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# Kinetic parameter estimation from TGA: Optimal design of TGA experiments

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## A B S T R A C T

This work presents a general methodology to determine kinetic models of solid thermal decomposition with thermogravimetric analysis (TGA) instruments. The goal is to determine a simple and robust kinetic model for a given solid with the minimum of TGA experiments. From this last point of view, this work can be seen as an attempt to find the optimal design of TGA experiments for kinetic modelling. Two computation tools were developed. The first is a nonlinear parameter estimation procedure for identifying parameters in nonlinear dynamical models. The second tool computes the thermogravimetric experiment (here, the programmed temperature profile applied to the thermobalance) required in order to identify the best kinetic parameters, i.e. parameters with a higher statistical reliability. The combination of the two tools can be integrated in an iterative approach generally called sequential strategy. The application concerns the thermal degradation of cardboard in a Setaram TGA instrument and the results that are presented demonstrate the improvements in the kinetic parameter estimation process.

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### Keywords:

Thermal gravimetric analysis

Kinetics

Parameter identification

Experimental design

Cardboard

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## 1. Introduction

This work is part of an ongoing research effort to develop a practical, universal, and minimal-time consuming computing tool that will be helpful in determining reliable kinetic parameters occurring in the modelling of any chemical and/or physical problem such as solids combustion, pyrolysis, calcination, stabilization, and other phenomena investigated in our laboratory. In building the reaction schemes for such solids decomposition, the estimation of kinetic parameters represents a crucial step in chemical modelling. This paper's focus is on the determination of kinetic parameters of solid thermal degradations from data obtained by a thermal gravimetric analysis (TGA) instrument. TGA is a technique for thermal analysis. A given definition of thermal analysis is "A group of techniques in which a physical property of a substance and/or its reaction products is measured as a function of temperature while the substance is subjected to a controlled temperature program" (Mackenzie, 1979). Thermal gravimetric analysis consists in measuring the time evolution of a

sample mass under given conditions of temperature. Two modes of thermogravimetry are generally found to be used in literature: isothermal mode, in which the sample mass is recorded as a function of time at constant temperature, and dynamic (or non-isothermal) mode, in which the sample is exposed to the effect of a temperature programme, usually at a linear rate. The majority of recent scientific studies deal with a single kinetic equation where graphical and/or linearization methods are used to identify the kinetic parameters (Varhegy, 2007). For instance, a review of several of these methods can be found in Galwey and Brown (1998) or in Brown et al. (2000). When the reaction scheme involves more than one reaction, standard graphic methods are non-adequate and the nonlinear fitting represents the only alternative. However, nonlinear numerical methods need to be implemented with precaution and efficiency to avoid the determination of physically non-acceptable values. As discussed later, kinetic parameters estimation from TGA data can give scattered and non-acceptable results. To avoid this drawback, a numerical estimation procedure to determine

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## Nomenclature

|               |   |
|---------------|---|
| $a$           | mass stoichiometric coefficient                             |
| $A$           | pre-exponential factor ( $s^{-1}$ )                         |
| $A_r$         | pre-exponential factor after reparametrisation ( $s^{-1}$ ) |
| $b$           | mass stoichiometric coefficient                             |
| $E$           | activation energy ( $J\ mol^{-1}$ )                         |
| $E_r$         | activation energy after reparametrisation ( $K^{-1}$ )      |
| $F$           | Fisher information matrix                                   |
| $J_1$         | fitting criterion   |
| $J_2$         | optimum design criterion                                    |
| $k_r$         | rate constant ( $s^{-1}$ )                                  |
| $p$           | parameter   |
| $R$           | gas constant ( $J\ mol^{-1}\ K^{-1}$ )                      |
| $t$           | time (s)  |
| $T$           | Temperature (K)   |
| $W$           | weighting matrix  |
| $x$           | state variable  |
| $X$           | sensitivity matrix  |
| $y$           | dependent variable or normalized mass                       |
| $z$ or $Z$    | output variable or total normalized mass                    |
| Greek symbols |   |
| $\beta$       | heating rate ( $K\ min^{-1}$ or $^{\circ}C\ min^{-1}$ )     |
| $\Gamma$      | experimental measurement (vector)                           |
| $\kappa$      | level of the indifference region                            |

the kinetic parameters from TGA experiments simultaneously under different thermal conditions was developed. Additionally, a technique based on the design of the optimal TGA experiments was conceived. The goal of this technique is to improve the reliability and the confidence in the estimated parameters by determining the best experience to achieve this goal.

The objective of this paper is to give a detailed presentation of the methodology that was developed and to provide some initial results for the thermal degradation of a complex solid, cardboard. In the first part, the methodology and the associated numerical tools for the kinetic parameter estimation and for determining the optimal TGA experiment are described. The theoretical background to parameter identification and experimental design is explained. Some practical information on the current application are also discussed. In the second part, the experimental device and the materials used are presented. Finally, the paper is concluded by a description of the first experimental results obtained with samples of cardboard.

## 2. Kinetic parameter estimation problem and optimal design problem

Kinetic studies with TGA instruments are typically conducted under isothermal conditions or non-isothermal conditions, i.e. with a linear time evolving temperature. Some experimental difficulties can exist with isothermal experiments: a significant part of the reaction may occur during the setting of the experimental temperature at the beginning of the experiment; for instance, see Maciejewski (2000) for more precision about this subject. One advantage of the isothermal conditions is the homogeneous sample temperature after the isothermal reaction temperature has been reached, whereas in non-

isothermal mode, a temperature gradient in the sample can occur due to the resistance of heat conduction in the sample and the resistance of outer heat transfer. A way for compensating for this effect is to use low heating rates. Isothermal and non-isothermal methods have been widely used in the literature but papers comparing the results obtained with the two methods are rare (Làzaro et al., 1998). Furthermore, it is not easy to compare the scientific studies published for a given product: the experimental conditions (equipment, technologies, operating conditions, sample conditioning, etc.) are often different and not always well known; moreover, the models, the data treatments and the computational methods are never the same (Maciejewski, 2000).

### 2.1. Direct problem: kinetic model

The first step consists in choosing the kinetic model, i.e. the mathematical model describing the time evolution of the different mass fractions during the thermal degradation process. The complexity of the chosen model depends on the desired objectives. The thermal degradation of heterogeneous and complex materials, such as waste or biomass, cannot be expressed in detail. Simplified reaction schemes with pseudo-components are generally used. At this stage, a key question is to decide whether heat and mass transfer processes have to be taken into account. A large majority of the works assume the regime of kinetic control, i.e. all influences of internal and external mass and thermal transfer are neglected and the sample is assumed to follow the programmed temperature of the thermobalance perfectly and to have a uniform temperature. However, sources of error related to the temperature undoubtedly exist: the placement and the accuracy of the thermocouple, the thermal lag between the sensor and the sample, and the effect of heats of reaction (Gallagher, 1998). Some authors have demonstrated the influence of experimental conditions (for example, Völker and Rieckmann, 2002, or Roduit et al., 1996). However, some experimental considerations allow the difference between the set-point temperature and the actual temperature of the sample to be minimized: a small sample (with a low mass) and a slow heating rate are generally preferred.

The class of models used in this work is the class of pure kinetic models. The kinetic model is based on a set of first order differential equations (ODE) and can be represented by the following form of equation:

$$\begin{aligned} \dot{y} &= f(t, y, p, x) & y(t=0) &= y_0 \\ z &= g(t, y) \end{aligned} \quad (1)$$

where  $t$  is the time,  $y$  and  $\dot{y}$  are the set of dependent variables characterizing the solid kinetic and their derivatives with respect to time,  $p$  represents the set of kinetic parameters to be identified and  $x$  represents the other variables of the model such as temperature;  $z$  corresponds to the model output to compare with the evolution of loss mass measured with the thermobalance. If  $z$  represents the measured total mass, it can be obtained by summing all the solid partial mass  $y$ . In this work, all the kinetics are assumed to be modelled with a first order Arrhenius kinetic model and the state variables  $y$  are the solid normalized mass, i.e. divided by the initial mass of the sample. The kinetic parameters are respectively the pre-exponential factor and the activation energy for each reaction of the chosen model.

The numerical method for solving the set of ordinary differential equations is based on the algorithm developed by Kaps–Rentrop (Press et al., 1992).

## 2.2. Inverse problem: kinetic parameter estimation

Once the kinetic scheme and the associated equations have been established, the kinetic parameter estimation problem can be examined. The minimisation criterion used for identifying the kinetic parameters is given by the squared differences of the model output with the measured normalized total mass for one or several experiments. Under a vectorial form, the criterion can be written as follows:

$$\min_{\mathbf{p}} J_1(\mathbf{p}) = \min_{\mathbf{p}} \frac{1}{N_{\text{ex}} N_{\text{mi}}} (\mathbf{\Gamma} - \mathbf{Z})^T \mathbf{W} (\mathbf{\Gamma} - \mathbf{Z}) \quad (2)$$

where  $\mathbf{Z}$  and  $\mathbf{\Gamma}$ , are respectively the vectors of computed and measured normalized total mass.  $\mathbf{W}$  is the inverse measurement error covariance matrix. We have an approximate value of the measurement variance thanks to blank experiments (experiments with no sample), where the signal is constant for some rather long lengths of time (and temperature). From several blank experiments, the variance have been estimated to about  $10^{-5}$ .

A version of the Levenberg–Marquardt method was applied for the parameter estimation problem (Press et al., 1992).

Preliminary results have proven that this inverse problem was badly conditioned; as some sensitivity coefficient values were very small. The sensitivity coefficients for the pre-exponential factors are generally small compared to the coefficients for activation energies. In practice, this implies that the Levenberg–Marquardt method only modified a few kinetic parameters (parameters with the highest values for the sensitivity coefficients) in order to improve the minimisation criterion, and some parameters were not changed (parameters with the lowest values for the sensitivity coefficients). We proceeded with a reparametrization in order to improve the parameter estimation procedure. This reparametrization consisted in modifying the parameters to achieve a better homogeneity in the parameter value magnitude and in their sensitivity coefficient magnitude. Two new kinetic parameters,  $A_r$  and  $E_r$ , were defined from the original ones,  $A$  and  $E$ , by the following relations:

$$\begin{aligned} A_r &= \log A \\ E_r &= \frac{E}{R} \end{aligned} \quad (3)$$

The new expression of the rate constant must be equal to the original and is given by the following equation:

$$k_r = \exp A_r \exp\left(-\frac{E_r}{T}\right) = A \exp\left(-\frac{E}{RT}\right) \quad (4)$$

The benefits of the reparametrization have been presented in a previous paper concerning the thermal degradation of cellulose (Reverte et al., 2007).

## 2.3. Optimal design problem

One of the aims of the optimum experimental design is to plan experiments in order to maximize the statistical reliability of some unknown parameters estimated from the experimental data (Bauer et al., 2000). In our case, we use the approach of

optimum experimental design to determine what are the TGA experiment(s) to perform, called subsequently optimal experiment(s), for estimating the best kinetic parameters. Here, best parameters mean the parameters with a higher statistical reliability. In a recent paper, an author states that the laws of mathematical statistics cannot be useful in finding kinetic parameters with Thermal gravimetric analysis (Varhegy, 2007). According to this paper, statistics would not be useful because the most important experimental errors of TGA runs are usually neither random nor independent but concern the difference between the measured temperature and the actual one. We agree that the generally encountered assumption that the sample has a uniform temperature equal to the furnace temperature is very restrictive but we think that some statistics tools can be helpful for the design of TGA runs. Experimental errors exist such as those due to the measurements of mass and temperature or due to the heterogeneity of the sample. Our own experience with thermobalances is that these devices are very sensitive to the influence of many factors.

The precision of the estimated parameters can be linked to the notion of the joint confidence region; the word *joint* indicates that all the estimated parameters are taken into account simultaneously. The joint confidence region defines a bounded closed subset of the parameter space that contains the true value of the parameters with a given probability.

The Fisher information matrix  $\mathbf{F}$  combines some information on the output measurement error by means of the weighting matrix  $\mathbf{W}$ , and some information on the sensitivity of the model output with respect to the parameters through the sensitivity matrix  $\mathbf{X}$ :

$$\mathbf{F} = \mathbf{X}^T \mathbf{W} \mathbf{X} \quad (5)$$

For nonlinear model in the parameters, the inverse of Fisher information matrix ( $\mathbf{F}^{-1}$ ) is an approximation of the parameter variance–covariance matrix; in fact, it provides the Cramer–Rao lower bound on the parameter variance–covariance matrix (Walter and Pronzato, 1997). It can be demonstrated that the volume of the joint confidence region is proportional to the square root of the determinant of the inverse Fisher information matrix. So, the minimum-sized joint confidence region corresponds to the maximum of  $\mathbf{F}$  determinant. An experiment maximizing  $\mathbf{F}$  will then be deemed to be optimal. However, because of the nonlinearity of the model, the matrixes  $\mathbf{X}$  and  $\mathbf{F}$  depend on the values of parameters. An iterative approach can be envisaged with an improvement for the parameter estimates at each iteration. This iterative approach, which is generally called sequential strategy, alternatively combines parameter identification and design of experiments to improve the value of the parameters.

In this work, we assume that a standard thermobalance is used; only the variations of the total mass of solid and of the cell temperature can be recorded in the course of time. The variables characterizing a particular experiment are:

- the initial mass of the sample,
- the nature and the flow rate of the vector gas,
- the programmed temperature profile applied to the sample.

Because a pure kinetic model is used in this work, no mass or thermal transfer is taken into account. The solid sample is assumed homogeneous in temperature and composition. The initial mass of the sample and the flow rate and the

properties of the vector gas have no influence with such a model. In conclusion, the only input available to improve the experimental conditions is the programmed profile of the cell temperature. In other words, we look for the temperature profile applied to the thermobalance in order to improve the precision and the reliability of kinetic parameters for a chosen kinetic model. One possible approach for the numerical resolution of this problem requires the discretization of the temperature profile into finite subintervals inside the interval of operation. Mathematical functions must be defined to represent the evolution of the temperature in every subinterval. In order to avoid complex and unrealizable temperature profiles, the mathematical functions chosen are linear functions for the temperature in respect of time. Another advantage of using linear functions is that they will be easy to programme with the thermobalance. From a practical point a view, the problem consists then in determining the heating rate, i.e. the slope of the temperature, for each time subinterval. The optimum design problem can then be written as follows:

$$\min_{\beta} J_2(\mathbf{p}) = \min_{\beta} \det(\mathbf{F}^{-1}) \quad (6)$$

where  $\beta$  is the vector of the successive values of the heating rate.

Once all the values of  $\beta$  are defined, the evolution of different masses is computed by numerical integration on each time subinterval. To avoid unrealistic temperature profiles, lower and upper bounds are defined for the values of  $\beta$ ; these bounds must be chosen according to the thermogravimetric device used.

To solve this optimization problem, the well known method of modified simplex with constraints was used (Nelder and Mead, 1965). Several parameters needed to be defined: reaction time, number of subintervals, length of each subinterval, class of mathematical functions chosen. All these parameters can be fixed and/or adapted by the numerical procedure. In this work, they were all fixed.

#### 2.4. Indifference region

Because the criterion  $J_2$  defined in Eq. (6) is neither explicit nor practical to analyse, we need an explicit indicator for the quantification of the improvement in the identified parameters gained through the optimal experiment(s). The indicator used in this paper is the length of the indifference interval for each identified parameter.

A indifference region of level  $\kappa$  (or  $\kappa$ , indifference region) in the parameter space represents the locus of points  $\mathbf{p}$  where (Bard, 1974)

$$|J_1(\mathbf{p}) - J_1(\mathbf{p}^*)| \leq \kappa \quad (7)$$

$J_1(\mathbf{p}^*)$  is the value of the minimization criterion (Eq. (2)) with the identified optimal parameters  $\mathbf{p}^*$ . The region in the parameters space where the inequality defined in Eq. (7) is true represents the locus where the values of  $\mathbf{p}$  can be changed without significantly modifying the optimal value of the criterion  $J_1$ . The indifference region can be viewed as a measure of the sensi-

tivity of the determination of parameters. A large indifference region would mean that  $\mathbf{p}$  can be chosen far away from  $\mathbf{p}^*$  without deteriorate the quality of fitting, and thus leading to a bad determination of the model. By writing the second order Taylor formula for the function  $J_1(\mathbf{p})$ , it is easy to develop an approximate indifference interval for each identified parameter  $p_i$ :

$$\mathbf{p}_i \in \left[ p_i^* - \left( \frac{2\kappa}{H_{ii}} \right)^{1/2}, p_i^* + \left( \frac{2\kappa}{H_{ii}} \right)^{1/2} \right] \quad (8)$$

where  $\kappa$  is the allowed maximum for the absolute value of the difference between  $J_1(\mathbf{p})$  and  $J_1(\mathbf{p}^*)$  (see Eq. (7)).  $\kappa$  can be chosen as a percentage of the optimal minimization criterion; for instance, a 5%—indifference region corresponds to  $|J_1(\mathbf{p}) - J_1(\mathbf{p}^*)| < \kappa = 0.05 J_1(\mathbf{p}^*)$ .  $H_{ii}$  represents the diagonal elements of the Hessian matrix computed for  $J_1(\mathbf{p}^*)$ . Practically, they are computed by second order central finite difference with  $\varepsilon = 10^{-5}$ :

$$H_{ii} = \frac{J_1(\mathbf{p}_1, \dots, p_i^*(1+\varepsilon), \dots, p_{np}^*) + J_1(\mathbf{p}_1, \dots, p_i^*(1-\varepsilon), \dots, p_{np}^*) - 2J_1(\mathbf{p}^*)}{(\varepsilon p_i)^2} \quad (9)$$

From Eq. (8), much information about the indifference region can be gained by the analysis of the Hessian matrix. The relative sensitivities between the parameters  $p_i$  can be estimated from the respective lengths of the indifference intervals.

### 3. Experimental instruments and materials

Experiments were carried out with a SetaramTM 92-16.18 thermogravimetric analyser (TGA). The thermogravimetric unit is composed of a thermobalance: an electronic microbalance using a system of a balance beam and a furnace composed of a vertical tubular graphite tube. Operating temperatures ranged between room temperature and 1750 °C. Cylindrical platinum crucibles were used. Experiments were conducted under a flow of an inert gas (nitrogen) at a constant flow-rate (33 ml min<sup>-1</sup>) controlled with a mass flow controller. Because the buoyancy exerted on the sample decreases with increasing temperature, an apparent mass gain is observed (about 1 mg). So a preliminary “blank experiment” was carried out before each experiment. A “blank experiment” consists in doing an experiment, identical to the actual experiment, except that there is no sample (an empty crucible is used). The evolution of measured mass of the blank experiment is subtracted from the recorded mass of the “actual experiment”. Finally, in order to protect the balance from reaction with an incoming reactant gas stream, nitrogen was passed through the balance chamber for 4 h before each experiment.

Cardboard is a complex material, essentially composed of cellulose, hemicelluloses and lignin, and represents about 30% of municipal solid waste. Few studies have been devoted to the kinetics of its thermal degradation (David et al., 2003). The cardboard samples came from various forms of packaging. They were finely pulverized by cryogenic grinding. For all the experiments presented below, the sample mass was the same (3.5 mg). With such a small mass, we assume the thermal gradient inside the sample is small.

**Table 1 – Kinetic parameters and indifference intervals for thermal degradation of cardboard; one set of parameters is identified for each thermogravimetric experiment**

| Experiment: heating rate (°C min <sup>-1</sup> ) | log A <sub>1</sub> (min <sup>-1</sup> ) | E <sub>1</sub> (J mol <sup>-1</sup> ) | log A <sub>2</sub> (min <sup>-1</sup> ) | E <sub>2</sub> (J mol <sup>-1</sup> ) | a           | b           |
|--|---|---------------------------------------|---|---------------------------------------|-------------|-------------|
| #1: 5  | 21.30 ∈ [20.09–21.69]                   | 115,249 ± 1887                        | 10.91 ∈ [7.17–14.67]                    | 74,136 ± 2136                         | 0.35 ± 0.08 | 0.30 ± 0.06 |
| #2: 10   | 22.27 ∈ [21.86–22.68]                   | 117,502 ± 1972                        | 10.00 ∈ [7.00–12.98]                    | 65,730 ± 5490                         | 0.37 ± 0.08 | 0.31 ± 0.06 |
| #3: 15   | 22.04 ∈ [21.65–22.43]                   | 115,016 ± 1911                        | 11.67 ∈ [8.52–14.79]                    | 73,055 ± 5814                         | 0.35 ± 0.08 | 0.30 ± 0.06 |

## 4. Results

### 4.1. Identification of kinetic parameters of cardboard degradation

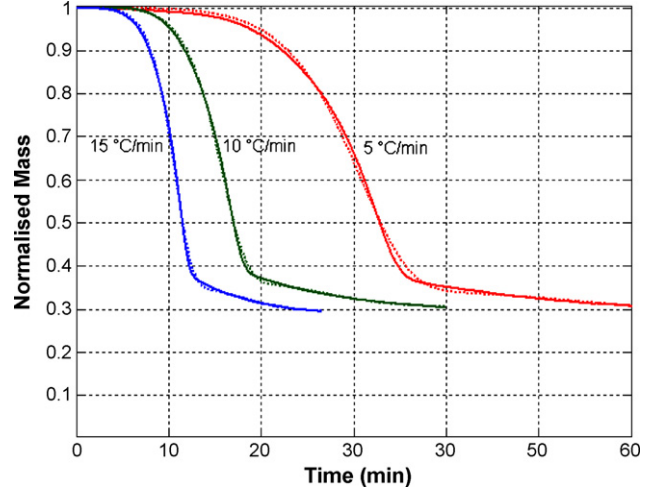
The reaction scheme assumed here for the thermal degradation of cardboard was proposed by David et al. (2003): cardboard  $\xrightarrow{k_1}$  a I1 + a' G1 and a I1  $\xrightarrow{k_2}$  b char + b' G2.

The cardboard, noted C, is degraded by two successive reactions. Gaseous products (G1) and an intermediary solid specie (I1) are produced by the first reaction; a solid residue, called char, and other gases (G2) are the products of a second reaction. Mass stoichiometric coefficients a, a', b and b' were defined for representing the mass proportion between solid and gaseous products for each reaction. The kinetic model (or direct model) for the solid species associated with the reaction scheme is

$$\begin{aligned} \frac{dy_C}{dt} &= -k_1 y_C = -A_1 \exp\left(-\frac{E_1}{RT}\right) y_C \\ \frac{dy_{I1}}{dt} &= a[k_1 y_C - k_2 y_{I1}] = a \left[ A_1 \exp\left(-\frac{E_1}{RT}\right) y_C - A_2 \exp\left(-\frac{E_2}{RT}\right) y_{I1} \right] \\ \frac{dy_{char}}{dt} &= b k_2 y_{I1} = b A_2 \exp\left(-\frac{E_2}{RT}\right) y_{I1} \\ z &= y_C + y_{I1} + y_{char} \end{aligned} \quad (10)$$

where  $y_C$ ,  $y_{I1}$ ,  $y_{char}$  and  $z$  respectively represent the normalized mass of cardboard, solid intermediary, solid residue and the total normalized mass.  $T$  is the temperature. A first order Arrhenius kinetic model is used for the two reactions, then six parameters must be identified: the four Arrhenius parameters ( $A_1$ ,  $E_1$ ,  $A_2$ ,  $E_2$ );  $a$  and  $b$ , the two mass stoichiometric coefficients.

The thermogravimetric data recorded during the non-isothermal decomposition of the cardboard sample for three heating rates (5, 10 and 15 °C min<sup>-1</sup>) were used for the determination of the kinetic parameters of the model given above. For each experiment, 2951 items of experimental data were recorded (2951 was fixed with the default sampling time for the first experiment). The experimental conditions such as sample mass, atmosphere and gas flow rate were identical in all experiments. In Fig. 1, the experimental data are presented and compared with the theoretical curves computed with the identified kinetic parameters. Experimental data correspond to solid lines, while dashed lines represent the calculated curves. First, the kinetic parameters were identified separately for each experiment and their values are given in Table 1. Simulated curves and experimental curves are very close because the optimal set of parameters was found independently for each experiment. By examination of Table 1, we notice that while the kinetic parameter values are close for each experiment, they are, however, different; the more scattered values are for the parameters of the second reaction (log A<sub>2</sub> and E<sub>2</sub>) identified for the experiment with an heating



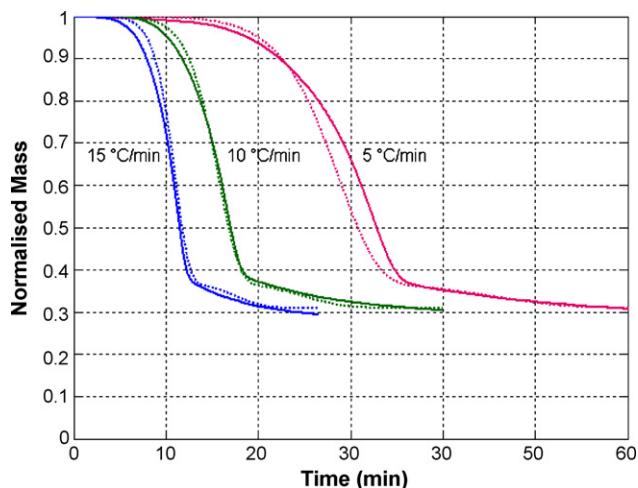
**Fig. 1 – Thermal decomposition of cardboard at 5, 10 and 15 °C min<sup>-1</sup>. Comparison between experimental curves (—) and fitted curves (---) using Eq. (10). The kinetic parameters are different for each fitted curve.**

rate of 10 °C min<sup>-1</sup>. The indifference intervals for each parameter are also given in Table 1. They are larger for the parameters of reaction (2). This result proves the model is more sensitive to the parameters of the first reaction.

In a second step, the identification procedure was carried out again with the three sets of experimental data (heating rate of 5, 10 and 15 °C min<sup>-1</sup>) as a whole. The kinetic parameters obtained are given in Table 2. Except for the coefficients  $a$  and  $b$ , the new values of the parameters are significantly different compared to the previous values given in Table 1. If the minimization criterion (Eq. (2)) for each experimental curve is compared using either the parameters identified for each experiment or the parameters identified for all the experiments, we found a ratio of about 10:  $J_1$  is respectively equal to  $6.0 \times 10^{-5}$ ,  $2.9 \times 10^{-5}$  and  $4.1 \times 10^{-5}$  for the experiment with a heating rate of 5, 10 and 15 °C min<sup>-1</sup> with the parameters identified for each experiment and equal to  $80.9 \times 10^{-5}$ ,  $15.8 \times 10^{-5}$  and  $64.1 \times 10^{-5}$  with the parameters identified for all the experiments. However, the comparison of the indifference

**Table 2 – Kinetic parameters and indifference intervals for thermal degradation of cardboard based on a unique identification using the three thermogravimetric experiments**

|  |                         |
|--|-------------------------|
| Experiment: heating rate (°C min <sup>-1</sup> ) | 5/10/15                 |
| log A <sub>1</sub> (min <sup>-1</sup> )          | 27.33 ∈ [26.66 – 27.99] |
| E <sub>1</sub> (J mol <sup>-1</sup> )            | 142,045 ± 1010          |
| log A <sub>2</sub> (min <sup>-1</sup> )          | 17.24 ∈ [16.28 18.20]   |
| E <sub>2</sub> (J mol <sup>-1</sup> )            | 103,185 ± 2571          |
| a  | 0.37 ± 0.05             |
| b  | 0.31 ± 0.05             |



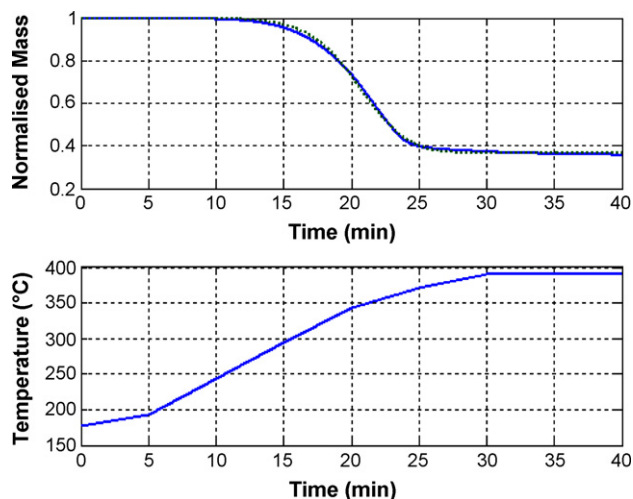
**Fig. 2 – Thermal decomposition of cardboard at 5, 10 and 15 °C min<sup>-1</sup>. Comparison between experimental curves (—) and fitted curves (---) using Eq. (10). The kinetic parameters are the same for each fitted curve.**

intervals shows they have been reduced with the unique set of parameters. This is particularly true for the parameters of the second reaction. We can conclude that parameters simultaneously found for several experiments with different operating conditions allow a reduced estimated range (i.e. smaller indifference intervals) but with worse fitting capabilities. This last point can be visualised with Fig. 2 where the experimental data are compared with the theoretical curves obtained with a unique set of kinetic parameters. We can observe the fitting capabilities mainly deteriorate for the experiment with a heating rate of 5 °C min<sup>-1</sup>.

#### 4.2. Optimal design of a thermogravimetric experiment

The first step is to look for the thermogravimetric experiment that makes it possible to find the kinetic parameters with the smallest minimum-sized joint confidence region. As stated before, a total experiment time and a number of intervals, in which the temperature will linearly evolve, must be chosen. Moreover, initial values for the parameters are needed. In this study, we present the case where height intervals of 5 min were fixed for the optimal experiment sought. The maximum possible heating rate allowed was 10 °C min<sup>-1</sup> so as to try to avoid too high a temperature gradient inside the sample. The values of the parameters identified for the experiment with a heating rate of 10 °C min<sup>-1</sup> were chosen as initial kinetic parameters and the heating rates for each subinterval were fixed to 10 °C min<sup>-1</sup> for initialisation. About 1400 iterations were necessary to maximize the criterion  $J_2$ : its value increased from  $2 \times 10^2$  to  $3.9 \times 10^{16}$ . The optimal values for the eight different heating rates are respectively 3.29, 10.00, 10.00, 10.00, 5.52, 3.89, 0.00 and 0.00. The optimal temperature profile can be viewed in the lower part of Fig. 3.

After the evaluation of the optimal experiment, we now need to carry it out. So, in a second step, a thermogravimetric experiment, whose programmed temperature profile is equal to the optimal temperature profile evaluated in the previous step, is carried out. From these new experimental data, a kinetic parameter identification procedure can be started. The optimal experiment has to be simulated with the model.



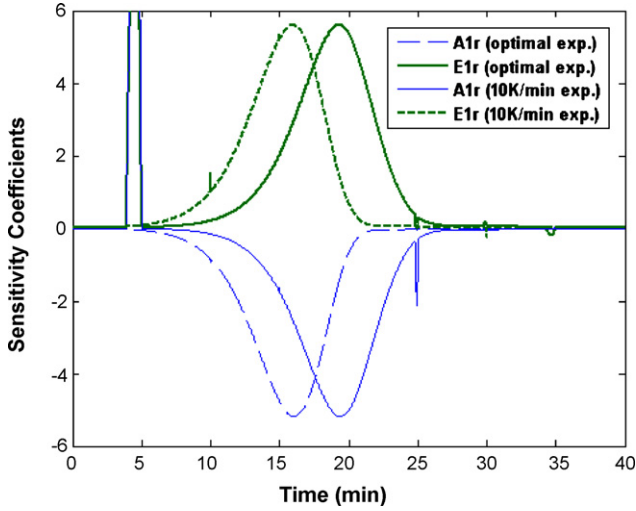
**Fig. 3 – Upper figure: Comparison between experimental curves (—) and fitted curves (---) with the kinetic parameters identified from the optimal experiment. Lower figure: Optimal temperature profile computed for the thermal decomposition of cardboard.**

The ODE system is resolved using the optimal temperature profile as inputs for the variable  $T$ . The results of the parameter identification are given in Table 3. The comparison with the results obtained for the experiment with a constant heating rate of 10 °C min<sup>-1</sup> (same number of experimental data) shows that the values of fitted parameters have evolved and a smaller indifference interval can be noticed; it is particularly true for the two mass stoichiometric coefficients with a reduction of their indifference interval by a factor between 4 and 6. In order to estimate the quality of the new kinetic parameters, the experimental curve and model-predicted mass evolution versus time are compared in Fig. 3 (upper part). The two curves are very close. However, if we consider the numerical value of the criterion  $J_1$ , its value increases from 0.086 (fitting with the experiment with a constant heating rate of 10 °C min<sup>-1</sup>) to 0.206 (optimal experiment).

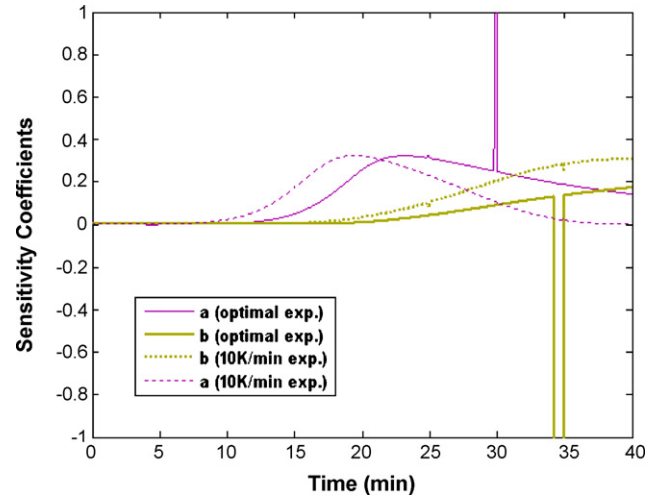
In attempting to analyse the results obtained, it can be observed that, as expected, the optimal experiment seems to allow the improvement of the parameters; this is confirmed from a numerical point of view: a very large increase in the criterion  $J_2$  and a reduction in the indifference intervals for all the parameters are observed. Unfortunately, firm explanations cannot be drawn about the “shape” of the temperature profile computed for the optimal experiment. In a previous study, the optimal temperature profile for identifying the kinetic parameters of the thermal degradation of cellulose (Reverte et al., 2007) were researched; the reaction schemes for the cellulose degradation are fairly well known and we used a scheme consisting in two concurrent reactions (Bradbury et al., 1979). The results showed that the heating rate of the time intervals where the main mass loss occurs were significantly reduced during the optimal experiment. We interpreted this to mean that the numerical procedure had increased the duration of the main degradation phase by reducing the heating rate. This length of time corresponded to the intervals in which the sensitive coefficients had the highest values. It was proven by the plot of the sensitive coefficients and it was observed that the duration where the main thermal degradation took place corresponded to the times where the parameters were the most sensitive to the measured data.

**Table 3 – Kinetic parameters and indifference intervals for thermal degradation of cardboard; comparison between the experiment with a constant heating rate of  $10^\circ\text{C min}^{-1}$  and the optimal experiment**

| Experiment: heating rate ( $^\circ\text{C min}^{-1}$ ) | $\log A_1$ ( $\text{min}^{-1}$ ) | $E_1$ ( $\text{J mol}^{-1}$ ) | $\log A_2$ ( $\text{min}^{-1}$ ) | $E_2$ ( $\text{J mol}^{-1}$ ) | $a$             | $b$             |
|--|----------------------------------|-------------------------------|----------------------------------|-------------------------------|-----------------|-----------------|
| 10   | $22.27 \in [21.86-22.68]$        | $117,502 \pm 1972$            | $10.00 \in [7.00-12.98]$         | $65,730 \pm 5490$             | $0.37 \pm 0.08$ | $0.31 \pm 0.06$ |
| Optimal run  | $24.04 \in [23.81-24.27]$        | $130,189 \pm 1284$            | $10.00 \in [9.65-10.35]$         | $44,143 \pm 3278$             | $0.45 \pm 0.02$ | $0.37 \pm 0.01$ |

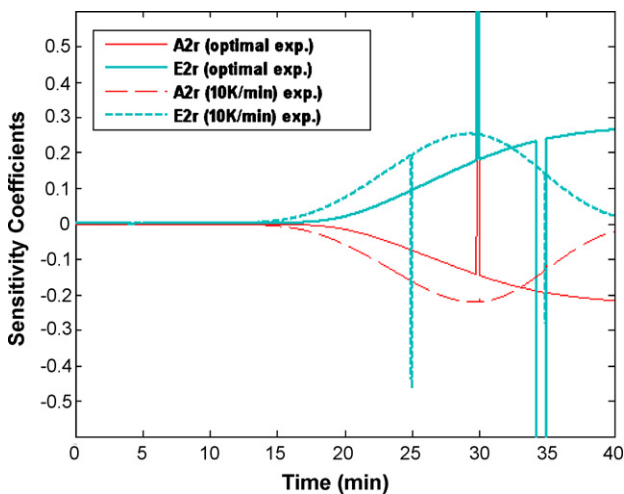


**Fig. 4 – Time evolution of sensitivity coefficients for parameters  $A_{1r}$  and  $E_{1r}$  with the optimal temperature profile (continuous line) and with a constant heating rate of  $10\text{ K min}^{-1}$  (dashed line).**



**Fig. 6 – Time evolution of sensitivity coefficients for parameters  $a$  and  $b$  with the optimal temperature profile (continuous line) and with a constant heating rate of  $10\text{ K min}^{-1}$  (dashed line).**

In the case of the cardboard experiments no such conclusion is drawn. It seems rather obvious that the optimal temperature profile was elaborated for a quick heating without going beyond a temperature of  $400^\circ\text{C}$ . Some information can be deduced from the plot of the evolution of sensitivity coefficients over time (Figs. 4–6). Even with the applied reparametrization, differences in magnitude exist for the sensitivity coefficients. The time evolution of the sensitivity coefficients for parameters  $A_{1r}$  and  $E_{1r}$  with the optimal experiment and with the experiment at a constant heating rate are plotted in Fig. 4. The two kinetic parameters of the first



**Fig. 5 – Time evolution of sensitivity coefficients for parameters  $A_{2r}$  and  $E_{2r}$  with the optimal temperature profile (continuous line) and with a constant heating rate of  $10\text{ K min}^{-1}$  (dashed line).**

reaction ( $A_{1r}$  and  $E_{1r}$ ) present the higher coefficient values (to compare with Figs. 5 and 6); these values increase with the progress of the mass loss. In fact, it is easy to show they are directly proportional to the time derivative of the mass loss: the maximum value of these two coefficients is approximately at a time of 20 min corresponding to the time of the maximum for the derivative of the mass loss. In Fig. 5, similar plots have been produced for the parameters  $A_{2r}$  and  $E_{2r}$ . The magnitude of the kinetic parameters of the second reaction ( $A_{2r}$  and  $E_{2r}$ ) is smaller and increases from about the middle of the simulation. The plotting of the estimated partial mass  $y_C$ ,  $y_{I1}$  and  $y_{\text{char}}$  (not shown here) proves that the sensitivity coefficients of  $A_{2r}$  and  $E_{2r}$  are directly proportional to the mass of produced char ( $y_{\text{char}}$ ). An identical comment can be made for the sensitivity coefficient of  $b$  (Fig. 6). Now, by comparing the two evolutions of sensitivity coefficients for a given parameter, we can better understand why the temperature remained constant at the end of the run. For the parameters of the first reaction, there is no significant difference, except a time delay can be observed in Fig. 4. Some real differences exist in the evolution of sensitivity coefficients for  $A_{2r}$  and  $E_{2r}$  (Fig. 5) and even for the coefficient  $a$  (Fig. 6): with a constant heating rate, these coefficients decrease during the end of the run, while with the optimal temperature profile (and the temperature maintained constant during the last subintervals), the coefficient values do not decrease. We can assume this to be one of the reasons explaining the final evolution of the temperature during the optimal run. Finally, the last remark concerns the “perturbations” observed for all the curves with the experimental experiment. These “perturbations” occur at a time when the heating rate is modified, and are without doubt due to a lack of precision in the numerical evaluation of the sensitivity coefficients at these instants.

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## 5. Conclusion

In this paper, we have presented some results concerning the evaluation of an optimal thermogravimetric experiment for increasing the reliability of kinetic parameter estimates. The results were illustrated by determining a kinetic model for cardboard thermal degradation. Through the approach explained above, parameters with a smaller joint confidence region and with reduced indifference intervals have been found. However, we need to confirm these first results with a thorough analysis; for example, what is the influence of the variables of the method whose values have been fixed here (number and length of subintervals, maximal heating rate, etc.)? What would be the benefit of combining the initial experimental run and the optimal run for the identification of kinetic parameters? How many TGA runs are necessary in order to obtain the same confidence criterion as the one that was obtained with the optimal run?

However, because of the poor extrapolation capacity of the fitted parameters, a conclusion of this work is that the model used here is without doubt not suitable to well represent the thermal degradation of cardboard under different operating conditions. Different models must be tested with the presented procedure. In a near future, we plan to use a similar approach based on the experimental optimal design for the model discrimination, i.e. the evaluation and the realization of optimal TGA experiments for discriminating the best kinetic model among several proposed models.

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