

# New Method for Kinetic Analysis of Decomposition of Biomass Materials—Based on Critical Analysis of Moll Method

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**ABSTRACT:** Moll method used in extracting the kinetic parameters of thermal decomposition of biomass materials is theoretically analyzed and the limitation of the method is critically examined. It is demonstrated that Moll method can only be used under strict conditions within narrow temperature intervals. In light of the idea of Moll method and also in view of the limitations of Moll method, a two-point data set method is developed for the kinetic analysis of the decomposition of biomass materials in air, using single heating rate mass-loss curve. The method is justified by comparing the resulted kinetic

parameters with those by integral and differential methods. Compared with Moll method, the new method is applicable to the mass-loss data within wide temperature intervals, whereby the kinetic parameters (especially the activation energy) can be evaluated without any prior knowledge of reaction order, with fairly high reliability. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 524–530, 2009

**Key words:** biomass materials; Moll method; thermal decomposition; kinetic model

## INTRODUCTION

During the past several decades, the decomposition kinetics of biomass materials has been a subject of a number of investigations in both fields of fire safety engineering and chemical engineering. Generally, the thermal decomposition of biomass materials can be modeled by the following rate equation:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp(-E/RT)f(\alpha) \quad (1)$$

where  $\alpha$  is the mass-loss fraction,  $\beta$  (K/min) the heating rate,  $E$  (kJ/mol) the apparent activation energy,  $A$  ( $\text{min}^{-1}$ ) the preexponential factor, and  $R$  the gas constant.  $T$  (K) is the absolute temperature. The specific form of  $f(\alpha)$  represents the reaction model function. A considerable number of mechanisms have been suggested, which may control the different mass-loss processes for cellulose and biomass under different fuel and heating conditions. The corresponding forms of the model function  $f(\alpha)$  with derivations were frequently stated in the

literature.<sup>1,2</sup> A special reaction model function is  $f(\alpha) = (1-\alpha)^n$ , where  $n$  represents the apparent order of reaction.

The approaches to extract the kinetic triplet based on the above expression can be generally divided into two categories according to the kind of data used, i.e., differential method by using derivative thermogravimetry (DTG) data and integral method using thermogravimetry (TG) data. The emphasis in these methods is on finding a way to plot the data so as to provide a rapid visual assessment of the kinetic parameters  $E$  and  $A$ . However, in practical extraction of the kinetic triplet, trial regression tests are generally required to achieve the suitable model function  $f(\alpha)$  for both differential and integral methods. In this aspect, although the reaction order model  $f(\alpha) = (1-\alpha)^n$  has now been recognized as a suitable model function for the decomposition of biomass materials, the  $n$  value has to be selected by intuition or blind guess rather than by consideration of firm guidelines. This limitation leads to great trouble in dealing with the decomposition data. Therefore, the techniques to obtain the kinetic parameters when the reaction order is unknown have been a subject of much concern over the past several decades.

In recent decades, a kind of multicomponent overall model has been developed to describe the mass-loss processes of biomass materials, such as almond

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TABLE I  
Features of the TG Curves for Wood and Leaf Samples in Air

Sample	Symbol <sup>a</sup>	$T_{m1}$ (°C) <sup>b</sup>	$T_{m2}$ (°C) <sup>b</sup>	Moisture (%)	Volatile (%)	Ash (%)
Fir	LF	332	466	8.0	80.6	11.4
	WF	312	440	12.6	81.0	6.4
Masson pine	LMP	320	472	10.3	81.9	7.8
	WMP	312	456	12.2	86.6	1.2

<sup>a</sup> The initials "L" and "W" in this column denote leaf and wood, respectively.

<sup>b</sup> DTG peak temperatures (for each sample there are two peaks).

shells,<sup>3,4</sup> pine and eucalyptus woods,<sup>5</sup> and other wood species.<sup>6</sup> In such models, each pseudocomponent corresponds to one apparent reaction order, which is evaluated by optimization computation. However, for optimization computation, it is well known that for any objective function (OF) with several parameters to be determined, in mathematics, there may be even infinite sets of parameters able to meet the demand of the error of OF, and thus, the achieved reaction order values as well as the activation energy and preexponential factor values are most likely to be short of kinetic significance. Alternatively, the isoconversional methods suggested by Freeman,<sup>7</sup> Ozawa,<sup>8</sup> and Flynn and Wall<sup>9</sup> can evaluate the kinetic parameters without knowing the form of model function. These methods all require multih heating rates decomposition data. However, under different heating rates, the reaction mechanisms and the kinetic parameters may vary significantly.

Comparatively, for the reactions which satisfy that  $f(\alpha) = (1-\alpha)^n$ , we refer back to the work of Moll et al.<sup>10</sup> who ever derived a method to estimate the activation energy by DTG data with only one single heating rate, without prior knowledge of the reaction order. Gogers and Morris<sup>11</sup> also used the similar method in DTA analysis. However, so far, this method has not been widely used, mainly due to its instability in data treatment, as will be analyzed and clarified in the later sections of the present article. It seems that no other application of this method has appeared in the literature. In the current article, a theoretical and critical discussion is performed on Moll method whereby its limitations are fully elucidated. A simple two-point data set method is then developed, which removes the limitations of Moll method. Experimental data for the decomposition of several Chinese wood and leaf species are subject to the new method. The kinetic parameters evaluated by the new method are compared with those by integral and differential methods, whereby the reliability of the new method is justified. It is believed that the new methods can be generally applied in extracting the kinetic parameters of biomass materials by simple procedures.

## EXPERIMENTAL

The raw materials used in the investigation were, respectively, the wood and leaf of fir and masson pine collected from Qimen forest zone of China (Table I). These materials were first cut and then ground, thereby the average particle size was specified to be approximately 40  $\mu\text{m}$ . The grains of the sample were evenly distributed over the open sample pan of 5-mm diameter, loosely, with the initial amounts of the samples all kept to be 10 mg or so. The depth of the sample layer filled in the pan is about 0.5 mm. Thermal decomposition was observed in terms of the overall mass loss by using a STA 409C Thermobalance. Temperature calibration of TGA was performed with special concern, because in this device the thermocouple was not in direct contact with the sample. An air stream was continuously passed into the furnace at a flow rate of 60 mL/min (at normal temperature and atmospheric pressure). The temperature was increased to 750°C at a rate of 10°C/min. The heating rate of this order is generally considered able to ensure that no temperature gap exists between the sample and its surroundings. To test the transport effect under this heating rate and sample mass condition, we performed the experiments using the masson pine as an example with different sample masses for which the least being 4 mg and the most being 10.6 mg. The result indicated that the TG curves for different masses differed from each other only around the upper edge of the domain of evaluation, at temperatures starting around 500°C. We regarded one of the curves as a benchmark curve and evaluated the fit of any other curve (e.g., the  $j$ th curve) relative to this benchmark curve according to the following expression:

$$\text{fit}(\%) = \left( \sum_{i=1}^{N_j} [w_{ji} - w_{bi}]^2 / N_j \right)^{0.5}$$

where  $w$  is the mass percentage, the subscript  $b$  refers to the benchmark curve, and  $N_j$  the number of points on the  $j$ th curve. Acceptable agreements were achieved with the most fit being only 2.6, indicating that the effect of the transport processes is low. This

may be partly due to the low heating rate used in this study. The sample mass-loss percentage and its temperature were recorded continuously as a function of heating time. From the sample mass-loss percentage, the normalized mass-loss ratio of a sample can be determined and plotted versus the sample temperature as the TG curve. The DTG curves were obtained from the TG curves which were subject to Gaussian smoothing method.

## RESULTS AND DISCUSSION

### Critical analysis of Moll method

This section seeks to offer a critical theoretical analysis so as to achieve an insight into the limitations of Moll method. For the sake of brevity, we use  $c = 1 - \alpha$  (which represents the mass fraction of decomposition) in the following discussion. For  $f(c) = c^n$ , eq. (1) can be written as

$$V \equiv \frac{dc}{dT} = -\frac{A}{\beta} \exp(-E/RT) c^n \quad (2)$$

The basic assumption by Moll et al.<sup>10</sup> is that there exist two points of temperature  $T_1$  and  $T_2$ , which can be carefully selected from the TG data such that the corresponding values of  $c_1^n$  and  $c_2^n$  have difference little enough to be negligible. By this assumption, from eq. (2) the activation energy can be easily estimated by the following expression:

$$E = \frac{R \ln V_2/V_1}{1/T_1 - 1/T_2} \quad (3)$$

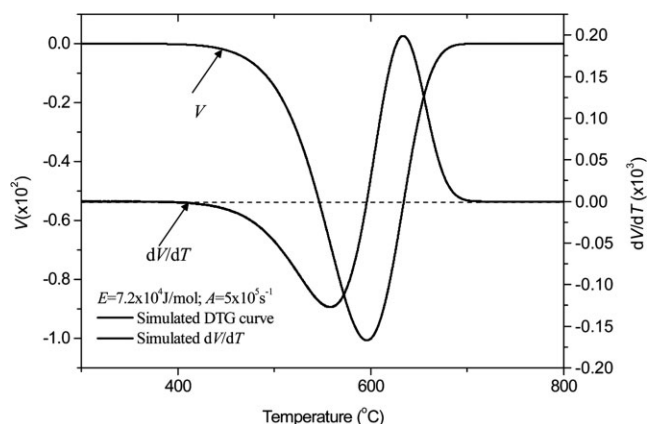
where  $V_1$  and  $V_2$  are obtained directly from the DTG data.

It is obvious that if the assumption of Moll method holds, the activation energy values can be easily evaluated by (3). When we vary the data set of  $(T_1, T_2)$  from lower temperatures to higher temperatures, we can even obtain the variation of the activation energy  $E$  with temperature, if  $E$  is not constant. However, from the above derivation, we can see that a hidden condition is implied in the assumption of Moll method, i.e., within the temperature interval between  $T_1$  and  $T_2$ , on the coordinate of temperature, the relative variation of  $V$  is higher than that of  $c^n$ , so that  $c_1^n \approx c_2^n$  while  $V_1$  and  $V_2$  have distinct difference. In mathematics, this hidden condition can be expressed as

$$\left| \frac{dV/dT}{V} \right| > \left| \frac{dc^n/dT}{c^n} \right| \quad (4)$$

From (2) we obtain

$$\frac{dV/dT}{V} = \frac{E}{RT^2} - \frac{A}{\beta} ne^{-E/RT} c^{n-1} \quad (5)$$



**Figure 1** Simulated curves of  $V$  and  $dV/dT$ , with  $E = 7.2 \times 10^4$  J/mol and  $A = 5 \times 10^5$  s<sup>-1</sup>.

In another aspect,

$$\left| \frac{dc^n/dT}{c^n} \right| = \frac{A}{\beta} ne^{-E/RT} c^{n-1} \quad (6)$$

For a general decomposition curve as shown in Figure 1, it is obvious that when  $T \geq T_{\max}$ , we have  $dV/dT \geq 0$ ,  $V < 0$ . Therefore, from (5) we obtain

$$\left| \frac{dV/dT}{V} \right| = \frac{A}{\beta} ne^{-E/RT} c^{n-1} - \frac{E}{RT^2} \quad (7)$$

Comparing (6) and (7) it is obvious that

$$\left| \frac{dV/dT}{V} \right| < \left| \frac{dc^n/dT}{c^n} \right| \quad (8)$$

Hence, we conclude that expression (4) does not hold when  $T \geq T_{\max}$ , and thus, Moll method is not suitable for the temperature range high than the peak temperature.

When  $T < T_{\max}$ , from Figure 1,  $dV/dT < 0$ ,  $V < 0$ . We have

$$\left| \frac{dV/dT}{V} \right| = \frac{E}{RT^2} - \frac{A}{\beta} ne^{-E/RT} c^{n-1} \quad (9)$$

So, when inequality (4) holds, we have

$$\frac{E}{RT^2} > \frac{2A}{\beta} ne^{-E/RT} c^{n-1} \quad (10)$$

Thus, it is concluded that (10) is a necessary condition for the use of Moll method when  $T < T_{\max}$ . However, for general variation range of decomposition temperatures and the activation energy of biomass materials, it can be easily verified that the above condition is very strict and cannot generally be satisfied.

Except for the above limitation, in the temperature interval of  $T < T_{\max}$  Moll method has other

difficulties in application. First,  $V$  has very low values within low temperatures, and thus, the data of  $V$  are generally highly “polluted” by data noise. Although Gaussian smoothing method is used, the error due to data fluctuation within low temperatures cannot be distinguished from kinetic signals. Therefore, the data of  $V_1$  and  $V_2$  may have great errors. Second, for the temperatures near the DTG peak, it is difficult to find two points with nearly the same values of  $c^n$ , because the  $V$  values there are generally very great. Finally, Moll method is very sensitive to the error of DTG data, not only within low temperatures. Here, we present an analysis on this sensitivity.

Assume  $V_2$  has an error of  $\varepsilon$ , for example,  $\varepsilon = 5\%$ , so the observed data  $V_2' = V_2(1+\varepsilon)$ . Assume  $V_1$  has no error. So

$$E' = R \frac{\ln(V_2'/V_1)}{1/T_1 - 1/T_2} = R \frac{\ln(V_2/V_1) + \ln(1+\varepsilon)}{1/T_1 - 1/T_2} \quad (11)$$

Hence

$$\frac{E' - E}{E} = \frac{\ln(1+\varepsilon)}{\ln(V_2/V_1)} \cong \frac{\varepsilon}{\ln(V_2/V_1)} \quad (12)$$

If it is expected that the error of the activation energy value is not enlarged due to the error of  $V_2$ , the following inequality should hold:

$$\left| \frac{E' - E}{E} \right| \cong \left| \frac{\varepsilon}{\ln(V_2/V_1)} \right| \leq \varepsilon \quad (13)$$

Therefore,  $V_2/V_1 \geq 2.7$  is required. However, because the two points have nearly the same values, this inequality does not hold in general. Hence, Moll method is highly sensitive to the error of DTG data.

In summary, for Moll method, only a narrow temperature interval can be used, with strict conditions (including inequality (10), and little data fluctuation and error of DTG curve) required. Therefore, it is not surprising that the method has not attracted wide application since it was proposed.

### Development of a new two-point data set kinetic method

With the above limitations of Moll method in mind, we tried to develop a new simple method that can be used to extract the kinetic parameters by one single heating rate data without any prior knowledge of reaction order  $n$ , with high reliability and wide temperature applicability. In what follows the basic idea underlying the new method is interpreted.

First, we address that Moll method has a good idea, i.e., trying to simplify the process of extracting the kinetic parameters by using constant (or nearly constant) items. Although, as indicated above, the

constant item (i.e.,  $c_1^n/c_2^n \approx 1$ ) suggested by Moll et al. is not so reasonable, the idea can be used in the present method development. In what follows, we try to use reasonable constant items for simplification of parameter extraction.

Second, we consider that the idea of using only a few data points (in Moll method only two points are used) for parameter extraction should be improved. As we know, any experimental data point obtained by thermogravimetry involves noises that arise from different sources, such as experimental random noises and buoyancy effect. With only a few data points used, the errors of these few points would affect the results in a great degree. In fact, we tried to use the experimental data to find data points suitable for Moll method, and then tried to get the kinetic parameters. However, we found this process is of high instability, and with different two-point data used, the parameters obtained vary significantly. Therefore, for the new method, we try to extract the kinetic parameters by regression calculation, which helps remove the effect of data noises by average effect.

With the above consideration in mind, we now begin to derive the new method.

For two points of decomposition, we have

$$\ln(-V_1) = \ln \frac{A}{\beta} - \frac{E}{RT_1} + n \ln c_1 \quad (14)$$

and

$$\ln(-V_2) = \ln \frac{A}{\beta} - \frac{E}{RT_2} + n \ln c_2 \quad (15)$$

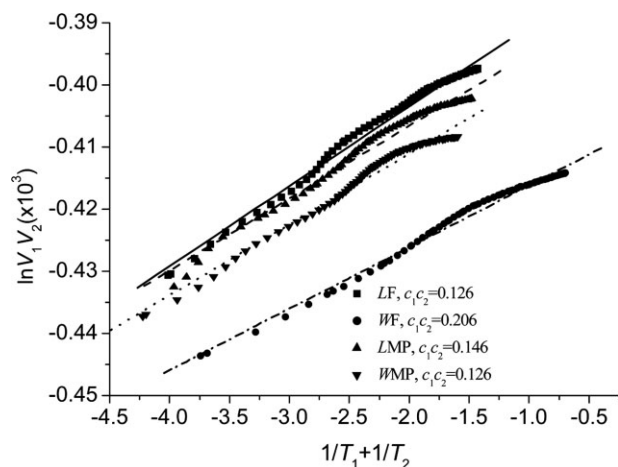
Subtracting (14) from (15) leads to a simple expression with elimination of the item involving the preexponential factor. It is just the famous Freeman and Carroll (FC) method. However, the difference processes of  $\ln(-V)$  and  $\ln c$  determine that the method may be greatly affected by the errors of  $V$ , and in most practical instances it was found that there is considerable difficulty in obtaining reliable values of kinetic parameters (including the reaction order  $n$ ) by the FC regression plot.

So, rather than using difference subtracting, we combine the above two expressions by addition:

$$\ln(V_1 V_2) = 2 \ln \frac{A}{\beta} - \frac{E}{R} \left( \frac{1}{T_1} + \frac{1}{T_2} \right) + n \ln c_1 c_2 \quad (16)$$

The major skill is that we select data points for which the values of  $c_1 c_2$  are kept constant. This idea of using constant items is same as that of Moll method. So, the regression plot of  $\ln(V_1 V_2)$  versus  $(1/T_1 + 1/T_2)$  should result in a straight line whose slope is  $-E/R$ , and the intercept is  $2 \ln A/\beta + n \ln c_1 c_2$ . Because the data sets of constant  $c_1 c_2$  are easy to be obtained from TG curve, and the regression does not





**Figure 2** The regression plots of  $\ln(V_1V_2)$  versus  $(1/T_1 + 1/T_2)$  for the first mass-loss steps of four biomass materials.

involve difference subtracting, the method is expected to hold high stability. We call the method as "Two-point Data Set Method." The method uses regression calculation in extracting kinetic parameters, and thus, removes the effect of the data errors by the average effect of regression. In addition, the method is applicable within wide temperature intervals.

Once the activation energy  $E$  is obtained, from (2)

$$\ln(-V) + E/RT = \ln(A/\beta) + n \ln c \quad (17)$$

the reaction order  $n$  and preexponential factor  $A$  can be calculated, respectively, from the slope and intercept terms of the regression plot of  $\ln(-V) + E/RT$  versus  $\ln c$ .

The method uses regression calculation in extracting kinetic parameters, and thus, removes the effect of the data errors by the average effect of regression. In addition, the method is applicable within wide temperature intervals.

### Application of new method in kinetic analysis of biomass materials decomposition

All samples subject to experiments in this work are found to give the same general shape for the TG-DTG curves. The evaporation of sorbed water occurring in the temperature range of 100–180°C constitutes an approximately 10% mass loss for all the leaf and wood samples. Following the water evaporation, the first major mass loss because of decomposition begins slowly and accelerates rapidly in the temperature range of 290–340°C. A second major mass loss follows the first one and reaches an overall mass loss of more than 90%. According to previous study by the authors,<sup>12</sup> the first DTG peak in air is largely due to the pyrolysis of hemicellulose and

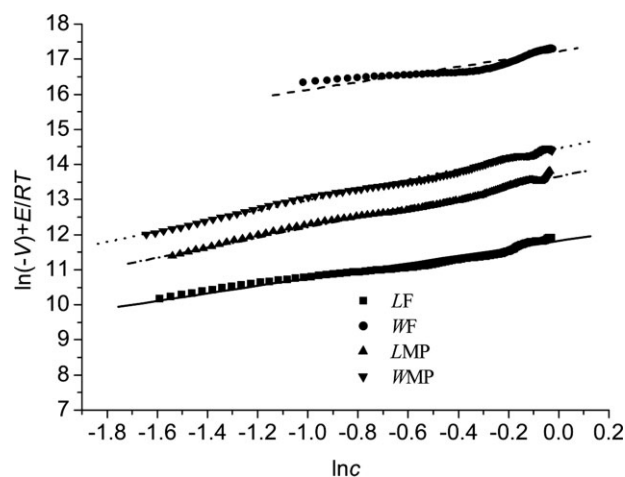
cellulose, and, in part, due to that of lignin, whereas the second DTG peak occurring at high temperatures is affected by oxidization in a considerable degree. Because of the complexity of the second reaction step, in this work, we only investigate the first step to examine the applicability of the two-point data set method.

The original experimental data (100 points/min, 10 K/min) were first extracted completely without any pretreatment. Generally, the data involved great noises with high-frequency fluctuations. Although a large number of smoothing algorithms have been developed ranging from polynomial algorithm to other techniques involving Fourier transformation and frequency filtering, the selection of smoothing parameters is always a difficult problem, because in theory there is always a tradeoff between the smoothing degree and the level of data fitting. In the previous work of the authors,<sup>13</sup> a systematic investigation on smoothing of decomposition data was presented and Gaussian algorithm was recommended for use. In the present work, we used Gaussian smoothing method to get TG and DTG data for analysis.

The temperature corresponding to the minimum of the first DTG peak is regarded as the separation point between the first mass-loss stage and the second. In this way the initial and residue solid mass fractions can be definitely determined.

The constant of  $c_1c_2$  is determined by the lower and upper limits of the TG data used for investigation. Some data within the lower and higher edge temperature intervals are not used for regression, because the corresponding DTG data involve great errors.

For example, for the leaf of fir, the range of  $c$  data used is 0.13 ~ 0.97, so for  $c_1$  varying within this range, the constant  $c_1c_2$  is determined to be 0.126 or so, so that  $c_2$  also varies within this range.



**Figure 3** The regression plots of  $\ln(c)$  versus  $\ln(-V) + E/RT$  for the first mass-loss steps of four biomass materials.

TABLE II  
Kinetic Parameters by Different Methods for Biomass Materials Samples in Air

Sample	Coats-Redfern method ( $n = 1$ )			Differential method ( $n = 1$ )			Two-point data set method				
	$E_I$	$\ln A_I$	$r_I$	$E_D$	$\ln A_D$	$r_D$	$E^*$	$r_1^*$	$\ln A^*$	$n^*$	$r_2^*$
LF	75.2	13.6	0.998	72.5	16.9	0.996	76.8	0.989	14.1	1.07	0.960
WF	95.6	18.5	0.998	95.8	22.5	0.990	99.6	0.988	19.5	1.10	0.846
LMP	72.9	13.2	0.999	66.8	15.8	0.992	84.1	0.978	16.0	1.45	0.986
WMP	78.5	14.8	0.995	68.8	16.5	0.988	86.0	0.982	16.8	1.47	0.994

The subscripts "I" and "D" represent the kinetic parameters, respectively, by integral and differential methods. The superscript "\*" represents the kinetic parameters by the proposed two-point set method.  $r_1$  represents the correlation coefficient of the regression plots of  $\ln(V_1V_2)$  versus  $(1/T_1+1/T_2)$  (Fig. 2), and  $r_2$  represents that of the regression plots of  $\ln(-V)$  versus  $\ln(-V)+E/RT$  (Fig. 3).

In previous research,<sup>12</sup> it has been indicated by integral method that the first step of biomass decomposition can be modeled by first-order reaction model function. Therefore, in the present work, we use the Coats-Refern integral method with condition of  $n = 1$  as a reference to testify the applicability of the two-point data set method. The regression expression of Coats-Redfern method with  $n = 1$  is

$$\ln\left[\frac{-\ln c}{T^2}\right] = \ln\frac{AR}{\beta E}\left[1 - \frac{2RT}{E}\right] - \frac{E}{RT} \quad (18)$$

In addition, with  $n = 1$ , we can determine the kinetic parameters by the following differential expression from (17):

$$\ln(-V/c) = \ln(A/\beta) - E/RT \quad (19)$$

By this expression, we can also obtain the kinetic parameters. The results, thus, obtained can be compared with those obtained by two-point data set method (as shown in Figures 2 and 3), to test the applicability of the method.

Table II presents the kinetic parameters by the above integral and differential methods as well as those by the two-point data set method. The results show that the plots of (16) and (17) both lead to high correlation coefficients. It can be seen that the integral method and differential method both lead to high correlation coefficients with good agreement, showing the decomposition of the first step can be modeled by first-order reaction. The agreement between the results by the new method with those by the integral and differential methods is fairly good. The reaction order values of the leaf and wood of masson pine differ from unity, maybe due to the effect of errors involved in DTG data. The difference of the results might be due to the addition process, because, as can be thought, if the two regression curves such as (14) and (15) are not so straight, the addition of the two curves would have higher curvature, leading to higher difference. It should be addressed for decomposition of polymers

with high chemical complexity, the reaction order has only apparent significance, so a fraction reaction order may also be reasonable.

## CONCLUSION

Moll method can extract activation energy by two data points, however, with high instability in practical application. A critical analysis is conducted on this limitation and it is found that Moll method can only be used for a narrow temperature interval with strict conditions. A new two-point data set method is proposed, for which a set of two-point data, the product of the mass fractions of the two points being kept constant, is subject to regression calculation to achieve an accurate estimation of activation energy, without any prior knowledge of reaction order. With activation energy obtained, the preexponential factor and reaction order can be achieved by differential regression equation.

The comparison of the results by the new method with those by integral and differential methods indicates that the method can be used in extracting the kinetic parameters of biomass materials decomposition. The difference of the results might be due to the addition process. The method can be used in the kinetic formulation of the smoldering combustion as well as the behavior of the interior of the bulk samples in fire, where heating rates are comparable with that used in this work.

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