

Nonisothermal n th-order DAEM equation and its parametric study – use in the kinetic analysis of biomass pyrolysis

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Nonisothermal n th-order distributed activation energy model (DAEM) was derived. Numerical solutions of the nonisothermal n th-order DAEM equation were performed. The influences of various parameters relevant to biomass pyrolysis on numerical results of the nonisothermal n th-order DAEM equation were also studied. Investigated parameters are heating rate, the mean of activation energy distribution, standard deviation of activation energy distribution, frequency factor and reaction order. The study results can be further responsible for determination of n th-order DAEM kinetic parameters from thermogravimetric analysis data of biomass.

KEY WORDS: distributed activation energy model, nonisothermal kinetics, pyrolysis, thermogravimetric analysis

1. Introduction

The distributed activation energy model (DAEM) has been proved very successful in kinetic analysis of complex material [1]. While our focus here is primarily on values of parameters relevant to biomass, the DAEM also applies to the pyrolysis of other materials, including coals [2–4], petroleum residues [5], resin chars [6] and oil shales [7].

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Numerical solutions of the reaction kinetic models are used to determine the kinetic parameters. To obtain realistic results, parameters affecting kinetic equations must be known. A detailed review of the influences of various parameters on the single-reaction model can be found in the literature [8]. Günes and Günes [9] investigated the influences of various parameters on the first-order DAEM. In this work, the n th-order DAEM equation has been derived and the influences of various parameters relevant to biomass pyrolysis on numerical solutions of n th-order DAEM have been performed.

2. Nonisothermal n th-order 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 [10]. The description here follows the total amount of volatiles released. The biomass constituents are numbered $i = 1, \dots, m$, and the released mass fraction for the i th constituent is $V_i(t)$. The contribution of i th reaction is described by the pseudo- n th-order equation:

$$\frac{d(V_i/V_i^*)}{dt} = k_i \left(\frac{V_i^* - V_i}{V_i^*} \right)^n, \quad (1)$$

where V_i^* denotes the total released mass fraction for the i th constituent, n the i th reaction order and k_i is the i th reaction rate.

It is assumed that k_i 's are given by Arrhenius expression [8]:

$$k_i = A_i e^{-E_i/RT}, \quad (2)$$

where A_i is the frequency or pre-exponential factor of the i th reaction process, E_i the activation energy of the i th reaction process, R the universal gas constant and T is the absolute temperature.

Substituting equation (2)–(1), after simple transformations and integrations of both sides gives

$$\frac{V_i^* - V_i}{V_i^*} = \left[1 - (1 - n) \int_0^t A_i e^{-E_i/RT} dt \right]^{\frac{1}{1-n}} \quad (3)$$

or

$$V_i = V_i^* \left\{ 1 - \left[1 - (1 - n) \int_0^t A_i e^{-E_i/RT} dt \right]^{\frac{1}{1-n}} \right\}. \quad (4)$$

If $i = 1$, the model is referred to as the single n th-order reaction model. In contrast the DAEM allows for a more complicated set of reactions by considering a continuous distribution of reactions. In the DAEM it is assumed that all k_i differ only in activation energy and the number of reactions is larger enough to permit the distribution of the activation energy to be expressed as a function $f(E)$. 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

$$dV^* = V^* f(E)dE, \tag{5}$$

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

$$\int_0^\infty f(E)dE = 1. \tag{6}$$

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

$$x = \frac{V}{V^*} = \int_0^\infty \left\{ 1 - \left[1 - (1 - n) \int_0^t Ae^{-E/RT} dt \right]^{\frac{1}{1-n}} \right\} f(E)dE \tag{7}$$

or

$$1 - x = \frac{V^* - V}{V^*} = \int_0^\infty \left[1 - (1 - n) \int_0^t Ae^{-E/RT} dt \right]^{\frac{1}{1-n}} f(E)dE, \tag{8}$$

where x is the mass fraction of releasing volatiles and $(1 - x)$ is the remaining mass proportion.

Usually $f(E)$ is taken to be Gaussian distribution with a mean activation energy E_0 and standard deviation σ , so

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(E-E_0)^2/2\sigma^2} \tag{9}$$

Substituting equation (9)–(8), rearranging equation (8), one gets the n th-order DAEM model equation:

$$1 - x = \int_0^\infty \frac{1}{\sigma\sqrt{2\pi}} \left[1 - (1 - n) \int_0^t Ae^{-E/RT} dt \right]^{\frac{1}{1-n}} e^{-\frac{(E-E_0)^2}{2\sigma^2}} dE \tag{10}$$

The thermogravimetric analysis (TGA) technique is extensively used to determine the relation between temperature and time in equation (10). Detailed

information about TGA can be found in the literature [11]. In this study, the $T = T_0 + \beta t$ equation is used, where T_0 is the pyrolysis initial temperature and β is heating rate.

Considering the $T = T_0 + \beta t$ equation, the nonisothermal *n*th-order DAEM equation is given below:

$$1 - x = \int_0^\infty \frac{1}{\sigma\sqrt{2\pi}} \left[1 - (1 - n) \int_{T_0}^T \frac{A}{\beta} e^{-E/RT} dT \right]^{\frac{1}{1-n}} e^{-\frac{(E-E_0)^2}{2\sigma^2}} dE. \quad (11)$$

It is noted that equations (3), (4), (7), (8), (10) and (11) subject to ($n \neq 1$). Assumptions and restrictions of the first-order DAEM, its equation for the nonisothermal processes is given for comparison [12]:

$$1 - x = \int_0^\infty \frac{1}{\sigma\sqrt{2\pi}} e^{-\int_{T_0}^T \frac{A}{\beta} e^{-E/RT} dT - \frac{(E-E_0)^2}{2\sigma^2}} dE. \quad (12)$$

3. Numerical solution of nonisothermal DAEM equation

Equation (11) involves a double integration, which is difficult to deal with. The inner dT integration is the temperature integral or Arrhenius integral, which has no exact analytical solution [13]. A large number of temperature integral approximations, with varying complexity and accuracy, have been presented [14]. In this study, the modified Junmeng–Fusheng approximation is used to replace the temperature integral, which is simple, accurate and reliable [15, 16].

$$\int_{T_0}^T e^{-E/RT} dT = \frac{E}{R} [p(u) - p(u_0)], \quad (13)$$

where

$$u = \frac{E}{RT}, \quad u_0 = \frac{E}{RT_0}, \quad (14)$$

$$p(u) = \frac{e^{-u} 0.99962u + 0.60642}{u^2 + 2.56879}. \quad (15)$$

To deal with the outer dE integration of equation (11), Simpson’s 1/3 rule is employed. For this purpose, a computer program developed in MATLAB language is used. Thus, the nonisothermal *n*th-order DAEM equation can be solved by using numerical techniques for certain $T_0, \beta, E_0, \sigma, A$ and n values.

4. Results and discussion

The objective of this analysis is to present the influences of various parameters relevant to biomass pyrolysis on the numerical results of the nonisothermal *n*th-order DAEM equation.

The effect of heating rate on numerical results is illustrated in figure 1, where it is seen that remaining mass fraction curves is shifted up the temperature scale by an increase in the heating rate.

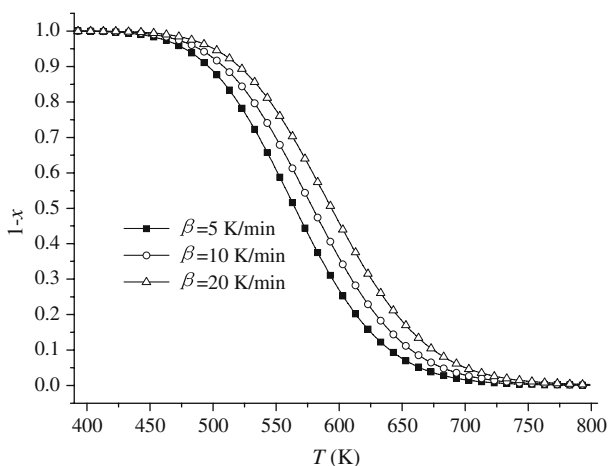


Figure 1. The effect of heating rate (β) on the numerical results ($T_0 = 393$ K, $E_0 = 125$ kJ/mol, $\sigma = 10$ kJ/mol, $A = 1.5 \times 10^9$ 1/s, $n = 2.0$).

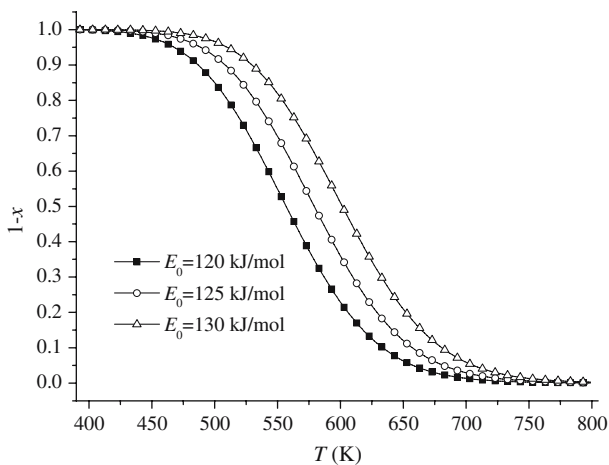


Figure 2. The effect of the mean activation energy (E_0) on the numerical results ($T_0 = 393$ K, $\beta = 10$ K/min, $\sigma = 10$ kJ/mol, $A = 1.5 \times 10^9$ 1/s, $n = 2.0$).

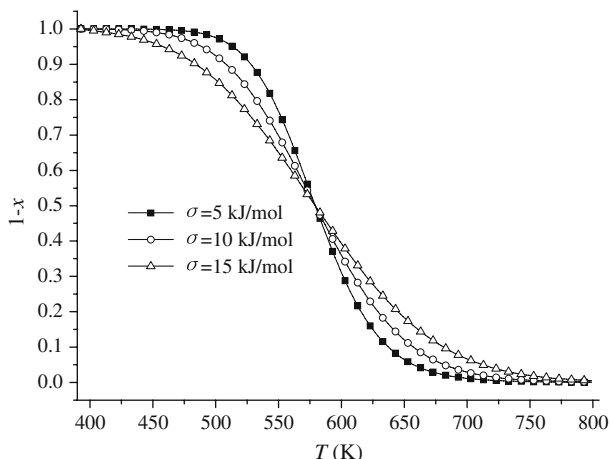


Figure 3. The effect of the standard deviation (σ) on the numerical results ($T_0 = 393$ K, $\beta = 10$ K/min, $E_0 = 125$ kJ/mol, $A = 1.5 \times 10^9$ 1/s, $n = 2.0$).

The effects of the mean activation energy (E_0) and standard deviation (σ) on numerical results are given in figures 2 and 3, respectively. Increase in E_0 values causes the remaining mass fraction ($1-x$) curves to lead towards right direction as parallel to each other. Increase in σ values causes slopes of ($1-x$) curves to get less.

The effect of the frequency factor (A) values on the numerical results is shown in figure 4. According to these curves, the increase in A values causes ($1-x$) curves to lead toward left direction.

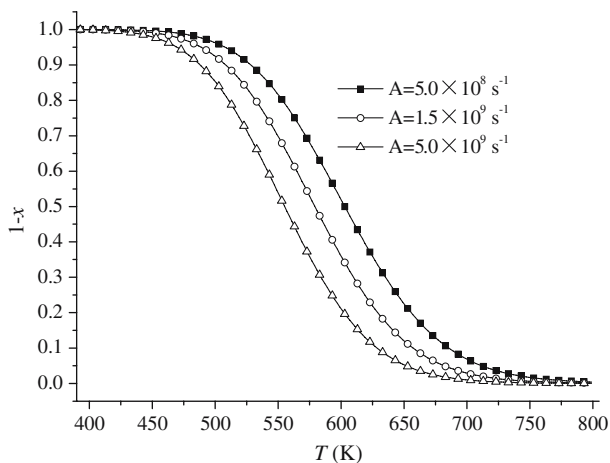


Figure 4. The effect of the frequency factor (A) on the numerical results ($T_0 = 393$ K, $\beta = 10$ K/min, $E_0 = 125$ kJ/mol, $\sigma = 10$ kJ/mol, $n = 2.0$).

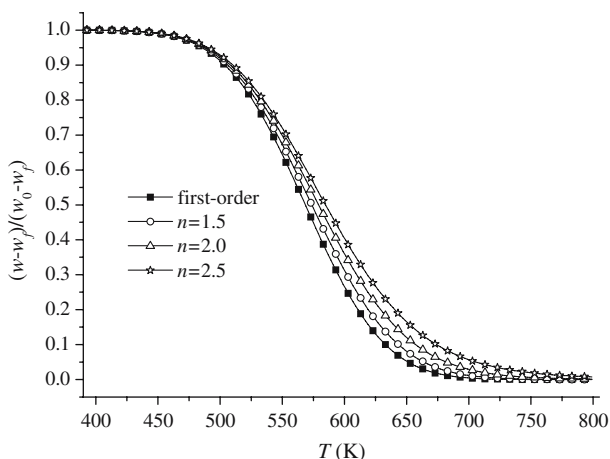


Figure 5. The effect of the reaction order (n) on the numerical results ($T_0 = 393$ K, $\beta = 10$ K/min, $E_0 = 125$ kJ/mol, $\sigma = 10$ kJ/mol, $A = 1.5 \times 10^9$ 1/s).

The effect of the reaction order (n) values on the numerical results is shown in figure 5. it is seen that increase in n values causes $(1-x)$ curves to lead toward right direction from figure 5.

5. Conclusion

Nonisothermal n th-order DAEM equation was derived and its parametric study was studied. The changing of heating rate, the mean of activation energy distribution, stand deviation of activation energy distribution, frequency factor and reaction order affects the form of remaining mass fraction curves. Those influences can be used to determine the kinetic parameters of nonisothermal n th-order equation from TGA data.

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