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# Critical consideration on the Freeman and Carroll method for evaluating global mass loss kinetics of polymer thermal degradation

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## Abstract

By means of regression analysis, an insight into the limitations of the widely used Freeman and Carroll method is offered, and it is indicated that the Freeman and Carroll method is essentially unstable for the determination of the reaction order. The reliabilities of the intercept and slope terms for any one regression equation are also investigated mathematically, suggesting that the slope term is in general easily to be determined accurately, whereas the intercept term has possibility to be obtained with great error. Based on these theoretical analyses, a new method to calculate the kinetic parameters for polymer thermal degradation is proposed, in which the three kinetic parameters are determined from the slopes of three regression equations described in this paper. The experimental data in the literature are used to verify the proposed method. By comparing the results from the Freeman and Carroll method and the proposed method respectively with those from the Doyle method, it is shown that the proposed method can be applied with a much better accuracy than the Freeman and Carroll method. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Dynamic thermogravimetry; Freeman and Carroll method; Unstable regression equation; Thermal degradation; Kinetic parameter

## 1. Introduction

During the past several decades, dynamic thermogravimetry, in which changes in weight are measured as a function of increasing temperature, has been widely used to study the kinetics of thermal decomposition reactions. Dynamic thermogravimetry has attracted widespread interest mainly due to its explicit advantages over isothermal methods. As pointed out

by Doyle [1], one dynamic mass-loss curve is equivalent to a large number of isothermal mass-loss curves. Other advantages of dynamic thermogravimetry have been summarized by Coats and Redfern [2] and Wendlandt [3]. With the development of different kinetic analysis methods, dynamic thermogravimetry has now been playing a very important role in the fields such as fuel property, fire research, fabric flammability, nuclear weapons effects, waste incineration, and aerospace technology, etc.

It is known that a wide range of practical problems is associated with the polymer thermal degradation. For example, the pyrolysis of biomass is related to the

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self-heating of cellulosic materials, the behavior of wood in fire, the role of inorganic salts as fire retardant for timber, etc. For the polymer thermal degradation, there has been an ongoing debate in the literature concerning the global kinetics of polymer pyrolysis. Global kinetics are of interest in modeling polymer decomposition in many applications in which trying to represent the full complexity of the polymer degradation process makes no sense. In general, the global kinetics of the pyrolysis are looked on as offering a clue to the key mechanistic steps in the overall weight loss process.

In the case of polymer degradation, global kinetic analysis of thermogravimetric data from a weight loss curve is based on the formal kinetic equation

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (1)$$

where  $\alpha$  is the fraction of material decomposed at time  $t$ ,  $n$  is the order of reaction, and  $k$  the rate constant.

The combination of this equation and the empiric Arrhenius expression gives the following relationship:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) (1-\alpha)^n \quad (2)$$

where  $A$  is the frequency factor,  $E$  is the activation energy of the reaction, and  $R$  the gas constant. Introducing the heating rate,  $\beta$ ,

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} (1-\alpha)^n \quad (3)$$

This is the fundamental expression of analytical methods to calculate kinetic parameters on the basis of TG data. Based on this expression, a considerable number of methods to derive kinetic parameters  $E$ ,  $n$ , and  $A$  from thermogravimetric curves have been developed. According to the kind of data used, the methods in general fall into two classes: integral method and differential method. Integral method utilizes weight loss versus temperature data directly, while differential method uses the rate of weight loss versus temperature. The most widely used integral kinetic methods are those developed by (a) Doyle [1], (b) Coats and Redfern [4], (c) Zsako [5], (d) Broido [6], (e) Reich and Stivala [7], and (f) Ozawa et al. [8], and the differential methods in common use are those derived by (g) Freeman and Carroll [9], (h) Newkirk [10], (i) Achar et al. [11], (j) Vachuska and Voboril

[12], and (k) Friedman et al. [13] From their mathematical derivations, it can be concluded that the methods (a),(b),(c),(e) and (i) can be applied only when the reaction order is priorly known, while the methods (d) and (h) may be used only when the reaction is of first order. In other words, for these methods the priori knowledge of the reaction mechanism is generally needed for calculating the kinetic data. However, it is just such a limitation that usually leads to great trouble in dealing with the thermogravimetric curve, because the reaction mechanism is in general not able to be determined in advance. In fact, the techniques to obtain the kinetic parameters when the reaction order (or mechanism) is unknown have been a subject of much concern over the past several decades.

The method (j) developed by Vachuska and Voboril [12] can be used to determine the kinetic parameters  $E$  and  $n$  simultaneously. However, this method involves the determination of  $d^2\alpha/dt^2$ , which cannot be obtained readily and accurately from the weight loss curve. Actually, such a disadvantage strongly weakens the accuracy of this method, and few applications of it can be found in literature. The methods (f) and (k) developed respectively by Ozawa and Friedman have been successfully used to study polymer thermal decomposition kinetics, without any priori knowledge of the reaction mechanism. The common disadvantage of the two methods is the requirement of several experiments with different heating rates.

Besides the Ozawa method and the Friedman method, the method developed by Freeman and Carroll (FC) [9] is another one widely used without any priori knowledge of the reaction order. The reaction order  $n$  (or mechanism) and the activation energy  $E$  can be determined from the equation

$$\frac{-(E/R)\Delta(1/T)}{\Delta \ln(1-\alpha)} = \frac{\Delta \ln(d\alpha/dt)}{\Delta \ln(1-\alpha)} - n \quad (4)$$

It is apparent that by plotting a graph of  $\Delta \ln(d\alpha/dt)/\Delta \ln(1-\alpha)$  versus  $\Delta T^{-1}/\Delta \ln(1-\alpha)$ , the parameters  $E$  and  $n$  can be calculated respectively from the intercept and the slope of the regression line (in what follows we call it the FC regression line). However, in most practical instances it was found that there is considerable difficulty in obtaining a reliable value of the reaction order  $n$  by the FC regression line [2]. By

means of the thermal decomposition of calcium carbonate, Sharp and Ventworth [14] also proved the invalidation of the FC method in determining the reaction order  $n$ . During their investigations it was found that the obtained reaction order values sensitively fluctuated with the number of the points selected for fitting the straight line. When the number of points was eight, the obtained reaction order was +0.55, whereas when 14 points were used, the reaction order was obtained to be -0.17. In addition, the FC method cannot be used directly to determine the pre-exponential factor  $A$ . These evidences hint that the FC method can only be used to determine the activation energy of the reaction accurately.

With the above limitations of the FC method in mind, this study seeks to develop a new method for deriving the kinetic data  $E$ ,  $n$ , and  $A$  accurately, without any priori knowledge of the reaction mechanism. We begin with a theoretical attempt to understand the reason for the limitations of the FC method in Section 2. Based on the theoretical analysis, in Section 3 we formally describe three equations which make up the new method. One of the equations is just the Eq. (4) derived by Freeman and Carroll. The parameters  $E$ ,  $n$ , and  $A$  can be determined accurately from the slopes, rather than the intercepts, of the regression lines according to the three equations respectively. The verification of the proposed method appears in Section 4, and Section 5 is a summary and conclusion section.

## 2. Insight into the limitations of the FC method

As pointed out in the last section, there exists lack of consistency in calculating the reaction order  $n$  from the intercept of the FC regression line. In the literature, this disadvantage has been considered to arise mainly due to the random error in the slope evaluation fluctuation [15]. However, no insight was offered into the sensitivity of the resulted reaction order value to the slope evaluation fluctuation until now, and it has been presumed that the FC method can be accurate on condition that the slope is determined with satisfactory accuracy. By contrast, this section seeks to indicate in terms of theoretical analysis that the regression Eq. (4) is in nature unstable for determining its intercept value. Due to this instability, a small error of the slope

estimator may lead to a great error of the intercept evaluation, so that the reaction order cannot be determined accurately by the FC method in essence, so long as any experimental fluctuation exists.

For convenience in the present discussion, we begin with a brief derivation of the FC method. Taking logarithms of both sides of Eq. (3), we have

$$\ln \left( \frac{d\alpha}{dT} \right) = \ln \frac{A}{\beta} - \frac{E}{RT} + n \ln (1-\alpha) \quad (5)$$

Suppose another temperature, referred to as  $T'$ , is randomly selected from the thermogravimetric curve. By analogy to Eq. (5) we obtain

$$\ln \left( \frac{d\alpha'}{dT'} \right) = \ln \frac{A}{\beta} - \frac{E}{RT'} + n \ln (1-\alpha') \quad (6)$$

where  $\alpha'$  is the fraction of material decomposed at temperature  $T'$ , and here for the convenience of representation,  $(d\alpha/dT)_{T=T'}$  has been expressed simply as  $d\alpha'/dT'$ . Subtracting Eq. (6) from Eq. (5) yields

$$\Delta \ln \left( \frac{d\alpha}{dT} \right) = -\frac{E}{R} \Delta \left( \frac{1}{T} \right) + n \Delta \ln (1-\alpha) \quad (7)$$

Dividing both sides by  $\Delta \ln(1-\alpha)$ , we have

$$(A) \quad \frac{\Delta \ln(d\alpha/dT)}{\Delta \ln(1-\alpha)} = -E \frac{\Delta(1/T)}{R \Delta \ln(1-\alpha)} + n \quad (8)$$

This expression is just the one used in the FC method (see Eq. (4)), but the derivation here is more concise than that of Freeman and Carroll. This equation is used in the proposed new method to determine the activation energy  $E$ . Hence, we mark this equation by (A) for sake of emphasis. As has been explained, dealing with the weight loss curve by the FC method comes down to fitting a straight line in terms of this equation. In a strictly mathematical sense, the FC regression line may be expressed as follows:

$$Y = \hat{a} + \hat{b}X \quad (9)$$

where  $X$  and  $Y$  are two variables related to each other by the least squares method, while  $\hat{a}$  and  $\hat{b}$  are two estimators. Corresponding to Eq. (8), we have the following relations:

$$X = -\frac{\Delta(1/T)}{R \Delta \ln(1-\alpha)} \quad (10)$$

$$Y = \frac{\Delta \ln(d\alpha/dT)}{\Delta \ln(1-\alpha)} \quad (11)$$

$$E(\hat{a}) = n \quad (12)$$

$$E(\hat{b}) = E \quad (13)$$

Here the notation  $E(\cdot)$  denotes the predicted value of the bracketed term. The terms  $\hat{a}$  and  $\hat{b}$  are respectively, the estimators of  $n$  and  $E$ .

For a specific thermogravimetric experiment, samples of the data point  $(X, Y)$  are measured and calculated randomly from the weight loss curve. In this sense,  $X$  and  $Y$  can be looked on as two observed variables, and it can be assumed that the two variables follow normal distribution. In general, different samples of  $(X, Y)$  lead to different values of  $\hat{a}$  and  $\hat{b}$ . In other words, the estimators  $\hat{a}$  and  $\hat{b}$  will fluctuate when the used sample changes from one to another. If the fluctuations of  $\hat{a}$  and  $\hat{b}$  both result to be small compared with their respective targets, i.e.  $n$  and  $E$ , the Eq. (9) may be referred to as a stable regression equation. If not, we call Eq. (9) an unstable regression equation, and the estimator with great fluctuation will be unreliable.

In mathematics, the fluctuations of  $\hat{a}$  and  $\hat{b}$  can be formulated by their standard deviations [16]:

$$\sigma_{\hat{a}} = \sigma \sqrt{\frac{\sum_{i=1}^N X_i^2}{N \sum_{i=1}^N (X_i - \bar{X})^2}} \quad (14)$$

$$\sigma_{\hat{b}} = \frac{\sigma}{\sqrt{\sum_{i=1}^N (X_i - \bar{X})^2}} \quad (15)$$

where  $\sigma$  is the standard deviation of  $Y$  around the regression line.

We define the relative errors of  $\hat{a}$  and  $\hat{b}$  as the ratios of  $\sigma_{\hat{a}}$  and  $\sigma_{\hat{b}}$  respectively to  $E(\hat{a})$  and  $E(\hat{b})$ , and expressed them as  $\tilde{\sigma}_{\hat{a}}$  and  $\tilde{\sigma}_{\hat{b}}$

$$\tilde{\sigma}_{\hat{a}} = \frac{\sigma}{n} \sqrt{\frac{\sum_{i=1}^N X_i^2}{N \sum_{i=1}^N (X_i - \bar{X})^2}} \quad (16)$$

$$\tilde{\sigma}_{\hat{b}} = \frac{\sigma}{E \sqrt{\sum_{i=1}^N (X_i - \bar{X})^2}} \quad (17)$$

The orders of magnitude of these two errors cannot be evaluated theoretically in a general sense. However, for the thermal decomposition of solid materials, the order of  $\tilde{\sigma}_{\hat{b}}$  can be inferred from the literature. So far,

some studies have been devoted to the polymer thermal degradation, in which the FC method and several other kinetic methods were used simultaneously in order to obtain relatively reliable kinetic data. It seems that for a specific experiment all these methods always resulted in approximately the same activation energy values. This hints that, for most cases, the activation energy  $E$  can be estimated by the FC method accurately, with a quite small error  $\tilde{\sigma}_{\hat{b}}$  obtained. A recent reference of this kind is that by Huang and Li [17]. By means of four kinetic methods, Huang and Li have obtained the kinetic parameters for cellulose and cellulose esters at 10°C/min in nitrogen, and it was found that the  $E$  values by the FC method differed little from those by other three methods. Another reference of this kind is that of Sharp and Ventworth [14], as has been stated in Section 1. During their investigation, the great fluctuation of the reaction order value by the FC method hinted at a very big order of  $\tilde{\sigma}_{\hat{a}}$ . However, with different numbers of points used, the obtained  $E$  values by the FC method were also found to differ not too much from those by other two methods. In fact, there has been a substantial agreement that the FC method can be used in the determination of the  $E$  values with satisfactory accuracy, and an investigation of the literature revealed that the obtained  $E$  value is generally in error by 5–15%, that is to say,  $\tilde{\sigma}_{\hat{b}} \sim 5\text{--}15\%$ . Here and in the following discussion we use the symbol ‘ $\sim$ ’ to mean ‘the order of magnitude is equal to’.

Combining Eqs. (16) and (17) yields the following relation

$$\frac{\tilde{\sigma}_{\hat{a}}}{\tilde{\sigma}_{\hat{b}}} = \frac{E}{n} \sqrt{\frac{\sum_{i=1}^N X_i^2}{N}} \quad (18)$$

Taking Eq. (10) into account, Eq. (18) can be rewritten as the following expression:

$$\frac{\tilde{\sigma}_{\hat{a}}}{\tilde{\sigma}_{\hat{b}}} \sim \frac{E\Delta(1/T)}{nR\Delta \ln(1-\alpha)} \quad (19)$$

For simplicity, let  $\alpha = 1-y$ . Here  $y$  is the fraction of material not yet decomposed at time  $t$ . To evaluate the order of magnitude of  $\tilde{\sigma}_{\hat{a}}/\tilde{\sigma}_{\hat{b}}$ , we define two functions  $z_1(T, T')$  and  $z_2(y, y')$  as

$$z_1 = \frac{1}{R} \left( \frac{1}{T} - \frac{1}{T'} \right) \quad (300 \leq T, T' \leq 1073) \quad (20)$$

$$z_2 = \ln y - \ln y' \quad (\varepsilon \leq y, y' \leq 1.0) \quad (21)$$

Eq. (19) can then be rewritten as

$$\frac{\tilde{\sigma}_a}{\tilde{\sigma}_b} \sim \frac{Ez_1}{nz_2} \quad (22)$$

In general, the thermal decomposition is carried out in an inert atmosphere from room temperature to about 800°C, meanwhile the fraction of material not decomposed decreases from 1.0 to  $\varepsilon$  continuously. Here  $\varepsilon$  is the fraction not yet decomposed when the temperature has been increased up to 800°C. In dealing with the weight loss curve by the FC method, the temperatures  $T$  and  $T'$  are selected randomly and independently, and the corresponding fractions  $y$  and  $y'$  are determined from the curve. Due to this procedure, the fractions  $y$  and  $y'$  can be looked on as two quantities independent of each other, with possible values ranging from  $\varepsilon$  to 1.0 for each of them.

Fig. 1 shows the graph of  $z_1$  versus  $T$  for various values of  $T'$ . Inspection of Fig. 1 indicates that for any fixed value of  $T'$ ,  $z_1(T)$  is on the order of  $10^{-5}$ – $10^{-4}$  over most of the interval of  $T$ . Stated in another way, for any two temperatures  $T$  and  $T'$  selected randomly from the weight loss curve, the following relation holds in almost all cases:

$$z_1(T, T') \sim 10^{-5} - 10^{-4} \quad (23)$$

In an analogous manner, the plot of  $z_2$  versus  $y$  for various values of  $y'$  shown in Fig. 2 reveals that

$$z_2(y, y') \sim 10^{-1} - 10^0 \quad (24)$$

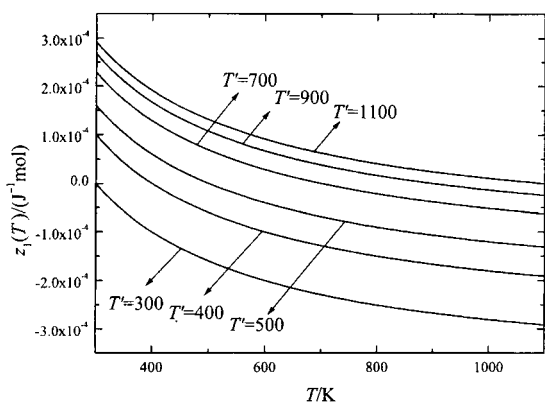


Fig. 1. Plot of  $z_1(T)$  vs.  $T$  for various values of  $T'$ .

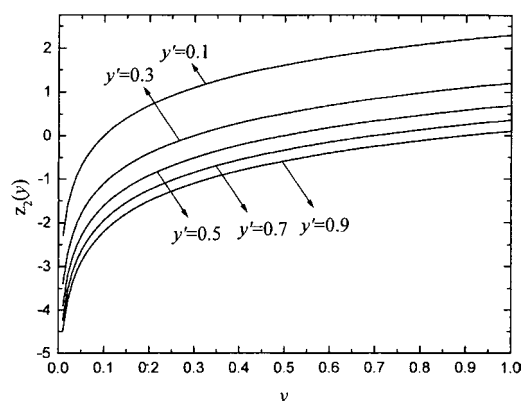


Fig. 2. Plot of  $z_2(y)$  vs.  $y$  for various values of  $y'$ .

is valid under general circumstances. Combining Eqs. (23) and (24) the order of magnitude of  $z_1/z_2$  can be obtained as the following expression:

$$\frac{z_1}{z_2} \sim 10^{-5} - 10^{-3} \quad (25)$$

It has been shown in the literature that the activation energy  $E$  is generally on the order of  $10^4$ – $10^5$  J/mol, and the reaction order  $n \sim 1$ . An investigation of the literature revealed that almost all the studies with few exceptions have supported these orders of magnitude. Some papers of this kind in recent years are those by Huang and Li [17], Jimenez et al. [18], Chang [19], Antal and Varhegyi [20], and Milosavljevic and Suuberg [21]. Taking this fact into account, substituting Eq. (25) into Eq. (22) yields:

$$\frac{\tilde{\sigma}_a}{\tilde{\sigma}_b} \sim 10^{-1} - 10^2 \quad (26)$$

Recalling the fact that  $\tilde{\sigma}_b \sim 5$ – $15\%$ , we can then obtain the following evaluation of the error term  $\tilde{\sigma}_a$ :

$$\tilde{\sigma}_a \sim 0.5 - 1500\% \quad (27)$$

We note in passing that since  $y$  is dependent on  $T$ , Eq. (27) is just an evaluation of the order of magnitude of  $z_1/z_2$  in a relatively rough sense. It can be inferred from the literature that under real situations  $Z_1/Z_2$  has generally an order of magnitude of  $10^{-5}$ – $10^{-4}$  (see, e.g. [14,18]), and therefore a more accurate evaluation of  $\tilde{\sigma}_a$  can be obtained:

$$\tilde{\sigma}_a \sim 0.5 - 150\% \quad (28)$$

Eqs. (27) and (28) both imply that when different sets of data points ( $T, \alpha$ ) and ( $T', \alpha'$ ) are selected stochastically from the weight loss curve, the values of  $\hat{\sigma}_{\hat{a}}$  would fluctuate from less than 1% to over 100%. It has been stated that  $\hat{a}$  is the estimator of the reaction order  $n$ . Therefore, it has been now clear that the FC method may lead to a great error for the  $n$  value, even if the error of the  $E$  value remains small. In mathematics, this result reveals that the regression Eq. (9) is in itself unstable for the determination of its intercept term. Just for the instability, the obtained value of the reaction order generally fluctuates greatly with the number of points used, as stated previously. Due to the inescapability of the experimental and measure fluctuations, the error of the  $E$  value cannot be reduced to extremely small. Hence, it can be concluded that the FC method cannot be used to determine the reaction order accurately in essence. Only by improving the FC method itself can the reaction order be expected to be determined with satisfactory accuracy.

### 3. Proposed method to obtain the kinetic data

Investigating the literature, it is interesting to note that although the intercept term of the FC regression equation showed weak reliability, almost all the regressions had acceptable correlation coefficient values. Before proceeding further into the detailed description of the new method, let us pause here to examine the regression reliabilities of the slope and intercept terms for any one general regression equation, underlying the interpretation of the principle of the new method.

For a set of observed data ( $X_1, Y_1$ ) ( $X_2, Y_2$ ), ..., ( $X_N, Y_N$ ), suppose the true relation between  $X$  and  $Y$  is  $Y = a + bX$ , while the regression line is  $Y = \hat{a} + \hat{b}X$ . By comparing the definition of the correlation coefficient  $r_{XY}$  with the expression of  $\hat{b}$ , the following relation can be achieved [22]:

$$\hat{b} = \left\{ \frac{\sum (Y_i - \bar{Y})^2}{\sum (X_i - \bar{X})^2} \right\}^{1/2} r_{XY} \quad (29)$$

where and in what follows summations are all over  $i = 1, 2, \dots, N$ . Combining Eq. (15) and (29) allows us to obtain the following expression:

$$\frac{\sigma_{\hat{b}}}{\hat{b}} = \frac{\sigma}{r_{XY} \sqrt{\sum (Y_i - \bar{Y})^2}} \quad (30)$$

This expression is the approximate relative error of the estimator  $\hat{b}$ . In practice we cannot know the value of  $\sigma^2$ , which is the variance of  $Y$  about the true line. Nevertheless, it can be estimated by the following unbiased deviation about the fitted line [23]:

$$s^2 = \frac{1}{N-2} \sum (Y_i - \hat{Y}_i)^2 \quad (31)$$

where  $\hat{Y}_i$  is the fitted value of  $Y$  on the fitted line:

$$\hat{Y}_i = \hat{a} + \hat{b}X_i \quad (32)$$

The summation term in Eq. (30) can be expressed by the following equality [22]:

$$\sum (Y_i - \bar{Y})^2 = \sum (\hat{Y}_i - \bar{Y})^2 + \sum (Y_i - \hat{Y}_i)^2 \quad (33)$$

Finally, we can rewrite the approximate relative error of  $\hat{b}$  by substituting Eqs. (31) and (33) into Eq. (30). Thus

$$\frac{\sigma_{\hat{b}}}{\hat{b}} = \frac{1}{r_{XY} \sqrt{N-2}} \frac{\sqrt{\sum (Y_i - \hat{Y}_i)^2}}{\sqrt{\sum (\hat{Y}_i - \bar{Y})^2 + \sum (Y_i - \hat{Y}_i)^2}} \quad (34)$$

It is clear that for a  $r_{XY}$  close to unity, the error of the slope term  $\hat{b}$  would be small on condition that the number  $N$  is big enough. Even for a small value of  $N$ , there is still possibility that a value of  $\hat{b}$  be achieved with minor error, due to the reduction effect of the later fractional term in the above equation. This equation provides a good interpretation of the reason for which the activation energy value resulted from the FC method usually has a reasonable accuracy. As stated previously, in the existing applications of the FC method, the values of  $r_{XY}$  were usually found to be close to unity, implying that the variables  $X$  and  $Y$  for the FC regression line had a closely positive relation. In view of this fact, reasonable accuracy of the activation energy  $E$  by the FC method is not surprising. The more important conclusion drawn from the above equation is that, if the parameter being examined appears in the slope term of any one general regression equation, this parameter would be expected likely to be determined accurately. This conclusion underlies the theory of the new method.

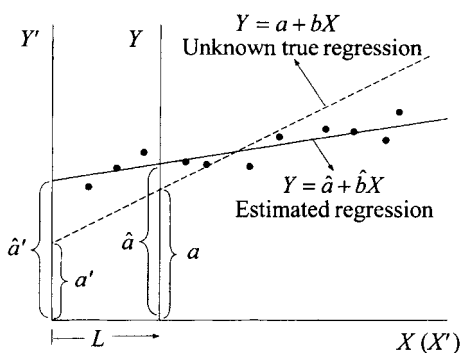


Fig. 3. Illustration of the unreliability of the intercept term for a general regression equation.

It should be pointed out, however, the intercept term for a general regression equation has not such a good feature. Fig. 3 is used here to make the point. This figure shows a general regression. Suppose the true regression  $E(Y) = a + bX$  is the dashed line shown in the figure. This is unknown to the statistician, who must estimate it as accurately as possible by observing  $X$  and  $Y$ . Suppose the estimated regression is  $Y = \hat{a} + \hat{b}X$ . The correlation coefficient  $r_{XY}$  is assumed to be close to unity, hinting at a closely positive relation between  $X$  and  $Y$ . Our emphasis here is on the reliability of the fitted intercept term  $\hat{a}$ . In Fig. 3, two coordinate systems are used to illustrate that a data set  $(X', Y')$  with unreliable fitted intercept value can be readily constructed, even if the sample correlation coefficient between  $X'$  and  $Y'$  is close to unity. It's evident that the relation of the two coordinate systems is

$$X' = X + L \quad (35)$$

$$Y' = Y \quad (36)$$

In the space  $(X', Y')$ , the true and the estimated regression lines can be expressed by  $X'$  and  $Y'$ , respectively as

$$Y' = (a - bL) + bX' \quad (37)$$

and

$$Y' = (\hat{a} - \hat{b}L) + \hat{b}X' \quad (38)$$

Combining these two equations, the error of the estimated intercept in this space can be obtained:

$$\hat{a}' - a' = (\hat{a} - a) + (b - \hat{b})L \quad (39)$$

It can be seen from Fig. 3 that the quantity  $\hat{a}' - a'$  has the same sign as  $b - \hat{b}$ . Hence, the error of the estimated intercept in the space  $(X', Y')$  is enlarged compared with that in the space  $(X, Y)$ . It's obvious that if  $L$  is taken to be big enough, the quantity  $\hat{a}'$  would finally become to differ from  $a'$  so much that the quantity  $|\hat{a}' - a'|/|a'|$  would exceed unity, hinting at a great error of the estimated intercept. Stated in another way, the data set  $(X', Y')$ , i.e.  $(X + L, Y)$ , would lead to a regression line with an unreliable intercept term. During this procedure, the correlation coefficient  $r_{XY}$  remains fixed, which can be justified by referring to the definition of  $r_{XY}$ . Hence, a conclusion can be drawn from this analysis, that is, with the correlation coefficient approximating unity, the intercept term is still likely to be greatly unreliable.

Based on the above arguments, we now proceed to describe the method for the determinations of the reaction order and the pre-exponential factor. In view of the above features of the slope and intercept terms for a general regression equation, the FC method may be improved upon by deriving two regression equations whose slope terms respectively involve the reaction order  $n$  and the pre-exponential factor  $A$ . The values of  $n$  and  $A$  can then be determined from the slope terms of the two equations. Based on this idea, we first refer back to Eq. (7) and derive the equation for the reaction order  $n$ . Rearrangement of Eq. (7) yields the following equation:

$$(B) \quad \frac{\Delta \ln(1 - \alpha)}{\Delta \ln(d\alpha/dT)} = \frac{E}{nR\Delta \ln(d\alpha/dT)} + \frac{1}{n} \quad (40)$$

The use of its slope term, i.e.  $E/n$ , is therefore an essentially better way to calculate the reaction order value, on condition that the activation energy  $E$  has been obtained using the FC regression equation. The above equation is marked by (B). Although the derivation is trivial, this regression equation is of major importance for the accurate determination of the reaction order  $n$ . In fact, for the solid material thermal degradation, the following order of magnitude is generally achieved (see, e.g. [14,18]):

$$\Delta \ln \left( \frac{d\alpha}{dT} \right) \sim 1 - 10 \quad (41)$$

Due to the fact that  $\Delta(1/T)/R \sim 10^{-5} - 10^{-4}$  and  $E \sim 10^4 - 10^5$ , the intercept term of Eq. (40) can be

shown, by the same analysis method for the FC regression equation, to have a relative error of 1–100 times the slope term. This result suggests that Eq. (40) is also unstable for the determination of its intercept term. However, the use of its slope term is expected to lead to an accurate  $n$  value, for the reason stated before.

The equation for the pre-exponential factor  $A$  can be derived based on the same idea. In doing so, we would refer back to Eqs. (5) and (6). Dividing both sides of them respectively by  $\ln(1-\alpha)$  and  $\ln(1-\alpha')$ , and then subtracting one from the other, we obtain

$$\Delta \left[ \frac{\ln(d\alpha/dT)}{\ln(1-\alpha)} \right] = \ln \frac{A}{\beta} \Delta \left( \frac{1}{\ln(1-\alpha)} \right) - \frac{E}{R} \Delta \left( \frac{1}{T \ln(1-\alpha)} \right) \quad (42)$$

Dividing both sides by  $\Delta(1/T \ln(1-\alpha))$  yields the following equation:

$$(C) \quad \frac{\Delta[\ln(d\alpha/dT)]/\ln(1-\alpha)}{\Delta[1/(T \ln(1-\alpha))]} = \ln \left( \frac{A}{\beta} \right) \frac{\Delta(1/\ln(1-\alpha))}{\Delta[1/(T \ln(1-\alpha))]} - \frac{E}{R} \quad (43)$$

Obviously the pre-exponential factor  $A$  can be obtained from the slope term of this equation. We mark this equation by (C) for the sake of emphasis. This regression equation is worth a few other words. It has been clear that using Eqs. (A) and (B) the activation energy  $E$  and the reaction order  $n$  can be obtained with permissible errors. However, when  $E$  and  $n$  have been obtained, the pre-exponential factor  $A$  should not be estimated by selecting only one data point ( $T, \alpha$ ) from the thermogravimetric curve and substituting the data and the values of  $E$  and  $n$  into Eq. (5). The reason is due to the fact that the measured data point ( $T, \alpha$ ) and the obtained estimators of  $E$  and  $n$  all contain errors, and using them to estimate  $A$  would certainly lead to additional error of the result. Another possible strategy for determining  $A$  is using Eq. (5) directly as the regression equation, in which the parameters of  $E$  and  $n$  are taken as the values obtained by the methods described earlier. However, it's obvious that the errors of  $E$  and  $n$  will still affect the reliability of the obtained value of  $A$ . For this reason, this strategy is also not recommended. By contrast, Eq. (43) is not directly affected by the errors of the values of  $E$  and  $n$ , and thus

it would be expected to result in the value of  $A$  with less error.

So far, we have completed the derivations of the three regression equations which consist of the new method to obtain the kinetic information for thermal degradation reactions. Eqs. (A)–(C) are respectively used to determine the activation energy  $E$ , the reaction order  $n$ , and the pre-exponential factor  $A$ . This method overcomes the disadvantage of the FC method in the theoretical sense, and therefore it is expected to result in reliable values of the kinetic parameters.

#### 4. Experimental verification of the proposed method

In our earlier paper [24], the thermal decomposition of six different samples of wood and leaves in nitrogen has been studied by using dynamic thermogravimetry. We give now one example for the verification of the above-explained method, using the experimental data published in the paper. The sample we take here is the leaves of oil-tea tree, whose botanical name is *Camellia oleifera*, and the initial weight of this sample is 5.73 mg. The sample was collected from Qimen forest zone in Anhui province of China. It was ground and the fraction passing 20 mesh was used for analysis. Thermal decomposition was observed in terms of the overall weight loss by using a WRT-3 thermobalance made by Shanghai Balance Instrument Plant. An atmosphere of dry nitrogen, oxygen-free, was passed into the furnace at a flow rate of 80 ml/min. The sample was used in a wide-mouth porcelain crucible lightly packed so as not to impede loss of volatile products. The temperature was increased from room temperature to 500°C at a rate of 15°C/min. The buoyancy effect was considered negligible, which was justified by some other researchers, e.g., Simons et al. [25].

Using the Doyle method, we have found the following kinetic data during the temperature interval from 154 to 275°C:

$$n = 2; E = 63.68 \text{ KJ/mol}; A = 1.953 \times 10^5 \text{ min}^{-1}.$$

To verify the above-suggested method, we selected several data points randomly from the weight loss curve, and fitted three lines respectively according to



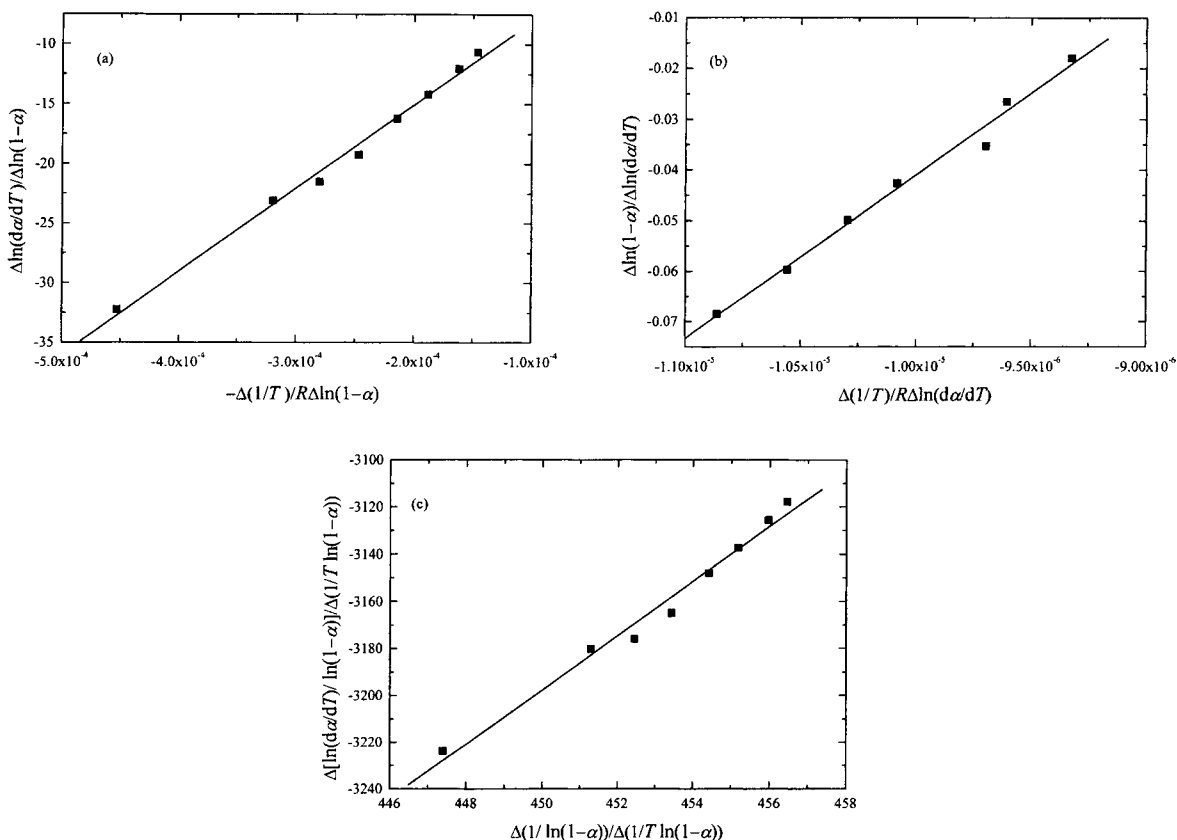


Fig. 4. Data calculated from the suggested method for (a) the activation energy, (b) the reaction order, and (c) the pre-exponential factor. The unit of  $T$  is K, and the unit of  $R$  is J/K mol. Note that plot (a) is just the one used in the FC method.

Eqs. (A)–(C). The regression lines are shown in Fig. 4. A direct test established that these plots showed very good linearity. For sake of comparison, the kinetic parameters have been calculated respectively by the FC method and the suggested method, and the results are shown in Table 1. It is apparent that a singular value of  $n$ , i.e.  $-1.11$ , has been achieved by the FC method. Contrarily, the comparison of the values of  $E$ ,  $n$ , and  $A$  by the proposed method with those by the Doyle method has shown good agreement. Table 2 is a

Table 1  
Kinetic parameters by different methods

|                 | $E$ (KJ/mol) | $n$   | $A$ ( $\text{min}^{-1}$ ) |
|-----------------|--------------|-------|---------------------------|
| FC method       | 69.83        | -1.11 | -                         |
| Doyle method    | 63.68        | 2.00  | $1.953 \times 10^5$       |
| Proposed method | 69.83        | 2.16  | $1.596 \times 10^6$       |

Table 2  
Regression results for the FC method and the proposed method

|            | FC method | Proposed method <sup>a</sup> |         |       |
|------------|-----------|------------------------------|---------|-------|
|            |           | (A)                          | (B)     | (C)   |
| $I^b$      | -1.11     |                              |         |       |
| $\sigma_I$ | 0.64      |                              |         |       |
| $S^c$      | 69833.0   | 69833.0                      | 32370.8 | 11.57 |
| $\sigma_S$ | 2397.9    | 2397.9                       | 1620.9  | 0.64  |
| $r$        | 0.996     | 0.996                        | 0.994   | 0.991 |

<sup>a</sup> (A), (B) and (C) correspond respectively to Eqs. (A), (B) and (C).

<sup>b</sup> Intercept term.

<sup>c</sup> Slope term.

summary of the regression results for the FC method and the proposed method. With reference to the table we can see that all the correlation coefficients approximate unity, implying that the points in each plot of

Fig. 4 are nearly in a line. Inspection of the standard deviations revealed that only the FC regression line resulted in an error of its intercept being of the same order as the intercept value itself, hinting at a great unreliability of the reaction order obtained by the FC method. This result illustrated the invalidation of the FC method in determination of the reaction order. On the other hand, as is clear from Table 2, the standard deviations for the suggested method are small compared with the corresponding estimator values, indicating that the suggested method has good accuracy in the determination of all the kinetic data.

## 5. Concluding remarks

Previous thermogravimetric studies showed that the FC kinetic method, for which no assumption about the reaction order is needed, has great instability in the determination of the reaction order  $n$ . In this paper, an insight into this limitation has been offered by means of the regression theory, which suggests that the regression line used in the FC method is in essence unstable for the calculation of the  $n$  value from the intercept term. Just for this instability, the  $n$  values by the FC method often fluctuate greatly with the number of points used for fitting.

For any one general regression equation, the reliabilities of the intercept and slope terms have also been investigated mathematically. It is shown that the slope term can be expected to be determined accurately on condition that the correlation coefficient is close to unity. Whereas even with the correlation coefficient approximating unity, the intercept term is still likely to be obtained with great error. Based on this analysis, a new method to determine the three kinetic parameters  $E$ ,  $A$ , and  $n$  accurately has been suggested. In the proposed method, the three kinetic parameters are determined respectively from the slopes of three regression lines. The comparison of the results respectively from the Doyle method, the FC method, and the proposed method has shown that the proposed method can be applied with a much better accuracy than the FC method. The proposed method can be used without a priori knowledge of the reaction order, which is needed for most of the other existing kinetic methods. Meanwhile, the proposed method removes the disadvantages of the FC method, and its statistical way of working up experimental data insures the accuracy in estimating the kinetic

parameters. The proposed method is therefore a reasonable improvement upon the FC method, and it can be applied in the study of global mass loss kinetics of polymer thermal degradation.

As a final remark, this work also reveals that when any one new kinetic method is developed, the reliabilities of its resulted parameters should be investigated in detail, by either experimental or theoretical means. Only with reliable kinetic parameters can the suggested method be recommended in use for the kinetic data of the thermal degradation reactions.

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