Applicability of bi-pseudo component separated-stage model for decomposition of lignocellulosic materials in air at multiple heating rates

Jiakun Dai · Naian Liu · Lifu Shu

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Abstract In our previous research (Liu et al., J Anal Appl Pyrol 63:303–325, 2002), the pseudo bi-component separated-stage model (PBSM) was suggested for the kinetic analysis on the decomposition of lignocellulosic materials in air at relatively lower heating rates. As a continuing work, this paper is intended to investigate the applicability of PBSM at different heating rates by experimental analyses. Decomposition of oil tea wood has been studied by means of non-isothermal thermogravimetric analysis in air atmosphere at 10–25 K min$^{-1}$ heating rates. A two-step parallel reaction kinetic model is used to optimize the kinetic parameters of these materials in air. Meanwhile, an improved PBSM is developed to describe the thermal degradation process of oil tea wood. Furthermore, a comparison between the kinetic results of parallel model and PBSM reveals realistic applicability of PBSM. It is concluded that the PBSM has relatively high accuracy for the first decomposition step in the lower temperature range, while fails to predict the thermal decomposition behavior in the char oxidative process which occurs in the higher temperature range.

Keywords Kinetic analysis · Thermal decomposition · Lignocellulosic material · PBSM

List of symbols

- $A$ Apparent pre-exponential factor (s$^{-1}$)
- $E$ Apparent activation energy (kJ mol$^{-1}$)
- $n$ Apparent reaction order
- $R$ Gas constant (kJ K$^{-1}$ mol$^{-1}$)
- $β$ Heating rate (K min$^{-1}$)
- $T$ Absolute temperature (K)
- $x$ Mass loss fraction
- $x_p$ Mass loss fraction corresponding to DTG peak
- $T_{initial}$ Initial decomposition temperature (K)
- $T_{final}$ Final decomposition temperature (K)
- $T_P$ Temperature of the DTG peak (K)
- $ΔT_P$ Variation amplitude of temperature corresponding to DTG peak (K)
- $Δβ$ Variation amplitude of heating rate (K min$^{-1}$)
- $T_{SP}$ Temperature corresponding to the minimum in the DTG curve (K)
- $TRFS$ Temperature range of first degradation stage
- $TRSS$ Temperature range of second degradation stage
- $BT_1$ Boundary temperature of TRFS
- $BT_2$ Boundary temperature of TRSS

Introduction

Biomass, as a renewable energy source, has great potential to contribute to the future energy mix in many countries. Besides the direct utilization of biomass combustion, gasification to produce fuel gas seems to be a promising method to increase the calorific value of biomass [1]. In biomass energy technologies, pyrolysis process is of key importance because this thermal degradation of solid fuels is present in both combustion and gasification [2, 3]. Meanwhile, thermal decomposition acts as the initial step...
to control the release of volatile fuel during fires which involve fuels of lignocellulosic materials.

As for the decomposition kinetics of biomass, it involves a high number of different reactions due to chemical complexity. Many researchers regarded the biomass as consisting of multiple pseudo components to simplify the decomposition kinetic analysis, thereby different apparent kinetic models were suggested to describe the mass loss behaviors of biomass, mostly based on the thermogravimetric (TG) data. Concerning biomass decomposition in oxidative atmosphere, Momoh et al. [4–7] pointed out that biomass decomposition mainly involves two stages of mass loss processes, with the first step due to wood devolutilization and the second by char oxidation. Consequently, the two-step kinetic models consisting of parallel or consecutive reactions of pseudo components have been widely applied to describe the global decomposition behavior of lignocellulosic materials [8–15]. The kinetic parameters for the pseudo components were generally evaluated by a nonlinear least-squares algorithm using the differential thermogravimetric (DTG) or thermogravimetric (TG) data. However, the least square method produced some skepticism. According to Várhegyi et al. [16, 17], the systematic errors of the thermal analysis could hinder the mechanistic application of the nonlinear least-squares.

Comparatively, Liu et al. [18] developed a new model, named “First Order Pseudo Bi-component Separated-stage Model (PBSM)”, to describe the decomposition behavior of lignocellulosic materials. The model describes the global mass loss by two pseudo components which decompose, respectively, within two separate temperatures ranges. In this model framework, the kinetic analysis of the main mass loss stage can be performed individually for which only linear regression is required. The temperature corresponding to the minimum in the DTG curve is regarded as the point of separation between two mass loss stages. The model was verified to be suitable for the mass loss processes of variable wood and leaf samples under relatively lower heating rates (mostly 10 K min\(^{-1}\)). In the subsequent researches by other authors [19, 20], it was verified that this model could be successfully applied for other types of solid fuels. However, it was also observed that with higher heating rates, the two mass loss steps may overlap within a relatively wide temperature ranges. In such cases, the hypothesis of PBSM may be invalid, and especially it may be difficult to identify the minimum temperature in DTG curves which was assumed in PBSM model to be the separation temperature \((T_{SP})\) between the two stages.

In this work, non-isothermal experiments with oil tea wood collected from Jiangxi province of China. After being dried for 24 h at 80 °C, 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\(^{-1}\) and the temperature was increased from atmosphere temperature to 800 K at the heating rates of 10–25 K min\(^{-1}\) with step of 5 K min\(^{-1}\). 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.

**Theoretical analysis**

Influence of heating rate on the decomposition temperatures of two pseudo components

The kinetic analysis of decomposition is based on the general rate equation:

\[
\frac{d\alpha}{dT} = \frac{A}{\beta} \exp(-E/RT)f(\alpha)
\]

(1)

where \(\alpha\) is the mass loss fraction, \(\beta\) the heating rate (K min\(^{-1}\)), \(E\) the activation energy (kJ mol\(^{-1}\)), \(A\) the pre-exponential factor (s\(^{-1}\)), and \(R\) the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)).

We begin the analysis by using the Kissinger equation [21, 22]:

**Experimental**

The raw material used for experiments was oil tea wood collected from Jiangxi province of China. After being dried for 24 h at 80 °C, 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\(^{-1}\) and the temperature was increased from atmosphere temperature to 800 K at the heating rates of 10–25 K min\(^{-1}\) with step of 5 K min\(^{-1}\). 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.
Table 1 Kinetic parameters of oil tea wood by two-step parallel model in literature [18]

<table>
<thead>
<tr>
<th>Step</th>
<th>$E$/kJ mol$^{-1}$</th>
<th>$\ln A$/s$^{-1}$</th>
<th>$n$</th>
<th>$T_p$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>First</td>
<td>80.7</td>
<td>5.0</td>
<td>1.0</td>
<td>583</td>
</tr>
<tr>
<td>Second</td>
<td>86.3</td>
<td>4.0</td>
<td>1.0</td>
<td>705</td>
</tr>
</tbody>
</table>

\[
\ln \beta - 2 \ln T_p + \frac{E}{RT_p} = \text{const} \tag{2}
\]

where $T_p$ is the peak temperature of DTG curve. The difference form of Eq. 2 is

\[
\frac{1}{\beta} \Delta \beta - \left( \frac{2}{T_p} + \frac{E}{RT_p} \right) \Delta T_p = 0 \tag{3}
\]

and

\[
\Delta T_p = \left( \frac{2}{T_p} + \frac{E}{RT_p} \right) \beta \tag{4}
\]

here, $\Delta T_p$ is the difference in peak temperatures for one pseudo component obtained from the DTG curves at two different heating rates. Naturally $\Delta T_p$ depends on the variation of heating rate. Since the two pseudo components generally hold different kinetic parameters, by using the kinetic parameters in Table 1 and Eq. 4, it is found that with increasing heat rate ($\Delta \beta > 0$), $\Delta T_{P_2} < \Delta T_{P_1}$ (here the subscripts ‘$P_1$’ and ‘$P_2$’ denote, respectively, the first and second DTG peaks), which indicates that the separation distance between the two DTG peaks, i.e., $\Delta T_{P_2} - \Delta T_{P_1}$, has an increase trend. Thus the temperature overlapping region between the reactions of the two pseudo components appears to be enlarged with the increase of heating rate, which may weaken the applicability of PBSM models.

Theoretical analysis of the applicability of PBSM

Recall PBSM adopts the following scheme:

\[
S_1 \xrightarrow{k_1} a_1R_1 + b_1V_1 (T < T_{SP})
\]

\[
S_2 \xrightarrow{k_2} a_2R_2 + b_2V_2 (T > T_{SP})
\]

where $S_1$ and $S_2$ are the pseudo components that decompose, respectively, in the lower and higher temperature regions, $R_i$ and $V_i$ ($i = 1, 2$) are, respectively, the residues and volatiles generated in reaction $i$. $T_{SP}$ is the temperature point corresponding to the minimum in the DTG curve. The mass loss processes are expressed as:

\[
\begin{align*}
\frac{dz_1}{dT} &= \frac{A_1}{\beta} \exp\left(-\frac{E_1}{RT}f_1(z_1)\right) & T < T_{SP} \\
\frac{dz_2}{dT} &= \frac{A_2}{\beta} \exp\left(-\frac{E_2}{RT}f_2(z_2)\right) & T > T_{SP}
\end{align*}
\tag{5}
\]

As shown in Fig. 1, the initial temperature for the second decomposition step ($T_{2\text{initial}}$) is defined as the left intersection point of the second separated DTG curve with the line of zero mass loss rate. Therefore:

\[
\frac{dz_2}{dT} = \frac{A_2}{\beta} \exp\left(-\frac{E_2}{RT}f_2(z_2)\right) = 0 & T < T_{2\text{initial}} \tag{6}
\]

\[
0 < \frac{dz_2}{dT} = \frac{A_2}{\beta} \exp\left(-\frac{E_2}{RT}f_2(z_2)\right) < \epsilon & T_{2\text{initial}} < T < T_{SP} \tag{7}
\]

In addition, we note that in previous researches (e.g., Refs. [7, 13]), the applicability of the parallel reaction model was verified, which holds the kinetic expression as

\[
\frac{dz_2}{dT} = \frac{1}{V_{1\infty} + V_{2\infty}} \left( V_{1\infty} \frac{A_1}{\beta} \exp\left(-\frac{E_1}{RT}f_1(z_1)\right) + V_{2\infty} \frac{A_2}{\beta} \exp\left(-\frac{E_2}{RT}f_2(z_2)\right) \right) & T_{1\text{initial}} < T < T_{2\text{final}} \tag{8}
\]

When the temperature difference between $T_{SP}$ and $T_{2\text{initial}}$ is sufficiently small, $\epsilon$ is a minterm, and then Eq. 8 can be rearranged as Eq. 5. In such cases, it is reasonable to use the temperature $T_{SP}$ as the separation point for the two steps. Using $T_{SP}$, the temperature boundary of two reaction stages can be determined. However, as implied in the last section, a wide overlapping region between the two steps may be induced with increase of heating rate. As a consequence, there will be a relatively larger temperature difference of $T_{SP} - T_{2\text{initial}}$, and the influence of $\epsilon$ on the kinetic analysis of the second mass loss step cannot be ignored. In this case, the use of $T_{SP}$ as the separation point of the two stages may be suspicious.

Results and discussion

Kinetic analysis for oil tea wood with two-step parallel reaction model

The decomposition of oil tea wood starts at around 500 K and completes at 775 K (Fig. 2). All the DTG curves show two similar peaks and the peak temperatures are list in

![Fig. 1 Illustration of definitions of feature points in DTG curve](image-url)
The kinetic law could be expressed by the following equation:

\[
\frac{dv_i}{dT} = \frac{1}{V_{1i} + V_{2i}} \left( V_{1i} \frac{dv_1}{dT} + V_{2i} \frac{dv_2}{dT} \right) \tag{9}
\]

\[
\frac{dv_i}{dT} = \frac{A_i}{\beta} \exp(-E_i/RT)(f(x_i) \quad (i = 1, 2) \tag{10}
\]

To obtain the kinetic parameters for each pseudo component, a nonlinear least-squares algorithm is applied to the mass loss curves (TG) at different heating rates. The NETZSCH Thermokinetics program is used to optimize the kinetic parameters. In order to test the different model functions of \( f(x) \), data from runs at 10, 15, 20, and 25 K min\(^{-1}\) are used, with the same number of experimental points for each run. To enable a visual comparison between the model functions of \( f(x) = (1 - x)^n \) and \( f(x) = (1 - x) \), the experimental and calculated TG curves are presented for the experiment at 10, 15, 20, and 25 K min\(^{-1}\) in Figs. 3 and 4, respectively. As can be observed, \( f(x) = (1 - x)^n \) holds better fitting results than the function of \( f(x) = (1 - x) \). At the same time, the optimized values of the kinetic parameters with the correlation parameters of \( R^2 \) and OF for different model functions are shown in Table 3. The analyses of \( R^2 \) and OF indicate that the model function of \( f(x) = (1 - x)^n \) is more reasonable to be used.

Kinetic analysis for oil tea wood with pseudo bi-composition separate-stage model

Here a new method is developed to evaluate the temperature ranges of the two reaction stages accurately. In Fig. 5, TRFS and TRSS are, respectively, the temperature ranges of the first and second steps, and BT\(_1\) and BT\(_2\) are the corresponding two boundary temperatures. Now that the temperature ranges of two stages are controlled by BT\(_1\) and BT\(_2\), well then the mass loss processes are expressed as:

![Fig. 2 Experimental curves for oil tea wood at heating rates of 10–25 K min\(^{-1}\)](image)

![Fig. 3 Experimental and simulated DTG curves of oil tea wood by two-step parallel model assuming \( f(x) = (1 - x)^n \)](image)

![Fig. 4 Experimental and simulated DTG curves of oil tea wood by two-step parallel model assuming \( f(x) = (1 - x) \)](image)

**Table 2** Degradation characteristics of oil tea wood at different heat rates

<table>
<thead>
<tr>
<th>( \beta/\text{K min}^{-1} )</th>
<th>( T_F/\text{K} )</th>
<th>( T_i/\text{K} )</th>
<th>( \Delta T_F = T_F - T_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>583</td>
<td>705</td>
<td>122</td>
</tr>
<tr>
<td>15</td>
<td>589</td>
<td>721</td>
<td>132</td>
</tr>
<tr>
<td>20</td>
<td>592</td>
<td>723</td>
<td>131</td>
</tr>
<tr>
<td>25</td>
<td>600</td>
<td>729</td>
<td>129</td>
</tr>
</tbody>
</table>
taking logarithm

where

The evaluation of BT1 (BT2) starts from Eq. 10 by taking logarithm

\[
\frac{dz}{dT} = \ln \frac{A}{\beta} - \frac{E}{RT} + n \ln(1 - x)
\]

(12)

for which we regard \(-1/T\) and \(\ln(1 - x)\) as the predictive variables, and \(\ln (dz/dT)\) as the response variable. Generally, when BT1 or BT2 is specified, the kinetic parameters of \(E_1, A_1, n_1\) (or \(E_2, A_2, n_2\)) can be evaluated from Eq. 12 by regression analysis, with a corresponding residual as

\[
\text{OF} = \left( \frac{1}{N} \sum_{i=1}^{N} (\alpha(i)_{\text{exp}} - \alpha(i)_{\text{cal}})^2 \right) / N
\]

(13)

where \(N\) is the number of experimental data. The value of OF function is related to the fitting degree in regression analysis. Therefore, by selecting an optimization of OF, the corresponding BT1 or BT2 is adjusted to be the most reasonable boundary temperature.

### Table 3 Simulation results by two-step parallel model with different model functions: kinetic parameters and statistics indicators

<table>
<thead>
<tr>
<th>β/K min(^{-1})</th>
<th>(E_1/\text{kJ mol}(^{-1})</th>
<th>(\ln A_1/\text{s}(^{-1})</th>
<th>(n_1)</th>
<th>(E_2/\text{kJ mol}(^{-1})</th>
<th>(\ln A_2/\text{s}(^{-1})</th>
<th>(n_2)</th>
<th>\text{OF}</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
<td>72.2</td>
<td>4.16</td>
<td>1</td>
<td>90.5</td>
<td>4.29</td>
<td>1</td>
<td>6.18 × 10(^{-6})</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>73.7</td>
<td>4.43</td>
<td>1</td>
<td>99.6</td>
<td>5.08</td>
<td>1</td>
<td>7.44 × 10(^{-6})</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>74.0</td>
<td>4.58</td>
<td>1</td>
<td>106.1</td>
<td>5.68</td>
<td>1</td>
<td>1.01 × 10(^{-5})</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>78.4</td>
<td>5.00</td>
<td>1</td>
<td>101.1</td>
<td>5.32</td>
<td>1</td>
<td>5.51 × 10(^{-6})</td>
</tr>
<tr>
<td>n</td>
<td>1</td>
<td>4.16</td>
<td>1.25</td>
<td>6.18</td>
<td>100</td>
<td>4.29</td>
<td>1</td>
<td>2.05 × 10(^{-6})</td>
</tr>
</tbody>
</table>

The boundary of TRFS is defined as BT1, and of the values of OF as a function of BT1 is illustrated in Fig. 6. The inflection point of functional curve is regarded as a criterion point (BT\(_{1\text{best}}\)). As shown in Fig. 6, the value of OF has a sharp increase after BT\(_{1\text{best}}\), suggesting that the agreement between the predicted and experimental data becomes worse greatly. Therefore, due to the better fitting degree in regression analysis, BT\(_{1\text{best}}\) is definitely specified as the boundary of TRFS, and the kinetic parameters can thus be extracted.

After the determination of BT\(_{1\text{best}}\) in Fig. 6, the kinetic parameters are obtained by Eq. 12 using linear regression method. The results obtained, respectively, by parallel model, PBSM using BT\(_{1\text{best}}\) and PBSM using \(T_{SP}\) are presented in Table 4. As can be seen, when the heating rates increase from 10 to 25 K min\(^{-1}\), BT\(_{1\text{best}}\) is almost equal to \(T_{SP}\). Therefore, it is reasonable to define \(T_{SP}\) as the separation point for the two mass loss steps. Meanwhile, the results in Table 2 have shown that the temperature overlapping region between two reactions is enlarged at the heating rates from 15–25 to 10 K min\(^{-1}\), which may destroy the basic assumption of PBSM. However, the pre-exponential factors \(A\) and activation energies \(E\) do not vary appreciably when using different kinetic models (PBSM and Parallel model). It is indicated that the assumption plays an exiguous role in applications of PBSM. It is considered that the evaluation of the reaction order \(n\) plays an important role in accurate kinetic analysis. As shown in Table 4, the reaction order \(n\) evaluated from PBSM is higher than that by using parallel model. This may be interpreted by the concept of “adjusting function” proposed by Šestáková [23], who ever suggested the method of using an “adjusting function \(a(\alpha)\)” multiplied with the ideal model function of \(f(\alpha)\) to represent the reasonable model function \(h(\alpha)\), which is expressed as \(h(\alpha) = f(\alpha)\cdot a(\alpha)\), where \(a(\alpha) = (1 - \alpha)^n\). The value of \(n\) varies and the adjusting function effectively counteracts the effect of overlapping region, which makes the PBSM applicable in the first reaction stage.
Kinetic analysis for the second decomposition step

The value of $BT_{2\text{best}}$ is determined as shown in Fig. 7, by the same method as above. The optimized values of fitting parameters for the second reaction stage tested by PBSM and parallel model are shown Table 5, in which the values of $BT_{2\text{best}}$ and $T_{\text{SP}}$ are also presented.

It is interesting to note that the differences between $BT_{2\text{best}}$ and $T_{\text{SP}}$ are significant at all heating rates. Therefore, the temperature ranges of the second mass loss stage are almost different by the two models (using $BT_2$ and $T_{\text{SP}}$). It can be seen from Table 5 that the kinetic parameters optimized by PBSM using the boundary temperature of $BT_{2\text{best}}$ differ from those by PBSM considering $T_{\text{SP}}$.

When the boundary of second stage is specified to be $BT_{2\text{best}}$ or $T_{\text{SP}}$, the calculated activation energy is about 75–90 kJ mol$^{-1}$ or 60–75 kJ mol$^{-1}$. Comparison of OF values shows that the kinetic parameters using $BT_{2\text{best}}$ achieve a higher fitting degree, and thus the “relatively correct” onset point ($BT_{2\text{best}}$) is used to evaluate the kinetic parameters. However, the kinetic parameters by PBSM differ significantly from those by the parallel model. Compared with the parallel model, a worse OF is obtained by using PBSM, which implied that the PBSM could not be suitable to describe the second kinetic process. The adjusting function $a(x) = (1 - x)^n$ may fail to counteract the influence of overlapping region with the change of heating rate. According to previous investigations [14, 24], the order of reaction depends on biomass component (cellulose, hemicelluloses or lignin) being degraded under pyrolysis conditions. Cellulose degradation mostly follows a first order reaction ($n = 1$); lignin follows higher order reaction during thermal degradation ($n > 1$). However, the second stage in the higher temperature range is mostly due to the combustion of char, which differs from the mechanism of lignin pyrolysis. Therefore, the model function of $f(x) = (1 - x)^n$ is not reasonable to describe the behavior of the second decomposition stage. Furthermore, the PBSM is not sufficient to describe the process of char oxidation or combustion. This may be due to the additional complexity of the reactions taking place with the char matrix as the char is heated. It is probably not a question of the model function but due to that the model is too simple for describing the processes. Therefore, an appropriate model to independently describe the second stage needs to be further investigated.

Table 4 Simulation results by PBSM and two-step parallel model for the first decomposition step: kinetic parameters and separation points

<table>
<thead>
<tr>
<th>$\beta$/K min$^{-1}$</th>
<th>$E_1$/kJ mol$^{-1}$</th>
<th>$\ln A_1$/s$^{-1}$</th>
<th>$n_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$BT_{1\text{best}}$ (644 K)</td>
<td>92.2</td>
<td>6.90</td>
</tr>
<tr>
<td></td>
<td>$T_{\text{SP}}$ (645 K)</td>
<td>91.6</td>
<td>6.84</td>
</tr>
<tr>
<td></td>
<td>Parallel model</td>
<td>86.0</td>
<td>5.49</td>
</tr>
<tr>
<td>15</td>
<td>$BT_{1\text{best}}$ (650 K)</td>
<td>86.9</td>
<td>6.25</td>
</tr>
<tr>
<td></td>
<td>$T_{\text{SP}}$ (650 K)</td>
<td>86.9</td>
<td>6.25</td>
</tr>
<tr>
<td></td>
<td>Parallel model</td>
<td>84.0</td>
<td>5.43</td>
</tr>
<tr>
<td>20</td>
<td>$BT_{1\text{best}}$ (659 K)</td>
<td>89.2</td>
<td>6.45</td>
</tr>
<tr>
<td></td>
<td>$T_{\text{SP}}$ (660 K)</td>
<td>88.2</td>
<td>6.36</td>
</tr>
<tr>
<td></td>
<td>Parallel model</td>
<td>86.6</td>
<td>5.79</td>
</tr>
<tr>
<td>25</td>
<td>$BT_{1\text{best}}$ (664 K)</td>
<td>87.5</td>
<td>6.14</td>
</tr>
<tr>
<td></td>
<td>$T_{\text{SP}}$ (665 K)</td>
<td>87.2</td>
<td>6.09</td>
</tr>
<tr>
<td></td>
<td>Parallel model</td>
<td>88.6</td>
<td>5.97</td>
</tr>
</tbody>
</table>
Conclusions

In this paper, by formula derivation, it is found that the activation energy and the DTG peak temperature both control the shift of DTG peak temperatures with the variation of heating rates. For the decomposition of oil tea wood, the separation distance between the two DTG peaks has an increase trend with the increase of heating rate. A narrower temperature overlapping region between two pseudo components reactions appears in higher heating rate.

The two-step parallel model assuming $n$-order function is successful to describe the decomposition of oil tea wood in air, and the obtained kinetic parameters were used as a benchmark to evaluate the applications of PBSM. Based on the comparison between PBSM and two-step parallel model, in the lower temperature range, the adjusting function plays an important role in counteracting the influence of overlapping region with the change of heating rate, while in higher temperature range, it fails to counteract the influence of overlapping region. It is summarized that the model of PBSM is suitable in the lower temperature range, while in the higher temperature range, PBSM needs more improvements to improve its applicability. Meanwhile, the wider temperature overlapping region has a slight influence on the application of PBSM for lower heating rates.

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Table 5 Simulation results by PBSM and two-step parallel model for the second decomposition step: kinetic parameters and separation points

<table>
<thead>
<tr>
<th>$\beta$ K min$^{-1}$</th>
<th>$E_2$ kJ mol$^{-1}$</th>
<th>$\ln A_2$ s$^{-1}$</th>
<th>$n_2$</th>
<th>OF</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 BT$_{2\text{best}}$ (660 K)</td>
<td>79.1</td>
<td>4.15</td>
<td>0.79</td>
<td>$2.2 \times 10^{-6}$</td>
</tr>
<tr>
<td>$T_{SP}$ (645 K)</td>
<td>67.3</td>
<td>3.28</td>
<td>0.74</td>
<td>$6.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>Parallel model</td>
<td>125.0</td>
<td>6.81</td>
<td>0.99</td>
<td>$1.4 \times 10^{-6}$</td>
</tr>
<tr>
<td>15 BT$_{2\text{best}}$ (677 K)</td>
<td>74.8</td>
<td>3.69</td>
<td>0.58</td>
<td>$3.9 \times 10^{-6}$</td>
</tr>
<tr>
<td>$T_{SP}$ (650 K)</td>
<td>60.1</td>
<td>2.59</td>
<td>0.51</td>
<td>$7.3 \times 10^{-6}$</td>
</tr>
<tr>
<td>Parallel model</td>
<td>112.2</td>
<td>6.00</td>
<td>0.94</td>
<td>$2.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>20 BT$_{2\text{best}}$ (674 K)</td>
<td>91.5</td>
<td>4.90</td>
<td>0.67</td>
<td>$4.4 \times 10^{-6}$</td>
</tr>
<tr>
<td>$T_{SP}$ (660 K)</td>
<td>76.5</td>
<td>3.79</td>
<td>0.60</td>
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</tr>
<tr>
<td>Parallel model</td>
<td>126.2</td>
<td>7.14</td>
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<tr>
<td>25 BT$_{2\text{best}}$ (684 K)</td>
<td>75.3</td>
<td>3.65</td>
<td>0.47</td>
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<tr>
<td>$T_{SP}$ (665 K)</td>
<td>63.7</td>
<td>2.80</td>
<td>0.42</td>
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<tr>
<td>Parallel model</td>
<td>130.3</td>
<td>7.48</td>
<td>0.88</td>
<td>$1.1 \times 10^{-6}$</td>
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References