of pyrolysis models based on a calibrated semi-empirical approach. We consider the case of polyvinyl chloride (PVC) and first develop two models to simulate PVC pyrolysis. The development is based on: a standard one-dimensional model formulation used to describe heat and mass dynamics inside the PVC material combined with global one-step pyrolysis chemistry; cone calorimeter test data used for model calibration; and two parameter estimation techniques used to optimize the model calibration process. The models that are produced are different but provide similar mass loss rate predictions for conditions corresponding to calibration test data (i.e. high values of the radiation intensity, \( G > 50 \) kw/m², relatively thin samples, \( L = 6 \) mm, and thermally insulated back surface conditions).

We then present a comparison of predictions made by the PVC pyrolysis models in an upward flame spread problem. The flame spread problem is characterized by low values of the thermal feedback (values of the gauge heat flux vary between 10 and 20 kw/m²), i.e. conditions that lie outside of the domain of calibration of the pyrolysis models. The PVC pyrolysis models are found to produce conflicting predictions. The large variations in the predicted burning behavior suggest that the models have limited value when applied to flame spread problems because of uncertainties in their level of accuracy. Thus, the domain of validity of semi-empirical pyrolysis models is limited to the set of conditions that are used during model calibration. This may be an unacceptable restriction for models intended for general-purpose use,
especially given the fact that the exact domain of validity of the proposed pyrolysis models remains typically unspecified.

This restriction may be overcome in several ways. One way is to adopt a more comprehensive strategy for model calibration, for instance by using thermo-gravimetric analysis (TGA) data, differential scanning calorimetry (DSC) data, and/or simultaneous thermal analysis (STA) data in addition to bench-scale data (cone calorimeter or fire propagation apparatus). A more comprehensive strategy for model calibration may also require better instrumented bench-scale tests, for instance tests that produce in-sample solid temperature data (e.g., front and back surface temperature data) in addition to mass loss rate data. The present study also suggests that it is important to include data from cone calorimeter tests performed with low values of the radiation intensity, preferably below 20 kW/m².

Finally, it is worth emphasizing that while semi-empirical models provide a cost-effective approach to pyrolysis modeling and are an attractive option for engineering-level fire modeling applications, the present study also suggests that there is a strong need to develop more fundamental approaches that rely on detailed descriptions and accurate estimates of “true” physical and chemical properties. Detailed comprehensive pyrolysis models are the preferred approach for a general-purpose treatment of pyrolysis.

References