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Effect of separation points on kinetic parameters in pseudo component separated stage model

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Abstract In pseudo bi-component separated-stage model (PBSM), the effect of the TG value at separation points on the kinetic parameters is studied by residual and theoretical analysis. Simultaneously, a new method to determine the point that is the end of 1st reaction or the initial of 2nd reaction is developed. The investigations have improved the calculation procedure of PBSM. We performed thermogravimetry (TG) analysis on oil tea wood with two-step consecutive model and parallel model. Comparison between the results of the two models and improved PBSM shows well agreements. The influence of different separation points on kinetic parameters is presented.

Keywords Kinetic analysis · Thermal decomposition · Lignocellulosic material · PBSM · Mass percentage

Introduction

The thermo-oxidative degradation of various polymer and lignocellulosic materials has been investigated by TG and DTG simultaneous analysis performed in oxidative atmosphere [1–7]. It was indicated that at the progressive heating of polymer in oxidative atmosphere, three or four complex processes occur successively [4, 5]. Meanwhile, many authors pointed out that the mass losses of lignocellulosic materials decomposition in air showed a two-step decomposition profile, with the first step due to wood devolatilization and the second for char oxidation (e.g., Momoh et al. [6, 7]). Consequently, the kinetic models consisting of parallel or consecutive reactions of pseudo components have been widely applied to describe the global kinetic behavior in thermo-oxidative degradation [8–15]. Generally, the kinetic parameters are extracted from the differential thermogravimetric (DTG) or thermogravimetric (TG) data by a nonlinear least square algorithm. However, the least square method received some skepticism. According to Varhegyi et al. [16, 17], the systematic errors of the thermal analysis could hinder the mechanistic application of the non-linear least-squares.

Comparatively, Liu et al. [18] developed a new two-step model, named "First Order Pseudo Bi-component Separated-stage Model (PBSM)", to describe the decomposition behavior of lignocellulosic materials. The model deals with the global mass loss by two pseudo components which decompose, respectively, within two separate temperature ranges, therefore, no nonlinear least square algorithm is required. The model was verified to be suitable for the mass loss processes of variable wood and leaf samples under relatively lower heating rates. The basic idea of PBSM model is based on the experimental observations of that DTG curves at lower heating rates frequently show two nearly separate peaks with relatively narrow overlapping region. Liu's work regarded the minimum in DTG curve as the point of separation between two mass loss stages. However, if two reactions that occur within a narrow overlapping region, the separation point defined previously is not the accurate one where one reaction ends and the other starts. The mass percentage of this point cannot be defined as $w_{1\infty}$ and w_{20}. Therefore, how to select the value of $w_{1\infty}$ and w_{20} on TG curve is worth studying.

In the present study, non-isothermal TG analysis on oil tea wood has been studied to understand the decomposition behavior of oil tea wood in air atmosphere. A new method is used to evaluate $w_{1\infty}$ and $w_{2\infty}$ by residuals analysis. For

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the evaluation of w_{20}, a theoretical derivation is carried out to study the influence of w_{20} on kinetic parameters of second reaction. Meanwhile, two-step consecutive reaction model and parallel reaction model are both applied on the experimental data so that the way of taking value of $w_{1\infty}$ in PBSM can be further verified.

Experimental

The raw material used for experiments is oil tea wood collected from Jiangxi province of China. After being dried for 24 h at 80 °C, the material was cut and then ground. A fraction of the material with dimension in 150–300 μm was used for experiments. The grains of samples were distributed over the open sample pan of 5 mm diameter loosely, with the initial amounts of the samples all kept to be nearly 10 mg. The depth of the sample layer filled in the pan was about 0.5 mm. Thermogravimetrical analysis (TGA) under air atmosphere was carried out on thermobalance NETZSCH STA 409C, controlled by PC compatible system. In this device the thermocouple was not in contact with the sample directly. The temperature calibration of TGA was performed by Curie Point Standards. In tests, air flow was controlled to be 50 mL/min and the temperature was increased from atmosphere temperature to 750 °C at the heating rates of 5–25 K/min with step of 5 K/min. The experiment reproducibility was proved by reasonable agreement between the data obtained from two runs under the same experimental conditions. The DTG curves extracted from the TG data were smoothed by means of Gaussian smoothing algorithm.

Results and discussion

The procedure to determine the point of separation

When overlapping reactions occur, it is sometimes difficult to locate on the TG curve an unambiguous point where one reaction ends and the other starts. By use of DTG curve, the temperature corresponding to the minimum in the DTG curve can be regarded as the demarcation point [18, 19], which is shown in Fig. 1. The separation point is defined as T_{sep}, at which the corresponding value on TG curve is, respectively, defined as $w_{1\infty}$ and w_{20}. In Fig. 1, subscripts onset and offset, respectively, correspond to the initial of reaction and the end of reaction. It is assumed that the initial of overall reaction is T_{onset1} and the end of overall reaction is $T_{offset2}$. In PBSM, the initial and residual solid mass fractions corresponding to the two separate reactions are defined, respectively, in the definite lower and higher

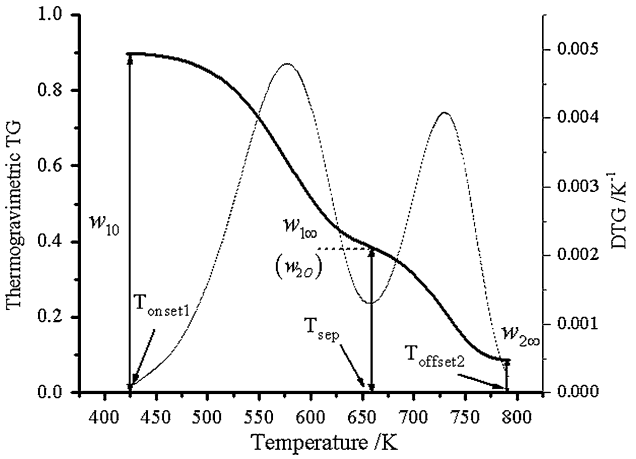

Fig. 1 Illustration of separation point T_{sep}, T_{onset1} and $T_{offset2}$ defined in PBSM

temperature ranges, and accordingly the global mass loss kinetics can be expressed as:

$$\begin{cases} \frac{d\alpha_1}{dT} = \frac{A_1}{\beta}\exp(-E_1/RT)f_1(\alpha_1) & T_{onset1} < T < T_{sep} \\ \frac{d\alpha_2}{dT} = \frac{A_2}{\beta}\exp(-E_1/RT)f_2(\alpha_2) & T_{sep} < T < T_{offset2} \end{cases} \quad (1)$$

In Eq. 1, mass loss fraction α_1 and α_2 are decided by

$$\alpha_1 = \frac{w_{10} - w_1}{w_{10} - w_{1\infty}} \quad (2)$$

$$\alpha_2 = \frac{w_{20} - w_2}{w_{20} - w_{2\infty}} \quad (3)$$

where α is the sample mass loss fraction and w is the mass percentage of solid. The subscripts 0 and ∞ refer to the initial and residual amounts, and the subscripts 1 and 2, respectively, correspond to the pseudo components 1 and 2. However, due to reactions that occur within the same temperature range, it is more reasonable to use an extrapolation procedure such as that shown in Fig. 2 to determine approximately where the first reaction starts and the second

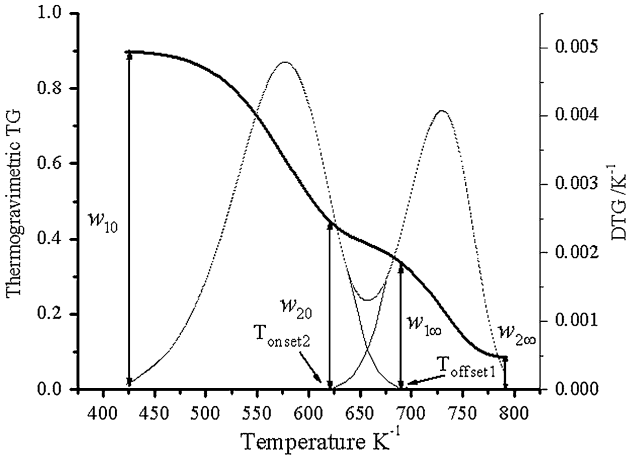

Fig. 2 Illustration of separation point $T_{offset1}$ and T_{onset2} defined in PBSM

reaction begins. The mass percentage $w_{1\infty}$ and w_{20} need more accurate evaluations. By estimating from Figs. 1 and 2, it is assumed that the temperature at T_{offset1} is greater than that at T_{sep} by 30 K, and T_{onset2} is lower by 30 K. As follow, to sustain this conjectural method, more analytical results are performed.

Evaluation of the offset of first mass-loss reaction $w_{1\infty}$

A new method to evaluate the mass percentage at the end of first mass-loss reaction accurately is developed here. By taking logarithm of Eq. 1, the following equation is get

$$\ln \frac{\mathrm{d}\alpha_1}{\mathrm{d}T} = \ln \frac{A}{\beta} - \frac{E}{RT} + n \ln (1 - \alpha_1) \tag{4}$$

for which we regard $-1/T$ and $\ln (1 - \alpha_1)$ as predictive variables, and $\ln \mathrm{d}\alpha_1/\mathrm{d}T$ as a responsive variable. Generally, when $w_{1\infty}$ is specified, the mass loss fraction α_1 is decided from Eq. 2, and the kinetic parameters of E_1, A_1, and n_1 can be evaluated from Eq. 4 by linear regression analysis, with a corresponding residual obtained:

$$R = \left(\sum_{i=1}^{N} (\alpha(i)_{\text{exp}} - \alpha(i)_{\text{cal}})^2 \right) / N \tag{5}$$

where N is the number of experimental data of the first mass loss reaction. The value of the R function is related to the quality of fit in regression analysis. Therefore, the more exact $w_{1\infty}$ is chosen, the smaller value of R should be given. The kinetic parameters are optimized to achieve a higher quality of fit. By use of the minimum in the functional curve as shown in Fig. 3, it is easy to determine an accurate $w_{1\infty}$. The values of $w_{1\infty}$ are given at different heating rates in Table 1. When the predicted values of $w_{1\infty}$ are taken by calculation, the corresponding values of T_{offset1} can be obtained by use of TG curves in Fig. 6. As

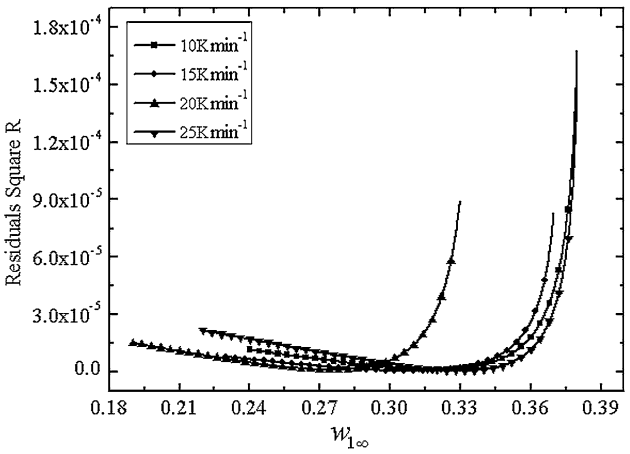

Fig. 3 The relationship between residual square R and $w_{1\infty}$ at different heating rates (10, 15, 20, and 25 K/min)

Table 1 The mass percentage and temperature at 1st reaction offset point T_{offset1} (by calculation) and T_{sep}

β (K/min)	$w_{1\infty}$ (T_{sep})	$w_{1\infty}$ (T_{offset1})	T_{sep} (K)	T_{offset1} (K)
10	0.3726	0.3169	645	645 + 27
15	0.3643	0.3080	650	650 + 26
20	0.3277	0.2730	660	660 + 26
25	0.3732	0.3288	665	665 + 23

Table 2 Comparison of kinetic parameters for oil tea wood with selecting different offset points T_{sep} and T_{offset1} (heating rates 10, 15, 20, 25 K/min)

β (K/min)		E_1 (kJ/mol)	ln A_1 (s^{-1})	n_1
10	T_{sep}	63.7	4.01	0.86
	T_{offset1}	91.6	6.84	1.89
15	T_{sep}	65.9	4.12	0.81
	T_{offset1}	86.9	6.25	1.70
20	T_{sep}	65.4	4.05	0.89
	T_{offset1}	89.2	6.45	1.85
25	T_{sep}	70.3	1.42	0.88
	T_{offset1}	87.5	6.14	1.63

shown in Table 1, the realistic offset point of first reaction T_{offset1} is almost greater than T_{sep} by 20–30 K. Due to the corresponding minimum of R, it is reasonable to take value of mass percentage at T_{offset1}, when using Eq. 2. In this way, the kinetic parameters can be further extracted. The comparison of kinetic parameters in Table 2 indicates that the deviations of $w_{1\infty}$ bring the great errors of kinetic parameters.

To enable a visual comparison to be made between the two procedures by T_{sep} and T_{offset1}, the mathematical Eq. 4 is integrated numerically with the corresponding kinetic constants (in Table 2). Experimental and simulated curves of TG are represented for experiment at 10, 15, 20, and 25 K/min in Figs. 4 and 5. Compared to the T_{sep} analysis in Fig. 4, the other kinetic parameters optimized by using point T_{offset1} achieve a high quality of fit in Fig. 5.

Evaluation of the onset of second mass-loss reaction w_{20}

By the same method, the onset of second reaction (w_{20}) is evaluated, whereas an accurate w_{20} is difficult to determine from the minimum point in Fig. 6. A set of horizontal lines is shown in this figure, which indicates there is no specific functional relationship between residuals square R and w_{20}. Furthermore, the value of w_{20} may have no influence on the kinetic parameters (E_2, A_2, and n_2) of second reaction. The following analyses can sustain this conclusion.

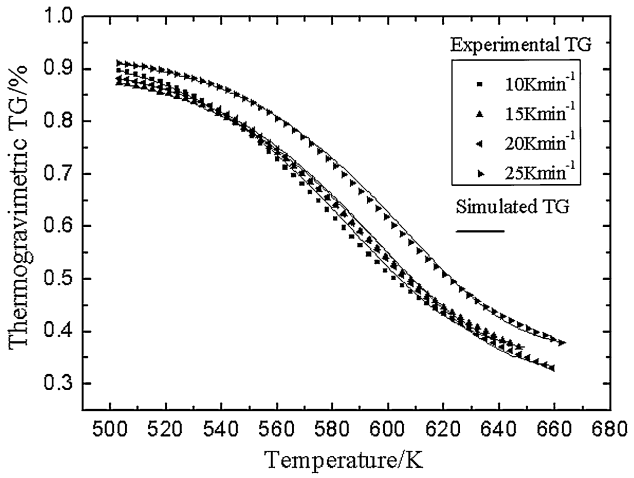

Fig. 4 Comparison of experimental TG in first reaction stage and simulated curves with selecting different offset points T_{sep}

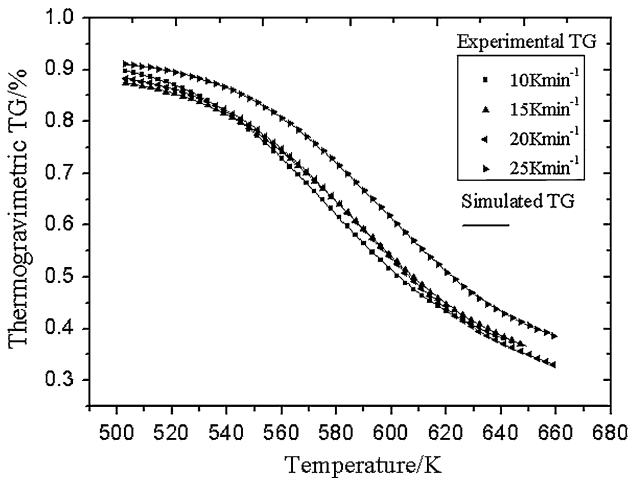

Fig. 5 Comparison of experimental TG in first reaction stage and simulated curves with selecting different offset points $T_{offset1}$

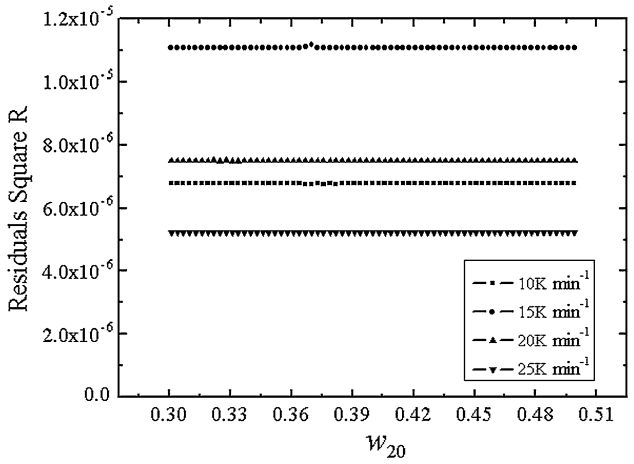

Fig. 6 The relationship between residual square R and w_{20} at different heating rates (10, 15, 20, and 25 K/min)

Formula derivation starts from Eq. 1. By taking logarithm of this equation, we can obtain:

$$\ln \frac{\mathrm{d}\alpha_2}{\mathrm{d}T} = \ln \frac{A_2}{\beta} - \frac{E_2}{RT} + n_2 \ln (1 - \alpha_2) \tag{6}$$

substituting Eq. 3 into Eq. 6:

$$\ln \left(\mathrm{d}\left(\frac{w_{20} - w}{w_{20} - w_{2\infty}} \right) \Big/ \mathrm{d}T \right) = \ln \frac{A_2}{\beta} - \frac{E_2}{RT} + n_2 \ln \left(1 - \frac{w_{20} - w}{w_{20} - w_{2\infty}} \right)$$

$$\ln \frac{-\mathrm{d}w/\mathrm{d}T}{w_{20} - w_{2\infty}} = \ln \frac{A_2}{\beta} - \frac{E_2}{RT} + n_2 \ln \left(\frac{w - w_{2\infty}}{w_{20} - w_{2\infty}} \right)$$

$$\ln \left(-\frac{\mathrm{d}w}{\mathrm{d}T} \right) - \ln (w_{20} - w_{2\infty}) = \ln \frac{A_2}{\beta} - \frac{E_2}{RT} + n_2 \ln (w - w_{2\infty}) - n_2 \ln (w_{20} - w_{2\infty})$$

$$\ln \left(-\frac{\mathrm{d}w}{\mathrm{d}T} \right) = -\frac{E_2}{R} \frac{1}{T} + n_2 \ln (w - w_{2\infty}) + \left(\ln \frac{A_2}{\beta} - (n_2 - 1) \ln (w_{20} - w_{2\infty}) \right) \tag{7}$$

The activation energy E_2 and reaction order n_2 are calculated from the slope of a plot of ln $(-\mathrm{d}w/\mathrm{d}T)$ versus $1/T$ and ln $(w - w_{2\infty})$, and the intercept gives the pre-exponential factor. The predictive variables are independent on the value of w_{20}, so that the corresponding estimation parameters (E_2 and n_2) can be evaluated without an accurate w_{20}. In the case, the pre-exponential factor A_2 is the only kinetic parameter controlled by w_{20}.

Here, w_{20} is assumed to be the real mass percentage of second reaction onset. An intercept is given:

$$C = \ln \frac{A_2}{\beta} - (n_2 - 1) \ln (w_{20} - w_{2\infty}) \tag{8}$$

If there is an error in w_{20}, defined as φ, the other intercept is:

$$C = \ln \frac{A_2'}{\beta} - (n_2 - 1) \ln (w_{20} + \varphi - w_{2\infty}) \tag{9}$$

by subtracting Eq. 8 from Eq. 9, the error of A_2 can be written:

$$\ln \frac{A_2'}{A_2} = (n_2 - 1) \ln (1 + \varphi/(w_{20} - w_{2\infty})) \tag{10}$$

compared to experimental data, a relatively greater error is defined as:

$$\frac{\varphi}{w_{20} - w_{2\infty}} = -0.2 \tag{11}$$

assuming a reasonable reaction order:

$$n_2 = 1.2 \tag{12}$$

substituting Eqs. 11 and 12 into Eq. 10, we can get the error of A_2

$$\frac{A_2'}{A_2} = 1.0377 \approx 1 \tag{13}$$

From Eq. 13, it is found that the relative error of pre-exponential factor due to the deviation of w_{20} is not more than 4%. Consequently, the effect of w_{20} on kinetic parameters of second mass loss can be ignored.

Evaluation of the offset of second mass-loss reaction $w_{2\infty}$

In Eqs. 2 and 3, $w_{2\infty}$ plays the same role as $w_{1\infty}$ in controlling the kinetic parameters, and the correlative discussion is also needed by using the same method in "Evaluation of the offset of first mass-loss reaction $w_{1\infty}$" section. From Fig. 7 and Table 3, though $w_{2\infty}$ has a relatively visible effect on the kinetic parameters of second reaction, however, the computed T'_{offset2} approximately equals to T_{offset2}. The previous procedure to determine where is the end of second mass loss reaction in Fig. 1 is acceptable.

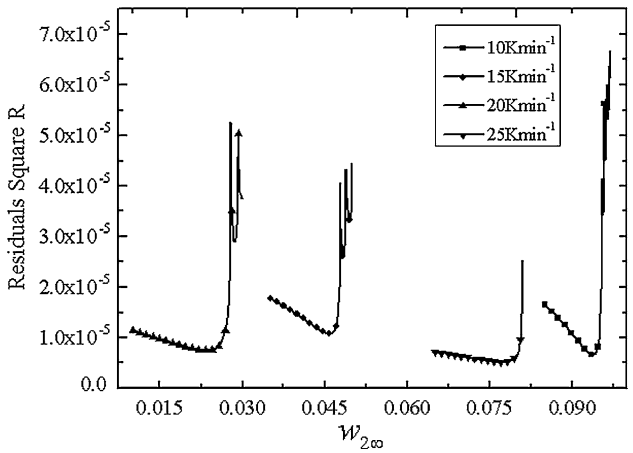

Fig. 7 The relationship between residual square R and $w_{2\infty}$ at different heating rates (10, 15, 20, and 25 K/min)

Table 3 The mass percentage and temperature at 2nd reaction offset point T_{offset2} and T'_{offset2} (by calculation)

β (K/min)	$w_{2\infty}$ (T_{offset2})	$w_{2\infty}$ (T'_{offset2})	T_{offset2} (K)	T'_{offset2}(K)
10	0.0942	0.0938	775	775 + 2
15	0.0449	0.0459	775	775-1
20	0.0242	0.0235	775	775 + 1
25	0.0758	0.0771	775	775-1

Kinetic analysis for the decomposition of oil tea wood

The decomposition of oil tea wood starts at around 500 K and completes at 773 K (Figs. 8, 9). All the DTG curves show two similar peaks and the separation points at different heating rates are list in Table 1. The characteristic of DTG curves is an indication that the overall reaction contains least two steps.

According to the inspection of literature, parallel reaction model and consecutive reaction model had been proved to be reasonable models to describe the decomposition of biomass because of its two stages characteristics. In order to estimate the kinetic parameters for each pseudo component, a nonlinear least-squares algorithm is applied to the mass loss curves (TG) at different heating rates by single curve analysis. In this study, the NETZSCH Thermokinetics program is used to optimize the kinetic

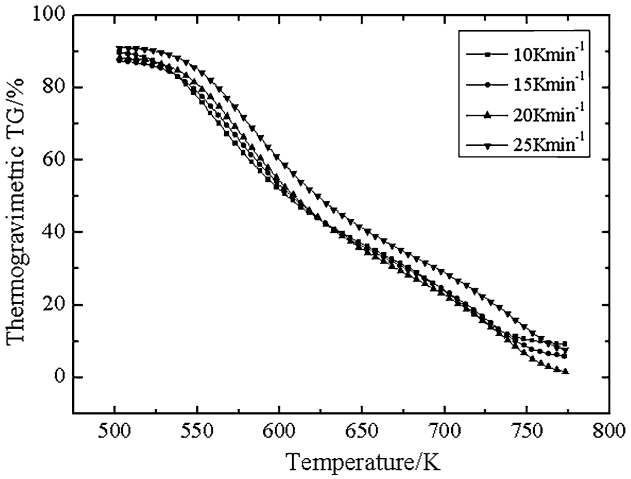

Fig. 8 Experimental TG curves for the experiment with oil tea wood at 10–25 K/min heating rates

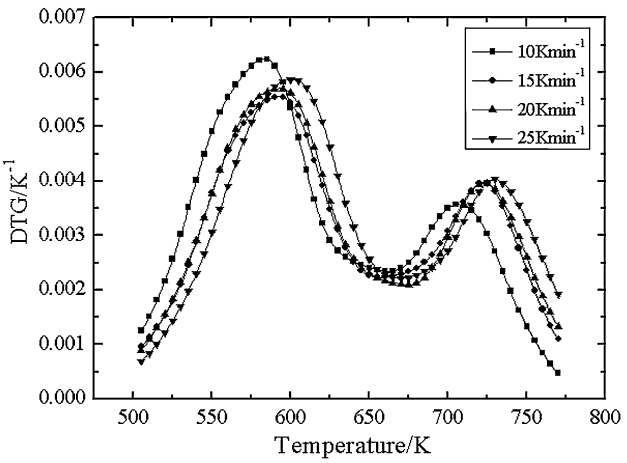

Fig. 9 Experimental DTG curves for the experiment with oil tea wood at 10–25 K/min heating rates

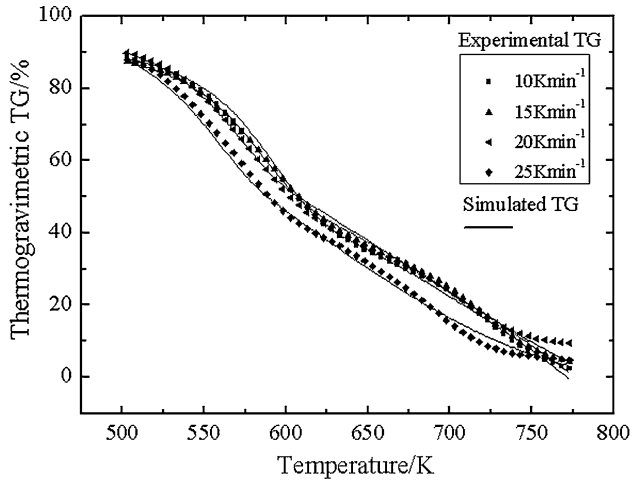

Fig. 10 Comparison of experimental TG curves of oil tea wood and simulated TG curves by two-step consecutive model assuming $f(\alpha) = (1-\alpha)^1$

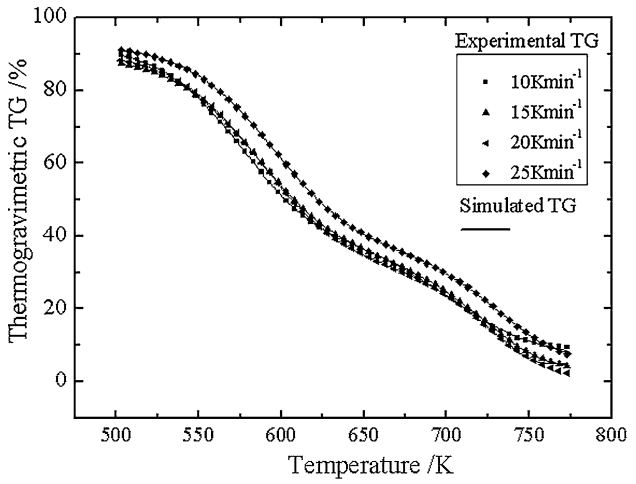

Fig. 12 Comparison of experimental TG curves of oil tea wood and simulated TG curves by two-step parallel model assuming $f(\alpha) = (1-\alpha)^n$

parameters. The fit between the simulated and experimental data is illustrated in Figs. 10, 11, and 12. As shown, the mechanism function of $f(\alpha) = (1-\alpha)^n$holds better fitting effect than the function of $f(\alpha) = (1-\alpha)^1$. Therefore, the former mechanism function is applied and the extracted kinetic parameters are shown in Table 4. The kinetic parameters by using consecutive model and parallel model are hardly changing with increase of heating rate, which indicates the two models are relatively successful to describe the reaction process. Therefore, it is reasonable to regard kinetic parameters (E_1, A_1, and n_1) in Table 4 as good benchmark for the rating of the PBSM model as can be seen from the calculated parameters (Table 2). When defining the mass percentage at T_{offset1} is $w_{1\infty}$, the simulated kinetic parameters in Table 2 are nearly equal to the

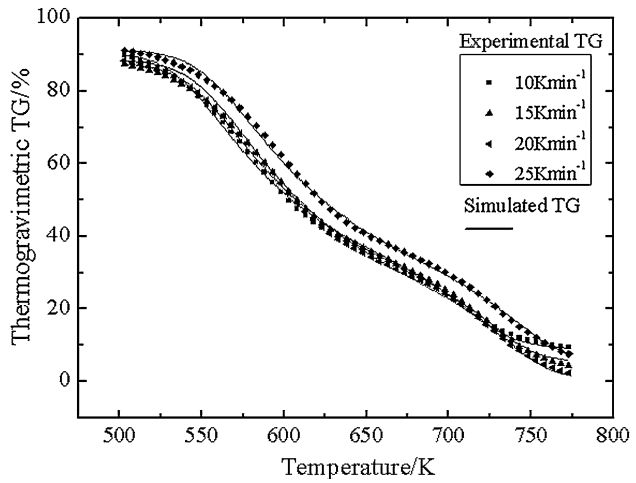

Fig. 11 Comparison of experimental TG curves of oil tea wood and simulated TG curves by two-step consecutive model assuming $f(\alpha) = (1-\alpha)^n$

Table 4 Comparison of kinetic parameters for decomposition of oil tea wood by two-step consecutive reaction model and parallel reaction model

β (*K*/min)	E_1 (kJ/mol)	ln A_1 (s^{-1})	n_1	E_2 (kJ/mol)	ln A_2 (s^{-1})	n_2
10						
Consecutive	86.3	5.52	1.54	125.8	6.97	1.14
Parallel	86.0	5.49	1.25	125.0	6.81	0.99
15						
Consecutive	83.7	5.40	1.35	114.2	6.16	1.00
Parallel	84.0	5.43	1.35	112.2	6.00	0.94
20						
Consecutive	86.0	5.73	1.44	128.7	7.35	1.00
Parallel	86.6	5.79	1.48	126.2	7.14	0.67
25						
Consecutive	88.1	5.92	1.40	131.7	7.60	1.00
Parallel	88.6	5.97	1.42	130.3	7.48	0.88

values in Table 4. It is farther indicated that selecting the value of $w_{1\infty}$ at T_{offset1} is more reasonable with comparison of T_{sep}.

However, as indicated in previous work [18], the basic idea of PBSM assumed that the pseudo components decompose, respectively, in two separate temperature regions. Therefore, when the decomposition of fractions overlapping region presents extensively, the application of PBSM is limited. Meanwhile, the investigation of separation points' effect on kinetic parameters in this article is only based on the experiment of oil tea wood. The effect of the decomposition of fractions overlapping region on kinetic parameters is ignored, so the corresponding problem motivates the need further investigations.

Conclusions

In this article, decomposition of oil tea wood has been studied by means of non-isothermal thermogravimetric analysis in air atmosphere at 10–25 K/min heating rates. For the common analysis of the TG measurements run, a satisfactory fit is obtained with consecutive model and parallel model. Compared to these successful models, the procedure of PBSM is further studied. By use of residual analysis and theoretical analysis, the effects of $w_{1\infty}$, w_{20} and $w_{2\infty}$ on kinetic parameters are evaluated. It is summarized in the following: (1) It is reasonable to take value of mass percentage at T_{offset1}, when estimating the kinetic parameters; (2) For the experimental data of oil tea wood, the realistic offset point of first reaction T_{offset1} is almost greater than T_{sep} by 20–30 K at different heating rates; (3) The value of w_{20} almost has no influence on the kinetic parameters (E_2, A_2, n_2) of second reaction; (4) Regarding the end point of overall reaction as T_{offset2} is acceptable.

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