

# A new Approach for the Reliable Estimation of Kinetic Parameters by Means of Dynamic DSC Experiments

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A new method for the assessment of the kinetic triplet (pre-exponential factor, Activation energy, kinetic model) better describing a thermal decomposition process is presented. The approach is based on the processing of three DSC thermograms collected under dynamic conditions using different heating rates. It has been shown that two of this basic set of runs allows the assessment “a priori” of the kinetic model suitable to describe the process under study (among reaction order and autocatalytic Sestak-Berggren model) while a successive multivariate procedure carried out considering these three set of data allows the assessment of the final estimate of the thermokinetic parameters. A number of examples are provided with the aim at showing that, when particular hypothesis are met, the extrapolation of the results lead to reliable previsions.

## 1. Introduction

In the context of a safety analysis involving thermal unstable compounds, a crucial point is concerned with the reliable prevision of the behaviour of these substances under different thermal conditions. This requires the knowledge of a kinetic model suitable both to describe the experimental data from which it has been identified (interpolation) and predict the behaviour of the system outside these conditions (Extrapolation). To this end two different strategies are possible: the model free and the model fitting approach (Burnham et al., 2007). The first class of techniques includes all the methods that allow the determination of the dependence of the activation energy on the conversion. The second class of methods are based on the strategies devoted to determine the best model that fit the experimental data. In both cases, the basic assumption which is considered valid is the so called single step hypothesis (Šimon, 2005). This assumption allows us to write the reaction progress as the product of two independent terms:

$$\frac{d\alpha}{dt} = K(T) f(\alpha) \quad (1)$$

the first depending only on the temperature ( $K(T)$ : Kinetic constant, which generally has an Arrhenius structure):

$$K(T) = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

and the second term  $f(\alpha)$  (reaction model) depending only on the conversion  $\alpha$ . A list of these models can be found in (Vyazovkin et al., 2011).

It should be underlined that the single step hypothesis is a strongest assumption that should be verified before the implementation of any successive identification procedure. A way by means this can be accomplished consider the plot  $E=E(\alpha)$  evaluated adopting a model-free method (Friedman method for example) and verifying that these values are constant (or at least almost constant) over the whole conversion interval:  $E=E(\alpha)=\text{const}$  for each  $\alpha$  belonging to  $[0,1]$ .

In the classic model fitting approach we try to determine the model better describing the experimental (isothermal or dynamic) DSC data evaluating the regression coefficient  $R^2$  determined considering a

number of different (reasonable) models. The expression of  $f(\alpha)$  that provide the highest value of  $R^2$  is considered as the best choice for the system under study. The major drawback of this approach is that this criterion does not provide an objective discrimination procedure due to the fact that the  $R^2$  values are generally comparable and close to one also considering different kinetic models. Another possible discrimination procedure try to select the best model describing the experimental data by means of the use of the so called  $y(\alpha)$  and  $z(\alpha)$  functions (Malek method) (Màlek, 1992). A good review of all these methods can be found in (Vyazovkin et al., 2011).

When the model fitting strategy is considered, semi-empirical models can be successfully taken into account especially when the complexity of the system under study prevents any mechanistic conclusion. The use of these models can be considered as a possible strategy which allows us to lump in an apparent kinetic scheme the complex nature of the real process under study. Equation 3 and 4 (Šimon, 2011) show the basic semi-empirical models that are generally taken into account.

$$RO(n): \quad f(\alpha) = (1 - \alpha)^n \quad (3)$$

$$SB(p, q): \quad f(\alpha) = \alpha^p (1 - \alpha)^q \quad (4)$$

Once determined the model which is considered valid for the description of the system under study (discrimination), the kinetic triplet [A, E,  $f(\alpha)$ ] can be identified using the approach suggested by (Militký et al., 1992). This approach requires the minimization of a suitable objective function. Due to the complex nature of the objective function, usually the sum of the squared errors, the success of this approach is strongly affected by the proper choice of the initial values of the parameters. If DSC dynamic techniques are considered, although a single dynamic DSC run contains all the information, more than one scan performed at different heating rates are required to identify the model correctly. The approach that will be discussed in the present work is based on the following assumptions: a thermal process in a dynamical DSC run is represented by a single peak; Equation 1 is valid, the semi-empirical models considered are: RO( $n$ ) (Equation 3) and SB( $p, q$ ) (Equation 4). The approach proposed by the authors allows the discrimination among RO( $n$ ) and SB( $p, q$ ) models without making any simplifying hypothesis and considering only the geometric structure of two DSC dynamic runs. Once established the kinetic model suitable at describing the system under study, a reliable initial estimate of the model's parameter is performed and the final estimate is determined by means of a suitable multivariate identification procedure.

## 2. Method Description

It has been shown (Sanchirico, 2012) that two DSC dynamic runs carried out at different heating rates are enough to the aim at determining the kinetic model (among Reaction Order (RO( $n$ )) and Sestak-Berggren autocatalytic (SB( $p, q$ )) model) better describing the experimental data. The analysis of the ratio  $\frac{q_i(T)}{q_j(T)}$  for

the specific heat powers performed using the Equation (5)

$$q_i(T) = K(T) f(\alpha_i) (-\Delta H_R), \quad i = 1, 2 \quad (5)$$

written for two different values of the heating rate,  $\beta_i$  and  $\beta_j$ , ( $\Delta H_R$  is the heat of reaction) and considering for  $f(\alpha)$  the expressions given by the Equations (3) and (4) lead to the conclusion that the simple fact that two dynamic DSC curves gathered in these conditions intercept in a point different than the origin allows us to conclude that RO( $n$ ) has to be ruled out and the application of SB( $p, q$ ) should provide:  $0 < p < 1$  and  $q > 0$ . The last circumstance highlights the autocatalytic nature of the process under study. On the contrary, if two curves do not intercept in a point different than the origin, RO( $n$ ) can describe the experimental data provided that  $n > 0$  and SB( $p, q$ ) is not applicable.

A first estimate of the exponents  $p$  and  $q$  can be obtained by means of the linear interpolation of the following variables (Relation a):

$$y_{i,j} = \frac{\ln\left(\frac{q_i}{q_j}\right)}{\ln\left(\frac{\alpha_i}{\alpha_j}\right)} \quad \text{vs} \quad x_{i,j} = \frac{\ln\left(\frac{1-\alpha_i}{1-\alpha_j}\right)}{\ln\left(\frac{\alpha_i}{\alpha_j}\right)} \quad (a)$$

(where the indexes  $i \neq j$  refer to a couple of runs carried out at different heating rates). The slope of this line is equal to  $q$  and intercept is equal to  $p$ :

$$y_{i,j} = p + q x_{i,j} \quad (6)$$

If  $RO(n)$  holds, by applying the Equation 6 we should get an intercept  $p=0$  and a slope  $q=n>0$ ; this result could be derived also considering (Relation b)

$$\ln\left(\frac{q_i}{q_j}\right) \text{ vs } \ln\left(\frac{1-\alpha_i}{1-\alpha_j}\right) \quad (b)$$

obtaining a line with slope equal to the reaction order  $n$ .

Once the model  $f(\alpha)$  is estimated its derivative  $f'(\alpha)$  can be used for the estimation of the activation energy and of the pre-exponential factor by means of the application of the extended Kissinger's method. This requires at least three experimental curves gathered during different dynamical runs carried out using different heating rates  $\beta_1 < \beta_2 < \beta_3$ . At this point, the different curves corresponding to different combinations of indexes  $((i, j)=(1, 2), (2, 3), (1, 3))$ , can be used also to verify the results gathered about the model using the first two runs. The values of the Arrhenius and kinetic model parameters assessed previously can be adopted as initial estimate in a successive optimization procedure carried out by means of multivariate Ordinary Least Square procedure that involves the search of the minimum over the parameter space of the sum of the squared errors built considering all the data collected at the different heating rates.

### 3. Results and discussion

In order to show the method illustrated above, in the following are reported the principal results obtained for the thermal decomposition of Cumene Hydroperoxide (80 % in Cumene) [CHP] and Dicumyl Peroxide (98% pure crystalline powder) [DCP]. These substances are important industrial intermediates belonging to the class of organic peroxides tending to decompose exothermically with a huge heat release and gas evolution. It is reported that CHP decomposes following an autocatalytic behavior (Sanchirico, 2012). On the contrary, it has been confirmed that the thermal decomposition of DCP follows a reaction order kinetic (Sanchirico, 2013). In both cases, DSC runs were performed using a PerkinElmer DSC 8000 instrument equipped with an Intracooler II cooling system. Both Dynamic and Isothermal runs were carried out using High Pressure capsules. Temperature ramps were performed using three different heating rates for each compound. The principal results and the conditions adopted for these experiments are reported in Table 1 while in Figure 1a and 1b are reported the corresponding DSC traces.

Table 1: Experimental conditions and principal results gathered during the Dynamic DSC runs carried out on DCP and CHP

Substance	Run	Sample mass (mg)	$\beta$ (K min <sup>-1</sup> )	$T_{\max}$ (K)	$-\Delta H_R$ (J g <sup>-1</sup> )
CHP	1	2.2	1.5	430	1,692
	2	2.1	10.0	459	1,638
	3	2.2	20.0	473	1,613
DCP	1	2.7	2.5	437	951
	2	2.8	10.0	455	908
	3	2.6	20.0	463	938

These curves have been considered with the aim of identifying the kinetic triplet concerned with both CHP and DCP. The analysis of the Figure 2b does not show evident intersection points among all the possible combinations of distinct curves while, at the opposite, in the case reported in Figure 1a are evident three distinct intersection points  $\Gamma_i \cap \Gamma_j$  (highlighted by arrows). These circumstances allow us to conclude that in the case of DCP  $RO(n)$  holds and in the case of CHP the Sestack-Berggren has to be taken into account. It has been demonstrated that a first estimate of the exponent  $n$  can be obtained by means of the linear interpolation of suitable variable (Equation 6) (Sanchirico, 2012). In Figure 2 is reported an example of these interpolations both for CHP and DCP.

In Table 2 are reported the results of these initial estimates  $[(p_0, q_0)$  for CHP and  $n_0$  for DCP] along with the corresponding evaluation temperature intervals. The evaluation temperature intervals are the temperature intervals over which the variables in Eq. 6 should be evaluated due to the fact that, if two curves are "too close" (as it is evident considering the values reported for  $q_i$  vs  $T$  over the tails), the experimental errors could amplify leading to a poor evaluation of these variables. Once determined a first estimate of the reaction orders, Extended Kissinger's method has been applied considering Eq. 7.

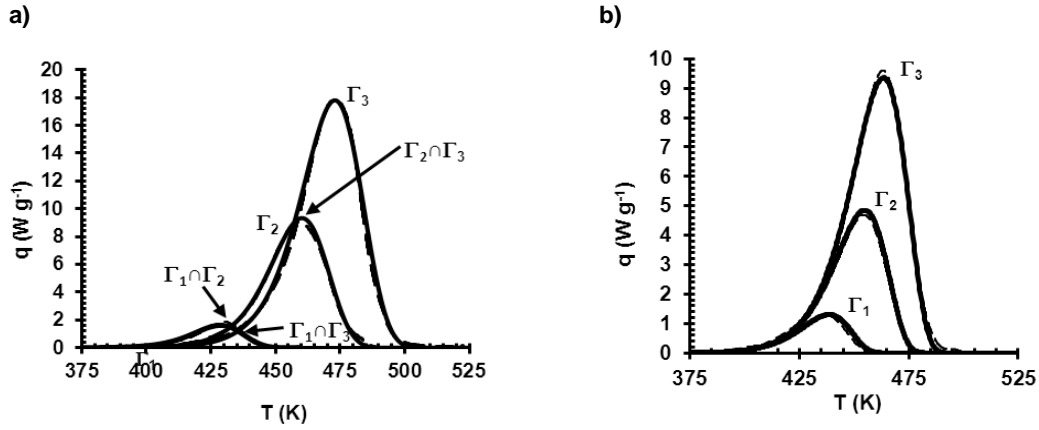


Figure 1: Calculated (solid) and experimental (dashed lines) results gathered during the DSC dynamic experiments on CHP (panel a) and DCP (panel b)

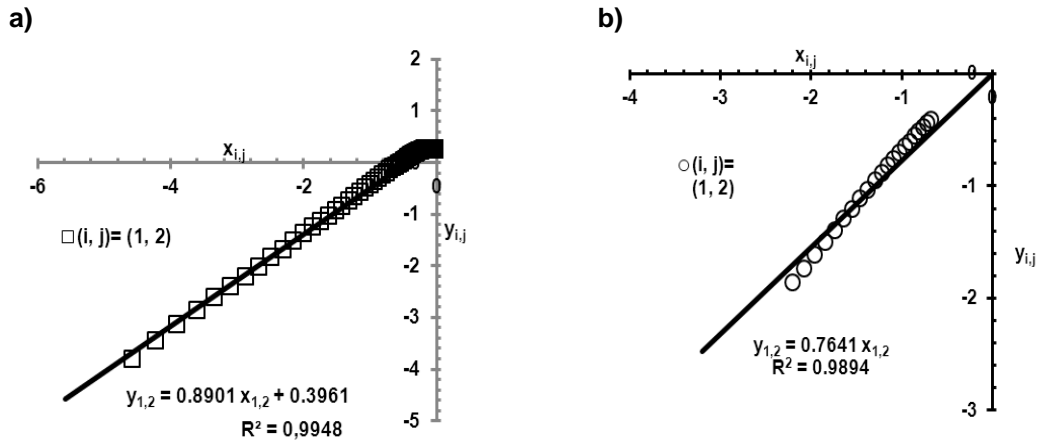


Figure 2: Examples of Regression lines used for the initial estimate of  $(p,q)$  [Panel (a): CHP] and  $n$  [panel (b): DCP]. (Indexes refer to some of the runs reported in Table 2)

Table 2: First estimates of the exponents evaluated considering the method proposed by the authors both for DCP ( $RO(n)$ ) and CHP ( $SB(p,q)$ )

Substance	Data Set at	Evaluation Temperature Range (K)	$P$	$q$	$n$
CHP	$\beta_1, \beta_2$	405-450	0.40	0.89	-
	$\beta_2, \beta_3$	425-480	0.52	1.09	-
	$\beta_1, \beta_3$	410-450	0.40	0.88	-
DCP	$\beta_1, \beta_2$	430-446	-	-	0.76
	$\beta_2, \beta_3$	439-480	-	-	1.05
	$\beta_1, \beta_3$	420-452	-	-	0.86

$$\ln\left(\frac{\beta_i}{T_{i,\max}^2}\right) = -\frac{E}{R T_{i,\max}} + \ln\left(\frac{AR}{E} \phi_o(\alpha_{i,\max})\right) \quad (i = 1, 2, 3) \quad (7)$$

where  $\phi_o(\alpha_{i,\max}) = -D[f(\alpha_{i,\max})]$ .

Considering the temperature at the maximum  $T_{\max,i}$  (see Table 1) for the different heating rates, the linear interpolation carried out considering the Equation 7, allowed the assessment of the Arrhenius parameters reported in Table 3.

Table 3: Initial and final estimates evaluated for the parameters concerned with the RO( $n$ ) and SB( $p,q$ ) models used to describe the thermal decomposition of DCP and CHP

Substance	Parameter	Initial estimate	Final estimate
DCP	A ( $s^{-1}$ )	$3.64 \cdot 10^{+12}$	$3.10 \cdot 10^{+13}$
	E ( $J \text{ mol}^{-1}$ )	125,870	133,892
	$n$	0.89	0.93
CHP	A ( $s^{-1}$ )	$1.31 \cdot 10^{+9}$	$3.728 \cdot 10^{+8}$
	E ( $J \text{ mol}^{-1}$ )	95,895	91,220
	$p$	0.44	0.45
	$q$	0.95	0.93

The final estimate of the parameters was determined by means of a multivariate ordinary least square (OLS) procedure carried out considering all the curves shown in Figure 1a and 1b and considering as initial guess for the vector parameter the values previously determined. It should be stressed that, if we consider the SB( $p,q$ ) model, the Equation 1 provides the trivial solution  $\alpha(T)=0$  if this equation is integrated considering the initial condition  $\alpha(T_0)=0$ . This fact, along with the extreme sensitivity of the solution in respect to the initial condition adopted to carry out the integration (Roduit et al., 2013) led to the integration of the equation (1) for the different heating rates  $\beta_i$  ( $i=1, 2, 3$ ) fixing for CHP a value of  $\alpha_0=10^{-3}$  and evaluating the initial temperatures  $T_{0,i}$  for which the experimental conversion assume this value. Thus, the experimental values considered for the OLS procedure were:  $T_i=[T_{0,i}, T_{final,i}]$ ,  $\alpha_i=[10^{-3} \ 1]$  and  $q_i=[q(T_{0,i}) \ q(T_{final,i})]$ , ( $i=1,2,3$ )

#### 4. Extrapolations

With the aim at showing that the identification procedure described above lead to estimates which can be used also for extrapolation purposes, a series of isothermal experiments were performed both on DCP and CHP and the results compared with the corresponding theoretical predictions. These results are reported in Figure 3 and, as it is evident from its analysis, clearly points out a good agreement between the experimental and the calculated curves both in the case of CHP and DCP.

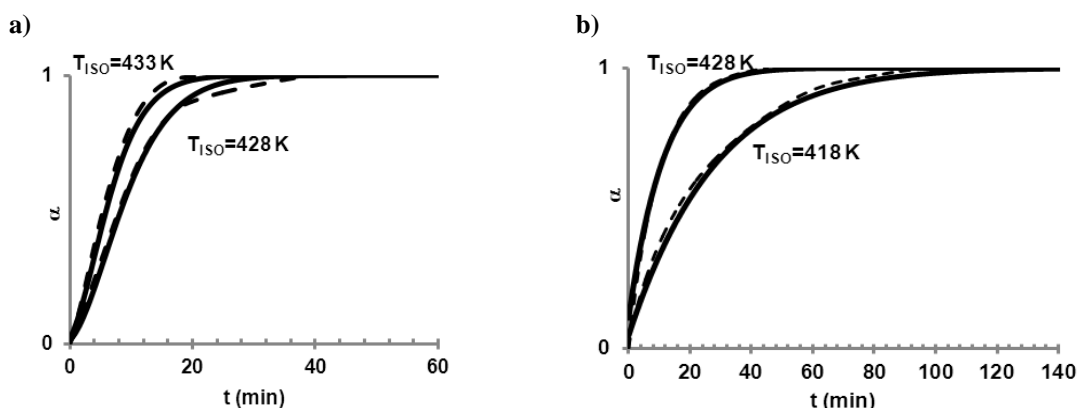


Figure 3: Experimental DSC Isothermal conversions (dashed) and calculated (solid) curves for CHP (panel a) and DCP (panel b). Temperatures are reported near the curves

#### 5. Conclusions

A method for the discrimination between two different kind of semi-empirical models (reaction order and autocatalytic Sestak-Berggren) has been proposed. It has been shown that two curves are enough to determine the kinetic model that better describe the experimental data and it has been pointed out that three dynamic DSC curves could provide a complete set of experimental data suitable to assess the complete kinetic triplet  $[A, E, f(\alpha)]$ . It has been shown that if two curves gathered using different heating rates intercept in a point different than the origin the model suitable at describing the system under study is the autocatalytic Sestak-Berggren model. At the opposite, if these intersection points doesn't exist, the RO( $n$ ) model should be taken into account. A procedure providing the initial guess of the kinetic parameters has been illustrated along with the successive multivariate least square algorithm for the final identification of the kinetic triplet  $[A \ E \ f(\alpha)]$  better describing the system under study

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