Potential kinetic model for thermal decomposition of complex organic compounds: Significance of parameters and engineering application

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ABSTRACT

This paper analyzes 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 on the use of the kinetic parameters for the design of industrial reactors.

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1. 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 Galwey [2] analyzed 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 re-condensation of low volatile product. He used the Hertz–Langmuir approach, relating the flux density of vapor 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 behavior 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

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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 tetrabromobisphenol A (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.

Shannon [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 toward 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 behavior. One of the proposed models is the potential one, in accordance with the following kinetic expression:

$$\frac{d\alpha}{dt} = k_o \exp\left(\frac{E}{RT}\right)[1-\alpha]^n \tag{1}$$

where α is the conversion degree and the pre-exponential factor k_o, 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. Burnham 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.

2. Kinetic model for a single reaction of decomposition

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

Solids B $\Rightarrow$ Volatiles V + solids R

can be the following:

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

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:

$$f(\alpha) = (1-\alpha)^n \tag{3}$$

Consequently,

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

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 behavior 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 differ 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 centers, 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.