Analysis of the relative strength of the singular values obtained from the non-parametric kinetic method

Ruben Ruiz-Femenia · Jose A. Caballero

Abstract The non-parametric kinetic method (NPK) is a method for the processing of thermoanalytical data, which does not make any assumption about the functionality of the reaction rate with the degree of conversion or with the temperature. This method has not been widely used due to its mathematical sophistication and difficulty of automation. The original NPK method uses only the first (maximum) singular value whereas additional information could be drawn from the remaining singular values. A hypothetical application of the NPK, which uses all the significant singular values (modified version of the NPK), is the separation of two or more steps of a complex decomposition reaction. Using simulated data, we have demonstrated that the modified version of the NPK is not useful to discriminate among the decomposition steps of a consecutive complex decomposition reaction scheme. Nevertheless, the analysis of the relative strength of the singular values is useful to assess the degree of separability of the temperature and conversion functions, which are the outcome of the NPK. Taking into account the relative magnitude of the first singular value with regard to the remaining singular values, we have proposed an automated two-scan version of the NPK method which guarantees two separable functions. As the separability of both temperature and conversion functions is the imperative assumption of the single-step kinetics

approximation, the two-scan NPK method can be used as a testing method for those methods based on this approximation, the model-free and model-fitting methods.

Keywords Solid-state kinetics · Non-isothermal kinetics · Single-step approximation · Non-parametric method (NPK) · Function separability

List of abbreviations

A	Matrix with the reaction rate $d\alpha/dt$ at different pairs of values of conversion (rows) and temperatures (columns) (s^{-1}) (see Eq. 5)
A_i	Activation energy for reaction i (s^{-1})
b_i	Stoichiometric coefficient of the gas product G_i in reaction i
E_i	Activation energy for reaction i (kJ mol^{-1})
$f(\alpha)$	Function depending exclusively on the fractional conversion (α)
f	Vector with the values of the function $f(\alpha)$
G_i	Gaseous product from reaction i
h	Vector with the values of the function $h(T)$ (s^{-1})
$h(T)$	Function depending solely on the temperature (T) (s^{-1})
M_{G_i}	Molecular mass of the gaseous product G_i (kg mol^{-1})
m_0	Initial sample mass (kg)
m	Aggregate reaction mass at time t (kg)
m_∞	Final aggregate reaction mass (kg)
N_{S0}	Initial amount of substance for the solid reactant (mol)
n	Number of consecutive steps in the reaction scheme for the decomposition of a solid reactant
ni	Number of experiments executed by means of a non-isothermal thermoanalytical technique (TG, DSC)

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nk	Number of rows of the matrix $\mathbf{A}$, each row corresponds to a fixed value of the conversion
nj	Number of rectangles used in a scan of the NPK method
nl	Number of columns of matrix $\mathbf{A}$, each column corresponds to a fixed value of the temperature
R	Gas constant, 8.314×10^{-3} kJ (mol K)$^{-1}$
r_i	Function to calculate the conversion α at time t for the ith experiment, $\alpha = r_i(T)$
s_i	Function to calculate the temperature T at time t for the ith experiment, $T = s_i(t)$
S_i	Solid product from reaction i in a reaction scheme with n consecutive decomposition steps
$\mathbf{S}_j$	Submatrix with the reaction rate dα/dt for interval j
T	Absolute temperature (K)
$\mathbf{T}$	Vector with the T values from T_0 to T_f spaced by an increment ΔT.
t	Time (s)
$\mathbf{W}$	Diagonal matrix with the singular values, Eq. 13.
X_i	Molar conversion for reaction i at time t
$X_{i\infty}$	Molar conversion for reaction i at the end of the process

Greek letters

α	The fractional conversion, $0 \leq \alpha \leq 1$
$\boldsymbol{\alpha}$	Vector with the α values from α_0 to α_f spaced by an increment $\Delta\alpha$
δ	Normalized value of the singular value ω (see Eq. 27)
$\Theta(T)$	Program temperature set in a non-isothermal experiment, $\Theta(T) = \partial T/\partial t$
λ	Index of separability of a matrix $\mathbf{A}$ (see Eq. 28)
$v_{i,j}$	Stoichiometric coefficient for solid compound S_j in reaction i
φ^j	Factor multiplying $\mathbf{u}^j$ to insure continuity with $\mathbf{u}^{j-1}$
$\Phi(T, \alpha)$	General function to calculate the rate of a process in condensed state
χ	Scaling factor, χ to rescale $\mathbf{v}_T^{\mathrm{ver}}$ (see Eq. 30)
ω	Singular value

Subscript

i	ith Non-isothermal experiment
k	kth Row of matrix $\mathbf{A}$ which corresponds to a fixed value of the conversion
l	lth Column of matrix $\mathbf{A}$ which corresponds to a fixed value of the temperature

Superscript

hor	Scan with horizontal rectangles in the two-scan NPK method (width $\gg$ height)
ver	Scan with vertical rectangles in the two-scan NPK method (height $\gg$ width)

Introduction

Solid-state reactions generally show a tangled interplay of various chemical and physical processes such as solid-state decomposition, reaction of gases with solids, phase transitions, diffusion, adsorption, and desorption. Full and exact kinetic description of such a complex multistep process would be very difficult since a detailed mechanism of the process could be unknown. The kinetics of this process can be studied using the single-step kinetics approximation, which assumes that the complex set of kinetic equations can be substituted by a sole single-step kinetic equation. The concept of single-step kinetics approximation was introduced by Simon [1]. The single-step kinetics approximation involves the imperative condition of the separability of both temperature and conversion functions. To check the separability of these functions, the Non-Parametric Kinetics method (NPK), developed by Serra et al. [2], could be very suitable. The NPK method is based on the mathematical procedure known as singular value decomposition (SVD), and the most important feature of this method is its ability to decouple the experimental values of the reaction rates into two linearly independent vectors containing information on the temperature and conversion functions without the need of any assumptions about the functionality of the reaction rate with the fractional conversion or with the temperature [3]. Thus the NPK method can be used as a testing method for those methods based on the single-step kinetics approximation, which use analytical forms of the temperature and/or conversion functions, i.e., the model-free and model-fitting methods [4]. Despite this ability of the NPK method, it has not yet become widespread. The reason was pointed out by Simon [4]: "*NPK is a perfect method for the description of kinetic data. It is quite surprising that it is not applied more extensively. A probable reason is that, on the first sight, it looks quite laborious and I guess it could be automated with difficulties.*" Sewry and Brown [5] also find the NPK method very interesting and state that it does not seem to have received the attention that it deserved, due to its mathematical sophistication and the fact that the matrix and non-linear regression calculations involved are not readily automated. Starink [6] also considers that the NPK method is accurate but, due to its mathematical complexity, has been applied very little.

The original NPK method [2] uses only the first (maximum) singular value computed by the SVD. Additional information could be drawn taking into account all the singular values from the SVD. Some authors have applied a modified version of the NPK method which uses the relative strength of all the significant singular values, to enable the discrimination among the steps of a complex decomposition reaction [7]. This modified version of the NPK

method requires a unique matrix for a sufficient range of the fractional conversion and temperatures. Since all the elements of this matrix cannot be experimentally obtained, a multivariate regression technique is applied [7–12]. However, other researchers doubt [13] about this technique due to the fact that some of the matrix elements are necessarily the result of extrapolation of the experimental data, whereas multivariate regression should be only applied for interpolation purposes. In this study, the analysis of the usefulness of the modified version of the original NPK has been performed to evaluate its ability to determine the number of steps in a consecutive reaction scheme. The results of this analysis reveal that the relative strength of each singular value cannot be connected with the existence of its associated reaction step. However, the analysis of the relative strength of the singular values is not a useless task. The relative magnitude of the first singular value with regard to the remaining singular values can be indeed used to assess the degree of separability of the functions $h(T)$ and $f(\alpha)$. In accordance with this result, we have developed an automated NPK algorithm to guarantee two separable functions. The main difference of the proposed two-scan NPK method with the original NPK method [2] is that the former uses two scans, whereas the original NPK method uses one scan. The two-scan NPK method has been programmed in Matlab (all the Matlab files are available on request).

Theoretical

Mathematical formulation of the single-step kinetics approximation

The rate of the processes in condensed state is generally a function of temperature (T) and the fractional conversion, α (hereinafter named conversion):

$$\frac{d\alpha}{dt} = \Phi(T, \alpha) \tag{1}$$

The single-step kinetics approximation assumes that the function Φ in Eq. 1 can be expressed as a product of two separable functions (independent of each other), with the first one, $h(T)$, depending solely on the temperature and the other one, $f(\alpha)$, depending solely on the conversion of the process:

$$\Phi(T, \alpha) = h(T)f(\alpha) \tag{2}$$

Combining Eqs. 1 and 2, it is obtained the rate of the complex multistep condensed state process, which is the mathematical formulation of the single-step kinetics approximation [4]:

$$\frac{d\alpha}{dt} = h(T)f(\alpha) \tag{3}$$

The concept of single-step kinetics approximation, introduced by Simon [4], resides in the interpretation of Eq. 3, which is not a true kinetic equation and may not be straightforwardly connected with the reaction mechanism.

Implementation of the original NPK method

The NPK method, as described in [2, 3, 14, 15], is also based on the single-step kinetics approximation; therefore, Eq. 3 is the basic relationship for the analysis of kinetic data. The purpose of the NPK method is to separate the effects of the experimental variables (α and T) on a total set of reaction rate data, leading to two separable functions, $f(\alpha)$ and $h(T)$, without any prior assumptions about their functionality. The experimental data required to apply the NPK method are obtained from ni experiments by means of a non-isothermal thermoanalytical technique (TG, DSC). Each experiment i is run at a different temperature program (the relationship between time and temperature reads $\Theta(t) = \partial T / \partial t$). Then, for experiment i two curves are obtained, together with their corresponding inverse curves:

$$\forall \Theta_i(t), \quad \begin{cases} \alpha = r_i(T), & T = r_i^{-1}(\alpha) \\ T = s_i(t), & t = s_i^{-1}(T) \end{cases} \tag{4}$$

The reaction rate of the processes in condensed state, Eq. 1, can be expressed as a surface in a three-dimensional space, where any point of this surface is determined by the corresponding pair of values of the conversion and the temperature. The reaction rate does not depend on the previous history of the process. This continuous surface can be discretized as an ($nk \times nl$) matrix $\mathbf{A}$, which rows correspond to different degrees of conversion, from α_1 to α_{nk}, and which columns refer to different temperatures, from T_1 to T_{nl} (the number of temperature values chosen, nl must be higher than the number of experimental curves, ni):

$$\mathbf{A} = \begin{pmatrix} f(\alpha_1)h(T_1) & \cdots & f(\alpha_1)h(T_l) & \cdots & f(\alpha_1)h(T_{nl}) \\ \vdots & & \vdots & & \vdots \\ f(\alpha_k)h(T_1) & \cdots & f(\alpha_k)h(T_l) & \cdots & f(\alpha_k)h(T_{nl}) \\ \vdots & & \vdots & & \vdots \\ f(\alpha_{nk})h(T_1) & \cdots & f(\alpha_{nk})h(T_l) & \cdots & f(\alpha_{nk})h(T_{nl}) \end{pmatrix} \tag{5}$$

Calculation of the reaction rate along experimental curves

The first step to build the matrix $\mathbf{A}$ from experimental data is the calculation of the derivative of α with respect to temperature at each α_k and for each experimental curve i. This value, $(d\alpha/dT)_{\alpha_k, \text{curve } i}$, is calculated from the

derivative of $r_i(T)$. As these derivatives depend on the temperature, it is first required to calculate the temperature at which the curve i reaches each α_k. This is accomplished using the inverse function $T_{\alpha_k,i} = r_i^{-1}(\alpha_k)$. The calculated values can be arranged in the $nk \times ni$ matrix $\mathbf{B}$, where the rows correspond to different conversion values, from α_1 to α_{nk}, while columns correspond to the different experimental curves, from 1 to ni:

$$B = \begin{pmatrix} \left(\frac{d\alpha}{dT}\right)_{\alpha_1,T_{\alpha_1,1}} & \cdots & \left(\frac{d\alpha}{dT}\right)_{\alpha_1,T_{\alpha_1,i}} & \cdots & \left(\frac{d\alpha}{dT}\right)_{\alpha_1,T_{\alpha_1,ni}} \\ \vdots & \cdots & \vdots & \cdots & \vdots \\ \left(\frac{d\alpha}{dT}\right)_{\alpha_k,T_{\alpha_k,1}} & \cdots & \left(\frac{d\alpha}{dT}\right)_{\alpha_k,T_{\alpha_k,i}} & \cdots & \left(\frac{d\alpha}{dT}\right)_{\alpha_k,T_{\alpha_k,ni}} \\ \vdots & \cdots & \vdots & \cdots & \vdots \\ \left(\frac{d\alpha}{dT}\right)_{\alpha_{nk},T_{\alpha_{nk},1}} & \cdots & \left(\frac{d\alpha}{dT}\right)_{\alpha_{nk},T_{\alpha_{nk},i}} & \cdots & \left(\frac{d\alpha}{dT}\right)_{\alpha_{nk},T_{\alpha_{nk},ni}} \end{pmatrix}$$

(6)

The second step is the calculation of dT/dt at each α_k and for each experimental curve i, by means of the derivative of $s_i(t)$. The time at which the curve i reaches α_k is calculated using the inverse function evaluated at the previously calculated $T_{\alpha_k,i}$:

$$t_{\alpha_k,i} = s_i^{-1}\left(T_{\alpha_k,i}\right) \tag{7}$$

Then, the following $nk \times ni$ matrix can be built:

$$C = \begin{pmatrix} \left(\frac{dT}{dt}\right)_{\alpha_1,t_{\alpha_1,1}} & \cdots & \left(\frac{dT}{dt}\right)_{\alpha_1,t_{\alpha_1,i}} & \cdots & \left(\frac{dT}{dt}\right)_{\alpha_1,t_{\alpha_1,ni}} \\ \vdots & \cdots & \vdots & \cdots & \vdots \\ \left(\frac{dT}{dt}\right)_{\alpha_k,t_{\alpha_k,1}} & \cdots & \left(\frac{dT}{dt}\right)_{\alpha_k,t_{\alpha_k,i}} & \cdots & \left(\frac{dT}{dt}\right)_{\alpha_k,t_{\alpha_k,ni}} \\ \vdots & \cdots & \vdots & \cdots & \vdots \\ \left(\frac{dT}{dt}\right)_{\alpha_{nk},t_{\alpha_{nk},1}} & \cdots & \left(\frac{dT}{dt}\right)_{\alpha_{nk},t_{\alpha_{nk},i}} & \cdots & \left(\frac{dT}{dt}\right)_{\alpha_{nk},t_{\alpha_{nk},ni}} \end{pmatrix}$$

(8)

The Hadamard product (multiplication element-by-element for matrices of the same dimension) for matrices $\mathbf{B}$ and $\mathbf{C}$ yields the $nk \times ni$ matrix $\mathbf{D}$, which contains the derivative of α with respect to time:

$$D = \left\{ \frac{d\alpha}{dt} \right\}_{k,i} = \left\{ \left(\frac{d\alpha}{dT}\right)_{\alpha_k,T_{\alpha_k,i}} \left(\frac{dT}{dt}\right)_{\alpha_k,t_{\alpha_k,i}} \right\}_{k,i} = B \circ C$$

(9)

Interpolation along the data curves

The last step to build $\mathbf{A}$ requires calculating $d\alpha/dt$ for each row (each α_k) and for all the selected temperature values $(T_1, \ldots, T_l, \ldots, T_{nl})$. This can be performed interpolating at each T_l through the row from matrix $\mathbf{D}$ corresponding to the same value of α_k

$$\left(\left(\frac{d\alpha}{dt}\right)_{\alpha_k,t_{\alpha_k,1}}, \cdots \left(\frac{d\alpha}{dt}\right)_{\alpha_k,t_{\alpha_k,i}}, \ldots, \left(\frac{d\alpha}{dt}\right)_{\alpha_k,t_{\alpha_k,ni}} \right).$$

This interpolation has been implemented using the Matlab function `interp1` with the cubic spline method.

Singular value decomposition

With the vectors $\mathbf{f}$ and $\mathbf{g}$ defined as:

$$\mathbf{f} = (f(\alpha_1), \ldots, f(\alpha_k), \ldots, f(\alpha_{nk}))^T \tag{10}$$

$$\mathbf{h} = (h(T_1), \ldots, h(T_l), \ldots, h(T_{nl}))^T \tag{11}$$

the matrix $\mathbf{A}$ can be written as an outer product:

$$\mathbf{A} = \mathbf{f}\mathbf{h}^T \tag{12}$$

Rewriting $\mathbf{A}$ in terms of the vectors $\mathbf{f}$ and $\mathbf{g}$ has the benefit of compressing the initial amount of data contained in $\mathbf{A}$, i.e., the $nk \times nl$ reaction rate values, into only $nk + nl$ values. The mathematical procedure accomplishing this task is the singular value decomposition (SVD). It takes a matrix such as $\mathbf{A}$ and decomposes it into three matrices:

$$\mathbf{A} = \mathbf{U}\mathbf{W}\mathbf{V}^T \tag{13}$$

where $\mathbf{U}$ and $\mathbf{V}$ are the orthonormal matrices, i.e., $\mathbf{U}^T = \mathbf{U}^{-1}$, $\mathbf{V}^T = \mathbf{V}^{-1}$ and $\mathbf{W}$ is a diagonal matrix containing the singular values of matrix $\mathbf{A}$. If $\mathbf{A}$ is (n, m) in size, then $\mathbf{U}$ is (n, m) in size, $\mathbf{V}$ is (m, m) in size, and $\mathbf{W}$ is (m, m). If only the first singular value is significant $(W_{1,1} \gg W_{2,2}, \cdots, W_{1,1} \gg, \cdots, W_{m,m})$, only the first columns of $\mathbf{U}$ and $\mathbf{V}^T$ are significant and all other columns may be ignored. These subsets of $\mathbf{U}$ and $\mathbf{V}$ are then vectors which are called $\mathbf{u}_1$ and $\mathbf{v}_1$, respectively. Similarly $W_{1,1}$ is called w_1. Then, matrix $\mathbf{A}$ can be approximated to:

$$\mathbf{A} = \mathbf{U}\mathbf{W}\mathbf{V}^T \simeq \mathbf{u}_1 w_1 \mathbf{v}_1^T \tag{14}$$

Applying the original NPK method to non-isothermal experiments

On account of the data acquired by a non-isothermal thermoanalytical technique, the whole α range (from 0 to 1) is not available over all of the temperature range. This difficulty has been overcome by other authors [2, 3, 14, 15], dividing up the total range of data into submatrices $\mathbf{S}^j$, each enclosing a different range of temperatures and α values (a two-dimensional interval j) to completely fill the area bounded by the TG curve at the lowest heating rate and the TG curve at the highest heating rate. These submatrices $\mathbf{S}^j$ can be drawn as rectangles in a α versus temperature plot (Fig. 1). If the height of each rectangle is kept constant, the method is called rigid NPK, and if a variable height is allowed for each rectangle, the method is called
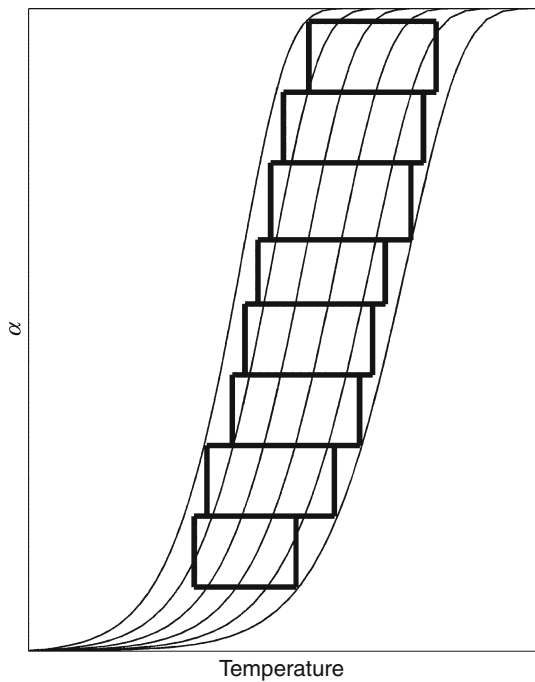
Fig. 1 Original NPK method using several *rectangles*, each one encloses a different range of temperatures and α values to fill the area bounded by the TG curve at the lowest heating rate and the TG curve at the highest heating rate

adaptive NPK [15]. The submatrices $\mathbf{S}^j$ are analyzed separately by the SVD obtaining the matrices $\mathbf{U}^j$, $\mathbf{W}^j$ and $\mathbf{V}^j$. As before, if only $\mathbf{W}^j_{11}$ is of relevance, then only the first columns of $\mathbf{U}^j$ and $\mathbf{V}^j$ are required:

$$S^j = U^j W^j V^{jT} \cong u^j w^j v^{jT} \tag{15}$$

The vectors $\mathbf{u}^j$, $\mathbf{v}^j$ are combined into one set by adding the second and subsequent vectors to the first, after multiplying each vector $\mathbf{u}^j$ by a suitable factor φ^j, and the corresponding $\mathbf{v}^j$ has to be divided by the same factor, keeping the product $u^j w^j v^{jT}$ constant. These factors can be calculated forcing successive matrices to share at least one row of data, which means that matrices $\mathbf{S}^j$ and $\mathbf{S}^{j+1}$ have a least one row for the same value of α. Finally, the two outcome vectors of the original NPK method can be expressed as:

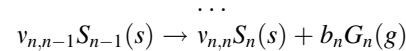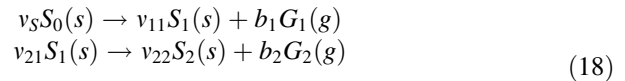$$f = \left(\mathbf{u}^1, \varphi^2 \mathbf{u}^2, \ldots, \varphi^j \mathbf{u}^j, \ldots, \varphi^{nj} \mathbf{u}^{nj} \right)^T \tag{16}$$

$$h = \left(\frac{w^1}{\varphi^1} \mathbf{v}^1, \frac{w^2}{\varphi^2} \mathbf{v}^2, \ldots, \frac{w^j}{\varphi^j} \mathbf{v}^j, \ldots, \frac{w^{nj}}{\varphi^{nj}} \mathbf{v}^{nj} \right)^T \tag{17}$$

where the value φ^1 is fixed equal to 1.

The modified version of the NPK

A modified version of the NPK method which uses only one rectangle has been employed instead of the original NPK method with several rectangles. The modified version of the NPK method has been applied with the purpose to enable the separation of two or more processes of a complex decomposition reaction [7–10]. The usefulness of this modified version of the NPK is below analyzed using a simulated complex decomposition reaction scheme, the decomposition of a solid compound S that undergoes n consecutive decomposition steps:

$$\begin{aligned} v_S S_0(s) &\rightarrow v_{11} S_1(s) + b_1 G_1(g) \\ v_{21} S_1(s) &\rightarrow v_{22} S_2(s) + b_2 G_2(g) \\ &\cdots \\ v_{n,n-1} S_{n-1}(s) &\rightarrow v_{n,n} S_n(s) + b_n G_n(g) \end{aligned} \tag{18}$$

where S_i is the solid product and G_i is the gaseous product from the reaction step i. This modification of the original NPK method is based on the utilization of the SVD as a method to decompose the matrix $\mathbf{A}$ into a weighted, ordered sum of separable matrices $\mathbf{B}_i$:

$$\mathbf{A} = \sum_i \mathbf{B}_i = \sum_i \mathbf{u}_i w_i \mathbf{v}_i^T \tag{19}$$

where $\mathbf{u}^j$ and $\mathbf{v}^j$ are the ith columns of the corresponding SVD matrices $\mathbf{U}$ and $\mathbf{V}$, Eq. 13, and w_i are the ordered singular values. Note that if only the first separable matrix $\mathbf{B}_1$ is considered (i.e., if only the first singular value w_1 is used), Eq. 19 turns into Eq. 14. The modified version of the NPK assumes that the existence of the step i is subject to the relative strength of the singular value associated with this step (w_i). A value of w_i below a certain tolerance implies that the step i does not exist. This modified version of the NPK method requires necessarily a unique matrix $\mathbf{A}$ which contains the reaction rate for all pair of values (α, T) inside the two-dimensional domain specified by the α range (from 0 to 1) and by the temperature range (from the initial temperature to the highest final temperature). This two-dimensional domain is drawn as a unique rectangle in a α versus temperature plot. When using thermoanalytical methods, changes of aggregate physical properties are observed, i.e., enthalpy and mass in the case of DSC, DTA, and TG. In thermogravimetric analysis, the definition of the conversion (or aggregated reacted fraction) is performed in terms of the aggregate reaction mass loss corresponding to the actual time (Δm) and the aggregate reaction mass loss corresponding to the end of the process (Δm_∞):

$$\alpha = \frac{\Delta m}{\Delta m_\infty} = \frac{m_0 - m}{m_0 - m_\infty} \tag{20}$$

where, m_0 is the initial sample mass, m is the aggregate sample mass at time, t, and m_∞ is the final aggregate

sample mass. The conversion for reaction i is defined as:

$$\alpha_i = \frac{X_i}{X_{i\infty}} \qquad (21)$$

where X_i is the molar conversion for reaction i at time t, and $X_{i\infty}$ is the molar conversion for the reaction i at the end of the process. The relationship between the aggregate conversion α (the value that can be experimentally measured) and the conversion for reaction i, α_i is:

$$\alpha = \sum_i \left(\frac{b_i M_{G_i} X_{i,\infty}}{\sum_i b_i M_{G_i} X_{i,\infty}} \right) \alpha_i \qquad (22)$$

where M_{G_i} is the molecular mass of the gaseous product G_i.

Applying Eq. 3 for each reaction step i and using Eq. 21, we obtain the following general expression for the reaction rate of the step i for the consecutive reaction scheme, Eq. 18:

$$\begin{cases} i = 1, & \frac{d\alpha_1}{dt} = h_1(T) f_1\left(\frac{(-v_S)X_{1,\infty}}{N_{S0}}(\alpha_i) \right) \\ i > 1, & \frac{d\alpha_i}{dt} = h_i(T) f_i\left(1 - \frac{(-v_{i,i-1})M_{i-1}X_{i,\infty}}{M_S} \frac{}{N_{S0}}(\alpha_{i-1} - \alpha_i) \right) \end{cases} \qquad (23)$$

where $X_{i\infty}$ is calculated from the stoichiometric coefficients according to the following expression:

$$\begin{cases} i = 1, & X_{1,\infty} = \frac{N_{S0}}{(-v_S)} \\ i > 1, & X_{i,\infty} = \frac{v_{i-1,i-1}}{(-v_{i,i-1})} \cdots \frac{v_{2,2}}{(-v_{3,2})} \frac{v_{1,1}}{(-v_{2,1})} \frac{N_{S0}}{(-v_S)} \end{cases} \qquad (24)$$

TG data have been generated taking into account the first 2 steps of the scheme reaction in Eq. 18. For only two decomposition steps, the particular case $M_1 v_{11} = M_S(-v_S) = 1$ and the first-reaction-order model $f(\alpha) = (1 - \alpha)^1$ for both steps, Eqs. 23–24 result into the following system of ordinary differential kinetic equations:

$$\begin{aligned} \frac{d\alpha_1}{dt} &= h_1(T)(1 - \alpha_1) \\ \frac{d\alpha_2}{dt} &= h_2(T)(\alpha_1 - \alpha_2) \end{aligned} \qquad (25)$$

The temperature function $h(T)$ for each reaction i is expressed by the Arrhenius equation:

$$h_i(T) = A_i e^{(-E_i/(RT))} \qquad (26)$$

where A_i and E_i are the pre-exponential factor and the activation energy, respectively, and R stands for the gas constant. The values chosen for the Arrhenius parameters for the first-reaction step are $A_1 = 1 \times 10^5$ s^{-1} and $E_1 = 73$ kJ kmol^{-1}, while for the second reaction step $A_2 = 1 \times 10^8$ s^{-1} and $E_2 = 120$ kJ kmol^{-1}. Six TG curves have been generated setting a constant heating rate $(\Theta_i(T) = \partial T/\partial t = \beta_i)$ with the following values: 1, 2, 4, 8,
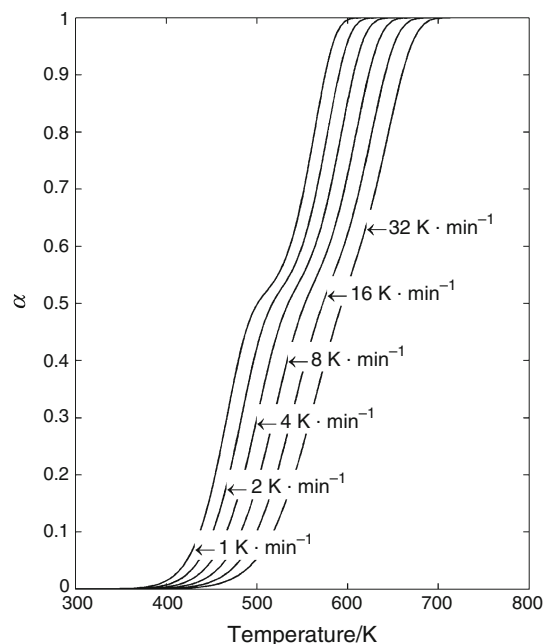

Fig. 2 TG main curves generated at 6 heating rates for a consecutive reaction scheme with two steps using the reaction order model with $n = 1$ and the Arrhenius function
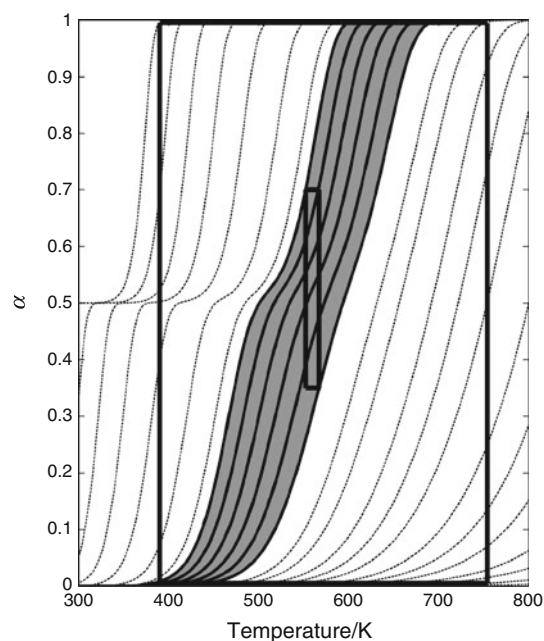

Fig. 3 TG main curves at 6 heating rates (1, 2, 4, 8, 16, and 32 K min^{-1}) (*solid lines*) and TG auxiliary curves (*dashed lines*) for two steps consecutive reaction scheme with a *small inscribed rectangle*, and a *large circumscribed rectangle* to the *shadowed area*, which is bounded by the TG main curve at the lower heating rate 1 K min^{-1} and by the TG main curve at the highest heating rate 32 K min^{-1}

16, and 32 K min^{-1} (Fig. 2). The application of the modified version of the NPK method to establish the number of steps requires a unique rectangle inscribed in the area bounded by

the TG experimental curve at lower heating rate $\beta_1 = 1$ K min^{-1} and by the TG experimental curve at the highest heating rate $\beta_6 = 32$ K min^{-1}. Nevertheless, the inscribed rectangle with the maximum height that can be drawn does not cover the whole α range; it starts at $\alpha = 0.35$ and ends at $\alpha = 0.70$ (Fig. 3, small rectangle inscribed in the shadowed area). If only one rectangle is allowed for this modified version of the NPK method, the solution is to employ more TG curves at lower and higher heating rates (they will hereafter be referred to as TG auxiliary curves). In the current example, it is necessary to decrease the heating rate until 1×10^{-6} K min^{-1} and increase the heating rate until 1×10^6 K min^{-1} in order to draw a unique circumscribed rectangle which contains the six TG experimental curves (Fig. 3, large circumscribed rectangle). Obviously, these heating rates cannot be carried out in real TG experiments (a heating rate of 1×10^{-6} K min^{-1} for a range temperature from 400 to 700 K, implies an experiment of 570 years long !).

Despite this insurmountable experimental fact, this analysis is continued to investigate if the SVD, applied to only one rectangle, can ascertain the number of steps. The TG auxiliary curves can be generated by computer simulation. Then, the SVD is applied using the large circumscribed rectangle (Fig. 3) that covers a range of α values from 0.005 to 0.995 and a temperature range from 390 to 754 K. For the parameters of the NPK method we chose a step size of 0.005 for α and a step size of 2 K for T. For each α value, the dependent variable $(d\alpha/dt)$ is calculated for each temperature by interpolating through the TG auxiliary and TG experimental curves. With these reaction rate values the matrix $\mathbf{A}$ (199 rows and 182 columns) is built and the SVD applied. The magnitude of each singular value has been normalized using the norm of the vector generated with all the singular values of $\mathbf{A}$:

$$\delta_i = w_i \bigg/ \sqrt{\sum_i w_i^2} \tag{27}$$

For this reaction scheme of two consecutive steps, the TG curves were generated assuming that the reaction rate of

each step has the same weighting factor (0.5) to the overall reaction rate. Accordingly, a successful outcome for the modified version of the NPK as a method to determine the number of steps should have led to only 2 weighty singular values $(w_1 \simeq w_2 \gg w_3, \ldots, \gg w_m)$ with same strength around $\delta_1 \simeq \delta_2 \simeq 0.5$. Nonetheless, the first singular value is $w_1 = 13.47$ (a normalized value of $\delta_1 = 0.998$) and the second singular value is $w_2 = 0.7810$ (a normalized value of $\delta_2 = 0.0579$). Therefore, the computed singular values from this matrix do not reveal that the scheme reaction consists in two consecutive reactions.

The same SVD procedure has been applied to the thermal decomposition process with three and ten steps for an in-depth analysis of the potential application of the modified NPK method. The case of a unique step has also been simulated to allow for comparison. In all the cases and for all the steps, $f(\alpha)$ is the reaction order model with $n = 1$, and $h(T)$ follows the Arrhenius law. Table 1 shows the pre-exponential factors (A_i) and the activation energies (E_i) used to generate the TG main curves for all the reactions schemes (Fig. 4). The TG auxiliary curves and the circumscribed rectangle to the TG main curves for the reaction scheme with one, three, and ten steps are shown in Figs. 5, 6, and 7, respectively. After applying the SVD decomposition to each reaction scheme, the first 10 singular values have been analyzed. The normalized values δ_i of the 10 singular values for each reaction scheme are shown in Fig. 8. As expected, the scheme reaction with only one step has only one significant singular value, $\delta_1 = 1$. For the multistep reaction schemes, the normalized value of the singular value does not match with the expected contribution of each step to the overall reaction rate. For the case of three consecutive steps, it would be expected that the 3 first singular values would have the same strength. However, the normalized value of the first singular value ($\delta_1 = 0.999$) is approximately 31 times higher than the normalized value of the second singular value ($\delta_2 = 0.0316$), and approximately 485 times higher than the normalized value of the third singular value ($\delta_3 = 0.0021$). The SVD analysis for the case of ten consecutive steps reaction scheme shows the same behavior:

Table 1 Parameters of the temperature function $h(T)$ for each reaction step i for the consecutive reaction schemes with 1, 2, 3, and 10 steps

1 Step	A_i/s^{-1}	1×10^6									
	E_i/kJ kmol^{-1}	90									
2 Steps	A_i/s^{-1}	1×10^5	1×10^8								
	E_i/kJ kmol^{-1}	73	120								
3 Steps	A_i/s^{-1}	5×10^5	4×10^6	1×10^8							
	E_i/kJ kmol^{-1}	78	100	128							
10 Steps	A_i/s^{-1}	5×10^3	5.6×10^7	1.1×10^8	1.7×10^8	2.2×10^8	2.8×10^8	3.3×10^8	3.9×10^8	4.4×10^8	5×10^8
	E_in/kJ kmol^{-1}	65	73	81	89	97	105	113	121	129	137

Fig. 4 TG main curves generated at 6 heating rates for a consecutive reaction scheme with 1 step (**a**), 3 steps (**b**), and 10 steps (**c**). In all the cases and for all the steps, the reaction order model with $n = 1$ and the Arrhenius function have been chosen
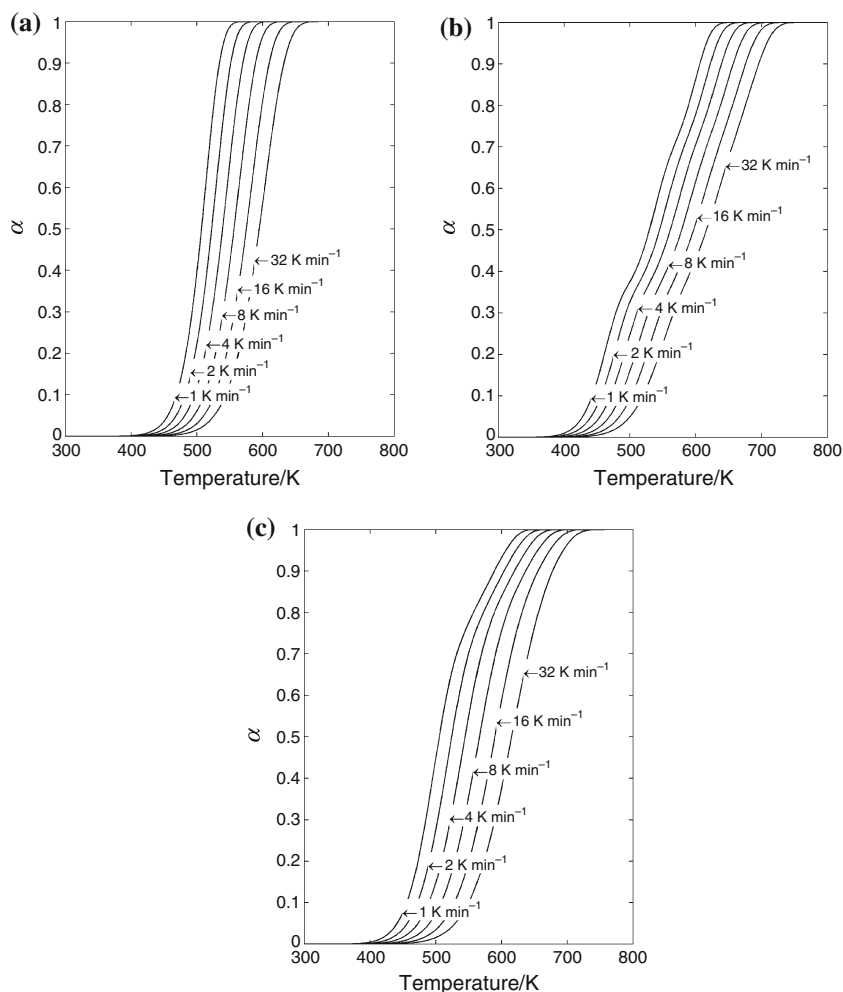
the first singular value has a much higher significance than the other 9 singular values (Fig. 8). These results confirm the conclusion drawn from the 2 steps scheme reaction, and reveal that the analysis of the relative strength of the singular values from a unique matrix **A** is not useful to elucidate the number of steps in a complex decomposition process.

Usefulness of the singular values relative strength analysis

The impossibility to determine the number of steps involved in the consecutive reaction scheme using all the singular values does not relegate the analysis of the relative strength of the singular values to a useless task. The relative magnitude of the first singular value with regard to the remaining singular values can be indeed used to assess the degree of separability of the functions $h(T)$ and $f(\alpha)$. As the imperative assumption of the single-step approximation is the separability of the two former functions, the degree

of separability can reveal the validity of the single-step approximation. An index of separability can be defined as the ratio of the power of the largest singular value (w_1) to the sum of the power of all the singular values [16]:

$$\lambda = w_1^2 / \sum_i w_i^2 \qquad (28)$$

The closer the matrix **A** is to being separable, the more dominant the first singular value (w_1) is over its counterparts. The most favorable case for compressing the reaction rate data occurs when the matrix **A** is reproducible to good approximation using only the biggest singular value ($w_1 \gg w_2 \gg w_3, \ldots, \gg w_m$). To guarantee that the two vectors **f** and **h** are linearly independent, the height of the rectangles defined in the NPK method should be set at the lowest possible values. The rank of the matrix **A** can be used to quantify the degree of separability of the vectors obtained through the SVD. If the rank is one, the matrix **A** can be exactly reconstructed as an outer product of two vectors, Eq. 12. This rank is equal to the non-zero elements of the diagonal matrix **W**, Eq. 13, which is the same that the

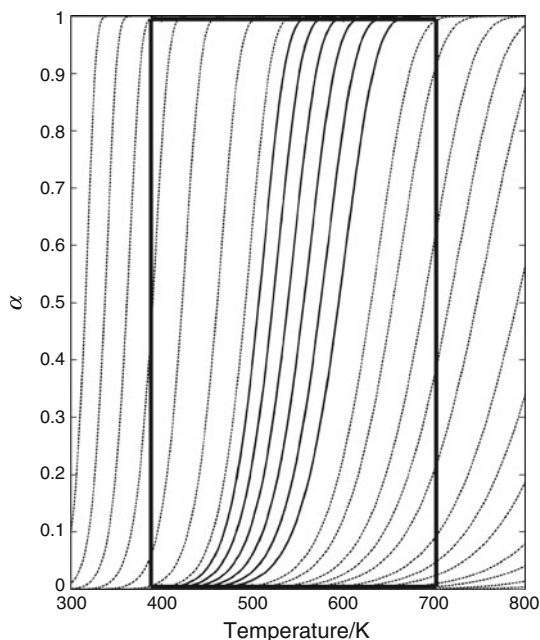**Fig. 5** TG main curves (*solid lines*) at 6 heating rates (1, 2, 4, 8, 16, and 32 K min^{-1}) and TG auxiliary curves (*dashed lines*) for only one-step reaction with a unique *circumscribed rectangle* to the TG main curves for the application of the SVD
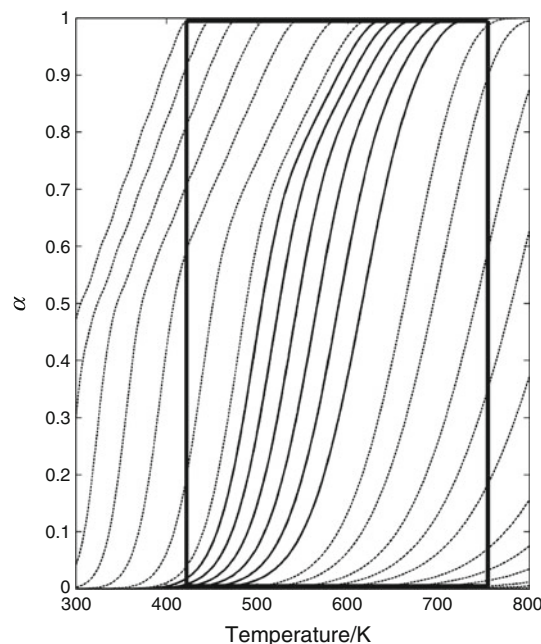

Fig. 6 TG main curves (*solid lines*) at 6 heating rates (1, 2, 4, 8, 16, and 32 K min^{-1}) and TG auxiliary curves (*dashed lines*) for 3 steps consecutive reaction with a unique *circumscribed rectangle* to the TG main curves for the application of the SVD
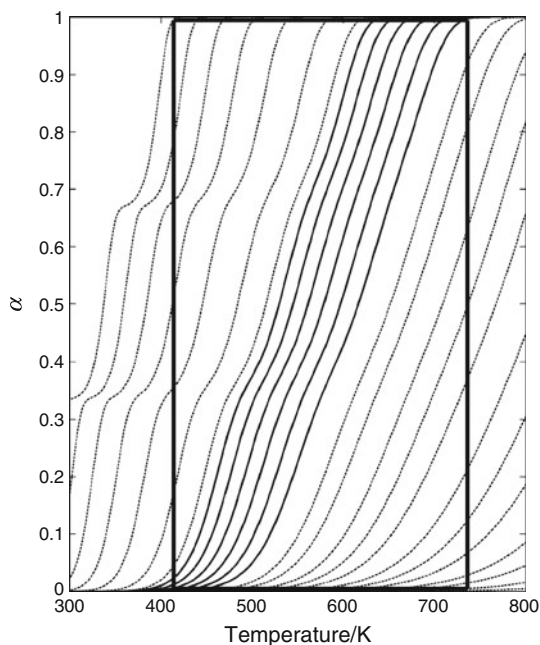
number of non-zero singular values. As the SVD uses a numerical algorithm, none of the singular values can be exactly zero. Then, it is necessary to specify a tolerance and consider zero any singular value below this tolerance. To
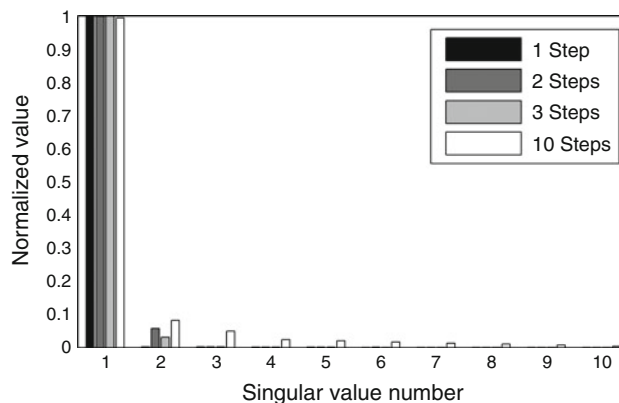

Fig. 7 TG main curves (*solid lines*) at 6 heating rates (1, 2, 4, 8, 16, and 32 K min^{-1}) and TG auxiliary curves (*dashed lines*) for 10 steps consecutive reaction with a unique *circumscribed rectangle* to the TG main curves for the application of the SVD

Fig. 8 Normalized value of the first 10 singular values for the four reaction schemes: only 1 step, 2 steps, 3 steps, and 10 consecutive steps

illustrate the effect of the rectangle height in the degree of separability, the SVD has been applied to two rectangles with different height (Fig. 9): one with the height used in the original NPK method extending from $\alpha = 0.50$ to $\alpha = 0.60$ ($\Delta\alpha = 0.1$), and other rectangle with a much smaller height extending from $\alpha = 0.545$ to $\alpha = 0.555$ ($\Delta\alpha = 0.01$). For both cases, the alpha step ($\Delta\alpha$) and the temperature step (ΔT) have been chosen to obtain 50 values for both variables inside the rectangle. Only for the small rectangle in Fig. 9 the index of separability is 1, which guarantees the separability of the two vectors **f** and **h**.
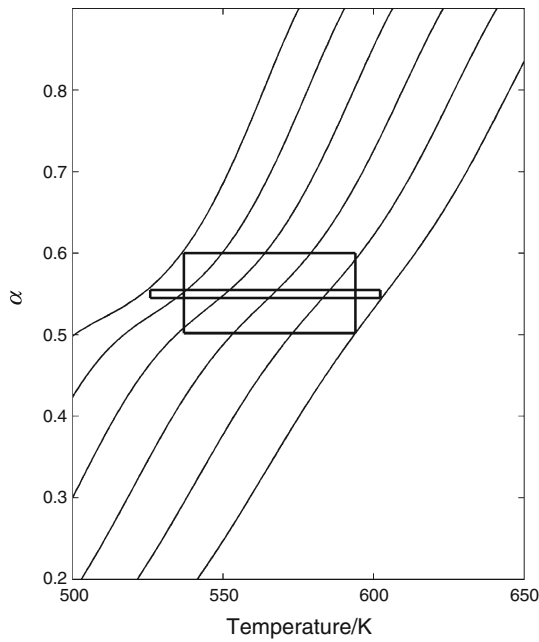
Fig. 9 Two *rectangles* with different height for the application of the SVD

Two-scan NPK method

To our knowledge, the authors who have used the NPK method have applied the rigid or the adaptive implementation, or a combination of both alternatives. Nevertheless, the original procedure for the NPK method presents difficulties that jeopardize its automatization. Each value of α matches with a unique element from vector **f**, so there is an injective correspondence (one-to-one) between the values of α and the elements of vector **f**. However, the same does not occur for vector **h**. After applying the NPK method, for each value of the temperature there is a correspondence with several elements from vector **h** (one-to-many). This fact introduces ambiguity in the method because only one of the possible values of vector **h** must be assigned to each value of the temperature.

An NPK method which utilizes two scans has been proposed to avoid this arbitrariness. The first scan uses horizontal rectangles (width $\gg$ height) to obtain a vector $\mathbf{u}^{\mathrm{hor}}_\alpha$, which has an unequivocal correspondence with a vector α^{hor} which elements are user-defined from α_0 to α_f with a fixed increment $\Delta\alpha$. And the second scan employs vertical rectangles (height $\gg$ width) to calculate a vector $\mathbf{v}^{\mathrm{ver}}_T$ which elements have an injective correspondence with the elements of vector $\mathbf{T}^{\mathrm{ver}}$, which is also selected by the user from T_0 to T_f with a step of ΔT (Fig. 10).

The first scan uses a number of horizontal rectangles (nj^{hor}), and the rectangle j is defined by the values of α^j_k and
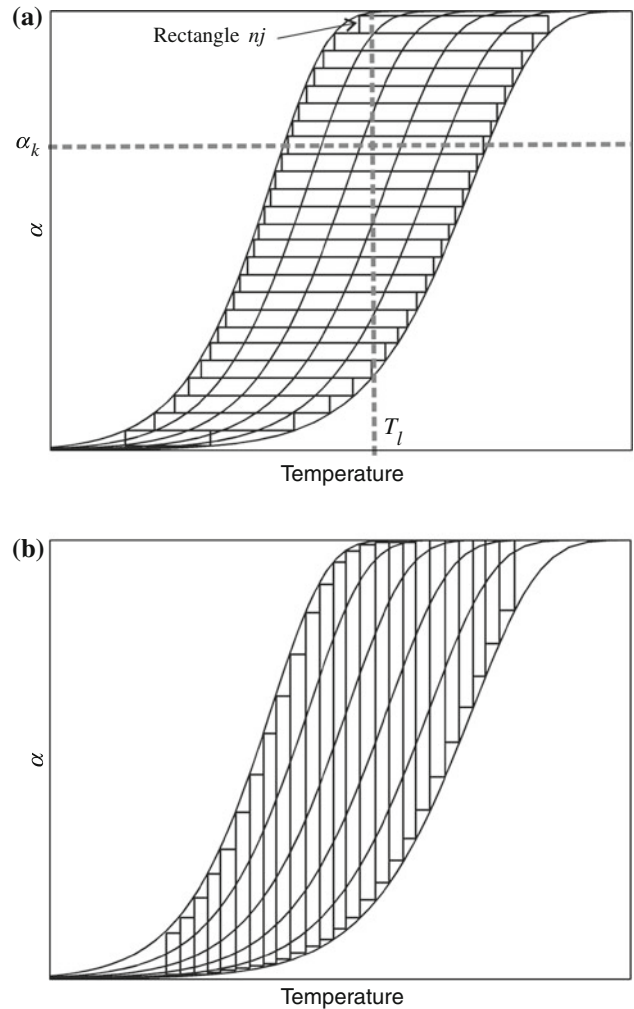

Fig. 10 Two-scan NPK method, *horizontal rectangles* (a) and *vertical rectangles* (b)

T^i_l contained in the vectors $\alpha^{\mathrm{hor},j}$ and $\mathbf{T}^{\mathrm{hor},j}$, respectively. The criterion to select the height of the horizontal rectangles and the width of the vertical rectangles, and therefore, the number of rectangles used is based on the index of separability previously defined, Eq. 28. The height (horizontal rectangles) and width (vertical rectangles) are selected to keep the index of separability equal to 1 (minus a specific tolerance). After applying the SVD to each horizontal rectangle of the first scan, the vectors $\mathbf{u}^{\mathrm{hor},j}$ and $\mathbf{v}^{\mathrm{hor},j}$ are obtained for each rectangle j. Using the steps described in "Applying the original NPK method to non-isothermal experiments" section, the nj^{hor} pair of vectors, $\mathbf{u}^{\mathrm{hor},j}$ and $\mathbf{v}^{\mathrm{hor},j}$, are combined into two vectors, $\mathbf{u}^{\mathrm{hor}}_\alpha$ and $\mathbf{v}^{\mathrm{hor}}$. But, only for vector $\mathbf{u}^{\mathrm{hor}}_\alpha$, each one of their elements corresponds with a unique element of vector α^{hor} (denoted by adding the subscript α to $\mathbf{u}^{\mathrm{hor}}$). This fact is illustrated in Fig. 10a, where for a fixed value of α_k, a parallel line to the

temperature axis only crosses one rectangle, whereas for a specific temperature value, T_l, a parallel line to the y axis crosses many rectangles. Hence, for a specific T_l, there exists a correspondence to many $v^{\mathrm{hor},j}$ (note that the subscript T has not been added to $\mathbf{v}^{\mathrm{hor}}$). Through a second scan using vertical rectangles with a small width, a non-arbitrary correspondence between T and v can be established. The outcomes from the second scan are the two vectors $\left(\mathbf{u}^{\mathrm{ver}}, \mathbf{v}_T^{\mathrm{ver}}\right)$, analogously to the first scan. After the two scans, the injective vectors $\mathbf{u}_\alpha^{\mathrm{hor}}$ and $\mathbf{v}_T^{\mathrm{ver}}$ we are aiming for cannot be directly chosen, because their outer product would modify the values of $\mathrm{d}\alpha/\mathrm{d}t$:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha,T} = \mathbf{u}_\alpha^{\mathrm{hor}}\mathbf{v}^{\mathrm{hor}} = \mathbf{u}^{\mathrm{ver}}\mathbf{v}_T^{\mathrm{ver}} \neq \mathbf{u}_\alpha^{\mathrm{hor}}\mathbf{v}_T^{\mathrm{ver}} \qquad (29)$$

The injective vectors $\mathbf{u}_\alpha^{\mathrm{hor}}$ and $\mathbf{v}_T^{\mathrm{ver}}$ can be selected keeping the original $\mathrm{d}\alpha/\mathrm{d}t$ values by rescaling one of the two vectors. Once $\mathbf{u}_\alpha^{\mathrm{hor}}$ is chosen, $\mathbf{v}_T^{\mathrm{ver}}$ is rescaled introducing a scaling factor, χ, in Eq. 29.

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha,T} = \mathbf{u}_\alpha^{\mathrm{hor}}\mathbf{v}^{\mathrm{hor}} = \chi\mathbf{u}^{\mathrm{ver}}\frac{\mathbf{v}_T^{\mathrm{ver}}}{\chi} \qquad (30)$$

The scaling factor, χ, is calculated assuming that $\mathbf{u}_\alpha^{\mathrm{hor}} = \chi\mathbf{u}^{\mathrm{ver}}$. The final outcome after the two-scan NPK method are the injective vectors $\mathbf{u}_\alpha^{\mathrm{hor}}$ and $\hat{\mathbf{v}}_T^{\mathrm{ver}} = \mathbf{v}_T^{\mathrm{ver}}/\chi$.

The two-scan NPK guarantees that the functions $h(T)$ and $f(\alpha)$ obtained are separable, and hence it makes useful for the analysis of the thermo analytical data, which starts assuming that the single-step kinetics approximation is valid. The separability of these functions is guaranteed adjusting the parameters of the NPK method: number and height of the horizontal rectangles and number and width of the vertical rectangles. To check if the single-step approximation remains valid, the TG curves are simulated taking the outcome ($h(T)$ and $f(\alpha)$) from the two-scan NPK algorithm at each programmed temperature $\Theta_i(T)$ (note that is not limited to a constant heating rate). An ordinary differential equation system (ODEs) with 2 equations has to be solved given the initial values of the conversion (α_0) and temperature (T_0):

$$\begin{matrix} \forall\Theta_i(t) \\ i=1,2,\ldots,ni^{\mathrm{sim}} \end{matrix} \rightarrow \left.\begin{matrix} \frac{\mathrm{d}\alpha}{\mathrm{d}t}=f(\alpha)h(T) \\ \frac{\mathrm{d}T}{\mathrm{d}t}=\Theta_i(t) \\ t=0\rightarrow\alpha_0,\ T_0 \end{matrix}\right\} \overset{\mathrm{solve\,an\,ODEs}}{\rightarrow} \alpha=r_i^{\mathrm{sim}}(T)$$

$$(31)$$

Then, the solution functions $r_i^{\mathrm{sim}}(T)$ are compared with the experimental TG curves for all the programmed temperatures, $\Theta_i(T)$. If the simulated data are not able to fit the experimental curves, it implies that a couple of two separable functions cannot be used to model the experimental data, and according to Simon [17] the single-step

approximation is too crude. On the contrary, a good fit guarantees that the single-step kinetics approximation is valid.

Conclusions

We have proved that the NPK modified version which uses only one rectangle cannot be used to elucidate the number of steps in a consecutive decomposition reaction scheme. This conclusion is based on two reasons. First, this application of the NPK method requires a unique matrix $\mathbf{A}$, but it is not possible to experimentally obtain all the elements of the matrix $\mathbf{A}$ for a sufficient range of α values and temperatures. The second reason relies on the fact that the relative strength of each singular value cannot be connected with the existence of its associated reaction step.

We have proposed the two-scan NPK method that guarantees to find a pair of separable functions, $h(T)$ and $f(\alpha)$, and then check if the single-step kinetics approximation is valid. Consequently, the two-scan NPK can be used as a testing method for the methods based on the single-step kinetics approximation, the model-fitting and model-free methods. The two-scan NPK method provides to the model-fitting method the advantage of performing the fit of the parameters of $h(T)$ and the fit of the parameters of $f(\alpha)$, separately. As demonstrated in [18], for the non-isothermal kinetic data and using the model-fitting method, almost any $f(\alpha)$ can satisfactorily fit the data at the cost of dramatic variations in the Arrhenius parameters ($h(T)$). The later is a consequence of the simultaneous fitting of all the parameters (compensation effect) [19]. With regard to the iso-conversional methods, as they are also based on the single-step approximation, the NPK has the benefit that allows for prior checking of the separability of functions $h(T)$ and $f(\alpha)$.

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