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Kinetic model identification and parameters estimation from TGA experiments

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Abstract

The presented work is a part of an ongoing research effort on the development of a general methodology for the determination of kinetic models of solid thermal decomposition under pyrolysis conditions with thermogravimetric analysis (TGA) devices. The goal is to determine a simple and robust kinetic model for a given solid with the minimum of TGA experiments. From the latter point of view, this work can be seen as the optimal design of TGA experiments for pyrolysis kinetic modelling. In this paper, a general procedure is presented and more precise results are given about the influence of the sensitivity matrix on the estimation of the kinetic parameters and about the important influence of the specific TGA runs used for parameter estimation on the precision of the fitted parameters. The first results are shown for simulated applications; in the final part, the presented results concern cellulose pyrolysis in a Setaram TGA device.

Keywords: Kinetic; Parameter estimation; Optimal design; TGA; Pyrolysis

1. Introduction

The development of design tools for industrial scale pyrolysis processes adapted to various waste or mixed waste involves correctly understanding and describing the chemical and physical phenomena occurring inside the pyrolysis vessel, i.e. the chemistry of the solid decomposition, the thermal transfer between wall, solid and gas phases, and also inside the solid phase. For instance, the modelling of thermal degradation of a large solid body generally requires solving heat and mass balance equations to compute the temperature and the gas composition at each location inside the material. The heat and mass source terms are calculated from the progress of the chemical reactions, which is itself computed from a reaction scheme involving the kinetic parameters. Because the assumption of a uniform temperature (or a constant heating rate) inside the process (for example fixed bed reactor, slumping bed in a rotary kiln, etc.) is too restrictive, the set of kinetic parameters should be unique and independent of the operating conditions. Moreover, before trying to evaluate the kinetic parameters, some other important choices must be made: Which reaction scheme and kinetic model is associated? How are the reaction rates computed (chemical reaction first or *n*th order, nucleation, phase boundary reaction, diffusion, etc.)? For example, in a previous study concerning the thermal degradation of cardboard, six reaction schemes have been checked without a real conclusion on the right one [1]. Another example is the wide range of literature about cellulose thermal degradation [2,3]; many kinetic laws and kinetic parameters have been proposed during the last decades.

The aim of our ongoing research effort is to bring answers to questions like these: What are the best kinetic parameters for a chosen model? What is the best (or rather the least worst) kinetic model between several candidates? How many experiments must be made to identify the kinetic model and kinetic parameters? What would be the optimal experiment(s) to identify the kinetic model and the kinetic parameters? What is the confidence in the estimated parameters? etc. Initially, all these questions are limited to the study of solid thermal

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degradation primary reactions with a thermogravimetric analysis (TGA).

In a previous stage [4,5], a numerical estimation procedure to simultaneously determine the kinetic parameters from TGA experiments under different thermal conditions was developed. This numerical procedure is used to recover the kinetic parameters of the given model. The parameter estimation problem is solved with a gradient type-method by minimizing the least square norm. In this paper, we present additional numerical techniques to help to determine the kinetic parameters and to design a more robust parameter estimation tool. We show how the examination of the sensitivity coefficients and the matrix sensitivity determinant can improve the analysis of kinetic estimation results. Finally, some first results concerning the optimal design of TGA experiments are presented. By optimal design, we mean ''what are the best experiments to do for the optimal determination of kinetic parameters?''.

2. Optimum experimental 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 [6]. In our case, the goal is then to use the approach of optimum experimental design to determine the optimal TGA run to perform in order to find the ''best'' kinetic parameters. By ''best'' parameters, we mean the parameters with a higher statistical reliability, i.e. with the highest associated confidence. Then we call the ''optimal experiment'', the one allowing us to determine these ''best'' parameters.

2.1. Initial kinetic parameter estimation problem

First, let us define the kinetic parameters estimation problem. The kinetic model used is given by the following equations:

$$\dot{\mathbf{y}} = \mathbf{f}(t, \mathbf{y}, \mathbf{p}, \mathbf{x}), \quad \mathbf{y}(t=0) = \mathbf{y}_0, \qquad z = g(t, \mathbf{y}) \tag{1}$$

where t is the time, $\mathbf{y}$ and $\dot{\mathbf{y}}$ are the set of dependent variables characterizing the solid kinetic and their derivatives with time, $\mathbf{p}$ the set of kinetic parameters to identify and $\mathbf{x}$ are the other variables of the model such as temperature; z corresponds to the model output to compare with the evolution of mass loss measured with the thermobalance. Generally, z is a linear combination of $\mathbf{y}$. All variables depend on time, except the kinetic parameters, which are assumed to be constant. The set of equations ($\mathbf{f}$ and g) defines the kinetic model.

In this work, all the kinetics are assumed to be modelled with a first order Arrhénius kinetic model and the dependant variables $\mathbf{y}$ are the solid normalized mass. Then the kinetic parameters are, respectively, the pre-exponential factor and the activation energy for each reaction of the chosen model.

The minimization criterion used for identifying the kinetic parameters is given by the squared differences between the model output and the measured data for one or several runs:

$$\min_{\mathbf{p}} J_1(\mathbf{p}) = \frac{1}{\mathrm{Nex} \cdot \mathrm{Nm}} \sum_{i=1}^{\mathrm{Nex}} \sum_{j=1}^{\mathrm{Nm}} w_{ij} (\eta_{ij} - z_{ij}(t_{ij}, \mathbf{y}, \mathbf{p}))^2 \tag{2}$$

Nex and Nm, respectively, represent the number of experimental runs and the number of measurements for each run. η_{ij} corresponds to the jth experimental measurement of the ith run. w_{ij} is a weighting factor used to give a relative importance to each term of the sum(s). The choice of w_{ij} is generally made so that the more a measurement is noise corrupted the less it will count in the sum(s). If the measurement errors are assumed to be independent and normally distributed with an expected zero value then the weighting factor is chosen as the inverse measurement error variance.

In vector form, the above expression can be written as:

$$\min_{\mathbf{p}} J_1(\mathbf{p}) = \frac{1}{\mathrm{Nex} \cdot \mathrm{Nm}} (\Gamma - \mathbf{Z})^{\mathrm{T}} \mathbf{W} (\Gamma - \mathbf{Z}) \tag{3}$$

Here, $\mathbf{Z}$ and $\mathbf{\Gamma}$ are, respectively, the vectors of computed total mass and measured mass. $\mathbf{W}$ is the inverse measurement error covariance matrix.

A version of Levenberg–Marquardt method was applied for the parameter estimation problem [7]. It is a quite stable, powerful and straightforward method that has been applied to a variety of optimization and inverse problems. The solution for vector $\mathbf{p}$ is achieved using the following iterative procedure:

$$\mathbf{p}^{k+1} = \mathbf{p}^k + \left[\mathbf{X}^{k\mathrm{T}} \mathbf{X}^k + \mu^k \Omega^k\right]^{-1} \mathbf{X}^{k\mathrm{T}} (\Gamma - \mathbf{Z}^k) \tag{4}$$

It is an iterative procedure where the superscript k defines the iteration number. $\mathbf{\Omega}$ and μ are, respectively, a damping matrix and a damping parameter. $\mathbf{X}$ represents the sensitivity matrix evaluated at each iteration k. The sensitivity matrix is given by:

$$\mathbf{X} = \left[\frac{\partial \mathbf{Z}^{\mathrm{T}}(\mathbf{p})}{\partial \mathbf{p}}\right]^{\mathrm{T}} = \begin{bmatrix} \frac{\partial z_{11}}{\partial p_1} & \cdots & & \frac{\partial z_{11}}{\partial p_m} \\ \frac{\partial z_{12}}{\partial p_1} & \cdots & & \\ \cdots & \frac{\partial z_{ij}}{\partial p_n} & \cdots & \cdots \\ \frac{\partial z_{\mathrm{Nex} \cdot \mathrm{Nm}}}{\partial p_1} & \cdots & & \frac{\partial z_{\mathrm{Nex} \cdot \mathrm{Nm}}}{\partial p_m} \end{bmatrix} \tag{5}$$

The elements of the sensitivity matrix $\mathbf{X}$ are known as the sensitivity coefficients. In the present work, a central finite-difference approximation is used to calculate the sensitivity coefficients. The sensitivity coefficient X_{ij} is the measure of the sensitivity of the estimated model output z_i with respect to changes in the parameter p_j. A small value of the magnitude of X_{ij} indicates that large changes in p_j yield small changes in z_i. It can easily be noticed that the estimation of the parameter p_j is extremely difficult in such a case, because basically the same value for total mass would be obtained for a wide range of p_j values.

As said before, the Levenberg–Marquardt method is an iterative procedure because of the non-linear nature of the

estimation problem and therefore the coefficients of the sensitivity matrix depend on the values of the unknown kinetic parameters. Moreover, it is necessary to give initial values for the unknown parameters in order to start the numerical computations. For each iteration, the successive steps are:

- model output is computed by the resolution of the set of differential equations (Eq. (1));
- minimization criterion is calculated by summing the squared differences for each computed model output at the sampling times of the measurements (Eq. (2));
- new values of parameters are estimated by Eq. (4).

Iterations continue until convergence of the estimated parameters is reached, i.e. when there is a negligible change in any component of **p**. However, because the Levenberg–Marquardt method is a local method, we are not sure of finding the global solution, i.e. the set of kinetic parameters giving the smallest value of the minimization criterion. Classically, the solution found by the numerical method will strongly depend on the initial values chosen for the parameters. We have to proceed to a reparametrisation of parameters in order to improve the parameter estimation procedure. This reparametrisation is presented in the next section.

2.2. Kinetic parameter reparametrisation

Beck and Arnold [8] have clearly shown the significant importance of the sensitivity coefficients for the parameter estimation. The inverse problem (or optimization problem) is less suitable if the sensitivity coefficient values are small. The fitting process can be improved if the sensitivity coefficient values are increased. As it will be shown later, the sensitivity coefficients for the pre-exponential factors are generally small compared to the coefficients for activation energy. It will then be more difficult to estimate the former because their variation will have little influence on the kinetic model output. In order to have a better homogeneity in the sensitivity coefficient magnitude, we proceed to the following reparametrisation of the kinetic parameters, where the two new kinetic parameters, A_r and E_r, are defined from the original ones, A and E, by the relations:

$$A_r = \ln(A), \qquad E_r = \frac{E}{R} \tag{6}$$

The only interest for the reparametrisation of the activation energies is to decrease the values of these parameters and then the differences of magnitude between all the parameters to estimate. The new expression of the kinetic constant (k_r) must be equal to the original one and is given by:

$$k_r = \exp(A_r)\exp\left(-\frac{E_r}{T}\right) \tag{7}$$

The influence of such reparametrisation on sensitivity coefficients will be shown in Section 3.

2.3. Joint confidence regions and parameter confidence intervals

Finding the best values of the set of parameters is just a part of the job of fitting. If possible, the precision of the parameter estimates must be known. 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. For example, let us suppose that a model has been generated from a set of data and a set of parameters has been found. With a new and different set of data, different parameter values will be estimated. This happens because of random variations in the measurements. If we plot the different sets of parameters in the parameter space then the plotting is not entirely random. If there are only two parameters, p_1 and p_2, and the different sets of parameters are plotted in a (p_1–p_2) plan, the orientation and the shape of the region covered by the plots are not random. A small region indicates precise parameter estimates.

The basic element is the Fisher information matrix **F** that combines some information on the output measurement error thanks to the weighting matrix **W**, and some information on the sensitivity of the model output (z) with respect to the parameters thanks to the sensitivity matrix **X** (Eq. (5)):

$$\mathbf{F} = \mathbf{X}^{\mathrm{T}}\mathbf{W}\mathbf{X} \tag{8}$$

For a non-linear model in the parameters, the inverse of the 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 [9]. The Fisher information matrix gives information on the parameter estimation quality in the neighborhood of the true parameter vector [10].

It can be demonstrated that the size of the joint confidence region is proportional to the Fisher information matrix. More precisely, the area of the joint confidence region is proportional to the determinant of the inverse Fisher information matrix:

$$\upsilon(\kappa) \propto \det{}^{1/2}(\mathbf{F}^{-1}) \tag{9}$$

So, the minimum sized joint confidence region corresponds to the maximum of the **F** determinant. In the mathematical sense, an experiment maximizing **F** will be said to be optimal. However, because of the non-linearity of the model, the matrixes **X** and **F** depend on the values of the parameters. If they are distant, the estimated parameters will have a large confidence region. An iterative approach to experimentation can be envisaged with an improvement on the parameter estimates after each iteration.

Practically, a scalar function of **F** is used as a criterion to find the optimal experiment. Several criteria exist (determinant, trace, condition number). Here, we use a criterion, called D-criterion, corresponding to the maximization of the determinant of the Fisher information matrix, equivalent to minimizing the geometric mean of the identification error:

$$\max_u J_2(\mathbf{p}) = \det(\mathbf{F}) \tag{10}$$

u represents the set of variables whose values are sought to minimize the criterion. We discuss the choice of u in the next section.

Moreover, an approximate confidence interval can be defined for each identified parameter:

$$p_i \in \left[p_i^* - \left(\frac{2\kappa}{H_{ii}} \right)^{1/2}, p_i^* + \left(\frac{2\kappa}{H_{ii}} \right)^{1/2} \right] \tag{11}$$

where κ is the allowed maximum value for the absolute value of the difference between $J_1(p)$ and $J_1(p^*)$. $\mathbf{p}^*$ is the fitted solution for $\mathbf{p}$. H_{ii} is the diagonal element of the Hessian matrix computed for $J_1(p^*)$. Practically, they are computed by second order central finite difference.

2.4. Optimum design with a thermogravimetric analyzer (TGA)

In this work, we assume that a classical thermobalance is used; only the variations of the total mass of solid and of the cell temperature can be recorded during the experimental time. What are the constant and time-varying controls or inputs to the process and what are the experimental conditions that characterize a particular experiment? We can distinguish:

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

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 and it is assumed that the solid sample temperature is the same as the cell temperature. So, with such a model, the initial mass of the sample and the flow rate and properties of the vector gas have no influence. In conclusion, the only input available to improve the experimental conditions is the programmed temperature profile of the cell.

In other words, we are looking for the temperature profile to apply to the thermobalance in order to improve the precision and the reliability of kinetic parameters for a chosen kinetic model, i.e. in minimizing the criterion defined in Eq. (10). To find the optimal temperature profile, we first divide the chosen time of reaction (t_f) into P intervals of equal length (Δt), so that the length of each interval is:

$$\Delta t = \frac{t_f}{P} \tag{12}$$

We seek the successive profiles, assumed linear, for each interval so that the temperature is given by (for the kth interval):

$$T(t) = T(k) + \left(\frac{T(k+1) - T(k)}{\Delta t} \right)(t - t(k)) \tag{13}$$

where $T(k)$ and $T(k+1)$ are the initial and final temperatures for the kth interval, respectively, at time $t(k)$ and $t(k+1)$. If we define β_k as the slope of the temperature for the kth interval, Eq. (13) can be expressed as:

$$T(t) = T(k) + \beta_k(t - t(k)) \tag{14}$$

The optimum design problem can then be written as:

$$\max_{\beta} \det(\mathbf{F}) \tag{15}$$

$\boldsymbol{\beta}$ is the vector of the successive values of β_k.

Lower and upper bounds are defined for the values of β_k; these bounds must be chosen according to the thermogravimetric device used.

2.5. The proposed procedure for the optimum experimental design with a TGA device

The procedure proposed in this paper is sketched in Fig. 1. The first stage corresponds to the choice of the model and the identifiability study of the model. The choice for the class of models used depends on the required objectives. In model classes, we broadly distinguish between "detailed models versus simple models" and "kinetic models versus multi-physics models". For a given class of models, i.e. simple kinetic models, it is possible to have several candidate models. For example, considering the huge literature about the kinetics of thermal degradation of cellulose [2,3,11–13], many reaction schemes and associated kinetic models have been proposed. The question is to know how to choose the best candidate knowing all the candidates are simplified models and they are more or less wrong. Assuming we are able to determine the best kinetic model, we need to check the identifiability of the chosen model. A definition of identifiability has been expressed as "if for the chosen model, there are several sets of searched parameters exactly corresponding to the same input–output behavior of the model then this latter is not uniquely identifiable" [9]. Several mathematical approaches exist for checking the identifiability of a model before conducting any experiments. However, for a non-linear model, the computations are generally long and tedious. In this paper, we do not discuss the first stage.

The second stage involves making an initial experiment. This first experiment is very important and must benefit from all the knowledge and expertise of the experimenter. From this first experiment, unknown parameters must be identified using a criterion liked that given in Eqs. (2) or (3). Classically, the main problem here is the choice of the initial parameters for running the numerical procedure. Success will often depend on the quality of the initialization.

The third stage is the computation of the confidence interval of the parameters found and the determination of the optimal experiment by the maximization of a criterion linked to the Fisher Matrix as defined in Eq. (15). This newly determined experiment will depend on the chosen model and the parameters fitted in the previous stage. Next, the second stage is repeated: the new experiment is carried out and new parameters are fitted. Finally, the precision of the new parameters is computed and compared to the previous

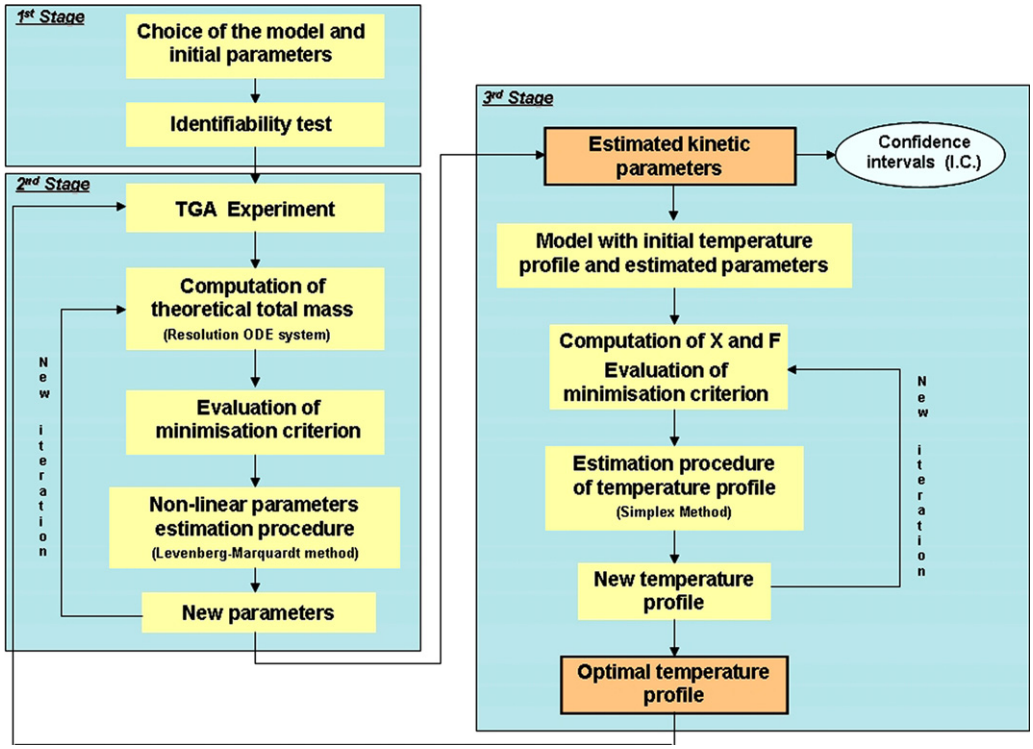

Fig. 1. General procedure for the estimation of kinetic parameters and for the determination of the optimum experimental run.

ones. If the results are satisfying then the procedure is stopped. If not, a new loop is generated. As said before, because of the non-linearity of the model, the determination of the optimal experiment depends on the parameters initially used. It is possible to find a new and different optimal experiment and then some new parameters after the conclusion of each loop.

3. Results

Some results using the procedure described in the previous sections and concerning the thermal degradation of cellulose are now presented. First of all, simulation results are given, i.e. the experimental data points are generated by a numerical model without or with artificial noise on the data; next, real experimental data from TGA apparatus is used. In both parts the kinetic parameters are first estimated with the computation of their confidence intervals; secondly, the optimal experiment is determined for final evaluation and comparison of the new confidence intervals. For all the presented results (experimental and simulations), 2951 values are used for each estimation runs.

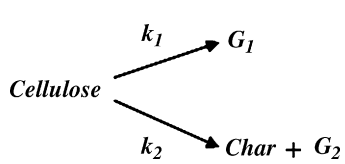

Fig. 2. Reaction scheme used for the thermal degradation of cellulose [11].

The reaction scheme used for describing the thermal degradation of cellulose is the scheme proposed by Bradbury et al. [11], given in Fig. 2.

3.1. Influence of the reparametrisation

As previously said in Section 2.2, the mathematical expressions of the kinetic constants, defined in Eqs. (6) and (7), have been used. The influence of such modifications is shown in Fig. 3, where the transient behaviors of the relative sensitivity coefficients are plotted for the four kinetic parameters of the model associated with the reaction scheme defined by Bradbury; the kinetic constants (k_1 and k_2) are expressed with a first order Arrhénius law. Because the unknown parameters can have different orders of magnitude, it is preferable for a more easy comparison and analysis to plot the relative sensitivity coefficients defined as:

$$X_{ij}^{+} = p_j X_{ij} = p_j \frac{\partial z_i}{\partial p_j} \tag{16}$$

Without reparametrisation (Fig. 3, left hand), the smallest relative sensitivity coefficients are observed with A_1 and A_2, which can involve difficulties in their estimation and a relatively high estimation error. When the reparametrisation process is applied (Fig. 3, right hand) then all the relative sensitivity coefficients have the same order of magnitude. Many trials without and with reparametrisation have been carried out and have proved that the computations during the estimation procedure are faster (the number of iteration is reduced) for

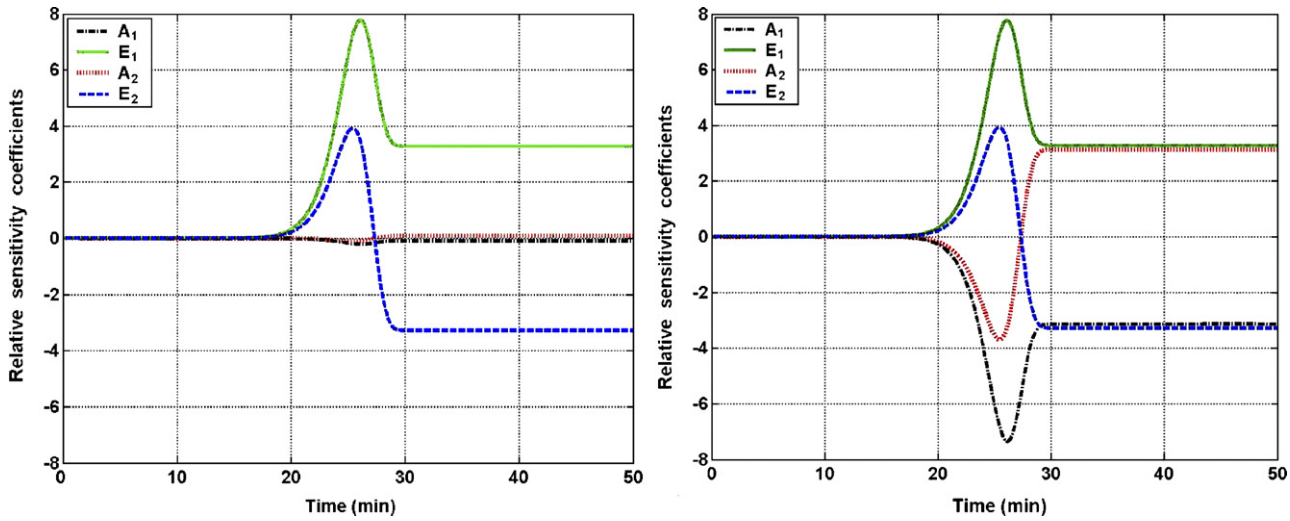

Fig. 3. The relative sensitivity coefficient evolutions without reparametrisation (left hand) and with reparametrisation (right hand).

Table 1
True and fitted parameters for cellulose degradation (simulation studies)

	True parameters	Fitted parameters (no noise)	Fitted parameters (0.5% noise)	Fitted parameters (2% noise)
A_1 (min^{-1})	3.75×10^{19}	3.75×10^{19}	2.87×10^{19}	2.17×10^{19}
E_1 (J mol^{-1})	234,904	234,904	233,632	232,248
A_2 (min^{-1})	3.88×10^{12}	3.88×10^{12}	1.33×10^{14}	1.48×10^{14}
E_2 (J mol^{-1})	160,967	160,967	178,859	179,437

finding the solution and/or the solution is more often found with reparametrisation.

3.2. Simulation studies

3.2.1. Kinetic parameters estimation

In order to check the real ability of the developed parameter estimation procedure, a TGA run has been simulated. Simulation results are primarily used to avoid one of the main drawbacks of the approach: we are sure that the kinetic model used is perfect and if it is a pure kinetic model (the case presented here), no thermal transfer can influence the kinetic of thermal degradation; moreover, the measurements are also assumed to be perfect.

The simulation consisted in computing the transient mass evolution for a given heating rate (10 °C min^{-1}) by the resolution of the two differential equations associated with the two parallel reactions in the scheme proposed by Bradbury (Fig. 2). We need to set values for kinetic parameters, these values are assumed to be "true" and are called true parameters in Table 1. The true parameters have been chosen as the values identified from an experimental TGA run in a preliminary step. Three cases have been simulated: first, no artificial noise has been added to the simulated data; in the second and third cases, a random value (white noise) between 0 and ±0.5% of the maximum value of the total normalized mass (i.e. 1.0), or between 0 and ±2%, is added to the computed mass. The values of the fitted parameters for all the cases are presented in Table 1. The fitted values are exactly the same ones as the true parameters when there is no noise on the data; the correct performances of the parameter estimation procedure are thus confirmed. With noise on the data, it is not possible to find the true parameters, differences exist between solution values and fitted values, mainly for the second reaction parameters. The differences between true parameters and fitted parameters increase with the noise level. However, if the mass loss curve is computed with the fitted parameters, we can see that this computed curve is very close to the solution curve used for the fitting process; for example, the curve used for the parameter estimation (2% noise level) and the mass loss curve computed with the parameters estimated are presented in Fig. 4. We can

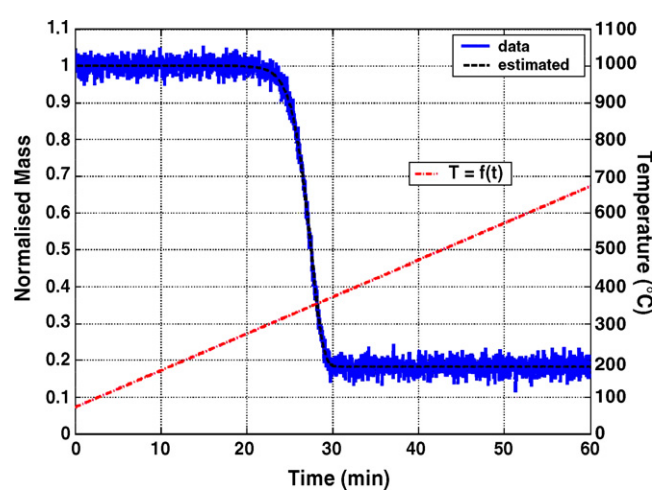

Fig. 4. Mass loss curves: simulated curve with noise on data and computed curve with fitted parameters.

Table 2
Fitted parameters from the first run (constant heating rate) and from the optimal run (optimal temperature profile)

	Fitted parameters (0.5% noise) after the first run	Fitted parameters (0.5% noise) after the optimal run	Fitted parameters (2% noise) after the first run	Fitted parameters (2% noise) after the optimal run
A_1 (min^{-1})	2.87×10^{19} [1.98–4.16 $\times 10^{19}$]	2.87×10^{19} [2.07–3.98 $\times 10^{19}$]	2.17×10^{19} [0.22–21.7 $\times 10^{19}$]	2.17×10^{19} [1.72–2.73 $\times 10^{19}$]
E_1 (J mol^{-1})	233,632 ± 1872	233,632 ± 1240	232,248 ± 1861	232,248 ± 995
A_2 (min^{-1})	1.33×10^{14} [0.92–1.92 $\times 10^{14}$]	1.33×10^{14} [1.11–1.60 $\times 10^{14}$]	1.48×10^{14} [1.17–1.88 $\times 10^{14}$]	1.48×10^{14} [1.32–1.66 $\times 10^{14}$]
E_2 (J mol^{-1})	178,859 ± 1850	178,859 ± 3668	179,437 ± 3203	179,437 ± 2021

Values in square parenthesis give the confidence intervals.

conclude that the fitted parameters are able to represent the thermal degradation of cellulose (at least for a run with a constant heating rate of 10 °C min^{-1}).

3.2.2. Determination of the optimal experiment

Now, we are trying to evaluate the optimal experiment for the cellulose from the kinetic parameters fitted with the noise data. We recall that we call "optimal experiment", the set of experimental data allowing the computation of the kinetic parameters with the best precision. It is no use trying to find precise estimates with the data without noise because we have shown the solution has been exactly determined in this case. As we explained before, the goal here is to find the temperature profile maximizing the criterion defined in Eq. (15), kinetic parameters being kept constant. In the case of the thermal degradation of cellulose, we have chosen a maximum reaction time of 1 h. The time of reaction has been divided in 12 intervals of 5 min. The 12 heating rates must be included between 0 °C min^{-1} (isothermal step) and 10 °C min^{-1} (maximum heating rate).

In the case of data with 2% level noise, the optimal temperature profile found is plotted in Fig. 5. The successive values of heating rates for each 5 min interval are: 7.08, 2.18, 2.25, 5.31, 3.81, 5.21, 8.17, 3.29, 3.00, 5.14, 7.32, and 7.94. The total mass, mass of cellulose and mass of char computed with the optimal temperature profile are also plotted in Fig. 5. These curves enable us to show that the thermal degradation is finished. The optimal temperature profile with 0.5% level noise is slightly different (not shown here) from the optimal temperature profile presented in Fig. 5; this is logical because the kinetic parameters used were not the same.

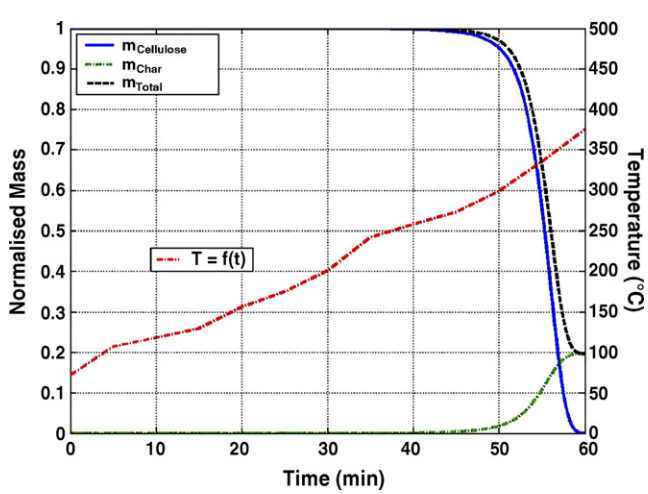

Fig. 5. The optimal temperature profile and the corresponding mass loss curves (total mass, cellulose and char).

Now in order to check if the found temperature profile is really optimal, a new kinetic parameters estimation is carried out (noise is again added on the simulated data) and simulated with this new optimal temperature profile. The initial values used for the parameters are the ones found during the previous step. A computation of the confidence intervals for each parameters is achieved and compared with the confidence intervals found during the previous step. All the results are listed in Table 2. We can observe the fitted values are the same ones in both cases, i.e. classical run (conventional temperature program with a constant heating rate run with a constant heating rate) and optimal run. However, the examination of the confidence intervals shows:

(i) in almost all cases, the confidence intervals are reduced with the optimal runs; there is one exception for E_2 with the 0.5% noise run;
(ii) for A_1 with the 2% noise run, a very large decrease (nearly 95%) can be observed;
(iii) with the 2% noise run, the decrease in the confidence intervals for E_1 and E_2 are, respectively, 46% and 37%.

This simulation study proved that it was possible to improve the precision of the estimated kinetic parameters. In the following section, we apply the methodology to an experimental example.

3.3. Experimental study

Experiments were performed using a Setaram™ 92-16.18 apparatus. The heating rate was first taken as 10 °C min^{-1} with a stable gas flow of nitrogen (33 ml min^{-1}). A small sample size of cellulose (11 mg) was used to ensure the kinetic regime of the decomposition.

Fig. 6 shows the experimental and model predicted mass evolutions versus time obtained with the developed algorithm. Some differences can be observed around the curve of the measured total weight loss. Other results, not shown here, have proved the curve fits better if a nth order Arrhénius model is used to model the kinetic constants. The values of the estimated parameters with their respective confidence intervals are given in the first column of Table 3.

From these estimated parameters, we have determined the optimal temperature profile. Here again, a time of reaction of 1 h has been divided in 12 intervals of 5 min with lower and

Table 3
Fitted parameters from the first experimental run (constant heating rate) and from the optimal experimental run (optimal temperature profile)

	Fitted parameters from the first run (10 °C min^{-1})	Fitted parameters from the optimal run
A_1 (min^{-1})	5.14×10^{19} [3.35–7.89 $\times 10^{19}$]	8.17×10^{19} [7.11–9.38 $\times 10^{19}$]
E_1 (J mol^{-1})	236,417 ± 2162	235,743 ± 859
A_2 (min^{-1})	3.95×10^{10} [2.78–5.61 $\times 10^{10}$]	4.26×10^{10} [3.66–4.96 $\times 10^{10}$]
E_2 (J mol^{-1})	137,871 ± 1760	137,630 ± 470

Values in square parenthesis give the confidence intervals.

upper bounds, respectively, of 0 and 10 °C min^{-1}. The successive optimal values of heating rates for each 5 min interval are (all given in °C min^{-1}): 8.44, 5.40, 8.32, 9.57, 4.07, 2.08, 1.00, 6.25, 6.51, 2.17, 7.98, and 6.85. The final corresponding maximization criterion, i.e. the determinant of **F**, is equal to 5.2×10^{15}; its value has increased from an initial value of 12.5 (the initial temperature profile was a constant heating rate of 10 °C min^{-1}).

The optimal experiment was performed by setting this optimal temperature profile on the TGA device used. The real experimental temperature profile and the experimental mass loss curve (solid curve) are shown in Fig. 7. From these experimental curves, a new kinetic parameters estimation process was run. The kinetic parameters obtained with their respective confidence intervals are presented in the second column of Table 3. The computed mass loss curve from these parameters is also plotted in Fig. 7.

From Table 3 and Fig. 7, we can conclude:

(i) the new fitted parameters are different from the previous ones fitted from the classical TGA run. The fitting errors are reduced; the minimization criterion values (Eq. (3)), respectively, give 4.6×10^{-4} (first fitting with a constant heating rate) and 2.6×10^{-4} (fitting with the optimal profile);
(ii) the confidence intervals of all parameters are reduced on average by 50–60% by using the optimal experiment;
(iii) during the optimal experiment, the heating rate of the time interval where the main mass loss occurs is significantly reduced (2.17 °C min^{-1}) from its initial value (10 °C min^{-1}).

This last point can be interpreted as if the numerical procedure had increased the duration of the main degradation phase by reducing the heating rate. Consequently, it is a method of improving the precision of the parameter estimates by increasing the period where the sensitive coefficients have the highest values. The relative sensitivity coefficient evolutions in the case of the optimal temperature profile are plotted in Fig. 8. Not surprisingly, the duration where the main thermal

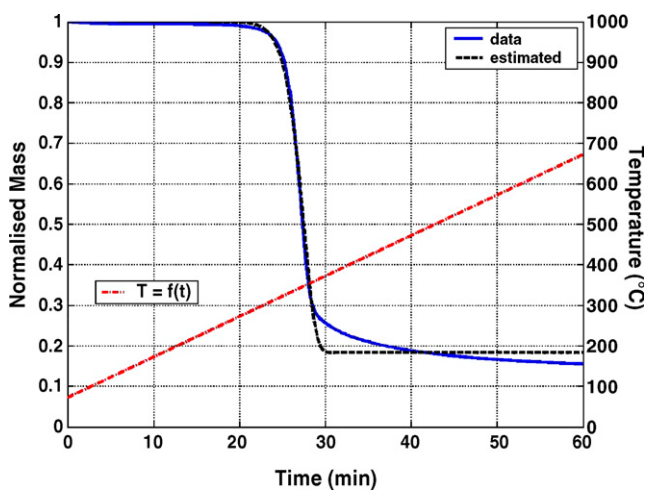

Fig. 6. The experimental mass loss curve and model predicted curve for cellulose (10 °C min^{-1}).

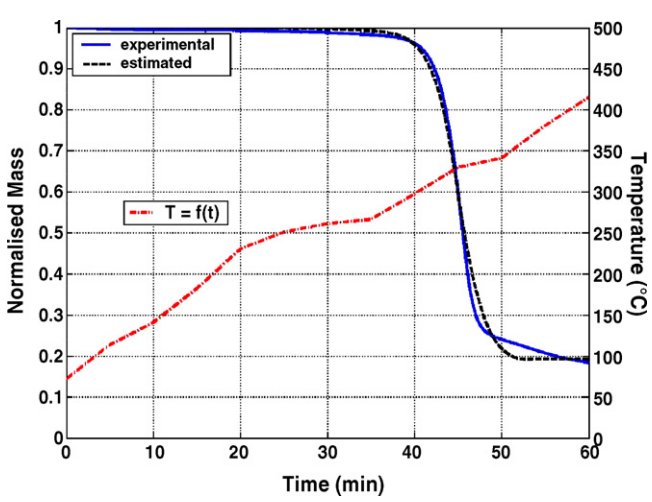

Fig. 7. The optimal temperature profile, experimental mass curve and computed mass curve with fitted parameters (total mass).

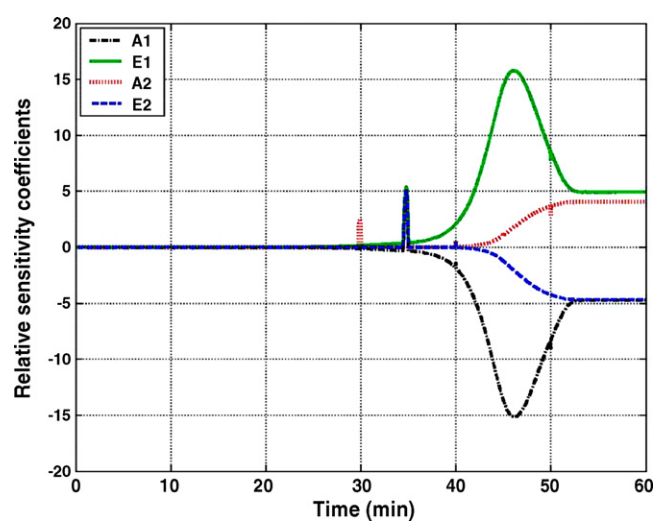

Fig. 8. The relative sensitivity coefficient evolutions (case of the optimal temperature profile).

degradation takes place corresponds to the times where the parameters are the most sensitive to the measured data; the information content of the experiment is then ‘‘richer’’. An optimal experiment can be viewed as a run where the amount of ‘‘rich’’ data has been maximized.

4. Conclusion

In this paper, we presented our first results concerning the evaluation of an optimal run with a thermobalance to increase the precision of kinetic parameter estimates. The simulation results are not as interesting as we hoped because, although the precision is improved, the kinetic parameter estimates are the same as those with the optimal experiment, even in the case where an artificial noise has been added on the simulated data. However, the experimental results with cellulose have shown that the proposed approach is promising with real data. It is rather challenging to observe that complex numerical computations give some solutions very close to the ones that an experimenter would propose for better resolution, i.e. to lengthen the time where the thermal degradation occurs, and very similar to the thermal profiles computed by a high-resolution thermogravimetry. With high resolution TGA devices, the heating rate of the sample material is dynamically and continuously modified in response to changes in the rate of decomposition of the sample: when no weight change is detected, the heating rate remains constant; whereas when a loss of weight is detected, the heating rate decreases in response to the increasing rate of mass loss and the system tries to keep it at the lowest value until the end of the loss of weight.

Now, we need to confirm these first results and prove the real benefits of the proposed approach; for example, by the evaluation of the number of TGA runs (isothermal or non-isothermal with a constant heating rate) necessary to obtain the same confidence intervals as those obtained with one optimal experiment, or by the comparison between the confidence intervals obtained with the proposed method with the confidence intervals of high resolution TGA device. Moreover, the optimal design with the TGA device will be used for the model discrimination, i.e. when several rival models are proposed and the ‘‘best’’ model is sought. Experimental optimal design can be useful for evaluating the best kinetic model among several models associated with different proposed reaction schemes or for discriminating the ‘‘best’’ expression to use for the computation of the kinetic constants.

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