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# Thermal decomposition and Pyrolysis of solid fuels: Objectives, challenges and modelling

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## ABSTRACT

The need to describe the complexity of the situation concerning fires with more accuracy and taking all the different phases of the fire behaviour (such as the ignition, its growing, its extinction...) into consideration, has led to a great effort from the international research community in the past few years to improve the performance of the numerical simulation codes. These 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 plays a significant role on the fire ignition and its evolution since it represents the fuel quantity supplied to the combustion process.

Then, the requirement of a more detailed characterization and description is one actual and important challenge. This is the objective of this article which deals with pyrolysis 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 pyrolysis, this article details the different steps required for its description, based on an experimental and numerical scaling-up approach. Examples of application are explained. Special focus is given on different scientific bolts, issues and challenges for pyrolysis modelling.

## KEYWORDS

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

## Nomenclature

$A_i$	Pre-exponential factor of the reaction $i$	$[s^{-1}]$
$C_s$	Solid material specific heat	$[kJ \cdot kg^{-1} \cdot K^{-1}]$
$dV$	Volume element	$[-]$
$E_i$	Apparent activation energy of the reaction $i$	$[kJ \cdot mol^{-1}]$
$HRR$	Heat release rate per unit area	$[kW \cdot m^{-2}]$
$L$	Thickness	$[m]$
$m$	Mass	$[kg]$
$m_0$	Initial mass of solid	$[kg]$
$m_\infty$	Mass at the end of the thermal decomposition	$[kg]$
$m_i(t)$	Mass at an arbitrary time	$[kg]$
$\dot{m}_p$	Mass-flow rate of pyrolysis	$[g \cdot s^{-1}]$
$\dot{m}_p''$	Mass flow rate of pyrolysis per unit area	$[g \cdot s^{-1} \cdot m^{-2}]$
$\dot{m}_{O_2}$	Mass-flow rate of oxygen	$[g \cdot s^{-1}]$
$\dot{m}_{O_2}''$	Mass flow rate of oxygen per unit area	$[g \cdot s^{-1} \cdot m^{-2}]$
$MLR$	Mass Loss Rate	$[g \cdot s^{-1}]$
$n_i$	Reaction order of the reaction $i$	$[-]$
$N$	Number of reaction of thermal decomposition	$[-]$
$\dot{q}_i$	Incident external heat flux	$[kW]$
$q_e''$	Incident external heat flux per unit area	$[kW \cdot m^{-2}]$
$\dot{q}_c$	Conductive heat flux	$[kW]$
$\dot{q}_{cv}''$	Convective heat flux	$[kW]$
$q_{cv}$	Convective heat flux per unit area	$[kW \cdot m^{-2}]$
$\dot{q}_r''$	Reradiative heat flux	$[kW]$
$q_{SR}''$	Reradiative heat flux per unit area	$[kW \cdot m^{-2}]$
$R$	Universal constant of gases equal to 0.082	$[l \cdot atm \cdot mol^{-1} \cdot K^{-1}]$
$T$	Temperature	$[K]$
$T_0$	Initial temperature of the air	$[K]$
$T_p$	Temperature of the solid at the back face	$[K]$
$V_R$	Regression rate	$[m \cdot s^{-1}]$
$x$	Distance	$[m]$
$Y_i$	Mass fraction of gas emissions due to reaction $i$	$[g \cdot g^{-1}]$
$Y_s$	Mass fraction of solid fuel	$[g \cdot g^{-1}]$
$Y_{F,s}$	Initial mass fraction of solid fuel	$[g \cdot g^{-1}]$
$Y_{F,g}$	Gaseous mass fraction of combustible	$[g \cdot g^{-1}]$
$Y_{O_2,g}$	Oxygen mass fraction in the gas	$[g \cdot g^{-1}]$
$Y_{O_2}$	Oxygen mass fraction	$[g \cdot g^{-1}]$
$\Delta H$	Enthalpy of the reaction	$[kJ \cdot kg^{-1}]$
$\alpha$	Progress of the reaction	$[-]$
$\beta$	Heating rate	$[^{\circ}C \cdot min^{-1}]$
$\rho_s$	Density of the solid	$[kg \cdot m^{-3}]$
$\delta_{CH}$ or $\varepsilon_{CH}$	Thickness corresponding to the chemical zone	$[m]$
$\delta_p$ or $\varepsilon_p$	Thickness affected by the thermal decomposition	$[m]$
$\delta_T$ or $\varepsilon_T$	Thickness thermally affected	$[m]$
$\delta_{O_2}$ or $\varepsilon_{O_2}$	Thickness of oxygen diffusion into the solid	$[m]$
$\delta_F$ or $\varepsilon_F$	Thickness of the reactive zone	$[m]$
$\tau_i$	Stoichiometric coefficient of the reaction $i$ of gas emissions	$[-]$
$\dot{\omega}$	Rate of the reaction	$[s^{-1}]$
$\delta$	Reaction order for oxygen mass fraction	$[-]$
$\vartheta_i$	Stoichiometric coefficient of a solid or liquid product of reaction $i$	$[-]$
$\chi$	Equivalent permeability function	

## INTRODUCTION

The material used in the buildings, furnishings and in different applications (for example transport) have evolved considerably in the past few years, generating new challenges and requirements concerning fire safety science (complexity). In parallel, the progress of the experimental investigations, computational capacities, as well as the knowledge permit to take into account and to describe other and more complex phenomena.

All around the world, fire safety engineering made a strong progress in developing the fire simulation models. For example, Fire Dynamics Simulator [1] or FireFoam [2]. Finally, the requirement of a better description of all the steps of 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 to solve: 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 ( $dV$ ) of the material as a function of temperature and atmosphere ( $\%O_2$ ). It expresses the relation between temperature, atmosphere and the kinetic's of thermal decomposition, which is considered as homogeneous at each time step in terms of temperature and composition. Thus, the sub-model of pyrolysis permits describing the kinetic of mass loss of a solid material and then the quantity of fuel brought to the combustion, currently nicknamed as the « source term ». It has a large influence on the ignition process (limits of flammability), growing fire, flame propagation and characteristics, gaseous emissions, extinction, etc.

However, the thermal decomposition model is just a part of the pyrolysis process of a solid fuel and it must be coupled to other ones in order to describe heat transfers (temperature), mass transfers ( $\%O_2$ , devolatilization transfer, reactive mixture, etc.) and the boundary conditions of the volume element considered for the pyrolysis modelling.

Classically four models of pyrolysis are proposed. They are empirical, thermal, polynomial and finally comprehensive models:

- With the empirical models, the methodologies are based on analysis of small-scale experimental data for extrapolation to larger scale experiments. Classically bench-scale data are extrapolated to larger scales due to the fact that results are expressed in relation to the surface of the material (surfacic assumption): mass loss rate, heat release rate and incident radiation are commonly expressed per unit area. Moreover, it is considered that no mass loss occurs before the surface has reached a critical ignition temperature.
- Thermal models increase the level of complexity. Reaction rates are not included in the thermal pyrolysis model however pyrolysis is represented by heat transfer rates. Decomposition is assumed to start when the material-dependent pyrolysis temperature is reached. Mass loss rate is mathematically determined by solving an energy balance at the thin pyrolysis front, and the chemical kinetic is not considered.
- The polynomial pyrolysis models are categorized as an intermediate step between thermal and comprehensive models. The simplifications incorporated into the thermal models are also principle here, but those models permit to take into account the environment: mass loss rate is tabulated as a function of incident heat flux and oxygen concentration. Each input parameter is described by the use of a polynomial equation, in which thermal parameters and enthalpies are masked in the coefficients of the polynomial.
- Comprehensive models include chemical kinetics, then the pyrolysis is described by reaction rates which are calculated based on local temperature. In many cases chemical kinetics is modelled by some form of an Arrhenius expression. The description of the pyrolysis requires properties which are determined from micro-scale apparatuses, e.g. thermo-gravimetric analysis (TGA), or differential scanning calorimetry (DSC).

Due to its performance, this method has been favoured by different authors recently.

In this context, the objective of the present contribution is to describe how to model the pyrolysis of a solid fuel, using a comprehensive approach. The development of the sub-model of thermal decomposition 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 pyrolysis of a solid. This is realized based on the scaling-up approach presented by Torero [3] and addressing both experimental and numerical aspects. Finally, the presentation of the different steps of development of a model of pyrolysis permits explaining the actual scientific challenges and issues.

In the first part, the challenges and the phenomenology associated with the pyrolysis of a solid are presented. Next, the steps of the development of the model of pyrolysis are detailed, treatment of the reaction mechanism, the kinetic law and the function of conversion. 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 PYROLYSIS

This first part is dedicated to a presentation of the pyrolysis phenomenon of a solid fuel.

The pyrolysis of a solid is represented by its mass loss and the quantity of combustible gases emitted which decide whether the combustion will occur or not. Thus, the coupling between the pyrolysis of the condensed phase and the combustion into the gaseous phase is very important: pyrolysis controls the fuel gases but it is dependent on the oxygen diffusion and the heat transfer (which permits the heating of the material) for its decomposition. This strong coupling is presented in Figure 1 and is summarized in Figure 2 [4].

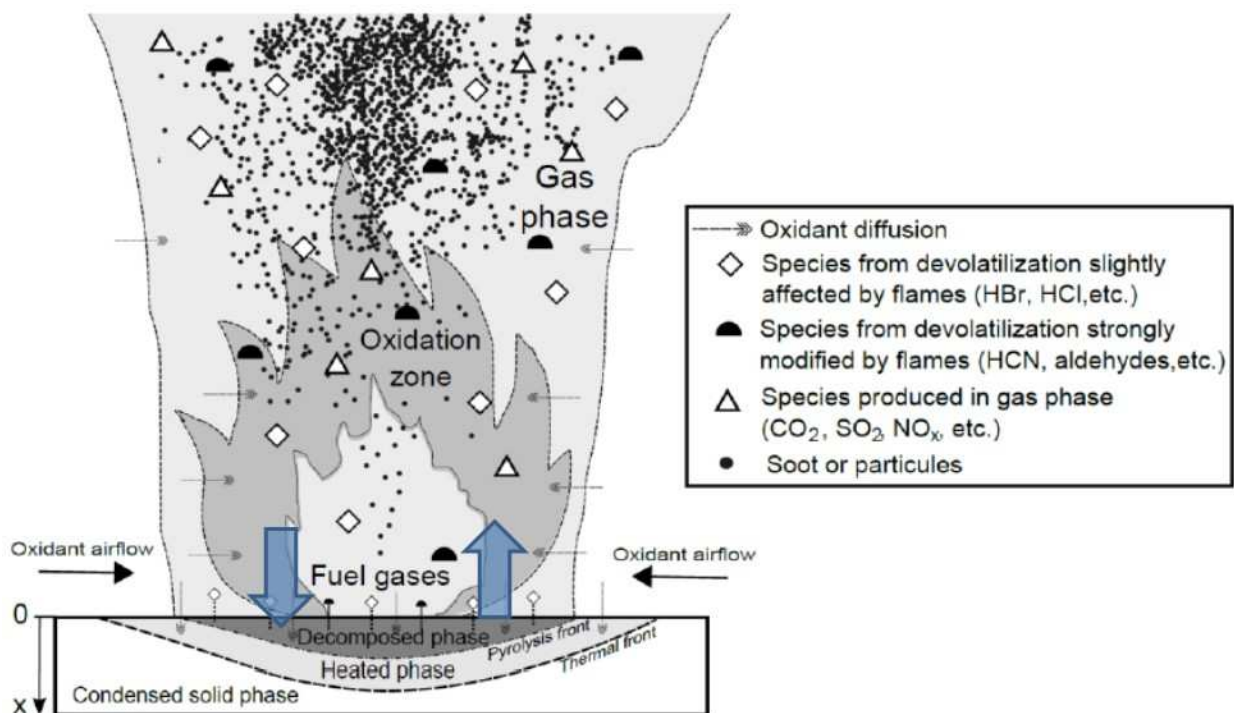


Figure 1: Illustration of the coupling between the pyrolysis and the combustion into the gaseous phase.



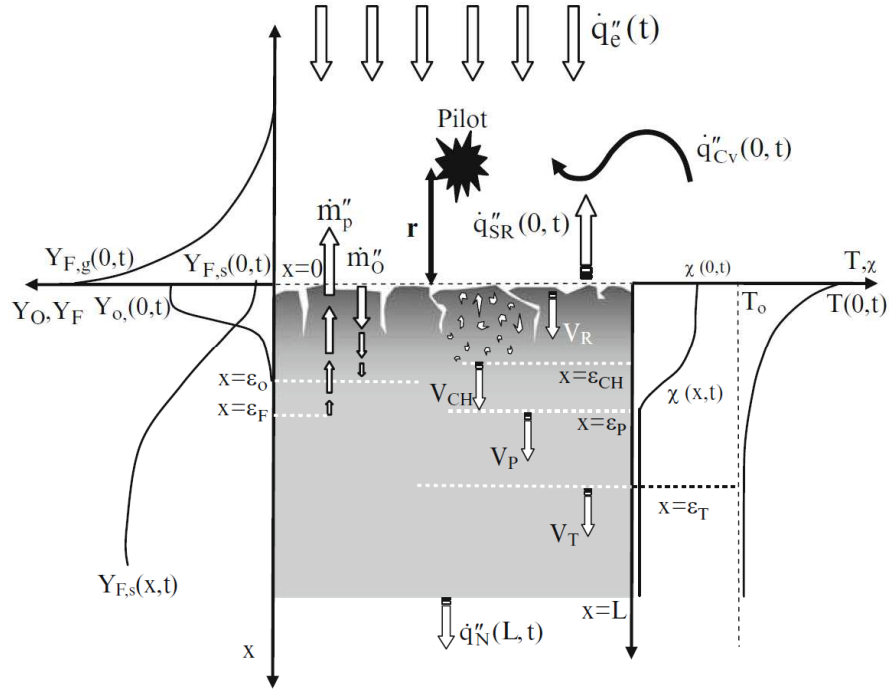


Figure 3: Simplified (1D.) representation of the phenomenon occurring during the pyrolysis of a solid [5]

From figure 3, pyrolysis is shown as a function of time [5] – in a simplified 1D approach:

- Temperature  $T(x, t)$ .
- Local mass fraction of combustible,  $Y_s(x, t)$ .
- Local mass fraction of oxygen,  $Y_{O_2}(x, t)$ .
- Mass fraction of residual solid fuel,  $Y_{F,s}(x, t)$ .
- Permeability,  $\chi(x, t)$ .
- Thickness of oxygen diffusion into the solid,  $\delta_{O_2}(x, t)$ .
- Thickness of the reactive zone,  $\delta_F(t)$ .
- Kinetic parameters values of each reaction,  $A_i$  the pre-exponential factor,  $n_i$  the order of the reaction  $i$ ,  $m_i$  the mass of  $i$ ,  $E_i$  the energy of activation.

In real situation, this dependence is spatial and so in 3 dimensions.

The mass loss rate due to the pyrolysis is expressed locally by Eq. (1) [5]:

$$\dot{m}_p'''(x, t) = Y_{F,s}(x, t) \sum_{i=1}^N \left[ A_i Y_{O_2}^{m_i}(x, t) Y_s^{n_i}(x, t) e^{-E_i/RT(x,t)} \right] \quad \text{Eq. (1)}$$

And for each volume element  $dV$  Eq. (2) [5]:

$$\dot{m}_p''(x, t) = \int_0^L \chi(x, t) \left[ Y_{F,s}(x, t) \sum_{i=1}^N \left( A_i Y_{O_2}^{m_i}(x, t) Y_s^{n_i}(x, t) e^{-E_i/RT(x,t)} \right) \right] dx \quad \text{Eq. (2)}$$

Thus, the objective is to represent the pyrolysis, which reclaims as presented in figure 4 (inspired from [6]):

- a model of pyrolysis,
- physical, chemical and thermal properties,
- and the description of coupling, heat and mass transfers.



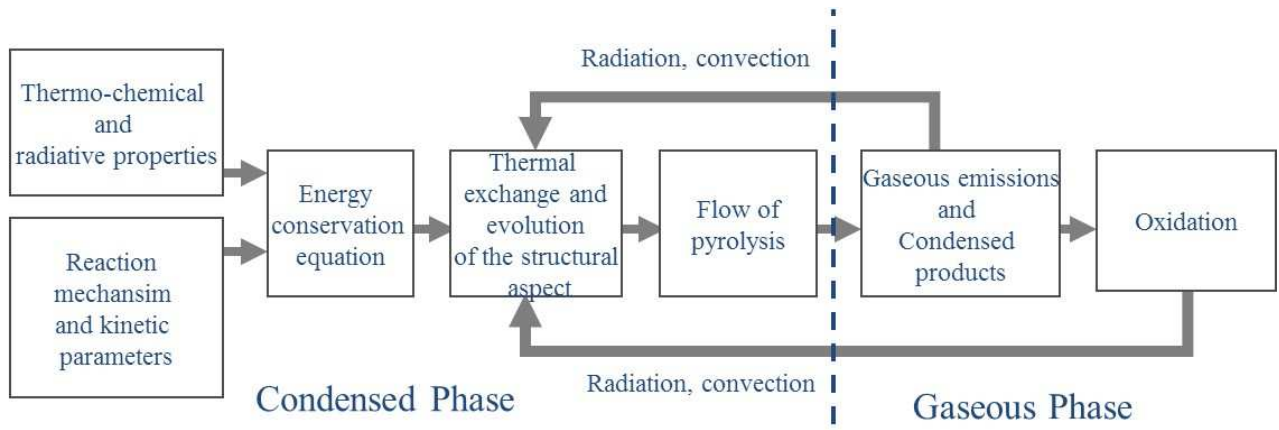


Figure 4: Pyrolysis of a solid fuel (Aspects represented are inspired from [6]).

Each one of this 3 aspects will be addressed. In a first part, we are interested in the model of pyrolysis.

## II. THE SUB-MODEL OF PYROLYSIS

The sub-model (or model) of pyrolysis presents the chemical evolution (reactions) with respect to the temperature, atmosphere and the kinetic of thermal decomposition of a volume element  $dV$  for the studied material which is considered as homogeneous in terms of temperature and composition at each time step.

Three main approaches are classically used in order to determine a model of pyrolysis [7]:

- Modelistic approach – Model fitting method: it consists of a list of models out of which one is selected that fits best with TGA non-isothermal experimental curves. In this method, the Arrhenius equations are referenced to the remaining mass in the sample holder. Then it requires the definition of  $A$ ,  $E$  and  $n$  for each reaction and those terms are defined as properties of the reaction. The model-fitting method is expressed in terms of the degree of conversion  $\alpha$ , which is equal to “0” at the beginning of the test and to “1” when all the mass has been decomposed. The degree of conversion that is an overall property of the transformation kinetics, is defined in 2.2.
- Isoconversionnal approach – Free model method: Kissinger [8], described a method to determine the pre-exponential factor, the activation energy and the reaction order of thermal decomposition of magnesite, calcite, brucite, kaolite and halloysite. The type of reactions observed with these minerals are single-staged. In these reactions, the solid is transformed into residue and gas. Kissinger’s method is based on the analysis of the conditions needed to attain the maximum reaction rate. The postulate is: if a reaction proceeds at a rate varying with temperature (*i.e.* possesses an activation energy), the position of the peak varies with heating rate if the others experimental conditions are kept unchanged. It permits then determining the evolution of the activation energy as a function of the degree of conversion of the reaction.  $E$  is dependent on  $\alpha$  (the progress of the reaction) and  $T$ . It does not use a reaction mechanism (just one reaction) but is based on Arrhenius form. The evolution of  $E$  permits presenting the mass loss rate. This approach is available in the case of 1 reaction 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 isoconversionnal one. This method requires the numerical and experimental individualization of each reaction peak, permitting to propose a mechanism of thermal decomposition. Each peak of mass loss rate is treated with a Kissinger method [8].

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. [9], Lautenberger & al. [10-12], Stoliarov & al. [13-15], Matala & al. [16], Bustamante Valencia [17], Rogaume and Fateh & al. [18-21], Batiot [22]. Those different groups consider the model fitting method, which is mostly used in the different software. Our interest will focus on the rest of this contribution through this approach. In the modelistic approach, an imposed and a less complex model is used to represent the detail kinetic of thermal decomposition. The model of pyrolysis required:

- A reaction mechanism, Eq. (3):





- 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 rate of variation and  $f(\alpha)$ , the function of conversion. The rate of variation is classically represented by a modified Arrhenius function, Eq. (4). Thus:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(-\frac{E}{RT}\right)f(\alpha) \quad \text{Eq. (4)}$$

where,  $T$  is the temperature,  $\alpha$  is the progress of the reaction,  $E$  is the energy of activation,  $A$  is the pre-exponential factor and  $R$  is the perfect gas constant .

### 2.1. Determination of the reactional mechanism

Four main methods are used to determine the reactional mechanism of thermal decomposition of a solid. In order to understand well, we can take the example of the work of Di Blasi [23] concerning the thermal decomposition of wood (see Figure 5).

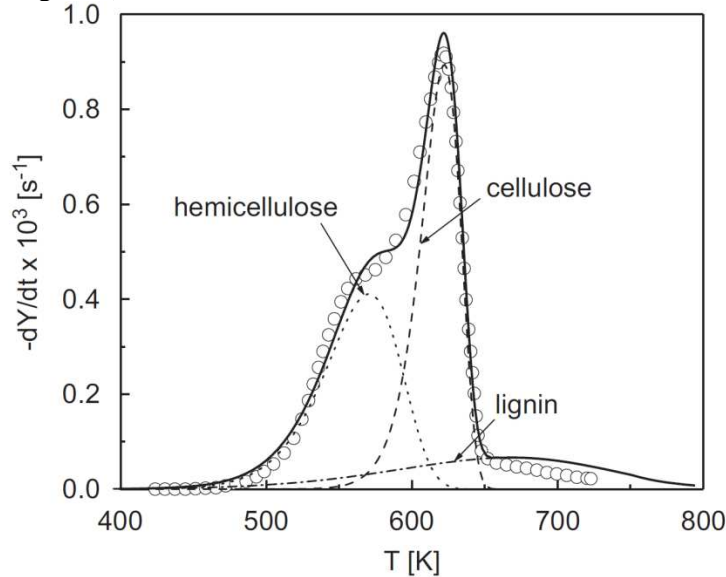


Figure 5: Comparison of experimental and numerical curves of thermal decomposition of the wood and its constituents at  $5^\circ\text{C}.\text{min}^{-1}$  [23]

- The lumped parameter approach (LPA) considers that the material is homogeneous. The thermal decomposition of this material is a multiple steps mechanism proposed by Di Blasi [23]:

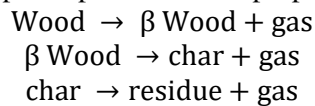


Figure 6: Example of multiple steps mechanism of thermal decomposition of wood using the lumped parameter approach (LPA) [23]

- 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. Considering the wood, it is composed of cellulose, hemicellulose and lignin. Then, 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 (as presented on figure 7 for the wood).
- In 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 good knowledge of the polymer decomposition steps [7].
- The other 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 in [24]. 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.
- The last one that is presented by Batiot [22] is an hybrid one. Associating the other approaches, notably permitting to develop a global mechanism, considering the constituent and the known functional properties. Concerning the wood, its thermal decomposition is described as [22]:

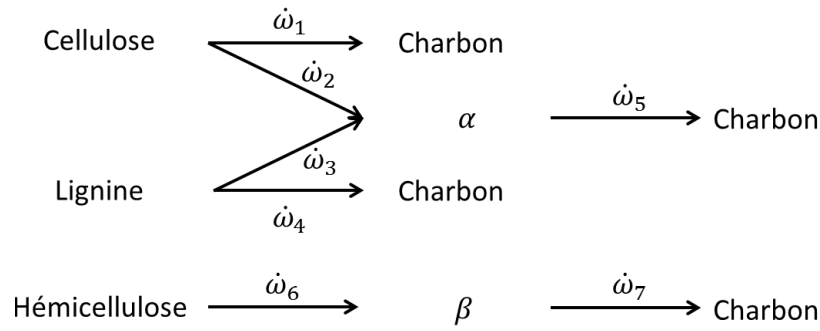


Figure 7: Mechanism of thermal decomposition of wood using the lumped parameter approach (LPA) [22]

Then, it currently appears that the LPA approach is the more acceptable and it has been used by several authors [4, 9-21]. 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) were heated 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 deduced.

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 [18]. Figure 8 presents respectively the evolution of the mass loss and of the mass loss rate, for two atmospheres and four heating rates [18].

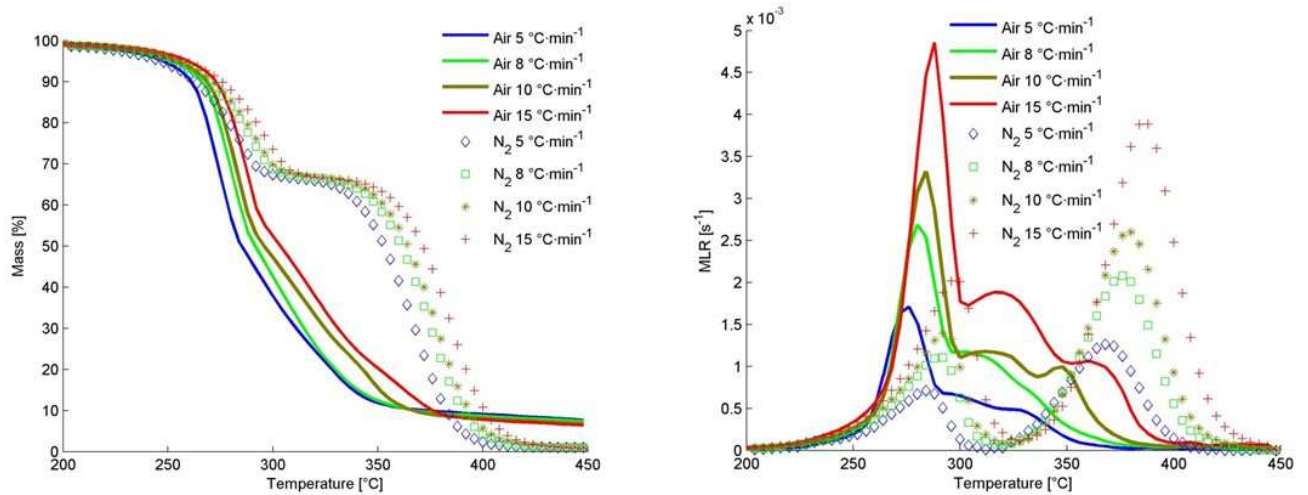


Figure 8: Evolution of the mass loss and the mass loss rate during the thermal decomposition of a PU foam at TGA scale [18].

It can be seen from the Figure 8 that the thermal decomposition of the PU foam is occurring in 2 global reactions of pyrolysis (under inert atmosphere) and in 3 reactions under air (oxidation). These reactions are presented in the table 1 [18].

No	Type of reaction	Temp. [°C]	Reactives	Products solid or liquid	Products gas
1	Pyrolysis	200–340	PPUF	$\rightarrow \nu_1 \cdot \text{Polyol}$	$+ \tau_1 \cdot [\text{Isocyanate}]$
2	Pyrolysis	340–450	Polyol	$\rightarrow \nu_2 \cdot \text{Residue}$	$+ \tau_2 \cdot [\text{Polyol} + \text{H}_2\text{CO} + \text{H}_2\text{O} + \text{CH}_4]$
3	Oxidation	200–275	PPUF + O <sub>2</sub>	$\rightarrow \nu_3 \cdot \text{Polyol}$	$+ \tau_3 \cdot [\text{Polyol} + \text{CO}_2 + \text{H}_2\text{O}]$
4	Oxidation	220–300	Polyol + O <sub>2</sub>	$\rightarrow \nu_4 \cdot \text{Char}$	$+ \tau_4 \cdot [\text{Polyol} + \text{H}_2\text{CO} + \text{CH}_4 + \text{CO} + \text{CO}_2 + \text{H}_2\text{O}]$
5	Oxidation	300–450	Char + O <sub>2</sub>	$\rightarrow \nu_5 \cdot \text{Residue}$	$+ \tau_5 \cdot [\text{Polyol} + \text{H}_2\text{CO} + \text{CH}_4 + \text{CO} + \text{CO}_2 + \text{H}_2\text{O}]$

Table 1: Reactions of thermal decomposition of a PU foam [18]

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 most 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. [25]. Several complex mechanisms 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 Kissinger [18] is as follows (Figure 9):

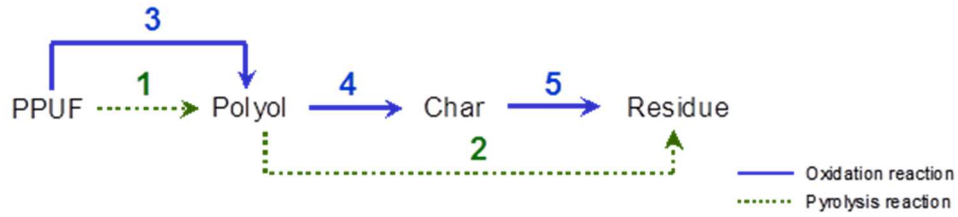


Figure 9: Mechanism of thermal decomposition of a PU foam [18]

## 2.2. Determination of the kinetic law

The rate of reaction of the solid phase is the multiplication of  $k(T)$ , the law of rate of variation and  $f(\alpha)$ , the function of conversion. The rate of variation is classically represented by a modified Arrhenius function (see Eq. 5).

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(-\frac{E}{RT}\right)f(\alpha) \quad \text{Eq. (5)}$$

where,  $T$  is the temperature,  $\alpha$  is the progress of the reaction,  $E$  is the energy of activation,  $A$  is the pre-exponential factor and  $R$  is the perfect gas constant.

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, Eq. (6):

$$\alpha = \frac{m_0 - m_i(t)}{m_0 - m_\infty} \quad \text{Eq. (6)}$$

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

The analytical form of the functions of conversion, which associates  $\alpha$  to  $f(\alpha)$ , permits to represent the large diversity of the reactions of thermal decomposition. Thus, different forms of law are proposed in order to represent the different kinds of reactions that can be met during the thermal decomposition process of solid fuel. Different functions of conversion are presented in the table 2 [7]:

Model		$f(\alpha)$
Reactional Order	ordre 0	1
	1 <sup>er</sup> ordre	$1 - \alpha$
	2 <sup>nd</sup> ordre	$(1 - \alpha)^2$
	ordre 3	$(1 - \alpha)^3$
	ordre $n$	$(1 - \alpha)^n$
Exponential law		$\alpha$
Power function	$P = 3/2$	$\frac{3}{2}\alpha^{1/3}$
	$P = 2$	$2\alpha^{1/2}$
	$P = 3$	$3\alpha^{2/3}$
	$P = 4$	$4\alpha^{3/4}$
	$P = n$	$n\alpha^{(1-1/n)}$

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

The choice of the law has to be done considering the global reactions, because the microscopic ones are not known. Classically the reactional order 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 studied solid, for example the degree of polymerization.

However, sometime, physical phenomena are indistinguishable from the kinetic, and it is necessary to use different conversion functions. It can be the case considering the oxygen diffusion into the solid, which impacts the kinetics of decomposition (cf Jander), eq. (7):

$$f(\alpha) = \left[ 1 - (1 - \alpha)^{\frac{1}{3}} \right]^2 \quad \text{Eq. (7)}$$

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:  $\dot{\omega} = k(\dot{T}) \cdot f(\alpha)$ :

$$\dot{\omega} = A e^{-\frac{E}{RT} m^n} \quad \text{Eq. (8)}$$

where,  $A$  is the pre-exponential factor,  $E_a$  is the energy of activation,  $R$  is the perfect gas constant,  $T$  is the temperature,  $m$  is the mass,  $n$  is the order of the reaction.

It is important to note that the law of Arrhenius has been developed for gas application and its use for the solid thermal kinetic representation can be questionable. Past works have shown that its application gives good results, nevertheless the theoretical justification of this one has not been yet done. Then, the actual works notably based on the transition states objective to clarify this application. The work of Batiot [22] have then permitted establishing firmly its application and its form, using a detailed upscaling approach, from the atoms to the solid at matter scale.

Moreover, Batiot & al. [26] have conducted a sensitivity analysis on the different parameters ( $A$ ,  $E$ ,  $n$ ) of this law to study response on the mass loss and the mass loss rate. They show not only the compensation effect between  $A$  and  $E$  but also the existence and the uniqueness of the solutions obtained for those parameters, in accordance with the works of Marquis & al. [27]. Because these parameters are micro-scale properties, they cannot be determined without using inverse optimisation methods, described below.

Each reaction  $i$  of the reactional mechanism has a rate  $\dot{\omega}_i$  defined by an Arrhenius law of the form, Eq. (9):

$$\dot{\omega}_i = A_i e^{-\frac{E_i}{RT}} \left( \frac{m_i}{m_o} \right)^{n_i} Y_{O_2}^\delta \quad \text{Eq. (9)}$$

From those expressions, the total mass loss rate of the solid (MLR<sub>i</sub> or  $\frac{dm_t}{dt}$ ) is expressed by the sum of the mass loss rate due to the  $i$  reactions of the reactional mechanism, Eq. (10):

$$MLR_i = \frac{dm_i}{dt} = \sum_{j \in J} \nu_j \omega_j - \sum_{k \in K} \omega_k \quad \text{Eq. (10)}$$

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

$$\frac{dm_t}{dt} = \sum_{i=1}^l \frac{dm_i}{dt} \quad \text{Eq. (11)}$$

Eq. 11 presented the calculation of the mass-loss rate of a given solid species. A similar calculation is presented in Eq. (12), but referenced to the mass of gas produced by a reaction: The yield of gases produced by a given reaction  $\dot{Y}_i$  (eq. (3)) is calculated as the product of the stoichiometric coefficient,  $\tau_i$  and the reaction rate  $\dot{\omega}_i$  (see table 1).

$$\dot{Y}_i = \tau_i \cdot \dot{\omega}_i \quad \text{Eq. (12)}$$

The rate of the reaction revealed four unknown parameters for each reaction:  $A$  the pre-exponential factor,  $E$  the energy of activation,  $n$  the order of the reaction and  $\nu$  the stoichiometric coefficient. The determination of those parameters cannot be done experimentally [22], and can be realised from different methods:

- The direct methods permit to determine the unknown kinetic parameters directly (mathematical resolution) from the experimental data, for example the mass loss rate evolutions. There are not time consuming, however there are only applicable for simple problems, here, for a mechanism of thermal decomposition with only one step.
- The metaheuristic methods, using inverse methods of optimization. In the literature, different methods are proposed and compared [28-29]. The algorithms of evolutionary type or behavioral type appear to be particularly well adapted to the difficult problems of optimization on strongly non-linear and very unstable models

Let us quote by example: the genetic algorithms (GA) [30] (the Genetic Algorithms Simulated Annealing), the Stochastic Hill Climber, the Shuffled Complex Evolution [31] or the particle swarm [32]. They are applied to the mass loss and (not systematically) to the mass loss rate evolutions. The differences between the different methods permit to resolve the problem of convergence, of not exploration of the whole space of the possible solutions. The global scheme of functioning of those algorithms is as follows (Figure 10):

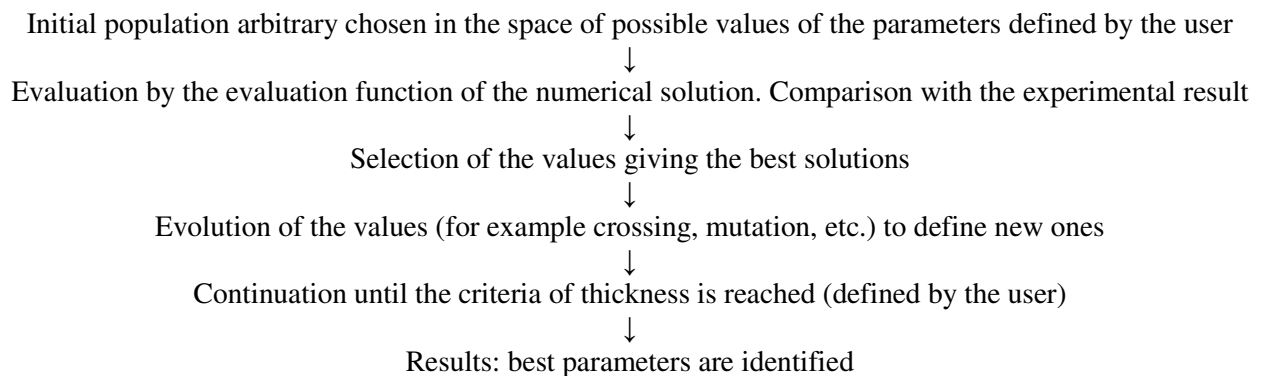


Figure 10: global scheme of functioning of the metaheuristic methods of optimization of the unknown parameters

- Another method is proposed by Bruns [33]. It is based on a Bayesian interference data analysis to model calibration. It treats the model parameters as quantities whose values are imprecisely known. These

uncertain model parameters are characterized by probability density functions (PDFs) instead of point estimates. The form of these PDFs are determined by a calibration process in which Bayes' theorem is used to update prior knowledge with experimental data. One advantage of this approach is that it permits a complete treatment of uncertainty.

In most of the cases, multi-step mechanisms of thermal decomposition are proposed, then metaheuristic methods are used. It uses an evaluation function that compares experimental and calculated curves. The accuracy between curves is called fitness  $\phi$ , Eq. (13). The improvement of fitness, means a best fitting between experiments and calculations. Optimum parameters are found with the maximisation of  $\phi$ . Thus, based on the comparison of experimental and calculated curves, the evaluation function has the main role in the modelling while it indicates to the code if the result is adequate or not. Different evaluation functions  $\phi$  are proposed as a function of the authors [9, 17, 34] and it is shown that this one has an influence on the solutions obtained [17, 22]. The following evaluation function is the one used by Rein & al. [9].

$$\phi = \sum_{\beta=1}^c \left[ \left( \int \left| \frac{dm^{Calc}}{dt} - \frac{dm^{Exp}}{dt} \right| dT \right)^{-1} + \psi \left( \int |m^{Calc} - m^{Exp}| dT \right)^{-1} \right]_{\beta} \quad \text{Eq. (13)}$$

Where,  $c$  is the number of heating rates that are compared (four in this research). This function is formed by the addition of two terms: the first term of the right hand side accounts for the absolute value of the difference between the experimental and calculated curves of MLR. The second term of the right hand side is the absolute value of the difference of the experimental and calculated curves of change in mass as a function of temperature. Due to several shortcomings of this function, other evaluation functions have been developed. In the following equation, the fitness is based on the classical method to calculate errors: the square of the difference between the two curves. It is in agreement with the evaluation function of Esperanza & al. [33]:

$$\phi = \sum_{\beta=1}^c \sum_{j=1}^k \left( \frac{dm_j^{Calc}}{dt} - \frac{dm_j^{Exp}}{dt} \right)^2_{\beta} \quad \text{Eq. (14)}$$

Where,  $k$  is the dimension of the vectors that are compared (only comparison of vectors of the same size are allowed). This equation is quite restrictive because of the second power of the error.

Another evaluation function has been proposed during the work of Bustamante Valencia [17-18], eq. (15).

$$\phi = \sum_{\beta=1}^c \left[ \cos[\angle(\vec{x}, \vec{y})] \cdot \left[ \frac{\|\vec{x} - \vec{y}\|}{\|\vec{x}\|} \right]^{-1} \right]_{\beta} \quad \text{Eq. (15)}$$

$$\vec{x} = \frac{dm^{Exp}}{dT}; \quad \vec{y} = \frac{dm^{Calc}}{dT}$$

Where,  $\vec{x}$  and  $\vec{y}$  are respectively arrays of experimental and calculated mass-loss rates as a function of temperature. These vectors are of the same dimension, *i.e.* the data points are taken at the same temperature. The definition of  $\phi$  takes into account the scalar product  $\langle \vec{x}, \vec{y} \rangle$  and the Euclidean norm of vectors  $\|\vec{x}\|$ .

Considering the example of application presented in Figures 7, 8 and the table 1, the total mass loss rate of the polyurethane foam [18] is defined as (see Eq. 16):

$$\frac{dm}{dt} = \sum_{i=1}^4 MLR_i = \frac{dm_{PPUF}}{dt} + \frac{dm_{Polyol}}{dt} + \frac{dm_{Char}}{dt} + \frac{dm_{residue}}{dt} \quad \text{Eq. (16)}$$

So:

$$\frac{dm}{dt} = (v_1 - 1)\omega_1 + (v_2 - 1)\omega_2 + (v_3 - 1)\omega_3 + (v_4 - 1)\omega_4 + (v_5 - 1)\omega_5 \quad \text{Eq. (17)}$$

with each reaction having a rate:

$$\dot{\omega}_i = A_i \exp\left(-\frac{E_i}{RT}\right) m_i^{n_i} y_{O_2}^{\delta} \quad \text{Eq. (18)}$$

During the previous study [18], the  $4 \times i$  (with  $i$  the number of reactions) so 20 unknown parameters have been determined by the Genetic Algorithms method [30]. In Eq. (18),  $\delta$  is equal to 0 when the reaction takes place without oxygen, and 1 for the thermos-oxidative reactions. The values obtained are presented in table 3.

Reaction	Parameter	Value	Range		Units
			High	Low	
PPUF pyrolysis	$E_1$	169.9	190	150	$\text{kJ} \cdot \text{mol}^{-1}$
	$A_1$	$6.09 \times 10^{13}$	$1 \times 10^{22}$	$1 \times 10^7$	$\text{s}^{-1}$
	$n_1$	0.91	1	0.1	—
	$\nu_1$	0.69	0.9	0.1	$\text{kg} \cdot \text{kg}^{-1}$
	$\tau_1$	—	$9 \times 10^9$	$1.5 \times 10^9$	—
Polyol pyrolysis	$E_2$	243.9	260	100	$\text{kJ} \cdot \text{mol}^{-1}$
	$A_2$	$4.42 \times 10^{17}$	$1 \times 10^{19}$	$1 \times 10^7$	$\text{s}^{-1}$
	$n_2$	1.26	1.5	0.1	—
	$\nu_2$	0.10	0.81	0.1	$\text{kg} \cdot \text{kg}^{-1}$
	$\tau_2$	$4.9 \times 10^9$	$9 \times 10^9$	$1.5 \times 10^9$	—
PPUF oxidization	$E_3$	214.1	240	161	$\text{kJ} \cdot \text{mol}^{-1}$
	$A_3$	$3.07 \times 10^{18}$	$1 \times 10^{20}$	$1 \times 10^7$	$\text{s}^{-1}$
	$n_3$	0.48	3	0.2	—
	$\nu_3$	0.44	0.7	0.1	$\text{kg} \cdot \text{kg}^{-1}$
	$\tau_3$	$8.9 \times 10^4$	$1.5 \times 10^5$	$3 \times 10^4$	—
Polyol oxidization	$E_4$	213.6	240	161	$\text{kJ} \cdot \text{mol}^{-1}$
	$A_4$	$1.26 \times 10^{18}$	$1 \times 10^{22}$	$1 \times 10^7$	$\text{s}^{-1}$
	$n_4$	0.95	3	0.3	—
	$\nu_4$	0.56	0.7	0.1	$\text{kg} \cdot \text{kg}^{-1}$
	$\tau_4$	$8 \times 10^5$	$2.2 \times 10^6$	$2 \times 10^4$	—
Char oxidization	$E_5$	160.8	240	160	$\text{kJ} \cdot \text{mol}^{-1}$
	$A_5$	$4.30 \times 10^{12}$	$3 \times 10^{15}$	$1 \times 10^{11}$	$\text{s}^{-1}$
	$n_5$	1.64	3	0.5	—
	$\nu_5$	0.25	0.8	0.1	$\text{kg} \cdot \text{kg}^{-1}$
	$\tau_5$	$3.4 \times 10^6$	$9 \times 10^6$	$1.7 \times 10^5$	—

Table 3: kinetic parameter values of the different reactions of thermal decomposition of a PU foam [18]

The figure 11 presents the comparison between the experimental and the numerical mass loss rate evolutions [18].



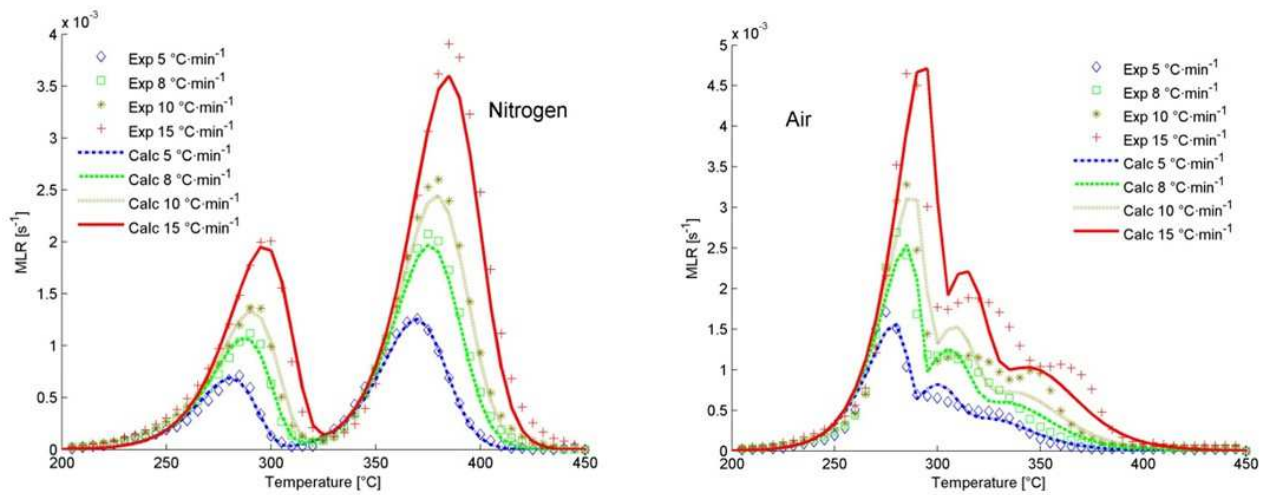


Figure 11: comparison of the experimental and the numerical mass loss rate evolutions [18]

The results show a very good agreement, the pyrolysis model (and then the reactional mechanism and the kinetic parameters) is 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 which, requires, notably, the determination of several thermo-physical properties of the studied fuel.

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

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

- The thermal conductivity  $k$  can be determined 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 an infra-red and a thermal camera approach, as done in [34-35].
- 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 pyrolysis process. Taking the example of the PU foam, which means that  $k$ ,  $\rho$ ,  $C_p$ ,  $\Delta H$ ,  $\varepsilon$ ... 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 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:
  - o It is very difficult to measure the conductivity  $k$  on porous matrix.
  - o It is not possible to measure  $k$  and  $C_p$  after a certain temperature (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 pyrolysis process, with notions of superposition of the reactions and so of the compound formed in the same temperature range. A solution for this difficulty would 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 developed by the team of S. Stoliarov in the University of Maryland, which uses the micro-calorimeter set-up to determine the heat of combustion or pyrolysis [36-37], or the Controlled Atmosphere Pyrolysis Apparatus (CAPA) to deduce the conductivity [38-39]. However, if the first method gives encouraging results, it does not permit isolating and determining the property values for each

intermediate compound. Then it can be applicable in case of one mechanism of thermal decomposition with only one reaction. Recent works on CAPA show how it can be used to parameterize the thermal transport properties for 6 reaction and 11 reaction mechanisms. It can be used for different materials, and the experiments performed under different atmospheres (pure nitrogen to air).

It appears to be very difficult to experimentally determine certain of those parameters, such 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 [11]. 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 » is used to determine the value of the thermo-physical properties, between the properties of the initial material and the final one:
  - o 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 in [38].

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

#### IV. MODELLING OF THE PYROLYSIS – SCALING-UP

As presented before, notably in Figures 1 and 2, the challenge remains the modelling of the pyrolysis 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 [3, 5] and adopted by [4, 18, 41] 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 [42], the Fire Propagation Apparatus [43] or the Controlled Atmosphere Pyrolysis Apparatus [38-39]. 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 [44], the Medium Burning Item [45], the Single Burning Item [46], permitting some investigation in two and three dimensions, with a flame propagation.
- At real scale, like realised for example by [47-48].

The modelling approaches use dedicated codes, like Gpyro [11-12] or Thermakin [13-15], 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 [49] have permitted its characterization using the cone calorimeter coupled with several gas analysers. Some results are presented on figure 12 for the mass loss rate (MLR) and the Heat Release Rate (HRR) [49].

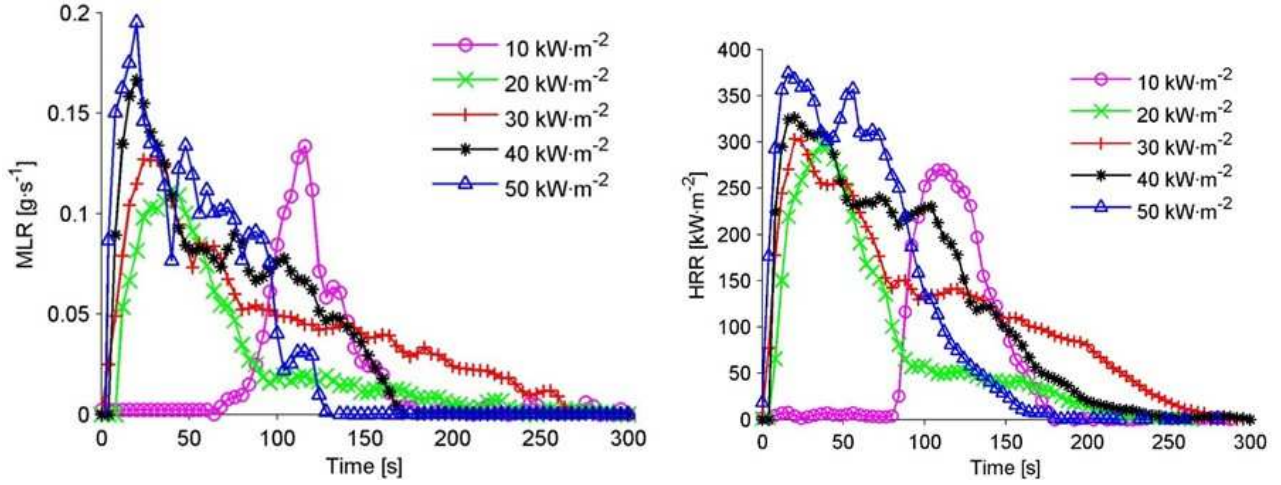


Figure 12: MLR and HRR evolution during the pyrolysis of a PU Foam using the cone calorimeter [49]

Dealing with the PU foam in their study of the behaviour of a railway seat, Guillaume & al. [41] have simulated, the cone calorimeter experiments at the specific condition of 50kW/m<sup>2</sup>. In this study, a simplified 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 13 [41]. The results show a good agreement permitting to validate the model at this scale.

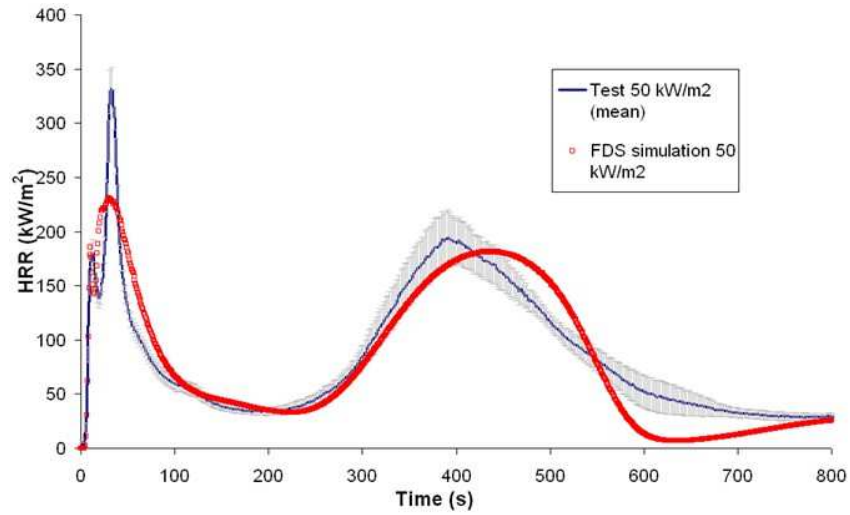


Figure 13: numerical and experimental evolutions of the HRR evolution during the pyrolysis of a railway seat using the cone calorimeter [41]

If classically the mass loss rate and the heat release rate are considered for the validation of the model, the work of Fateh & al. [50] shows that it is necessary to consider other parameters. Indeed, in their study of the pyrolysis of plywood [50], the authors compared two different mechanisms of thermal decomposition: one at 5 reactions (developed in [19], see Figure 14), and a simpler one at 3 reactions (see Figure 15) using Gpyro:

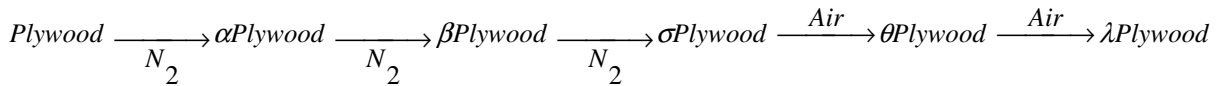


Figure 14: 5 steps mechanism of thermal decomposition of a plywood [19]

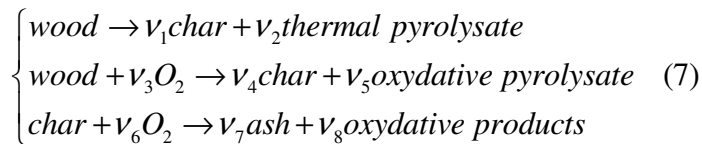


Figure 15: 3 steps mechanism of thermal decomposition of wood [19].

In order to estimate the ability of this 3 steps model to represent the thermal decomposition of plywood using Gpyro, Fateh & al [50] show that it is necessary to consider the temperature evolutions in the depth of the material and the thickness evolution of the intermediate compounds. Indeed, the authors show that the 3 steps model permits to represent very well the mass loss, the mass loss rate (Figure 16) as well as the temperatures at the front and back surfaces of the solid during its decomposition in the cone calorimeter at  $30 \text{ kW.m}^{-2}$  (Figure 17).

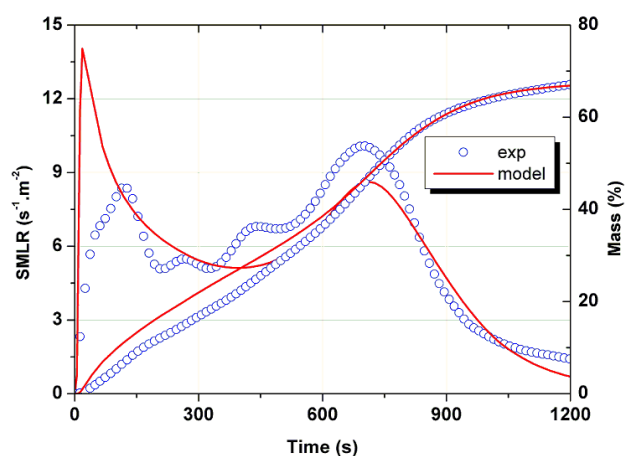


Figure 16: Experimental and numerical mass and mass loss rate evolutions as function of time at  $30 \text{ kW.m}^{-2}$  during the pyrolysis of plywood with the cone calorimeter – 3 steps mechanism [50].

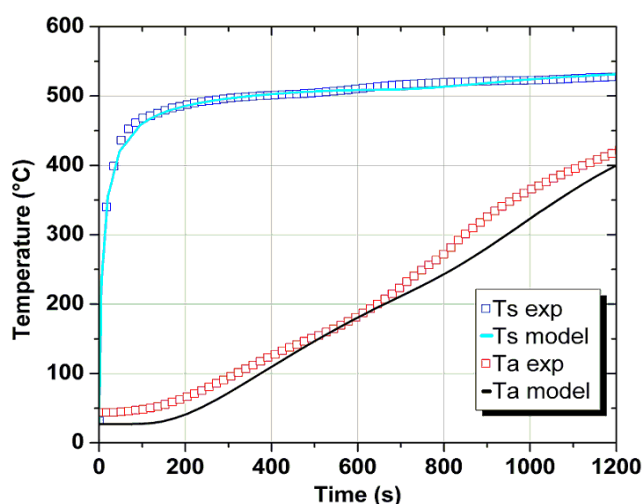


Figure 17: Experimental and numerical temperatures evolutions as a function of time ( $30 \text{ kW.m}^{-2}$ ) at the front and the back surface of the plywood sample during cone calorimeter study – 3 steps mechanism [50]

Nevertheless, even if the 3 step pyrolysis model predicts quite well the mass loss rate of the plywood, its capacity to reproduce the pyrolysis of the solid in depth is questionable. This 3 step pyrolysis model give us some non-physical results. Indeed, the figure 18 [50] represents the evolution of the mass fractions of the heterogeneous species and the evolution of the temperature along the thickness of the sample at 1000s for 2 types of the model.

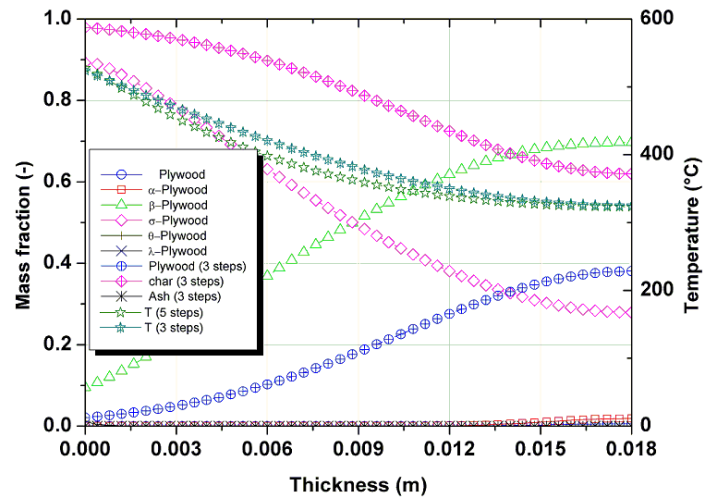


Figure 18: Evolutions of mass fractions of heterogeneous species as a function of time ( $30 \text{ kW.m}^{-2}$ ) at the back surface of the solid at 1000 s during cone calorimeter experiments, for the two mechanisms [50]

For the 3 step mechanism, virgin plywood is present all along the thickness of the sample and represents 40 %wt of the sample weight at the back surface of the solid. However at this time no more virgin material remains for the corresponding experiment.

At a higher scale, Guillaume & al. [41], in their scaling-up validation of the model - to represent the pyrolysis of a railway seat, have modelled some tests using a single burning item. The figure 19 [41] presents the comparison of the numerical and the experimental HRR evolutions at the Single Burning Item scale. A good agreement is obtained.

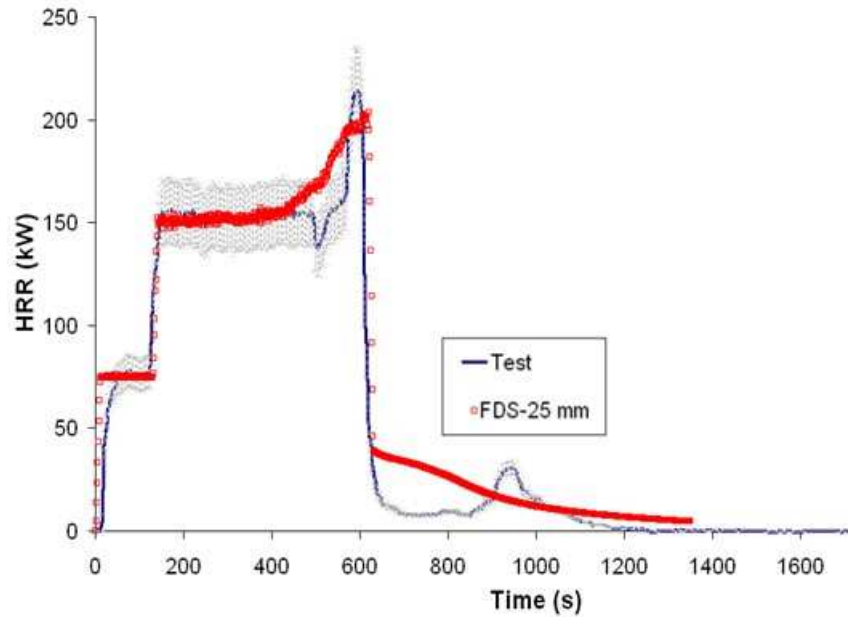


Figure 19: Numerical and experimental evolutions of the HRR evolution during the pyrolysis of a railway seat using a single burning item [41]

## V. DISCUSSION

From several years, many efforts are realized by the scientific community in order to improve the experimental and numerical investigations of the thermal decomposition and the pyrolysis of solid fuels. If progress has been done, different scientific obstacles persist, requiring specific focus and attention in the future: development, calibration, verification, and validation of predictive models of thermal decomposition and pyrolysis are the challenge.

This then requires experimental investigations in order to understand the phenomena occurring and to initiate, to develop and to validate the models. Thus, the efforts to support in the future concerns both the experimental investigations and the models development.

It is shown previously that in order to describe numerically the thermal decomposition and the pyrolysis of a solid fuel, it is necessary to develop a model of pyrolysis, to determine the physical, chemical and thermo-physical properties, to describe heat and mass transfers and finally to represent the coupling between the condensed and the gas phases. Current scientific shortcomings concern both each one of those aspects and are discussed below.

Those shortcomings are dependent on the complexity of the studied solid fuel. Indeed, the phenomenon occurring during the pyrolysis of non-charring fuel are different than the ones involved for charring materials. Other complexities are also generated when studying multicomponent solids as well as for the intumescent ones.

The first aspect concerns the experimental investigations of the thermal decomposition in order to propose a model of pyrolysis. The challenge is to obtain “good data” in controlled and known conditions and then to develop and to promote good practises when using the thermogravimetric apparatus.

Each reaction of the thermal decomposition has a kinetic defined by an Arrhenius law for which parameters are unknown. Those parameters are classically determined using different inverse methods of optimization, for which problems of convergence exist, not allowing then the exploration of the entire domain of the possible solutions. Thus, the development of more robust methods is necessary.

Another important aspect concern the determination of the thermal, chemical and physical properties for the modelling of the pyrolysis process. Different experimental techniques exist and are used (thermo-differential analysis, differential scanning calorimetry, micro-calorimeter, etc.). It is necessary to establish the conditions of implementation to guaranty the acquisition of “good results”. Moreover, another important challenge is the possibility of determination of those properties for each equivalent condensed phase of the kinetic mechanism of thermal decomposition, as a function of time. Complexity in those determination can be generated by the charring of the material, its intumescent properties or the mechanical transformations induced by its degradation and heating.

At this scale but also in the scaling-up approach, past studies have demonstrated the intake of the measurement of the gaseous emissions induced by the pyrolysis. Nevertheless, in most studies, only a qualification of the species emitted is realised. Efforts have to be made in order to quantify the gaseous emissions emitted by the pyrolysis and the thermal decomposition, both with intrusive or non-intrusive techniques.

The pyrolysis model is developed at a very small scale (matter scale), for some conditions which are not representative of real fires. A scaling-up approach is then used by different teams.

However, for increasing the scale, two aspects are important: the control and the knowledge of the initial and boundary conditions for the model input and initialization; a good realization of the tests for obtaining “good data” for the model validation (comparison of numerical and experimental results). Developments are required in order to propose specific bench scales, to established good methodologies and experiment conditions, etc. at matter scale but also during the scaling-up process, it is beneficial for the model development and validation, to establish some balance sheets of the species, of energy and of mass conservation. This requires precise quantification of what happen in the condensed phase as well as in the gas phase: chemical composition of the solid phase, gaseous emissions, heat transfers, porosity, pressure evolution, species diffusion, flowrates, etc. have to be quantified. Dedicated experimental set-up and analysis have to be developed in this sense, taking into account the complexity of the materials studied: charring, intumescence, structural evolutions (cracking, delamination...).

In longer period, the study of coupling between the condensed and the gaseous phases for a better description of the ignition-extinction processes and the flame propagation are required to perform. To do this, representative experimental tests must be developed and performed, and the model must be improved and developed.

Application of those different approaches and methodologies to multicomponent solids also remain a very important challenge in the future.

Due to all these factors the “IAFSS International Working Group on Measurement and Computation of Fire Phenomena” has been created and subgroup the “Condensed Phase Phenomena” within the IAFSS. Its objective is to better coordinate measurement and modeling efforts carried out in this field by various research

groups. The purpose of the Condensed Phase Phenomena subgroup is to facilitate data sharing among researchers in order to improve predictions of thermal decomposition and pyrolysis in fire.

## CONCLUSION

The description of the pyrolysis 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 pyrolysis is controlled by the phenomena taking place into the condensed phase but is dependent on the heat and the mass transfers associated to the gaseous phase.

The models of pyrolysis can be divided into four main categories: the empirical, the thermal, the polynomial and finally the comprehensive ones, depending on how pyrolysis is modelled. Empirical models are not pertinent to applications other than the geometry and materials which they have been validated for. Thermal models are feasible for materials with high activation energies and where little pyrolysis occurs before ignition. Polynomial models take the environment into account but the validity of scaling is yet to be established. Finally, the comprehensive methodologies are the most developed since it has the potential to be used for any application with quite a good accuracy. However it is more complex to develop and it requires many parameters. The present paper is making a state of the art of how to develop a comprehensive model of thermal decomposition of the solid fuels.

In the context of comprehensive models, the pyrolysis description requires three main parts: the development of a sub-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 thermal degradation.

Those different steps required to model the pyrolysis of a solid, are presented in the present contribution.

Different methods are used to develop a model of pyrolysis: the modelistic approach, the isoconversionnal and the hybrid (coupling the two last) ones.

However, the modelistic one is used the most, then the attention is focused on it. 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. Different approaches are used in order to propose a mechanism of thermal decomposition, where one can have different levels of complexity: one single reaction to several sequential or parallel reactions. In many studies, the lumped parameter approach is used, or the hybrid one proposed by Batiot [22]. Different functions of conversion are also proposed, it is a choice to be dependent on the characteristics of the reactions of thermal decomposition. Thus, classically a reactional order function is chosen. Concerning the rate of the reactions, it is described by a modified (for solid application) law of Arrhenius.

Four unknown parameters appear for each reaction of thermal decomposition and cannot be determined experimentally. Inverse metaheuristic methods of optimization are then used by the international community in order to define the best value of the kinetic parameters. To do this, evaluation functions are used in order to compare the experimental and the numerical results.

The development and the validation of the model of pyrolysis is realized at matter scale, using thermogravimetric analysis. A stake is then to evaluate the ability of the model to represent the pyrolysis at upper scale.

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 pyrolysis 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. Generally complexity is added step by step. First considering the modelling of experimental tests with cone calorimeter or the fire propagation apparatus. Tests with a flame propagation are subsequently studied until full scale situations.

Despite the progress of the research, different scientific obstacles persist, requiring specific focus and attention in the future. They concern notably: the experimental investigations whatever the scale in order to obtain “good” data as well as the control of the initial and boundary for the development and the validation of the models; the determination of the thermo-physical properties; etc. and in a longer period, the coupling between



the condensed and the gaseous phases for a better description of the ignition-extinction processes and the flame propagation.

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