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POTENTIAL KINETIC MODEL FOR THERMAL DECOMPOSITION OF COMPLEX ORGANIC COMPOUNDS: SIGNIFICANCE OF PARAMETERS AND ENGINEERING APPLICATION

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Highlights

- The potential model is useful for correlating isothermal and dynamic runs
- The significance of the kinetic parameters, especially E and n , is also discussed
- The potential model is compared with other correlation models

Abstract

This paper analyses the significance of the apparent activation energies and the reaction orders in potential kinetic models, their great interrelation and their influence in the design of reactors. The interrelation between the pre-exponential factor, the apparent activation energy and the reaction order is considered for a single reaction model and for a scheme of reactions. In addition, some simulated results of schemes of reactions were correlated satisfactorily by a single reaction model with surprising results concerning the activation energy and the reaction order. The potential model is compared with other correlation models proposed in literature. Finally, an analysis is presented of the use of the kinetic parameters for the design of industrial reactors.

Keywords: Kinetics, thermal decomposition, reaction order, activation energy

INTRODUCTION

Kinetic models for thermal decomposition of materials are useful for the characterization of material and for the design of reactors. Thermal decomposition can occur as a result of either pyrolysis, oxidative pyrolysis (or fuel-rich pyrolysis or poor-oxygen pyrolysis) and combustion (with oxygen excess). The kinetic models can be applied to solids, liquids or even solids that melt prior to their thermal decomposition. Decomposition runs carried out with thermobalances (TG) or with different types of

reactors – pyrolysers, fixed-bed, fluidized bed, entrained flow- have been used to obtain the kinetics of decomposition

Decomposition runs can be carried out at constant temperature (isothermal runs), at a constant heating rate (dynamic runs), or using ramps of heating rate and trams with constant temperature. Considering the decomposition of different materials (lignocellulosic materials, synthetic polymers, wastes, sludges, etc.), the kinetic models obtained must be analyzed taking into account that they are correlation models. These correlation models can be more representative of the actual decomposition, when the same kinetic model reproduces the experimental results for different operation conditions, using the same kinetic parameters: several dynamic runs, dynamic and isothermal runs, stepwise heating programs, etc..

Galwey and Brown [1] and Galvey [2] analysed the thermal decomposition of ionic solids, considering the nucleation of the product obtained and the mobility of extended defects in the crystal, including the surface material.

L'vov [3] presented a physical approach to the interpretation of the kinetics of thermal decomposition of inorganic solids. He proposed that the decomposition of solids is based on the mechanisms of congruent dissociative vaporization with the subsequent recondensation of low volatile product. He used the Hertz-Langmuir approach, relating the flux density of vapour with the equilibrium pressure, so deducing that the activation energy corresponds to the molar enthalpy of the decomposition.

Nevertheless the previous methods cannot be applied to organic polymers, which is the subject of this paper, although some considerations are useful for the comprehension of the decomposition of organic polymers.

Burnham and Braun [4] presented a kinetic analysis of complex material, considering two principal ways with non-first order kinetics: a) nucleation kinetic behaviour considering random initiation in a variety of sites expanding in space, and b) distributed reactivity reactions involving a mixture of labile and refractory reactions.

Yakobson [5] analyzed the self-fracturing of solids during chemical decomposition, showing the complexity of the dynamics of the decomposition front and the overall decomposition.

Ranzi et al. [6] and Marongiu et al. [7] studied the decomposition of melted polymers (polyethylene, polypropylene and polystyrene) considering a complex net of radical reactions: bond fissions, hydrogen abstractions, β -decompositions, intra-molecular

abstractions and terminations. The kinetic parameters are obtained considering the transient state theory. The reactions considered included chain fission reactions with activation energy around 250 kJ/mol and other reactions (H-abstraction, radical recombination, back biting, etc.) with activation energy around 50-110 kJ/mol.

Marongiu et al. [8] presented a semi-detailed kinetic scheme of the tetrabromobisphenolA (TBBA), constituted by more than 900 chemical reactions, and considering the vaporization processes of TBBA and other compounds. It involves about 60 components, pseudo species and their corresponding radicals. The validation of the kinetic scheme relied on several sets of experimental data (under isothermal and dynamic conditions with different heating rates) directly obtained from scientific literature. On the other hand, Font et al. [9] could also correlate the experimental data with the potential model, considering five processes: the TBBA volatilization and four chemical-vaporization processes.

Shanon [10] applied the activated complex theory to the first order thermal decomposition of inorganic compounds, comparing the predicted and experimental values of an atomic frequency of vibration factor. Font and García [11] applied the transition state theory for the solid decomposition of cellulose. This application of the theory is based on the assumption that the decomposition takes places on the outer surface, where there are only chemical bonds towards the inside part of the particle and it is reasonable to accept that the decomposition begins on the outer surface. This assumption was considered by analogy to the heterogeneous reactions on the surface of the catalyst, when the step controlling the reaction is the decomposition of the activated complex formed. During the reaction, new surfaces are formed as a consequence of the breakage or disappearance of the solid mass, and the reaction surface can change during the extension of the reaction.

For ionic solids, first order kinetic decomposition may be expected in decomposition of fine powders if particle nucleation occurs on a random basis and growth does not advance beyond the individual crystallite nucleated [2]. For organic polymers, there are many correlations of data assuming first order reactions, on the basis that the decomposition rate is directly proportional to the non-reacted solid. Nevertheless, there are many correlations that deviate from this behaviour. One of the proposed models is the potential one, in accordance with the following kinetic expression:

$$\frac{d\alpha}{dt} = k_0 \exp(E/RT) [1 - \alpha]^n \quad (1)$$

where α is the conversion degree and the pre-exponential factor k_0 , the apparent activation energy E and the reaction order n are the triplet kinetic parameters. These kinetic parameters must be considered only as correlation parameters.

For chemical engineers, an adequate and real correlation model is sufficient for the design of reactors, so the mechanistic aspects are less important, although they cannot be ignored. These correlation models can easily be used in simulation programs but the distribution of products must be obtained experimentally. On the contrary, the mechanistic models can give information above the distribution of products, although this distribution must be compared with the experimental one and primary and secondary decomposition must be taken into account. These models must be solved with simulation programs with limited accessibility.

Different kinetic models have been presented in literature. Burgham and Braun [4] have discussed the models corresponding to a generalized nucleation-type reaction, and in some cases these models reduce to the potential models, where only three kinetic parameters are considered: pre-exponential factor, apparent activation energy and reaction order.

The potential model is one of the most used in the correlation of solid decomposition in literature. It is very useful when comparing different results with compounds of similar structure [12]. It is also useful when correlating experimental data with different fractions or decomposition steps with distinct reactivity, in which each fraction must be correlated to a single model, and the different decompositions overlap, preventing a very exact model to be obtained; in this case, a single versatile model, such as the potential one, is sometimes sufficient for obtaining a satisfactory global decomposition model. In some cases, unusual values of apparent activation energy and /or reaction order are obtained. In this paper, an analysis of these cases is considered and discussed considering different factors, trying to provide some explanations on the chaos in solid state reaction kinetics. On the other hand, the influence of these rare values on the design of reactors is also analyzed. Nevertheless, it must be emphasized that the potential model cannot be applied satisfactorily to all kinetic data, and other models must be tested to select the best one.

KINETIC MODEL FOR A SINGLE REACTION OF DECOMPOSITION

In previous papers [13-15], it was deduced that a convenient expression for determining the decomposition of a solid, following the single reaction

can be the following:

$$-\frac{d\left[\frac{B}{B_o}\right]}{dt} = \frac{d(V/V_{inf})}{dt} = -\frac{d\left[\frac{W - W_{inf}}{W_o - W_{inf}}\right]}{dt} = \frac{d\alpha}{dt} = k_o \exp(E/RT)f(\alpha) \quad (2)$$

where B is the amount or fraction of the non-reacted solids, B_o the initial solids amount or fraction, V is the amount or fraction of volatiles, V_{inf} is the maximum value of V at time infinity, α is the conversion degree that equals V/V_{inf} , W is the solid amount or fraction sum of the non-reacted solids and the residue formed, W_{inf} is the amount or mass fraction of residue at time infinity, W_o is the initial amount or mass fraction (for a homogeneous material the initial mass fraction equals 1), k_o is the pre-exponential factor, E is the apparent activation energy and $f(\alpha)$ is a function conversion degree..

Different expressions for $f(\alpha)$ have been proposed in literature [1], but in this paper we limit the study to the potential model because many kinetic studies are based on this model:

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

Consequently,

$$\begin{aligned} -\frac{d\left[\frac{B}{B_o}\right]}{dt} &= \frac{d(V/V_{inf})}{dt} = -\frac{d\left[\frac{W - W_{inf}}{W_o - W_{inf}}\right]}{dt} = \frac{d\alpha}{dt} = k[1 - \alpha]^n = k\left[\frac{B}{B_o}\right]^n = \\ k\left[\frac{W - W_{inf}}{W_o - W_{inf}}\right]^n &= k\left[1 - \frac{V}{V_{inf}}\right]^n = k_o \exp(E/RT)\left[1 - \frac{V}{V_{inf}}\right]^n \end{aligned} \quad (4)$$

It must be emphasized that these models are simplifications of the complexity of the system, including many reactions, each of them including many elemental and radical reactions.

In many correlation models, the reaction order is assumed to be unity due firstly to simplicity, and secondly, because homogeneous behaviour is plausible, so the reaction rate is directly proportional to the non-reacted mass of the initial solid. Nevertheless, there are many factors for considering that the reaction order can different from unity:

no homogeneous nucleation for ionic compounds, sintering of particles, solid-gas reactions, coarse particles with heat and mass transfer, variation of the outer surface or active centres, heterogeneity of the sample with zones with different reactivity, etc.

The analysis presented in this paper is focused on the systems where the kinetic models follow an exponential law, but the analysis and conclusions could be adapted to each case.

INFLUENCE AND INTERRELATION OF THE KINETIC PARAMETERS

In this section, a short review of the influence of the kinetic parameters and their great interrelation is presented. The influence of the parameters on the variation of weight loss or volatiles evolved mass vs. temperature for dynamic runs (constant heating rate) is discussed.

It is well known that the curves of decomposition of a homogeneous material when the heating rate is changed, show a displacement with the greatest heating rates to the zone of high temperatures, as a consequence of the less available time for decomposition. It is also known that there is also a displacement of the TG curves, when changing only the pre-exponential factor. It can be tested that the curves obtained with the same value of the pre-exponential factor: heating rate ratio are coincident. This is congruent with the following simple mathematical deduction. In a dynamic run, the kinetic decomposition law can be written as:

$$\frac{d(V/V_{\text{inf}})}{dT} = (k_o/a) \exp(E/RT) \left[1 - \frac{V}{V_{\text{inf}}} \right]^n \quad (5)$$

where a is the heating rate ($a = dT/dt$). Consequently, the variation of V/V_{∞} vs. the temperature T is the same for the hypothetical runs with the same value of the ratio (k_o/a) . Note that the heating rate cannot explain any difference in any chemical mechanism, and if it does, it is because it interferes with heat transfer rates.

The great interrelation between the exponential factor and the activation energy is also well known [16]. In a previous paper, a parameter was defined in order to decrease the great interrelation between the pre-exponential factor, the activation energy and the reaction order [15]. This parameter is

$$A = k_o \left[\exp\left(-\frac{E}{RT_{\text{ref}}}\right) \right] (0.64)^n \quad (6)$$

where T_{ref} is a temperature of reference (a temperature inside the interval where the decomposition takes place). It has been tested that the use of this parameter in the optimization process decreases the great interrelation between the three parameters involved [15]. The compensation effect between the kinetic parameters (k_o , E , n) has also recently analysed [17].

In a dynamic run with a constant heating rate “a” and considering first order reaction, it can easily be deduced (doing $d^2(V/V_{\text{inf}})/dT^2$ equals zero) that the temperature T_{max} corresponding to the maximum decomposition rate can be obtained from the following expression:

$$\frac{k_o}{a} \exp\left(-\frac{E}{RT_{\text{max}}}\right) = \frac{E}{RT_{\text{max}}^2} \quad (7)$$

The previous expression, considering eq. (6) and taking into account that n equals unity for the case considered, can be written as:

$$\frac{A}{0.64a} \exp\left(-\frac{E}{R}\left(\frac{1}{T_{\text{max}}} - \frac{1}{T_{\text{ref}}}\right)\right) = \frac{E}{RT_{\text{max}}^2} \quad (8)$$

The value of T_{ref} used in eq. (6) must be close to the value T_{max} , corresponding to the maximum decomposition rate, but it can be different to T_{max} . For other reaction orders, the values of T_{max} are close to those obtained by eqs. (7) or (8), as will be seen later.

Figure 1 shows the variation of $1-V/V_{\text{inf}}$ vs. temperature in dynamic runs, where the influence of the apparent activation energy can be observed, but considering that the kinetic parameter A with a reference temperature T_{ref} is constant. The value T_{ref} has been chosen between the extensive range of decomposition of organic and inorganic compounds, but the same conclusion can be obtained with another value. It can be observed that a low value of apparent activation energy extends the TG curve. Considering the factor A , the kinetic eq. (4) can be written as

$$\frac{d(V/V_{\text{inf}})}{dT} = (k_o/a)(0.64)^n \left[\exp\left(-\frac{E}{RT_{\text{ref}}}\right) \right] \left[\exp\left(-\frac{E}{R}\left\{\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right\}\right) \right] \left[\frac{1 - \frac{V}{V_{\text{inf}}}}{0.64} \right]^n =$$

$$\frac{A}{a} \left[\exp\left(-\frac{E}{R}\left\{\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right\}\right) \right] \left[\frac{1 - \frac{V}{V_{\text{inf}}}}{0.64} \right]^n \quad (9)$$

From eq. (9), it is easy to deduce that a TG curve decay will be very sharp and centred approximately in T_{ref} for high values of the activation energy, maintaining the values of n , the heating rate and the factor A constant. For high values of E/R , if A is constant, the value of T_{max} is close to T_{ref} , and in the limit of E/R equals infinite, T_{max} equals T_{ref} .

Figure 1

In Figure 2, the influence of the reaction order can be observed. A reaction order of 5 has been selected to observe the influence of a high value (in literature, one can find high reaction orders in correlation models). Note also that the same parameter A is considered for all the cases, in order to obtain similar temperature ranges of decomposition, and consequentially the pre-exponential factors are different. It is deduced that a large value of n extends the TG curve, similarly to the effect of a low value of apparent activation energy, but there are some differences that can be clearly observed in the following Figure 3. On the other hand, it can also be observed that the decay of the curves takes place in the same temperature interval, so eqs. (7) and (8) deduced for first order reactions can be useful for obtain an approximate value of T_{max} for different values of n .

Figures 2 and 3

In Figure 3, there are two very similar TG curves, but with very different kinetic parameters. One of the curves has high activation energy and high reaction order and the other one a low activation energy and low reaction order. It can be observed that they are close, so many experimental data, from non-uniform materials and in the presence of small random effects, could be satisfactorily correlated with many sets of parameters, but with different values of reaction order and activation energy. Nevertheless, it must be noted that a low value of activation energy extends the TG curve on both sides, at the beginning and at the end of the weight loss, whereas a low value of n extends the TG curve at the end of the weight loss.

SIMULATION OF MULTIPLE REACTIONS AND CORRELATION TO A SINGLE REACTION

In many decomposition reactions, from the TG/DTG curves, it is possible to deduce that there are at least two, three or four initial or intermediate fractions, because there are two, three or four peaks in the DTG. Considering a simulation program, it is possible to deduce the best kinetic parameters for each fraction, in order to obtain a satisfactory correlation.

In many cases, the decomposition corresponding to each fraction is the sum of many reactions, so the kinetic parameters have no physical meaning associated to a compound. Frequently, high or low activation energy or reaction orders are obtained. In this section, some cases are discussed that can explain the kinetic parameters obtained in some correlations.

An analysis of the heating rate on the coupling of complex reaction was done by Flynn [18] to study the separation of the decomposition ranges and/or the decomposition rate peaks, changing the heating rate. Agrawal [19] also presented a discussion about the overall activation energy of a complex system for independent reactions and for competitive parallel reactions considering a single run. Their conclusions are compared with those obtained in this paper when three dynamic runs and three dynamic + isothermal runs are correlated together.

A) Independent reactions

The first cases considered correspond to a solid composed of five different fractions, each one following its own decomposition reaction, in accordance with the scheme

where S_i is the initial mass fraction of the component “i”, v_i and r_i are the yield factors of volatiles V_i and residue R_i corresponding to b_i mass of the initial component “i”. The maximum amount of volatiles obtained at time infinite of reaction is V_{iinf} , and the conversion degree α_i at any time equals the quotient between the volume evolved of volatiles V_i and the maximum value V_{iinf} . The total value V is the sum of the value V_i , and the maximum value V_{inf} is the sum of all V_{iinf} . The kinetic equations considered are the following:

$$\frac{d\alpha_i}{dt} = \left[k_{oi} \exp\left(-\frac{E_i}{RT}\right) \right] (1 - \alpha_i)^{n_i} \quad i=1 \text{ to } 5 \quad (10)$$

$$\alpha_i = \left[\frac{V_i}{V_{iinf}} \right] \quad (11)$$

For any time

$$\alpha = \sum \frac{V_{iinf}}{V_{inf}} \alpha_i = \frac{V}{V_{inf}} \quad (12)$$

and

$$V_{inf} = \sum V_{iinf} \quad (13)$$

A.1) Independent reactions. Parameter A and reaction order constant; different activation energy

Let us assume the kinetic parameters of each fraction shown in Table 1. In this case, the parameter A and the reaction order are the same for all the fractions, whereas the activation energy is different for each fraction. The simulated data are those obtained simulating the system with the five reactions, for three dynamic runs and three dynamic + isothermal runs, and consequently would correspond to the real data obtained from the decomposition of solid, with the behaviour assumed. The dynamic + isothermal runs have been obtained with a constant heating rate from 298 K to the set temperature and then maintaining the set temperature constant. In view of Figure 4, in which simulated and correlated data are plotted, any researcher would think that the solid is homogeneous, and the decomposition kinetics can be deduced considering only one fraction, so an optimization program is used to obtain the best parameters.

Following the ICTAC Kinetics Committee recommendation [20], Figure 5 shows the variation of $\ln$ reaction rate vs. $1/T$ for the different values of conversion degree between 0.05 and 0.95, in accordance with the iso-conversional method. Nearly parallel straight lines are obtained (slopes between 29140 and 31156 K⁻¹) indicating that a single reaction can be used for correlating the data obtained.

Figure 5

The program used to calculate the optimized parameters of the single reaction was the “Solver” tool of an Excel spreadsheet software, and the objective function was a combined sum of the square of differences between simulated and correlated values of $(1-V/V_{inf})$ and the sum of the square of differences of $d(V/V_{inf})/dT$ (all the correlations carried out in this paper have been done with this software). The expression for the objective function was the following:

$$O.F = \sum \left[(1 - V/V_{inf})_{real} - (1 - V/V_{inf})_{cal} \right]^2 + \text{factor} * \sum \left[(-d(1 - V/V_{inf})/dt)_{real} - (-d(1 - V/V_{inf})/dt)_{cal} \right]^2 \quad (14)$$

where the value of the factor is selected in order to obtain a good correlation, both in the TG and DTG data. The subscript “real” and “cal” refers to the real or simulated data generated by the system of equations and to the data obtained to the correlation with a single reaction respectively. The data selected for the runs has been from the values of

$(1-V/V_{inf})$ from 0.99 to 0.01 or to the lowest fraction of non- reacted solid indicated in the figures.

The variation coefficient V.C. used to analyse the differences between the real or simulated values and those obtained by all the correlations discussed in this paper is the following:

$$V.C. = \frac{\sqrt{\frac{[(1 - V/V_{inf})_{real} - (1 - V/V_{inf})_{cal}]^2}{np - m}}}{\text{mean value of } (1 - V/V_{inf})} \times 100 \quad (15)$$

where np is the number of points, m is the number of parameters optimized and the mean value of $(1-V/V_{\infty})$ is the mean of the real values considered, which equals 0.5. The points considered in the value of V.C. correspond to the interval where the ordinates of the TG curve vary significantly from the top value to the lowest one. This coefficient is used in all the correlations presented in this paper. The value of V.C. is useful to analyse the deviations of the correlations considered.

Figure 4 also shows the correlated results with a single reaction, and the parameters obtained. In this Figure and others presented in the following sections, the correlated lines are very close to the simulated ones, and apparently only one line can be observed. An intermediate value of activation energy is obtained and the values of the parameter A and the reaction order, different from unity, are close to those considered in the five fractions. The value of E/R is an intermediate value inside the variation range deduced previously $29140\text{--}31156 \text{ K}^{-1}$ by the iso-conversional method. Similar conclusions can be obtained for other values of A and n of the five fractions (the same values for the five fractions). Elder [21] considered a similar case, although with one single run, obtaining the same tendency in the conclusion: intermediate value of activation energy and similar reaction order. It is important to emphasize that the same set of parameters is used to correlate the data of six runs, three dynamic at different heating rates from 5 K/min to 20 K/min and three dynamic + isothermal runs at different conditions.

The procedure for simulating the results and then correlating presented previously is the same as those applied in the following sections.

A2. Independent reactions. Activation energy and reaction order constant; different pre-exponential factors.

In Table 2 and Figure 6, the activation energy of the first order reactions is the same for all the fractions, whereas the parameter A is different for each fraction. When correlating the data to an apparent kinetics of a single fraction, a low value of activation energy and the values of the parameter A and the reaction order higher than 1 are obtained. This conclusion was also suggested by Agrawal [19] when analysing the papers on coal pyrolysis. Note that, although there are some local deviations between data, the correlation can be considered acceptable, taking into account that the six runs are correlated to the same set of one single reaction parameters. With the suitable selection of parameters, the multiple reaction is not clearly apparent from the DTG runs, as can occur in many real cases. When applying the iso-conversional method to the simulated data, nearly parallel straight lines were also obtained with slopes between 28300 and 30400 K, indicating the suitability for correlating the data to a single reaction (ICTAC Kinetics Committee recommendation [20]).

A3) Independent reactions. Reaction order constant; different pre-exponential factors and activation energies.

In the third case presented in Table 3 and Figure 7, there are different values of the parameter A and the activation energy of the five first order reactions considered. In this case, the best correlation to a single reaction, although not perfect, leads to an intermediate value of apparent activation energy and a high value of reaction order. By applying the iso-conversional method to the simulated data, nearly parallel straight lines were also obtained with slopes between 28400 and 32400 K, indicating an acceptable possibility for correlating the data to a single reaction (ICTAC Kinetics Committee recommendation [20]).

A4) Independent reactions. Gaussian variation of activation energy

Two kinetic models can be considered assuming a Gaussian variation of the apparent activation energy, one with constant pre-exponential factor and another with constant parameter A. In both cases, infinite parallel reactions are considered, with a Gaussian distribution of apparent activation energy as a function of the volatile mass evolved. This is discussed as follows:

A4.1) Independent reactions. Gaussian variation of the activation energy with constant pre-exponential factor

The kinetic model proposed and used by some researchers [22, 23], considering first order reactions for each one of the parallel reactions, is the following:

$$1 - \alpha = \int_0^{\infty} \exp\left[-k_o \exp\left(-\frac{E/R}{T}\right)\right] D(E/R) d(E/R) \quad (16)$$

where the distribution function $D(E/R)$ is expressed as

$$D(E/R) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{((E/R) - (E_o/R))^2}{2\sigma^2}\right) \quad (17)$$

where E_o is the central value and σ is the standard deviation. Note the standard deviation refers to the values of E/R .

Figure 8 shows the simulated values of three dynamic runs and three dynamic + isothermal runs with the Gaussian distribution taking into account the kinetic values presented in Table 4, and considering 34 intervals of $\Delta(E/R)$. The distribution of the activation energy vs. maximum volatile mass evolved can also be observed in Figure 8.

Following similar procedure to that in the previous sections, the simulated values were correlated to a single potential order reaction. Values of E/R between 28400 and 33000 K were obtained by the iso-conversional method (ICTAC Kinetics Committee recommendation [20]).

The optimized parameters and the calculated values are also shown in Table 4 and Figure 8. It can be deduced that for the Gaussian distribution of energy assumed, the potential model can satisfactorily correlate the simulated results. The calculated activation energy is close to the average value of the Gaussian distribution and the reaction order is greater than unity.

For much wider Gaussian distribution, the results are not satisfactory, so there can be some experimental data that could be correlated by the potential model and non-satisfactorily by the Gaussian model and vice versa.

An extensive analysis of comparison of correlation of data by the potential model and the distributed energy models can be observed in the Burnham and Braun paper [4]. Braun et al. [24] observed that the same data of some dynamic runs can be correlated

either the Gaussian model or the potential model with reaction order different than 1. In this paper the analysis is extended considering dynamic and isothermal runs.

A4.2) Independent reactions. Gaussian variation of the activation energy with constant factor A.

This model is presented to emphasize the differences with respect to the previous Gaussian model. The kinetic

$$1 - \alpha = \int_0^{\infty} \exp \left[-\frac{A}{(0.64)^n} \exp \left(-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right) \right] D(E/R) d(E/R) \quad (18)$$

where it must be remembered that A equals $k_0[\exp(-E/RT_0)](0.64)^n$.

In the previous equation kinetic, the value of T_0 is selected in the decomposition range and the parameter A is considered constant instead of k_0 . Taking the same Gaussian distribution as that of the previous section, the simulated results coincide with those calculated almost exactly, with the activation energy close to the average value of the Gaussian distribution, the reaction order close to unity and parameter A also close to that assumed in the model. No Figure is presented due to the coincidence of simulated and calculated values. In this case, it is obvious that the compensation effect of the different reactions considered with the same value of parameter A causes the results obtained. In this case with the value of standard deviation taken into account, the Gaussian and potential models are equivalent.

A5.2) Conclusions of the analysis of the independent reactions.

Two conclusions can be summarized when obtaining a satisfactory correlation:

- It is possible that, although there is apparently only one fraction that correlates satisfactorily to one reaction, there can be different fractions with different activation energy.
- Intermediate values of activation energy and high values of reaction order obtained can be obtained from the correlation to a single reaction when many independent reactions are considered, but whose decompositions overlap leading to an apparent decomposition corresponding to only one fraction.

B) Competitive parallel reactions

The following analysis is carried out with a system with five competitive parallel reactions of a homogeneous material. In this case, the scheme of reaction can be written as

The equations representative of the process are the following:

$$\frac{d\alpha_i}{dt} = \left[k_{oi} \exp\left(-\frac{E_i}{RT}\right) \right] (1 - \sum \alpha_i)^{n_i} = \left[k_{oi} \exp\left(-\frac{E_i}{RT}\right) \right] (1 - \alpha)^{n_i} \quad i=1 \text{ to } 5 \quad (19)$$

$$\alpha_i = \left[\frac{V_i}{V_{iinf}} \right] \quad i=1 \text{ to } 5 \quad (20)$$

$$\text{For any time} \quad V = \sum \alpha_i V_{iinf} \quad (21)$$

In this case, the values α_i vary from zero to a value less than unity at time infinity, while the total conversion degree α varies from zero to 1 at time infinity. Table 5 and Figure 9 show the kinetic parameters and the simulated (with the five reactions) and correlated (to one single reaction) results when the five competitive parallel reactions have different activation energy, with the particularity that V_{iinf} is the same for the reactions. Therefore, the value V_{iinf} (value of V at time infinity) does not depend on the heating rate and equals any V_{iinf} (when the values $V_{i\infty}$ are different, the value V depends on the heating rate). It can be deduced that in this case, an intermediate value of apparent activation energy is obtained, and the reaction order is similar to the accepted values. The same conclusion is obtained by Agrawal [19] when discussing these systems with a TG run. In this paper however, the conclusion is valid when correlating six TG runs carried out at different operating conditions. By the iso-conversional method to the simulated data, the nearly parallel straight lines obtained have slopes between 20400 and 23400 K, indicating also an acceptable possibility for correlating the data to a single reaction (ICTAC Kinetics Committee recommendation [20]).

Nevertheless, it must be emphasized that when the value V_{iinf} is different for each fraction, the total V_{iinf} changes with the heating rate, so when this occurs, a system with parallel reactions must be selected. The example of Figure 9 has been selected to show that in some cases, although it could be thought that there is only one fraction that can react according to a single reaction, the real behaviour corresponds to a system with

many reactions. In other systems, there can be several peaks in the DTG curve, and this clearly shows that there are many different fractions involved.

C) Sequential reactions

A system with five sequential reactions has been simulated and then correlated by a single reaction. The scheme of reactions is the following:

In this case, the equations used have been the following [12]:

$$\frac{d\alpha_i}{dt} = \left[k_{oi} \exp\left(-\frac{E_i}{RT}\right) \right] (\alpha_{i-1} - \alpha_i)^{n_i} \quad i=1 \text{ to } 5 \quad (22)$$

where α_{i-1} for $i=1$ equals 1.

On the other hand

$$\alpha_i = \left[\frac{V_i}{V_{iinf}} \right] \quad i=1 \text{ to } 5 \quad (23)$$

$$\text{For any time } \alpha = \frac{1}{V_{inf}} \sum \alpha_i V_{iinf} = \frac{V}{V_{inf}} \quad (24)$$

The yield coefficient v_i equals V_{iinf} .

Table 6 and Figure 10 show details of the simulation with five reactions (considered as if it were real) and of the correlation obtained to a single reaction. Applying the iso-conversional method to the simulated data, nearly parallel straight lines obtained have slopes between 29300 and 30500 K (ICTAC Kinetics Committee recommendation [20]).

The correlation obtained is good. The activation energy obtained of the single reaction is close to the values considered in the five initial reactions. The reaction order is less than unity as occurs for nucleation-growth reactions, which can be considered as sequential reactions, and discussed in literature [4, 25]"Table 6

D) Zero reaction order and small apparent activation energy.

In some cases, in pyrolysis and oxidative pyrolysis of liquids melting solids, it is possible that the weight loss process is due to the evaporation of the sample inside the crucible that is under flow in the TG equipment. This case can be considered as a

diffusion of the volatile compound A through a steady zone of the carrier gas at the upper part of crucible. The mass flow of volatilized compound can be expressed as:

$$\text{Mass flow} = F_1 \frac{SMPD_{AB}}{RT(z_2 - z_1)p_{Bml}} [p_{A1} - p_{A2}] \approx F_2 \frac{MPD_{AB}}{RTz_2p_{Bml}} [p_{A1}] \approx F \frac{MPD_{AB,298}}{RTz_2p_{Bml}} \left[\frac{T}{298} \right]^{1.75} [p_{Ao} \exp(-B/T)] \quad (23)$$

where F_1 is a correction factor, considering that there can be small convection draughts inside the crucible, S is the constant section, M is the molecular weight of the volatilized compound, P is the total pressure, D_{AB} is the diffusivity of the volatilized compound A through the gas B, R is the gas constant, z_2 and z_1 are the heights of the upper part of the crucible and the level of the liquid inside the crucible, respectively, p_{A1} is the vapour pressure of compound A that equals the partial pressure of A in the layer of gas in contact with the liquid and p_{A2} equals the partial pressure of A in the upper part of the crucible. The vapour pressure p_A can have an exponential variation with respect to the absolute temperature (Antoine equation). In many occasions, the height of the liquid inside the crucible is very small in comparison with the height of the crucible, so “ $z_2 - z_1$ ” equals “ z_2 ” and the difference “ $p_{A1} - p_{A2}$ ” equals “ p_{A1} ”, because “ p_{A2} ” is very small or the difference “ $p_{A1} - p_{A2}$ ” is proportional to “ p_{A1} ”. Consequently, the vaporization rate does not depend on the mass in the crucible, and consequently the reaction order equals zero. The apparent activation energy mainly corresponds to the variation of the vapour pressure with temperature, although the increase of the diffusivity with temperature can also contribute to the apparent activation energy. An extensive analysis of this fact can be seen elsewhere [26].

When considering many species in the mixture, the kinetics of evaporation depends on the flow and thermodynamics, so the previous equation does not represent the complexity of the system. The pyrolysis/evaporation of waste oils was carried out [27,28], and a zero order reaction was also deduced for correlating the data satisfactorily. A low value of activation energy was obtained, which is in accordance with the variation of vapour pressure with temperature multiplied by $T^{1.75}$.

In addition to the zero reaction order and low activation energy, the pre-exponential factor in accordance with eqs (1) and (2) is inversely proportional to the initial mass; the high heating rates can promote the convective diffusion and increase the value of the pre-exponential factor inside a random variation [26-28].

Summarizing this phenomenon, when a zero reaction order and a low value of apparent activation energy are obtained when correlating the data, it is possible that an evaporation process takes place. Another aspect of the vaporization runs is the fact that the TG curves are not reproducible, due to the random behaviour.

E) Zero reaction order and high apparent activation energy.

There are some processes that can be correlated nearly satisfactorily with a zero order reaction order and a high value of apparent activation energy. Westerhout et al. [29] presented a review about the kinetics of the low-temperature pyrolysis of polyethylene, polypropylene and polystyrene. In accordance with data reported, there are several kinetic parameters triplets (activation energy, pre-exponential factor and reaction order). The values of reaction order presented are zero, one and intermediate values, considering in some cases intervals of decomposition degree. The activation energies vary in a large interval about 200 kJ/mol, including the cases with zero reaction order.

An explanation of the case corresponding to reaction order equals zero is the following. Assume a scheme of consecutive reactions

The reaction yields $v_1, v_2, \dots, v_i, \dots, v_N$ are equal to the maximum volatile mass fractions evolved at time infinity, $V_{1inf}, V_{2inf}, \dots, V_{iinf}, V_{Ninf}$ respectively. If all the reactions are considered to be first order, the kinetic constants for all the reactions and the maximum volatile fractions for each reaction are similar; the following expressions can be deduced:

$$\begin{aligned} \frac{d\alpha_1}{dt} &= \left[k_o \exp\left(-\frac{E}{RT}\right) \right] (1 - \alpha_1) & \alpha_1 &= \frac{V_1}{V_{1inf}} \\ \frac{d\alpha_2}{dt} &= \left[k_o \exp\left(-\frac{E}{RT}\right) \right] (\alpha_1 - \alpha_2) & \alpha_2 &= \frac{V_2}{V_{2inf}} \\ &\dots\dots\dots \end{aligned}$$

$$\frac{d\alpha_i}{dt} = \left[k_o \exp\left(-\frac{E}{RT}\right) \right] (\alpha_{i-1} - \alpha_i) \quad \alpha_3 = \frac{V_3}{V_{3inf}}$$

.....

$$\frac{d\alpha_N}{dt} = \left[k_o \exp\left(-\frac{E}{RT}\right) \right] (\alpha_{N-1} - \alpha_N) \quad \alpha_N = \frac{V_N}{V_{Ninf}} \quad (26)$$

Adding the previous equations, the following is obtained

$$\frac{d[\alpha_1 + \alpha_2 + \dots \alpha_i + \dots \alpha_n]}{dt} = \left[k_o \exp\left(-\frac{E}{RT}\right) \right] (1 - \alpha_N) \quad (27)$$

If all the maximum volatile mass fractions V_{iinf} are similar, and considering that the volume at time infinity equals the sum of all volumes at time infinity, it can be written that

$$V_{inf} = V_{1inf} + V_{2inf} + \dots V_{iinf} + \dots + V_{Ninf} = NV_{iinf} \quad (28)$$

On the other hand, the degree conversion of the overall process α equals

$$\alpha = \frac{V}{V_{inf}} = \frac{\alpha_1 V_{1inf} + \alpha_2 V_{2inf} + \dots \alpha_i V_{iinf} + \dots \alpha_N V_{Ninf}}{NV_{iinf}} = \alpha_1 + \alpha_2 + \dots \alpha_i + \dots \alpha_N \quad (29)$$

Assuming that there are many reactions, the degree conversion α_N of the last reaction is nil during most of the process, so eq. (25) becomes

$$\frac{d\alpha}{dt} \approx \left[k_o \exp\left(-\frac{E}{RT}\right) \right] \quad (30)$$

that corresponds to zero reaction order with high apparent activation energy. If the number of reactions is not very high, two consecutive reactions could be considered: the first one with zero reaction order and the second reaction with a positive reaction order between zero and the unity.

F). Very high apparent activation energy

No satisfactory models were obtained with relative high apparent activation energy, when considering several dynamic runs or dynamic and dynamic + isothermal runs. Only when taking into account a single dynamic run with a model with several sequential reactions, the apparent activation energy is much higher than that of the sequential reactions and with the same reaction order. No figures are presented because no more information can be obtained.

COMPARISON OF THE POTENTIAL MODEL WITH OTHER KINETIC MODELS

Many kinetic models for correlation of data can be found in literature. As commented previously, the potential model, with reaction order unity or different from unity, can represent an oversimplification of the process, with a complex mechanism (with initiation, propagation, end reactions, etc.), variation of the active centre/non-reacted mass ratio, autocatalytic reactions, mass and heat diffusion effects, sum of many reactions with different pre-exponential factor and/or activation energy, approximation of other kinetic models, etc.. Table 7 shows some frequently proposed models based on solid state reactions [1]. The comparison with the potential model is carried out considering the function $f(\alpha)$ and $g(\alpha)$ defined as

$$f(\alpha) = (1/k_o \exp(-E/RT))d\alpha/dt \quad (31)$$

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \quad (32)$$

that equals, in accordance with the mass balance expressed by eq. (1)

$$g(\alpha) = \int_0^t \left[k_o \exp\left(-\frac{E}{RT}\right) \right] dt \quad (33)$$

For the potential model

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{[1 - (1-\alpha)^{1-n}]}{1-n} \quad (34)$$

Figure 11 shows the variation of $g(\alpha)$ vs. α for the different models proposed, and the optimized parameters n and B of the potential model closest to the variation of $g(\alpha)$ vs. α . These parameters have been obtained by minimization of the objective function OF, sum of the squares differences between the values $g(\alpha)$ of the corresponding model and that calculated by eq. (33) with the correcting factor B , considering values α from 0.01, 0.02, 0.03, to 0.99. The optimization function in this case has been:

$$OF = \sum_{0.01}^{0.99} \left[g(\alpha) - B \frac{[1 - (1-\alpha)^{1-n}]}{1-n} \right]^2 \quad (35)$$

The variation coefficient VC has been calculated as

$$VC = 100 \frac{\sqrt{\frac{OF}{98-2}}}{(g(0.01) + g(0.99))/2} \quad (36)$$

where 98 is the number of points considered, 2 the number of parameters (n and A), and the mean value considered is the average value $g(\alpha)$ for the extremes values of α : 0.01 and 0.99.

Figure 11

The parameter B is a constant value for all the range studied, and when correlating data the value is included inside the pre-exponential factor. The potential model includes the contracting area model (R_2) and the contracting volume model (R_3), and it is close to the diffusion models $D1$, $D2$ and $D3$.

The value of reaction order n can be useful when correlating experimental data with the potential model to deduce that other models could probably correlate the data with more reliability than the potential model when the deviations between experimental data and those calculated by the potential models are consistent with the deviations of $g(\alpha)$ observed in Figure 11.

ANALYSIS OF THE REACTION ORDER AND THE APPARENT ACTIVATION ENERGY.

Table 8 summarizes the main conclusions obtained from the previous analysis, so when correlating the data by the potential model, the suggestions presented can be useful to analyse specific data. For some cases, the interpretation can be easy, and the model is consistent with a decomposition mechanism assumed.

An important aspect to be considered is to obtain a kinetic model from experimental data obtained from different operating conditions, dynamic runs and isothermal runs. With only dynamic runs, the kinetic parameters can also only be valid to simulate other results with intermediate heating rate. With dynamic and isothermal runs, or with ramps of heating rate, the correlation model is more plausible because it has been obtained in extensive operating conditions. The analysis carried out in this paper has been carried out with dynamic and isothermal runs to ensure that the kinetic parameters obtained from the correlation to a single reaction be more reliable than those obtained from only 1 or 3 dynamic runs.

On the other hand, the values obtained of activation energy and reaction order from the correlation to a single reaction, can be useful to select a system of parallel/consecutive

reactions to obtain a better correlation of the experimental data and to be representative of decomposition studied.

USE OF THE POTENTIAL MODEL FOR DESIGN OF REACTORS

An analysis of the application of the potential model obtained from several runs carried out in small reactors and thermo-balances to the design of industrial reactors is discussed. Some of the analyses are general to a kinetic model and others are specific for potential models.

Four general considerations can be presented to obtain an appropriate kinetic model for the chemical decomposition.

a) The size and particle diameter should be small enough to ensure that external and internal mass and heat transfer effects are negligible vs. the chemical decomposition.

b) Several runs must be carried out at different operating conditions (dynamic runs at different heating rate, isothermal runs, runs with temperature ramps, etc.) in order to obtain a kinetic model valid for any condition but inside the range studied. Extrapolations are risky.

c) The effect of the initial mass, the superior surface/mass ratio, the crucible height on the conversion degree should be studied; if the variation of conversion degree depends on the initial mass or superior surface/mass ratio, the process must be analyzed. If the apparent activation energy is high, the superior surface/mass ratio can probably be very important due to initiation reactions on the superior surface. On the contrary, if the apparent activation energy is low and the reaction order is close to zero, a vaporization process probably takes place and the crucible height also has a big influence. It was tested that heating rate can have a considerable influence in vaporization process [26-28]. When these effects are important, more runs must be carried out to deduce the corresponding parameters in the correlation model.

d) In combustion or oxidative pyrolysis processes, the kinetic constant can depend on the partial oxygen process, so some runs must be done at different atmospheres with distinct oxygen content.

In view of the previous analysis three cases can be considered.

1) Materials where the variation of all the conversion degrees corresponding to the different reactions only depends on the operating temperature and time, and with an appropriate kinetic model. In industrial reactors, if the external and internal diffusion of

mass and heat are negligible vs. chemical reaction, the kinetic models can be applied directly, taking into account the mass and energy balances. When the diffusion effects are important, complex models must be developed for the design of reactors.

2) Materials where the variation of one or some conversion degrees depends on the surface/mass ratio as a consequence of the development of the reactions depending on active centres at the surface. In this case, the kinetic constants obtained by TG or reactors, must be expressed as a function of the ratio external surface/mass, and consequently the kinetic constant must be used in the design of the reactors, taking into account the corresponding value of the surface/mass ratio at industrial conditions (ind.cond.) and at laboratory conditions (lab.cond.):

$$k_{o,ind.cond.} = k_{o,lab} \frac{(S/W_o)_{ind.cond.}}{(S/W_o)_{lab.cond.}} \quad (37)$$

3) Materials where the variation of one or some degrees conversion corresponds to vaporization process.

In this case, the extrapolation of the data obtained from TG runs or other reactors to the design of industrial reactor must be done considering the vaporization process. In the vaporization process, the volatilization rate is directly proportional to the surface, and the variation rate of degree α (defined as W/W_o because there is no residue). is also inversely proportional to the initial mass, so the apparent kinetic constant is directly proportional to the ratio (S/W_o) . On the other hand, the kinetic constant also depends on the height of the crucible, in which the volatiles diffuse from the liquid surface to the surrounding atmosphere and on the heating rate probably as a consequence of the contribution of convective diffusion. So the

$$k_{o,ind.cond.} = k_{o,lab} \frac{(S/W_o)_{ind.cond.}}{(S/W_o)_{lab.cond.}} (\text{diffusion factor})(\text{heating rate factor}) \quad (38)$$

$(S/W_o)_{ind.cond.}$ is the ratio between the initial height or thickness of the liquid layer and the liquid density, so it must be a design parameter to be taken into account.

The diffusion factor considers the diffusion of the vapours inside the crucible, so the apparent kinetic constant is inversely proportional to the crucible height in pure vaporization processes with small samples, but in the case of reactors, this factor can be estimated by the following equation:

$$\text{diffusion factor} = \frac{(1/L_{ind.cond.})}{(1/L_{lab.cond.})} = \frac{L_{lab.cond.}}{L_{ind.cond.}} \quad (39)$$

where $L_{ind.cond.}$ is the equivalent diffusion length for the industrial conditions and $L_{lab.cond.}$ is the crucible height in TG apparatus or the equivalent diffusion length reactors.

The equivalent length for reactors can be calculated as the ratio between the diffusion coefficient D of vapours and the mass transfer coefficient k_c , which can be estimated through specific correlations of the Sherwood number (Sh) with the Reynolds number (Re) and Prandtl number (Pr), as explained elsewhere [26]. Schematically, the following expressions can be written:

$$L_{ind.cond} = D / k_c \quad (40)$$

The previous equation is based on the “Phoney film theory”, in which it is assumed that the resistance to the mass transfer is equivalent to that of a layer with a thickness L_{equiv} , which is valid for turbulent gas flows [28]. Consequently, the approximation performed in this section will depend on the assumptions considered.

On the other hand, in many processes, the relationships between the dimensionless numbers are presented by the following equation [30]
:

$$Sh = a Re^n Pr^m \quad (41)$$

$$\text{Sherwood number} = Sh = k_c d_p y_{gas,ml} / D \quad (42)$$

where d_p is a physical magnitude (normally diameter of tube, packing, etc.), $y_{gas,ml}$ is the average of the inert gas concentration between that at the surface and that of the fluid (this is normally close to unity) and D is the diffusivity.

It can be deduced that an error in the estimation of the overall diffusivity is of relatively small importance, because normally the exponent “ m ” of the Prandtl number is 0.3-0.4 in the correlations proposed in literature. From eqs. (40) and (42), it is deduced that:

$$L_{equiv} = D / k_c = D d_p y_{gs,ml} / (Sh D) = d_p y_{gas,ml} / Sh \quad (43)$$

Finally the heating rate factor can also be considered, if this effect has been studied. If not considered, this factor is unity.

In some cases, the kinetic parameter obtained refers to a process, including vaporization and kinetic decomposition, as in the case of pyrolysis of olive oil [31]. A similar analysis to that previously presented can be done, but with some modifications as a consequence of the particularity of the case.

CONCLUSIONS

The potential model with any value of reaction order (unity or another value) is very flexible to correlate some experimental data with parallel or consecutive reactions. Although the values of apparent activation energy and reaction order must only be considered as correlation parameters, they can have a physical/significance in some cases, as indicated in the paper. The values obtained from the correlation to a single reaction can also be useful to propose a system of reactions more complex but more reliable of the decomposition studied. The application to the design of industrial reactors is presented taking into account the analysis carried out previously.

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Table 1. Five independent reactions with different activation energy.

Assumed kinetic parameters of the simulated data with five independent reactions

$$A_1=A_2=A_3=A_4=A_5=0.1469 \text{ min}^{-1}; T_{\text{ref}}=890 \text{ K}$$

$$k_{o1}=7.580 \cdot 10^{18} \text{ min}^{-1}; E_1/R=40000 \text{ K}$$

$$k_{o2}=2.753 \cdot 10^{16} \text{ min}^{-1}; E_2/R=35000 \text{ K}$$

$$k_{o3}=1.000 \cdot 10^{14} \text{ min}^{-1}; E_3/R=30000 \text{ K}$$

$$k_{o4}=3.632 \cdot 10^{11} \text{ min}^{-1}; E_4/R=25000 \text{ K}$$

$$k_{o5}=1.319 \cdot 10^9 \text{ min}^{-1}; E_5/R=20000 \text{ K}$$

$$n_1=n_2=n_3=n_4=n_5=1$$

$$V_{1\text{inf}}=V_{2\text{inf}}=V_{3\text{inf}}=V_{4\text{inf}}=V_{5\text{inf}}=V_{\text{inf}}/5$$

—

Kinetic parameters of the single reaction

$$A=0.1545 \text{ min}^{-1}; T_{\text{ref}}=890 \text{ K}$$

$$k_o=1.747 \cdot 10^{14} \text{ min}^{-1}$$

$$E/R=30400 \text{ K}$$

$$n=1.13$$

$$V.C=1.3 \%$$

Table 2. Five independent reactions with different parameter A.

Assumed kinetic parameters of the simulated data with five independent reactions

$$A_1/4=A_2/2=A_3=2 \cdot A_4=4 \cdot A_5=0.1469 \text{ min}^{-1}; T_{\text{ref}}=890 \text{ K}$$

$$k_{o1}=4 \cdot 10^{14} \text{ min}^{-1}; E_1/R=30000 \text{ K}$$

$$k_{o2}=2 \cdot 10^{14} \text{ min}^{-1}; E_2/R=30000 \text{ K}$$

$$k_{o3}=1 \cdot 10^{14} \text{ min}^{-1}; E_3/R=30000 \text{ K}$$

$$k_{o4}=5 \cdot 10^{13} \text{ min}^{-1}; E_4/R=30000 \text{ K}$$

$$k_{o5}=2.5 \cdot 10^{13} \text{ min}^{-1}; E_5/R=30000 \text{ K}$$

$$n_1=n_2=n_3=n_4=n_5=1$$

$$V_{1\text{inf}}=V_{2\text{inf}}=V_{3\text{inf}}=V_{4\text{inf}}=V_{5\text{inf}}=V_{\text{inf}}/5$$

—

Kinetic parameters of the single reaction

$$A=0.1474 \text{ min}^{-1}; T_{\text{ref}}=890 \text{ K}$$

$$k_o=7.010 \cdot 10^{13} \text{ min}^{-1}$$

$$E/R=29420 \text{ K}$$

$$n=1.6$$

$$V.C=1.8 \%$$

Table 3. Five independent reactions with different parameter A and E/R.

Assumed kinetic parameters of the simulated data with five independent reactions

$$A_1 \cdot 4 = A_2 \cdot 2 = A_3 = A_4 / 2 = A_5 / 4 = 0.1469 \text{ min}^{-1}; T_{\text{ref}} = 890 \text{ K}$$

$$k_{o1} = 6.88 \cdot 10^{15} \text{ min}^{-1}; E_1/R = 35000 \text{ K}$$

$$k_{o2} = 4.73 \cdot 10^{14} \text{ min}^{-1}; E_2/R = 32500 \text{ K}$$

$$k_{o3} = 1 \cdot 10^{14} \text{ min}^{-1}; E_3/R = 30000 \text{ K}$$

$$k_{o4} = 2.11 \cdot 10^{13} \text{ min}^{-1}; E_4/R = 28000 \text{ K}$$

$$k_{o5} = 1.45 \cdot 10^{12} \text{ min}^{-1}; E_5/R = 25000 \text{ K}$$

$$n_1 = n_2 = n_3 = n_4 = n_5 = 1$$

$$V_{1\text{inf}} = V_{2\text{inf}} = V_{3\text{inf}} = V_{4\text{inf}} = V_{5\text{inf}} = V_{\text{inf}}/5$$

Kinetic parameters of the single reaction

$$A = 0.1606 \text{ min}^{-1}; T_{\text{ref}} = 890 \text{ K}$$

$$k_o = 7.010 \cdot 10^{13} \text{ min}^{-1}$$

$$E/R = 30572 \text{ K}$$

$$n = 1.81$$

$$V.C = 3.4 \%$$

Table 4. Gaussian distribution of apparent activation energy.

Pre-exponential factor k_o constant	Parameter A constant
Assumed kinetic parameters for the simulation $k_o = 1 \cdot 10^{14} \text{ min}^{-1}$ Central value $E_o/R = 30000 \text{ K}$ Standard deviation $\sigma = 1500 \text{ K}$ Minimal value of $E/R = 25000 \text{ K}$ Maximum value of $E/R = 34900 \text{ K}$ $n = 1$	Assumed kinetic parameters for the simulation $T_o = 890 \text{ K}$ $A = 0.1469 \text{ min}^{-1}$ Central value $E_o/R = 30000 \text{ K}$ Standard deviation $\sigma = 1500 \text{ K}$ Minimal value of $E/R = 25000 \text{ K}$ Maximum value of $E/R = 34900 \text{ K}$ $n = 1$
Kinetic parameters of the single reaction $k_o = 1.028 \cdot 10^{14} \text{ min}^{-1}$ $E/R = 29411 \text{ K}$ $n = 2.41$ $V.C = 3.5 \%$	Kinetic parameters of the single reaction $T_o = 890 \text{ K}$ $A = 0.1473 \text{ min}^{-1}$ $k_o = 1.033 \cdot 10^{14} \text{ min}^{-1}$ $E/R = 30023 \text{ K}$ $n = 1.001$ $V.C = 0.05\%$

Table 5. Five competitive reactions with different E/R values.

Assumed kinetic parameters of the simulated data with five competitive reactions

$$A_1=A_2=A_3=A_4=A_5=0.1469 \text{ min}^{-1}; T_{\text{ref}}=890 \text{ K}$$

$$k_{01}=4.79 \cdot 10^8 \text{ min}^{-1}; E_1/R=15000 \text{ K}$$

$$k_{02}=1.32 \cdot 10^9 \text{ min}^{-1}; E_2/R=20000 \text{ K}$$

$$k_{03}=1 \cdot 10^{14} \text{ min}^{-1}; E_3/R=30000 \text{ K}$$

$$k_{04}=7.58 \cdot 10^{18} \text{ min}^{-1}; E_4/R=40000 \text{ K}$$

$$k_{05}=2.09 \cdot 10^{21} \text{ min}^{-1}; E_5/R=45000 \text{ K}$$

$$n_1=n_2=n_3=n_4=n_5=1$$

$$V_{1\text{inf}}=V_{2\text{inf}}=V_{3\text{inf}}=V_{4\text{inf}}=V_{5\text{inf}}=V_{\text{inf}}$$

Kinetic parameters of the single reaction

$$A=0.5146 \text{ min}^{-1}; T_{\text{ref}}=890 \text{ K}$$

$$k_0=4.992 \cdot 10^9 \text{ min}^{-1}$$

$$E/R=20059 \text{ K}$$

$$n=1.02$$

$$V.C=2.1 \%$$

Table 6. Five sequential reactions with constant E/R values.

Assumed kinetic parameters of the simulated data with five sequential reactions

$$A_1=A_2=A_3=A_4=A_5=0.1469 \text{ min}^{-1}; T_{\text{ref}}=890 \text{ K}$$

$$k_{01}=1 \cdot 10^{14} \text{ min}^{-1}; E_1/R=30000 \text{ K}$$

$$k_{02}=1 \cdot 10^{14} \text{ min}^{-1}; E_2/R=30000 \text{ K}$$

$$k_{03}=1 \cdot 10^{14} \text{ min}^{-1}; E_3/R=30000 \text{ K}$$

$$k_{04}=1 \cdot 10^{14} \text{ min}^{-1}; E_4/R=30000 \text{ K}$$

$$k_{05}=1 \cdot 10^{14} \text{ min}^{-1}; E_5/R=30000 \text{ K}$$

$$n_1=n_2=n_3=n_4=n_5=1$$

$$V_{1\text{inf}}=V_{2\text{inf}}=V_{3\text{inf}}=V_{4\text{inf}}=V_{5\text{inf}}=V_{\text{inf}}$$

Kinetic parameters of the single reaction

$$A=0.04186 \text{ min}^{-1}; T_{\text{ref}}=890 \text{ K}$$

$$k_0=2.254 \cdot 10^{13} \text{ min}^{-1}$$

$$E/R=29976 \text{ K}$$

$$n=0.53$$

$$V.C=1.6 \%$$

Table 7. Kinetic models of thermal decomposition.

Model	Kinetic law $f(\alpha)$	Integral result $g(\alpha)$	Comparison with Potential method		
			n	B	VC (%)
First order	$(1-\alpha)$	$-\ln(1-\alpha)$	1	1	0
Potential	$(1-\alpha)^n$		n	1	0
Avrami-Erofeyev (A ₂)	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$	0.10	1.61	10
Avrami-Erofeyev (A ₃)	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$	-1.12	2.67	14
Avrami-Erofeyev (A ₄)	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$[- \ln(1-\alpha)]^{1/4}$	-2.86	4.27	15
Contracting Area (R ₂)	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)]^{1/2}$	0.5	0.5	0
Contracting Volume (R ₃)	$2(1-\alpha)^{2/3}$	$[1-(1-\alpha)]^{2/3}$	0.33	0.66	0
Diffusion (D ₁)	$1/(2\alpha)$	α^2	0.69	0.46	10
Diffusion (D ₂)	$[- \ln(1-\alpha)]^{-1}$	$[(1-\alpha)\ln(1-\alpha)] + \alpha$	0.90	0.29	9.3
Diffusion (D ₃)	$[3(1-\alpha)^{2/3}][2(1-(1-\alpha)^{1/3})]$	$[1-(1-\alpha)^{1/3}]^2$	1.22	0.086	6.3
Power law (P ₂)	$2\alpha^{1/2}$	$\alpha^{1/2}$	-1.59	2.35	10
Power law (P ₃)	$3\alpha^{2/3}$	$\alpha^{1/3}$	-3.74	4.22	13
Power law (P ₄)	$4\alpha^{3/4}$	$\alpha^{1/4}$	-6.67	6.83	13

Table 8. Analysis of the apparent activation energy E and the reaction order n .

Description	Observation
$n=1$	Particle nucleation occurs on random basis and growth does not advance beyond the individual zone implied. It is possible that many parallel reactions are involved in the apparent single reactions.
$n=0$ or low and high value of E	Consecutive reactions with evolution of volatiles in the different reactions
$-n=0$ or low and low values of E; pre-exponential factor inversely proportional to initial mass ; possible influence of heating rate, random behaviour	Evaporation process or evaporation process + kinetic thermal decomposition
E low and/or n high	There are probably many fractions or reactions in the system correlated to a single reaction.
E low and n small or E high and n high	Analyze the interrelation between both parameters, in order to see if other acceptable kinetic parameters can also correlate the results.
Potential model is not satisfactory	See deviations considered in Figure 11 and/or try to correlate with a Gaussian distribution of activation energy.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Five independent reactions with different parameter A

Figure 6

Figure 7

Figure 8

Five competitive reactions with different parameter E/R

Figure 9

Figure 10

Figure 11