Insight into torrefaction of woody biomass: Kinetic modeling using pattern search method

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ABSTRACT

Torrefaction aroused as a promising pretreatment technique that can improve the fuel properties and thermochemical conversion performance of biomass. The kinetics of biomass torrefaction is fundamental for the investigation of torrefaction reaction mechanisms, and the simulation and optimization of torrefaction processes. The commonly used empirical reaction model has some theoretical drawbacks in describing the kinetics of biomass torrefaction. In this study, the torrefaction kinetics of beech wood was studied using thermogravimetric analysis (TGA) at isothermal temperatures of 493, 523 and 553 K. The nth-order kinetic model was presented to analyze the kinetic experimental data at all torrefaction temperatures simultaneously. The pattern search method was used to optimize the kinetic parameters of the nth-order model for biomass torrefaction. Predicted results from the nth-order model with the optimal kinetic parameters were compared with the experimental data and indicated that the nth-order model satisfactorily predicted the experimental data of beech wood torrefaction at different torrefaction temperatures.

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1. Introduction

In recent decades, biomass containing varying amounts of cellulose, hemicellulose, lignin and small amounts of extractives has attracted attention considering its renewability, abundancy and carbon-neutral [1,2]. However, biomass has high moisture content, low heating value and energy density, poor grindability, hygroscopicity, and structural heterogeneity [3,4]. Those obstacles are associated with the effective utilization of lignocellulosic biomass, especially in the conversion efficiency of biomass as well as economical transportation, handling, and storage [5].

To overcome the recalcitrance of biomass and upgrade the production of high-quality solid biofuel, some pretreatment technologies can be used, whereas torrefaction is a promising one [6,7]. Torrefaction is the mild pyrolysis of biomass within a relatively low-temperature range of 200−300 °C under inert condition [8,9]. Generally, torrefied biomass losses about 30% of the original mass, but retains 90% of the initial energy content [10]. Compared with raw biomass, torrefied biomass has better storage and transportation characteristics, and improved fuel properties, such as lower O/C and H/C ratios, higher energy content and density, better grindability, and hydrophobicity [11,12].

Beech wood used for heat or energy is a clean solid fuel containing low nitrogen, sulphur and ash content [13,14]. In general, combustion of beech wood for the production of heat or electricity is relatively inefficient whereas the gasification of beech wood for fuel gas has commonly been used [15]. However, because of its high moisture content and thermal instability (some light volatiles would release even if it was heated at low temperatures below 250 °C), beech wood gasification may result in the formation of tars in gasification reactors, which may easily cause blockages, plugging, corrosion, and catalyst deactivation, resulting in serious

operational and maintenance problems [16]. According to Prins et al. [17], higher gasification efficiencies can be achieved for solid fuels with lower O/C ratios. Gasifying raw woody biomass directly makes it over-oxidized under high-temperature conditions in the gasifier, therefore, highly oxygenated raw wood biomass is not an ideal solid fuel for gasification from an exergetic point of view [15]. Wood can be gasified more efficiently using torrefaction than conventional direct gasification [15,18−24].

The kinetics of biomass torrefaction is fundamental to investigate the reaction mechanisms of biomass torrefaction and essential to characterize and optimize biomass torrefaction processes for industrial applications (see Fig. 1) [25,26].

Recently, several kinetic models have been proposed for kinetic analysis of biomass torrefaction [27−32]. For example, Świechowski et al. [27] used an empirical reaction model with an exponential form function to describe the torrefaction kinetics of the pruned Oxytree biomass. The same empirical reaction model was found to fit the torrefaction kinetic experimental data of municipal solid waste [32], pine, fir and spruce [33], and wheat straw [34]. However, the empirical model has only a statistical meaning but no physical meaning. Di Blasi and Lanzetta [35] proposed a classical two-step kinetic model and obtained the corresponding kinetic parameters for xylan torrefaction. The two-step kinetic model was also employed to describe the experimental torrefaction kinetic curves of willow with the same parameter set [36]. The two-step kinetic model involves the intermediate product. It is difficult to experimentally measure the intermediate product and therefore to validate the model using experimental data.

In literature, another type of kinetic model, so-called nth-order model successfully described the kinetics of biomass thermochemical conversion, such as biomass pyrolysis [37], biomass torrefaction [38,39], biomass combustion [40]. According to Burnham [41], the nth-order model had the flexibility to fit the reaction
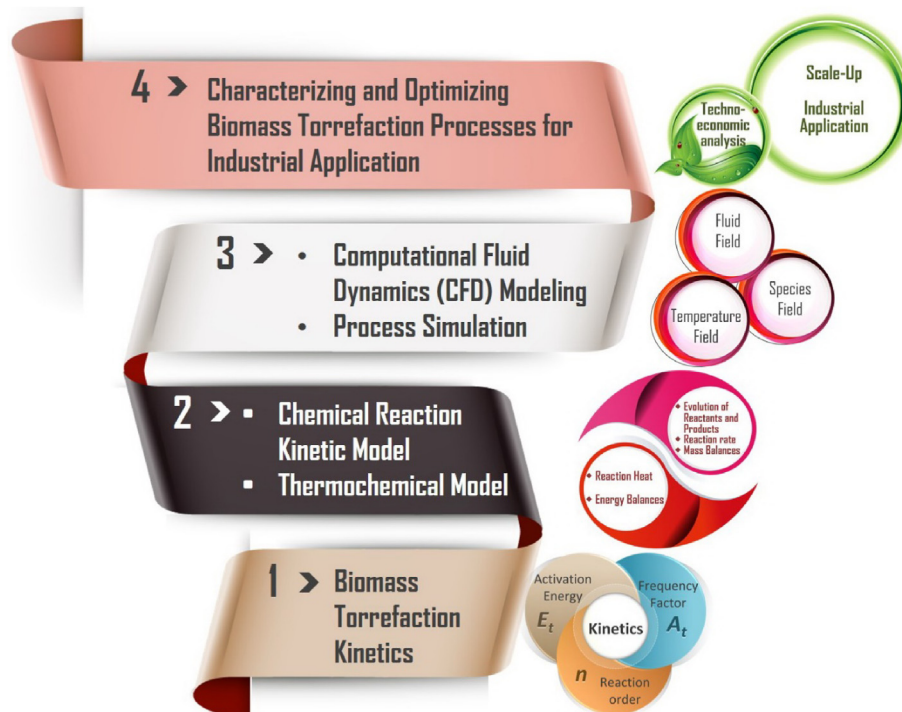

Fig. 1. Importance of the kinetics in the industrial application of biomass torrefaction.

profile of some solid-state reactions, especially the thermal decomposition of solid fuels (e.g., coal, oil shale, polymer, and biomass). Evenly, the nth-order reaction model has been considered as a legitimate tool for treating complex reactivity distributions [42]. Considering the novelty of the nth-order model, we used it to analyze the kinetics of beech wood torrefaction under isothermal conditions and to present the pattern search method in order to estimate the corresponding kinetic parameters.

2. Materials and experiments

2.1. Materials

The beech wood, collected from a farm located in Suqian City, Jiangsu Province, China, was used as the sample for the investigation of biomass torrefaction kinetics. After milling and sieving into less than 0.25 mm in diameter, the samples were dried at 105 °C (378 K) for 24 h for further analyses. The proximate analysis of the sample was performed according to the method presented in our previous review paper [43]. The ultimate analysis was performed in an elemental analyzer (vario EL cube, Elementar Analysensyteme GmbH, Germany). The lower heating value (LHV) of the sample was measured in an oxygen bomb calorimeter (XRY-1B, Shanghai Changji Geological Instruments Co., Ltd., China). The physicochemical analysis results of the beech wood are listed in Table 1.

2.2. Torrefaction kinetics measurement

The isothermal thermogravimetric analysis (TGA) was employed for the kinetic investigation of beech wood torrefaction. The thermogravimetric analyzer (TGA 7, PerkinElmer, Inc., USA) was used for kinetic measurement. Pure nitrogen was used as purge gas with a flow rate of 60 mL min^{-1}. Three torrefaction temperatures (493, 523 and 553 K) were considered in this study. The mass loss during TGA was recorded. The TGA experiments at each torrefaction temperature were repeated in triplicate and the mean value was used for further analysis.

3. Kinetic models for biomass torrefaction

3.1. Empirical reaction model

In the literature [27,32], an empirical exponential form function was usually used to describe the mass loss curves of biomass during torrefaction at differenttemperatures:

$$w(t) = w_0 \cdot \exp(-k \cdot t) \tag{1}$$

where $w(t)$ is the mass (g) after torrefaction time t, w_0 is the initial mass (g), k is the reaction rate constant (s^{-1}) which is usually

Table 1
The physicochemical properties of the beech wood sample.

Property	Value	Measure standard
Proximate analysis (on dry basis), wt.%		
Volatile matter content	83.1 ± 0.6	ASTM E872-82
Fixed carbon content (by difference)	16.3	
Ash content	0.6 ± 0.1	ASTM D1102-84
Elemental analysis (on dry ash-free basis), wt.%		
C content	45.83 ± 0.09	
H content	6.35 ± 0.04	
O content (by difference)	47.51	
N content	0.31 ± 0.01	
Energy content, MJ kg^{-1}		
Low heating value (LHV)	17.1 ± 0.6	ASTM D5865-13

described by the Arrhenius law:

$$k(T) = A_t \exp\left(-\frac{E_t}{R \cdot T}\right) \tag{2}$$

where R is the universal gas constant (8.3145 J mol^{-1} K^{-1}), T is the absolute temperature (K), A_t and E_t are the frequency factor (s^{-1}) and apparent activation energy (J·mol^{-1}) for biomass torrefaction.

Substituting Equation (2) into Equation (1) yields:

$$w(t) = w_0 \cdot \exp\left[-A_t \exp\left(-\frac{E_t}{R \cdot T}\right) \cdot t\right] \tag{3}$$

For the empirical reaction model (Equation (3)), when $t \to \infty$, then $w(t) \to 0$. That contradicts the fact that biomass can't totally be converted during torrefaction. In this aspect, the empirical reaction model has some theoretical drawbacks in describing the torrefaction kinetic behaviors.

3.2. First- and nth-order models

To avoid the theoretical drawback of the empirical reaction model, the first- and nth-order models have been introduced in this study. In those models, biomass decomposes into torrefed products and torrefaction volatiles through a one-step reaction. The reaction rate can be expressed in the following kinetic equation:

$$\frac{d\alpha}{dt} = A_t \cdot e^{-E_t/R \cdot T} \cdot f(\alpha) \tag{4}$$

where α is the degree of conversion (dimensionless), $f(\alpha)$ is the reaction mechanism function which is usually described by the nth-order kinetic mechanism function:

$$f(\alpha) = (1 - \alpha)^n \tag{5}$$

where n is the reaction order (dimensionless).

Substituting Equation (5) into Equation (4) results in:

$$\frac{d\alpha}{dt} = A_t \cdot e^{-E_t/R \cdot T} \cdot (1 - \alpha)^n \tag{6}$$

By separation of variables and integration, we get

$$\int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = \int_0^t A_t \cdot e^{-E_t/R \cdot T} dt \tag{7}$$

For isothermal torrefaction conditions, temperature is maintained constant during torrefaction, the term $A_t e^{-E_t/RT}$ remains constant and Equation (7) can be integrated into the following form:

$$\begin{cases} -\ln(1-\alpha) = A_t \cdot e^{-E_t/R \cdot T} \cdot tn = 1\frac{1 - (1-\alpha)^{1-n}}{1-n} \\ \quad = A_t \cdot e^{-E_t/R \cdot T} \cdot tn \neq 1 \end{cases} \tag{8}$$

The degree of conversion, α, at a given time can be determined by the TGA mass loss data during torrefaction:

$$\alpha = \frac{w_0 - w(t)}{w_0 - w_f} \tag{9}$$

where w_f is the infinite time steady-state mass for biomass torrefaction.

From Equations (8) and (9), the first- and nth-order models for

biomass torrefaction can be obtained:

$$w(t)=\begin{cases} w_0-\left(w_0-w_f\right)\left[1-\exp\left(-A_t\cdot e^{-E_t/R\cdot T}\cdot t\right)\right] & n=1 \\ \\ w_0-\left(w_0-w_f\right)\left\{1-\left[1-(1-n)A_t\cdot e^{-E_t/R\cdot T}\cdot t\right]^{1/(1-n)}\right\} & n\neq 1 \end{cases}$$

(10)

For the above first- and nth-order models, when the time, t, is long enough, the mass of solid residue, $w(t)$, approaches to w_f.

For the first-order model, Equation (10) can be rearranged into the following equation:

$$w(t)=w_0\exp\left(-A_t\cdot e^{-E_t/R\cdot T}\cdot t\right)$$
$$+w_f\left[1-\exp\left(-A_t\cdot e^{-E_t/R\cdot T}\cdot t\right)\right]\text{first}-\text{order}$$

(11)

Based on the above equation for the first-order model, when the time is short, $w_f\left[1-\exp\left(-A_t\cdot e^{-E_t/R\cdot T}\cdot t\right)\right]\approx 0$, then $w(t)\approx w_0\exp\left(-A_t\cdot e^{-E_t/R\cdot T}\cdot t\right)$, which is close to the above empirical model.

Based on the above analyses, it is expected that when t is short, the new model is close to the empirical model, whereas the deviations between the first- and nth-order models and the empirical model increase with increasing t.

If the parameter values of the above models are given, the mass loss results as a function of torrefaction time can be calculated. Fig. 2 showed the parametric study results of the first- and nth-order models for biomass torrefaction, which reflected the influences of the various model parameters on the numerical results of the nth-order model. From Fig. 2, it was obtained that the nth-order model had the flexibility to present various reaction profiles with different reaction order values.

4. Parameter estimation for the models

Since the first- and nth-order models are applied simultaneously to describe the kinetic experimental data of biomass torrefaction at different torrefaction temperatures, the parameter estimation should be needed. For this purpose, the following objective function is established, which uses the sum of the squared errors between the experimental data and model prediction [44]:

$$\text{O.F.}\left(n,A_t,E_t,w_f\right)=\sum_{j=1}^{m_i}\sum_{i=1}^{m_{d,i}}\left(w_{\exp,ij}-w_{\text{cal},ij}\right)^2$$

(12)

where the subscripts exp and cal refer to the experimental data and data calculated from the first- or nth-order models, the subscripts i and j represent the i-th data point and a point in the j-th torrefaction temperature, respectively. When the first- or nth-order model is used with certain parameter values, the w_{cal} and then O.F. values can be computed. The kinetic parameters can be optimized by minimizing the above objective function (12).

If the experimental data at only one temperature is considered for the kinetic analysis of biomass torrefaction, the model parameters can be easily estimated using a common nonlinear optimization method, e.g., least square method, the Levenberg-Marquardt method [45]. It is difficult to determine the parameters using the common nonlinear optimization methods when the experimental
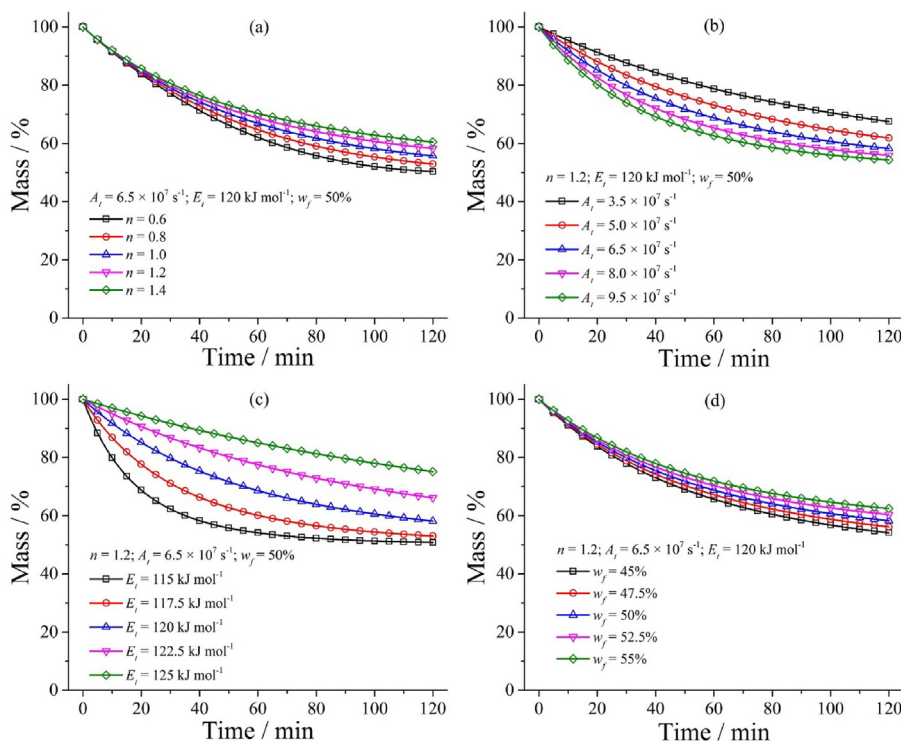

Fig. 2. The parametric study of the first- and nth-order models for biomass torrefaction at $T = 553$ K. (a) n; (b) A_t; (c) E_t; (d) w_f.

data at all the torrefaction temperatures are considered. In this paper, the pattern search method was used to determine the optimal model parameters minimizing the objective function (12).

The pattern search method is an evolutionary technique that is suitable for solving nonlinear optimization problems in various scientific and engineering fields [46]. The method is a direct search, derivative-free method which can process the optimization problem in finite steps with fast convergence without any information about the derivatives of the objective function [47,48]. It was successfully applied in the parameter estimation of the distributed activation energy model for biomass pyrolysis [49,50] and the kinetic model for bio-oil aging [51]. In the implementation of the pattern search method, the search is performed by moving the variable vector in the exploratory and/or pattern move directions [52].

The above optimization calculations were performed in the MATLAB software environment. The corresponding pseudo-code of the parameter estimation of the first- and nth-order models for kinetic modeling of biomass torrefaction were shown in Fig. 3.

5. Results and discussion

5.1. Comparison of kinetic models

Świechowski et al. [27] used the empirical reaction model to fit the experimental kinetic data of the pruned Oxytree biomass torrefaction at different torrefaction temperatures and obtained the corresponding k values (as presented in Fig. 4). The $\ln(k)$ and $-1000/(R \cdot T)$ values were calculated and also included in Fig. 4. A linear regression analysis of the relationship $\ln(k)$ vs. $-1000/(R \cdot T)$ was performed and the kinetic parameters of the empirical reaction model can be obtained: $E_t = 33.37$ kJ mol^{-1}, and $A_t = 7.84 \times 10^{-2}$ s^{-1}. Fig. 5 showed the experimental data and the predicted mass loss curves for the pruned Oxytree biomass torrefaction at different torrefaction temperatures (473, 493, 513, 533, 553 and 573 K) with the empirical model. The experimental data could be described well by the empirical reaction model with the resulting kinetic parameters. It was noteworthy that Świeichowski et al. [27] just

```
•   Step 1: Input experimental data
        T1: (t1, wexp,1)  T2: (t2, wexp,2)  T3: (t3, wexp,3)
•   Step 2: Define the variables and nth-order model
        Variables: n, At, Et, wf
        for i=1:length(datapoint)
            if n=1
                wcal,1(i)=f1(t1(i))  wcal,2(i)=f1(t2(i))  wcal,3(i)=f1(t3(i))
            else if
                wcal,1(i)=f2(t1(i))  wcal,2(i)=f2(t2(i))  wcal,3(i)=f2(t3(i))
            end for if
        end for i
•   Step 3: Define the objective function
        errsum=0
        for j=1:3
            for i=1:length(datapoints)
                errsum = errsum+(wexp,j(i)-wcal,j(i))^2
            end for i
        end for j
        Output errsum
•   Step 4: Initial guess and constraints of variables
        X0: {n0, At0, Et0, wf0}   lb: {nlb, Atlb, Etlb, wflb}   ub: {nub, Atub, Etub, wfub}
•   Step 5: Pattern search optimization
        Set options of pattern search method
        Pattern Search (@objective function, x0, lb, ub, options)
•   Step 6: Output and statistical analysis
        Output: 1) Optimization iterative calculation results; 2) Model parameters
        Statistical analysis:
                1) Coefficience of determination
                2) Model prediction and its comparison with experimental data
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Fig. 3. The pseudo-code of the parameter estimation of the first- and nth-order models for isothermal torrefaction kinetics.

T / K	k / s⁻¹	E_t / kJ·mol⁻¹	A_t / s⁻¹	R²
473	1.59×10^{-5}			
493	2.21×10^{-5}			
513	3.42×10^{-5}	33.37 ± 1.597	7.84×10^{-2}	0.989
533	4.29×10^{-5}			
553	5.16×10^{-5}			
573	7.21×10^{-5}			

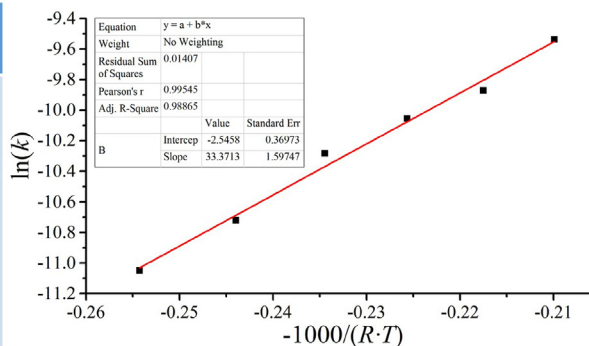| Equation	y = a + b*x	
Weight	No Weighting	
Residual Sum of Squares	0.01407	
Pearson's r	0.99545	
Adj. R-Square	0.98865	
	Value	Standard Err
B Intercep	-2.5458	0.36973
Slope	33.3713	1.59747

Fig. 4. Calculations of the empirical reaction model parameters for the pruned Oxytree biomass torrefaction.

considered the torrefaction time range from 0 to 60 min. Fig. 5 also showed the calculated mass loss curves from the first-order model with the kinetic parameters ($n = 1$, $w_f = 20.2$, $E_t = 34.47$ kJ mol⁻¹, and $A_t = 1.30 \times 10^{-1}$ s⁻¹). It was seen that (1) in the time range between 0 and 120 min the curves calculated from the first-order model were very close with the data calculated from the empirical reaction model; (2) when $t > 120$ min, the deviations between the data calculated from the first-order model and the empirical model became larger and larger. The reason for the deviations was given in the section 'First- and nth-order models', in this case, the value of 200 min was dependent on the values of kinetic parameters.

5.2. Kinetic analysis of beech wood torrefaction

The mass loss data obtained from isothermal TGA at different temperatures for the torrefaction of the beech wood sample were normalized according to the method presented in our previous papers [53,54]. The normalized mass loss values at different torrefaction temperatures for typical torrefaction time were listed in
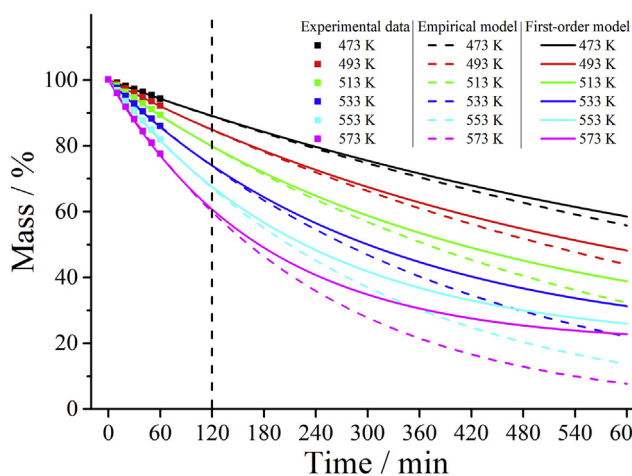
Fig. 5. Comparison between the empirical and first-order models for the pruned Oxytree biomass torrefaction.

Table 2
Mass loss data of beech wood at different torrefaction temperatures.

Temperature/K	Torrefaction time/min				
	30	60	90	120	150
493	96.52	95.55	94.64	94.08	93.66
523	90.92	87.79	85.76	83.72	82.32
553	75.56	68.36	63.73	60.41	57.62

Table 2, where it could be obtained that higher temperature facilitated a faster mass loss during torrefaction. This indicated that the thermal decomposition reaction intensified and torrefaction volatile products released faster when the beech wood sample underwent torrefaction at the higher temperatures. Similar results were found in the torrefaction kinetics of various types of biomass [55–57].

The first- and nth-order models have different expressions and both models were used for kinetic modeling of beech wood torrefaction. The pattern search method was employed to perform the parameter estimation. Before the optimization calculations, the initial guesses and the low and upper constraints of the model parameters should be provided. According to the value ranges for those model parameters published in the literature [25,36,39,58,59], the constraints of the model parameters were determined and listed in Table 3. The corresponding initial guesses were chosen to be close to the median values of the parameter constraints.

The optimization calculations for the first-order model using the pattern search method, including the best objective function value at each iteration, function evaluations per interval, and mesh-size at each iteration were showed in Fig. 6, which indicated that the objective function decreased with iteration and the optimization problem could be solved with fast convergence using the pattern search method.

According to the optimization calculations using the pattern search method for the kinetic modeling of beech wood torrefaction, the parameter values of the first- and nth-order models can be obtained and listed in Table 4. The predicted curves calculated from the first- and nth-order models with the optimal parameter values and the experimental data of beech wood torrefaction at different torrefaction temperatures were shown in Fig. 7. The coefficients of determination (R^2) between the experimental data and the curves predicted from the 1st- and nth-order models at different torrefaction temperatures were calculated and also showed in Fig. 7. From the comparison illustrated in Fig. 7, it was observed that (1) comparing with the first-order model, the nth-order model provided more accurate prediction for describing the kinetic experimental data of beech wood torrefaction, (2) the nth-order model was effective and accurate enough ($R^2 > 0.97$) for the kinetic description of beech wood torrefaction.

According to the nth-order model coupled with the optimal kinetic parameters, the curves of beech wood torrefaction with interpolated and extrapolated torrefaction temperatures of 503, 533 and 563 K were predicted and plotted in Fig. 8.

Table 3
The initial guesses and constraints of the model parameters.

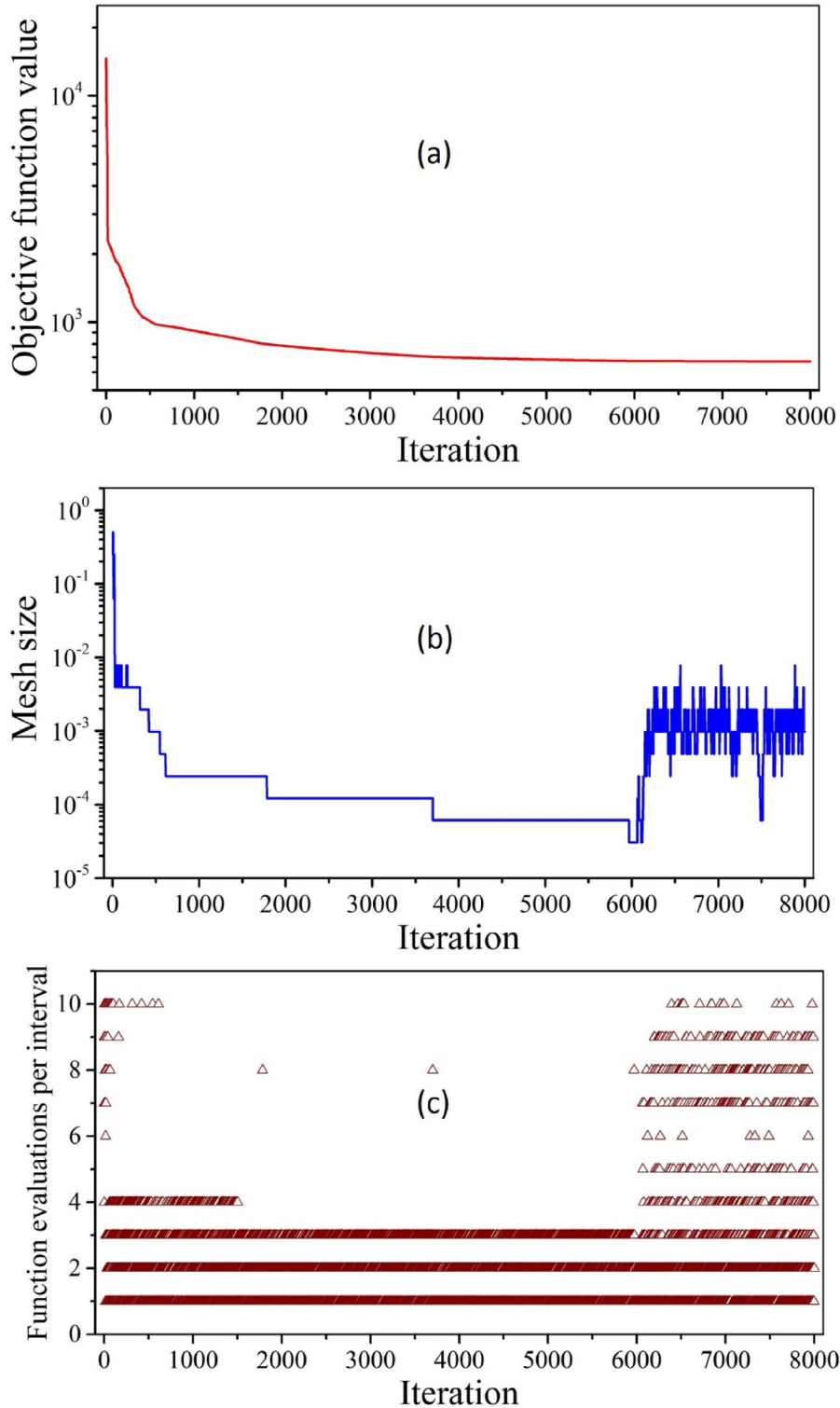|	first-order model	nth-order model ($n > 1$)	nth-order model ($n < 1$)
Initial guess	$A_t = 1.6 \times 10^5$ s^{-1} $E_t = 100$ kJ mol^{-1} $w_f = 40\%$	$A_t = 1.6 \times 10^5$ s^{-1} $E_t = 100$ kJ mol^{-1} $w_f = 40\%$ $n = 2.0$	$A_t = 1.6 \times 10^5$ s^{-1} $E_t = 100$ kJ mol^{-1} $w_f = 40\%$ $n = 0.8$
Constraints	A_t: $(1.0 \times 10^{-5}, 8.0 \times 10^8)$ s^{-1} E_t: $(10, 300)$ kJ mol^{-1} w_f: $(10, 54.3)$ %	A_t: $(1.0 \times 10^{-5}, 8.0 \times 10^8)$ s^{-1} E_t: $(10, 300)$ kJ mol^{-1} w_f: $(10, 54.3)$ % n: $(1.01, 5.5)$	A_t: $(1.0 \times 10^{-5}, 8.0 \times 10^8)$ s^{-1} E_t: $(10, 300)$ kJ mol^{-1} w_f: $(10, 54.3)$ % n: $(0.5, 0.99)$

Fig. 6. Optimization calculation results for the first-order model using pattern search method. (a) Best objective function value at each iteration; (b) Mesh size at each iteration; (c) Function evaluations per interval.

Table 4
The parameter values of the first- and nth-order models for beech wood torrefaction.

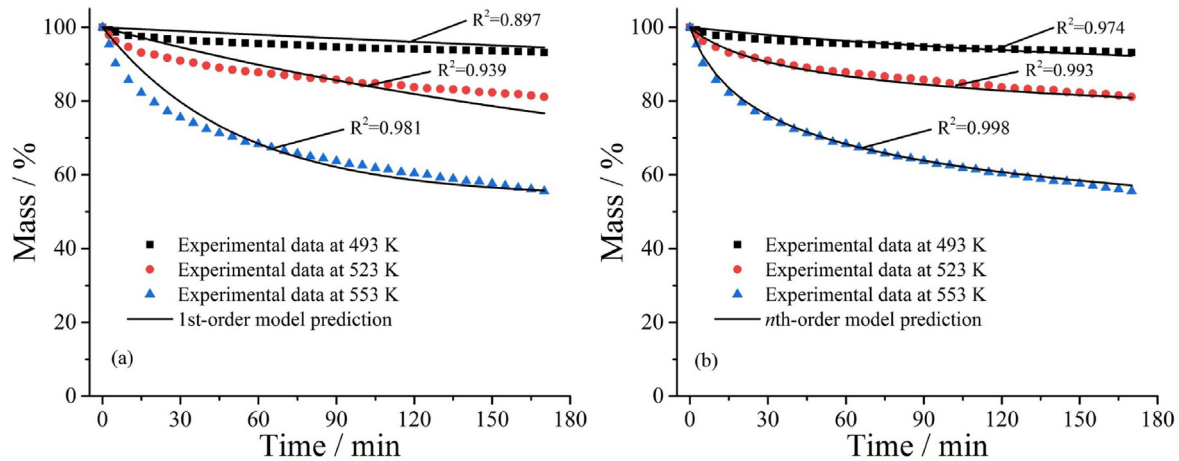| Parameter	first-order model	nth-order model
A_t/s^{-1}	6.00×10^7	3.89×10^8
$E_t/kJ \ mol^{-1}$	119.41	122.89
$w_f/\%$	54.30	44.83
n	1.00	2.68
O·F.	673.94	102.48

Fig. 7. Comparison between the experimental data and curves predicted from the (a) first- and (b) nth-order models.
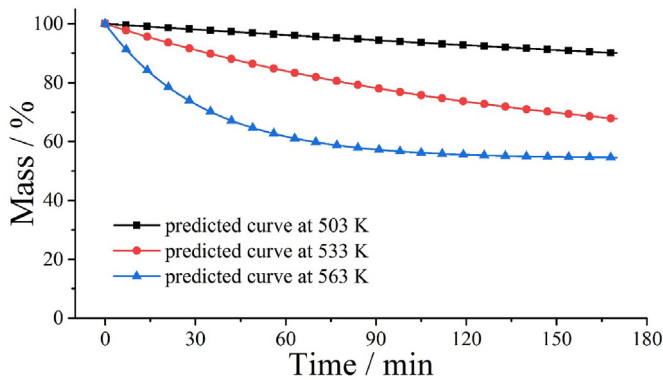

Fig. 8. The predicted curves at 503, 533 and 563 K from the nth-order model with the optimal kinetic parameters for beech wood torrefaction.

6. Conclusions

(1) The isothermal TGA at three torrefaction temperatures of 493, 523, and 533 K was employed to investigate the torrefaction kinetics of beech wood. The experimental results showed that high temperature facilitated the thermal decomposition reactions during torrefaction.

(2) The pattern search method was used for the parameter estimation of the model by fitting the experimental data at all torrefaction temperatures simultaneously. The optimization calculation results showed that the pattern search method worked well for the determination of the model parameters.

(3) The nth-order model provided a more accurate prediction than the first-order model in describing the kinetics of beech wood torrefaction. The activation energy, frequency factor,

and reaction order for the beech wood torrefaction were $E_t = 123 \ kJ \ mol^{-1}$, $A_t = 3.89 \times 10^8 \ s^{-1}$, and $n = 2.68$.

Credit author statement

Hanqi Duan (co first-author): Physicochemical characterization of biomass; Data processing, Writing - original draft; Zhiqing Zhang (co first-author): Thermogravimetric analysis of biomass; Optimization calucaltions, Writing - original draft preparation; Md. Maksudur Rahman: Pre-treatment of experimental data, Reviewing and editing; Xiaojuan Guo: Writing — Reviewing and editing; Xingguang Zhang: Writing — Reviewing and editing; Junmeng Cai: Supervision; Writing; Programming; Writing, Reviewing and editing.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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