Thermal decomposition of solid fuels. Objectives, challenges and modelling

To cite this article: Thomas Rogaume 2018 J. Phys.: Conf. Ser. 1107 022001

View the article online for updates and enhancements.
Thermal decomposition of solid fuels. Objectives, challenges and modelling

Thomas ROGAUME

Institut Pprime, UPR 3346 CNRS, Université de Poitiers, ISAE-ENSMA, France

thomas.rogaume@univ-poitiers.fr

ABSTRACT

The progress of computing means, the complexity of the situation concerning fires, the need to describe with more accuracy all the different phases of the fire behaviour (such as the ignition, its growing, its extinction…) has led to a great effort in the past few years of the international research community to improve the performance of the numerical simulation codes. Those codes consist of different sub-models in order to simulate the different physical, thermal and chemical aspects of the fire, such as the thermal decomposition. This one plays a significant role on the fire evolution since it represents the fuel quantity that supplies the combustion process. Then, the requirement of a more detailed characterization and description is one actual and important challenge. This is the challenge of this keynote lecture which is dealing with thermal decomposition of solid fuels in the conditions of fire, addressing both the experimental investigations and the modelling development aspects.

After a presentation of the objectives and challenges of thermal decomposition, this lecture details the different steps required for its description, based on an experimental and numerical scaling-up approach. Examples of application are done. Special focus is highlighted on different scientific bolts and issues for thermal decomposition modelling.

KEYWORDS

Thermal decomposition, solid fuels, model of pyrolysis, scaling-up, heat transfer, mass transfer, Arrhenius, thermo-physical properties.
INTRODUCTION

The buildings, the furnishings, the material used in different applications (for example transport) have evolved considerably in the past few years, generating new challenges and requirements concerning fire safety science (complexity). Then, all around the word, fire safety engineering met a strong development. This one uses models of fire simulation, for example Fire Dynamics Simulator [1] or FireFoam [2]. Finally, the requirement of a better description of all the steps of a fire, particularly the non-established events (such as ignition, fire growing, extinction…) is principal and conductible to several works to improve those models.

The Computational Fluid Dynamics (CFD) models are composed by several sub-models, each one has specific functions: heat transfer, radiation, flows and turbulence, combustion… and pyrolysis. Specifically, the sub-model of pyrolysis permits describing the chemical evolution (reactions) of a small volume element (dV) as a function of temperature and the atmosphere (%O₂). It expresses the relation between temperature, atmosphere and the kinetic of thermal decomposition of a volume element dV of one material, which is considered at each time step homogeneous in terms of temperature and composition. Thus, the sub-model of pyrolysis permits describing the kinetic of mass loss of one solid material and then the quantity of fuel brought to the combustion. Currently nicknamed the « source term », it has a large influence on the ignition process (limits of flammability), on fire growing, on flame propagation and characteristics, on the gaseous emissions, etc.

However, the pyrolysis model is just a part of the description of the thermal decomposition process of a solid fuel, and it must be coupled to other ones in order to describe heat transfers (temperature), mass transfers (%O₂, devolatilization transfer, reactive mixture, etc.) and the boundary conditions of the volume element considered for the pyrolysis modelling.

In this context, the objective of the present contribution is to describe how to model the thermal decomposition of a solid fuel. The development of the sub-model of pyrolysis and its characteristics will be presented, as well as its coupling with other sub-models, permitting taking into account the strong coupling between the condensed and the gaseous phases and to describe the thermal decomposition of a solid. This is realized based on the scaling-up approach presenting by Torero [3] and addressing both experimental and numerical aspects. Finally, the presentation of the different steps of development of a model of thermal decomposition permits explaining the actual scientific challenges and issues.

In the first part, the challenges and the phenomenology associated with the thermal decomposition of a solid are presented. Next, the steps of the development of the model of pyrolysis are detailed, treating of the reaction mechanism, the kinetic law and the function of conversion. An attention is brought on the Arrhenius law and on the determination of the kinetic parameters associated to this one. The modelling of the heat and mass transfers requires the knowledge of the values of different thermal, physical and chemical parameters. Their investigations and limits are presented. At the end, the scaling-up validation of the model is addressed.

The different aspects are illustrated by examples of applications on several materials, at different scales.

I. DEFINITION AND PHENOMENOLOGY OF THE THERMAL DECOMPOSITION

The thermal decomposition of a solid represents its mass loss and then the quantity of combustible gases emitted and that permits the combustion to take place (or not). Thus, the coupling between the thermal decomposition of the condensed phase and the combustion into the gaseous phase is very important: thermal decomposition controls the fuel gases but is dependant of the oxygen diffusion and the heat transfers permitting the heating of the material, for its decomposition. This strong coupling is presented on figure 1 and is summarized on figure 2, inspired from [4]:
Figure 1: illustration of the coupling between the thermal decomposition and the combustion into the gaseous phase.

Figure 2: presentation of the coupling between the condensed and the gaseous phases during the combustion of a solid fuel. Inspired from [4]

It is shown that the thermal decomposition is dependant of the local oxygen concentration, the local temperature as well as the structure and the properties of the material (solid fuel) studied. Its description reclaims 3 parts: a sub-model of pyrolysis; the determination of physical, chemical and thermal properties; and the coupling with other sub-models to describe heat and mass transfers. Those 3 aspects will be addressed.

However, due to the multitude and the complexity of the phenomenon to characterize and to model, it is classical to study independently the gas phase and the condensed one. Concerning the condensed phase, the interaction with the gas one is just considered using an external heating source (classically an external heat flux) and a local diffusion of oxygen. Torero [5] proposes a monodimensional representation of the phenomenon occurring into the solid, figure 3. When a solid, initially at ambient temperature is exposed to an external heat flux ($q_i$ or $q_e$),
part of this heat flux permits the heating of the material by conduction ($\dot{q}_c$) and a part is lost by reradiation of the surface ($\dot{q}_r$ or $\dot{q}_{SR}$). Its temperature starts to increase in depth and as a function of time. If the temperature is sufficient to break the link between the condensed molecules (energy of linking), the solid starts to decompose at a flow rate ($\dot{m}_p$). The initial mass fraction of solid fuel ($Y_{F,s}$) is consumed to produce gaseous components ($Y_{F,g}$), while some oxygen can diffuse into the solid matrix ($Y_{O_2,g}$). Heat and mass transfers into the condensed phase are dependant of its permeability $\chi$.

![Diagram](image)

**Figure 3:** simplified (1 Dimension) representation of the phenomenon occurring during the thermal decomposition of a solid [5]

The energy balance of the controlled volume is defined by the equation:

$$\frac{\partial [\rho_s C_s T]}{\partial t} = \frac{\partial}{\partial x} \left[ k_s \frac{\partial T}{\partial x} \right] + \frac{\partial}{\partial x} \left[ \omega^{s}_C \rho_p C_p T_p \right] - \frac{\partial}{\partial x} \left[ \omega^{o}_C \rho_p C_p T_0 \right] + \frac{\partial}{\partial x} \left[ \rho_s V_R C_s T \right] + \dot{q}_{RAD}$$

$$+ \sum_{i=1}^{N} \Delta H_{f,i} \rho_s \left[ A_i Y^{m}_O V^{m}_F \exp^{E_i/R} \right]$$

With the last term describing the energy due to the $n$ reactions of thermal decomposition.
From figure 3, it is shown that the thermal degradation depends on as a function of time [5] - 1D approach:
- Temperature T(x,t).
- Local mass fraction of combustible, Y_s(x,t).
- Local mass fraction of oxygen, Y_O2(x,t).
- Mass fraction of residual solid fuel, Y_Fs(x,t).
- Permeability, χ(x,t).
- Thickness of oxygen diffusion into the solid, δ_O2(x,t).
- Thickness of the reactive zone, δ_F(t).
- Kinetic parameters values of each reaction, A_i, the pre-exponential factor, n, the order of the reaction i, m_i, the mass of i, E_i the energy of activation.

The mass loss rate due to the thermal decomposition is expressed locally by [5].
\[ \dot{m}_p(x,t) = \sum_{i=1}^{N} A_i Y_s^{m_i}(x,t) Y_{O2}^{n_i}(x,t) e^{-E_i/RT(x,t)} \]

And for each volume element dV [5]:
\[ \dot{m}_p(x,t) = \int_0^L \chi(x,t) \left[ Y_F(x,t) \sum_{i=1}^{N} A_i Y_s^{m_i}(x,t) Y_{O2}^{n_i}(x,t) e^{-E_i/RT(x,t)} \right] d\chi \]

The objective is thus to represent the thermal decomposition, which reclaims a model of pyrolysis, physical, chemical and thermal properties, and the description of coupling, heat and mass transfers, as presented figure 4 (inspired from [6]).

Figure 4: thermal decomposition of a solid fuel. Aspects to be represented (inspired from [6]).

In a first part, we are interested in the model of pyrolysis.

II. THE MODEL OF PYROLYSIS

The sub-model (or model) of pyrolysis expresses the chemical evolution (reactions) with the relation between temperature, atmosphere and the kinetic of thermal decomposition of a volume element dV of the material studied which is considered at each time step homogeneous in term of temperature and of composition.

Three main approaches are classically used in order to determine a model of pyrolysis [7]:
- Modelistic approach – Model fitting method: it uses a define reaction mechanism with an Arrhenius formulation. Then it requires the definition of A, E_a and n for each reaction and those terms are defined as properties of the reaction.
- Isoconvertional approach – Free model method: it permits determining the evolution of the activation energy as a function of the degree of conversion of the reaction. E_a is dependant of α (the progress of the reaction) and T. It does not use a reaction mechanism (just one reaction) but is based on an Arrhenius form. The evolution of E_a permits presenting the mass loss rate. This approach is available in the case of 1 reaction of thermal decomposition, or when the steps are clearly separated (no interaction) and chronologic (not parallel).
- The hybrid approach is a combination of the modelistic and the isoconversional one. Each peak of mass loss rate is treated with a Kissinger method.

Recently (in the past 15 years), great efforts have been made by the international scientific community in order to develop more detailed and performant models of pyrolysis, for example by Rein & al. [8], Lautenberger & al. [9-11], Stoliarov & al. [12-14], Matala & al. [15], Rogaume and Fateh & al. [16, 18-21], Bustamante Valencia [17]. Those different groups consider the model fitting method, which is used the most in the different software. Our interest will focus on the rest of this contribution through this approach. With the modelistic approach, an imposed and more or less complex model is used to represent the detail kinetic of thermal decomposition and model of pyrolysis required:

- A reaction mechanism:

\[
\dot{ω}_v = \frac{m_1}{m_2}
\]

- A kinetic law and a function of conversion. The rate of reaction of the solid phase is the multiplication of \( k(T) \), the law of variation of the rate and \( f(\alpha) \), the function of conversion. The variation of the rate is classically represented by a modified Arrhenius function. Thus:

\[
\frac{dα}{dt} = k(T) f(α) = A \exp\left(-\frac{E}{RT}\right) f(α)
\]

with \( T \) the temperature, \( α \) the progress of the reaction, \( E \) the energy of activation, \( A \) the pre-exponential factor and \( R \) the constant of the perfect gases.

### 2.1. Determination of the reactional mechanism

Four main methods are used to determine the reactional mechanism of thermal decomposition of a solid:

- The lumped parameter approach (LPA) considers that the material is one, homogeneous. The thermal decomposition is the one of this material.

- The constituent approach considers that a material is composed of several constituents and that its thermal decomposition is the sum of the one of each component – Example: wood is composed of cellulose, hemicellulose and lignin, so its mechanism of thermal decomposition is the one of the cellulose, the one of the lignin and the one of the hemicellulose. This approach is quite simple, but it neglects the facts that can cause some interactions between the constituents. This is the case for the wood…

- The functional approach. The thermal decomposition is described as functional groups, due to the well-known fragmentation of the polymers. This last one is very precise but time consuming and it requires a well knowledge of the polymer decomposition steps [7].

- The last one consists of describing all the elementary reactions of thermal decomposition, as it is classically done for the reactions into the gas phase. One example is presented into [22]. However due to the complexity of the solid structures and of the thermal decomposition it is inapplicable for safety science engineering and multicomponent materials for example.

Then, it currently appears that the LPA approach is the more acceptable and it has been used by several authors [4, 8-21]. It relies on the use of results of thermal decomposition of the solid studied from thermogravimetric analysis, which can be coupled to detailed gas analysis, like a Fourier transformed infra-red spectrometer, gas chromatography or mass spectrometer. During those experimental investigations, very small samples of solid (few mm and mg) are heating up under a controlled atmosphere (inert, oxygen %) from the ambient temperature to several hundred degrees (1000°C) at a controlled heating rate, classically from 5 to 20°C/min. The mass loss is measured as a function of the time and (knowing the heating rate) the temperature, as well as the gaseous emissions (if possible). The mass loss rate is secondly deducted.

The evolutions of the mass loss and the mass loss rate obtained for different experimental conditions permit the determination of the reactional mechanism.

For example, the thermal decomposition of a polyurethane foam is studied [16]. Figure 5 presents respectively the evolution of the mass loss and of the mass loss rate, for two atmospheres and four heating rates [16].
Figure 5: evolution of the mass loss and the mass loss rate during the thermal decomposition of a PU foam at TGA scale [16].

From those results, it is shown that the thermal decomposition of the PU foam is taking place by 2 global reactions of pyrolysis (under inert atmosphere) and 3 more reactions under air (oxidation). Those reactions are presented into the table 1 [16].

| No | Type of reaction | Temp. [°C] | Reactives | Products solid or liquid | Products gas |
|----|------------------|------------|-----------|-------------------------|--------------|
| 1  | Pyrolysis        | 200 – 340  | PPUF      | $\tau_1$ [Isocyanate]   |              |
| 2  | Pyrolysis        | 340 – 450  | Polyol    | $\tau_2$ [Polyol + H₂O + CO₂ + CH₄] |              |
| 3  | Oxidation        | 200 – 275  | PPUF + O₂ | $\tau_3$ [Polyol + CO₂ + H₂O] |              |
| 4  | Oxidation        | 220 – 300  | Polyol + O₂ | $\tau_4$ [Polyol + H₂CO + CH₄ + CO + CO₂ + H₂O] |              |
| 5  | Oxidation        | 300 – 450  | Char + O₂ | $\tau_5$ [Polyol + H₂CO + CH₄ + CO + CO₂ + H₂O] |              |

Table 1: reactions of thermal decomposition of a PU foam [16]

The main challenge consists of determining a more realistic mechanism, and classically several can be proposed [17]. The evolutions of the gaseous emissions are thus of best importance. The accuracy of modelistic approaches does not depend on the resolution technique, but rather on the description of the apparent chemical reaction pathway. It is then interesting to focus on the complexity level of the reaction mechanism, which has been done by Marquis & al. [23]. Several mechanisms complexity with various levels of sophistication (number of linked reactions) are studied using a new statistical technique. The analysis shows the possibility to simplify the initial reaction mechanism’s complexity, without influencing the accuracy of forecasts.

From the reactions analysis, the reactional mechanism of the PU foam proposed by [16] is (Figure 6):

Figure 6: mechanism of thermal decomposition of a PU foam [16]
2.2. Determination of the kinetic law

The rate of reaction of the solid phase is the multiplication of \( k(T) \), the law of variation of the rate and \( f(\alpha) \), the function of conversion. The variation of the rate is classically represented by a modified Arrhenius function.

\[
\frac{d\alpha}{dt} = k(T) f(\alpha) = A \exp \left( -\frac{E}{RT} \right) f(\alpha)
\]

with \( T \) the temperature, \( \alpha \) the progress of the reaction, \( E \) the energy of activation, \( A \) the pre-exponential factor and \( R \) the constant of the perfect gases.

The model-fitting method is expressed in terms of the degree of conversion: equal to 0 at the beginning of the test and to 1 when all the mass has been decomposed. The degree of conversion is defined as:

\[
\alpha = \frac{m_0 - m_i(t)}{m_0 - m_\infty}
\]

With \( m_0 \) the mass at the beginning, \( m_i(t) \) the mass at an arbitrary time, \( m_\infty \) the mass at the end of the process.

Different functions of conversion can be used [7], some are presented into the table 2:

| Model          | \( f(\alpha) \) |
|----------------|------------------|
| Batch 0        | 1                |
| 1st order      | \( 1 - \alpha \) |
| 2nd order      | \( (1 - \alpha)^2 \) |
| 3rd order      | \( (1 - \alpha)^3 \) |
| nth order      | \( (1 - \alpha)^n \) |
| Exponential law| \( \alpha \)      |

*Tableau 2: Different functions of conversion into the model of pyrolysis, from [7]*

Classically the function \( f(\alpha) = (1 - \alpha)^n \) is used, since it is adequate to represent only the kinetic aspect, with \( n \) which may be linked to a degree of complexity of the solid studied, for example the degree of polymerization.

Special attention: sometime, physical phenomena are indistinguishable from the kinetic, and it is necessary to use a different conversion functions. It can be the case considering the oxygen diffusion into the solid, which impacts the kinetic of decomposition (cf Jander):

\[
f(\alpha) = \left( 1 - (1 - \alpha)^{3/2} \right)^2
\]

Concerning the rate of the reactions, it is described by a modified (for solid application) law of Arrhenius. Then, the rate of each reaction is: \( \dot{\omega} = k(T). f(\alpha) \):

\[
\dot{\omega} = A e^{-\frac{Eam}{RT}}
\]

with \( A \) the pre-exponential factor, \( E_a \) the energy of activation, \( R \) the constant of perfect gases, \( T \) the temperature, \( m \) the mass, \( n \) the order of the reaction.
During this study, the 4i so 20 unknown parameters have been determined by using inverse optimisation methods, described below.

Each reaction of the reactional mechanism has a rate $\dot{\omega}_i$ defined by an Arrhenius law of the form:

$$\dot{\omega}_i = A_i e^{-\frac{E}{RT}} \left( \frac{m_i}{m_e} \right)^{b_i}$$

From those expressions, the total mass loss rate of the solid (MLR$_i$) or $\frac{dm_t}{dt}$ is expressed by the sum of the mass loss rate due to the i reactions of the reactional mechanism:

$$MLR_t = \frac{dm_t}{dt} = \sum_{j=l} v_j \omega_j = \sum_{k=K} \omega_k$$

With $m_t$ the mass of the intermediate compounds, and i the number of intermediate species, J the number of reactions of thermal decomposition of the mass I and K the number of reactions permitting the gain of mass i. If $m_t$ the total mass, so

$$\frac{dm_t}{dt} = \sum_{i=1}^l \frac{dm_i}{dt}$$

The rate of the reaction revealed four unknown parameters for each reaction: A the pre-exponential factor, $E_a$ the energy of activation, n the order of the reaction and $\nu$ the stoichiometric coefficient. The determination of those parameters cannot be done experimentally [21], and is realised using inverse methods of optimization. Different methods are proposed, there are compared into [26-27]. Let us quote by example: the genetic algorithms (GA) [28], the Genetic Algorithms Simulated Annealing, the Stochastic Hill Climber, the Shuffled Complex Evolution [29] or the particle swarm [30]. There are applied to the mass loss and (not systematically) to the mass loss rate evolutions. There use an evaluation function permitting to estimate the convergence between the numerical solutions obtained with the optimised parameters and the experimental ones. Different evaluation functions $\phi$ are proposed as a function of the authors [8, 17, 31] and it is shown that this one have an influence on the solutions obtained [17, 21].

Considering the example of application presented figures 5 and 6 and the table 1, the total mass loss rate of the polyurethane foam [16] is:

$$\frac{dm}{dt} = \sum_{i=1}^4 MLR_i = \frac{dm_{PUR}}{dt} + \frac{dm_{Polyol}}{dt} + \frac{dm_{Char}}{dt} + \frac{dm_{Residue}}{dt}$$

So:

$$\frac{dm}{dt} = (v_1 - 1)\omega_1 + (v_2 - 1)\omega_2 + (v_3 - 1)\omega_3 + (v_4 - 1)\omega_4 + (v_5 - 1)\omega_5$$

With each reaction having a rate:

$$\dot{\omega}_i = A_i \exp \left( \frac{-E_i}{RT} \right) m_i^{n_i}$$

During this study, the 4i so 20 unknown parameters have been determined by the Genetic Algorithms method [16]. The values obtained are presented into the table 3.
Table 3: kinetic parameter values of the different reaction of thermal decomposition of a PU foam [16]

The figure 7 presents the comparison between the experimental and the numerical mass loss rate evolutions [16].

![Figure 7: comparison of the experimental and the numerical mass loss rate evolutions [16]](image_url)
The results show a very good agreement, the pyrolysis model (and then the reactional mechanism and the kinetic parameters) are validated at this particular scale, the matter one. However, just the kinetic aspect of the thermal decomposition is represented and it is now necessary to be able to represent the thermal behaviour of a real fuel, considering the thermal and mass transfers. A scaling-up approach is used, it requires notably the determination of several thermo-physical properties of the fuel studied.

### III. DETERMINATION OF THE THERMO-PHYSICAL PROPERTIES

In order to be able to simulate the heat and mass transfers during the thermal decomposition of a solid, it is necessary to determine different thermo-physical properties:

- The thermal conductivity \( k \). This can be done by the flash method, or using guarded hot plate.
- The density \( \rho \).
- The specific heat \( C_p \), using a differential scanning calorimetry.
- The enthalpies of the reactions \( \Delta H \), using a differential scanning calorimetry.
- The radiative properties (emissivity, absorptivity), using and infra-red and a thermal camera approach, as done in [32-33].
- The heat of combustion, using a bomb calorimeter.

However, it is very important to note that those properties must be determined for all the intermediate compounds formed throughout the thermal decomposition. Taking the example of the PU foam, which means that \( k, \rho, C_p, \Delta H, \epsilon \ldots \) must be determined for the initial PU foam (PPUF), the “Polyol”, the Char and the Residue. The determination of the certainty of those properties is one of the main actual problems faced by the international community, due to several reasons:

- The experimental limitations: indeed, for several parameters, the experimental investigations are not adequate and show major limitations. For example:
  - It is very difficult to measure the conductivity \( k \) on porous matrix.
  - It is not possible to measure \( k \) and \( C_p \) after a certain temperature, the one of thermal decomposition. Indeed, the gaseous emissions generated by the thermal decomposition will affect irreversibly the set-up used.

Some authors used a TGA/DSC apparatus for the determination of \( C_p \) and \( \Delta H \), however it is shown that the precision of the measure is quite low and the \( C_p \) value has to be corrected by the mass loss.

- The possibility to isolate each intermediate compounds in order to be able to realize the measurements of those properties. In fact, it is very difficult to isolate and to extract the condensed materials formed during the thermal decomposition process, with notions of superposition of the reactions and so of the compound formed for same temperature range. A solution should be to decompose the solid until the temperature of formation of each intermediate compound, if possible, and to stop the test. This may permit isolating each compound. Nevertheless, when cooling, the structure of the material will be modified, and that will make an important impact on the measurements.

New experimental approaches are actually developed by the team of S. Stoliarov in the University of Maryland, using for example the micro-calorimeter set-up to determine the heat of combustion or of thermal decomposition [34-35], or the Controlled Atmosphere Pyrolysis Apparatus (CAPA) to deduce the conductivity [36-37]. However, if the first method gives encouraging results, it does not permit isolating and determining the properties values for each intermediate compounds and it can, then, just be applicable in case of one mechanism of thermal decomposition with only one reaction. Concerning the second one (CAPA), it is limited to specific materials and conditions (gasification).

Then it appears to be very difficult to experimentally determine certain of those parameters, as \( k, \rho, C_p, \Delta H \). Two alternative solutions are actually used:

- The parameters are determined by inverse optimization methods, for example using Gpyro [10]. Nevertheless, this solution cannot be considered satisfactory, because this is like the addition of some degrees of liberty, some mathematical fitting methods with more variables, the thermochemical properties. Moreover a compensation phenomenon can be observed due to the large unknown parameters (the kinetics and the thermochemical ones). Finally, the values obtained can have no physical sense.
- Classically « weighting (average) law » are used to determine the value of the thermos-physical properties, between the properties of the initial material and the ones of the final one:
  - Or, equivalent properties are taken for all the intermediate compounds, as for just one equivalent material.
o Or, a linear evolution of the properties between the initial and the final materials is considered. An example is presented into [38].

Special attention: the determination of the thermo-physical properties for the total range of temperature of the thermal decomposition, and for all the intermediate compounds into the kinetic mechanism is essential for the modelling of the thermal decomposition. However, it is one of the main bottlenecks actually, requiring huge efforts of the scientific community.

IV. MODELLING OF THE THERMAL DECOMPOSITION – SCALING-UP

As presented before, notably on figures 1 and 2, the challenge remains the modelling of the thermal decomposition at real scale, then considering the interactions between both the condensed and the gaseous phases. This requires the description of the heat and mass transfers between these two. The scaling-up approach presented by [5] and adopted by [4, 17, 39] is used: it is based on experimental investigations to determine the initial and boundary conditions for the simulation, and to furnish results permitting a comparison with the numerical ones, for the validation (or not) of the model.

Several bench scales are classically used with the principle consisting of the addition of complexity in increasing scale:

- Firstly, at small scale, using the cone calorimeter [40], the Fire Propagation Apparatus [41] or the Controlled Atmosphere Pyrolysis Apparatus [36-37]. This permits to work in one-dimension, with heat and mass transfers but without a flame propagation.
- At product scale, using for example the radiant panel, the IMO-LIFT [42], the Medium Burning Item [43], the Single Burning Item [44], permitting some investigation in two and three dimensions, with a flame propagation.
- At real scale, like realised for example by [45-46].

The modelling approaches use dedicated codes, like Gpyro [10-11] or Thermakin [12-13], or consists of the implementation of the model of pyrolysis and the thermo-physical properties previously presented in a generalized CFD code, like FDS [1] or Firefoam [2] and to simulate the experimental configurations studied.

Several studies consider those different approaches and just some examples are given. Considering the PU Foam previously studied at matter scale, the works of [47] have permitted its characterization using the cone calorimeter coupled with several gas analysers. Some results are presented on figure 8 for the mass loss rate (MLR) and the Heat Release Rate (HRR) [47].

![Figure 8: MLR and HRR evolution during the thermal decomposition of a PU Foam using the cone calorimeter [47]](image)

Dealing with the PU foam in their study of the behaviour of a railway seat, Guillaume & al. [39] have simulated, at the specific condition of 50kW/m², the cone calorimeter experiments. In this study, the model of pyrolysis and the thermo-physical properties have been introduced into the FDS code. The results obtained concerning the Heat Release Rate are presented on figure 9 [39]. The results show a good agreement permitting to validate the model at this scale.
Figure 9: numerical and experimental evolutions of the HRR evolution during the thermal decomposition of a railway seat using the cone calorimeter [39]

If classically, the mass loss rate, the mass loss rate and the heat release rate are considered for the validation of the model, the work of Fateh & al. [48] shows that it is necessary to consider other parameters, like the temperature evolutions in the depth of the material and the thickness evolution of the intermediate compounds.

At a higher scale, Guillaume & al. [39], in their scaling-up validation of the model - to represent the thermal decomposition of a railway seat, have modelled some tests using the single burning item. The figure 10 [39] is presenting the comparison of the numerical and the experimental HRR evolutions at the Single Burning Item scale. A good agreement is obtained.

Figure 10: Numerical and experimental evolutions of the HRR evolution during the thermal decomposition of a railway seat using the single burning item [39]

CONCLUSION

The description of the thermal decomposition of the solid fuels is of the best interest and importance. It has a large influence on the ignition process, the kinetic of the fire development, its extinction and on the characteristics of the flame and its propagation.

The thermal decomposition is controlled by the phenomena taking place into the condensed phase but is dependent of the heat and the mass transfers associated to the gaseous phase. Thus, its description requires the
development of a model of pyrolysis which simulate the kinetic of decomposition of the solid phase, the
determination of the thermo-physical properties of the condensed compounds, and, finally, the description of
the heat and mass transfers which determine the conditions of the degradation. Then, different steps are required
to model the thermal decomposition of a solid.

Different methods are used to develop a model of pyrolysis, however, the modelistic one is used the most. It
requires a mechanism of thermal decomposition and a kinetic law, which - is composed by a function of
conversion and by a law of variation of the rate, adopting a modified Arrhenius form. The development and
the validation of the model of pyrolysis is realized at matter scale, using thermogravimetric analysis.

The determination of the values of the thermo-physical properties is necessary for the modelling of the heat and
mass transfers into the condensed phase but it remains an important challenge.

The modelling of the thermal decomposition is realised by a scaling up approach, permitting furnishing
experimentally the initial and boundary conditions as well as results for the model application and development.

ACKNOWLEDGMENTS

The author wishes to thank: the “Institut des Risques Industriels Assurantiels et Financiers” for their technical
and human support into the HESTIA platform ; his colleagues, particularly Benjamin Batiot, Jocelyn Luche,
Marc Poisson and Franck Richard ; his past and present PhD students.

REFERENCES

[1] FDS – Fire Dynamics Simulator and Smokeview. NIST, 100 Bureau Drive, Gaithesburg, MD, USA
http://www.fire.nist.gov/FDS
[2] FireFOAM, http://www.openfoam.org/. FM Global, http://code.google.com/p/firefoam-dev/.
[3] Torero J., Scaling up fire. Proceedings of the Combustion Institute, 34:99-124, 2013.
[4] Marquis D., Caractérisation et modélisation multi-échelle du comportement au feu d’un composite pour son
utilisation en construction navale. Thèse de doctorat, Université de Nantes, Ecole des Mines de Nantes, 2010.
[5] Torero J.L., Flaming ignition of solids fuels, SFPE Handbook of fire protection Engineering 4th edition,
National fire protection association, 2.260–2.276, 2008.
[6] Marquis D. & al. Impact de la connaissance des propriétés matériaux dans les simulations incendies – GDR
Feux, LEMTA Nancy 2011.
[7] Witkowski A, Stec A. Hull R., Thermal decomposition of polymeric materials. SFPE Handbook of fire
protection engineering, 5th edition, 167-254, 2016.
[8] Rein G., Lautenberger C., Fernandez Pello A.C., Torero J.L., Urban D.L., Application of genetic algorithms
and thermogravimetry to determine the kinetics of polyurethane foam in smoldering combustion.
Combustion and Flame, 146, p. 95-108, 2006.
[9] Lautenberger C., Rein G., Fernandez-Pello A.C. – The application of a genetic algorithm to estimate
material properties for fire modeling from Bench-Scale Fire Test Data. Fire Safety Journal, vol. 41, p. 204-
214, 2006.
[10] Lautenberger C. – Gpyro – A generalized pyrolysis model for combustible solids. Users’ Guide (2009)
http://code.google.com/p/gpyro/.
[11] Lautenberger C., Fernandez-Pello A.C. Generalized Pyrolysis Model for Combustible Solids. Fire Safety
Journal, vol. 44, pp. 819–839, 2009.
[12] Stoliarov S., Crowley S., Walters R.N., Lyon R.E. – Prediction of the burning rates of charring polymers.
Combustion and Flame, vol. 157-11, p. 2024-2034, 2010.
[13] Stoliarov S., Leventon I.T, Lyon R.E., Two-dimensional model of burning for pyrolyzable solids. Fire and
Materials, vol. 38, pp. 391-408, 2014.
[14] Stoliarov S. Parameterization and Validation of Pyrolysis Models for Polymeric Materials. Fire
Technology, vol. 52-1, pp 79–91, 2016.
[15] Matała A. Estimation of solid phase reaction parameters for fire simulation (Master’s thesis). Helsinki
University of Technology, Finland, 2008.
[16] Rogaume T., Bustamante Valencia L., Guillaume E., Richard F., Luche J., Rein G., Development of the
thermal decomposition mechanism of polyether polyurethane foam using both condensed and gas phase
release data. Combustion Science and Technology, vol. 183, pp. 627-644, 2011.
[17] Bustamante Valencia L. Experimental and numerical investigation of the thermal decomposition of materials at three scales: application to polyether polyurethane foam used in upholstered furniture. PhD thesis, Université de Poitiers, Ecole Nationale Supérieure de Mécanique et d’Aérotechnique, 2009.

[18] Fateh T., Rogaume T., Luche J., F. Richard, Jabouille F. Kinetic and mechanism of the thermal degradation of a plywood by using thermogravimetry and Fourier-transformed infrared spectroscopy analysis in nitrogen and air atmosphere. Fire Safety Journal, vol. 58, pp. 25-37, 2013.

[19] Fateh T., Rogaume T., Luche J., F. Richard, Jabouille F. Modeling of the thermal decomposition of a treated plywood from thermo-gravimetry and Fourier-Transformed Infrared Spectroscopy experimental analysis. Journal of Analytical and Applied Pyrolysis, vol. 101, pp. 35-44, 2013.

[20] Fateh T., Rogaume T., Richard F., Joseph P. Experimental and modelling studies on the kinetics and mechanisms of thermal degradation of poly (methyl methacrylate) in nitrogen and air. Journal of Analytical and Applied Pyrolysis, vol.120, pp. 423-433, 2016.

[21] Batiot B. Étude et modélisation de la cinétique de décomposition thermique des matériaux solides. Application à la dégradation du bois en cas d’incendie. Thèse de doctorat, Université de Poitiers, Ecole Nationale Supérieure de Mécanique et d’Aérotechnique, 2014.

[22] Gascoin N., Navarro-Rodriguez A., Gillard P., Mangeot A., Kinetic modelling of high polyethylene pyrolysis : Part1. Comparison of existing methods. Polymer degradation and stability, vol. 97, pp. 1466-1474, 2012

[23] Marquis D., Batiot B., Guillaume E., Rogaume T., Influence of reaction mechanism accuracy on the chemical reactivity prediction of complex charring material in fire condition. Journal of analytical and applied pyrolysis, vol. 118, pp. 231-248, 2016.

[24] Batiot B., Collin A., Richard F., Rogaume T. Sensitivity and uncertainty analysis of Arrhenius parameters in order to describe the kinetic of solid thermal degradation during fire phenomena. Fire Safety journal, vol. 82, pp. 76-90, 2016.

[25] Marquis D., Guillaume E., Camillo A., Rogaume T., Richard F. Existence and uniqueness of solutions of a differential equation system modelling the thermal decomposition of polymer materials. Combustion and Flame vol. 160, Issue 4, pp. 818-829, 2013.

[26] Lautenberger C., Fernandez-Pello C., Optimization Algorithms for Material Pyrolysis Property Estimation, Proceedings of 11th IAFSS, 2011

[27] Siarry P., Dréo J., Pétrowski A., Taillard E. Métapeuristiques pour l’optimisation difficile. Ed Eyrolles, ISBN13: 978-2-212-11368-6, 2003.

[28] Houck C., Joines J., A genetic algorithm for function optimization: a matlab implementation. North Carolina State University Edward P. Fitts Department of Industrial and Systems Engineering Report NCSU IE TR 95-09, 1995.

[29] Duan Q.Y., Gupta V.K., Sorooshian S., Shuffled Complex Evolution Approach for Effective and Efficient Global Minimization. Journal of Optimization Theory and Applications, Vol. 76:501-521, 1993.

[30] Eberhart R., Kennedy J. A new optimizer using Particle Swarm Theory. Sixth international Symposium on Micro Machine and Human Science, 1995.

[31] Esperanza M., Garcia A., Font R., Conesa J. Pyrolysis of varnish based on a polyurethane. Journal of Analytical and Applied Pyrolysis 52: 151-166, 1997.

[32] Boulet P., Parent G., Acem Z., Rogaume T., Fateh T., Zaida J., Richard F., Characterization of the radiative exchanges when using a cone calorimeter for the study of the plywood pyrolysis. Fire safety journal vol. 51, pp. 53-60, 2012.

[33] Acem Z., Brissinger D., Collin A., Parent G., Boulet P., Quach T.H.Y., Batiot B., Richard F., T. Rogaume T., Surface temperature on a carbon composite sample during thermal degradation. International Journal of Thermal Sciences, vol. 112, pp.427-438, 2017.

[34] Stoliarow S., Raffan-Montoya F., Walters R., Lyon R.E., Measurement of the global kinetics of combustion for gaseous pyrolyzates of polymeric solids containing flame retardants. Combustion and flame, vol.173 Issue 1, 2016.

[35] Ding Y., McKinnon M.B., Stoliarow S.L., Fontaine G., Bourbigot S. Determination of kinetics and thermodynamics of thermal decomposition for polymers containing reactive flame retardants: Application to poly(lactic acid) blended with melamine and ammonium polyphosphate. Polymer Degradation and Stability, Volume 129, pp. 347-362, 2016.
[36] Semmes M, Liu X, McKinnon MB, Stoliarov SI, Witkowski A. A model for oxidative pyrolysis for corrugated cardboard. In: Proceedings of the Eleventh International Symposium on Fire Safety Science; 2014.

[37] Swann J.D., Ding Y., McKinnon M.B., Stoliarov S.I., Controlled atmosphere pyrolysis apparatus II (CAPA II): A new tool for analysis of pyrolysis of charring and intumescent polymers. Fire Safety Journal, Vol. 91, pp. 130-139, 2017.

[38] Linteris G.T., Lyon R.E., Stoliarov S.I., Prediction of the gasification rate of thermoplastic polymers in fire-like environments. Fire Safety Journal, Volume 60, pp. 14-24, 2013.

[39] Guillaume E., Camillo A., Rogaume T., Application and Limitations of a Method Based on Pyrolysis Models to Simulate Railway Rolling Stock Fire Scenarios. Fire Technology, 50, pp. 317-348, 2014.

[40] ISO 5660-1:2002, Reaction to fire tests – Heat release, smoke production and mass loss rate – Part 1 Heat release rate (cone calorimeter method). Second edition 2002.

[41] ISO 12136:2011, Reaction to fire tests -- Measurement of material properties using a fire propagation apparatus.

[42] ISO 5658-2:2006, Reaction to fire tests - Spread of flame - Part 2: Lateral spread on building and transport products in vertical configuration.

[43] ISO 21367:2007, Plastics - Reaction to fire - Test method for flame spread and combustion product release from vertically oriented specimens.

[44] EN 13823:2014, Reaction to fire tests for building products – Building products excluding flooring exposed to the thermal attack by a single burning item.

[45] The Dalmarnock Fire Tests: experiments and modelling, (Eds.) G. Rein, C. Abecassis Empis, R. Carvel, University of Edinburgh, November, 2007, ISBN 978-0-9557497-0-4.

[46] Guillaume E., Didieux F., Thiry A., Belivier A., Real-scale Fire Tests of One Bedroom Apartments with Regard to Tenability Assessment, Fire safety journal, vol. 70, pp. 81-97, 2014.

[47] Bustamante Valencia L., Rogaume T., Guillaume E., Rein G., Torero J.L., Analysis of principal gas products during combustion of polyether polyurethane foam at different irradiance levels. Fire Safety Journal, vol. 44, issue 7, pp. 933-940, 2009.

[48] Fateh T., Rogaume T., Richard F., Modeling of the pyrolysis of plywood exposed to heat fluxes under cone calorimeter. 11th International Symposium on Fire Safety Science, 2014.