Pattern search method for determination of DAEM kinetic parameters from nonisothermal TGA data of biomass

Junmeng Cai*

*College of Power Engineering, University of Shanghai for Science and Technology,
Shanghai 200093, P. R. China*
E-mail: caijunmeng7321@163.com

Liqun Ji

*College of Management, University of Shanghai for Science and Technology,
Shanghai 200093, P. R. China*
E-mail: jilq0@163.com

The most accurate and up-to-date approach to modeling biomass pyrolysis is to adopt the distributed activation energy model (DAEM). In this study, a pattern search method to be used for the determination of DAEM kinetic parameters from the nonisothermal thermogravimetric analysis (TGA) data of biomass has been introduced. The method has been applied to the nonisothermal TGA data of peanut shell sample, and DAEM kinetic parameters of biomass samples have been determined. Calculated model results from determined kinetic parameters have been compared with nonisothermal TGA data of biomass.

KEY WORDS: distributed activation energy model (DAEM), thermogravimetric analysis (TGA), pattern search method, biomass

1.   Introduction

The scarcity of natural fuel resources and the increase in biomass have led to renewed interest in converting biomass into useful energetic products [1]. In recent years, thermochemical processes have become some of the most promising ways for obtaining useful products from biomass [2]. The study of the kinetic

behavior of thermal decomposition is fundamental for design and control of those processes.

The models explaining the thermal decomposition of biomass may be investigated under two main headings as pseudo-mechanistic model involving one or more reactions and distributed activation energy model (DAEM) [3]. The most accurate and up-to-date approach to modeling the thermal decomposition of biomass is to adopt DAEM [4].

Determination of DAEM kinetic parameters has some mathematical difficulties because of the complex structure of DAEM equation. In the previous studies, these parameters were established using methods such as (1) Marquardt nonlinear regression method [5, 6]; (2) Flexible Simplex method [7]; (3) direction search method based on the grid technique [8]. In their studies, the frequency factor is assumed as constant.

In this study, a pattern search method to be used for the determination of DAEM kinetic parameters (including the frequency factor) from the nonisothermal thermogravimetric analysis (TGA) data of biomass has been presented.

2.   Nonisothermal DAEM equation

The DAEM for biomass pyrolysis may be applied to either the total amount of volatiles released, or to the amount of an individual volatile constituent [9]. The description here follows the total amount of volatiles released. The biomass constituents are numbered $i = 1 \ldots n$, and the released mass fraction for the ith constituent is $V_i(t)$. The contribution of the ith reaction is described by the first-order equation:

$$\frac{\mathrm{d}V_i}{\mathrm{d}t} = k_i \left(V_i^* - V_i \right), \tag{1}$$

where V_i^* denotes the total released mass fraction for the ith constituent. So that $V_i^* - V_i$ is the amount of unreacted volatile remaining at time t.

The amount of volatiles released by this one constituent is obtained by integration of equation (1), giving:

$$V_i = V_i^* - V_i^* \exp\left[-\int_0^t k_i \mathrm{d}t \right]. \tag{2}$$

If $i = 1$, the model is referred to as the single first-order reaction model (SFOR). In contrast the DAEM allows for a more complicated set of reactions by considering a continuous distribution of reactions. In the DAEM the dependence on volatile number i is replaced by a continuous dependence on activation energy E, so that the total amount of volatile available for release from the biomass is taken to be a distribution satisfying

$$\mathrm{d}V^* = V^* f(E) \, \mathrm{d}E, \tag{3}$$

where $f(E)$ is the distribution of activation energies and

$$\int_0^\infty f(E)\,\mathrm{d}E = 1. \tag{4}$$

Thus the total amount of volatile material released up to time t is given by

$$V = V^* - V^* \int_0^\infty \exp\left[-\int_0^t k(E)\,\mathrm{d}t\right] f(E)\,\mathrm{d}E. \tag{5}$$

Usually, the distribution $f(E)$ is taken to be a Gaussian distribution with mean activation energy E_0 and standard deviation σ. Assuming that $k(E) = k_0 \exp(-E/RT)$, expression (5) becomes

$$1 - \frac{V}{V^*} = \frac{1}{\sigma\sqrt{2\pi}} \int_0^\infty \exp\left[-k_0 \int_0^t \exp\left(-\frac{E}{RT}\right)\mathrm{d}t - \frac{(E-E_0)^2}{2\sigma^2}\right]\mathrm{d}E, \tag{6}$$

where k_0 is the frequency factor, R is the universal gas constant, and T is the absolute temperature.

In the nonisothermal TGA, the sample is heated by using a linear heating rate:

$$T = T_0 + \beta t, \tag{7}$$

where T_0 is thermal decomposition initial temperature and β is the heating rate.

Considering equation (7), the nonisothermal DAEM equation is given below:

$$1 - \frac{V}{V^*} = \frac{1}{\sigma\sqrt{2\pi}} \int_0^\infty \exp\left[-\frac{k_0}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right)\mathrm{d}T - \frac{(E-E_0)^2}{2\sigma^2}\right]\mathrm{d}E. \tag{8}$$

3. Determination of DAEM kinetic parameters

The read values of certain T from TGA curve are written in their parts in the following equation:

$$1 - \frac{V}{V^*} = \frac{w_T - w_\mathrm{f}}{w_0 - w_\mathrm{f}} = x \tag{9}$$

and the remaining mass fraction is determined. In the above equation, w_0 is the initial weight, w_f the final weight and w_T the weight at temperature T of the sample analyzed by nonisothermal TGA.

In the calculation, the form of the objective function to optimize kinetic parameters (including k_0, E_0, and σ) of nonisothermal DAEM equation is

$$O.F. = \sum_{i=1}^{n_\mathrm{d}} \left(x_{i,\mathrm{cal}} - x_{i,\mathrm{exp}}\right)^2, \tag{10}$$

where $x_{i,\text{cal}}$ and $x_{i,\text{exp}}$ are calculated and experimental values of the remaining mass fraction, respectively, n_{d} is data number.

In the literature [10], obtained values for k_0 are between 10^4 and $10^{30}\,\text{s}^{-1}$, for E_0 are between 50 and $350\,\text{kJ/mol}$, for σ between 5 and $70\,\text{kJ/mol}$. Using certain k_0, E_0, and σ values between these limits, equation (8) can be solved by a computer program, which employs Simpson's 1/3 rule for integration, and $x_{i,\text{cal}}$ are obtained. Values of $x_{i,\text{exp}}$ can be obtained from TGA data of the sample. Kinetic parameters searched for the sample studied on will be about k_0, E_0, and σ values where *O.F.* has minimum value.

In order to determine the k_0, E_0, and σ values minimizing *O.F.* value, a certain optimization technique will be used. It is difficult to obtain information about gradient or higher derivations of the objective function without explicit expression. Therefore, the optimization algorithm should be derivative-free, robust with respect to local optima and should be require as least function evaluations as possible to find the optimum.

In this study, we propose the use of a pattern search method, which is a derivative-free, direct search method, and superior to other direct search methods such as Powell method and Simplex method in both robustness and number of function evaluations [11]. Pattern Search algorithm proceeds according to a series of exploratory moves and pattern moves. The exploration starts from an initial point using the specified step size in each coordinate direction. If the adjacent move is accepted according to the objective function, the step is considered successful. Otherwise, the step is retracted and replaced by a step in the opposite direction, which in turn is retained depending upon whether it succeeds or fails. When all coordinates (variables) have been investigated, the exploratory move is completed. The resulting point is termed as the base point. If a pattern direction exists after the completed exploratory move, the search procedure proceeds to the pattern move. A pattern move consists of a single step from the present base point along the line from the previous base point to the current base point. In the case of a successful pattern move, the line search along the pattern direction is conducted until there is no further acceptable move. On the other hand, if the exploratory move does not produce improvement, then the pattern move is discarded and the search returns to the exploratory search to find a new pattern direction. In such situation, the step sizes of the variables are adjusted. The step sizes will be increased first until the user-specified limit is reached. If this fails, the step sizes will be decreased, and the exploratory moves are repeated. For more details of pattern search method, readers are referred to the literature [12].

4.   Results and discussion

For numerical examples, nonisothermal TGA data of peanut shell are used. Ultimate analysis of peanut shell is given in table 1. Nonisothermal TGA data

Table 1
Ultimate analysis of peanut shell (wt%, db).

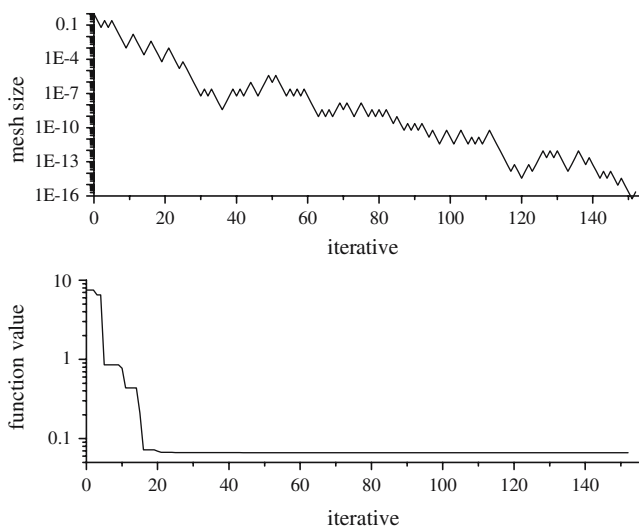|	
Carbon	45.468
Hydrogen	5.578
Oxygen	40.517
Others	8.437

Figure 1. Function value and mesh size versus iterative.

of peanut shell sample have been obtained with a heating rate of 10 K/min and a nitrogen flow rate of 25 ml/min.

In this study, we use the pattern search tool of the software MATLAB to compute the values of DAEM kinetic parameters. The MATLAB Genetic Algorithm and Direct Search Toolbox contains the generalized pattern search method developed by Torczon [13]. The pattern search algorithm can handles those optimization problems that are difficult to solve with traditional optimization techniques, including problems that computation of the objective function is discontinuous, highly nonlinear, stochastic, has unreliable or undefined derivatives.

Figure 1 plots function value and mesh size versus iterative for calculation of the pattern search method with the initial values given in table 2. It can be seen that the iterative computation is convergent. k_0, E_0, and σ values where *O.F.* has minimum value 0.06625 are given in table 2.

Calculated remaining mass fraction curves are compared with nonisothermal TGA data in figure 2. The correlation coefficient between calculated

Table 2
DAEM kinetic parameters for the biomass sample.

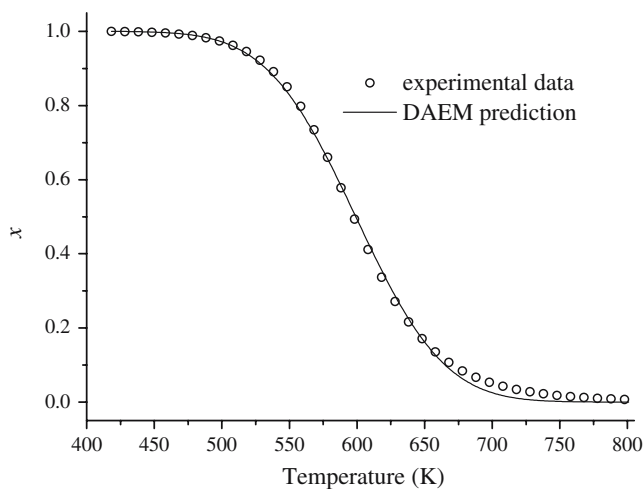|	A(1/s)	E_0(kJ/mol)	σ(kJ/mol)	Function value
Initial value	1.0×10^{10}	150	10	7.498
Final value	6.0218×10^{13}	183.3	15.06	0.06625

Figure 2. Comparison of remaining mass fraction curves calculated from the distributed activation energy model with nonisothermal TGA data.

remaining mass fraction and experimental data is up to 0.99968. It can be seen that DAEM fits the experimental data very well.

5.　Conclusion

DAEM kinetic parameters used in the explanation of thermal decomposition process can be determined easily from nonisothermal TGA data of sample and through a pattern search method. Determined kinetic parameters can be used for design and control of thermal decomposition process.

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