Simulation of the pyrolysis of charring polymers: influence of the porous media properties

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ABSTRACT

Recent large-scale experiments of cable tray fires have shown that the composition of the cable-sheath materials have a strong influence on the fire growth and spread. Thus, the correct prediction of the fire scenario requires the characterization of the sheath materials thermal and thermokinetic parameters. Yet, this task may be tricky for the materials whose pyrolysis generally leads to the formation of a porous residual. Whereas the physical constants related to the material degradation kinetics and to the virgin material properties can usually be determined using thermogravimetric analysis and differential scanning calorimetry, the porous residue properties are difficult to obtain and rarely available for pyrolysis models validation.

The present paper deals with the simulation of reference cone calorimeter experiments carried out on PVC samples. An extension to porous media of the pyrolysis model of the CALIF3S-ISIS fire simulation software, developed at IRSN and validated on non-charring polymers, is used for the simulations. Special attention is paid to the modelling of the thermal diffusion effects in the porous residuals. On the one hand, based on the intrinsic conductivity of the different media (virgin material, intumescent intermediate state, char and gases), several effective conductivity models are tested to evaluate the relevant range for the global material conductivity. On the other hand, it is observed that the porous residuals of PVC generally contain large pores due to the material intumescence. That is why a radiative conductivity is included in the model to account for the radiative transfer in the pores. Without precise knowledge of the PVC residuals morphology, a Penetrable Sphere Model (PSM) is chosen to represent the porous medium geometry. This model is parametrized by a constant porosity deduced from the experimental data, and a variable pore size. It allows deducing a porous medium radiative conductivity which is added to the usual effective conductivity.

It is shown that, in the particular case of PVC pyrolysis, the uncertainty on the purely conductive effects induces a very limited dispersion on the simulation of the Heat Release Rate (HRR), since all the considered models yield very similar results. Conversely, the sensitivity of the radiative conductivity and therefore of the pyrolysis kinetics to the PSM pore size is much larger. The optimal pore size with respect to the HRR temporal evolution is of the same order as the pore size observed in some PVC residuals. Finally, pyrolysis simulations are performed with this optimized parameter for different cone heater induced heat fluxes and sample sizes. A good overall agreement is found between the experimental and the numerical HRR evolution, except for the thinnest sample for which the numerical HRR is overestimated. More generally, this work shows that further effort on the morphological description of the porous residuals and on the modelling of the radiative transfer is required if one aims at performing predictive pyrolysis simulations.

KEYWORDS

Fire chemistry; pyrolysis; porous media; heat transfer; Penetrable Spheres Model; Rosseland approximation
INTRODUCTION

In recent years, fire spreading along cable trays in Nuclear Power Plants (NPP) has been widely studied in large scale facilities [1,2]. The influence of large scale parameters such as the cable trays loading, spacing, width, the cables arrangement and the presence of a wall has been demonstrated. But recent large-scale experiments carried out in the framework of the OECD PRISME program led by French "Institut de Radioprotection et de Sûreté Nucléaire" (IRSN) have shown that the cable-sheath materials may also have a strong influence on the fire growth and spread [2,3]. In particular, the comparison between 5-horizontal trays experiments containing halogenated (i.e. PVC) or non-halogenated (mainly PE/EVA, compounds with mineral fire retardants) materials has shown that the initial HRR growth and the peak HRR are larger for PVC cable-sheaths than for non-halogenated cable-sheaths, but that the effective heat of combustion is larger for the latter than for the former. Yet, two approaches aiming at predicting cable tray fire scenarios have been developed in the last ten years. On the one hand, large-scale models such as the FLASH-CAT model [1] consist in predicting the fire Heat Release Rate from the large scale geometrical characteristics of the cable tray configuration. This requires a correct prediction of the horizontal and vertical spreading rates by accounting for the influence of the cable-sheath materials thermal properties. On the other hand, comprehensive pyrolysis models have been used together with computational fire dynamic simulations to study cable fire scenarios [4]. They require the characterization of the cable-sheath materials thermal and thermokinetic parameters. Unfortunately, although they can be predictive for non-charring polymers such as PMMA [5,6], the prediction of the degradation rates of polymers such as PVC or PE/EVA compounds with fire retardants stumbles over the correct characterization of the thermal properties of the porous residuals generated during the pyrolysis process. Therefore, these unknown parameters are generally set using an optimization procedure [7]. In particular, all the diffusive effects occurring in the heat transfer balance may be tied together in a single elliptic term which includes the pure conduction and a Rosseland-like radiative conductivity.

The purpose of the present paper is to evaluate the sensitivity of pyrolysis models to the uncertainty on the pure conductivity and radiative conductivity of porous pyrolysis residuals. An extension of the pyrolysis model of the CALIF’S-ISIS [8] fire simulation software developed at IRSN and validated on non-charring polymers [6] is considered here. It will be tested against the PVC characterized and tested by Stoliarov et al. [7]. Therefore, after a description of the extended pyrolysis model for porous materials and of the hypotheses on unknown parameters [6,8], the sensitivity of the pyrolysis model to parameters involved in usual pure conductivity and radiative conductivity submodels will be analysed. Then, a comparison between the numerical results and reference cone calorimeter experiments will be presented.

MODEL DESCRIPTION

General features

The pyrolysis model developed in the CALIF’S-ISIS fire simulation software [8] allows simulating the thermal degradation of solid materials, involving \( N_R \) parallel or sequential reactions and a set of \( N_g \) gaseous species. Each solid material \( M_j \) is composed of a constitutive solid species \( S_j \) of intrinsic density \( \rho_j \), a micro-porosity \( \varphi_j \) and a macro-porosity \( \Phi_j \). Let \( \rho_j^0 = \rho_j(1-\varphi_j) \) denote the microporous solid density (mass of solid species \( S_j \) over the volume occupied by \( S_j \) and the micro-pores), and \( \rho_j \) denote its partial density (mass of solid species \( S_j \) over an arbitrary volume element). Thus, if \( X_j = \rho_j \) denotes the microporous solid volume fractions \( (j = 1 \text{ to } N_w) \), the total macro-porosity reads \( \Phi = 1 - \sum_j X_{w,j} \). Let also \( \bar{X}_j = X_j(1-\Phi_j) \) be the gas volume fraction of material \( M_j \), with \( \sum_j \bar{X}_{w,j} = 1 \), which is used to ensure volume conservation. Then, the gas transport in the porous material is modelled by the Darcy law, the continuity equation and the transport equation related to each gaseous species \( G_j \) \( (j = 1 \text{ to } N_g) \). The material permeability and the species diffusion can be kept constant since the model shows a negligible sensitivity to these parameters on a wide range of values. The total enthalpy conservation equation considered for non-porous materials is extended by including the terms related to the gas transport, namely accumulation, convection and pressure work.

Thermal degradation scheme and material properties

A two-step degradation scheme [7] is used to describe the pyrolysis of PVC, but a formulation of the pyrolysis gases is proposed according to several studies of gas analysis [9]. Indeed, the first step of the thermal degradation of PVC ((C\(_2\)H\(_5\)Cl)\(_{10}\)) consists in the ejection of Chlorine acid (HCl) and heavy hydrocarbons, mainly Benzene (C\(_6\)H\(_6\)), in the second step, a wide range of hydrocarbons is produced; among them are acetylene (C\(_2\)H\(_2\)) and hydrogen (H\(_2\)). Therefore, the retained degradation scheme is
\[
\begin{align*}
S_1 & \rightarrow \mu_1 S_1 + v_1 G_1 + v_2 G_2 \\
S_2 & \rightarrow \mu_2 S_2 + v_2 G_1 + v_4 G_3 + v_5 G_4
\end{align*}
\]
with \[
\begin{align*}
S_1 & \equiv (C,H_3Cl)_{\alpha}, \quad S_2 \equiv (CH)_{1.73a}(HCl)_{0.14a} \quad S_3 \equiv C_n \\
G_1 & \equiv HCl, \quad G_2 \equiv C,H_2, \quad G_3 \equiv C,H_4, \quad G_4 \equiv H_2
\end{align*}
\]
Here \(S_1\) denotes the virgin PVC, \(S_2\) is an intermediate pseudo-species and \(S_3\) is the char residual. \(\mu_i\) and \(v_j\) are the yields of solid and gaseous products evaluated according to the species conservation and the characterized products yields \([7]\): \(\mu_1 = 0.44, v_1 = 0.504\) and \(\mu_2 = 0.056\) for the first reaction, and \(\mu_2 = 0.47, v_3 = 0.184, v_4 = 0.33\) and \(v_5 = 0.016\) for the second one. The considered Arrhenius constants, heats of pyrolysis associated with each step, the virgin material specific heat, density and conductivity are those reported in Ref. \([7]\), as well as each material’s surface emissivity. Note that the present pyrolysis model allows recovering the correct mass loss evolution measured by thermogravimetric analysis depicted in Ref. \([7]\). The specific heat and intrinsic conductivity of \(S_2\) are taken equal to those of the virgin material, and one chooses the properties of coal for \(S_3\).

**Micro- and macro-porosity**

Without further knowledge of the morphology of the solid materials resulting from the PVC degradation, one assumes arbitrarily that the micro-porosity is caused by mass loss and that macro-porosity is due to intumescence, the latter being probably caused by a strong gas ejection across a partially melt material. Thus, intumescence affects the intermediate material and the char residual in the same way. If \(\beta_j\) denotes the intumescence factor of material \(M_j\), one sets \(\beta_1 = 1\) and \(\beta_2 = \beta_3 = 7\) \([7]\). In these conditions, since the PVC density is \(\rho_1 = 1430\) \(\text{kg/m}^3\), the microporous solid densities and macro-porosities are: \(\rho_1^0 = 1430\) \(\text{kg/m}^3\), \(\rho_2^0 = \mu_1 \rho_1^0 = 629.2\) \(\text{kg/m}^3\), \(\rho_3^0 = \mu_1 \mu_2 \rho_1^0 = 295.7\) \(\text{kg/m}^3\), \(\Phi_1 = 0\) and \(\Phi_2 = \Phi_3 = 1 - 1/\beta_2 = 0.857\).

**Conductive heat transfer models**

Various models can be proposed to deduce an effective conductivity \(\lambda_{\text{eff},\alpha}\) from the microporous solids conductivities \(\lambda_j\) and volume fractions \(X_j\) and from the gas conductivity \(\lambda_g\) and volume fraction \(X_g\) (i.e. macro-porosity \(\Phi\)). The arithmetic and harmonic volumetric averages \(\lambda_{\alpha}\) and \(\lambda_{\perp}\) correspond to stratified structures oriented parallel or perpendicular to the heat flux, and provide the largest and the lowest possible values for \(\lambda_{\text{eff}}\) for given volume fractions, regardless of the morphology \([10]\). The tighter upper and lower Hashin & Shtrickman bounds \([10,11]\) can also be applied if isotropy is assumed. As a rule, the arithmetic average \(\lambda_\alpha\) is used in the following. Numerical tests of the sensitivity to the various formulations are presented in Fig. 2. In this study, the conductivity \(\lambda_g\) of gaseous species is about 0.1 \(\text{W/m}^\circ\text{K}\) \([12]\). The conductivity reported in \([7]\) for the PVC is applied for the virgin material, \(\lambda_1 = 0.17\) \(\text{W/m}^\circ\text{K}\). For the intermediate microporous solid, one assumes that the solid species is PVC and that the micropores are filled with gases, which yields \(\lambda_2 = 0.13\) \(\text{W/m}^\circ\text{K}\). For the final microporous residual, a similar argument, this time with coal as a solid species, yields \(\lambda_3 = 0.22\) \(\text{W/m}^\circ\text{K}\).

![Fig. 1. PSM reconstruction example (left: 2D; center: 3D) with porosity 0.857 and sample of PVC carbon residue observed in CFS PRISME tests [2] (right).](image)

**Morphology and radiative transfer models**

The geometrical shape of the PVC carbon porous residuals is very complex and the conductive and radiative heat transfer may depend on their geometrical features, such as porosity, specific surface area, characteristic length and isotropy. Since measuring those properties experimentally is extremely difficult, they can be modelled by the means of a conceptual representation. For lack of direct information on the morphology of the PVC carbon residual, the well-known Penetrable Sphere Model (PSM) \([13]\) is chosen to represent it, since the spherical void inclusions are reminiscent of the gas bubbles observed in the experimental samples. Pictures of
a PSM sample with a porosity of 0.857 are shown in Fig. 1, along with a photo of a carbon residue cut off from a PVC sample after its pyrolysis.

Considering the size of the pores in the PVC residuals, the radiative transfer in the porous medium may increase the heat diffusion and must be accounted for. One assumes that the solids are opaque and gray materials, and that the radiative transfer in the intumescent intermediate species and char can be modelled by a Rosseland approximation, as proposed by Roudani et al. [14] for alveolar media. The local average temperature $T$, specific surface area $S$ and surface emissivity $\varepsilon$ of the solid interfaces are taken into consideration in Roudani’s model, as well as the conductivity coefficient $\lambda_c$ and a form factor $\omega_s$. The Rosseland radiative conductivity $\lambda_{eff, r}$ reads

$$\lambda_{eff, r} = \frac{8(1-\lambda_c)^2\varepsilon\sigma T^3}{\omega_s S}$$

(2)

For a PSM with such a high porosity as considered in this study, the conductivity coefficient $\lambda_c$ is nearly 0, and $\omega_s$ is set equal to 0.5. The surface area reads $S = 3(1 - \phi) \log \left( \frac{1}{1-\phi} \right) / R$, where $R$ is the sphere radius. Finally, the total effective conductivity is the sum of the conductive part and the radiative part: $\lambda_{eff} = \lambda_{eff, c} + \lambda_{eff, r}$.

**NUMERICAL RESULTS**

For the simulations, the independence with respect to the time step $\delta t$ and cell size $\delta x$ is ensured with $\delta t = 0.1$ s and $\delta x = 0.012$ mm. The heat release rate per unit area is related to the sum of the heat release rates per unit area of all three gaseous fuels by $q' = \sum q_j'' = \sum \Delta h_j m_j''$ where $\Delta h_j$ is the heat of combustion value reported in [15], namely 21.6, 41.5 and 141.8 MJ/kg for $C_6H_6$, $C_3H_8$ and $H_2$ respectively. The experimental heat release rate per unit area is deduced from the measured oxygen consumption during the cone calorimeter experiment. This measure is usually preferred from mass loss-derived measures which are usually noisier. After ignition, a time dependent correction is added to the initial value of external heat flux (EHF) to account for the intumescence, which leads to a surface movement towards the heater of the PVC sample. An additional 15kWm$^{-2}$ of incident radiative heat flux is also applied in the total EHF to simulate the presence of the flame.

**Sensitivity analysis to conductivity parameters**

The sensitivity to the radiative conductivity is considered first. In this case, the only unknown parameter in Eq. 4 is the spherical pore radius. All other things being equal, the surface area decreases and the radiative conductivity increases with $R$. The sensitivity of the HRR to the PSM radius and the comparison to the experimental results obtained for 6 mm PVC samples under 75 kW/m$^2$ are shown in Fig. 2. The optimal sphere radius for the intermediate and char species is found to be 2.8 mm, which is larger than the 1 mm pores observed on the experimental residue in Fig. 1. An example of test without radiative heat transfer is also presented for comparison, and shows that the radiative transfer must be accounted for to simulate the pyrolysis of PVC. Conversely, comparisons of different effective conductivity models, namely the arithmetic and harmonic averages as well as the upper and lower Hashin & Strickman bounds are also depicted in Fig. 2. The limited influence of the effective conductivity model on PVC pyrolysis is due to the very large porosity of the intermediate and carbon residue, and therefore to the small conductive transfers compared to the radiative contribution: $\lambda_{eff, r}$ ranges from 0.07 to 2.99 Wm$^{-1}$K$^{-1}$, compared to the maximum species conductivity, $\lambda_3 = 0.21$ Wm$^{-1}$K$^{-1}$ for the final microporous residual.

**Comparison to other cone calorimeter experiments**

Without further information about the experimental mass loss rate of PVC pyrolysis, the experimental HRR under various conditions and the corresponding simulation results are compared in Fig. 3. This HRR is also decomposed into the parts associated with the first and the second reaction. The optimal pore size previously determined is used to evaluate the radiative conductivity. As observed earlier, the HRR curves exhibit a first peak just after ignition (10 s) associated with the first pyrolysis reaction, which mostly consists in the ejection of chloride acid and a small fraction of heavy fuels. The two subsequent are associated with the second pyrolysis reaction by which most of the flammable volatiles are released. The numerical time evolution of the heat release rate is in a good qualitative agreement with the experimental one for all cases. In particular, for tests performed on 6 and 9 mm thick samples the initial HRR peak and the average HRR are well reproduced, for the sample tested under 50 kW/m$^2$, the experimental HRR curve is delayed due to the initial cycles of extinction. However, the peak HRR is clearly overestimated for the 3 mm thick sample test. In all cases, the partial heat release rates associated with the first and the second pyrolysis steps exhibit a sharp decay. The
final decay, sharper numerically than experimentally, is usually explained by a smoldering process which possibly occurs in the late stage of the material degradation. But more generally, the abrupt ending of both pyrolytic reactions may be due to an oversimplification in the two-step degradation model; possible missing intermediate reactions, which are difficult to be observed in thermogravimetric analysis, could yield smoother transitions.

![Graphs showing heat release rate per unit area comparison between cone calorimetry experiments and numerical simulations.](image)

Fig. 2. Comparison of heat release rate per unit area between cone calorimetry experiment and numerical simulations. Left: influence of the PSM pore radius in the Rosseland radiative conductivity approximation. Right: influence of the pure conductivity model. PVC sample thickness: 6 mm. Imposed heat flux: 75 kW/m².

![Graphs showing heat release rate per unit area comparison between cone calorimetry experiments and numerical simulation results.](image)

Fig. 3. Comparison of heat release rate per unit area between cone calorimetry experiments and numerical simulation results for 3 mm (d), 6 mm (a, b, c) and 9 mm(e) sample thickness and 50 kW/m² (a), 75 kW/m² (b, d, e) and 92 kW/m² (c) imposed heat flux.

**CONCLUSION**

The present study is an attempt to assess the sensitivity of pyrolysis models to the pure thermal conductivity and radiative conductivity variations resulting from the uncertainties on the PVC porous residuals properties. In this respect, the HRR results show little sensitivity to the pure effective conductivity model, but a strong sensitivity to the pore radius which parametrises the Penetrable Sphere Model underlying the radiative conductivity estimation. Without further knowledge of the residuals geometry, the optimized pore size value allows a good agreement between the experimental and simulated HRR time evolution.

As a consequence, the residue morphology of such porous residuals should be better described if one aims at predicting the pyrolysis rate of such materials. In highly intumescent materials such as PVC, the radiative
transfer seems to be dominant due to the large pore size and the relatively low gas conductivity. Note that, considering the large porosity and pore size and the possible semi-transparency of the solid species, the Rosseland approximation used to model the radiative transfer is not necessarily valid, and more relevant models should be used in a predictive approach. Despite the fact that the obtained radiative conductivity is model-dependent, the importance of radiative heat transfer during such process is evidenced. Further attention should be paid in this topic if a more accurate prediction is expected. Conversely, non-intumescent compounds filled with mineral fire retardants are expected to induce highly conductive mineral residuals with limited radiative effects if the pores are small. In this case, more attention should be paid on the modelling of the pure effective conductivity.

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