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Highlights

- Kinetic processes with models F0, D1, and Pn are simulated

- A process of two overlapping independent steps (D3+F0) is simulated

- The Fraser-Suzuki function (FSF) adjustability is evaluated for each case

- The FSF fit leads to erroneous results on curves with sharp peaks and sudden decays

Some limitations of the Fraser-Suzuki function for fitting thermokinetic curves

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Abstract

Mathematical deconvolution (MD) can offer a simple way to solve independent multistep kinetics. However, there are always doubts about the cases in which it loses efficiency.

This work analyzes the adjustability of the Fraser-Suzuki function (FSF) for processes with F0, D1, and Pn models. Curves $d\alpha/dt$-t for were simulated and fitted using the FSF for each case. Their kinetic parameters were determined and compared with the real ones. Furthermore, an example of deconvolution was analyzed. The results show that the FSF fit does not lead to satisfactory results when applied to $d\alpha/dt$ vs t curves that show sharp peaks and sudden decays.

This short communication is not intended to discourage MD use since it has led to correct parameters in many investigations. However, the aim is to show examples of limitations so that the analyst can choose other appropriate approaches. Therefore, MD should always be used with caution and judgment.

Keywords: Fraser-Suzuki function, Multistep kinetic, Kinetic models, Deconvolution, Thermogravimetry, DSC

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1. Introduction

The change in the temperature of a material directly affects the movement of the molecules that compose it [1]. This phenomenon can cause physical-chemical changes in the material, such as decomposition, phase transitions, polymerization, diffusion, among others. Furthermore, thermal stimulation will affect its kinetics [1]. Here, thermal analysis techniques play an essential role in the understanding and analysis of these processes and their kinetics.

Thermal analysis (TA) comprises a set of techniques that study some physical-chemical properties of a material as a function of time and temperature, according to a program pre-established by the analyst. The most widely used techniques are thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) [2]. TGA obtains an integral signal of the mass changes of the sample, which can be expressed as the conversion (α), while DSC produces a differential heat flux signal that can be proportional to $d\alpha/dt$ [2,3]. Therefore, time, temperature, α, and $d\alpha/dt$ data can be obtained using TA. In this way, the rate of heterogeneous one-step reactions can be parameterized according to:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{Ea}{RT}\right) f(\alpha) \tag{1}$$

where A and Ea are the pre-exponential factor and activation energy, respectively, R is the universal gas constant, and T is the absolute temperature. The function $f(\alpha)$ represent a wide variety of ideal kinetic models, some of which are in Table 1. The flexible Šesták-Berggren (SB) model can be used, $f(\alpha) = c(1 - \alpha)^n \alpha^m$, where by varying the coefficients n and m, all the ideal models are obtained [4]. Furthermore, the SB model allows observing deviations from the ideal models due to inhomogeneity in the shape or size of the particles [4].

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Table 1. Most common kinetic models $f(\alpha)$ used in thermokinetic analysis and the corresponding c, n and m values for their equivalence with the Šesták-Berggren function

Kinetic model	Symbol	$f(\alpha)$	c	n	m
One-dimensional phase boundary controlled reaction (zero-order)	F0	1	1	0	0
One-dimensional diffusion	D1	$1/2\alpha^{-1}$	0.5	0	-1
Two-dimensional diffusion	D2	$[-\ln(1-\alpha)]^{-1}$	0.973	0.441	-1.002
Three-dimensional diffusion (Jander equation)	D3	$3/2(1-\alpha)^{2/3}/[1-(1-\alpha)^{1/3}]$	4.431	0.951	-1.004
Random nucleation followed by an instantaneous growth of nuclei (first-order)	F1	$1-\alpha$	1	1	0
Random nucleation and growth of nuclei through different nucleation and nucleus growth models (Avrami Erofeev eq. n≠1)	An	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$	A2: 2.073 A3: 3.192	0.807 0.748	0.515 0.693
Two-dimensional phase boundary controlled reaction (contracting cylinder)	R2	$(1-\alpha)^{1/2}$	1	0.5	0
Three-dimensional phase boundary controlled reaction (contracting sphere)	R3	$(1-\alpha)^{2/3}$	1	0.667	0
Power law	P2	$2\alpha^{1/2}$	2	0	0.5
Power law	P3	$3\alpha^{2/3}$	3	0	0.667
Power law	P2/3	$2/3\alpha^{-1/2}$	0.667	0	-0.5

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Generally, thermally induced processes have multiple steps, which makes kinetic analysis more complex [5,6]. Multistep processes show kinetic curves with convolved peaks due to overlapping events. Furthermore, the individual steps can present competitive, consecutive, or independent kinetic schemes [7]. In some cases, kinetic multistep can be detected by visual inspection of the curves. However, the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) recommends isoconversional kinetic analysis of data for identification of multistep processes [3,6]. During the last decades, many approaches have been developed to obtain quality kinetic analysis in multistep processes, depending on the reaction schemes. These approaches include mathematical deconvolution (MD) [8], kinetic deconvolution analysis (KDA) [9,10], and formal kinetic analysis (FKA) [11,12].

Particularly, the MD has been presented as a useful and simple tool for the deconvolution of independent parallel processes in complex $d\alpha/dt$-t curves [8]. Here, the constituent peaks of the complex profile are separated empirically using a mathematical function given in Equation (2) [5,6].

$$\frac{d\alpha}{dt} = \sum_{i=1}^{N} F_i(t) \tag{2}$$

where $F_i(t)$ is an empirical function, t is the time, and N is the total number of reaction steps (i).

According to Perejón et al., the Fraser-Suzuki function (FSF) can be used for the deconvolution of overlapping independent processes [8]. Equation (3) allows us to adequately simulate the intrinsic asymmetry of the kinetic curves, regardless of the kinetic model of the solid-state reaction [6,8,13].

$$y = a_0 \exp\left[-\ln 2 \left[\frac{\ln\left(1 + 2a_3\frac{x-a_1}{a_2}\right)}{a_3}\right]^2\right] \tag{3}$$

where a_0, a_1, a_2 and a_3 are the amplitude, position, width at half height, and asymmetry of the curve, respectively. Once the deconvolution of the possible steps has been carried out, different methods can be applied to determine the kinetic triplets of each of them. Some methods are isoconversional methods, Combined Kinetic Analysis (CKA), among others.

The MD with the FSF has shown good results in the deconvolution of many multistep processes with a wide variety of kinetic models. Some examples are thermokinetic analyzes of PVC [8], BiFeO$_3$ [14], hydrotalcite [13], polysilazane and polysiloxane [15], polydimethylsiloxane silicone [16], 4-vinylbenzyl chloride [17], ammonium fluorosilicates [18], CL-20 polymorphs [19], among others. The MD with the FSF presents great flexibility in capturing the reaction profile [8]. However, it should always be used with caution and judgment, as the results a can be misleading [5].

This short communication evaluates some limitations of the FSF to adjust processes with models of zero order, one-dimensional diffusion, and power law. Kinetic curves were simulated for each one. The $d\alpha/dt$-t curves were fitted using FSF. Then, the kinetic parameters of the original and fit curves were obtained by CKA to compare their values. Finally, as an example, a process was simulated with two overlapping independent steps (D3+F0). The curves were deconvoluted with the FSF, and the kinetic parameters were obtained by CKA.

2. Obtaining and analysis of kinetic curves

Thermal analysis curves were simulated by generating time, temperature, α, and $d\alpha/dt$ data sets. The curves were obtained according to Equation (4) for non-isothermal heating programs (1, 2, 5, and 10 K/min). The simulations were done in Python 3.9 using the fourth-order Runge-Kutta integration method.

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$$\frac{d\alpha}{dt} = \sum_{i=1}^{N} l_i (cA)_i \, e^{\left(-Ea_i/RT\right)} (1-\alpha_i)^{n_i} \alpha_i^{m_i} \quad \text{with} \quad \sum_{i=1}^{N} l_i = 1 \quad \text{and} \quad \sum_{i=1}^{N} l_i \alpha_i = \alpha \quad (4)$$

where l_i is the contribution i-th reaction step

The $d\alpha/dt\text{-}t$ curves were fitted with the Fityk 1.3.1 software using the FSF with the Levenberg–Marquardt algorithm [8]. Then, the kinetic parameters of each step were obtained by CKA in Python [18,20]. The CKA consists of Equation (5) linearization through the parameters n and m optimization. The data sets are jointly fitted for α between 0.1 to 0.9. In this way, Ea is obtained from the slope and $\ln(cA)$ from the ordinate to the origin.

$$\ln\left(\frac{\frac{d\alpha}{dt}}{(1-\alpha)^n \alpha^m}\right) = \ln(cA) - Ea_i/RT \quad (5)$$

3. Results and discussion

3.1. Analysis for one-step processes with kinetic models F0, D1, and P3

Three one-step events were simulated with models F0, D1, and P3, and Ea = 146 kJ/mol and $\ln(A/s^{-1})$ = 11.5. Figure 1 shows the curves obtained for F0 (a and b), D1 (c and d), and P3 (e and f).
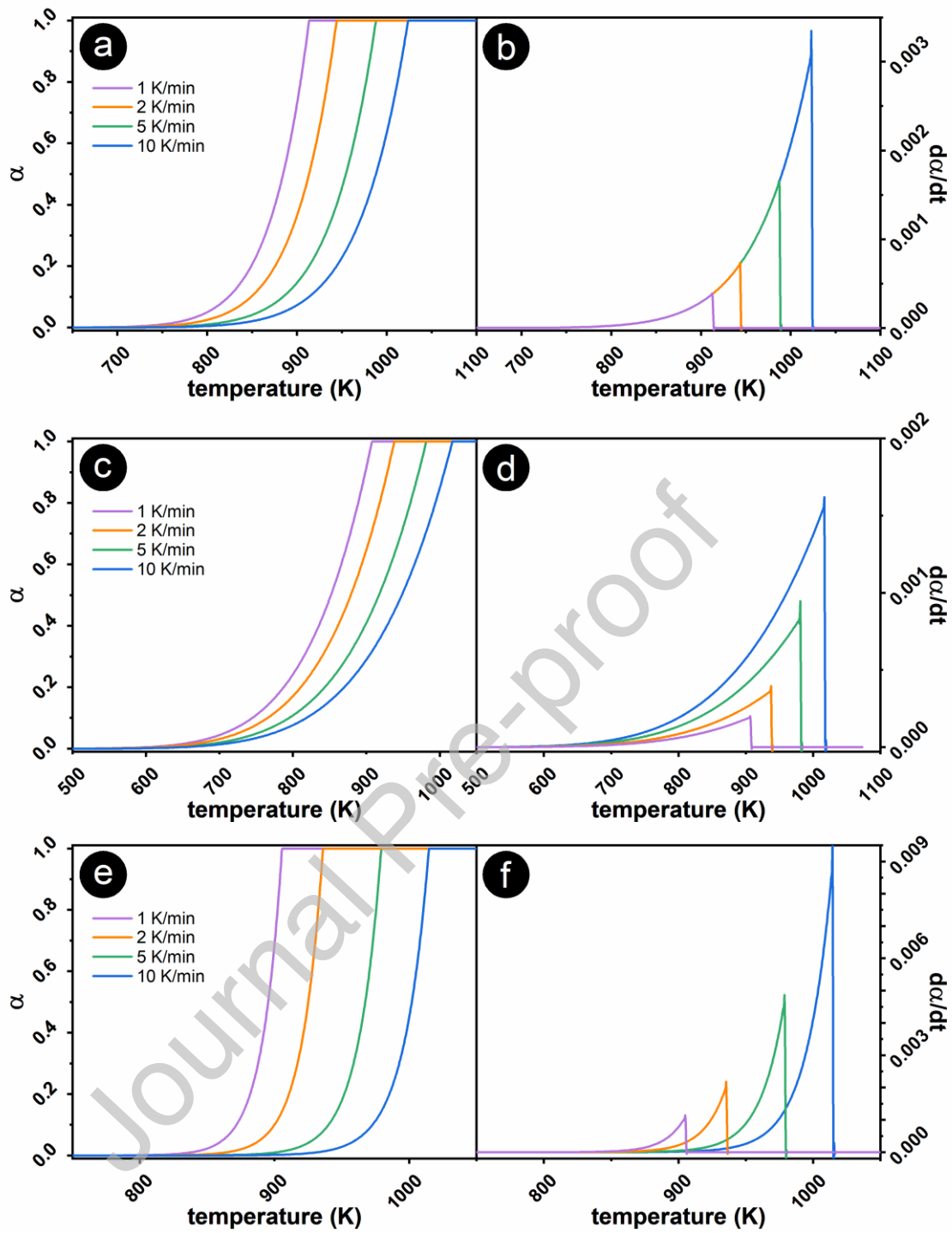
Figure 1. Simulated thermokinetic curves for processes with models F0 (a and b), D1 (c and d), and P3 (e and f)

The rate curves of all processes in Figure 1 show sharp peaks. The trends are typical of exponential functions, in agreement with the Arrhenius equation, combined with power function for the D1 and P3 models, according to $f(\alpha)$. Once the maximum is reached, the curves fall sharply parallel to the *y*-axis. In particular, the $d\alpha/dt$-T curves of the F0 model overlap because there is no dependence on the degree of conversion.

The $d\alpha/dt$-t curves were fitted with the FSF. The results of the F0, D1, and P3 models are presented in Figures 2, 3, and 4, respectively. Table 2 summarizes the SFS parameters.
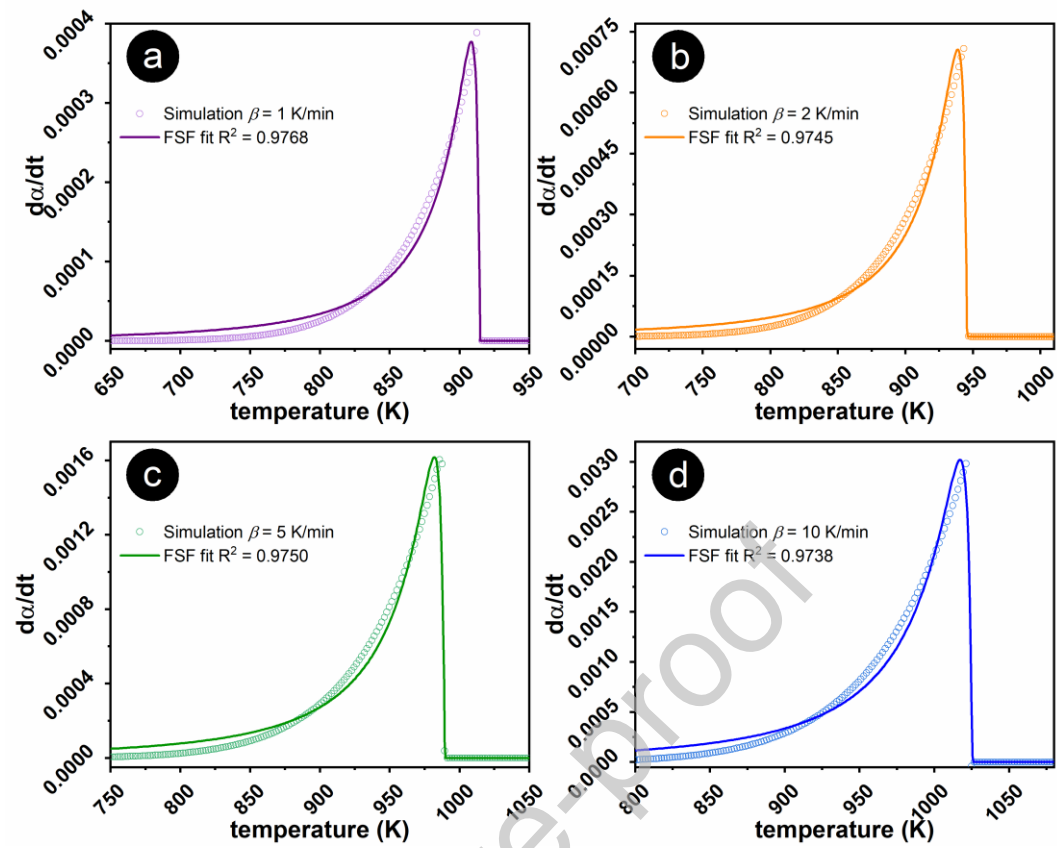
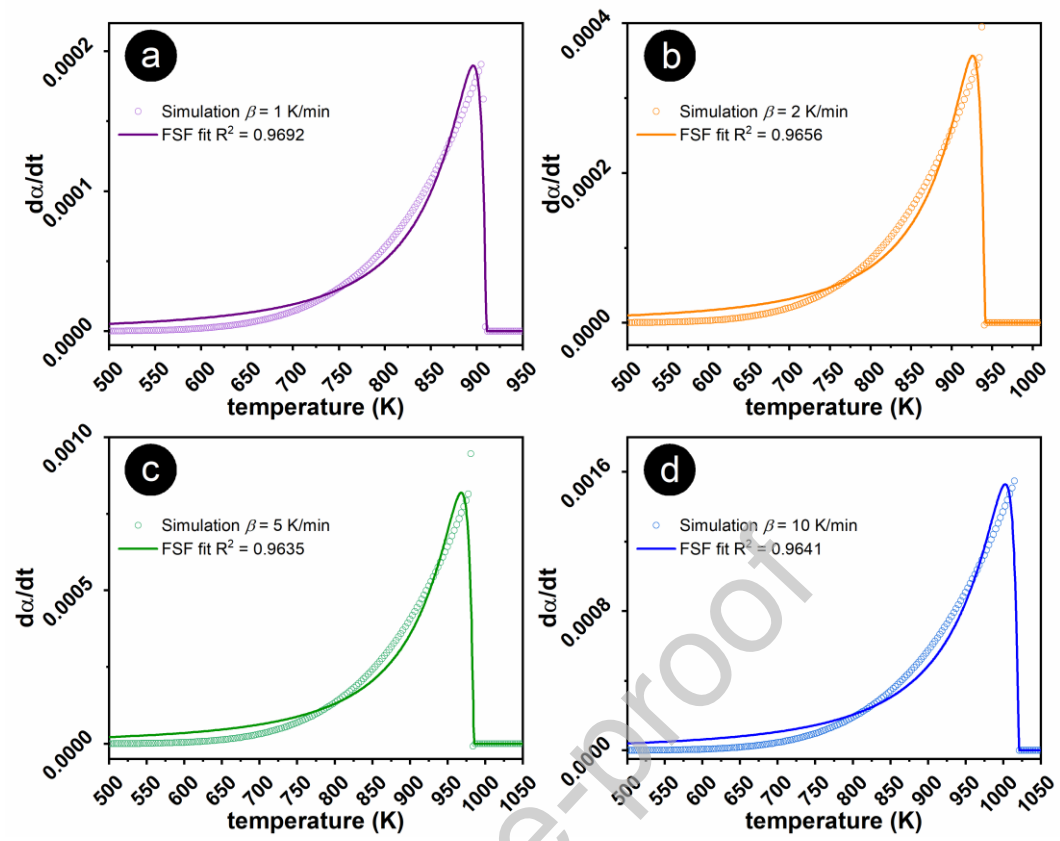**Figure 2. Thermokinetic curves of the F0 process fitted with the FSF**

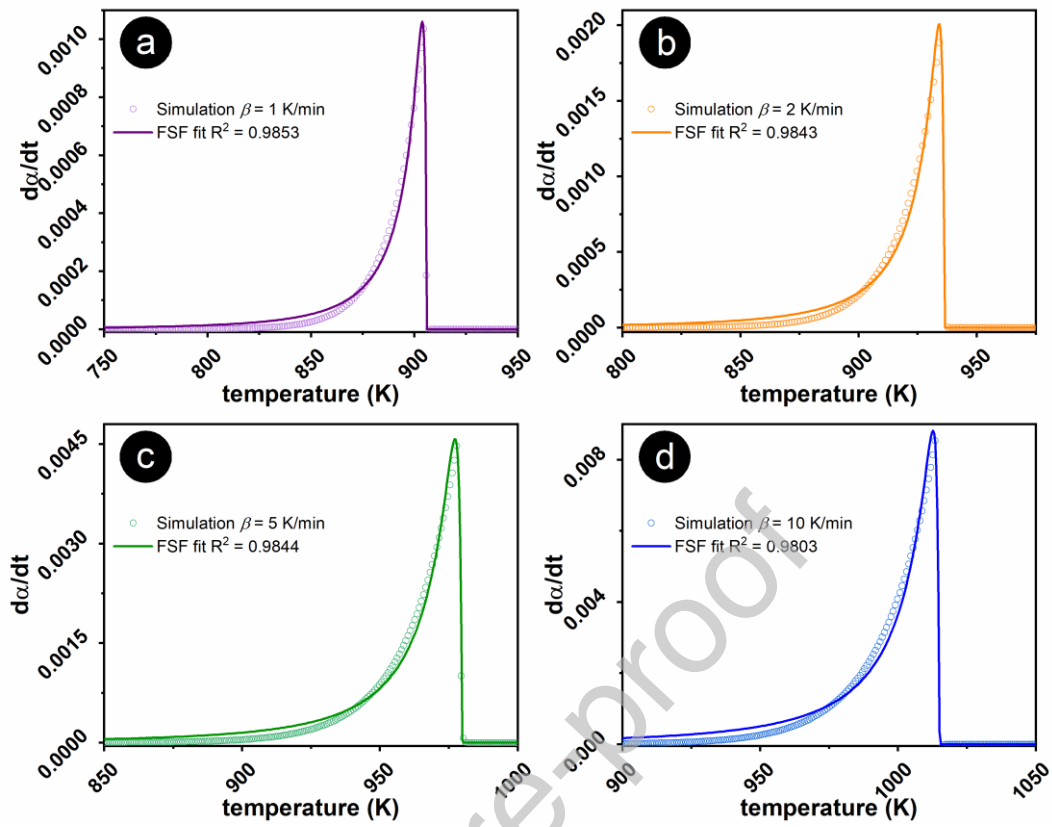**Figure 3. Thermokinetic curves of the D1 process fitted with the FSF**

Figure 4. Thermokinetic curves of the P3 process fitted with the FSF

Table 2. FSF fitting parameters of the experimental curves

Kinetic model	β (K/min)	a_0	a_1	a_2	a_3	R^2
F0	1	3.772691×10^{-4}	20114.16	1200.211	-1.54629	0.9768
	2	7.065953×10^{-4}	10966.52	647.7814	-1.533831	0.9745
	5	1.617904×10^{-3}	4905.264	284.9098	-1.526068	0.9750
	10	3.02133×10^{-3}	2664.424	153.3814	-1.520201	0.9738
D1	1	1.89775×10^{-4}	35876.22	2615.267	-1.445398	0.9692
	2	3.569372×10^{-4}	18831.62	1391.783	-1.455291	0.9656
	5	8.18936×10^{-4}	8040.328	610.0183	-1.450062	0.9635
	10	1.529519×10^{-3}	4226.96	329.0099	-1.442418	0.9641
P3	1	1.060705×10^{-3}	13838.2	427.7882	-1.523173	0.9853
	2	2.010286×10^{-3}	7829.149	220.4755	-1.549876	0.9843
	5	4.581993×10^{-3}	3648.97	98.37072	-1.532083	0.9844
	10	8.815951×10^{-3}	2037.326	47.65701	-1.61234	0.9803

The FSF fit shows good R^2 values for the four heating rates. Note that the fit "sacrifices" the start of the process to adjust the decay. The fitted curves show that the process begins at temperatures lower than the real ones. Although the FSF is very flexible due to its four adjustable parameters, it is not enough to fit the kinetic equation due to intrinsic mathematical differences in the functions.

For comparison, CKAs were performed on the original simulated curves and those fitted with the FSF. The results are presented in Table 3 and Figures 5, 6, and 7.

Table 3. Kinetic parameters obtained by CKA

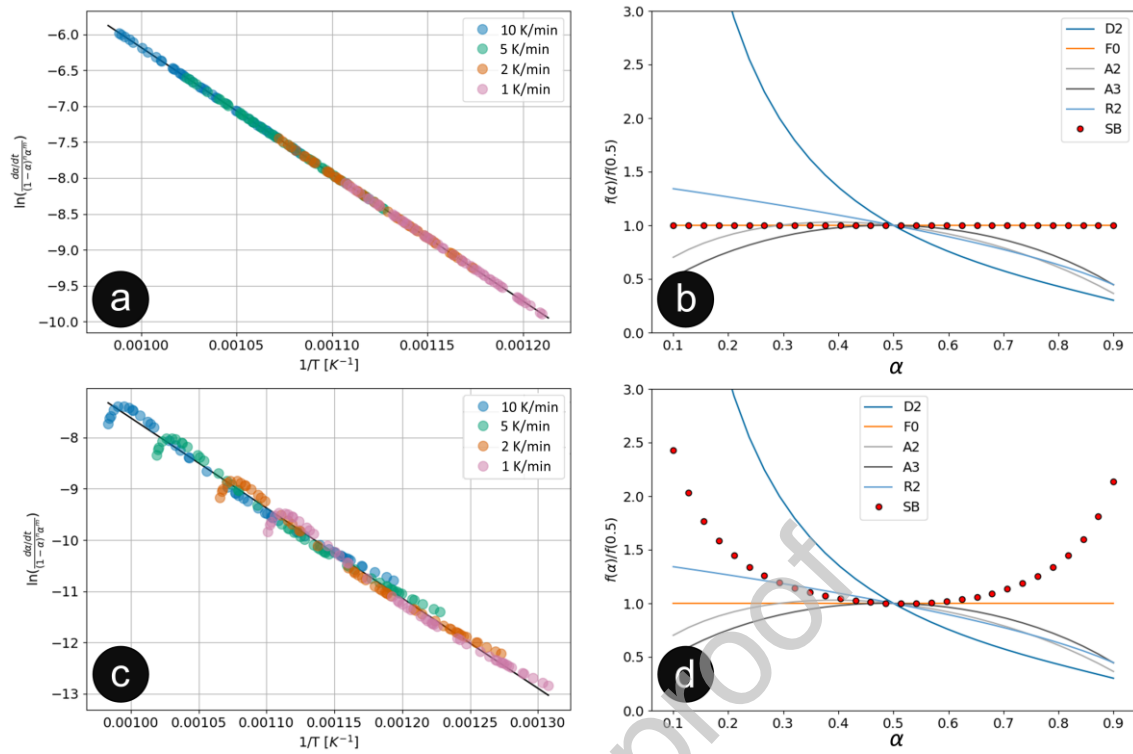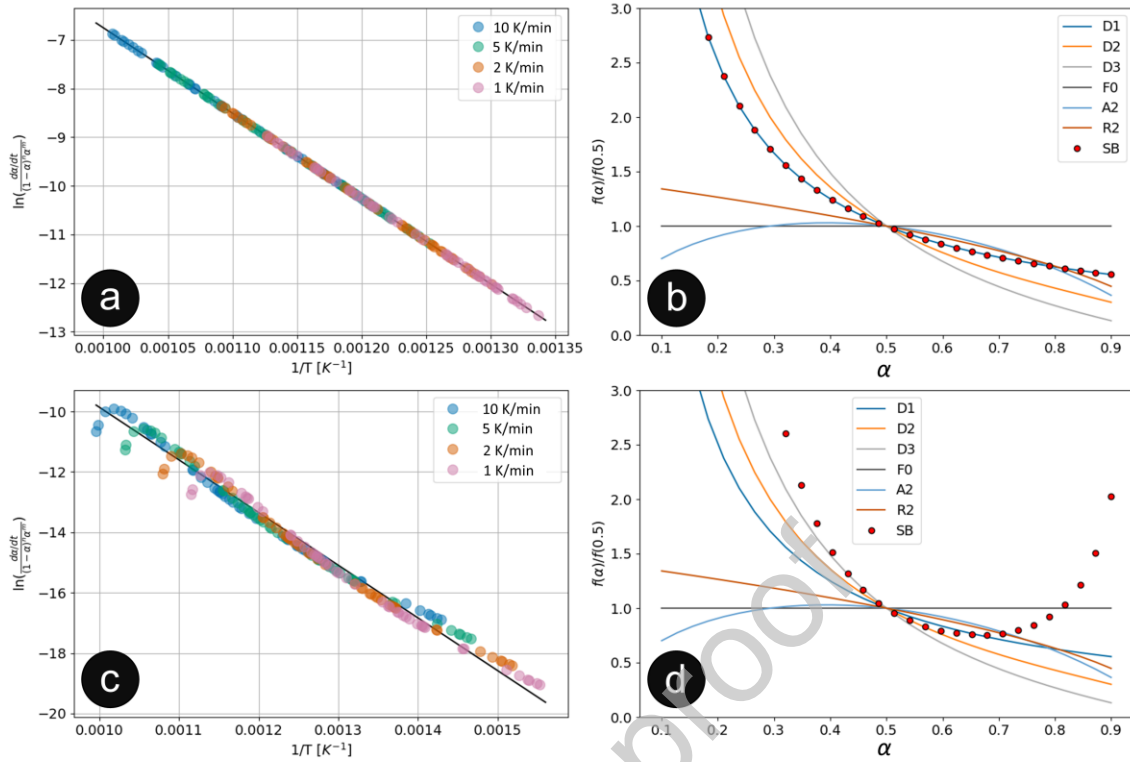| Kinetic model	F0		D1		P3	
CKA from:	Simulated data	FSF fit	Simulated data	FSF fit	Simulated data	FSF fit
Ea (kJ/mol)	146.00	146.4	146.00	145.0	145.99	142.5
$\ln(cA/s^{-1})$	11.5	10.0	10.8	7.6	12.6	11.5
n	0.000	-0.776	0	-1.64	0	-0.359
m	0.000	-0.835	-1	-3.29	0.667	0.648
R^2	1.0	0.994	1.0	0.990	1.0	0.996

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Figure 5. CKA results of the simulated (a and b) and fitted (c and d) curves for the F0 process

Figure 6. CKA results of the simulated (a and b) and fitted (c and d) curves for the D1 process
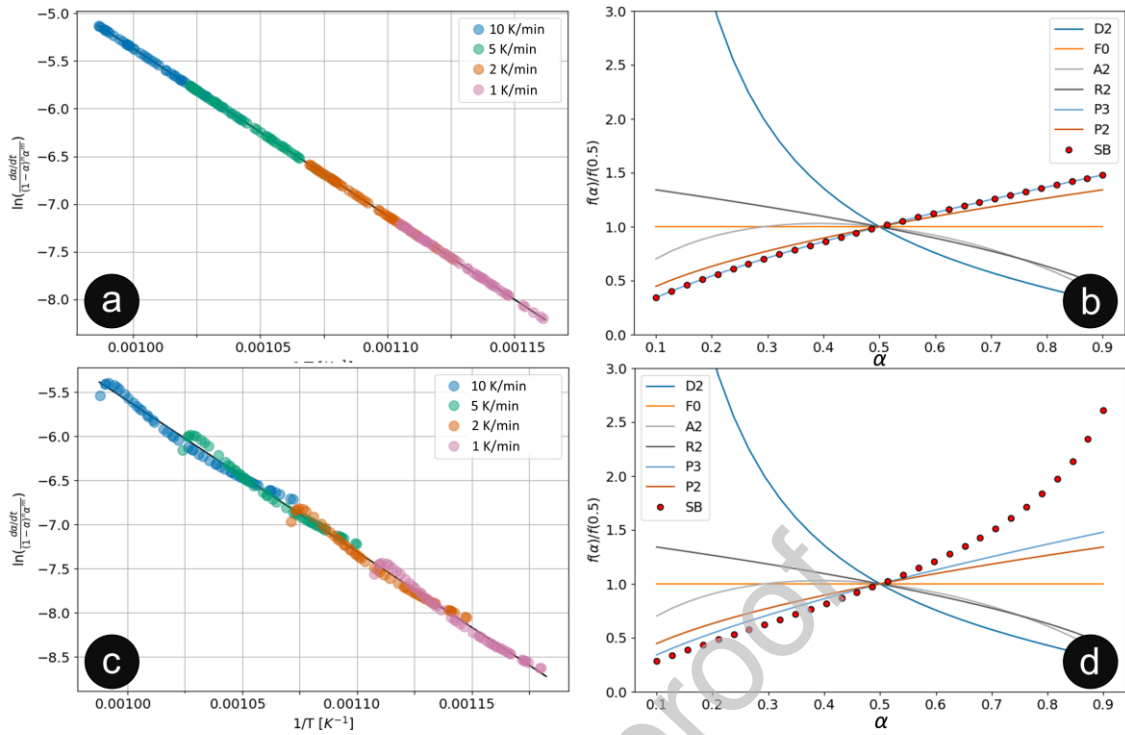
Figure 7. CKA results of the simulated (a and b) and fitted (c and d) curves for the P3 process

As expected, the original data show perfect fits, leading to the correct kinetic triplets (Figures 5 (a and b), 6 (a and b), and 7 (a and b)). Note the values of c presented in Table 1 for each model. On the other hand, the fit of the FSF curves presents R^2 very close to 1. This fact can lead to wrong conclusions. The Ea values are comparatively acceptable, while the $\ln(cA)$ present relative errors of 13, 30, and 9% for the F0, D1, and P3 models, respectively. Furthermore, Figures 5 (d), 6 (d), and 7(d) show considerable deviation correct kinetic models. For the event F0, the model obtained does not fit any ideal model and does not make physical sense. At low conversion, the D1 model overlap with D3 model. Finally, for P3 at low conversion, it is close to the correct model but deviates considerably at high conversion. Similar results to the P3 model were observed for P2 and P2/3 models (Supplementary Material).

These results show that MD is not efficient with processes that follow this type of kinetic models. As an empirical rule, the FSF fit does not lead to satisfactory results when applied to $d\alpha/dt$ vs t curves that show sharp peaks and sudden decays.

This short communication is not intended to discourage the use of the MD since it has led to correct parameters in many investigations. However, the aim is to show examples of limitations so that the analyst can choose other appropriate approaches [5,6]. Therefore, MD should always be used with caution and judgment.

3.2. Analysis of an example of two-step independent process

A process of two independent parallel steps was simulated with the kinetic parameters presented in Table 4. The first step corresponds to an D3 model, while the second step to an F0. Figure 8 shows the obtained α-T curves.

Table 4. Simulated kinetic parameters and those obtained from the deconvoluted curves

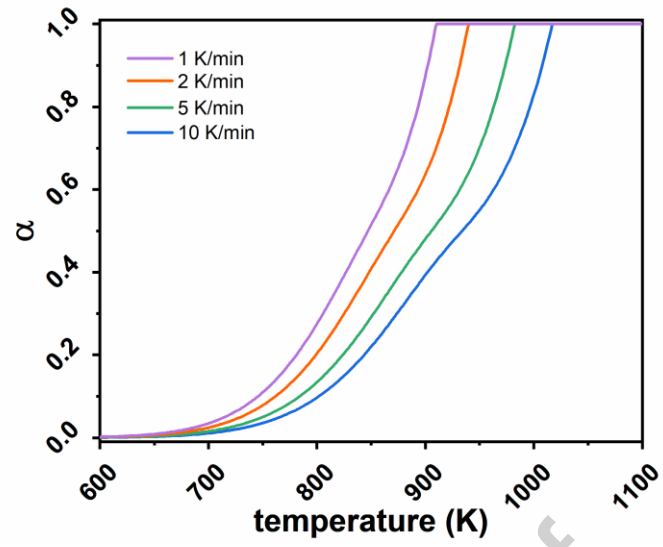| Step	1		2	
Data	Simulation	Deconvolution	Simulation	Deconvolution
Ea (kJ/mol)	196	235	150	174
$\ln(cA/s^{-1})$	21	26.8	12	10.8
n	0.951	1.84	0	-2.16
m	-1.004	-0.754	0	-3.09
Contribution	0.4	0.34	0.6	0.66
R^2	-	0.997		0.983

Figure 8. Simulated α-T curves for two independent process steps with models D3 and F0

According to the ICTAC recommendations, an isoconversional analysis is important to detect multistep kinetics [3,6]. Figure 9 presents a Friedman analysis of the simulated curves. As expected, the values of Ea_α as a function of α show a complex process of at least two steps. This indicates that a multistep analysis is necessary. In this case, the MD process offers a possible solution since the reactions are assumed to be independent parallel.
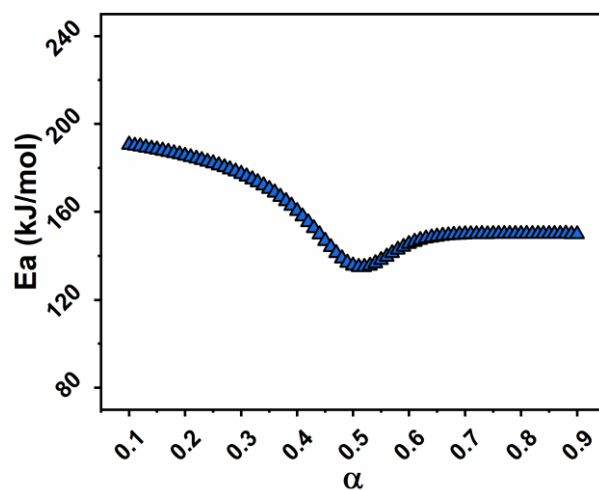
Figure 9. Activation energy as a function of α obtained from the Friedman isoconversional analysis of the simulated curves

The $d\alpha/dt$-t curves were fitted with the FSF. The results are presented in Figure 10. Furthermore, Table 5 summarizes the fitted parameters of the FSF for each step.
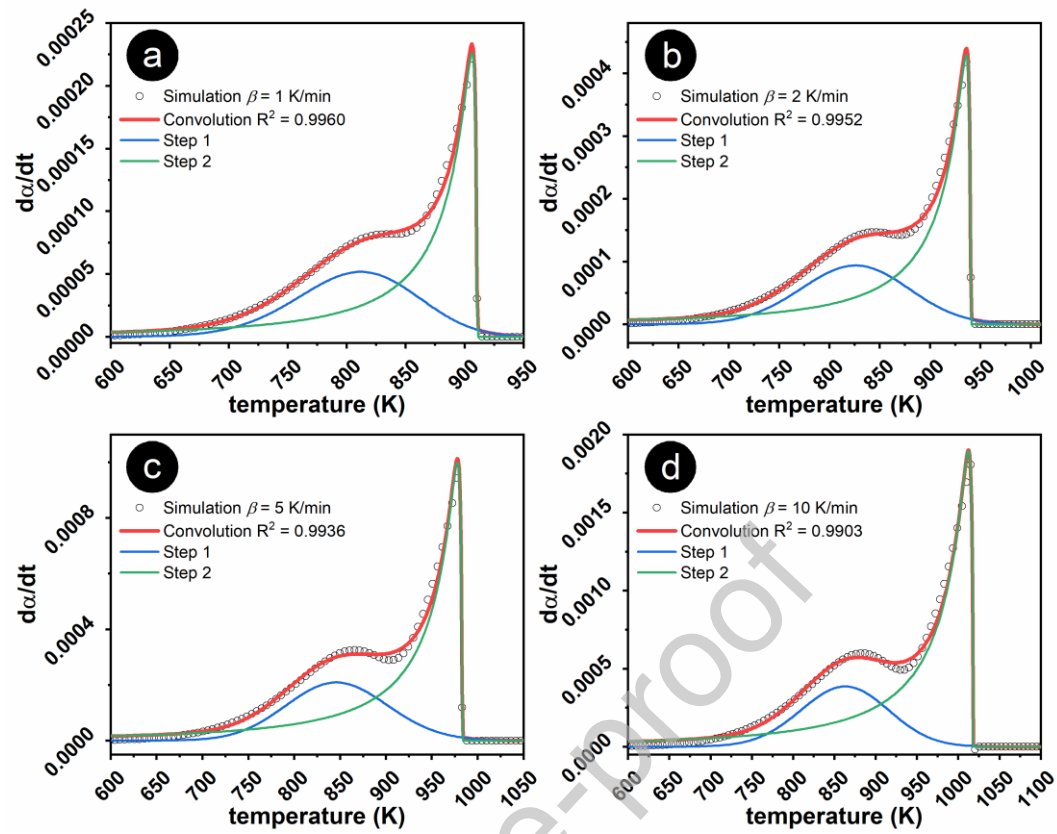
Figure 10. Mathematical deconvolution of the $d\alpha/dt$ curves for the experiments performed at 1 (a), 2 (b), 5 (c), and 10 K/min (d)

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Table 5. Fitting parameters of FSF for deconvolution of the experimental curves

Step	β (K/min)	a_0	a_1	a_2	a_3	l	R^2
1	1	5.178920×10^{-5}	30233.54	7205.412	-0.09172675	0.375	0.9960
	2	9.380564×10^{-5}	15537.58	3781.106	-0.02768397	0.355	0.9952
	5	2.089674×10^{-4}	6453.194	1565.234	0.02479655	0.330	0.9936
	10	3.862962×10^{-4}	3329.196	751.5814	-0.01962577	0.286	0.9903
2	1	2.263912×10^{-4}	35885.77	933.3918	-1.732851	0.625	0.9960
	2	4.297205×10^{-4}	18831.08	504.6524	-1.73959	0.646	0.9952
	5	1.001166×10^{-3}	8037.966	223.8179	-1.751883	0.670	0.9936
	10	1.898922×10^{-3}	4225.071	124.1021	-1.764803	0.714	0.9903

The fit show good values of R^2 for the four heating rates. Also, visually the fit seems correct. As in the first case analyzed, the start of the deconvoluted F0 step occurs at a lower temperature than for the real process. This fact will affect the previous step.
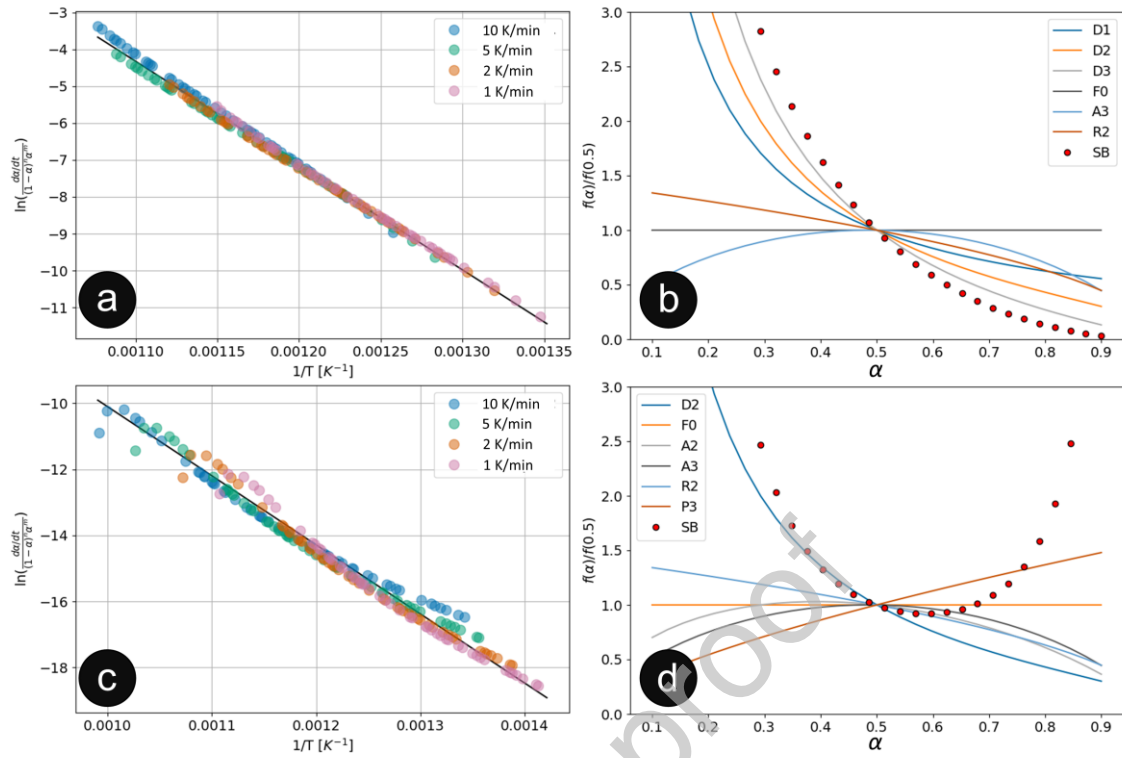The CKA results of each step are presented in Figure 6 and Table 4.

Figure 11. CKA and graphs $f(\alpha)/f(0.5)$ vs α of the obtained models for steps 1 (a) and 2 (b)

The CKA results of the deconvoluted steps lead to considerably different kinetic parameters from the real ones, as indicated in Table 4. The relative errors of steps 1 and 2 were 20 and 16% for Ea and 28 and 10% for $\ln(cA)$, respectively. On the other hand, Figures 11 (b) and (d) show that the models obtained from both steps are not correct, mainly for step 2.

MD and CKA R^2 values close to 1 can lead to serious errors. Sbirrazzuoli has shown that the high flexibility of the equations used generates the existence of local minima that describe the data but may not have a real physical meaning [7]. Therefore, statistical analysis does not always allow discriminating between different kinetic models.

For this example, the results obtained after the MD+CKA are incorrect. However, the error of the kinetic parameters will depend on the number, characteristics, and degree of overlap of the steps. Furthermore, it should be noted that kinetic models may deviate from ideality [8]. In those cases, the curves of these models might not decay drastically and better fit the FSF. However, it can be advisable to use the values obtained as starting parameters in a nonlinear regression applying KDA or FKA [5,10,18]. Furthermore, we must emphasize that MD can only be applied to independent reactions. Their application to consecutive schemes leads to erroneous kinetic triplets. Finally, it is always advisable to carry out curve reconstructions and predictions to verify and validate the kinetic parameters obtained.

4. Conclusions

This work analyzes the adjustability of the FSF for processes with models F0, D1, and Pn. Thermokinetic curves were simulated for each case. The rate equation remains an exponential function (Arrhenius equation) when it is F0, while for D1 and Pn, it is combined with a power function ($f(\alpha)$). These $d\alpha/dt$ vs t curves are characterized by generating with sharp peaks and sudden decays.

The simulated $d\alpha/dt$ vs t curves were fitted using the FSF. Visual analysis indicates that the adjustment "sacrifices" the start of the process to adjust the decay. The fitted curves show that the process starts at temperatures lower than the real ones. Although the FSF is very flexible due to its four adjustable parameters, it is not sufficient to fit the kinetic equation due to intrinsic mathematical differences in the functions. Also, good values of R^2 can confuse the analyst into wrongly accepting the fit.

The kinetic parameters were determined for the new FSF-fitted curves and compared with the real ones. The values of Ea were comparatively acceptable, while those of $\ln(cA)$ present relative errors of up to 30%. The n and m values of the SB model lead to deviation and confusion in determining the correct kinetic model. Here, the CKA of the FSF curves also presents R^2 very close to 1. This fact can lead to erroneous conclusions.

Finally, an example of overlapping processes was shown, simulated with kinetic models D3 and F0. Deconvolution with FSF showed a good overall visual fit. However, the obtained kinetic parameters were considerably different from the real ones.

Therefore, the results show that the FSF fit does not produce satisfactory results when applied to $d\alpha/dt$ vs t that show sharp peaks and sudden decays. The error of the kinetic parameters will depend on the number, characteristics, and degree of overlap of the steps. Furthermore, it should be noted that kinetic models may deviate from ideality. In those cases, the curves of these models might not decay drastically and better fit the FSF. However, it can be advisable to use the values obtained as starting parameters in a nonlinear regression applying KDA or FKA.

Finally, this short communication is not intended to discourage MD use since it has led to correct parameters in many investigations. However, the aim is to show examples of limitations so that the analyst can choose other appropriate approaches. Therefore, MD should always be used with caution and judgment in independent parallel reactions.

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Graphical abstract
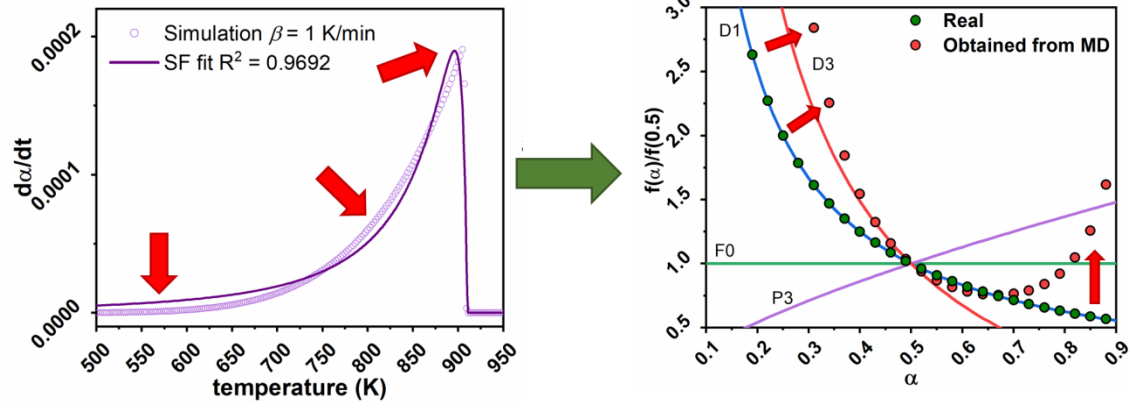
Authors' Contributions

Alexander C. Resentera: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Software, Writing - Original Draft, Writing - Review & Editing.

Mario H. Rodriguez: Resources, Visualization, Writing - Review & Editing, Funding acquisition.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: