Journal of Thermal Analysis and Calorimetry, Vol. 78 (2004) 1029–1041

SMOOTHING AND DIFFERENTIATION OF THERMOGRAVIMETRIC DATA OF BIOMASS MATERIALS

H. X. Chen[1], *N. A. Liu* [2*], *L. F. Shu*[3] *and R. W. Zong*[1]

[1]State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China
[2]State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China; Center for Public Safety Research and Department of Engineering Mechanics, Tsinghua University, Beijing 100084, P. R. China
[3]Research Institute of Forest Ecology, Environment and Protection, Chinese Academy of Forestry, Wanshou Shan, Beijing 100091, People's Republic of China

(Received November 23, 2003; in revised form February 7, 2004)

Abstract

Due to the experimental errors, the chemical effect of minor reactions, and some physical effects of heat and mass transfer, there usually exists much noise in the mass loss data resulted from thermal decomposition experiments, and thus high quality smoothing algorithm plays an important role in obtaining reliable derivative thermogravimetric (DTG) curves required for differential kinetic analysis. In this paper three smoothing methods, i.e. Moving Average smoothing, Gaussian smoothing, and Vondrak smoothing, are investigated in detail for pre-treatment of biomass decomposition data to obtain the DTG curves, and the smoothing results are compared. It is concluded that by choosing reasonable smoothing parameters based on the spectrum analysis of the data, the Gaussian smoothing and Vondrak smoothing can be reliably used to obtain DTG curves. The kinetic parameters calculated from the original TG curves and smoothed DTG curves have excellent agreement, and thus the Gaussian and Vondrak smoothing algorithms can be used directly and accurately in kinetic analysis.

Keywords: average smoothing, biomass, decomposition, Gaussian method, smoothing, Vondrak method

Introduction

Smoothing algorithm plays a basic and important role in the treatment of thermogravimetric curve. During the past several decades, dynamic thermogravimetry has been widely used in the fields such as fuel property, fire research, fabric flammability, waste incineration etc., to study the solid phase decomposition kinetics [1–6]. Generally, the solid phase thermal decomposition can be expressed by the equation

* Author for correspondence: E-mail: liunai@ustc.edu.cn

1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

$$A(solid) \rightarrow B(solid) + C(gas)$$

The irreversibility is promised by the condition of well-controlled air steam, which carries the volatile away as soon as it forms, so that the reverse reaction would not occur. For dynamic thermogravimetry, the calculation of kinetic parameters is based on the assumption that the mass loss due to the reaction can be described by the following rate equation:

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

where α is the mass loss fraction, β the heating rate, E the activation energy, A the pre-exponential factor, and R the gas constant. T is the absolute temperature. The specific form of $f(\alpha)$ represents the hypothetical model of the reaction mechanism. Published methods of deriving kinetic parameters from thermogravimetric (TG) data center about Eq. (1) itself or its integral form, respectively referred to as differential and integral methods. Upon using differential methods (e.g. Kissinger [7], Freeman–Carroll [8]), the derivative thermogravimetric (DTG) curve used for analysis is achieved by the differentiation of TG data *vs.* temperature. Due to the chemical complexity of the decomposition reaction and the experiment errors, the TG curve contains much noise and when calculating the DTG curve the noise can be enlarged greatly due to numerical differentiation. Hence, for any differential analysis method, reasonable smoothing algorithm is required to free the data from their short-term instability in order to provide improved representations of TG and DTG curves.

In mathematics, there have been wide varieties of smoothing algorithms ranging from polynomial algorithm to other techniques involving Fourier transformation and frequency filtering. However, few discussions have been proposed in literature to investigate the different smoothing algorithms used for thermogravimetric data. In Sbirrazzuoli's paper [9], the convolution method using a polynomial with intervals of seven successive points was applied in data smoothing. Várhegyi and Till [10] employed spline smoothing method to smooth and differentiate high pressure TG data. They also suggested that the Savitzky–Golay [11] method can be used to deal with the data of thermogravimetry–mass spectrometry. In principle, the smoothing and fitting performances of DTG curve are both of basic importance for the accuracy of differential kinetic analysis. However, few discussions can be found in literature concerning the smoothing parameter selection aiming at achieving optimum smoothing and fitting performances of DTG curve.

In this paper, three smoothing techniques (Moving Average smoothing, Gaussian smoothing, and Vondrak smoothing) are used in the investigation of TG and DTG curves of biomass decomposition and the smoothing qualities of them are compared in detail. This work is carried out as a part of a study on the decomposition behavior of biomass in fire [12, 13]. Although the overall mass losses of biomass decomposition are controlled by some primary reactions, rate-determining reactions are accompanied by many other less important reactions (in the sense that they contribute little to the mass loss). Hence, the great noise and flutter on the achieved TG curves are in great degree due to these less important reactions. This chemical complexity has led researchers to study biomass decomposition by apparent kinetic analysis, which has been looked on as offering a clue to

the key mechanistic steps in the overall mass loss process. Reliable smoothing algorithm actually plays a basic role in the pretreatment of the TG curves for apparent differential kinetic analysis.

Methodology

Moving average smoothing (mean filter smoothing)

For a series of equally spaced data sampled from TG curves, moving average smoothing simply takes the mean values of all data points within a small specified window as the new value of the middle point within the window, as described by the following general expression:

$$\alpha'(T_j) = \sum_{k=-n}^{n} c_k \alpha(T_{j+k}) \tag{2}$$

where α' is the smoothed data of α, $c_k \equiv 1/(2n+1)$. The index j is the running index of the original ordinate data table. The smoothing array consists of $2n+1$ points, where n is the half-width of the smoothing window. When the smoothing window moves on until the end temperature, the obtained data of $\alpha'(T)$ make up of the whole smoothed TG curve. Until now, moving average smoothing (mean filter smoothing) is almost the simplest algorithm for noise reduction.

Savitzky–Golay [11] smoothing can be thought of as a generalized moving average, since it can also be described by the general expression Eq. (2), but with different mass coefficients compared with the above simplest average procedure. The idea of Savitzky–Golay filtering is to approximate the underlying function within the moving window not by a constant (whose estimate is the average), but by a polynomial of higher order, typically quadratic or quartic. In other words, the Savitzky–Golay smoothing essentially performs a local polynomial regression to determine the smoothed value for each data point. This method is superior to simple adjacent averaging because it tends to preserve features of the data such as peak height and width, which are usually 'washed out' by adjacent averaging. Nevertheless, this paper only examines the simplest moving average smoothing and compares it with the Gaussian and Vondrak smoothing methods. As will be stated later, the theoretical transfer functions of the three methods can all be expressed explicitly. In what follows the so-called 'moving average smoothing' denotes the simplest average method. The application of Savitzky–Golay smoothing algorithm in the pre-treatment of decomposition data will be investigated in our future paper.

Gaussian smoothing

For Gaussian smoothing

$$\alpha'(T_j) = \frac{1}{W_j} \sum_{i=1}^{N} p_i \alpha(T_i) \exp[-(T_j - T_i)^2 / 2a^2] \tag{3}$$

where $W_j = \sum_{i=1}^{N} p_i \exp[-(T_j - T_i)^2/2a^2]$, p_i and N are, respectively, the mass and number of experimental data, a is the semi-bandwidth of the Gaussian function. Generally the biomass decomposition data can be looked on as being of equal weights. Obviously this smoothing algorithm is in essence a weighed average of experimental thermogravimetric data using the Gaussian function as the weight function. The degree of smoothing is determined by *a,* and when *a* increases, the smoothing quality also increases. Compared with moving average smoothing, Gaussian smoothing can be used to smooth the points at the two boundaries of the temperature intervals examined, and also it does not require the points to be equally spaced.

Vondrak smoothing

The Vondrak smoothing method can also be used to smooth unequally spaced data. It minimizes the quantity

$$Q = F + \varepsilon S \tag{4}$$

where $F = \sum_{i=1}^{N} p_i [\alpha'(T_i) - \alpha(T_i)]^2$, $S = \sum_{i=1}^{N-3} [\Delta^3 \alpha'(T_i)]^2$. F is the objective function of the weighed least square method, and is referred to as the degree of fitting of Vondrak smoothing. S is the sum of squares of the third-order difference of smoothed data. This term reflects the degree of smoothing and is called the smoothness of Vondrak. The smoothed curve is a compromise between the absolute fitting curve (where $\varepsilon \to 0$) and the absolute smoothed curve (where $\varepsilon \to \infty$). The degree of compromise is thus determined by ε.

Frequency filtering

The noises we wish to filter out generally vary greatly in short temperature intervals. In the frequency domain, these noises correspond to high frequency components. Theoretically if we filter out these components using low-band filters, the curve with noises will be smoothed. In this sense, the methods for the removal of noise are also often called frequency filters.

In fact the three smoothing techniques stated above can be characterized as such frequency filters. Generally, any linear filtering process can be expressed as a convolution of the raw data with an appropriate shaped window which corresponds to the transfer function in frequency domain. For moving average smoothing method, by assuming that the measurements are equally spaced and weighed, the theoretical transfer function is

$$H(f) = \frac{1}{2n+1} \frac{\sin(2n+1)\pi f\Delta}{\sin \pi f\Delta} \tag{5}$$

where f is the frequency, Δ is the sample interval.

The transfer function corresponding to Gaussian smoothing (for equally spaced and weighted measurements) is

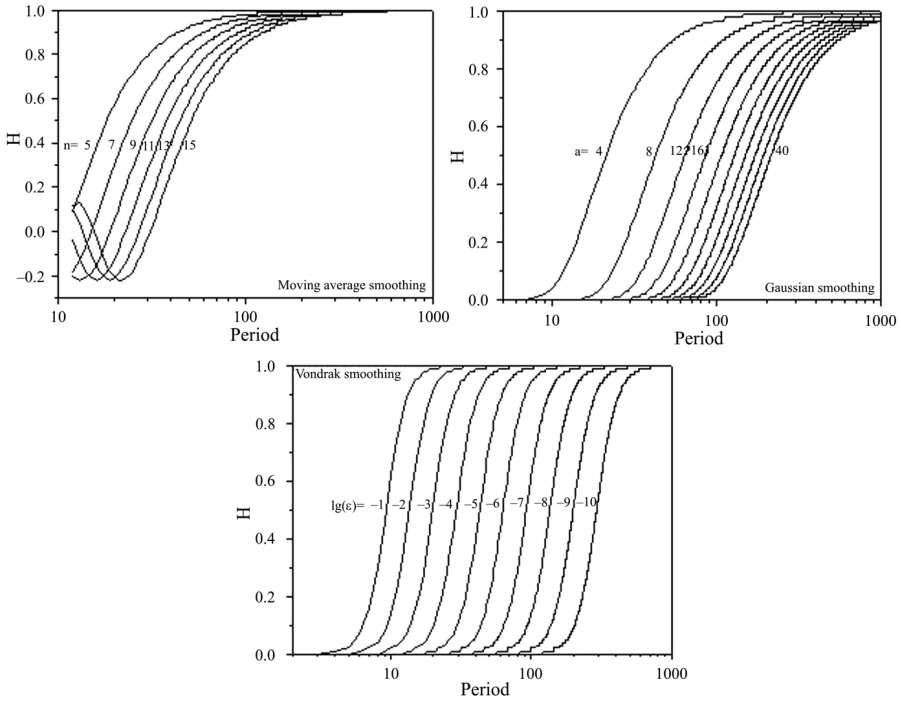

Fig. 1 Transfer functions of moving average, Gaussian and Vondrak smoothing methods

$$H(a,f)=\exp(-2\pi^2 f^2 a^2) \tag{6}$$

and that corresponding to the Vondrak smoothing is

$$H(\varepsilon,f)=(1+\varepsilon^{-1}(2\pi f)^6)^{-1} \tag{7}$$

For any filtering method, if the transfer function has a sharp transition band during a short frequency interval, it is naturally easy to realize a reasonable simulation to theoretical low-band or high-band filtering, and thus achieve high smoothing ability. In this sense, as implied in Fig. 1, the Vondrak method may achieve better smoothing compared with the other two methods.

Experimental

The raw materials used in the investigation were respectively the wood and leaf of oil-tea, loquat, camphor tree. These materials were first cut and then ground, thereby the average particle size was specified to be approximately 100 μm. The grains of the sample were evenly distributed over the open alumina crucible of 5 mm diameter, loosely, with the initial amounts of the samples all kept to be 5 mg or so. The depth of the sample layer filled in

the crucible was about 0.5 mm. Thermal decomposition was observed in terms of the overall mass loss and heat of DSC signal by using a Netzsch STA 409C Thermobalance. An air stream was continuously passed into the furnace at a flow rate of 50 mL min^{-1} (at normal temperature and atmospheric pressure). The temperature was increased to 800°C at a rate of 5 K min^{-1}. The heating rate of this order is generally considered able to ensure that no temperature gap exists between the sample and its surroundings [14].

Results and discussion

In each experiment, a thermogravimetric (TG) curve and a differential scanning calorimetry (DSC) curve were obtained. From Fig. 2 it can be seen that the DTG curve obtained directly through the differentiation of the raw TG curve fluctuates greatly. These fluctuant data are difficult to be used in kinetic analysis. Theoretically, the DTG and DSC curves have similar variation trend since the mass loss process is generally accompanied by heat release or absorption. This feature can be identified in Fig. 2. All the experimental data obtained in this work were subject to the three smoothing algorithms. The example to be presented corresponds to the experimental data with relatively high noise level, using which we can examine the smoothing power of the methods extensively.

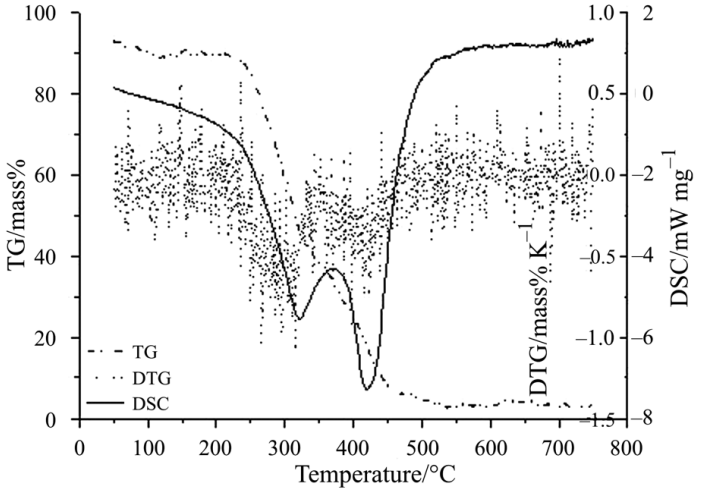

Fig. 2 Experimental decomposition curves for oil-tea wood samples in air at a heating rate of 5°C min^{-1}

The choice of smoothing parameters

The parameters of a and ε determine the degree of smoothing and should be chosen according to feature of the raw data, using the transfer functions. Generally, we can first evaluate the cutoff frequency f_c by power spectrum analysis, and then use the transfer function to determine the smoothing parameters. In principle, the purpose of filtering is to remove the noise components whose frequencies are higher than f_c. Hence, by com-

bining with f_c, we calculate the smoothing parameters by setting the transfer functions close to zero. In this way, the noise components with frequencies higher than f_c are completely removed, and those with frequencies within the transition region of the transfer function are partly removed, and other components are completely preserved.

Figure 3 indicates that the power spectrum density (PSD) of the decomposition data distributes within a short frequency domain. When f>0.025, the value of PSD is close to zero. We assume that the noise level is much lower than the level of kinetic signals. Hence we can use frequencies around f=0.025 as the estimations of the cutoff frequency. Overhigh estimation of cutoff frequency may induce that some noise components cannot be removed as expected. In the following examples, we use 38 as cutoff period, and so according to the transfer functions, the parameters of a=18 and $\varepsilon=10^{-7}$ are used, respectively, for Gaussian and Vondrak smoothing.

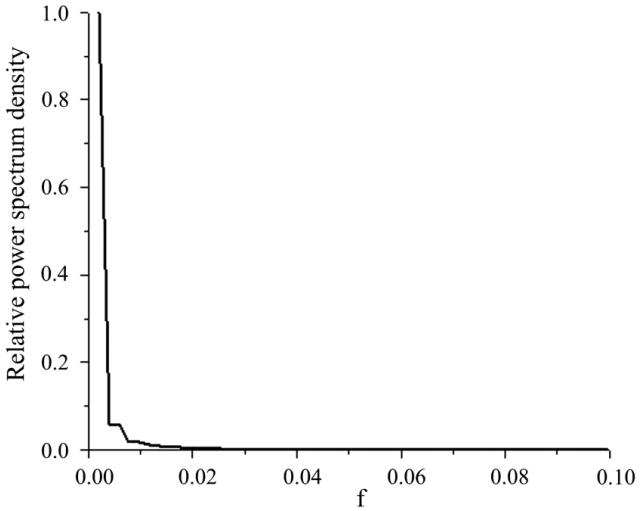

Fig. 3 Relative power spectrum density of original TG data for oil-tea wood samples decomposed in air at a heating rate of 5°C min^{-1}

Smoothing results and comparison

Figure 4 shows the original and smoothed TG curves and the corresponding DTG curves by first-order forward difference of TG data. For moving average smoothing, we vary the window width and find that the method can generally filter out extremely high components, but the local smoothing degree is not satisfactory. Figure 4a indicates that although the contour of two DTG peaks resulted from smoothing and differentiation of TG data can be observed to have almost the same variation trend as that of the DSC curve, the obtained DTG data still involve much noise and are difficult to be used in differential kinetic analysis.

The Gaussian and Vondrak smoothing methods can be compared by the parameters of a=18 and $\varepsilon=10^{-7}$, respectively, since the parameters are resulted from a constant cutoff frequency as stated above. Comparing the two methods in Fig. 5, we can see that the two

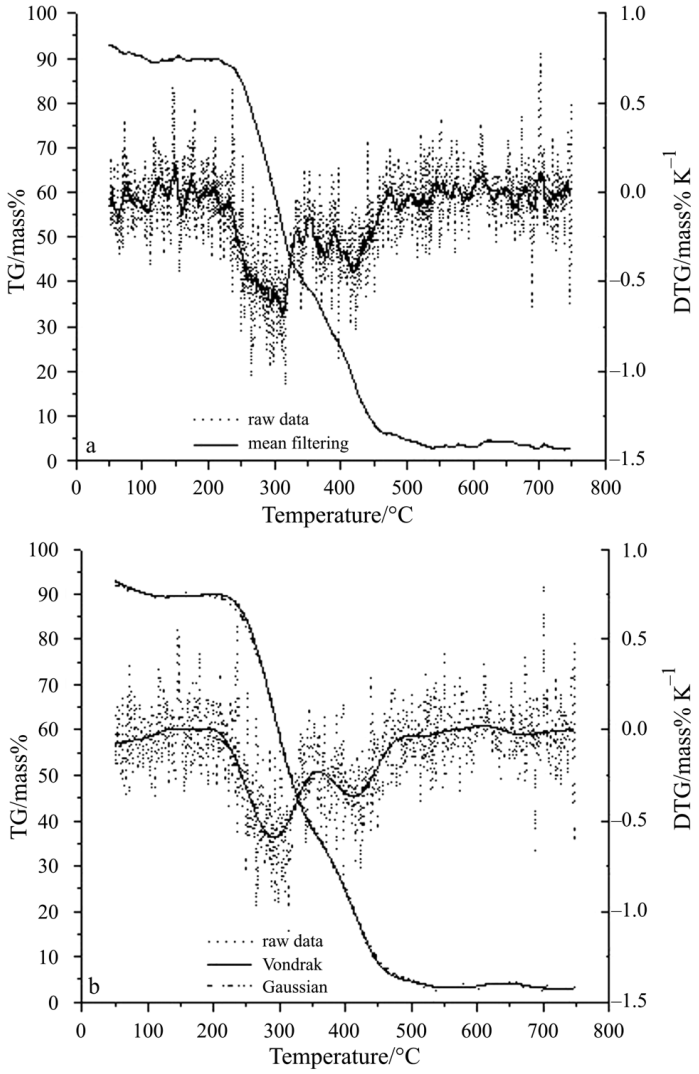

Fig. 4 The original and smoothed TG/DTG curves for the oil-tea wood samples decomposed in air at a heating rate of 5°C min^{-1}.
a – mean, N=5; b – Gaussian a=18; Vondrak $\varepsilon=10^{-7}$

DTG peaks resulted from the Gaussian method are not distinct like those from Vondrak method, while the ratios of the width of half height to the height of the two peaks are higher than those in the Vondrak smoothing result. The resolution quality of DTG peak is very important for peak separation. In our previous work [13], a simple kinetic description, named as 'First Order Pseudo Bi-component Separate-stage Model (PBSM-O1)', was developed based on the experimental results and integral analysis method. Differential methods are expected to be used to verify the model, for which the smoothing degree

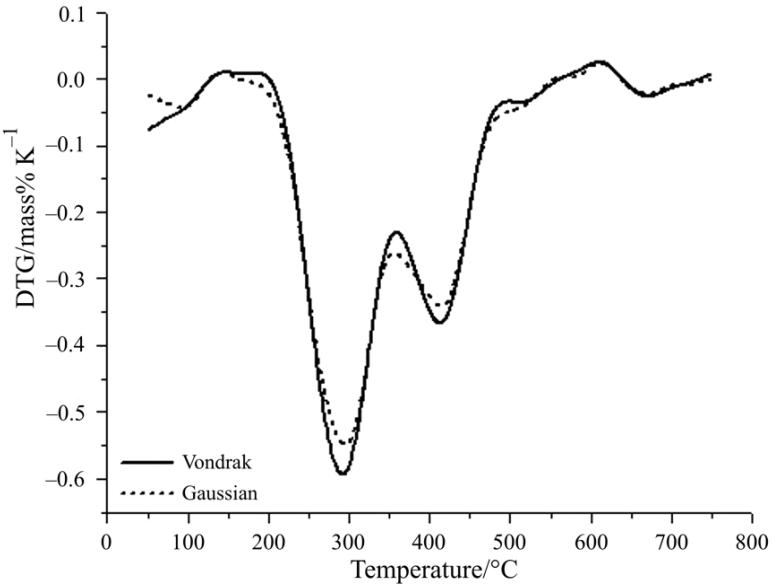

Fig. 5 Comparison of the smoothed DTG curves for the oil-tea wood samples decomposed in air at a heating rate of 5°C min^{-1}. Gaussian, a=18; Vondrak, ε=10^{-7}

of DTG curve and especially the quality of DTG peaks are of great importance. In this sense, the Vondrak smoothing method has advantage over Gaussian algorithm.

Evaluating the methods using simulated curves

In order to get more detailed knowledge, we use simulation to evaluate the methods. The general accepted integral form of non-isothermal kinetic data

$$g(\alpha)=\int_{o}^{\alpha}\frac{d\alpha}{f(\alpha)}=\int_{T_0}^{T}\frac{A}{\beta}\exp(-E/RT)dT\approx(AE/\beta R)P(u)$$

with (8)

$$P(u)=\int_{\infty}^{u}-(e^{-u}/u^2)du, u=E/RT$$

and first order reaction mechanism $f(\alpha)=1-\alpha$ are used.

Rational approximation [15] is used here to evaluate the value of $P(u)$:

$$P(u)=\frac{e^{-u}}{u}\frac{u^3+18u^2+86u+96}{u^4+20u^3+120u^2+240u+120} \quad (9)$$

The simulated TG curve is used to obtain the simulated DTG curve by numerical differentiation. A normal noise (mean value equals zero and standard variation is 1) is added to the simulated TG curve to generate noisy curve. Then Gaussian and Vondrak

methods are used to smooth the curve, and then obtain the DTG curves by numerical differentiation. Figure 6 shows the application of the two methods for the smoothing and differentiation of the simulated noisy TG curve with different smoothing parameters. It is obvious that the DTG curves tend to become smooth with the increase of a or the decrease of ε, while the peaks turn to become broaden and shorten. In Fig. 6a, the smoothing result with a=5 is almost identical with the simulated DTG curve within the peak domain, however, there still have great variations near the beginning and the end of the data series. When the value of a increases, these variations decrease gradually, while the peak begins to become broaden and shorten. The similar tendency exists in the Fig. 6b.

There is some understanding of the great variations near the beginning and the end. For the TG data, the kinetic signals excluding noises generally vary quite slowly during the lower and higher ends of the temperature interval, and hence are easy to be 'polluted' by local noises. In fact, the noises during these ranges may vary with nearly the same order as

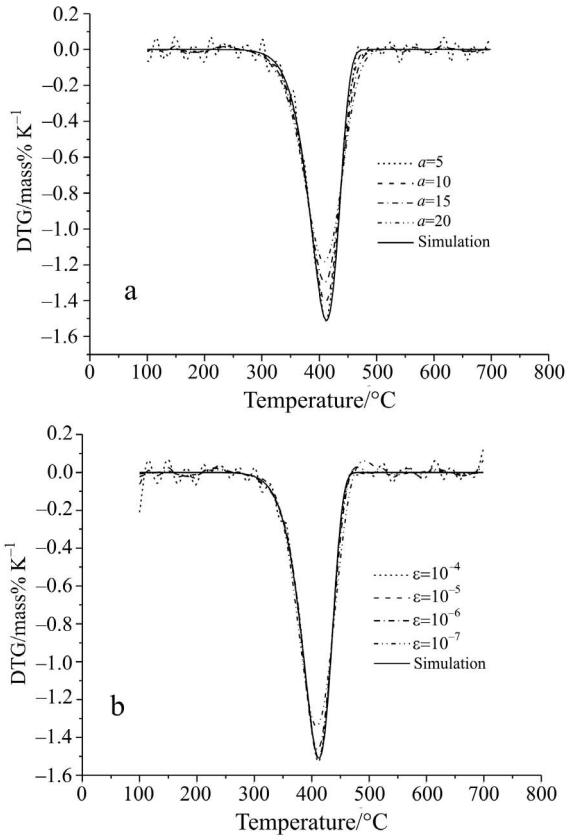

Fig. 6 DTG curves from the smoothed and simulated TG curve with normal noise by numerical differentiation. The different parameters are applied to smooth the TG curve with noise. E=150 kJ mol^{-1}, A=10^{11} min^{-1}, β=10°C min^{-1}
a – Gaussian smothing; b – Vondrak Smothing

the kinetic signals, and additionally, since the noises are generally of various frequencies, the DTG curve by the numerical differentiation of TG data is inevitably affected by the noise. There also exist some spurious variations occurring at the beginning and the end which are due to the smoothing method itself. The so-called end effect of the two methods is illustrated by Feissel [16]. The Vondrak method shows the end effect more seriously than Gaussian method, which in some extreme cases could be a severe drawback.

So a compromise must be found between the removal of the great variations near the two ends and the distortion in the peak domain. As for the smoothing of the simulated TG curve with normal noise, we can choose a =10–15 and $\varepsilon = 10^{-5}$–10^{-6}. We can see that the curve with a=5 and the one with $\varepsilon = 10^{-5}$ in Fig. 6 are close to the simulated DTG curve within the peak domain, but the first curve has more serious variations near the beginning and the end than the second. In this sense, Vondrak method with suitable parameter may be better than Gaussian method. As for the experimental TG curve, it has various noises, arising from experimental errors, secondary reactions, and physical transport effects, which are more complex than normal noise. We must choose a higher value of a and lower value of ε to smooth the TG curve to suppress these noises. According to the PSD, Gaussian method with a=18 and Vondrak method with $\varepsilon = 10^{-7}$ are used to smooth TG curves for the oil-tea wood samples, as presented in Fig. 4. These values of the parameter a and ε are also validated here.

Verification of the smoothing methods

Kinetic parameters of the biomass decomposition are computed to test the usefulness of the smoothing methods. First we use the integral Coats–Redfern method [17] (in the kinetic scheme of PBSM-O1) to analyze the original TG data, then use the differential method [18] to analyze the smoothed DTG data. Table 1 gives the kinetic parameters of oil-tea wood samples decomposed in air at a heating rate of 5°C min^{-1} and Fig. 7 gives

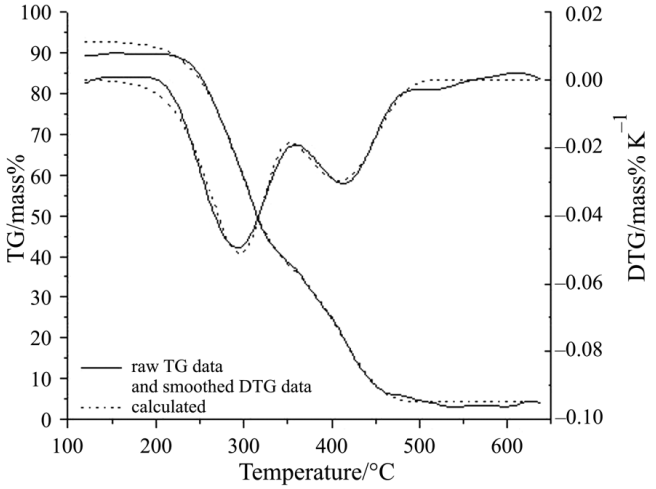

Fig. 7 Comparison of the experimental and calculated TG-DTG curves for the oil-tea wood samples decomposed in air at a heating rate of 5°C min^{-1}

Table 1. Kinetic parameters for the mass loss of the oil-tea wood samples by PBSM-01

	E_1/ kJ mol^{-1}	A_1/min^{-1}	E_2/ kJ mol^{-1}	A_2/min^{-1}
TG	74	$1.74 \cdot 10^4$	88	$1.02 \cdot 10^4$
DTG	80	$6.31 \cdot 10^4$	82	$3.16 \cdot 10^3$

the calculated curves. The results show that the two group parameters have good coincidence and the experimental and calculated curves have excellent agreement. So the smoothed curves can be used directly and accurately in the kinetic analysis.

Conclusions

Smoothing helps 'clean up' noisy information from raw data in order to make the data easy for human interpretation. When smoothing is performed to eliminate the measurements noise, the choice of the appropriate degree of roughness should take into account the spectrum of the quantity measured as well as the error spectrum of the measurements. The fluctuations in the decomposition data are attributed to different sources including the experimental noises, secondary reactions, and physical transport effects, and so are difficult to be avoided simply by using as low as possible sample masses. Since the noises can induce high fluctuations in the DTG curve due to numerical differentiation calculation, smoothing is of basic importance for differential thermal analysis.

In this paper three smoothing methods, i.e. moving average smoothing, Gaussian smoothing, and Vondrak smoothing, are investigated in detail for pre-treatment of biomass decomposition data to obtain the DTG curves. By choosing reasonable smoothing parameters based on the spectrum analysis of the data, the Gaussian smoothing and Vondrak smoothing can be reliably used to obtain DTG curves. The kinetic parameters calculated from the original TG curves and smoothed DTG curves have excellent agreement, indicating that both the Gaussian and Vondrak smoothing algorithms can achieve kinetic parameters with enough accuracy.

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This work was sponsored by National Natural Science Foundation of China under Grants 50346038 and 50323005, the China NKBRSF project (No. 2001CB409600), the Anhui Excellent Youth Scientist Fundation (2004–2005), the Specialized Research Fund for the Doctoral Program of Higher Education and the National Key Technologies R&D Programme (2001BA510B09-03).

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