

TWO-STEP KINETIC MODELS FOR THERMAL DECOMPOSITION OF FOREST COMBUSTIBLES: THREE KINETIC SCHEMES

N.A. Liu and H.X. Chen

State Key Laboratory of Fire Science, University of Science and Technology of China
Hefei, Anhui 230026, P. R. China

ABSTRACT

In fire research, simplified kinetic models of thermal decomposition of charring combustibles with high simulation accuracy are of great importance in modelling of solid ignition and fire propagation. In this work, the wood and leaf samples of oil tea, China fir, *Michelia maudiae*, China Gugertree, and masson pine were subject to thermogravimetric experiments in air atmospheres, in order to gain a deep understanding over the three kinetic schemes, *i.e.* consecutive, parallel and separate schemes. It is found that the three kinetic schemes all lead to mass fractions and kinetic parameters which correlate reasonably well with the decomposition processes, and the two conversion processes intersect within a quite narrow temperature range. Theoretical analysis indicates that with separate features in decomposition processes, the three kinetic schemes may be compatible in kinetic sense, and thus the consecutive and parallel schemes can be simplified by the separate kinetic scheme with high accuracy and reliability. It is also implied that the remarkable differences in the kinetic models and parameters in literatures may be due to the different materials and experimental techniques or conditions used.

KEYWORDS: Thermal decomposition, Forest combustible, Kinetic model, Two-step kinetic scheme

INTRODUCTION

As a primary step essential for solid ignition and fire propagation, the thermal decomposition of forest combustibles has been a major concern in fire research community, however, reliable and accurate kinetic description is still a subject of intense debate, mainly due to the great chemical complexity involved. In early research, Schwenker and Beck¹ succeeded in isolating 37 products from the degradation of cellulose (which is one of the major components of forest species), suggesting the great difficulties faced by the detailed chemical analysis. Instead, apparent kinetic analysis has witnessed great success in recent decades, in which the kinetic modelling definitely defines, on one hand, the kinetic scheme, *i.e.* the combination of single reaction steps, and on the other hand, the reaction type for each reaction step. In principle, the apparent kinetic analysis intends to provide an apparent model with compact formulation and few model parameters, which has been a topic of continuing interest for fire scientists. Apparent kinetic analysis has been successfully used to describe the decomposition of the major components of forest species, *i.e.* cellulose, lignin and hemicellulose at varying levels of detail (see review²⁻⁴). However, for the overall decomposition process of any forest material, kinetic modeling has always been a source of puzzlement and controversy since the decomposition occurs via much more complex mechanisms. Different kinetic schemes and reaction types were suggested with various kinetic parameters. The kinetic schemes most suggested are the overall kinetic scheme⁵⁻⁹, consecutive kinetic scheme¹⁰⁻¹² and parallel kinetic scheme¹³⁻²⁰. In the overall kinetic scheme, a homogeneous reaction model is developed for the entire conversion stage. Although with simple expressions, this scheme is short of kinetic significance since it cannot reflect the decomposition kinetic complexity. For the consecutive kinetic scheme, only a few reports are available which used sequential steps to describe the decomposition¹². The most suggested kinetic scheme seems to be the three independent parallel reaction diagram correlating the decompositions of hemicellulose, cellulose and lignin¹⁶⁻²². A most recent report of this scheme is on the non-isothermal kinetics of wood chips and an energy crop (thistle) by this scheme¹⁷. Comparatively, some authors¹³⁻¹⁵ claimed the kinetic model can be simplified by two parallel pseudo components, in light of the fact that the decomposition tests obviously shows two major peaks. Additionally, first-order and irreversible reaction type has

been suggested by most authors, however, even with the same reaction type, different kinetic parameters were frequently reported.

Most researches were conducted in inert atmospheres which help prevent the products from reacting with air. However, for the purpose of developing reasonable sub-models of decomposition for fire modeling, air atmosphere should be used instead to reflect the oxidation effect. Importantly, the work in oxidization atmosphere^{8-9,14} indicated that although the secondary mass loss peak is largely affected by the oxidation effect, apparent kinetic analysis is feasible with high reliability.

Compared with the above cited general kinetic schemes, another simplified scheme, *i.e.* separate kinetic scheme, was proposed by Liu *et al.*²³, which holds compact formulations. However, the correlation of this scheme with the general consecutive and parallel schemes remains to be investigated. The major issue is the great variations in both kinetic schemes (including reaction types) and kinetic parameters, which seem to be the present focus of debate for the decomposition of forest combustibles. However, one viewpoint of the authors is that these variations may be mainly due to the large variety of raw materials used, the different pyrolysis techniques and different experimental conditions used. By the same set of decomposition data, this work intended to systematically investigate and compare the three two-step kinetic schemes, *i.e.* consecutive kinetic scheme, parallel kinetic scheme, and separate kinetic scheme, whereby the compatibility and difference among the three different kinetic schemes are expected to be deeply understood.

MATERIALS AND METHODS

Materials

The raw materials used were respectively the wood and leaf of Oil tea (*Camellia Oleifera*), China fir (*Cunninghamia lanceolata* (Lamb.)Hook.), *Michelia maudiae* (*Michelia maudiae* Dunn), China Gugertree (*Schima superba* Gardner & Champ.), and masson pine (*Pinus massoniana*). These materials were collected from Jiangxi province of China. In laboratory, the materials were first cut and then ground, with particle size being approximately 40 μ m.

Thermogravimetric Analysis

The samples were subject to thermogravimetric experiments by using a STA 409C Thermobalance, for which the temperature calibration was performed by Curie Point Standards. The samples were evenly distributed over the open sample pan of 5 mm diameter, loosely, with the initial weight all kept to be lower than 10 mg. The depth of the sample layer is about 0.5 mm. An air stream was continuously passed into the furnace at a flow rate of 50 ml/min. The temperature was increased to 750°C at a rate of 10°C/min for all samples. Different masses (4 to 10 mg) were used for masson pine to check the effect of mass and heat transport effects, and the results showed acceptable agreements, indicating that the physical transport effect is low. For oil tea wood sample, tests by 5 different heating rates from 5°C/min to 25°C/min (with step of 5°C/min) were performed. In another case, nitrogen was used for oil tea wood sample at heating rate of 5°C/min.

Kinetic Analysis Methods

Data pretreatment

In each test, with the original data the normalized mass-loss fraction is determined and plotted versus temperature as the thermogravimetric (TG) curve. The derivative thermogravimetric (DTG) curve is calculated by smoothing and differentiation of the TG curve with respect to temperature.

In kinetic analysis, the differential methods, including differential model-fitting methods (*e.g.* Freeman-Carroll method), iso-conventional methods (*e.g.* Friedman method), and Direct Nonlinear Regression (DNR) method based on fitting of mass loss rate data by optimization, all use derivative thermogravimetry (DTG) data. For these differential methods noise suppression by smoothing

algorithm is of primary importance, since in mathematics the DTG data is obtained by the numerical differentiation of TG data, and the noises of TG data will be greatly enlarged by the numerical differentiation, leading to DTG data with high fluctuations. However, for thermal analysis the smoothing method and relevant parameters are still too often selected by intuition or blind guess rather than by consideration of firm guidelines. In our previous research²⁴, it was indicated that Gaussian algorithm can be effectively applied in the smoothing of decomposition data, and thus this method and suggested smoothing parameter are utilized in this paper.

Kinetic models and analysis methods

Consecutive, parallel and separate kinetic schemes are used to investigate the kinetic modeling of decomposition of forest combustibles. For the former two schemes, Direct Nonlinear Regression method is used to seek the reasonable kinetic model functions and relevant kinetic parameters. For the separate kinetic scheme, Coats-Redfern method²⁵ is used. First order reaction type is assumed, which has been recognized by most researchers.

Model-free methods including Friedman and OFW methods are used to verify the two-stage kinetic scheme and also suggest the reasonable initial parameters for direct nonlinear regression.

RESULTS AND DISCUSSION

Features of Mass Loss Curves for Forest Materials

The decomposition characteristics as shown in Figs. 1 and 2 are quantified by several feature temperatures with the corresponding mass fractions and devolatilization rates (Table 1). All samples hold the same general shape for the TG-DTG curves. After the water evaporation occurring within 100 to 180°C, the first major mass loss begins slowly and accelerates rapidly within 290 to 340°C, followed by a second major mass loss which reaches an overall mass loss of 85 to 90% at nearly 500°C. As the heating rate increases, the TG curves as expected shift to higher temperature regions (Fig. 2) and show the same variation modes. As indicated in literature, the heating rates used should promise there's no temperature gap between the sample and its surroundings.

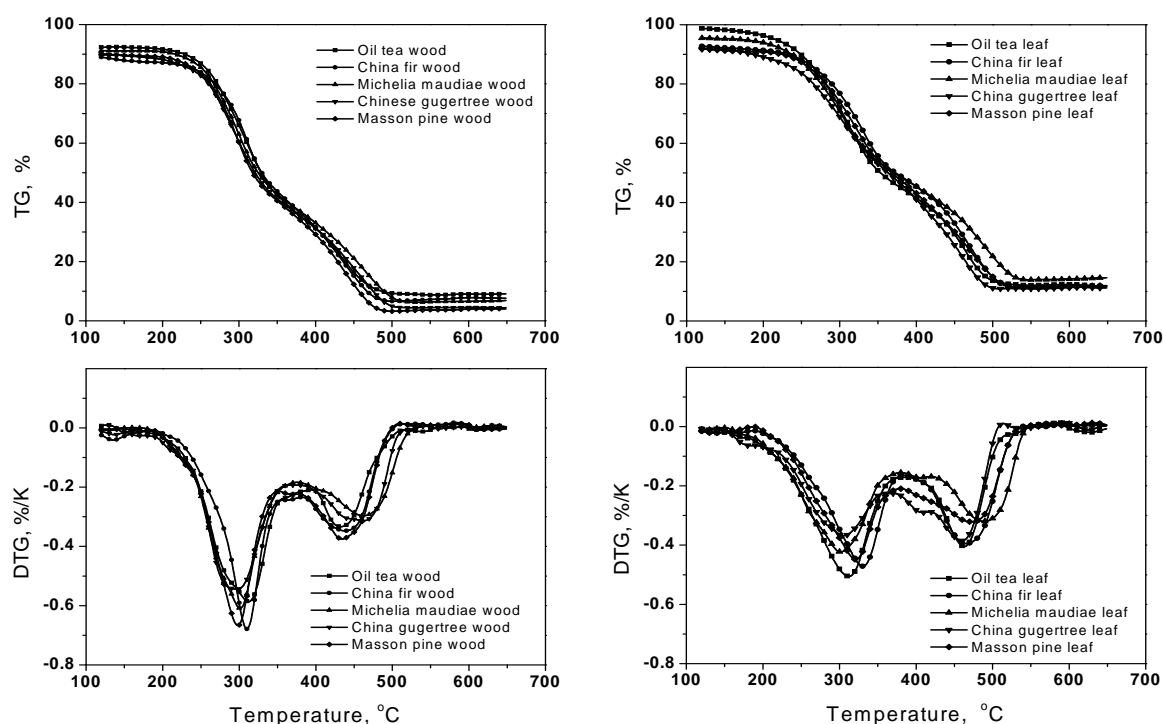


FIGURE 1. TG-DTG curves of forest combustible samples in air at 10°C/min

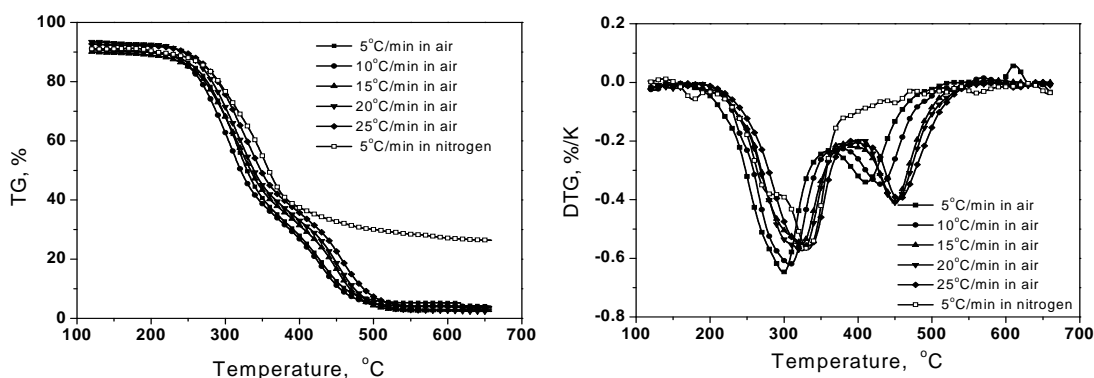


FIGURE 2. TG-DTG curves of oil-tea wood in air at different heating rates of 5 to 25°C/min and in nitrogen at 5°C/min

TABLE 1. Decomposition characteristics of forest combustible samples: temperatures and mass fractions

Samples	Symbol	β (°C/min)	T_{p1} (°C) ^a	T_{p2} (°C) ^a	DTG _{p1} (%/K) ^b	DTG _{p2} (%/K) ^b	M_{onset} (%) ^c	M_{end} (%) ^d
China fir leaf	LF	10	331	466	0.47	0.40	91.7	11.3
China fir wood	WF	10	318	444	0.68	0.35	89.2	3.7
Michelia maudiae leaf	LM	10	302	488	0.42	0.32	95.3	13.9
Michelia maudiae wood	WM	10	302	461	0.61	0.30	91.1	6.3
China gugertree leaf	LG	10	306	460	0.37	0.38	91.6	10.9
China gugertree wood	WG	10	298	463	0.55	0.31	89.4	4.4
Masson pine leaf	LMP	10	321	470	0.45	0.32	90.9	11.4
Masson pine wood	WMP	10	298	434	0.67	0.37	89.3	3.2
Oil tea leaf	LOT	10	313	463	0.51	0.41	97.4	12.5
Oil tea wood	WOT	5	300	412	0.66	0.35	89.8	5.3
		10	308	431	0.62	0.35	90.5	4.0
		15	324	450	0.55	0.41	89.4	2.7
		20	324	450	0.57	0.41	89.6	0.2
		25	333	455	0.56	0.40	92.1	4.1
N ₂		5	333		0.56		91.8	25.6

^a Temperatures of DTG peaks. ^b Mass loss rate at temperatures of DTG peaks.

^{c, d} Mass fractions at the beginning and end temperatures (determined by DTG curve) of decomposition

The decomposition results in nitrogen can be used as reference by which we can examine the decomposition mechanism in air atmosphere at lower temperatures (where pyrolysis rather than oxidation plays a major role). As shown in Fig. 2, the mass loss in nitrogen evidences a large DTG peak with a shoulder and a long tail, while under different conditions two or three distinct DTG peaks can be observed^{10,13,18}. No matter how many peaks be observed, they have been determined to be ascribed to the pyrolysis of hemicellulose and cellulose, accompanied by lignin pyrolysis which generally occurs slowly over a very broad range of temperatures^{3,18}. It is observed from Fig. 2 that up to about 350°C, the DTG curves in air and nitrogen are practically compatible, showing that the material does not undergo significant oxidation. Above 350°C, a new peak is observed in air, which is

largely due to the oxidation of char since little residue is left at the end. This behaviour has been reported by other authors¹⁸. This comparison indicates that the first DTG peak in air is largely due to the pyrolysis of hemicellulose and cellulose, and in part due to that of lignin, while the second DTG peak is affected by oxidization in a considerable degree.

Two-step Kinetic Modeling of Forest Combustibles

Justification of two-step kinetic scheme by model free analysis

The dependence of the activation energy on the mass fraction obtained by model free analysis using data at different heating rates helps identify the apparent reaction steps involved in decomposition. The Friedman method is expressed as:²⁶

$$\ln[\beta_i(d\alpha/dT)_{\alpha,i}] = \ln[A_\alpha f(\alpha)] - E_\alpha / RT_{\alpha,i} \quad [1]$$

Here E is the activation energy, A the pre-exponential factor, and R the ideal gas constant. The variable α denotes the mass loss fraction. The subscript i represents an ordinal number of the experiment conducted at the heating rate β_i . In contrast, the Ozawa-Flynn-Wall (OFW) method²⁶ uses the integral form of the rate equation with Doyle's approximation²⁷:

$$\ln(\beta_i) = \ln \frac{A_\alpha E_\alpha}{R} - \ln G(\alpha) - 5.3305 - 1.052 \frac{E_\alpha}{RT_{\alpha,i}} \quad [2]$$

where $G(\alpha) = \int_0^\alpha 1/f(\alpha) d\alpha$. The advantage of model free methods lies in the fact that they can be used to evaluate the activation energy without any prior knowledge of the model function $f(\alpha)$. However, as indicated by Vyazovkin²⁵, the activation energy evaluated by model free methods is just an average value of the activation energies for multi-step reactions. Agrawal²⁸ even claimed that the model free method of Friedman yields meaningless values of the activation energy for multi-step reactions. Nevertheless, the model free analysis acts as a preliminary stage by which the multi-step feature of a decomposition process can be detected from the dependence of the activation energy on the reaction degree. Additionally, the estimated activation energy means a great help to deliver reasonable initial values for nonlinear regression computations.

The data of oil tea wood sample by 5 heating rates were subject to both Friedman and OFW methods. The Gaussian smoothing algorithm suggested in our recent work²⁴ is used here to obtain smoothed DTG data. When activation energy is evaluated, the pre-exponential factor is evaluated as the average value over all dynamic heating rates in terms of [1] and [2]. For both methods the plots of activation energy E and pre-exponential factor $\ln A$ versus conversion show obvious two-stage feature (Fig. 3), separated at the conversion of nearly 0.6 to 0.7, which clearly indicates that the overall process can be modeled by two-step kinetic scheme, in apparent kinetic sense. Based on this result, we prefer the two-step kinetic scheme rather than the three-step scheme since for kinetic modeling, the increase in the number of model parameters has no physical or chemical meaning, and also complicates the application of parameters for practical uses.

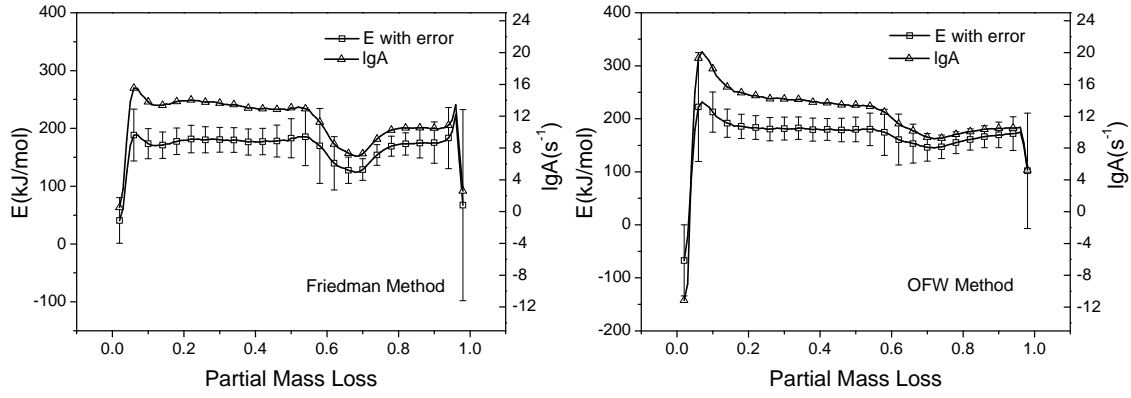
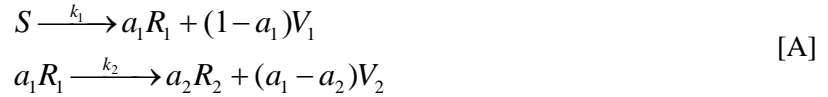


FIGURE 3. Model free analysis on decomposition of oil tea wood sample by Friedman and OFW methods. Heating rates used: 5°C/min, 10°C/min, 15°C/min, 20°C/min, 25°C/min

Two-step consecutive kinetic scheme

This scheme consists of two independent reactions corresponding to the decomposition of two pseudo-components, as follows:



where S is the original sample, R_i and V_i are respectively the residue and volatiles generated in reaction i and the yield coefficient a_i is expressed as grams of R_i divided by grams of reacted fuel ($S_0 - S$), where S_0 is the initial solid amount. The maximum amounts of volatiles $V_{i\infty}$ evolved by reactions 1 and 2 are respectively $(1 - a_1)$ and $(a_1 - a_2)$. Consequently a_1 equals $(1 - V_{1\infty})$ and a_2 equals $(1 - V_{1\infty} - V_{2\infty})$.

Based on mass balance the rate equations can be developed:

$$\frac{d\alpha_1}{dT} = \frac{A_1}{\beta} \exp(-E_1 / RT) (1 - \alpha_1)^{n_1}
 \tag{3}$$

$$\frac{d\alpha_2}{dT} = \frac{A_2}{\beta} \exp(-E_2 / RT) (\alpha_1 - \alpha_2)^{n_2}
 \tag{4}$$

where $\alpha_i = V_i / V_{i\infty}$ ($i = 1, 2$), n_i ($i = 1, 2$) is the apparent reaction orders. Here the Arrhenius equation is assumed for the rate constant terms. The overall degree conversion α is expressed as:

$$\alpha = \frac{w_0 - w}{w_0 - w_\infty} = \frac{V}{V_\infty} = \frac{V_1 + V_2}{V_{1\infty} + V_{2\infty}} = \frac{V_{1\infty} \alpha_1 + V_{2\infty} \alpha_2}{V_{1\infty} + V_{2\infty}} = r \alpha_1 + (1 - r) \alpha_2
 \tag{5}$$

where w is the weight fraction of the sample, and the subscripts 0 and ∞ denote respectively the initial and final decomposition temperatures. The term r is the yield coefficient of the first mass loss stage.

Multivariate nonlinear regression is used for simulation which allows a direct fit of the model to the data without any transformation and approximations. Another advantage is that there are no limitations with respect to the complexity of the model. The computation is conducted to minimize the objective function, OF , defined as:

$$OF = \sum_{i=1}^N (\alpha_{i,\text{exp}} - \alpha_{i,\text{cal}})^2 \quad [6]$$

where N is the number of data points, and the subscripts “exp” and “cal” mean experimental and calculated data. The parameters to be optimized are the activation energies (E_1 , E_2), the pre-exponential factors (A_1 , A_2), and the yield coefficient r . $V_{2\infty}$ is available from the mass loss curve, the a_1 and a_2 are then easily determined. The first-order reaction type recognized by most authors is assumed. The simulation is conducted by a 5th-degree RUNGE-KUTTA embedding method with automatic optimization of the interpolation nodes. The mean relative error of the nonlinear regression is defined as:

$$\text{Dev} = 100\% \frac{\sqrt{\sum_j [(d\alpha/dT)^{\text{exp}} - (d\alpha/dT)^{\text{calc}}]^2} / (N_{\text{data}} - N_{\text{parameter}})}{\max[-(d\alpha/dT)^{\text{exp}}]}$$

where N_{data} is the number of data points and $N_{\text{parameter}}$ is the numbers of independent parameters employed in the model (A_i , E_i , r_i , $i = 1, 2$).

From the simulation results shown in Table 2 and Fig. 4, it is obvious that there is a good agreement between the experimental and predicted results, indicating that in all cases, a two-step consecutive scheme consisting of decompositions of two pseudo components describes well the process. The kinetic data always result in low values of mean relative error (generally lower than 1, when the conversion fraction α is in unit of percent).

TABLE 2. Simulation results by two-step consecutive, parallel and separate reaction schemes: kinetic parameters and separation point

Sample	Consecutive scheme				Parallel scheme				Separate scheme	
	lgA(s ⁻¹)	E(kJ/mol)	r	T*(°C)	lgA(s ⁻¹)	E(kJ/mol)	r	T*(°C)	lgA(s ⁻¹)	E(kJ/mol)
LF	3.9	72.3	0.5	373	3.9	72.3	0.5	373	4.3	77.4
	6.6	126.0	4	383	6.6	126.0	3	383	6.7	128.6
WF	6.5	97.4	0.5	343	6.5	97.5	0.5	343	6.4	97.5
	4.8	96.2	3	334	4.8	96.2	2	334	4.9	99.6
LM	2.7	57.3	0.5	362	2.7	57.2	0.5	361	3.2	62.7
	4.5	100.2	6	374	4.5	100.2	6	374	4.1	94.6
WM	5.5	84.9	0.5	337	5.5	84.9	0.5	337	5.3	85.0
	3.3	79.1	5	330	3.3	79.2	4	331	4.9	102.5
LG	1.9	49.5	0.5	374	1.9	49.5	0.5	373	2.7	58.0
	6.0	115.2	5	362	6.0	115.5	4	362	5.4	107.8
WG	4.6	76.3	0.5	341	4.6	76.2	0.5	341	5.0	81.5
	4.0	88.6	6	337	4.0	88.6	6	338	5.6	110.0
LMP	4.0	71.9	0.5	363	4.0	71.8	0.5	363	4.0	72.8
	4.1	91.5	1	351	4.1	91.5	0	352	4.8	101.8
WMP	5.9	89.3	0.5	333	5.9	89.2	0.5	333	5.8	88.6
	4.7	95.0	4	333	4.7	95.1	4	333	4.8	97.5
LOT	2.6	55.5	0.6	360	2.6	55.5	0.6	361	2.8	59.0
	8.0	143.7	3	379	8.0	143.7	3	382	7.0	130.9
WOT	5.9	89.5	0.6	342	5.9	89.5	0.6	341	5.6	88.4
	4.7	93.77	0	322	4.7	93.77	0	321	5.7	109.3

Note: T^* denotes the end temperature of the first step (the first row for each sample) and the initial temperature for the second step (the second row for each sample).

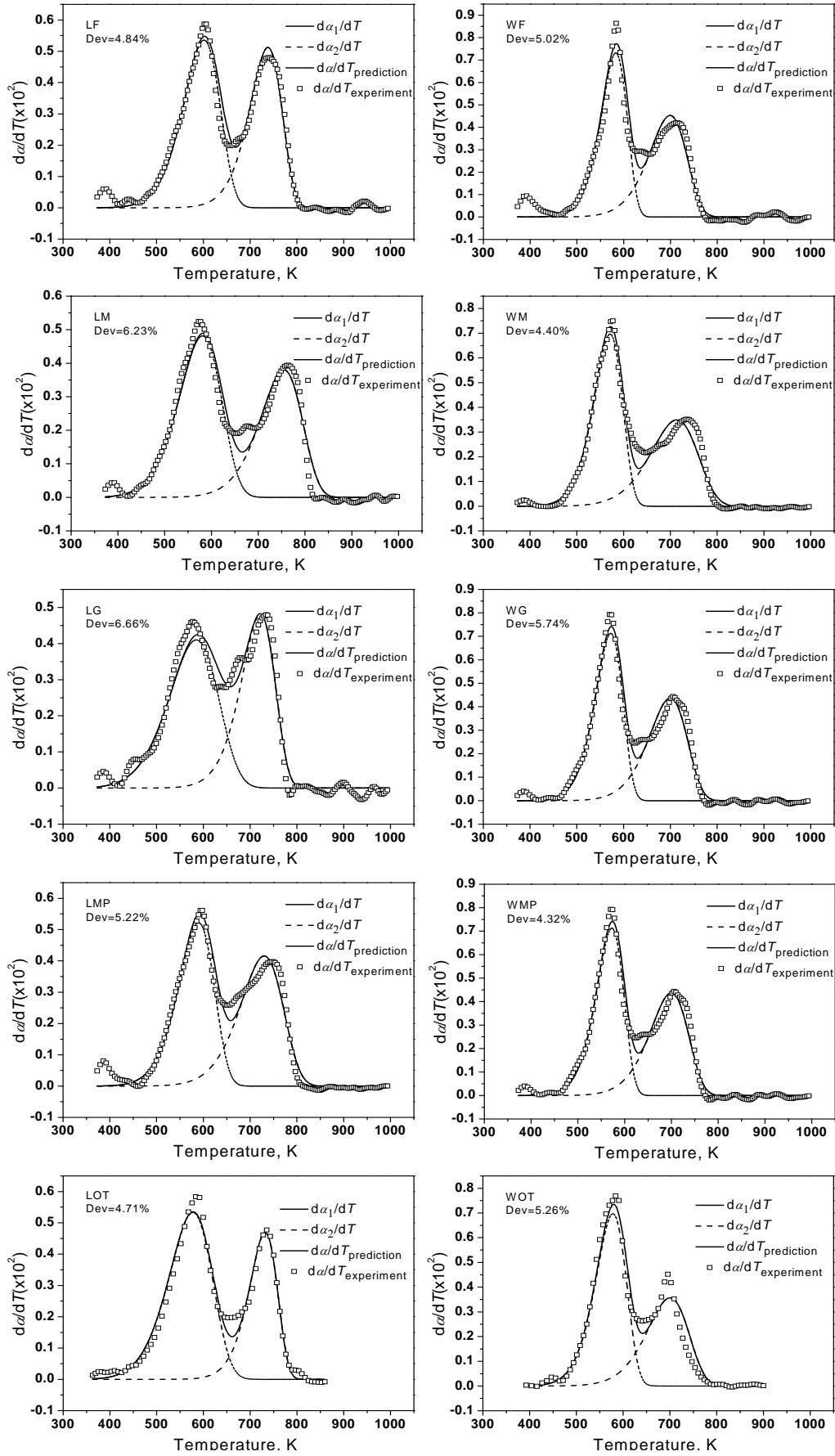


FIGURE 4. Comparison between the prediction and experiments by the consecutive kinetic schemes for different samples

A more important point can be observed from Fig. 4 that the two consecutive steps behave almost separate and can be regarded as decomposing independently during two separate temperature ranges. This result means that the second component starts its decomposition nearly when the decomposition of the first component ends. As shown in Fig. 4, the two steps share only a quite narrow temperature range, in which the mass fractions and rate signals are both very weak. We especially extract the feature temperatures of 95% conversion fraction of the first step and 5% conversion fraction of the second step from the simulation results, as shown in Table 2. The results clearly indicate that in all cases, the two steps just overlap within nearly 10°C. This result strongly implies that the decomposition of lignocellulosic materials can also be modeled by two-step separate kinetic scheme.

Two-step parallel kinetic scheme

An alternative way to model the decomposition of lignocellulosic materials is by two parallel reactions expressed as



where S_1 and S_2 are two different pseudo components which decompose with different kinetic parameters, and R_i and V_i ($i = 1,2$) are respectively the residue and volatiles generated from component i . The yield coefficients a_i and b_i are expressed as grams of R_i or V_i divided by grams of the reacted solid fuel ($S_{0i} - S_i$, $i = 1,2$), where S_{0i} is the initial amount of component i .

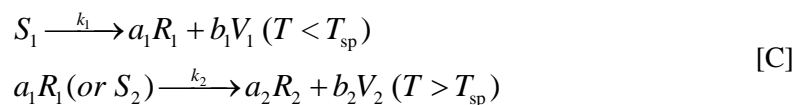
The kinetic law is:

$$\frac{d\alpha_i}{dT} = \frac{A_i}{\beta} \exp(-E_i / RT)(1 - \alpha_i)^{n_i} \quad (i = 1,2) \quad [7]$$

The overall degree conversion α is same as [5]. Nonlinear regression algorithm is used for simulation. As shown in Table 2, the kinetic parameters for parallel kinetic scheme are almost equal to those for consecutive kinetic scheme, thus leading to nearly the same simulation plots (which are omitted here for space limitations). This can be clarified by comparing the rate equation systems for the two kinetic schemes, from which we can see they differ from each other only in that the term $(\alpha_1 - \alpha_2)$ in (4) is replaced by $(1 - \alpha_2)$ in [7]. In other words, the mathematical form of the parallel scheme exactly fits to the situation for the consecutive scheme of that when the first step almost ends, the second step just begins. This is just the real situation for the present consecutive scheme. Therefore, it is not surprising that the simulation results of the two kinetic schemes show so good agreement. However, it should be addressed that in kinetics only when the two reaction steps have separate feature can the two kinetic schemes lead to nearly the same simulation results. In fact, just from equations [7] there's possibility that the two reaction steps overlap greatly and even progress simultaneously. Therefore, the present results for two-step parallel kinetic scheme are in essence a further indication that the decomposition can be modeled by two-step separate kinetic scheme.

Two-step separate kinetic scheme

In terms of the above analysis, we now directly simulate the experimental data by two-step separate kinetic scheme, in order to check it's compatibility with the former two kinetic schemes. The separate kinetic scheme are expressed as:



where T_{sp} is the separation point for the two reaction steps. Obviously, this scheme differs from schemes [A] and [B] in that the two pseudo components decompose within lower and higher separate temperature stages. The rate equations are:

$$\frac{d\alpha_1}{dT} = \frac{A_1}{\beta} \exp(-E_1/RT) f_1(\alpha_1) \quad T < T_{sp} \quad [8]$$

$$\frac{d\alpha_2}{dT} = \frac{A_2}{\beta} \exp(-E_2/RT) f_2(\alpha_2) \quad T > T_{sp} \quad [9]$$

where $f_i(\alpha_i)$ ($i = 1, 2$) is the model function representing the reaction type. Note that the above two equations are completely independent and the conversion fractions are defined within separate temperature stages, rather than in overall temperature stage as used by the former two kinetic schemes. The temperature corresponding to the minimum in the DTG curve between the two peaks is regarded as the separation point. The mass fractions α_1 and α_2 in turn represent the overall mass fraction α at separate temperature stages. The rate equations can be easily evaluated by many classical methods, *e.g.* Coats-Redfern method²⁸ as expressed by:

$$\ln\left[\frac{g_i(\alpha_i)}{T^2}\right] = \ln\left[\frac{A_i R}{\beta E_i}\right] \left[1 - \frac{2RT}{E_i}\right] - \frac{E_i}{RT} \quad [10]$$

where $g_i(\alpha)$ ($i = 1, 2$) is defined as the integral form of the reciprocal of $f_i(\alpha)$. A plot of $\ln[g_i(\alpha_i)/T^2]$ against $1/T$ should result in a straight line of slope $-E_i/R$ for the correct reaction mechanism, as underlies the method to find the suitable model function $g_i(\alpha_i)$ (or $f_i(\alpha_i)$). The apparent activation energy E_i and frequency factor A_i can be calculated from the regression line in the light of [10].

The separate kinetic scheme holds some advantages over the consecutive and parallel schemes. Firstly, the overall kinetic parameters can be determined by the separate scheme, while for the other two schemes, only the parameters respectively for the two-step reactions can be evaluated. Secondly, optimization computation is required in the consecutive and parallel schemes for which there is great difficulty in the selection of the initial values of parameters, since in mathematics there may be even many sets of parameters able to meet the demand of the error of OF.

The different model functions usually employed for solid state reactions of reaction order type (O0, O1, O2, O3), phase boundary controlled type (R2, R3) and diffusion type (D1, D2, D3, D4) are used for trial test to determine the most reasonable model function $f_i(\alpha_i)$. For the detailed expressions of these types of model function, refer to²³. It is found that the first-order reaction type leads to the highest correlation coefficients for both reaction steps in nearly all the cases. In Fig. 5 we compare the regression results for oil tea wood by different model functions, from which it is clearly that the first-order function holds the best linearity. From Table 2 we can see the kinetic parameters by the three kinetic schemes are comparative. This deeply suggests that the three kinetic schemes are completely compatible.

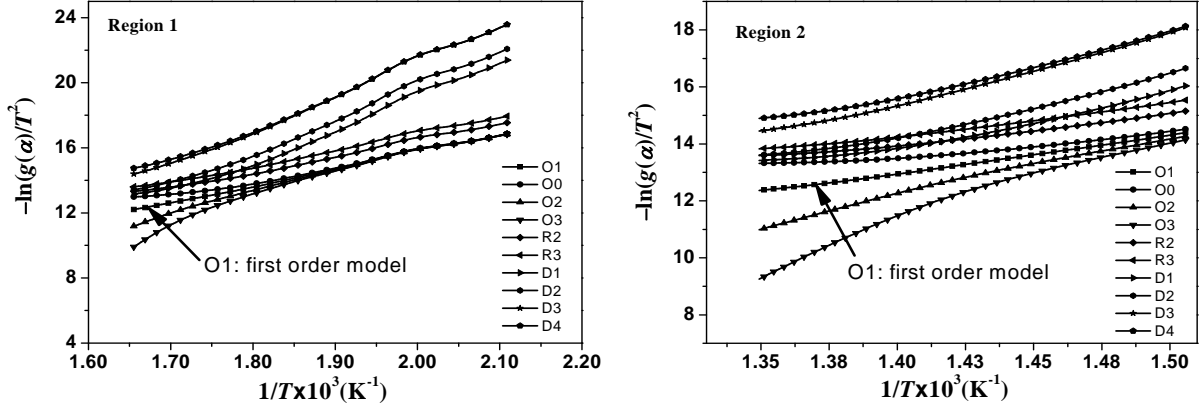


FIGURE 5. Coats-Redfern regression of two-step separate kinetic scheme for oil tea wood sample

Theoretical comparison of the three kinetic schemes

We refer back to the definition of the reaction fraction in consecutive and parallel schemes:

$$\alpha_i = \frac{V_i}{V_{i\infty}} = \frac{W_{i0} - W_i}{W_{i0} - W_{i\infty}} \quad (i=1,2) \quad [11]$$

When with separate feature in the two mass loss steps in decomposition, we can write:

$$W_{1\infty} = W_{20} \quad [12]$$

When $T < T_{sep}$, here T_{sep} is the separation temperature of the two steps, since $\alpha_2=0$, from [5] and [12] we can derive:

$$\frac{d\alpha}{dT} = \frac{W_{10} - W_{1\infty}}{W_{10} - W_{2\infty}} \frac{d\alpha_1}{dT} \quad [13]$$

Similarly, when $T > T_{sep}$,

$$\frac{d\alpha}{dT} = \frac{W_{20} - W_{2\infty}}{W_{10} - W_{2\infty}} \frac{d\alpha_2}{dT} \quad [14]$$

The above formulations [13] and [14] clearly indicates with separate feature the formulations consecutive and parallel schemes can be simplified to separate scheme.

CONCLUSION

An extensive investigation on the thermal decomposition of forest combustibles in air atmospheres is presented. The simulation by three two-step kinetic schemes, *i.e.* consecutive scheme, parallel scheme and separate scheme, all lead to well agreement between predictions and experiments comparative kinetic parameters, strongly indicating that the decomposition of forest material has separate feature in kinetics, and the two steps can be regarded as decomposing during nearly two separate temperature stages. It is thus indicated that the complex kinetic schemes such as consecutive and parallel ones can be simplified to separate kinetic scheme. The results imply that the variations in reported kinetic schemes and parameters are probably just due to the great variation in of raw materials, experimental techniques and operating conditions used. In kinetics, the different kinetic schemes and parameters due to different authors may be consistent, since the three kinetic schemes show high compatibility in

kinetics. Especially the two-step separate kinetic scheme holds highly simple mathematical formulation and computation procedures, and so it is of high feasibility for the description of the overall mass loss behaviors for forest materials and can be used as a sub-model for ignition and fire propagation simulations.

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