G Rein, 2008, From Pyrolysis Kinetics to Models of Condensed-phase burning, Invited Paper, in Recent Advances in Flame Retardancy of Polymeric Materials, Vol. 19, M. Lewin (ed.), BCC.

FROM PYROLYSIS KINETICS TO MODELS OF CONDENSE-PHASE BURNING

Guillermo Rein
BRE Centre for Fire Safety Engineering
University of Edinburgh, UK

ABSTRACT

The state-of-the-art of fire modelling is currently hindered due to a poor capability to model the burning of solid fuels. Current fire modelling tools provide good predictions of the thermal effects of a fire (*e.g.* the resulting thermal environment) but fail to predict properly the fire development (*e.g.* flame spread and fire growth). The consequence is that current fire modelling cannot predict the transient evolution of the heat release rate of a fire. Several studies have developed methodologies to overcome this limitation. The few applications available until now offer promising results but require further investigation. The development of fire spread models that can accurately predict the ignition and burning of solid-fuels will be a major advancement. The polymer and fire safety industries could use this knowledge to produce state-of-the-art flame retardants based on first principles.

In this work, the effects of the kinetic parameters of a one-step and a two-step pyrolysis are studied by combining it with a simple heat transfer model. The production of pyrolyzate before ignition is the main focus. The predictions in PMMA for the onset of pyrolysis in wide range of heat fluxes show good agreement with the measurements. The predicted surface temperature at the onset is not the same for different heat fluxes, indicating that the pyrolysis temperature is a non-physical concept. The sensitivity of the results to variations of the kinetic parameters is investigated and show large sensitivity to the pre-exponential factor and the activation energy, and relatively sensitivity to yield values. There are clear indications of potential for compensation between parameters and mechanisms and this is a concern when complex mathematical model are employed.

The issue of the required level of complexity in the models for parameter-estimation is a concern. Simplifications are required where the necessary precision does not warrant the inclusion of higher levels of complexity. This paper advocates for the use of blind predictions in combination with sensitivity studies and the identification of the simplest model that can predict the experimental data. Results are presented here in that direction.

INTRODUCTION

The last decade has seen a surge of computational modelling been applied to fire protection engineering. The use of fire modelling tools is only expected to grow at even faster rates in the short and long terms. But the robustness of the state-of-the-art of fire modelling is currently hindered by a poor capability to model the burning of solid fuels.

Current fire modelling tools provide good predictions of the thermal effects of a fire (*e.g.* the resulting thermal environment) but fail to predict properly the fire development (*e.g.* fire growth and/or the heat released rate). The consequence is that currently, fire modelling cannot predict the transient evolution of the heat release rate of a fire in a non-trivial scenario. This was shown in the international comparison study of fire forecast conducted for the Dalmarnock Fire Tests [1]. The study revealed that the accuracy of fire modelling to predict fire growth (ie the heat released rate) is in general poor and the sensitivity of the results is large.

Several studies are developing methodologies to overcome this limitation, and the few applications available until now offer promising results but require further investigation. In the opinion of the author, this topic will be one of the most important research objectives in fire engineering of the incoming decade.

Fire simulations required submodels of the solid phase to predict flame spread and fire growth over solid fuels. These submodels allow calculating the pyrolyzate rate based mainly on two factors, the heat transfer into the solid and a pyrolysis kinetic mechanism. The heat transfer problem was reasonable solved long ago and approximate solutions are part of the fire science curriculum. But the pyrolysis problem suffers from our limited ability to quantify and model the chemical kinetics. This precludes fire models from calculating the reaction rates, and thus fire growth and fire spread, from first principles.

A few methodologies have been proposed to extract the kinetics parameters governing the thermal degradation of solids from bench-scale tests based on calorimetry and mass loss. These methodologies stem from the same fundamental idea consisting on a heat transfer and degradation models and the hypothesis of a particular chemical mechanism. Then, the solution of the model is fit to the experimental results to extract the parameters. These parameters can then potentially be used as input to the submodels of fire spread. However, the selection of the underlying chemical mechanism and the heat and mass transfer and degradation models are assumptions that compromise the quality of the parameters. The effects of the assumptions in the heat transfer are easier to understand since our quantitative knowledge in heat transfer is relatively mature. The effects of the underlying chemical mechanism in the resulting parameters have not been sufficiently studied.

IGNTION OF A SOLID FUEL

This discussion is centered on how heating of a solid fuel leads to flaming ignition. Smouldering or self-heating ignition are not considered. The extension to other condense-phase fuels (*i.e.* liquid and gels) is not addressed here but can be done building upon this discussion. When a solid material is subjected to an external heat source, a series of physical and chemical phenomena are initiated as the energy reaches the surface of the material. The most important process in the solid phase is the production of pyrolyzate gases and that is the focus on this section. For a review of solid-phase processes leading to ignition, see [2]. Processes in the gas phase, the mixing with the oxidizer and the formation of a flame, are not considered here. Mass transfer inside the solid can be important in some problems, like those involving porous media or reduced oxygen transport to the solid surface.

For simplicity, the ignition process is described in a one-dimensional semi-infinite slab with coordinate y for the depth. To determine the pyrolyzate production it is necessary to solve for the evolution of the temperature inside the solid fuel. External heat is applied to the top surface. The temperature of the solid, initially at ambient T_0, increases as the heat reaches the surface of the slab. The highest temperatures are reached close to the surface, and in-depth energy transfer by conduction and radiation will result in an increase in temperature of the deeper parts of the slab. A schematic of a generic solid material undergoing heating is presented in Figure 1.

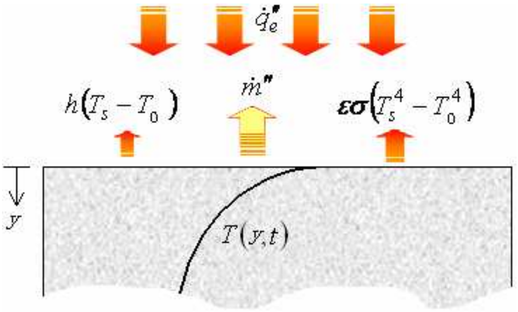

Figure 1. Solid heating and evolution of the pyrolysis reactions

Before flaming ignition occurs, pyrolyzate gas needs to be produced. Pyrolysis is an endothermic process that decomposes a solid into gas changing the chemical composition, usually into smaller chains and molecules. It takes place via several chemical reactions like Eq. (1). In oxidizing atmospheres, *e.g.* air, pyrolysis is accompanied by oxidation at the fuel surface. The effects of the surface oxidation reactions in ignition and flaming combustion are still poorly understood [2].

$$solid \rightarrow \nu_1\ residue + (1 - \nu_1)\ gas \tag{1}$$

In the case of a consecutive two-step pyrolysis, the general mechanism is:

$$solid \rightarrow \nu_1 \beta\text{-}solid + (1 - \nu_1)\ gas \tag{2}$$
$$\beta\text{-}solid \rightarrow \nu_2\ residue + (1 - \nu_2)\ gas \tag{3}$$

It is known that many solid decomposition mechanisms are affected by the presence of oxygen [4, 6]. These oxidation reactions can be included in the mechanism as parallel reactions. In general, the decomposition mechanism of a solid is made of many consecutive and parallel steps but only a few are important. How many steps are required to model the phenomena under study is one of the most important issues to be resolved. Thermogravimetric behavior helps in principle to address this question but limited information exist in the literature for the materials of most interest.

The reaction rate is a strong function of the temperature and is typically quantified using Arrhenius-type reaction rate $\dot{\omega}$. This is given by:

$$\dot{\omega}_i = \frac{dw_i}{dt} = A_i\, exp\left(-\frac{E_i}{RT}\right) w_i^n \tag{4}$$

Where A_i is the pre-exponential factor, E_i the activation energy, w_i the mass fraction of the reacting solid species, and n the reaction order (typically between 0.5 and 2). Equation (4) assumes that the reaction rate does not dependence on the oxygen concentration, which is valid for pyrolysis reaction. In conditions where oxygen transport is not reduced, the oxygen concentration near the surface is neatly constant and thus the assumption is also valid for oxidation reaction taking place near the surface.

Within the region where the temperature of the solid has increased above ambient, chemical activity leads to the production of pyrolyzate. Most production takes place at the surface but in-depth production of gases could be significant too near but below the surface. These gases move upwards and outwards the surface. Total gas production rate is given by the cumulative sum of surface and in-depth pyrolysis [2]. The definition of the onset of pyrolysis commonly uses the concept of a pyrolysis temperature, below which the solid fuel can be considered inert. It is important to note that the pyrolysis temperature is not a physical property but an approximate notion useful to decide on the onset of the reaction. Pyrolysis gases flow out of the slab top surface to the outside and mix with the surrounding air. When a sufficient concentration of pyrolyzate is reached close to a pilot flame, flaming ignition takes place. Alternatively, in the absence of a pilot, the pyrolyzate need to reach both a sufficiently high concentration and temperature for spontaneous ignition.

QUANTIFYING FIRE PARAMETERS OF FUELS

Recent studies have presented methodologies that use standard test methods and advanced optimization techniques to establish reduced reaction schemes and their associated. The methodologies stem from the same fundamental idea consisting on the combination of a heat transfer model with a decomposition model and the hypothesis of a particular chemical mechanism. Then, the mathematical solution of the model is fit to the experimental results to extract the parameters. These values explain the test results for the given modelling assumptions and the chemical mechanism. These procedures have only been applied so far to a reduced number of materials for a very limited set of conditions and thus currently remain research tools. However, they offer a great potential to future fire spread modelling concepts. These are briefly reviewed here.

Rein *et al.* [4] proposed a methodology where the kinetic parameters governing the thermal and oxidative degradation of solid fuels are determined using thermogravimetric data and a genetic algorithm. The method is applied to polyurethane foam and a quantified new 5-step mechanism was proposed. The model was used to produce blind predictions of thermogravimetric data showing good results. The kinetic scheme was then successfully used outside the realm of thermogravimetry to model the ignition, propagation and extinction of smouldering combustion of polyurethane foam. This application demonstrated the applicability of the method and proof the versatility of the kinetic scheme outside the realm of thermogravimetry. Lautenberger *et al.* [5] used a genetic algorithm to estimate the fire parameters of solid burning from cone calorimeter data. A pyrolysis model for thick solid fuels was combined with genetic algorithm to estimate the material properties for two charring materials (redwood and red oak) and polypropylene. This work has recently been extended to a generalized pyrolysis model able to simulate the behavior of charring, intumescent and smouldering materials and including some blind predictions [6].

The underlying idea in these methodologies is that the physics of the process needs to be as complete as possible. If the energy equation is missing an important transfer mode, or the chemical mechanism does not include an important step, the model could not be use to predict new data different from that used in the parameter-estimation study. For this reason, most parameter-estimation models in the literature include most of the known mechanisms. This has results in rather complex models.

The main drawback from large complexity is the potential black-box effect. This happens when the modelling is not providing understanding of the processes at hand but only predictions of a complex process, sometime intractable predictions. This effect might lead to mere numerical fitting of results instead of physical modelling. Moreover, a large number of uncertain parameters often results in compensation of one mechanism with other, *e.g.* a lower activation energy with a higher pre-exponential factor [4] or lower in-depth absorption with higher conductivity. Other more convoluted cases of compensation are possible. Thus, there are potential drawbacks in disproportionate complexity that have arrived via the computing revolution and the currently enormous computing power available.

The compromise solution lays within the two extremes of disproportionate complexity and excessive simplicity. Simplifications are required where the necessary precision does not warrant the inclusion of higher levels of complexity. One important element that helps resolving the issue is the identification of the simplest model that predicts the experimental data. The require level of modelling complexity could to be investigated and justified starting from this point.

PYROLYSIS MODEL

The combination of a heat transfer model with solid degradation is studied here for the simpler scenario of the onset of pyrolysis of a fuel slab. Results are applied to PMMA. The main objective is to investigate the robustness of the results based on variations of the parameters ad an investigation of the sensitivity of the modelling results. The model used here is deliberately simple and its development follows from the rule that simplifications are required where the necessary precision does not warrant the inclusion of higher levels of complexity.

Energy conservation is cast as an initial-boundary value problem of a parabolic heat transfer equation in 1-D in Cartesian coordinates corresponding to the slab in Figure 1. The following form of the energy equation is solved:

$$\rho c \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial y^2} + \frac{\partial \dot{q}''_a}{\partial y} \tag{5}$$

Where $\dot{\mathrm{q}}'''_{\mathrm{a}}$ is the in-depth radiation absorption and its derivative is given by:

$$\frac{\partial q''_a}{\partial y} = \varepsilon \dot{q}''_e \kappa \, exp(-\kappa y) \tag{6}$$

An emissivity ε of 1 is assumed. The energy conservation Eq. (5) neglects the endothermic and exothermic contributions of the pyrolysis and the oxidation rates respectively. This assumption is valid for high external heat fluxes (see below discussion on the decoupling of heat transfer and pyrolysis). The inclusion of in-depth absorption is important to predict the heating near the exposed surface of the slab. In-depth radiation distributes the heat within a very thin layer of material (in the order of 1 mm) resulting in a reduction of the re-radiation and convection heat losses at the surface. The boundary conditions applied to Eq. (5) are:

$$h\left(T_S - T_0\right) - \varepsilon\sigma\left(T_S^4 - T_0^4\right) + k\frac{\partial T_S}{\partial y} = 0 \tag{7}$$

$$\frac{\partial T_S}{\partial y} = 0 \tag{8}$$

Where the temperature at the top surface $T(0,t)$ as T_S. A convective heat transfer coefficient h of 10 W/m^2 was assumed. The initial conditions are that the entire slab is at ambient temperature T_0 The reaction rates are expressed as Arrhenius-type of Eq. (4) and two mechanisms are investigated, a one-step or two-step pyrolysis. The total mass loss is obtained by integrating the mass loss over the entire depth of the slab as:

$$\dot{m}'' = \rho \int_{0}^{\infty} \left[(1-\nu_1)\dot{\omega}_1 + (1-\nu_2)\dot{\omega}_2 \right] dy \quad (9)$$

This equation assumes that the in-depth pyrolyzate flows well out of the slab. This is a good approximation if in-depth heating is limited to shallow layers or the permeability of the material is large.

The solid decomposition problem is decoupled from the heat transfer. First, the heat transfer solution is obtained by integrating Eq. (5) with conditions (7) and (8). Then, the resulting temperature profile is used to calculate the reaction rates (Eq. (4)) and then the mass loss is calculated using Eq. (9). The decoupling of the two mechanisms assumes than the pyrolysis has a negligible effect on the temperature evolution and vice versa. This assumption is valid before ignition and shortly after it. When the mass loss rate is small, a high external heat flux is much large than the heat absorption rate by pyrolysis and thus this heat sink can be neglected. The low importance of the pyrolysis heat sink near the material surface can be quantified. According to [6], the heat of pyrolysis of PMMA is 0.54 kJ/g. Thus, a pyrolyzate rate of 1 g/s/m^2 requires just 5% of the energy received from an external radiant flux of 10 kW/m^2 or less than 1.5% of 40 kW/m^2. After ignition, the pyrolysis front penetrates inside the material and gradually reduces the material density on the top surface. This modifies the location of the free surface and the heat penetration. When the pyrolysis front moves some depth into the slab, the decoupled assumption creates on top an insulating layer of inert material that could be seen as the effect of a char layer. Nonetheless, this assumption is a strong one and fall outs after ignition. It needs to be studied further to identify the balance between energy transfer and in-depth pyrolysis where decoupling is valid. In this study, only the onset of pyrolysis is studied.

This simple theoretical framework allows studying the solid phase processes leading to the flaming ignition of a solid fuel. During burning, the process is further complicated by the presence of the flame that radiates to the fuel surface and modifies the boundary conditions. But the same foundation mechanisms and general modelling frame would apply. It is recommended that first a simple case is understood before more complex mechanisms are added. The addition of too many mechanisms could results in the model being a black box where the understanding of the process is obscured by intractable mathematical behavior.

RESULTS AND DISCUSSION

The simple model developed above is used here with some of the parameters estimated in [6]. Table 1 shows the values for the base-case. The thermal and mass loss results in the slab at different depths for PMMA at 40 kW/m^2 are presented in Figure 2. The top surface reaches a temperature of 300°C after 100 s. Up to 100 s, the pyrolyzate is being produced in a thin layer less than 2 mm thick. The slab is subjected to a monotonously increasing mass loss that reaches 0.18 g/s/m^2 at 100 s.

Table 1. Parameter values for the base-case used in the pyrolysis model for PMMA. The secondary reaction is not used in the based case but added to investigate the associated sensitivity.

	Value		Value		Value
ρ	950 kg/m^3; average value from [6]	A_1	5.58e11 1/s from [6]	A_2	1e11 1/s
k	0.4 W/mK ; average value from [6]	E_1	170 kJ/mol from [6]	E_2	124 kJ/mol
c	1650 J/kg/K average value from [6]	n_1	1.1 from [6]	n_2	1.14
κ	4200 1/m [6]	ν_1	0 for 1-step from [6] and 0.5 for the 2-step	ν_2	0.05

The model is used to predict the time for the onset of pyrolysis. An arbitrarily very small value of mass loss rate is chosen as the threshold to detect the onset in the numerical results. *e.g.* 0.01 g/s/m^2 is chosen here but other very small values can be chosen leading to the same conclusions. Results are investigated for a wide range of external heat fluxes. Figure 3 shows the results. The comparison with the measurements from Dakka *et al.* [3] for PMMA shows very good agreement. This is remarkable given that the parameters in [6] were obtained independently from the experiments in [3] and show that the simple model used here is capturing the thermal degradation behaviour of the slab. The results can be used for further deductions. Investigation of the predicted surface temperatures at the onset of pyrolysis shows values from 280 to 500 °C depending on the external heat flux. This implies that the pyrolysis temperature is a non-physical concept as mentioned before and that pyrolysis production depends on the heating rate and thermal history as well as on the temperature of the solid.

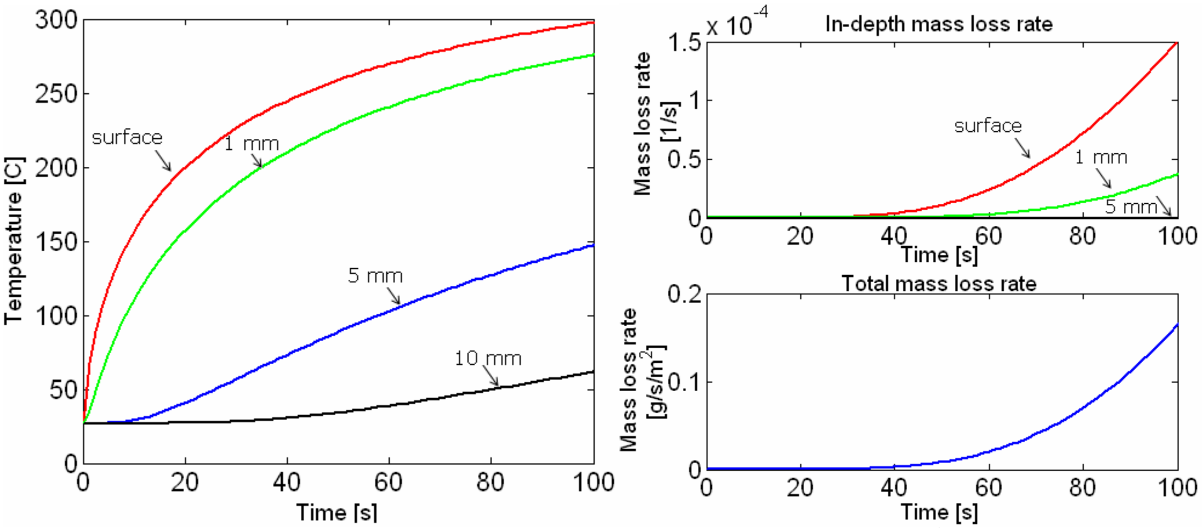

Figure 2. Predicted temperature and mass loss evolution in the PMMA slab for 40 kW/m^2 external heat flux. Left) Temperature evolution at different depths; Top right) mass loss rate at different depths; Bottom right) total mass loss rate from the slab.

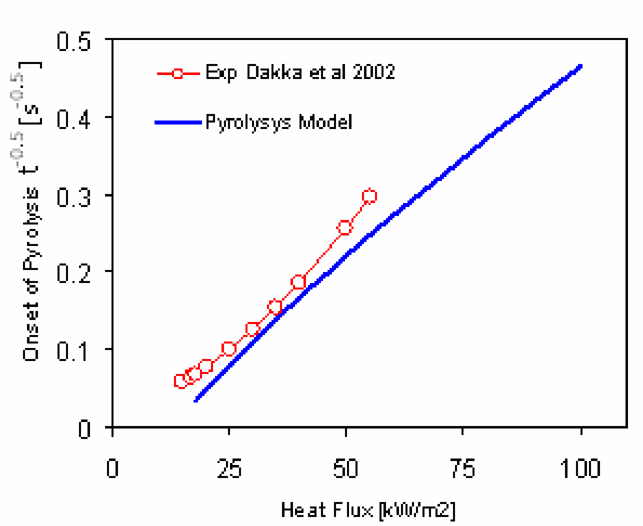

Figure 3. Comparison of predictions of the onset of pyrolysis for PMMA and measurements [3] in a wide range of external heat fluxes.

The model can be used to asses the sensitivity of the results to wide variations of the kinetic parameters. Figure 4, 5 and 6 show the effect of changing the pre-exponential factor, the activation energy and the solid yield for the one-step mechanism. The mass loss rate curve is very sensitive to the three parameters, specially the pre-exponential factor and the activation energy. As the factor increases or the activation energy decreases, the reaction rate and the mass loss rate increases following the Arrhenius dependence. This is indicative of clear potential for compensation of one parameter value with the other. A global peak value is observed in the mass loss curve of most reactive kinetics after which the mass loss rate plateaus or decreases. This peak is indicative that the top layer of the slab has largely reacted and the inert material left is acting as an insulating layer. After the peak, only charring behavior applies. Because the parameters used here are for PMMA, which is non-charring material, the predictions after the peak are not representative of PMMA but are presented only for qualitative purposes. The predicted onset of pyrolysis is weakly dependant on the solid yield value but strongly dependant on the other two parameters. As the pre-exponential factor increases or the activation energy decreases, the onset of pyrolysis decreases.

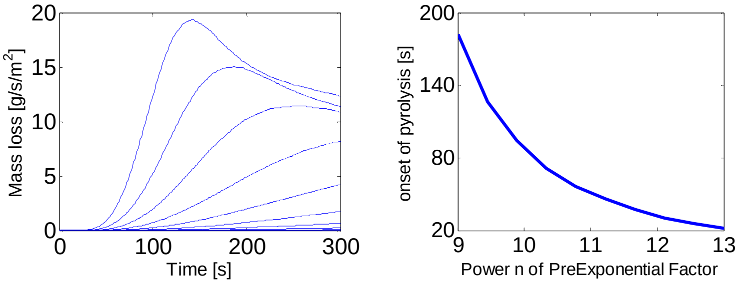

Figure 4. Sensitivity to pre-exponential factor values for 40 kW/m^2 heat flux. Left) mass loss rate vs time for factor from 1e7 to 1e13; Right) predicted onset of pyrolysis vs. power factor values.

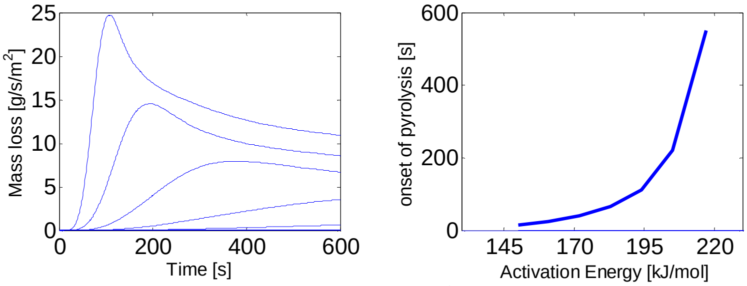

Figure 5. Sensitivity to activation energies values for 40 kW/m^2 heat flux. Left) mass loss rate vs. time for energies from 150 to 250 kJ/mol; Right) predicted onset of pyrolysis vs. energy values.

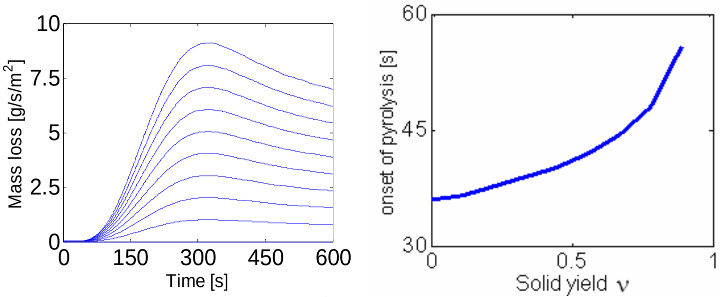

Figure 6. Sensitivity to solid yield values for 40 kW/m^2 heat flux. Left) mass loss rate vs. time for yields from 0 to 1; Right) predicted onset of pyrolysis vs. solid yield.

The effect of the two-step mechanism in the results is presented in Fig 7 for the pre-exponential factor of the second reaction Eq. (2). The results are not equivalent to those with the one-step mechanism. Two groups of resulting mass loss curves are seen; one for fast secondary reaction A_2>1e9 1/s (larger mass loss rates) and for slow secondary reaction A_2<1e6 1/s (lower mass loss rates). This behavior stems from the limiting reaction rate in the consecutive reactions. For pre-exponential factor values below 1e6 1/s, the second pyrolysis step is slower and thus limits the mass loss rate. For values above 1e9 1/s, the first step is the limiting step. This dynamics have a small effect on time for the onset of pyrolysis (results not shown) but results in a non-linear effect in the predicted peak mass loss.

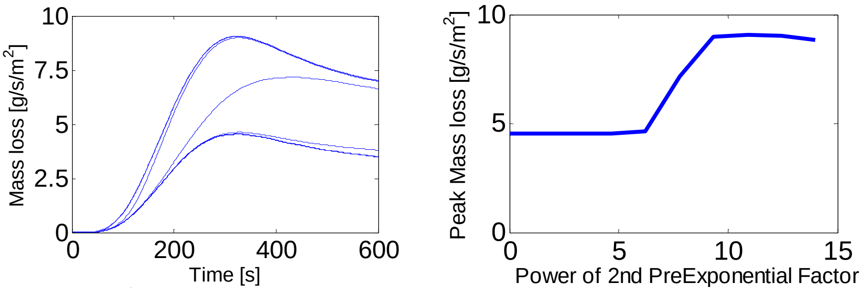

Figure 7. Sensitivity to 2nd pre-exponential factor values for 40 kW/m^2 heat flux. Left) mass loss rate vs. time for factor from 0 to 1e14; Right) peak pyrolysis rate vs. power factor values.

CONCLUSIONS

In this work, the effects of the kinetic parameters of a one-step and a two-step pyrolysis mechanisms are studied. The degradation model is combined with a simple heat transfer model to model the production of pyrolyzate before ignition. The parameter values for PMMA from Lautenger *et al.* [6] are used. The predictions for the onset of pyrolysis in wide range of heat fluxes show good agreement with the measurements for PMMA from Dakka *et al.* [3], showing that the simple model used here is capturing the thermal degradation behaviour of the slab before ignition. The predicted surface temperatures at the onset of pyrolysis show values ranging from 280 to 500 °C depending on the external heat flux, implying that the pyrolysis temperature is a non-physical concept.

The sensitivity of the results to variations of the kinetic parameters is investigated and shows that mass loss rates are very sensitive to the pre-exponential factor and the activation energy and relatively sensitive to yield values. There are patent potential for compensation between parameters and mechanisms. This is a concern when complex mathematical models are employed in the study of chemical kinetics since the estimation of kinetic parameters from thermogravimetry analysis and other experiments carries a significant uncertainty. The sensitivity of the results to the heat transfer parameters has not be investigated thoroughly here but the preliminary results (not show) indicates large temperature and mass loss variations with small parameters changes.

This paper advocates for the use of blind predictions (as done in previous studies) in combination with sensitivity studies and the identification of the simplest model that can predict the experimental data to resolve the issue of the balancing complexity in models. Results are presented here in that direction.

ACKNOWLEDGEMENTS

The author thanks the rich discussion with Jose Torero and the helpful comments of Lucas Bustamante.

REFERENCES

[1] G. Rein, CA Empis and R Carvel, The Dalmarnock Fire Tests: Experiments and Modelling, School of Engineering and Electronics, University of Edinburgh, 2007. ISBN 978-0-9557497-0-4. http://www.era.lib.ed.ac.uk/handle/1842/1152

[2] JL Torero, Flaming Ignition of Solid Fuels, in SPFE Handbook, 4th Ed, 2008 (in press).

[3] S Dakka, G Jackson, JL Torero, Mechanism controlling the degradation of PMMA prior to piloted ignition, Proceedings of the Combustion Institute 29, pp. 281–287 (2002).

[4] G Rein, C Lautenberger, AC Fernandez-Pello, JL Torero, DL Urban, Application of Genetic Algorithms and Thermogravimetry to Determine the Kinetics of Polyurethane Foam in Smoldering Combustion, Combustion and Flame 146, pp. 95-108 (2006).

[5] C Lautenberger, G Rein, AC Fernandez-Pello, The Application of a Genetic Algorithm to Estimate Material Properties for Fire Modeling from Bench-Scale Fire Test Data, Fire Safety Journal 41, pp. 204-214 (2006).

[6] C Lautenberger, AC Fernandez-Pello, A Generalized Pyrolysis Model for Combustible Solids, 5th International Seminar on Fire and Explosion Hazards, Edinburgh, UK, April 2007.

G Rein, 2008, From Pyrolysis Kinetics to Models of Condensed-phase burning, Invited Paper, in Recent Advances in Flame Retardancy of Polymeric Materials, Vol. 19, M. Lewin (ed.), BCC.