Pyrolysis of Medium Density Fibreboard: Optimized Search for Kinetic Scheme and Parameters via Genetic Algorithm Driven by Kissinger's Method

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ABSTRACT

The pyrolysis kinetics of charring materials plays an important role in understanding material combustions especially for constructions materials with complex degradation chemistry. Thermogravimetric analysis (TGA) is frequently used to study the heterogeneous kinetics of solid fuels, however, there is no agreed method to determine the pyrolysis scheme and kinetic parameters for charring polymers with multiple components and competing reaction pathways. This study develops a new technique to estimate the possible numbers of species and sub-reactions in pyrolysis by analysing the second derivatives of TG (DDTG) curves. The pyrolysis of a medium density fibreboard (MDF) in nitrogen is studied in detail, and the DDTG curves are used to locate the temperature of peak mass-loss rate for each sub-reactions. Then, based on the TG data under multiple heating rates, the Kissinger's method is used to quickly find the possible range of values of the kinetic parameters (A and E). These ranges are used to accelerate the optimization of the inverse problem using genetic algorithm (GA) for the kinetic and stoichiometric parameters. The proposed method and the kinetic scheme found are shown to match the experimental data and are able to predict accurately results at different heating rate better than the Kissinger's method. Moreover, the search method (K-K method) is highly efficient, faster than the regular GA search alone. Modelling results show that as the TG data available increases, the interdependence among kinetic parameters becomes weak and the accuracy of first-order model declines. Furthermore, conducting TG experiment under multiple heating rates is found to be crucial in obtaining good kinetic parameters.

KEYWORDS

pyrolysis; kinetics; thermogravimetry; optimization; combustion; fire

1. Introduction

To predict the burning behaviour and toxic species production, a better understanding of the material pyrolysis behaviours is required. Two major mechanisms are involved in the pyrolysis process: the physical heat transfer and the chemical reaction. The heat transfer process is determined by the materials thermo-physical properties, and the chemical decomposition is mainly determined by the compositions and structures of the material [1]. Therefore, developing an appropriate pyrolysis model and understanding the corresponding effects are crucial in order to simulate the ignition, spread and extinction of fire.

Thermogravimetric analysis (TGA) is the most common methodology to analyse the pyrolysis kinetics with a heating rate normally lower than 100 K/min. In the literature, the pyrolysis kinetics and properties of some “pure” materials such as wood [1-5], polyurethane foams [6,7] and PMMA [8] are most studied. Composite materials used in buildings such as medium density fibreboard (MDF) are rarely studied due to its complex physiochemical properties. In several studies (e.g. [4,9]), TGA is performed based at only a single heating rate at the low range of less than 10 K/min and it is believed that the lower heating rates give lower experimental uncertainty than the high heating rates. The pyrolysis rate is often expressed by an Arrhenius equation like the gas-phase reactions. The corresponding kinetic parameters can be inversely obtained by modelling the thermogravimetry (TG) experiments [7], and then inputting the parameters into a fire model (e.g. FDS [10], Gpyro [11]) to predict complex combustion dynamics under various and transient heating rates. Nevertheless, the heating rate in real fires will vary over a wide range, depending on the scale and scenario: smouldering fires [7,12], compartment fires [13], and large-scale wildfires [14]. For this reason, whether the proposed kinetic scheme and parameters, estimated

at a low and constant heating rate, are suitable for other heating conditions has been questioned and investigated in several studies [6-8,15].

In the literature pyrolysis models with different schemes have been proposed to simulate TG data at either a single heating rate [16,17] or multi heating rates [18-20]. However, when a complex reaction scheme is used, the large number of unknown kinetic parameters can make the modelling process difficult or even impractical. Determination of kinetic parameters by graphical techniques such as model-free methods can be applied but these approaches are only suitable for reactions that are well separated. Since the late 1990s, with the increase of computational capability new optimization techniques including the genetic algorithms (GA) [7,12,21-23], PEAKFIT [24,25] and least-squares method [4,26] have been adopted for the estimation of kinetic parameters. Subsequently, new decomposition models such as the multi-component/step model [1] and the distributed activation energy model (DAEM) [2,3,27] have also been developed for pyrolysis. Along with the rising degrees of explanation, the complexity and uncertainty of proposed kinetics schemes and parameters increases while a significantly longer computational time is required. Moreover, the uniqueness and suitability of these kinetic models and parameters for real fires becomes more uncertain [28]. The optimization techniques require initial guess of property values based on user experiences or literature data. The guess process could be tedious, arbitrary and lack of scientific support.

In this work, the TG experiment is conducted for a MDF sample under four heating rates ranging from 5 to 80 K/min. The second derivatives of TG (DDTG) curves are used to identify the number and location of sub-reactions. The reaction rate is expressed by the Arrhenius law, and the values of kinetic parameters (A and E) are estimated by the Kissinger's method based on the TG data under three heating rates.

The results are then coupled with the more accurate search of genetic algorithm (GA) for all kinetic and stoichiometric parameters. At last, the found kinetic parameters are used to blind predict the unused TG data of other heating rates, and the results are then compared among different search methods and parameters from the literature. This new technique is denoted as K-K method for simplification.

2. Experimental results and analysis

The current study investigated two MDF panels made by a local (New Zealand) manufacturer with thicknesses of 25 and 18mm, same as [9]. As specified by the manufacturer, the MDF panels are made of radiata pine with PF resin (<10%) and paraffin wax (~0.6%) to improve binding. TG experiments are conducted with a simultaneous DSC–TGA SDT Q600 thermal analyser (TA Instruments). In each experiment, the alumina (Al_2O_3) cups without lids, 90 μL and 3 mm diameter, were used.

The inner part of the MDF panel is collected to minimize the environmental contamination. After equipment calibrations, the sample of 10–15 mg, half-filled the alumina cup, was used in each experiment. The TG experiments have been conducted in nitrogen at four heating rates of 5, 20, 60, and 80 $^{\circ}\text{C}/\text{min}$, with a purge flow rate of 100 mL/min . The decomposition in nitrogen may simulate the environment in flaming fires where oxygen is consumed before reaching the pyrolysis front [6]. Each MDF sample in TG experiment was subjected to two consequent runs: (1) dehydrating the sample under a peak temperature 130 $^{\circ}\text{C}$, and (2) after cooling down, linearly increasing the temperature range from 20 to 1000 $^{\circ}\text{C}$. Three repeating experiments were conducted for each experiment. TGA experiments and the results showing an excellent repeatability (uncertainty within 3%), and insensitive to sample size, hence

confirming that the full heterogeneity of MDF in the reported data is captured. Figure 1 shows the experimental TG curves and their differentiated curves (DTG) of MDF at four heating rates. More experimental detail can be referred to Reference 9.

Figure 1. Experimental TG curves of MDF (a) mass fraction, and (b) mass-loss rate at four heating rates.

2.1 Estimation of pyrolysis steps

It is generally believed that a complicated pyrolysis reaction consists of several apparent sub-reactions, denoted by several peaks and shoulders at the overall DTG curves [1,3,6]. For well separated sub-reactions [6] it is not hard to determine the peak temperatures, however, for materials with strong overlapped sub-reactions such as wood [4], it is always a challenge to locate these peaks. Multiple peaks and shoulders are also observed for MDF DTG curves in Fig. 1b, indicating the existence of multiple decomposition reactions. Additionally, the similar shapes of DTG curves indicate that the samples experienced similar pyrolysis process under a wide range of heating rates (5-80 K/min), as observed by many other researchers for different materials and TG experiments [5-8].

If a component i only goes through one non-oxidative decomposition reaction, the decomposition rate may be expressed by the n-order Arrhenius equation as

$$\omega_i = \frac{d\alpha_i}{dt} = A_i \exp\left(-\frac{E_i}{RT}\right) (1 - \alpha_i)^{n_i} \quad (1)$$

where the volatile conversion is expressed by the normalized mass fraction as

$$\alpha_i = 1 - \frac{m_i}{m_{i,0}} \quad (2)$$

In Eq. (1), A_i , E_i , and n_i are the pre-exponential factor, activation energy, and reaction order (i.e. kinetic triplet). Given the constant heating rate, $\beta = dT/dt$, the total mass-loss rate (DTG) can be simulated by lumping the reaction rates of all components as

$$DTG = \frac{d(m/m_0)}{dT} = \sum_{i=1}^N f_i \frac{d(1 - \alpha_i)}{dT} \quad (3)$$

where $f_i = m_{i,0}/m_0$ denotes the initial mass fraction of component i ($\sum f_i = 1$).

Accordingly, the |DDTG| data can be simulated as

$$|DDTG| = \left| \frac{d^2(m/m_0)}{dT^2} \right| = \left| \sum_{i=1}^N f_i \frac{d^2\alpha_i}{dT^2} \right| \geq 0 \quad (4)$$

When a major component i (relative large f_i) is near the maximum decomposition rate $f_i(d(1 - \alpha_i)/dT) \Big|_{T \rightarrow T_{p,i}} \rightarrow \max$, denoted by the peak temperature ($T_{p,i}$), the absolute value of its second derivative will exponentially drop to zero, $\left| f_i(d^2\alpha_i/dT^2) \Big|_{T \rightarrow T_{p,i}} \rightarrow 0 \right.$. Therefore, if no other major reaction peaks nearby, the value of |DDTG| is very likely to drop rapidly to a local minimum.

Figure 2: Experimental curves of (a) $|DDTG|$ and (b) DTG of MDF at a heating rate of 5 K/min with four modelled sub-reactions in search (III).

Figure 2a presents the $|DDTG|$ curve at a heating rate of 5 K/min where the data scatter is small due to the low heating rate, and the corresponding DTG curve is given in Fig. 2b as a reference. Clearly, four local minimums can be observed in the $|DDTG|$ curve, which are also observed for other larger heating rates except that data scatter in $|DDTG|$ curves are also larger. Hence, four major sub-reactions are expected to take place, and four corresponding peak temperatures should locate within a small range near these local minimums, as shown in Fig. 2a. Additionally, this MDF is made mainly by radiata pine and less than 10% resin. The pyrolysis of radiata pine may consist of 3 parallel reactions as typical softwood: hemicellulose, cellulose and lignin [4]. Therefore, we propose a 4-step and 4-component pyrolysis scheme to explain the

decomposition of MDF in nitrogen,

where ν_i is the stoichiometric coefficient of char yield in pyrolysis of component i ($= r, h, c$, and l). Figure 2b shows an example simulation of the mass-loss rate in each reaction by the proposed kinetic scheme.

2.2 Estimation of A and E by Kissinger's method

When the decomposition of component i reaches the maximum at peak temperature of $T_{p,i}$, the peak reaction rate becomes

$$\omega_{i,p} = \left(\frac{d\alpha_i}{dt} \right)_p = A_i \exp \left(- \frac{E_i}{RT_{p,i}} \right) (1 - \alpha_{i,p})^{n_i} \quad (9)$$

where subscript “ p ” denotes at the peak reaction rate. Then, the second derivative of α_i with respect to T satisfies

$$\left(\frac{d^2 \alpha_i}{dT^2} \right)_p = \frac{A_i}{\beta} \exp \left(- \frac{E_i}{RT_{p,i}} \right) \left[-n(1 - \alpha_{i,p})^{n_i-1} \left(\frac{d\alpha_i}{dT} \right)_p + (1 - \alpha_{i,p})^{n_i} \frac{E_i}{RT_{p,i}^2} \right] = 0 \quad (10)$$

which leads to

$$n \left(\frac{d\alpha_i}{dT} \right)_p = (1 - \alpha_{i,p}) \frac{E_i}{RT_{p,i}^2} \quad (11)$$

Combining Eqs. (9) and (11) gives

$$\frac{\beta E_i}{A_i RT_{p,i}^2} = \exp \left(- \frac{E_i}{RT_{p,i}} \right) n (1 - \alpha_{i,p})^{n_i-1} \quad (12)$$

Using Kissinger's approximation [18],

$$n(1 - \alpha_{i,p})^{n_i-1} = 1 + (n_i - 1) \frac{2RT_{p,i}}{E_i} \approx 1 \quad (13)$$

the logarithm of Eq. (12) becomes

$$\ln\left(\frac{\beta}{T_{p,i}^2}\right) = -\frac{E_i}{RT_{p,i}} + \ln\left(\frac{A_i R}{E_i}\right) \quad (14)$$

and for two heating rates (β_1 and β_2), the difference is

$$\ln\left(\frac{\beta_1}{\beta_2}\right) = -\frac{E_i}{R}\left(\frac{1}{T_{p,i,1}} - \frac{1}{T_{p,i,2}}\right) + \ln\left(\frac{T_{p,i,1}}{T_{p,i,2}}\right)^2 \quad (15)$$

As discussed above, the peak temperature is very likely to take place near the local minimum of the |DDTG| curve. For the first approximation, we choose the temperature at the local minimum as the peak temperature for each sbu-reaction, and

plot $\frac{1}{T_{p,i}}$ against $\ln\left(\frac{\beta}{T_{p,i}^2}\right)$ under different heating rates. The TG data of 5, 20 and

60 K/min is used to determine kinetics parameters, as plotted in Fig. 3, while the case

of 80 K/min is used later for validation. The activation energy can be estimated from

the slope of $-\frac{E_i}{R}$ by a linear fit of three experimental points, and substituting back

into Eq. (14) gives the pre-exponential factor. Table 1 lists the obtained $T_{p,i}$, A_i , and

E_i as well as fitting condition (R^2) for the proposed 4-step kinetics under three heating.

Figure 3: Correlations of heating rates and peak temperatures

Table 1. Kinetics parameters and possible range via Kissinger's Method.

Reactions	β (K/min)	$T_{p,i}$ (K)	R^2 (-)	$T_{p,i} \pm 5$ (K)	E_i (kJ/mol)	E_i range (kJ/mol)	$\lg A_i$ ($\lg(s^{-1})$)	$\lg A_i$ range ($\lg(s^{-1})$)
Resin	5	483	0.9728	[478, 488]	130	[102, 175]	11.8	[8.8, 16.5]
	20	509		[504, 514]				
	60	518		[513, 523]				
Hemi-cellulose	5	568	1.0000	[563, 573]	157	[125, 207]	12.1	[9.2, 16.7]
	20	591		[586, 596]				
	60	611		[606, 616]				
Cellulose	5	620	0.9941	[615, 625]	192	[153, 254]	13.9	[10.6, 19.0]
	20	646		[641, 651]				
	60	661		[656, 666]				
Lignin	5	661	0.9972	[656, 666]	196	[160, 252]	13.2	[10.3, 17.5]
	20	689		[684, 794]				
	60	707		[702, 712]				

2.3 A quick analytical estimation of TG curves

Unlike the homogeneous gas-phase reaction, the kinetic triplets, A_i , E_i , and n_i for heterogeneous solid reactions are purely fitting parameters without consolidated physical meanings. Mathematically, the value of A_i and E_i determines the location and magnitude of the reaction, and there is a linear compensation effect between $\lg A_i$ and E_i [7,12]. The value of n_i defines the shape and symmetry of the reaction [18], and recent research showed that the kinetic triplets could be interdependent [12,28]. So far, there is no simple way to determine the value of n_i . For a quick estimation, both the

first- and second-order ($n_i = 1$ and 2) reaction model are tested for all four reactions.

The initial mass fraction of four species are selected from the literature: $f_r = 0.09$ (by manufacturer), $f_h = 0.28$, $f_c = 0.38$, and $f_l = 0.25$ [29]. Since the final mass fraction after pyrolysis is about 0.2 as shown in Fig. 1a, we assume a same stoichiometric coefficient for all reaction, $\nu_i = 0.2$. All selected parameters are summarized in Table 2. Figure 4 compares experimental DTG curve at 5 and 80 K/min with the quick simulation using the analytically estimated parameters above. Although the global matching condition is not as good as that from complex search methods, this quick estimation is still able to capture the location of DTG curve at both lowest and highest heating rates, probably because A_i and E_i are estimated from multiple heating rates. Moreover, with $n_i = 1$ the major peak of DTG curve still can be well predicted probably because the reaction order of the fastest sub-reaction, cellulose decomposition, is close to 1. Clearly, the reaction order n_i plays an important role on achieving a better match with the experiment: a larger n_i gives a flatter curve with fixed A_i and E_i . Therefore, we can estimate that $n_r \gg 2$, $n_h \sim 2$, $n_c \sim 1$, and $n_l \gg 2$, which will be helpful to set the initial guess and search range in a complex and more accurate search scenario.

Figure 4: Comparison between experimental DTG data and prediction with analytically estimated kinetic parameters at (a) 5 K/min, and (b) 80 K/min.

3. Accurate and accelerated search for kinetic parameters

3.1 Genetic algorithm

A Genetic Algorithm (GA) is a heuristic search method, imitating the principles of biological adaption based on Darwinian survival-of-the-fittest theory [30]. In a GA, the candidate solutions represent the individuals in a population that evolves with time in a predetermined environment. During the evolution process, GA will generate a set of individuals carrying several genes to produce the generations. The genes are the trial values of the undetermined parameters, which would evolve along the searching process with the bad genes being eliminated from the new generation.

Therefore, GA can be coupled with a decomposition model to search for values of kinetic and stoichiometric parameters that gives the best fit between the model outputs and the experimental results [7,21,22]. Here, the searched parameters include the kinetic triplets (A_i , E_i , and n_i), initial mass fractions (f_i) and char yields (ν_i). The individual number of 100-500 was used for each parameter, and in general a total generation less than 1000 can achieve the convergence. The search goal is to achieve a minimum error with the experimental TG data, defined as

$$\Phi_k = \gamma \frac{\sum |m_{cal,i} - m_{exp,i}|}{\sum m_{exp}} + (1 - \gamma) \frac{\sum |\dot{m}_{cal,i} - \dot{m}_{exp,i}|}{\sum \dot{m}_{exp}} \quad (16)$$

where both mass and mass-loss rate are considered with a same weight coefficient ($\gamma = 0.5$); subscripts *exp* and *cal* denote the experimental and calculated results; the summations are evaluated for each experiment data in the temperature range (from 300 to 1000 K). In order to improve the uniqueness of solution, TG tests conducted under different heating rates can be optimized simultaneously by simply adding the

number of experimental data points. The GA codes in both Matlab and Gpyro [11] are used to perform the search.

3.2 Optimized search methods and ranges

Although GA is able to produce a large search space in complex landscape to avoid trapping in numerous local maxima and minima, it may require a lot of computational time when the number of optimized parameter gets large. Furthermore, if the search ranges is too large or misplaced, it takes an even longer time to converge, and becomes more difficult to get good solutions. However, if a good initial guess and an appropriate research range are provided, the fast and better convergence is very likely to achieve.

The analysis in Section 2.3 proves that the A_i and E_i determined by the temperature at the local minimum of $|\text{DDTG}|$ curve, using Kissinger's method, is able to fix the location of DTG curve under a wide range of heating rates. Thus, if the reaction order (n_i) is optimized with fixed A_i and E_i from Kissinger's method, it may help to get a higher degree of fit to experiments, and reduce the converging time because of fewer optimized parameters. On the other hand, as shown in Fig. 2, the temperature at peak reaction rate ($T_{p,i}$) is likely to locate within a small range around the local minimum of $|\text{DDTG}|$ curve. Here, we choose a range of peak temperature as ± 5 K of the local minimum of $|\text{DDTG}|$ curve. Using the same Kissinger's method, the range of A_i and E_i can be found, as listed in Table 1. Same initial values of parameters as the analytical estimation in Section 2.3 are selected, and the range of search is set as roughly 50 – 200% of the initial guess for blind search. The range of reaction order (n_i) is inspired by the shape variation of DTG curves in Fig. 4. The optimized searched range is also summarized in Table 2, which is much narrower compared to

the blind search range.

Three search methods are proposed and conducted with GA under both blind and optimized search ranges:

- (I) Fix A_i and E_i , vary n_i (11 parameters) with TG data at 5 K/min;
- (II) Vary A_i , E_i , and n_i (19 parameters) with TG data at 5 K/min;
- (III) Vary A_i , E_i , and n_i (19 parameters) with TG data at 5, 20, 60 K/min.

In addition, the performance of first-order reaction model is also tested under both one (5 K/min, same as [9]) and three heating rates (5, 20, 60 K/min):

- (IV) Varying A_i , E_i , fixing $n_i = 1$ (15 parameters).

For each search scenario, multiple searches are performed. A good solution can be found after hundreds of generations till the relative error (Φ) between experiment and simulation no longer decreases (i.e. convergence). Due to the random nature of GA and the interdependences among parameters, the converging condition of GA can be random and various under different repeating runs, GA codes, or computers, but the overall trend should be clear. At the same time, a different group of good solutions will be obtained in each run. The best solution is listed in Table 2, and the range of other good solutions is also listed in Table S1 in the supply material. The converging time is recorded under a fixed condition: GA code in Matlab with default search settings, a population of 100, and running at a PC with Intel i7-3770 (3.40 GHz $\times$ 8) CPU. The average converging time of 10 runs for each method is reported in Table 2 as a reference to determine the search speed.

Table 2. Optimized searching range, and the best solutions of kinetic parameters for search method (I-IV).

Species	Parameter	Anal. /initial guess	Blind search range	Optimized search range	Search (I)		Search (II)		Search (III)		Search (IV)		MDF [26]	Pine [4]
					Blind	Opt.	Blind	Opt.	Blind	Opt.	5 K/min [9]	5,20,60 K/min		
Resin	$\lg A_r (\lg(s^{-1}))$	11.8	[5, 20]	[8.8, 16.5]	11.8	11.8	15.8	14.3	12.1	13.6	0.9	4.3	5.64	-
	E_r (kJ/mol)	130	[50, 300]	[102, 175]	130	130	164	152	133	149	35.4	64	81	-
	n_r (-)	1; 2	[0.5, 10]	[2, 10]	5.1	5.5	6.3	4.2	2.7	4.7	1	1	1.29	-
	f_r (%)	9	[5, 10]	[5, 10]	10.0	10.0	9.1	6.7	9.0	9.9	9.5	9.8	14	-
	v_r (%)	20	[0, 50]	[10, 40]	10.4	9.4	22.3	11.2	27.3	11.6	63.4	10.9	-	-
Hemi-cellulose	$\lg A_h (\lg(s^{-1}))$	12.1	[5, 20]	[9.2, 16.7]	12.1	12.1	8.7	9.2	15.7	12.9	5.51	10.2	13.82	6.35
	E_h (kJ/mol)	157	[50, 300]	[125, 207]	157	157	120	126	194	165	87.5	135	178	100
	n_h (-)	1; 2	[0.5, 10]	[1, 3]	3.7	2.9	2.4	2.5	5.6	2.4	1	1	3.0	1.0
	f_h (%)	28	[5, 50]	[14, 50]	42.8	39.3	33.2	41.5	49.6	31.7	26	21.4	43	45
	v_h (%)	20	[0, 50]	[10, 40]	9.4	9.0	14.3	24.5	10.9	11.5	13.6	15.8	-	-
Cellulose	$\lg A_c (\lg(s^{-1}))$	13.9	[5, 20]	[10.6, 19.0]	13.9	13.9	8.4	10.7	13.6	13.6	12.3	11.8	12.85	17.4
	E_c (kJ/mol)	192	[50, 300]	[153, 254]	192	192	128	154	188	189	173.5	166	180	236
	n_c (-)	1; 2	[0.5, 10]	[0.2, 2]	0.70	0.74	0.52	0.64	0.81	0.84	1	1	0.8	1.0
	f_c (%)	38	[5, 50]	[19, 50]	33.9	35.7	39.9	33.1	32.4	40.8	39.5	60.5	33	40
	v_c (%)	20	[0, 50]	[10, 40]	27.1	28.8	17.2	13.1	14.8	24.8	5.8	27.2	-	-
Lignin	$\lg A_l (\lg(s^{-1}))$	13.2	[5, 20]	[10.3, 17.5]	13.2	13.2	8.6	10.8	12.5	16.3	0.061	8.8	5.30	0.56
	E_l (kJ/mol)	196	[50, 300]	[160, 252]	196	196	144	163	240	238	39.0	148	106	46
	n_l (-)	1; 2	[0.5, 25]	[2, 10]	20.1	16.5	7.2	8.7	21.1	10.4	1	1	3.0	1.0
	f_l (%) ^a	25	-	-	13.3	14.3	17.8	18.7	9.0	17.6	25	8.3	8.5	15
	v_l (%)	20	[0, 50]	[10, 40]	7.2	6.3	25.9	14.7	44.6	27.2	28.6	22.0	-	-
Modeling Error	$\Phi_{\min}$ (%)	25.7; 26.4	-	-	3.0	3.0	1.9	2.2	5.0	5.0	5.4	9.7	6.5	18.3
Predict 80 K/min	Φ_{80} (%)	19.8; 23.6	-	-	7.8	7.5	24.2	14.7	6.2	6.4	23.9	8.4	7.7	31.3
Searched parameter No. ^b		-	-	-	11	11	19	19	19	19	15	15	-	-
Avg. Conv. time (min) ^c		-	-	-	7	4	66	23	93	32	-	-	-	-
Time range (min)		-	-	-	[3,11]	[2, 5]	[32, 124]	[6, 35]	[17,151]	[11,45]	-	-	-	-
Converging rate		-	-	-	Fast	Fast	Slow	Normal	Slow	Normal	Normal	Normal	-	-

^a The value of f_l is determined as $f_l = 1 - f_r - f_h - f_c$, and is not searched.

^b The modelling parameters are highlighted in the table, the number of which is equal to the number of genes used in GA.

^c The convergence time is averaged for 10 repeating runs under a fixed condition; the time for search (IV) is not reported due to a different search range.

3.3 Search results and comparisons

In order to test the reliability of these parameters under different heating rates, the best solution is used to predict the unused TG data at 80 K/min, and the relative error (Φ_{80}) is calculated (Table 2) for comparison. For each search scenario, the predicted DTG curves using best solution at 5 and 80 K/min are plotted in Fig. 5, and the predictions for 20 and 60 K/min are also plotted in Fig. S1 in the supply material. Figure 5 shows that all three search methods are able to give a good match to the experimental DTG curve at 5 K/min, where the relative error ranges from 1.9% to 5%, comparable to the uncertainty of repeating experiments. Therefore, it proves that the proposed 4-step decomposition scheme is reasonable and GA is able to find good solutions.

For search (III), the relative error is slightly large because three heating rates are modelled at the same time to acquire the best solution for all three heating rates, rather than only for 5 K/min. Regarding the prediction of 80 K/min, search (III) gives the best match as expected, because maximum TG data and kinetic parameters are used in the search. While for the same reason, using the raw and blind search range the convergence becomes very slow, and sometimes it fails to get a good solution. However, with the narrowed and optimized search range, the convergence becomes faster, using 1/3 the time of blind search.

Figure 5: Comparison between experimental DTG data ($\circ$) and predictions ($-$) at 5 and 80 K/min with the parameters at Table 2 for search scenarios (I-III).

For search (I), although only one heating rate and 11 parameters are used, it predicts both experiments of 5 and 80 K/min well. The major reason is that the values of A_i and E_i are estimated based on a wide range of 3 heating rates (Section 2.2), which is able to fix the location of each sub-reaction. Note that the convergence is fast ($t = 7$ min) even with a wide and blind search range. Therefore, despite of halving the time in the optimized search, whether or not to narrow search range becomes less important.

For search (II), it is able to give the best match to the experiment of 5 K/min ($\Phi=1.9\%$), but the prediction of 80 K/min is off and unstable (See Table S1). Meanwhile, the time for convergence is long, comparable to that of search (III). Due to the interdependence among kinetic parameters, without additional constraints a wide range of parameter values can be found to satisfy only one heating rate, which usually cannot predict other heating rates well. In current case, the search completely focuses on matching the TG data of 5 K/min while neglects the compatibility for other heating rates. In optimized search (II), the failure in predicting 80 K/min tends to mitigate because the search range is narrowed by Kissinger's method which including the information three heating rate. However, the convergence can become difficult and slow, especially near the final solution, due to a misled search: the best solution to match 5 K/min tends to approach that in blind search (II) which is actually outside the optimized search range.

In summary, conduction TG experiments at multiple heating rates is crucial to determine the kinetic parameters and predict real and complex pyrolysis conditions, lack of which cannot be compensated by advances in search skills. Two search scenarios are recommended: the (blind or optimized) search (I) is fastest and accurate, and optimized search (III) most efficiently accurate. Similar to Fig. 2b, the modelled sub-reactions for (I) Blind (5 K/min), and (III) Optimized (80 /min) are plotted in Fig. 6 as a reference.

Figure 6: Experimental DTG curve of MDF with four modelled sub-reactions in (left) Blind Search (I) at 5 K/min, and (right) Optimized search (III) at 80 K/min.

3.4 Discussions on kinetic parameters

In previous work [9], the DSC data was used to identify the possible peak temperature of each sub-reaction, and the first-order reaction ($n_i = 1$) was forced in the search of TG data at 5 K/min, as search method (IV). The degree of search freedom was reduced where only 15 parameters were searched, and the best solution is listed in Table 2. Figure 7a re-plots the searched result in [9] and shows that $n_i = 1$ with a group of very different A_i and E_i can give a fair match to 5 K/min, implying a strong interdependence among A_i , E_i and n_i under the minimum TG data. However, it gives an unreasonable prediction for 80 K/min. There can be two possible reasons: (1) the improper search objective, only one heating rate was searched as discussed above, and (2) the improper assumption of first-order reaction.

To identify the reason, three heating rates (5, 20, 60 K/min) are searched at the same time with $n_i = 1$. The modelling results and predictions are listed in Table 2 and plotted in Fig. 7b. Apparently, forcing $n_i = 1$ is not able to give a reasonable match to a wide range of heating rates. In particular, the decompositions of resin and lignin are not well simulated, and note

that their reaction orders (n_r and n_l) were found to be much larger than 1 in previous searches (I-III). On the other hand, the peaks of hemi-cellulose and cellulose decompositions are reasonably captured, probably because their reaction order (n_r and n_l) were found to be close to 1. Therefore, the kinetic triplets are not completely compensative to each other, unless the fixed reaction order does not deviate much from the best value. Since the mass loss of lignin is relatively small, assuming first-order reaction in many cases (e.g. [4]) can give a reasonable explanation for the wood pyrolysis.

Figure 7: Comparison between experimental DTG data ($\circ$) and predictions ($—$) at 5 and 80 K/min with the parameters at Table 2: (a) fix $n_i = 1$ search 5 K/min [9], (b) fix $n_i = 1$ search 5, 20, 60 K/min, (c) MDF [26], and (d) pine [4].

For comparison, the kinetic parameters of MDF from Becidan [26], and pine from Gronli [4] are also cited in Table 2, and used to simulate the DTG curves at 5 and 80 K/min, as shown in Fig. 7c and d. The char yield of each step in [4,26] is not provided, and is assumed to be 20% here. Figure 7c shows that using the parameters obtained from a different MDF sample in [26] can give a fair match with current experiments at both 5 and 80 K/min. It is possible that those two MDF samples have similar compositions and structures. Also, that the parameters in [26] was evaluated at an intermediate heating rate of 40 K/min may also explain the similar match conditions in two extreme heating rates.

Figure 7d shows that for simply applying kinetic parameters of pine cannot give good predictions for MDF probably because of large differences in composition and structure. However, the DTG peak locations are well predicted, implying that the pyrolysis of MDF may be treated as a co-pyrolysis of resin and softwood. This co-pyrolysis can be described by the parallel reactions, the interactions among which are small. At the same time, two features are found:

1. The activation energies (E_i) fall into a small range for multi heating rates: in search (III), 149-200 kJ/mol. However, it is found as 35-173 kJ/mol in [9], 116-167 kJ/mol in [5], and 46-236 kJ/mol in [4]. This supports the finding by Di Blasi [1] that the range of 46-236 kJ/mol in [4] has to be modified as 147-193 kJ/mol for multi heating rates.
2. The activation energy tends to increase with the peak temperature. In order words, the activation energy increases from resin to lignin as the peak temperatures follows resin < hemicellulose < cellulose < lignin. This feature differs from [4] and current search (II) where the activation energy has no noticeable trend with the components.

In fact, these features are deductions of Eq. (15): the activation energy determines the offset distance of peak temperature from low to high heating rate, therefore the activation

energies of different sub-reactions are similar due to the similarity of DTG curves between different heating rates, which leads to similar offset distances of peak temperatures for different sub-reactions. Therefore, that only one heating rate investigated in [4] and [9] as well as search (II) is believed to cause the differences. It also supports that the kinetic triplets can vary in a large range and have a strong independence to each other especially under limited TG data. More importantly, conducting TG experiments under different heating rates are important to determine a suitable kinetic scheme and parameters for complex pyrolysis scenarios.

CONCLUSIONS

A new technique, so called K-K method, is proposed to fast and accurately predict the material pyrolysis kinetics at multi heating rates by analysing $|\text{DDTG}|$ curves and coupling the Kissinger's method with GA. The TG experiments of a MDF sample at four heating rates are conducted and analysed for demonstration. The major findings includes:

- (1) The observed four local minimum in $|\text{DDTG}|$ curves suggests that a 4-step and 4-component kinetic scheme is able to describe the pyrolysis of MDF in nitrogen. The proposed method may be useful to determine the kinetic schemes of other unknown complex materials.
- (2) The Kissinger's method is used to quickly find the possible ranges of kinetic parameters (A and E). These ranges can be fed into GA and accelerate the search for more accurate kinetic and stoichiometric parameters. Comparison shows that the proposed methods and kinetic scheme are able to match the experimental data better than the Kissinger's analytical method and the first-order model. Meanwhile, the search method is highly efficient and straightforward, faster than the regular GA search alone.

- (3) As the TG data available increases, the interdependence among kinetic parameters becomes weak, and the accuracy of first-order model may declines. Conducting and using TG experiment under multiple heating rates is crucial to obtain good and unique kinetic parameters, and to better predict the pyrolysis in real fires scenarios under complex heating conditions.

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NOMENCLATURE

A	pre-exponential factor (s^{-1})
E	activation energy (kJ/mol)
f	mass fraction of component
m	mass of sample or char residue (mg)
$\dot{m}''_{\text{exp}}$	experimental mass-loss rate (s^{-1})
$\dot{m}''_{\text{Try}}$	model predicted mass-loss rate (s^{-1})
n	reaction order
N	number of components
R	ideal gas constant (J/mol/K)
T	sample temperature (K)
t	time (s)

Greek symbols

α	volatile conversion
β	heating rate (K/min)
ν	stoichiometric coefficient of char yield
Φ	relative error of fitting
ω	reaction rate (s^{-1})

Superscript and Subscript

cal	calculation
exp	experiment
i	component
p	peak

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