

Determination of activation energy of decomposition reaction from thermo gravimetric analysis

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Date of Submission: 10-07-2024

Date of Acceptance: 20-07-2024

ABSTRACT: The determination of activation energy (E_a) is crucial for controlling reaction rates, particularly for decomposition reactions. Recent research has focused on the theoretical analysis of decomposition reaction kinetics to calculate E_a from a single thermogravimetric analysis (TGA) data sheet. This approach leads to the formulation of ordinary differential equations, which are then solved numerically using the fourth-order Runge-Kutta method. In this work, pseudo-order (PO) and Šesták-Berggren (SB) models are employed for comparison with the established Coats-Redfern (C-R) method. The results demonstrate that the proposed general analysis not only provides a better description of experimental data compared to the C-R method but also offers deeper insights into the reaction mechanism. Furthermore, this approach has the potential to be extended or modified to determine the E_a of other gas-solid reactions.

KEYWORDS: Activation energy, Reaction kinetic, Thermogravimetric analysis, Thermal decomposition

I. INTRODUCTION

Thermogravimetric analysis (TGA) is a vital technique for evaluating the thermal behavior of materials. TGA measures the change in sample mass as a function of temperature over time. Typically, a TGA experiment is conducted under a constant heating rate (β), as defined by equation (1).

$$\beta = \frac{T - T_0}{t} \quad (1)$$

where T_0 and T are the initial temperature and the temperature at time t , respectively.

The literature reports numerous studies employing TGA to investigate decomposition reactions [1,2]. This involves introducing a specific

gas flow to the sample chamber during the TGA run [3]. For a pure solid sample, the resulting change in mass is referred to as the conversion (α), as defined by equation (2).

$$\alpha = \frac{m_0 - m}{m_0} \quad (2)$$

where m_0 and m represent the initial mass and the mass of the sample at time t , respectively.

Several established methods exist for determining the E_a of a decomposition reaction from TGA data. These include isoconversional methods (Friedman, Flynn-Wall-Ozawa, Kissinger) [4] and the invariant kinetic parameters (IKP) method [5]. While valuable, these methods typically require data sets acquired at different heating rates. For reactions following pseudo-order (PO) kinetics, the Coats-Redfern equations allow calculating E_a from a single TGA run [6]. Subsequently, Flynn [7] extended the problem raised by Coats and Redfern by employing a finite-difference method. However, for reactions beyond PO kinetics, the Šesták-Berggren (SB) equation offers a more general framework for describing reaction kinetics. This work proposes a novel approach that employs the general forms of the PO and SB models to analyze decomposition reaction kinetics using data from a single TGA experiment. To validate this approach, we utilize previously published TGA datasets..

II. THEORITICAL ANALYSIS

The kinetics of a decomposition reaction can be expressed as equation (3).

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (3)$$

where $k(T)$ is the rate constant, and $f(\alpha)$ is the conversion function.

Based on the Arrhenius law, the temperature dependence of the rate constant, $k(T)$, is expressed by equation (4).

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where A is the pre-exponential constant, T is the temperature, and R is the gas constant.

Furthermore, differentiation of equation (1) yields the relationship $dt = dT/\beta$. Consequently, the kinetic equation for the decomposition reaction is given by equation (5).

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

By rearranging and integrating equation (5), a general expression is obtained (equation (6)).

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (6)$$

where $g(\alpha)$ is the integral conversion function. The determination of the mathematical formula for $g(\alpha)$ requires knowledge of the expression $f(\alpha)$. In kinetic analysis of decomposition reactions, the PO model (equation (7)) and the SB model (equation (8)) are frequently employed [8,9].

- PO model: $f(\alpha) = (1-\alpha)^n$ (7)

- SB model: $f(\alpha) = \alpha^m (1-\alpha)^n$ (8)

where n is the order of reaction, and m is a power parameter.

Using the PO model and applying a Taylor expansion for the exponential term, Coats-Redfern [6] derived a solution to equation (6). This solution relates α to T and is known as the Coats-Redfern (C-R) equations, presented in Equations (9) and (10).

- or $n \neq 1$: $\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left(\frac{AR}{\beta E_a}\right) - \frac{E_a}{RT}$ (9)

- or $n = 1$: $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E_a}\right) - \frac{E_a}{RT}$ (10)

Fitting Equation (9) to conversion data often requires assuming an n -value of 1.5 or 2. While the Coats-Redfern approach can be fundamentally extended to other forms of $f(\alpha)$, obtaining an analytical solution for $g(\alpha)$ can be challenging, particularly for the SB model. Fortunately, equation (5) represents an ordinary differential equation. This characteristic enables numerical solutions using techniques like the Runge-Kutta method [10]. Present research has investigated directly fitting the conversion data calculated from TGA to equation (5) via numerical methods, eliminating the need to find an analytical solution.

III. RESULTS AND DISCUSSION

TGA data can be differentiated to yield the derivative thermogravimetry (DTG) curve. A greater number of peaks in the DTG curve signifies a more complex reaction mechanism [11]. Because each kinetic model represents a particular decomposition reaction mechanism, current approaches necessitate an unchanged mechanism during the analysis. Therefore, equation (5) will only be applied within a temperature range where the DTG curve exhibits a single peak.

3.1. DTG with non-overlapped peaks

This scenario represents the simplest case. As an example, a TGA data sheet from the study by Suliga et al. [12] was chosen. In this work, the thermal stability of a resin system (bis-(epoxycyclohexyl)-methylcarboxylate and Aradur 917) modified with 5 wt% octa-functional POSS (Polyhedral Oligomeric Silsesquioxane), labeled CY-1/Anhydride/octa-POSS (4), was evaluated using TGA under nitrogen flow ($\beta = 10$ °C/min) [12]. **Figure 1a** displays the corresponding DTG curve, which exhibits two distinct peaks within separate temperature ranges: the first occurring between 183-185 °C and the second between 314-402 °C. The corresponding conversion curve is presented in **Figure 1b**.

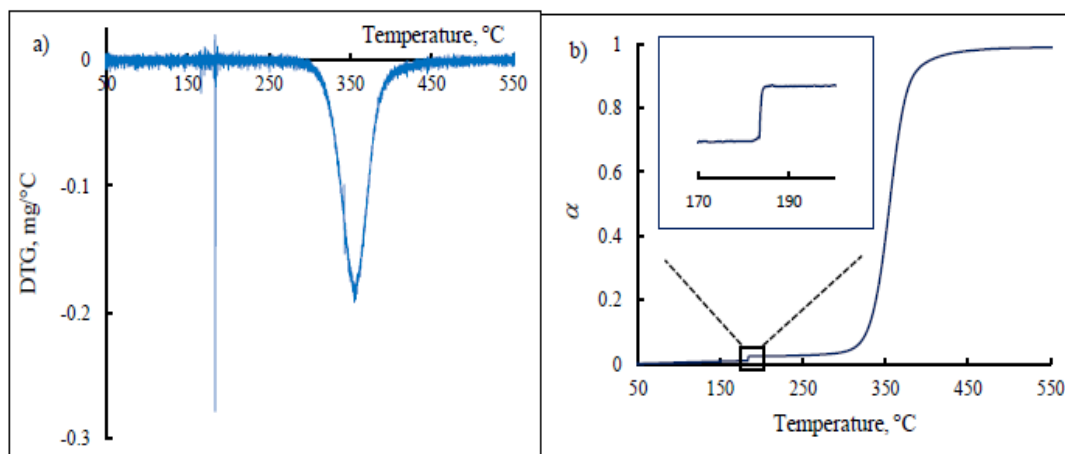


Figure 1 Curves of a) DTG and b) conversion of CY-1/Anhydride/octa-POSS (4) (Data from [12])

Table 1 Kinetic parameters of thermal decomposition of CY-1/Anhydride/octa-POSS (4) sample

Temperature range	Kinetic model	Parameters	R^2	A	E_a , kJ/mol
183-185 °C	PO	$n = 56.0$	0.8864	1.1×10^{79}	712.3
	SB	$n = 2.1, m = -1$	0.8798	6.4×10^{85}	790.5
	C-R				
	$n = 1$		0.8418	5.8×10^{106}	958.4
	$n = 1.5$		0.8420	1.7×10^{107}	962.5
314-402 °C		$n = 2$	0.8422	5.2×10^{107}	966.7
	PO	$n = 2.4$	0.9995	1.7×10^{24}	312.1
	SB	$n = 2.5, m = 0.1$	0.9995	6.8×10^{23}	306.6
	C-R				
	$n = 1$		0.9694	4.3×10^{10}	156.2
	$n = 1.5$		0.9870	5.1×10^{13}	190.6
	$n = 2$		0.9929	5.1×10^{17}	231.2

Both the PO and SB models were applied to Equation (5), while the C-R equations were directly fitted to the conversion data within the two temperature ranges of 183-185 °C and 314-402 °C. The resulting kinetic parameters are summarized in Table 1. In the lower temperature range (183-185 °C), the low R^2 values and unreasonable values obtained for the A and E_a suggest that the weight loss observed in this range is not a result of a chemical reaction. Conversely, the good fits achieved by both the PO and SB kinetic models when applied to the conversion data in the higher temperature range (314-402 °C) indicate that the thermal decomposition of CY-1/Anhydride/octa-POSS (4) within this range is controlled by a chemical reaction. Furthermore, the small m -value

of 0.1 obtained from the SB model suggests the slightly effect of autocatalysis [13]. It is also noteworthy that as the n -value in the C-R equations increase, the results approach those obtained from the PO model.

3.2. DTG with overlapped peaks

To illustrate a more complex scenario, we selected the TGA data sheet for diclofenac sodium loaded cellulose fiber (labeled LA) from the study by Dilebo et al. [14] The TGA of the LA sample was conducted under nitrogen flow at a heating rate of 10 °C/min. As depicted in Figure 2a, the DTG curve exhibits two overlapping peaks within the temperature ranges of 200-290 °C and 290-365 °C.

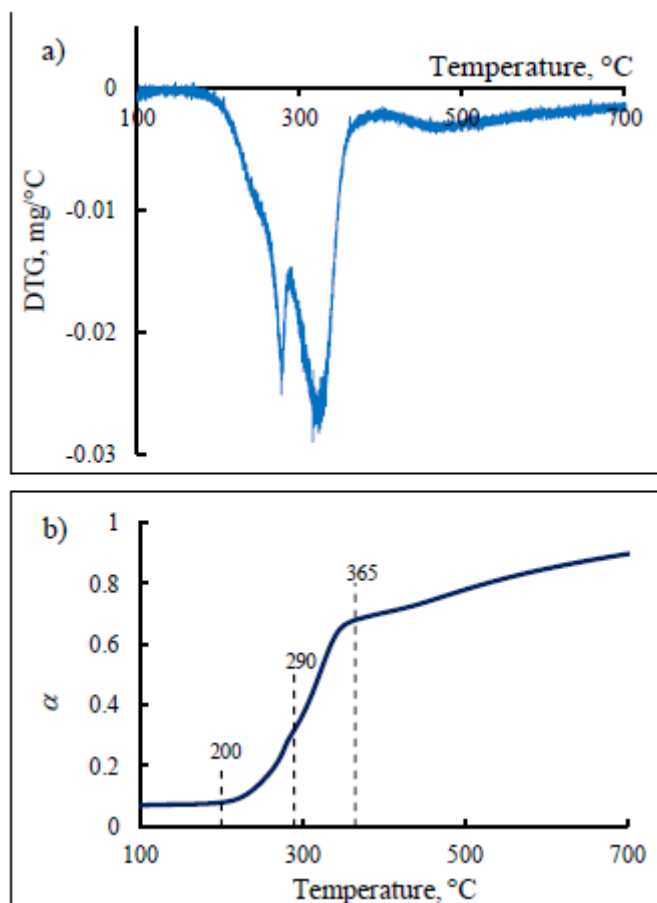


Figure 2 Curves of a) DTG and b) conversion of LA (Data from [14])

Table 2 Kinetic parameters of thermal decomposition of LA sample

Temperature range	Kinetic model	Parameters	R^2	A	E_a , kJ/mol
200-290 °C	PO	$n = 2.2$	0.9993	7.5×10^4	80.8
	SB	$n = 2.85, m = 0.18$	0.9993	7.5×10^4	78.8
	C-R				
		$n = 1$	0.9474	0.57	31.6
		$n = 1.5$	0.9442	0.95	33.4
290-365 °C	PO	$n = 8.9$	0.9923	1.0×10^{26}	298.8
	SB	$n = 7.8, m = 6.7$	0.9984	4.7×10^2	13.6
	C-R				
		$n = 1$	0.9612	3.4	38.3
		$n = 1.5$	0.9702	33.8	47.6
	$n = 2$	0.9760	4.2×10^2	58.1	

The kinetic parameters obtained from the fitting of conversion data with Equation (5) using the PO and SB models, and the C-R equations, are presented in Table 2. Within the temperature range of 200-290 °C, the E_a derived from the C-R equations is approximately 2.5 times lower than that obtained from the PO and SB models. A comparison of the R^2 values suggests that the PO

and SB models exhibit a better agreement with the experimental data than the C-R equations. The value of m in the SB model is low ($m = 0.18$), indicating a weak autocatalytic effect on the reaction kinetics. Notably, Tudjia et al. [15] previously reported that diclofenac sodium undergoes strong thermal decomposition between 202 and 300 °C under similar TGA conditions.

Therefore, it is reasonable to assume that the weight loss of LA within the 200-290 °C range can be attributed to the decomposition of diclofenac sodium, which can be modeled as a homogeneous reaction.

Within the higher temperature range of 290-365 °C, the PO and SB models again demonstrate a superior ability to describe the kinetic data compared to the C-R equations. The study by Jandura et al. [16] has previously shown that the DTG curve of cellulose fiber exhibits a single peak at 337 °C, which corresponds to the decomposition of cellulose. Consequently, the peak observed in **Figure 2a** between 290-365 °C can be attributed to the decomposition reaction of cellulose within the LA sample. The SB model yields a high value of $m = 6.7$, indicating a significant autocatalytic effect on the kinetics of cellulose decomposition within the LA sample. As presented in **Table 2**, the E_a derived from the SB model is notably lower compared to the values obtained from other models. This observation is consistent with the notion that autocatalysis contributes to a decrease in E_a , a conclusion supported by previous researches [17,18]. Analyzing solely the conversion curve (**Figure 2b**) presents a substantial challenge in elucidating the two distinct mechanisms occurring within the temperature range of 200-365 °C.

IV. CONCLUSION

To determine the E_a of the decomposition reaction, the PO and SB kinetic models were employed for theoretical analysis, resulting in ordinary differential equations. These equations were then solved numerically and fitted to the experimental conversion data obtained from TGA. The calculated value of E_a was subsequently determined. Validating the TGA results from two previous studies reveals that the present analysis provides a better description of the experimental data than the C-R equations. Moreover, the SB model can be used to discuss the characteristic mechanism underlying the decomposition reaction. Although this approach is successful in determining E_a for the selected TGA datasheet, it is challenging to apply to complex decomposition reactions featuring multiple overlapped peaks in the DTG curve.

CONFLICTS OF INTEREST

There is no conflict of interest among authors, and the involved institutions.

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