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PARAMETRIC STUDY OF THE NONISOTHERMAL n^{th}-ORDER DISTRIBUTED ACTIVATION ENERGY MODEL INVOLVED THE WEIBULL DISTRIBUTION FOR BIOMASS PYROLYSIS

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This paper describes the influences of some parameters relevant to biomass pyrolysis on the numerical solutions of the nonisothermal n^{th}-order distributed activation energy model (DAEM) involved the Weibull distribution. Investigated parameters are the integral upper limit, the frequency factor, heating rate, the reaction order and the shape, scale and location parameters of the Weibull distribution. Those influences can be used for the determination of the kinetic parameters of the nonisothermal n^{th}-order Weibull DAEM from thermoanalytical data of biomass pyrolysis.

Keywords: *biomass pyrolysis, distributed activation energy model (DAEM), non-isothermal kinetics, numerical solution, Weibull distribution*

Introduction

There are many models which are used to explain biomass pyrolysis, which can be investigated under two main headings: (1) single-reaction and (2) multi-reaction models. Detailed information on these models is available in the literatures [1–6]. The most accurate and up-to-date approach to modeling biomass pyrolysis is to adopt the distributed activation energy model (DAEM) [7–10].

The numerical solutions of the kinetic model equations are used to determine the kinetic parameters. To obtain realistic results, parameters affecting the numerical solutions of the model equations must be known. A detailed review of the influences of various parameters on the single-reaction models can be found in the literature [11]. Güneş and Güneş investigated the influences of various parameters on the nonisothermal first-order DAEM involved the Gaussian distribution [12]. Cai *et al.* performed a parametric study of the n^{th}-order Gaussian DAEM [13]. In this study, the influences of various parameters relevant to biomass pyrolysis on the numerical results of the nonisothermal n^{th}-order DAEM involved the Weibull distribution have been investigated.

Theory

The non-isothermal n^{th}-order DAEM involved the Weibull distribution and its numerical solutions

The DAEM is one type of the multi-reaction models. Assumptions and restrictions of the n^{th}-order DAEM, and the derivation of its equations can be found in the literature [13]. The nonisothermal n^{th}-order DAEM equation is given below:

$$1-x=\begin{cases}\displaystyle\int_0^{\infty}\exp\left[-\int_{T_0}^{T}\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T\right]f(E)\mathrm{d}E & \text{first-order}\\ \displaystyle\int_0^{\infty}\left[1-(1-n)\int_{T_0}^{T}\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T\right]^{\frac{1}{1-n}}f(E)\mathrm{d}E & n^{\text{th}}\text{-order}\,(n\neq 1)\end{cases} \quad (1)$$

In the above equation, E is the activation energy, A is the frequency factor, R is the ideal gas constant, β is heating rate, n is the reaction order, T is the absolute temperature, T_0 is the initial reaction temperature, x is the mass fraction of releasing volatiles and $f(E)$ is the distribution of activation energies.

Usually, $f(E)$ is taken to be a Gaussian distribution. However, with the selection of an appropriate distribution function for the molecular activation energies in mind, it may thus be advantageous to select an asymmetric distribution for modeling the kinetics of biomass pyrolysis, such as the Weibull distribution, over a sym-

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metric one (e.g., Gaussian) [14]. Furthermore, the Weibull distribution is mathematically flexible:

$$f(E)=\frac{\delta}{\eta}\left(\frac{E-\gamma}{\eta}\right)^{\delta-1}\exp\left[\left(\frac{E-\gamma}{\eta}\right)^{\delta}\right] \quad (2)$$

In the above equation, η is the scale parameter, and δ is the shape parameter, γ is the threshold or location parameter and $E\geq\gamma\geq 0$, $\eta>0$, $\delta>0$. δ is expressed in dimensionless, γ, η and E are expressed in kJ mol^{-1}.

The mean of the distribution equals the mean activation energy and is given by

$$\mu=\gamma+\eta\Gamma\left(\frac{1}{\delta}+1\right)=E_0 \quad (3)$$

The variance of the distribution is given by

$$\sigma^2=\eta^2\Gamma\left(\frac{2}{\delta}+1\right)-\eta^2\Gamma^2\left(\frac{1}{\delta}+1\right) \quad (4)$$

where $\Gamma(2/\delta+1)$ is the Gamma function.

The Weibull distribution has some interesting properties and generates a variety of distributions [15]. For $\delta=1$, the Weibull distribution coincides with the exponential distribution. For values of $\delta>1$, the distribution becomes 'bell shaped', but becomes positively skewed. As δ increases, the Weibull distribution approaches the Gaussian distribution more and more closely [16].

Choosing a threshold value of activation energy (γ), implies that reactions with activation energies less than this value do not occur. Therefore, the lower limit of the outer dE integral in the Eq. (1) should be replaced with $E=\gamma$. Then, the nonisothermal n^{th}-order DAEM involved the Weibull distribution is obtained and given below.

Equation (5) involves a double integration, which is difficult to deal with. The inner dT integration is termed the temperature integral or Arrhenius integral, which does not have an exact analytical solution [17]. A large number of temperature integral approximations, with varying complexity and accuracy, have been presented [18–20]. In this work, we use the approximation proposed by Cai *et al.* [21] to evaluate the temperature integral.

$$\int_{T_0}^{T}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T=\frac{E}{R}[p(u)-p(u_0)] \quad (6)$$

where

$$u=\frac{E}{RT},\ u_0=\frac{E}{RT_0} \quad (7)$$

$$p(u)=\frac{\mathrm{e}^{-u}}{u^2}\frac{u+0.25403\ln u+0.36665}{u+0.24598\ln u+2.41457} \quad (8)$$

To deal with the outer dE integration of Eq. (5), Simpson's 1/3 rule is employed. For this purpose, a computer program developed in Mathematica language is used. Detailed information about the Mathematica software system can be found in the literature [22]. Thus, the nonisothermal n^{th}-order DAEM equation can be solved by using some numerical techniques for certain A, β, T_0, γ, δ, η and n values.

$$1-x=\begin{cases}\displaystyle\int_{\gamma}^{\infty}\frac{\delta}{\eta}\left(\frac{E-\gamma}{\eta}\right)^{\delta-1}\exp\left[-\int_{T_0}^{T}\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T-\left(\frac{E-\gamma}{\eta}\right)^{\delta}\right]\mathrm{d}E & \text{first-order}\\ \displaystyle\int_{\gamma}^{\infty}\frac{\delta}{\eta}\left(\frac{E-\gamma}{\eta}\right)^{\delta-1}\exp\left[-\left(\frac{E-\gamma}{\eta}\right)^{\delta}\right]\left[1-(1-n)\int_{T_0}^{T}\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T\right]^{\frac{1}{1-n}}\mathrm{d}E & n^{\text{th}}\text{-order}\ (n\neq 1)\end{cases} \quad (5)$$

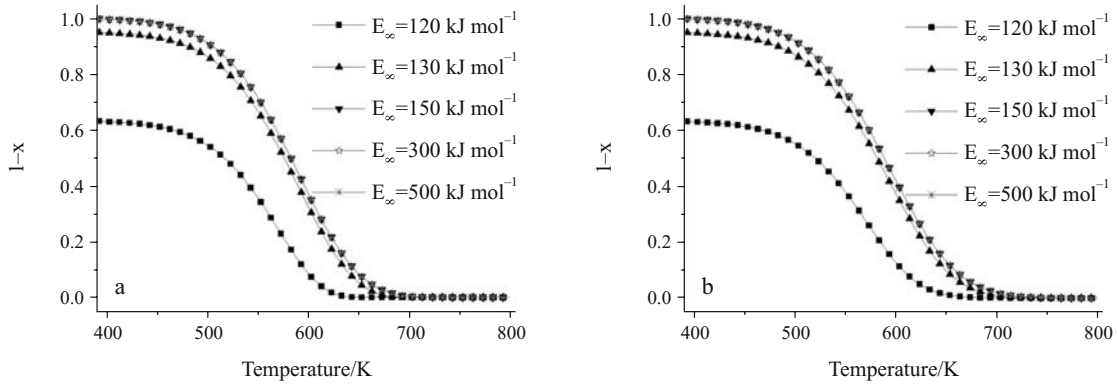

Fig. 1 The effect of upper limit of dE integral on the numerical results ($A=2.5\cdot10^8$ s^{-1}, β=20 K min^{-1}, T_0=393 K, γ=25 kJ mol^{-1}, δ=11, η=95 kJ mol^{-1}); a – first-order, b – n^{th}-order, n=1.5

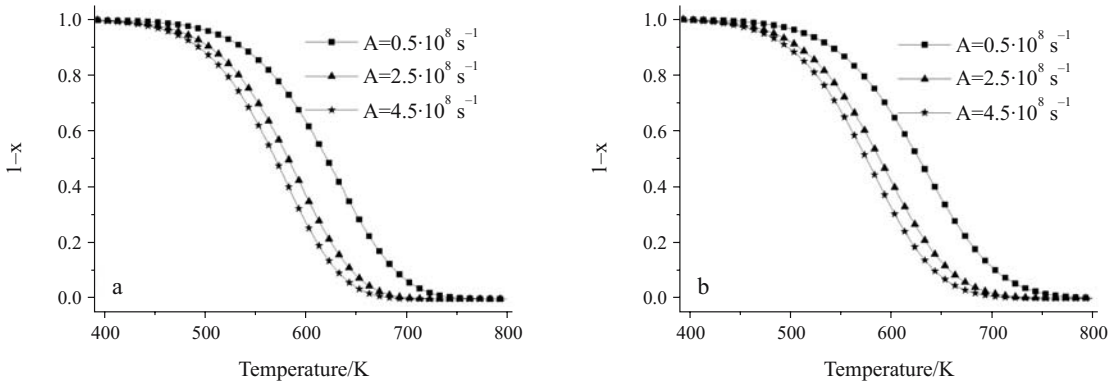

Fig 2 The effect of the frequency factor (A) on the numerical results (β=20 K min^{-1}, T_0=393 K, γ=25 kJ mol^{-1}, δ=11, η=95 kJ mol^{-1}); a – first-order, b – n^{th}-order, n=1.5

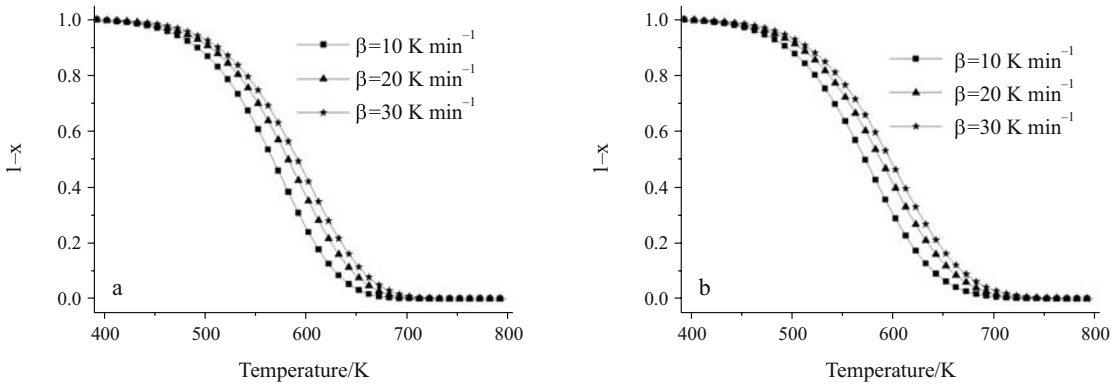

Fig. 3 The effect of heating rate (β) on the numerical results (A=2.5·10^8 s^{-1}, T_0=393 K, γ=25 kJ mol^{-1}, δ=11, η=95 kJ mol^{-1}); a – first-order, b – n^{th}-order, n=1.5

Application

For applications, the experimental data taken from the literature for the non-sothermal pyrolysis of peanut shell have been used. The thermogravimetric data for the pyrolysis of peanut shell have been taken from the literature [23]. Figure 8 shows the comparison of the n^{th}-order Weibull DAEM predicted pyrolytic conversion with the experimental data. It is noted that the results of this paper have been used in the process of obtaining the n^{th}-order Weibull DAEM prediction. Figure 8 demonstrates that the n^{th}-order Weibull DAEM fits the experimental data very well.

Results and discussion

For numerical integration of Eq. (1), the outer dE integration upper limits must be determined. For the parameters values relevant to biomass pyrolysis, the influences of upper limit (E_∞) of dE integral on the numerical results of the nonisothermal n^{th}-order DAEM equation is shown in Fig. 1. At the beginning of pyrolysis reaction, the remaining mass proportion ($1–x$) must be close to 1. Whereas in Fig. 1, it is observed that remaining mass proportion is less than 1 for E_∞<130 kJ mol^{-1} values. When more than 150 kJ mol^{-1} values are used for E_∞, the results are more accurate and closely proximate to each other. Therefore, 300 kJ mol^{-1} value can be used for the upper limit of the dE integral.

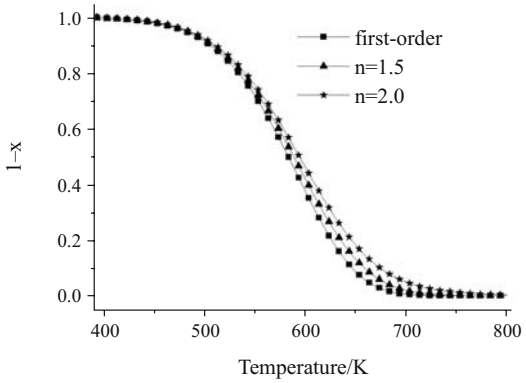

Fig. 4 The effect of the reaction order (n) on the numerical results (A=2.5·10^8 s^{-1}, β=20 K min^{-1}, T_0=393 K, γ=25 kJ mol^{-1}, δ=11, η=95 kJ mol^{-1})

The effect of the frequency factor (A) values on the numerical results is shown in Fig. 2. According to these curves, increase in A values causes (1–x) curves to lead to left direction.

The effect of heating rate on numerical results is illustrated in Fig. 3, where it is seen that remaining mass fraction curves is shifted up the temperature scale by an increase in heating rate.

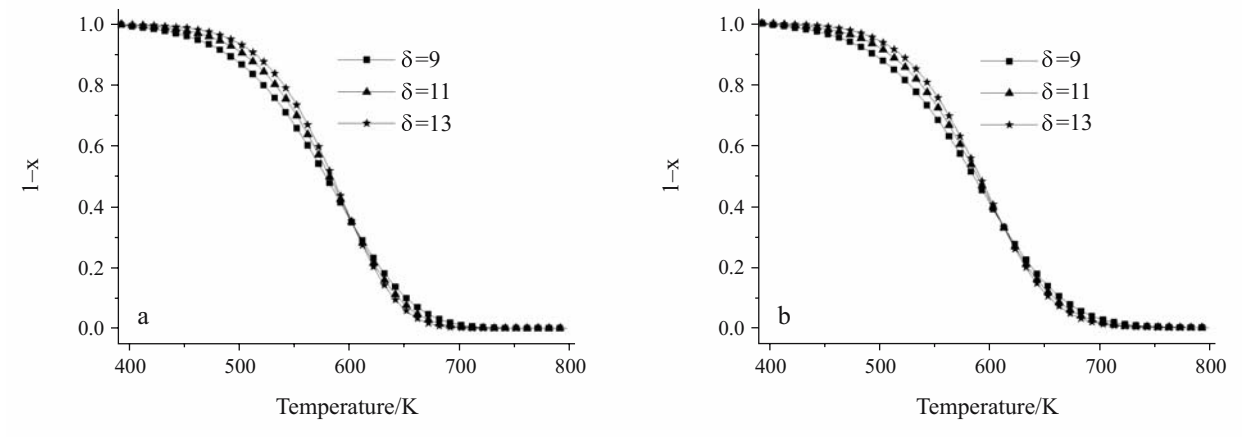

Fig. 5 The effect of the shape parameter of the Weibull distribution (δ) on the numerical results (A=2.5·10^8 s^{-1}, β=20 K min^{-1}, T_0=393 K, γ=25 kJ mol^{-1}, η=95 kJ mol^{-1}); a – first-order, b – n^{th}-order, n=1.5

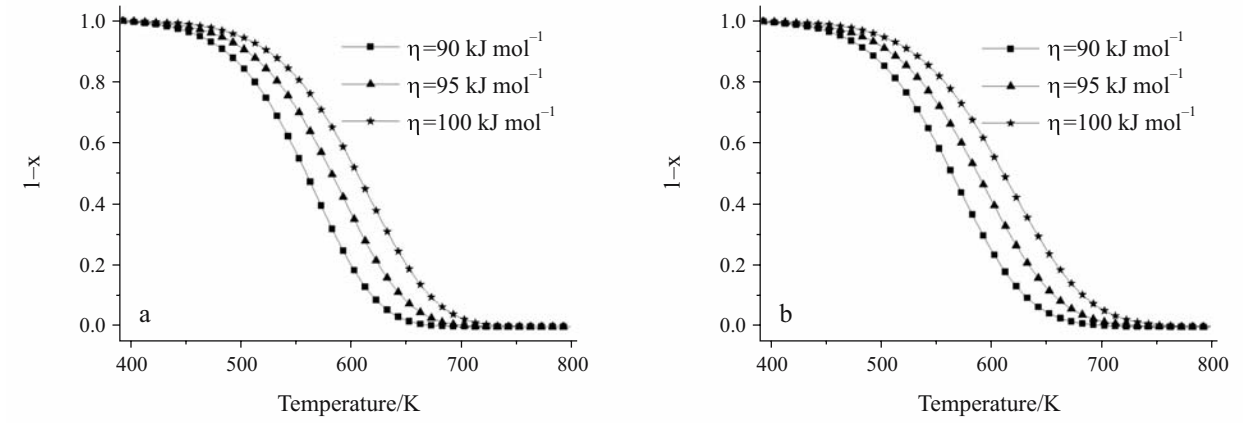

Fig. 6 The effect of the scale parameter of the Weibull distribution (η) on the numerical results (A=2.5·10^8 s^{-1}, β=20 K min^{-1}, T_0=393 K, γ=25 kJ mol^{-1}, δ=11); a – first-order, b – n^{th}-order, n=1.5

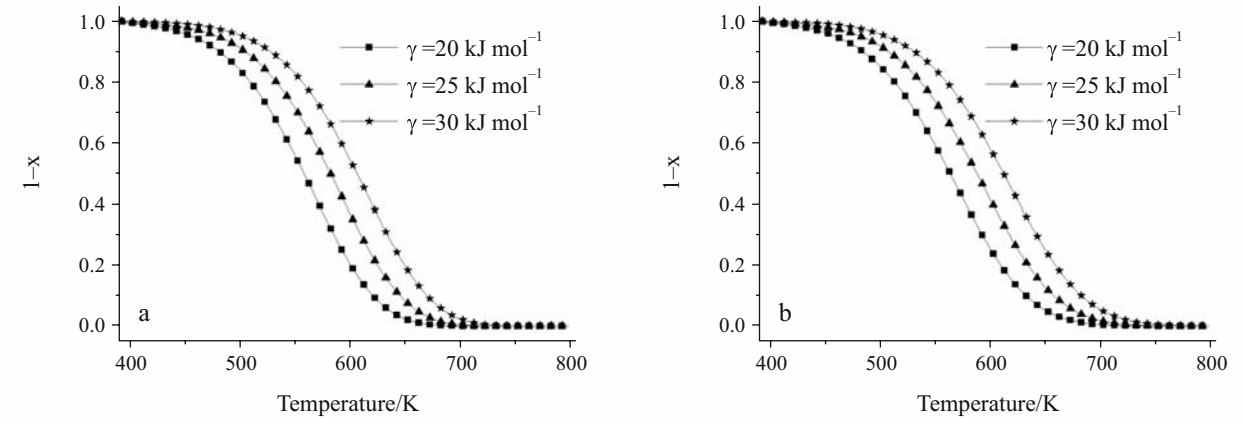

Fig. 7 The effect of the location parameter of the Weibull distribution (γ) on the numerical results (A=2.5·10^8 s^{-1}, β=20 K min^{-1}, T_0=393 K, δ=11, η=95 kJ mol^{-1}); a – first-order, b – n^{th}-order, n=1.5

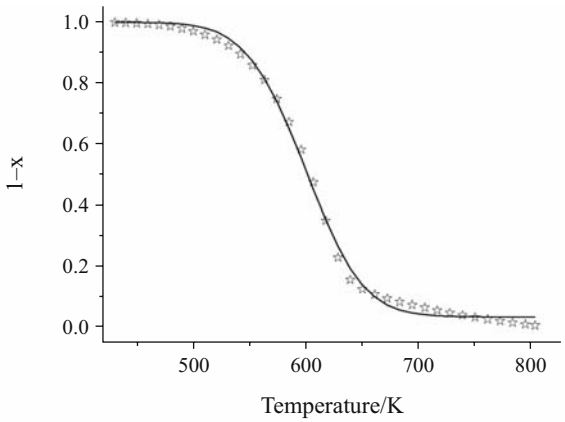

Fig. 8 Comparison between experimental data and the n^{th}-order Weibull DAEM prediction (✶ – experimental data; —— – the n^{th}-order Weibull DAEM prediction)

The effect of the reaction order (n) values on the numerical results is illustrated in Fig. 4, from which it is seen that increase in n values causes ($1–x$) curves to lead toward right direction.

The effect of the shape parameter of Weibull distribution (δ) on the numerical results is depicted in Fig. 5. Increase in δ values causes slopes of the remaining mass fraction ($1–x$) curves to get less.

The influences of the scale parameter (η) and the location parameter (γ) of Weibull distribution on the numerical results are given in Figs 6 and 7, respectively. Increase in η and γ values causes the remaining mass fraction ($1–x$) curves to lead towards right direction as parallel to each other.

Conclusions

In the numerical solutions of the nonisothermal n^{th}-order DAEM involved the Weibull distribution for the parameters values as the characteristic biomass pyrolysis kinetics, 300 kJ mol^{-1} value can be used for the upper limit of the outer dE integral. The changing of the frequency factor, heating rate, the reaction order and the shape, scale and location parameters of the Weibull distribution affects the form of remaining mass fraction curves. The results are helpful to the determination of the kinetic parameters of the nonisothermal n^{th}-order Weibull DAEM from the thermoanalytical data of biomass pyrolysis.

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