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Smoothing and Differential of Thermogravimetric Data

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Abstract: High quality data smoothing is frequently required in the 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, 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.

Key words: TG; DTG; smoothing; Vondrak method; Gaussian method; average smoothing; filtering

0 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. Generally, the solid phase thermal decomposition can be expressed by the equation

$$A(\text{solid}) \rightarrow B(\text{solid}) + C(\text{gas})$$

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:

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

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 Equation (1) itself or its integral form, respectively referred to as *differential* and *integral* methods. Upon using *differential methods* (e. g. Kissinger [1], Freeman-Carroll [2]), derivative thermogravimetric (DTG) curve used for analysis is achieved by the differentiation of TG data versus 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 numeri-

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cal differentiation. Hence, for thermogravimetric curve, 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 N. Sbirrazzuoli's[3] paper, the convolution method applied used a polynomial with intervals of seven successive points. Gabor Varhegyi[4] compared the experimental data to the values calculated from their neighboring points by third-order polynomial interpolation. Their results were just acceptable. 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[5~6]. 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 plays a basic role in the pretreatment of the TG curves for apparent kinetic analysis.

1 Methodology

1.1 Moving Average Smoothing (Mean Filter Smoothing)

For a series of equally spaced data sampled from TG curves $\alpha(T_i)$ $(i = 1 \sim N)$, 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 expression:

$$\alpha'(T_j) = \frac{1}{2n+1}\sum_{k=-n}^{n}\alpha(T_{j-k}) \qquad (2)$$

where α is the original data, α' is the smoothed data. 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 from low temperature to high temperature, the obtained data $\alpha'(T)$ make up of the smoothed thermogravimetric curve.

Another average smoothing method is Savitzky-Golay [7] smoothing method. This method uses simplified least-square-fit convolution for smoothing and the result is better than that of mean filter smoothing. Its weight coefficients are different from those of mean filter smoothing, but the smoothing theorem is the same. Here we just use mean filter smoothing to represent this sort of methods, for its transfer function can be expressed explicitly.

1.2 Gaussian Smoothing

For Gaussian smoothing

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

where $W_j = \sum_{i=1}^{n} p_i\exp[-(T_j - T_i)^2/2a^2]$, p_i and N are respectively the weight and number of experimental data, a is the semi-bandwidth of the Gaussian function. Obviously this smoothing algorithm is in essence a weighted 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 doesn't require the points to be equally spaced.

1.3 Vondrak Smoothing

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

$$Q = F + \varepsilon S \qquad (4)$$

where $F = \sum_{i=1}^{N} p_i[\alpha'(T_i) - \alpha(T_i)]^2$, $S = \sum_{i=1}^{N-3} [\Delta^3\alpha'(T_i) - \alpha(T_i)]^2$. F is the objective function of the weighted 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 $\varepsilon \rightarrow 0$) and the absolute smoothed curve (where $\varepsilon \rightarrow \infty$). The degree of compromise is determined by ε.

1.4 Frequency Filtering

The noises we wish to filter out change greatly in short temperature intervals. In the frequency domain, these noises correspond to high frequency components. Theoretically if we can filter out these components using low-band filters, the curve with noises will be smoothed.

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 appropriated shaped window, or transfer function. Assuming equally spaced and weighted measurements, the theoretical transfer function corresponding to the mean filter smoothing method is

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

the one corresponding to the Gaussian smoothing is

$$H(\alpha, f) = \exp(-w\pi^2 f^2 \alpha^2)$$

and the one corresponding to the Vondrak method is

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

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

The quality of digital filters depends on the broadness of transitional band of the frequency transfer function. From the figures of transfer functions (Figure1), it can be noticed that while none of the method provides a sharp frequency cutoff, the Vondrak method has a steeper behavior as a frequency filter than the

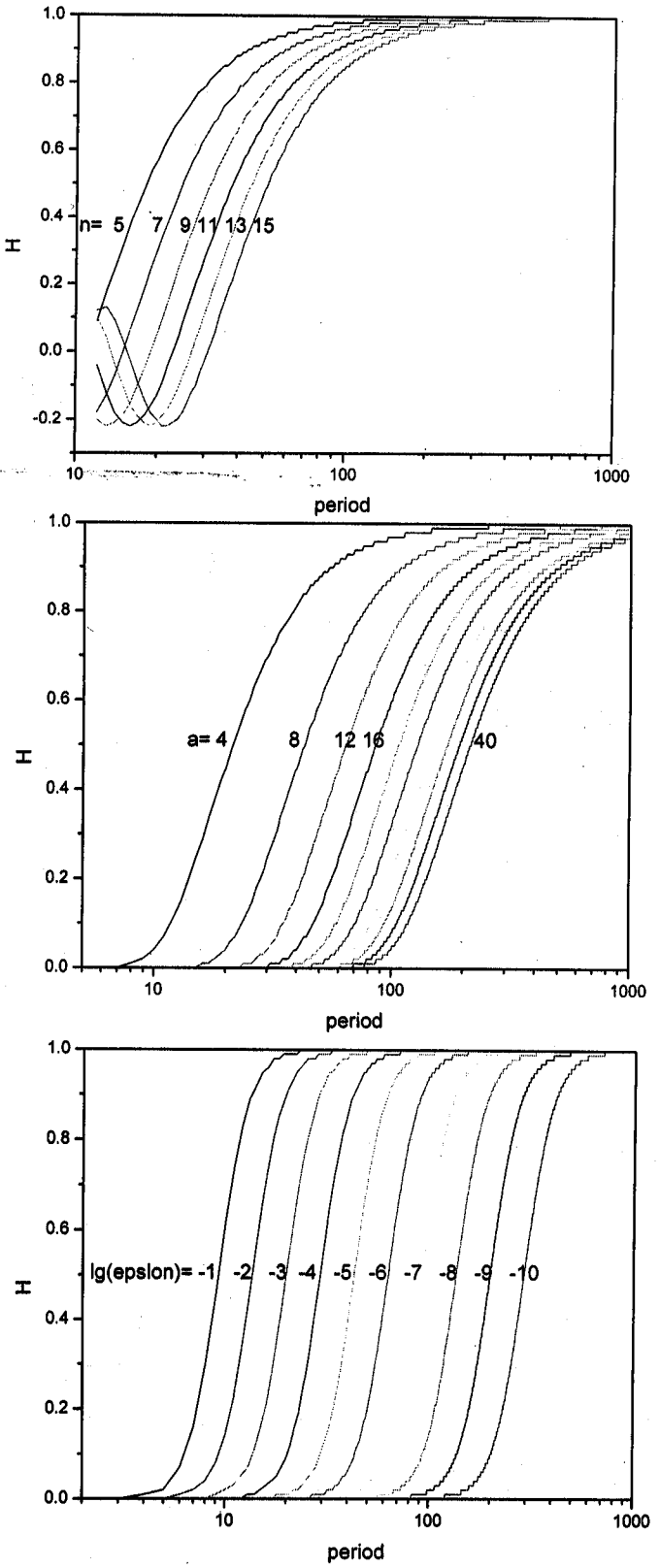

Fig. 1 Transfer functions of average, Gaussian and Vondrak smoothing

other two methods.

2 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 10 °C 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 [8].

3 Discussion

In each of our experiments, a thermogravimetric (TG) curve and a differential scanning calorimetry (DSC) curve can be obtained. The derivative thermogravimetric (DTG) curve is the differential of the TG curve.

Figure 2 shows the DTG curve. It can be seen that the DTG curve got directly through the differentiation of the TG raw curve flutters greatly. These fluctuant data are difficult to use in the kinetic analysis. Theoretically, the shapes of the DTG and DSC curve are similar if the mass loss process accompanies with heat release or absorption. Figure 2 has showed the global tendency. We hope to get a smooth DTG curve. So the TG curves must be pretreated before being transferred to the DTG curves. Three smoothing methods have been used and the results are given in the following. (We smoothed many experimental curves and got good results. Here, we just give one of them for simplicity.)

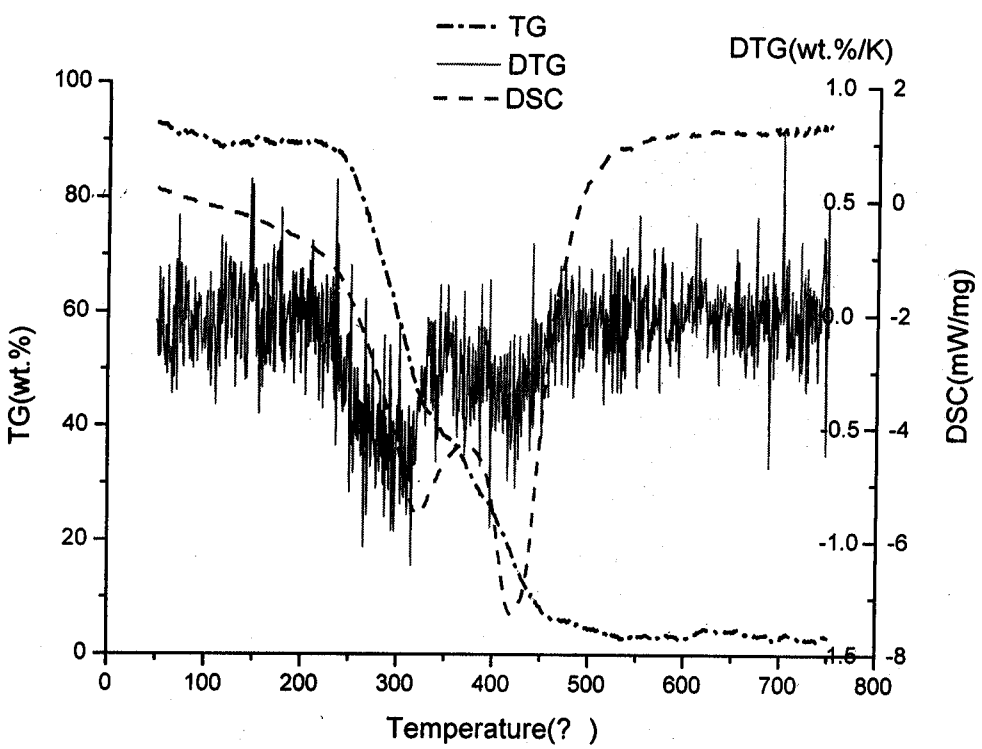

Fig. 2 Experimental curves

3.1 The choice of parameters

The choice of the method and degree of smoothing is dependent on the goals of the analysis it performed for. The parameters of α and ε determine the degree of smoothing and should be chosen according to the raw data, using the transfer functions. If we want to filter out the components which frequency is higher than a given value, then using this value as cutoff frequency, we can choose the corresponding parameters.

In order to determine the cutoff frequency, we compute the power spectrum method of the raw data and get the power spectrum density(PSD) distribution. Figure 3 shows that the main PSD is within a short frequency domain. Where $f > 0.025$, the value of PSD is close to zero. So we can use any frequency which satisfies $f > 0.025$ as cutoff frequency. In other word, we can use any period which satisfies $P < 40$ as cutoff period. In the following smoothing examples, we use 38 as cutoff period, so according to the figures of transfer functions(Figure 1), the parameters of $a = 18$ and $\varepsilon = 10^{-7}$ are chosen.

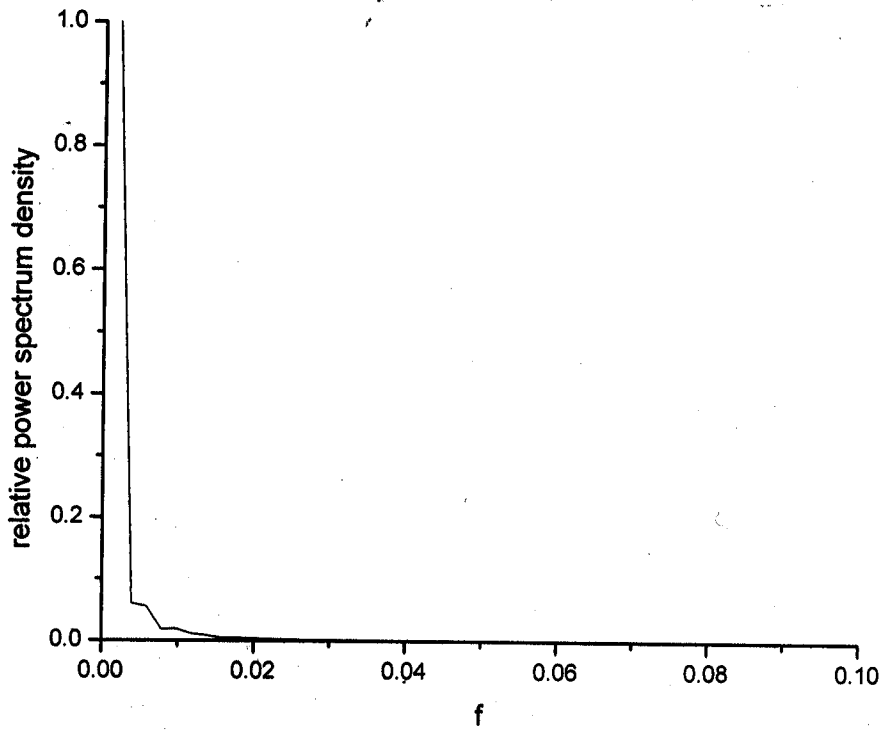

Fig. 3 Relative power spectrum density of original TG data of oil-tea wood

3.2 Smoothing results and comparison

Figure 4 shows the original and smoothed TG curves and the corresponding DTG curves, using first-order forward difference.

From figure 4 – 1, we can notice that the average smoothing method filters out very high frequency components, but leaves some high frequency components. The DTG curve still fluctuates greatly. However, the contour of two peaks like the DSC curve has appeared more clearly. This method is not good enough for kinetic analysis.

Comparing the two methods' DTG results in detail (Figure 5), we can see that the Gaussian method smoothes the data too much and the two peaks of the DTG curve are not distinct like those of Vondrak method. (Of course, the smoothed results are determined by the parameters of α and ε) We can see that the ratios of the width of half height to the height of the two peaks are bigger than those in the Vondrak smoothing result. This quality is very important in the peak separation. A simple kinetic description, named as 'First Order Pseudo Bi-component Separate-stage Model (PBSM-01)', is developed based on the experimental results and integral analysis method[9]. We hope to use differential methods to verify the model. So the smoothed DTG curve and the quality to separate peaks

easily and precisely are required. In this meaning, the performance of Vondrak smoothing is better.

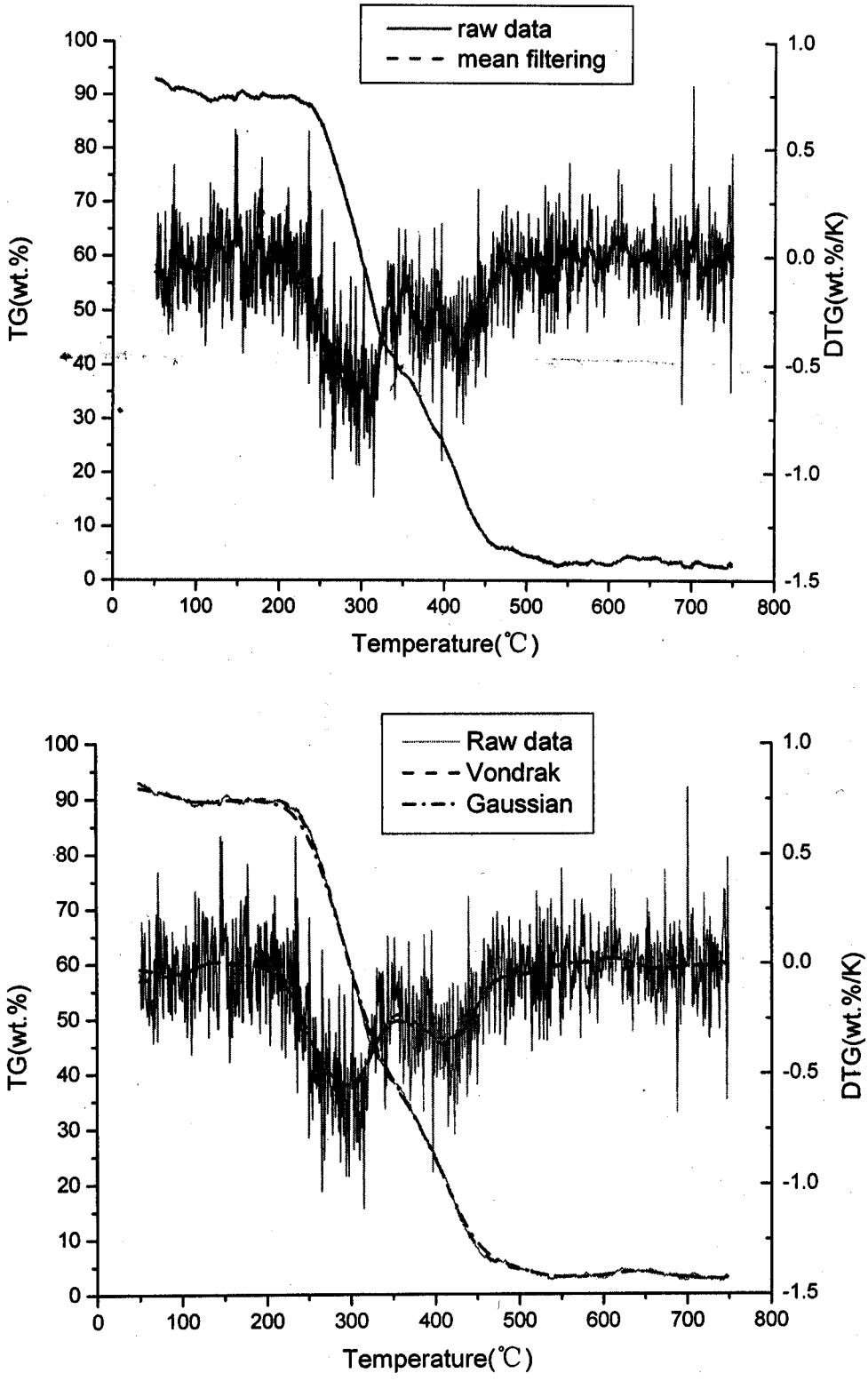

Fig. 4 The original and smoothed TG/DTG curves

(4 -1: mean N = 5 ; 4 -2: Guassian a = 18, Vondrak ε = 10 -7)

3. 3 Evaluating the methods using simulated curves

In order to get more detailed knowledge, we use simulation to evaluate the methods. The general ac-

cepted integral form for analysis of non-isothermal kinetic data

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_{T_0}^{T} \frac{A}{\beta}\exp(-E/RT)\,dT \approx (AE/\beta R)P(u)$$

with

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

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

Approximating equation for used here is rational approximation[10]

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

According to the simulated TG curve, we can get DTG curve. First we use Gaussian and Vondrak methods to smooth the simulated curve. Then a normal noise (mean value equals zero and standard variation is 2) is added to simulated TG curve, and the smoothing methods are performed again.

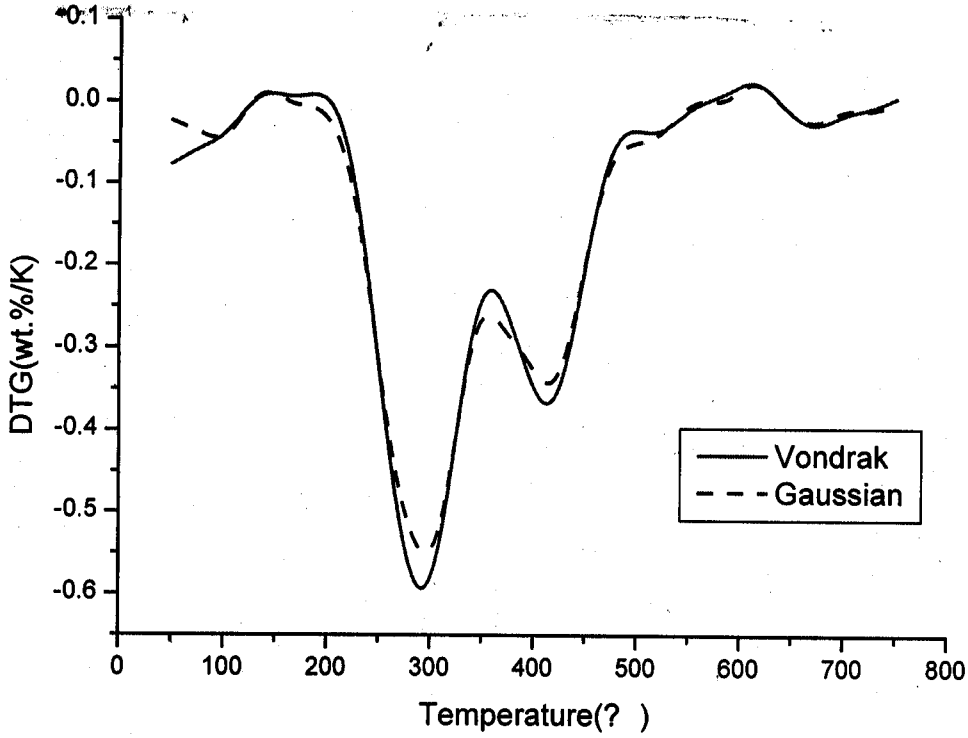

Fig. 5 Comparison of the DTG curves (Gaussian, a = 18; Vondrak, $\varepsilon = 10^{-7}$)

The smoothing results give some spurious variations occurring at the beginning and the end of mass loss process in Figure 6. In down figure (TG + noise), this effect is more serious. Vondrak smoothing is more sensitive to such variations. This end effect of the two methods is illustrated by Feissel[11]. The Vondrak method shows end effects more seriously than Gaussian method, which in some extreme cases could be a severe drawback. If the numbers of peaks in the DTG curve is hard to determine, the Gaussian method is better to use. And in the kinetic analysis, the Vondrak smoothing result may be better, because it is more close to the original curve in interval of the peak.

3.4 Verification of the smoothing methods

Kinetic parameters of the biomass pyrolysis are computed to test the usefulness of the smoothing methods. First we use integral method(C - R method[12]) to analyze the original TG data, then use differential method[13] to analyze the smoothed DTG data. The kinetic mechanism is "PBSM-O1" (First Order Pseudo Bi-component Separate-stage Model) [9]. Table1 gives the kinetic parameters of oil-tea pyrolysis in air and Figure7 gives the calculated curves. The results show that the two group parameters have good coincidence and the experimental & calculated curves have excellent agreement. So the smoothed curves can be

used directly and accurately in the kinetic analysis.

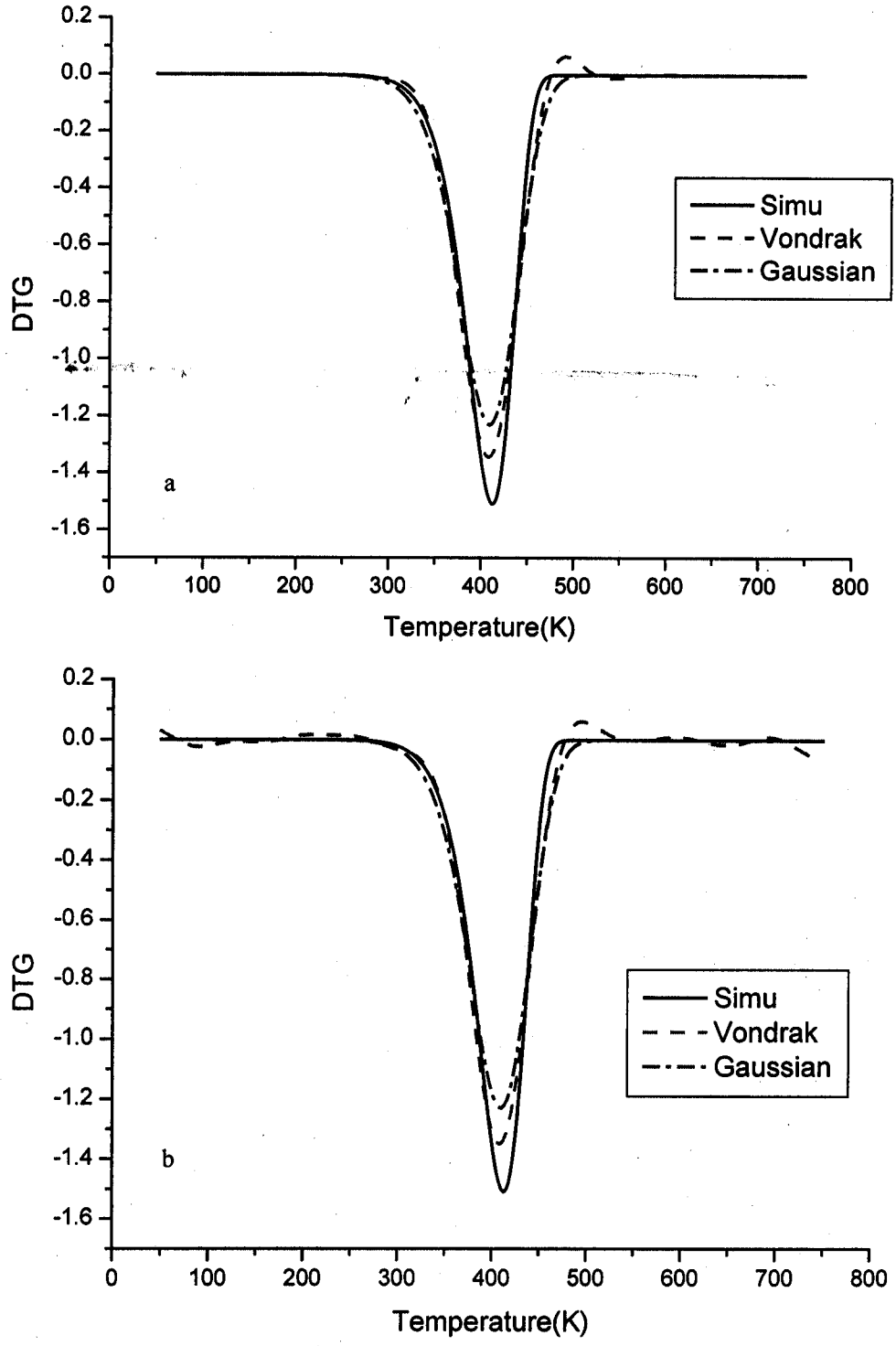

Fig. 6 Simulated and smoothed DTG curves ($E=150KJ/mol$, $A=10^{11}$, $\beta=10K/min$)
(a: TG without noise; b: TG with noise)

Tab. 1 kinetic parameters for the mass loss of the oil-tea wood by PBSM-O1

	E1(kJ/mol)	A1(min^{-1})	E2(kJ/mol)	A2(min^{-1})
TG	74	1.74e4	88	1.02e4
DTG	80	6.31e4	82	3.16e3

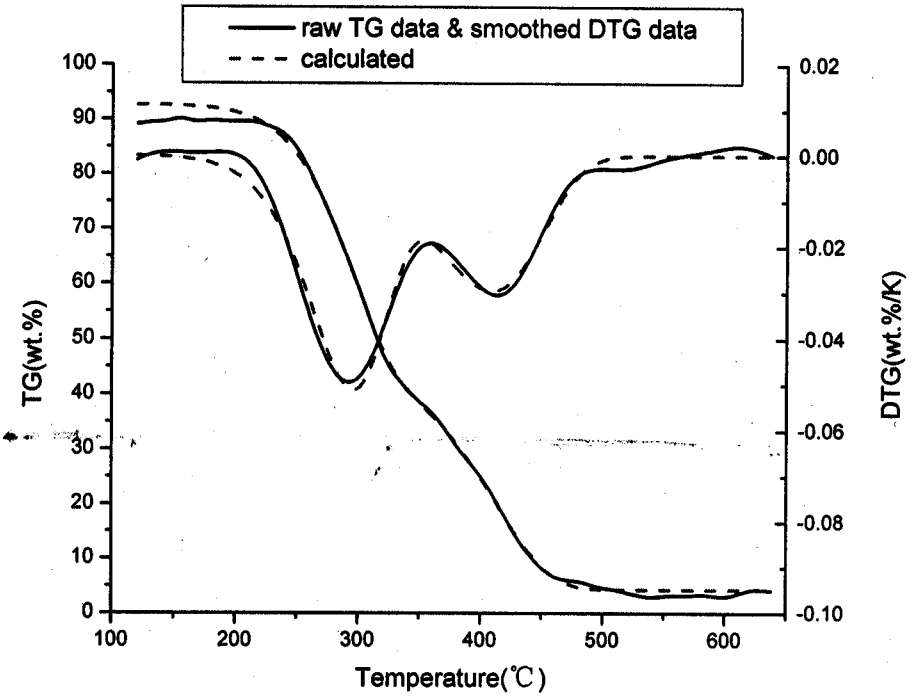

Fig. 7 Comparison of the experimental and calculated TG-DTG curves for the oil-tea wood

4 Conclusion

Smoothed data do not contain any additional information, however, smoothing "cleans up" noisy data to make information in the data more easily accessible to human interpretation. In this paper, we have used three different smoothing methods to reduce the high-frequency noise in the experimental curves. After smoothing, the curves can be used directly and accurately in the kinetic analysis.

According to the quality of the smoothing results and the figures of transfer functions, we can conclude that the Gaussian and Vondrak smoothing methods can meet the requirement effectively. And according to the raw data and the degree of smoothing, the method and parameters can be chosen.

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热重数据的平滑和微分

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摘要:在热分析技术中,经常要采用高质量的数据平滑方法。本文采用3种平滑方法来得到微分热重(DTG)数据,并比较了效果。从应用于实验数据和模拟数据的效果来看,可以认为Vondrak和高斯光滑方法有各自的优点,并且好于平均光滑方法。从原始TG数据计算的动力学参数和从平滑得到的DTG数据计算得到的参数很好的一致。这表明平滑算法是有效的,可以直接地应用于热动力学分析中。

关键词:热重;微分热重;平滑;滤波
中图分类号:O643.13^{+}4 **文献标识码**:A

研究进展

大空间早期火灾智能监测与电气火灾隐患检测系统

随着我国经济建设的飞速发展,伴随着大空间建筑的迅速增加,各类大空间建筑火灾也频繁发生,财产损失和人员伤亡极为严重。大空间建筑火灾防治,成为迫切需要解决的重大问题之一。统计数据分析表明,电气原因引发的火灾呈上升趋势,电气火灾隐患早期发现对减少火灾发生有至关重要的作用,所以对电气线路和设备的隐患进行非接触式、定量、实时可见的在线诊断也成为热安全领域内备受关注的一项关键技术。

解决大空间建筑火灾探测灵敏度与可靠性之间的巨大矛盾是现代消防技术的一项世界性难题,一直是世界各国火灾科学及消防科技工作者关注的前沿课题。大空间建筑火灾尤其是存在遮挡和环境干扰的时候,常规的感烟、感温探测器由于火灾燃烧产物在空间传播受空间高度和面积的影响,难以正常发挥效用。项目组采用"双波段图像型火灾探测技术"和"光截面图像感烟火灾探测技术"、"激光图像感烟火灾探测技术"和"智能化空间自动定位灭火技术"等取得了国内外多项专利的技术手段,使大空间火灾探测识别与空间定位灭火扑救问题得到了较好地解决。在电气火灾隐患防治方面,研究人员依据一定的热力设备存在的能量交换准则,通过扫描热力设备表面温度场,反演此工作模式下的相应立体温度场,形成了可快速诊断热安全故障隐患的在线检测技术。

该成果中的《利用彩色影像三基色差分进行火灾探测与定位的方法》2003年11月获第八届中国专利金奖,《光截面图像感烟火灾探测技术》于2003年8月获美国发明专利。

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