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Macro-TG apparatus and data processing method for the kinetic analysis of cooking oil tar

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ABSTRACT

The curves of combustion characteristics of cooking oil tar in pipe were obtained by using a self-designed thermogravimetric (TG) device with a large capacity. The wavelet transform was introduced into the thermogravimetric data smoothing and differentiation analysis according to the experimental results, and the orthogonal test method was used to find the optimized wavelet parameters. The wavelet transform results were compared with the traditional 'Moving Average', 'Gaussian Smoothing' and 'Vondrak Smoothing' methods and it shows that the signal-to-noise ratio of the measurement is increased and root-mean-square (RMS) error is decreased. The kinetic parameters calculated from the original TG curves and smooth differential thermogravimetric (DTG) curves are in good agreement, thus the wavelet transform smoothing algorithms can be used directly and accurately in the thermokinetic analysis.

KEYWORDS

Wavelet transform;
Thermogravimetric;
Cooking oil tar;
Smoothing;
Thermokinetic.

INTRODUCTION

Thermogravimetric (TG) analysis was one of the techniques for studying the primary reaction in the decomposition of solids and has been widely used. Because the heating rate, particle size, sample quantity and atmosphere, buoyancy, the specimen container and loading the close level and many other factors, makes the instrument by the original curve often contain a lot of noise, which can bring bigger distortion. In the thermal analysis, kinetic equation of linear regression is usually transformed into form, and from the slope and intercept related kinetic parameters[1]. For the use of DTG kinetic analysis method, as the DTG data is determined by thermogravimetric data obtained by numerical differentiation, in smaller calculation step conditions, even weaker intensity noise may also be due to differential calculation and the serious distortion of the numerical derivative results, without smoothing TG curve of DTG curve smoothness is very poor, the noise is amplified, the impact on the overall judgment of the trend curve and parameters. Adaptive wavelet Transform method was used to deal with thermogravimetric experiment data, and the reliability, validity result was contrastive studied compared to all kinds of traditional analysis methods.

ADAPTIVE WAVELET DENOISING

The principle of wavelet denoising

Dohono put forward the method of wavelet threshold filtering method in the minimum mean square error effectively and can achieve very good results. Its theoretical basis is Besov space signal energy is mainly focused on a limited number of coefficients, but the noise energy is distributed in the wavelet domain. By wavelet decomposing signal coefficients than noise coefficient, therefore using threshold method to be able to retain the signal factor, and most of the noise coefficient decreases to zero[2].

Assume noise signal

$$y_i = x_i + no_i, i = 1, 2, 3, \cdots, N \quad (1)$$

In For (1) y is Original signal, *x* is useful signal, no is noise signal. Wavelet decomposition according to Eq.1, get the wavelet detail coefficients. Wavelet decomposition process according to Eq.2 and Eq.3.

$$a_l^{j-1} = 2^{-1} \sum_{k \in Z} \overline{p_{k-2l}} a_k^j \quad (2)$$

$$b_l^{j-1} = 2^{-1} \sum_{k \in Z} (-1)^k p_{1-k+2l} a_k^j \quad (3)$$

a is profile coefficient, *b* is coefficient for details, *p is* wavelet coefficient, $\bar{p}$ is anti-*p*, *j is* decomposition series, *l* is decomposition coefficients. For the discrete sampling signal $x(n)$, this can make $a_n^J = x(n)$.

Through the decomposition formula are iterative, can approximate coefficient of multilayer wavelet detail coefficients of decomposition and the lowest layer was. And then set a threshold, the threshold below the detail coefficients are set to zero. And the preservation of the wavelet detail coefficients above a threshold, the reconstruction of the reconstruction algorithm, to obtain the signals after noise reduction. Reconstruction is achieved by iterative reconstruction formula, the reconstruction formula for

$$a_k^j = \sum_{l \in Z} p_{k-2l} a_l^{j-1} + \sum_{l \in Z} (-1)^k \overline{p_{1-k+2l}} b_l^{j-1} \quad (4)$$

Wavelet transform denoising process

Wavelet analysis for noise reduction process is as follows, the process of decomposition, a wavelet, and then the noise signals by *N* wavelet decomposition. Effect of threshold process, for each layer of the decomposed coefficients obtained for choosing a threshold, and the detail coefficients for soft threshold. The reconstruction process is coefficient denoising by wavelet reconstruction after the recovery of the original signal.

Threshold processing

Wavelet analysis for noise reduction is the core step of signal after the wavelet coefficients threshold determination. The threshold selection directly influences the quality of noise reduction. Soft threshold based on Stein unbiased risk estimation (rigrsure), length of log threshold (sqtwolog), heuristic SURE threshold (heursure), Minimax variance threshold (minimaxi)[3-6].

(1) Rigrsure is based on Stein Unbiased Risk Estimation and adaptive threshold selection principle.
(2) Heursure is a heuristic threshold selection rule, is the optimal threshold selection.
(3) Sqtwolog uses the form of fixed threshold, the threshold size is sqt (2×log (length (x)))
(4) Minimax is used to select the threshold minimax principle, extreme value it produces a minimum mean square error, but not without error.

When the high frequency part of signal is very small in the noise field, threshold rules Minimaxi and Rigrsure more conservative, that is not easy to lose valuable components in the signal, but only to remove the less noise. Sqtwolog threshold selection rule can remove noises effectively. Heursure is a kind of compromise. After the threshold rule selection signal generates a threshold, and then all of the detail coefficients of wavelet decomposition of the soft thresholding. Processing formula as Eq.5 shows, *t* as the field value, *X* raw signal, $\bar{x}$ the signal after de-noising.

$$\bar{x} = \begin{cases} x - \operatorname{sgn}(x)t, |x| > t > 0 \\ 0 \end{cases} \quad (5)$$

The inverse wavelet transform using wavelet coefficient threshold processing, to reconstruct the signals after noise reduction.

EXPERIMENT

Materials

Cooking oil tar in this study was obtained from a refectory of a high school, which can accommodate 1500 students. The kitchen next to dining-room plunge into use for five years, the cooking oil fog discharge

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pipe cleared for every tow month. The cooking oil tar select form the fog discharge pipe wall and the accumulated time was two month and chose the black and dense substance as the samples. Proximate and elemental analysis of cooking oil tar is given in TABLE 1.

TABLE 1 : Proximate and elemental analysis of cooking oil tar

Proximate analysis				Elemental analysis				
$\omega_{水}$ /%	$\omega_{挥}$ /%	$\omega_{灰}$ /%	$Q_{ar,net}$ /(kJ·kg^{-1})	α(O) /%	α(C) /%	α(H) /%	α(N) /%	α(S) /%
13.30	72.50	8.20	22587.10	27.12	40.74	7.103	1.738	0.074

Macro-TG apparatus

Thermogravimetric system built for pyrolysis studies of cooking oil tar is shown schematically in Figure 1. The main components of the system were a balance sensor which provided a means of measuring weight changes in all runs, a cylindrical quartz reactor with inlet for the carrier gas (N_2:O_2=4:1) and outlet for the volatiles and tars, a temperature controlled furnace and a computer to continuously record the weight and temperature for samples and record the temperature for the furnace during the entire reaction period.

The quartz reactor measured 350 mm in length by an internal diameter of 40 mm and was externally heated by a 3 kW temperature controlled furnace. The effective heating zone of the quartz reactor was about 250 mm. The sample basket was 30mL nickel crucible and approximately 15 g of sample was placed in the crucible. And then it was freely hung by a suspension wire from one end of the Level into the furnace tube. A type-K thermocouple located directly above the crucible was introduced to register the sample temperature during pyrolysis process and another type-K thermocouple located directly down the crucible to register the furnace temperature. The Macro-TG reactor is capable of pyrolyzing samples up to 1300°C at prefixed heating rate (in the range of 0-100°C/min). Subsequently, approximately 15 g weights, with the bottom of which was slightly put on the electronic balance, was also suspended by a suspension wire and then connected to another end of the Level.

The carrier gas was firstly introduced at a large rate of flow to purge residual impurities within the system, and then was established at 200ml/min. When the electronic balance output was stable, the furnace power was turn on for the pyrolysis to begin. As the sample begun to decompose, the balance output would change.

According to the Level Law, the weight loss of the sample would be equal to the weight increase of the electronic balance output. Thus, the change in the mass of the sample would be known. Simultaneously, the mass-change to time and reaction temperature was recorded on a personal computer at sampling rates of 1 s. In order to simulate the atmosphere of cooking fog discharge pipe, a vapor arise was installed in the gas system, which can proved wet air.

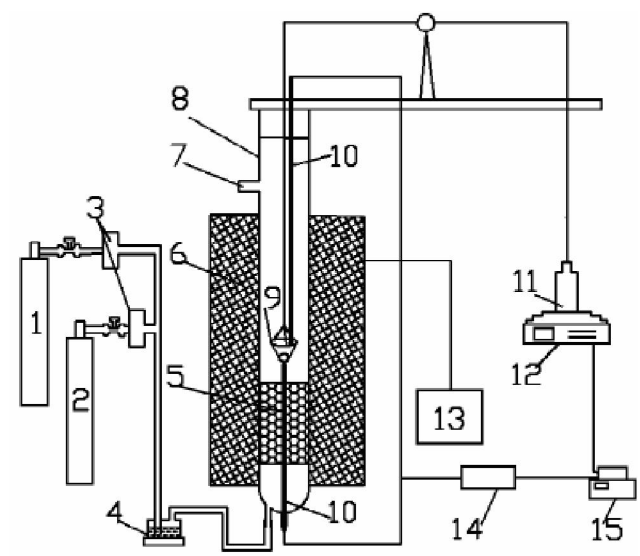

Figure 1 : Diagram of the laboratory scale themobalance (Macro-TG)

1. N_2 cylinder, 2. O_2 cylinder, 3. Flow meter, 4.vapor arise, 5. Porous ceramic, 6.Furnace, 7.Out let and gas collector, 8.quartz reactor, 9.nickel crucible, 10.Thermocouple, 11.200g weight, 12.Electronic balance, 13.Furnace controller, 14.Temperature collector (USB2816), 15.computer

In this study, experiments were conducted at heating rates of 5, 15 and 25°C/min. Samples were heated from room temperature to 1000 °C at the respective heating rate and then held at 1000 °C for 10 min. When the experiments were finished, the furnace power was turned off but the carrier gas was kept flowing until the reactor was cooled down to the room temperature. All experiments were carried out at atmospheric pressure.

WAVELET ANALYSIS DENOISING PROCESSING OF THERMOGRAVIMETRIC DATA

According to the above experiments to get TG curve of grease in 5 °C/min, and calculated DTG curves as Figure 2.

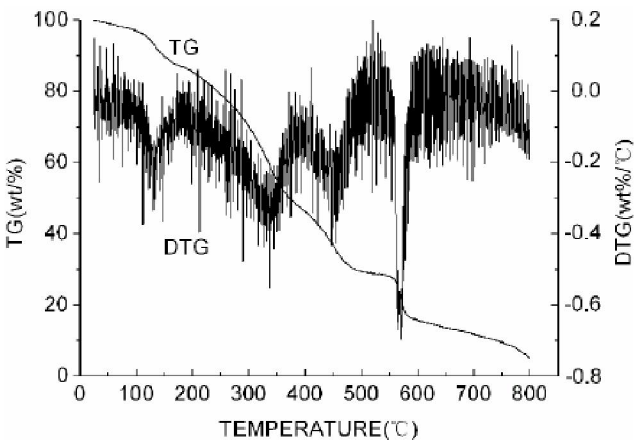

Figure 2 : Experiment results of TG and DTG

By using the principle of adaptive wavelet denoising choice is orthogonal wavelet decomposition of different layers respectively. Choose a different threshold rules for noise reduction. The noise signal reconstruction function to reconstruct coefficient decomposition after.

According to the threshold selection rule (rigrsure, sqtwolog, heursure, minimaxi), soft and hard threshold selection (soft, hard), threshold multiplication (one, sln, mln), wavelet layers (3,4,5), choose the wavelet (sym8, db3, db4), five parameters of orthogonal experiment. Comparison of the simulation results, while test number is N=$C_4^1 \times C_2^1 \times C_3^1 \times C_3^1 \times C_3^1$=216, threshold selection rule is sqtwolog, soft threshold, threshold multiplication is mln, wavelet layers is 3, wavelet as db4, the results is the best. The original DTG and wavelet DTG curve is shown in Figure 3. After the treatment to compare the effect of different parameters were showed in Figure 4, part of calculating results as follow (part of results).

In order to compare wavelet transform in thermogravimetric data smoothing processing advantage, select the moving average method, Gaussian Smoothing, Vondrak smoothing, comparison of denoising effect as shown in Figure 5.

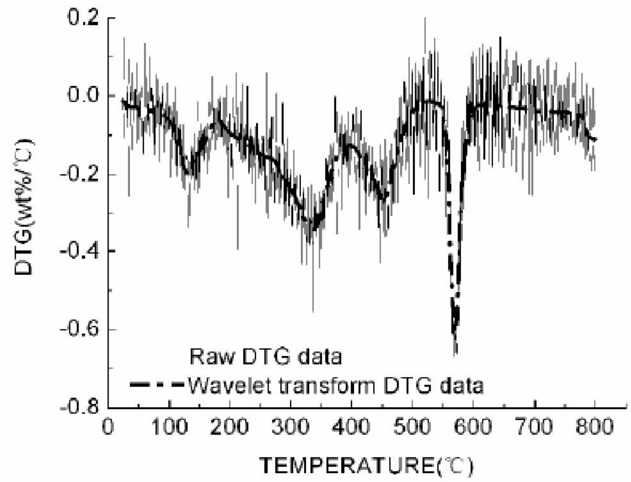

Figure 3 : Original results compared to denoising result of DTG

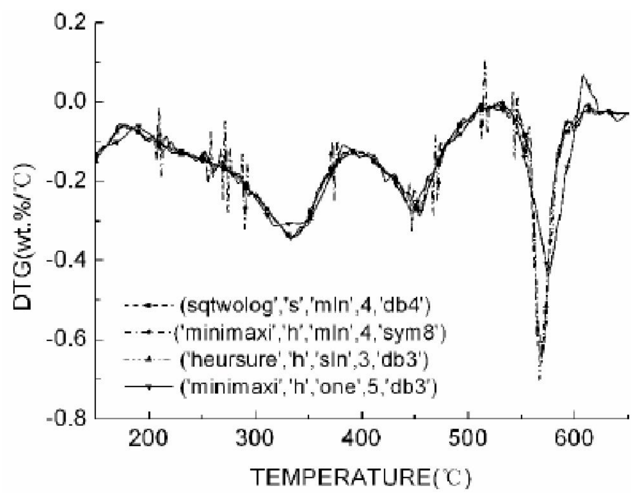

Figure 4 : Denoising result using deferent threshold parameter

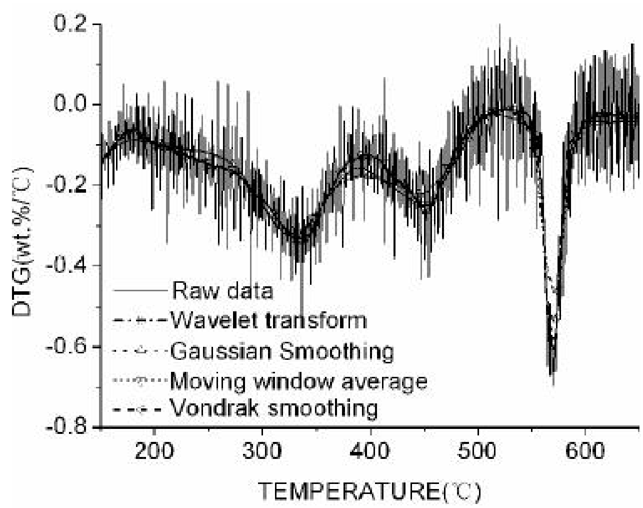

Figure 5 : Denoising result using deferent threshold

Wavelet transform is used to place DTG curve effective Gauss white noise, but also can speed characteristic signal retained very good burning, maximum close to the original data of the combustion rate. Moving average method will filter out part of the high frequency components, but also retains the Ministry of high frequency components, the curve is not smooth, and the maximum peak reduction.

The Peak of Gauss smoothing method is small than the Vondrak average method, but the peak width increases, and the peak value are small than the wavelet transforms method. In order to noise reduction effect comparison of different treatment methods, the original signal is recorded as $f(n)$, wavelet estimation signal recorded as $f'(n)$, the wavelet estimation of signal to noise ratio (R_{SNR}) (Wei Liang, *et al*, 2009) is defined as Eq.6.

$$R_{SNR} = 10\log\left[\frac{\sum_n f'^2(n)}{\sum_n (f(n) - f'(n))^2}\right] \quad (6)$$

The RMS error between the original signal and estimate signal were defined as Eq.7.

$$E_{RMSE} = \sqrt{\frac{1}{n}\sum_n (f(n) - f'(n))^2} \quad (7)$$

While the signal-to-noise ratio is high, the RMS between original signal and estimate the signal is small. Estimation of signal is more close to the original signal, denoising effect is better.

TABLE 2 : Denoising result using deferent threshold

Denoising methods	R_{SNR} /dB	E_{RMSE} /%	570℃peak error %	570℃peak load %
wavelet transform	14.68	0.0955	1.70	1.40
Moving window average	12.54	0.1037	11.21	5.33
Vondrak smoothing	11.69	0.1641	4.11	1.77
Gaussian Smoothing	11.35	0.1819	5.65	2.63

Comparing Figure 4 and Figure 5, combined with the results in TABLE 2 we can see that based on the adaptive wavelet denoising method is the highest signal-to-noise ratio, RMS error is the smallest, peak error and peak load are also the smallest, the method for data smoothing control force is the best, and it has good effect to bigger noise fluctuation signal processing.

DEMONSTRATED EFFECTIVENESS IN DENOISING METHOD OF WAVELET

To smooth the curve of TG is designed to provide reliable DTG curve to calculate the kinetic parameters for the differential method, Integral method is less affected by noise. The kinetic parameters obtained by comparing the differential method and integral method, to verify the effectiveness of the wavelet denoising algorithm. The oil tar combustion is a very complicated chemical reaction process, which including many reactions occur simultaneously. These reactions are often difficult to distinguish exact analyzed. The weight loss strict platform does not exist on the curve as these effects. There is not an exacted point on the TG curve corresponding to a clear point at the end of a reaction process and a reaction process. The minimum points on the DTG curve were regarded as the turning point of the four weight loss stages. The combustion process of the oil was described by the first-order reaction, and the kinetic parameters of the original TG curve were calculated by Coats-Redfern (P. Luangkiattikhun, *et al*, 2008) integral method. The kinetic parameters of the smoothed DTG curve were calculated by differential method.

TABLE 2 gives the kinetic parameters of oil samples in air at 5 °C/min heating combustion curve rate using the results obtained by two methods. The kinetic parameters of oil samples in air at 5°C/min heating combustion rate were calculated by two methods and showed in TABLE 2, and there is little difference between the corresponding parameters. The simulation curve and experimental curve matches well and can be see in Figure 6. The wavelet denosing method can be safely used in the thermal analysis, and the method has enough accuracy in the calculation of kinetic parameters.

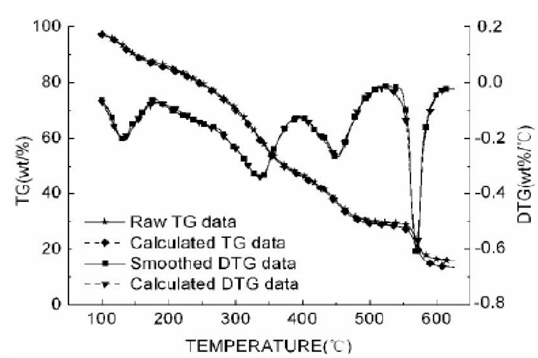

Figure 6 : Comparison of experiment and calculated TG-DTG

TABLE 3 : Kinetics parameter with different measure

method	activation energy E(kJ/mol)	frequency factor A(min^{-1})
TG integral method	68.18	5.900×10^{7}
	48.88	4.821×10^{5}
	153.32	3.028×10^{10}
	175.45	1.406×10^{10}
DTG differential method	70.33	3.312×10^{7}
	51.69	9.308×10^{6}
	151.67	5.422×10^{10}
	177.31	1.690×10^{10}

CONCLUSIONS

A thermogravimetric system was designed according to the characteristics of cooking oil tar, in which a large amount of sample (about 10 g) can be examined. Wavelet transform was introduced to the thermogravimetric data smoothing and differentiation analysis according to the experiment results, and the orthogonal test method was used to find the optimize wavelet parameter. Adaptive wavelet method overcomes the moving average method not smooth in the smoothed curve. This method can not only effectively filter out the noise signal to prevent signal distortion, and can guarantee the denoised signal smooth, provides certain reference value processing thermogravimetric data for future.

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