J Therm Anal Calorim (2009) 98:325–330
DOI 10.1007/s10973-009-0325-8

Kinetic analysis of wheat straw pyrolysis using isoconversional methods

J. M. Cai · L. S. Bi

Received: 1 October 2008 / Accepted: 14 January 2009 / Published online: 6 August 2009

Abstract The pyrolysis of wheat straw has been carried out by means of thermogravimetric analysis in inert atmosphere. The samples were heated over a range of temperatures that includes the entire range of pyrolysis with three different heating rates of 5, 10 and 20 K min^{-1}. The activation energy values as a function of the extent of conversion for the pyrolysis process of wheat straw have been calculated by means of the Flynn–Wall–Ozawa isoconversional method, the Vyazovkin–Sbirrazzuoli isoconversional method and an iterative isoconversional method presented in this article. The results have showed that there are small differences between the activation energy values obtained from the three methods, and the pyrolysis process reveals a dependence of the activation energy on conversion and have indicated the validity of the iterative integral isoconversional method. The effective activation energy for the pyrolysis of wheat straw is 130–175 kJ mol^{-1} in the conversion range of 0.15–0.85. Furthermore, the prediction of the pyrolysis process under isothermal conditions from the dependence of the activation energy on the extent of conversion has been presented.

Keywords Model-free kinetics · Pyrolysis · Biomass

J. M. Cai (✉) · L. S. Bi
School of Agriculture and Biology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China
e-mail: jmcai@sjtu.edu.cn

Introduction

Agricultural residues such as wheat straw have been usually considered as pyrolytic raw materials for the production of bio-oil or fuel gas [1–3]. The development of the pyrolysis process requires an optimization of the operating conditions in order to assure both acceptable gas outlet composition and an energy recovery, which makes the process economically satisfactory [4]. A good knowledge of the kinetics is fundamental to the optimization of the pyrolysis process [5].

The determination of reaction kinetics of wheat straw pyrolysis using thermogravimetric analysis (TGA) was investigated in some literature.

Nonisothermal TGA has proved to be one of the best techniques to study the kinetics of biomass pyrolysis and it has been extensively used. There are many methods for analyzing nonisothermal TGA data [6]. These kinetic methods can be divided into model-fitting and isoconversional methods [7, 8]. When applied to nonisothermal data, the model-fitting methods tend to produce highly unreliable values of kinetic parameters [9, 10]. This problem can be resolved when using isoconversional methods. Isoconversional methods allow estimating the activation energy as a function of conversion without previous assumptions on the reaction mechanism model. The basic assumption of these methods is that the reaction rate for a constant extent of conversion depends only on the temperature and the reaction mechanism model is independent of the heating rate [11]. Isoconversional methods allow describing not only the kinetics of single step processes, but also the kinetics of multi-step processes to be detected via a variation of the activation energy with the extent of conversion [12]. For the complex solid-state reaction processes, the apparent activation energy calculated by isoconversional methods is a global energy that may include several

reactions as well as physical transformations [13]. To use these methods, a series of experiments at different heating rates has to be performed.

The main purpose of this article is to investigate the kinetics of wheat straw pyrolysis. The specific objectives of this article are:

(a) to approach the kinetics of wheat straw pyrolysis via thermogravimetric measurements;
(b) to determine the activation energy using isoconversional methods and to verify the validity of an iterative integral isoconversional method.

Experimental

The experiments were carried out on a thermogravimetric analyzer STA 449C developed by Netzsch Instruments, Inc. The atmosphere used was nitrogen with a flow rate of 60 mL min^{-1} for the pyrolysis experiments.

All the experiments were carried out under dynamic conditions over a range of temperatures that includes the entire range of decomposition, with heating rates of 5, 10 and 20 K min^{-1}. The mass of the sample used was around 2 mg, and under these conditions the heat transfer limitations can be neglected.

The extent of conversion, α, was calculated according to Eq. 1, where m_0 is the initial and m_∞ is the final mass. The initial loss of mass corresponding to water evaporation was disregarded. Figure 1 shows the data of the extent of conversion versus temperature at different heating rates.

$$\alpha = \frac{m_0 - m(T)}{m_0 - m_\infty} \tag{1}$$

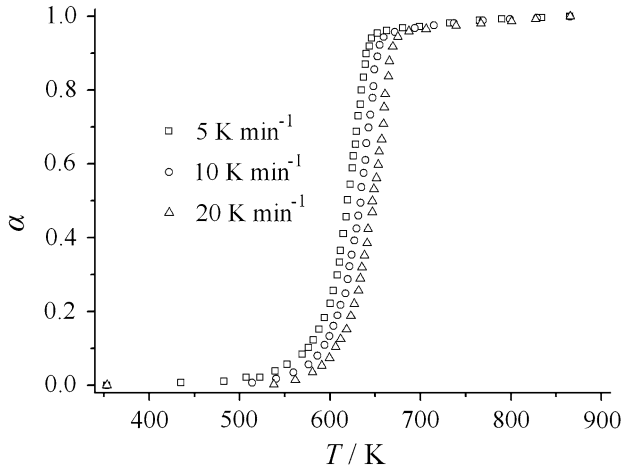

Fig. 1 Conversion of wheat straw pyrolysis as a function of temperature

Model-free isoconversional kinetics

For nonisothermal conditions when the temperature is raised at a constant heating rate, the reaction rate of thermally stimulated solid-state reactions can be generally described by Pilling and Seakins [14]:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha) \tag{2}$$

where T is the absolute temperature, β is the heating rate, A is the frequency factor, E is the activation energy, R is the universal gas constant, and $f(\alpha)$ is the differential conversion function which describes the dependence of the reaction rate on the extent of conversion.

The integration of Eq. 2, after rearranging, yields

$$g(\alpha) = \frac{A}{\beta} \int_0^T e^{-E/RT} dT = \frac{AE}{\beta R} \int_x^\infty u^{-2} e^{-u} du = \frac{AE}{\beta R} p(x) \tag{3}$$

where $g(\alpha) = \int_0^\alpha f(\alpha)^{-1} d\alpha$ is the integral form of the conversion function and $x = E/RT$.

The $p(x)$ function which is usually termed as the temperature integral has no exact analytical solution, and therefore, Eq. 3 cannot be expressed in a closed form. It can be solved by using either approximations or numerical integration [15]. The isoconversional integral methods differ according to the approximation used to calculate the $p(x)$ function [16].

The isoconversional method independently developed by Flynn and Wall [17] and Ozawa [18] uses the Doyle approximation [19]:

$$p(x) = 0.0048 e^{-1.0516x} \tag{4}$$

From Eqs. 3 and 4, it follows

$$\ln(\beta) = \ln\left(\frac{AE}{Rg(\alpha)}\right) - 5.331 - 1.0516 \frac{E}{RT} \tag{5}$$

Based on the above equation, the equation of the Flynn–Wall–Ozawa isoconversional method for evaluating the activation energy is given as

$$\ln(\beta_i) = \ln\left(\frac{A_\alpha E_\alpha}{Rg(\alpha)}\right) - 5.331 - 1.0516 \frac{E_\alpha}{RT_{\alpha,i}} \tag{6}$$

where subscripts i and α designate a given value of heating rate and the extent of conversion, respectively. Equation 6 is practically linear with respect to $T_{\alpha,i}^{-1}$ and thus allows E_α to be found from the slope of the plot of $\ln(\beta_i)$ versus $T_{\alpha,i}^{-1}$.

Coat and Redfern [20] suggested the following approximation for the $p(x)$ function:

$$p(x) = x^{-2} e^{-x} (1 - 2/x) \tag{7}$$

Generally, the part of $(1 - 2/x)$ of the approximation (7) is neglected, and an oversimplified approximation (8)

$$p(x) = x^{-2}e^{-x} \tag{8}$$

is actually used [21].

Submitting Eq. 8 into Eq. 3 and taking the logarithm, we have that

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \ln\left(\frac{A_\alpha R}{E_\alpha g(\alpha)}\right) - \frac{E_\alpha}{RT_{\alpha,i}} \tag{9}$$

The left-hand side of Eq. 8 is linear with respect to the inverse temperature, $T_{\alpha,i}^{-1}$. This enables the activation energy to be evaluated via the slope of a straight line $Y = a + bX$, where Y is $\ln(\beta_i/T_{\alpha,i}^2)$, $X = T_{\alpha,i}^{-1}$, and $b = -E_\alpha/R$. The above isoconversional method was proposed by Vyazovkin and Sbirrazzuoli, which is named here the Vyazovkin–Sbirrazzuoli isoconversional method [22].

Due to the development of computing technologies and software products, there is no special limitation to the use of numerical iterative methods in the determination of the activation energy [23–25]. Here we give an iterative isoconversional method.

The $p(x)$ function can be expressed by the following formula

$$p(x) = \int_x^\infty u^{-2}e^{-u}\mathrm{d}u = x^2e^x h(x) \tag{10}$$

where

$$h(x) = x^{-2}e^{-x}\int_x^\infty u^{-2}e^{-u}\mathrm{d}u \tag{11}$$

The $h(x)$ function has no exact analytical solution, and can be expressed as '$x + x^2e^x$ExpIntegralEi[$-x$]' in the Mathematica software developed by Wolforam Research, Inc. ExpIntegralEi[x] stands for the exponential integral function which can be numerically integrated.

From Eqs. 3, 10 and 11, it follows

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2 h(E_\alpha/RT_{\alpha,i})}\right) = \ln\left(\frac{A_\alpha R}{E_\alpha g(\alpha)}\right) - \frac{E_\alpha}{RT_{\alpha,i}} \tag{12}$$

According to the above expression, the iterative procedure for the estimation of the activation energy is as follows:

Step 1. Supposing $h(E_\alpha/RT_{\alpha,i}) = 1$ to estimate the initial value of the activation energy, $E_\alpha^{(0)}$ according to the slope of the plot of $\ln(\beta_i/T_{\alpha,i}^2)$ versus $T_{\alpha,i}^{-1}$.
Step 2. Using $E_\alpha^{(0)}$ to calculate $h(E_\alpha/RT_{\alpha,i})$, from the slope of the plot of $\ln[\beta_i/T_{\alpha,i}^2/h(E_\alpha/RT_{\alpha,i})]$ versus $T_{\alpha,i}^{-1}$ calculating a new value of the activation energy $E_\alpha^{(1)}$.
Step 3. Replacing $E_\alpha^{(0)}$ with $E_\alpha^{(1)}$, repeating step 2, until $|E_\alpha^{(0)} - E_\alpha^{(1)}| < \varepsilon$, where ε is a defined small quantity such as 0.001 kJ mol^{-1}.

Results and discussion

To apply the isoconversional methods, one has to determine the values of T_α. These values have been evaluated from the experimental data via a nonlinear interpolation. In this study, the MATLAB software has been used to perform the interpolation procedure. Detailed information about the implementation of the nonlinear interpolation by means of the MATLAB software can be found in the literature [26]. The α versus T_α data for the pyrolysis of wheat straw at different heating rates are listed in Table 1.

The plots of $\ln(\beta_i)$ versus 1.0516×10^3 $(RT_{\alpha,i})^{-1}$ corresponding to several conversion degrees of the pyrolysis process are shown in Fig. 2. As it can be obtained that there is linearity for all cases so the activation energy may be calculated from the corresponding slope by means of the Flynn–Wall–Ozawa isoconversional method. The determination coefficients corresponding to linear fittings in Fig. 2 together with the resultant activation energy values are listed in Table 2. As it can be seen that the determination coefficients are higher than 0.99141 for all cases.

Figure 3 shows the plots of $\ln(\beta_i/T_{\alpha,i}^2)$ versus 10^3 $(RT_{\alpha,i})^{-1}$ corresponding to several conversion degrees of the pyrolysis process. By virtue of the Vyazovkin–Sbirrazzuoli isoconversional method, straight lines with the slopes $-E_\alpha$ are obtained. The determination coefficients corresponding to linear fittings in Fig. 3 together with the resultant activation energy values are shown in Table 3. From the results included in Table 2, the determination coefficients are higher than 0.99022 for all cases.

Table 1 The α versus T_α data for the pyrolysis of wheat straw at different heating rates

α	T_α/K		
	5 K min^{-1}	10 K min^{-1}	20 K min^{-1}
0.15	588.091	602.074	617.921
0.2	597.069	609.495	624.399
0.25	603.218	617.182	630.839
0.3	608.370	620.075	634.000
0.35	611.026	623.428	637.898
0.4	614.070	627.614	641.322
0.45	617.935	630.920	644.962
0.5	619.261	633.920	646.610
0.55	623.010	635.478	650.266
0.6	625.236	638.756	653.302
0.65	628.065	640.213	655.500
0.7	629.849	642.717	658.626
0.75	633.049	645.719	659.770
0.8	634.851	647.830	661.460
0.85	638.066	649.051	664.899

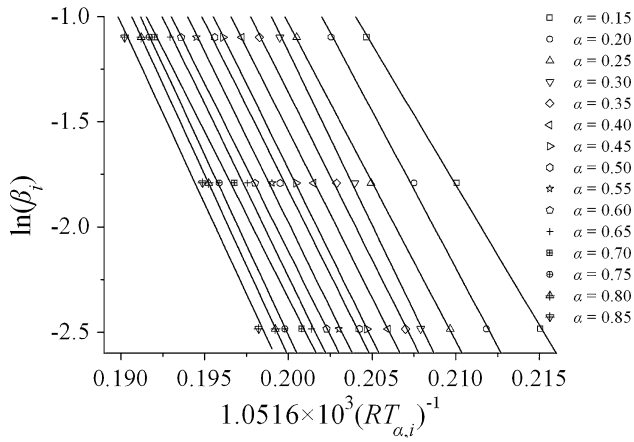

Fig. 2 The dependence of $\ln(\beta_i)$ versus $1.0516 \times 10^3 (RT_{\alpha,i})^{-1}$ at the different values of α (*solid lines* are linear fitting corresponding to different α)

Table 2 The determination coefficients (R^2) corresponding to linear fittings in Fig. 2 together with the resultant activation values (E_α)

α	E_α/kJ mol^{-1}	R^2
0.15	133.463 ± 2.915	0.99952
0.2	149.282 ± 5.898	0.99844
0.25	150.953 ± 2.917	0.99963
0.3	164.706 ± 6.281	0.99855
0.35	158.822 ± 5.093	0.99897
0.4	158.381 ± 1.429	0.99992
0.45	161.612 ± 1.656	0.99990
0.5	160.010 ± 8.630	0.99710
0.55	162.693 ± 5.993	0.99864
0.6	159.512 ± 1.342	0.99993
0.65	164.002 ± 8.831	0.99711
0.7	157.638 ± 7.604	0.99768
0.75	171.270 ± 3.070	0.99968
0.8	172.978 ± 0.392	0.99999
0.85	171.810 ± 15.994	0.99141

As indicated in Fig. 4, the values of E_α calculated by the three isoconversional methods mentioned in "Model-free isoconversional kinetics" section presented a great accordance although the Flynn–Wall–Ozawa method gave slightly higher values than the iterative method and the Vyazovkin–Sbirrazzuoli method gave slightly lower values than the iterative method. The small differences among the activation energy values determined by means of three isoconversional methods are due to the fact that the different approximations are used to calculate the temperature integral in these methods.

As results from Fig. 4, the activation energy for the pyrolysis of wheat straw is about 130–175 kJ mol^{-1} ($\alpha = 0.15$–0.85). According to this E_α dependence, it can be concluded that the pyrolysis of wheat straw follows

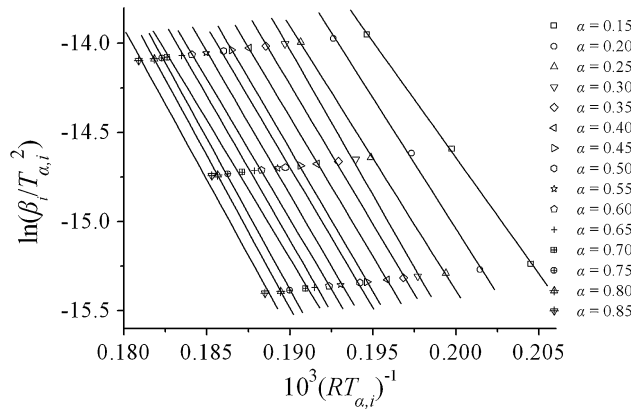

Fig. 3 The dependence of $\ln(\beta_i/T^2_{\alpha,i})$ versus 10^3 $(RT_{\alpha,i})^{-1}$ at the different values of α (*solid lines* are linear fitting corresponding to different α)

Table 3 The determination coefficients (R^2) corresponding to linear fittings in Fig. 3 together with the resultant activation values (E_α)

α	E_α/kJ mol^{-1}	R^2
0.15	130.325 ± 3.136	0.99942
0.20	146.830 ± 6.268	0.99818
0.25	148.486 ± 3.002	0.99959
0.30	162.875 ± 6.666	0.99833
0.35	156.634 ± 5.420	0.99880
0.40	156.119 ± 1.437	0.99992
0.45	159.454 ± 1.806	0.99987
0.50	157.748 ± 9.011	0.99675
0.55	160.502 ± 6.367	0.99843
0.60	157.115 ± 1.479	0.99991
0.65	161.792 ± 9.352	0.99667
0.70	155.059 ± 8.064	0.99730
0.75	169.361 ± 3.292	0.99962
0.80	171.129 ± 0.476	0.99999
0.85	169.839 ± 16.882	0.99022

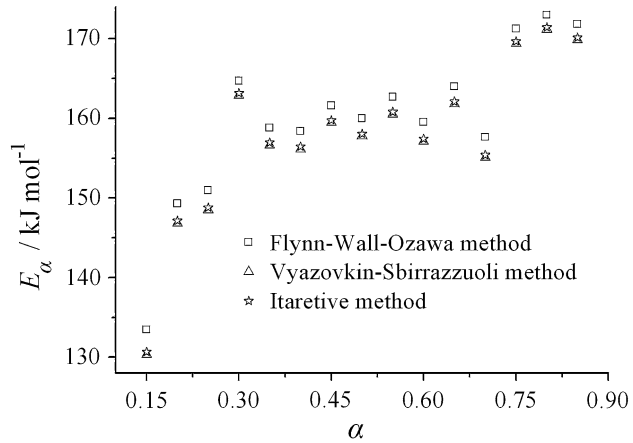

Fig. 4 The activation energy values as a function of the extent of conversion obtained by different isoconversional methods

Table 4 Isoconversional kinetic predictions: time to reach the α at T_0 under isothermal conditions

α	t_α/min				
	$T_0 = 550$ K	$T_0 = 575$ K	$T_0 = 600$ K	$T_0 = 625$ K	$T_0 = 650$ K
0.15	25.422	7.340	2.350	0.824	0.313
0.2	45.498	11.232	3.115	0.958	0.322
0.25	68.895	16.741	4.577	1.388	0.461
0.3	104.093	22.064	5.322	1.439	0.480
0.35	110.189	24.781	6.311	1.793	0.561
0.4	135.148	30.542	7.813	2.229	0.700
0.45	171.961	37.650	9.355	2.599	0.797
0.5	192.756	42.891	10.817	3.046	0.945
0.55	222.396	48.208	11.870	3.269	0.994
0.6	241.767	54.117	13.723	3.884	1.211
0.65	291.856	62.492	15.214	4.147	1.249
0.7	378.758	63.624	16.424	4.725	1.496
0.75	470.911	93.837	21.389	5.488	1.563
0.8	551.455	108.056	24.254	6.135	1.725
0.85	566.989	112.465	25.528	6.524	1.852

multi-step kinetics expressed by different apparent activation energies.

The dependence of E_α on α is enough to predict the isothermal kinetics from nonisothermal data, as in Eq. 13 [27–29].

$$t_\alpha = \frac{\int_0^{T_\alpha} e^{-E_\alpha/RT}\mathrm{d}T}{\beta e^{-E_\alpha/RT_0}} \tag{13}$$

where t_α is the time to reach the extent of conversion α at a given temperature, T_0, under isothermal conditions.

Solving Eq. 13 for different conversion degrees, the pyrolysis process of wheat straw at some temperatures has been predicted. The results obtained are shown in Table 4.

Conclusions

The dependence of E_α on α has been determined from the isoconversional kinetic analysis of nonisothermal thermogravimetric data of the pyrolysis of wheat straw. An iterative integral isoconversional method was presented and used for the kinetic analysis of wheat straw pyrolysis. The Flynn–Wall–Ozawa and Vyazovkin–Sbirrazzuoli methods were also used for the determination of the dependence of E_α on α. The results have shown that the differences among the activation energy values obtained by means of the three isoconversional methods are very small, which indicated the validity of the iterative integral isoconversional method. The effective activation energy corresponding the pyrolysis of wheat straw is 130–175 kJ mol^{-1} ($\alpha = 0.15$–0.85). Using the dependence of E_α on α, the isothermal pyrolysis process has been predicted.

Acknowledgements Financial support was obtained from National Natural Science Foundation of China (Project No. 50806048) and National Undergraduate Innovative Test Program in Shanghai Jiao Tong University (Project No. 081024807). The authors are grateful to the anonymous referees who provided valuable comments and suggestions to improve the article.

References

1. Lanzetta M, Di Blasi C. Pyrolysis kinetics of wheat and corn straw. J Anal Appl Pyrol. 1998;44:181–92.
2. A. Balestrino, F. Bassini, P. Pelacchi. On the control of a pyrolysis process. In: 2007 international conference on clean electrical power, 21–23 May 2007. p. 409–14. doi: 10.1109/ICCEP.2007.384246.
3. Henrich E, DInjus E, Rumpel S, Stahl R. A two-stage pyrolysis/gasification process for herbaceous waste biomass from agriculture, 1–15. In: Bridgewater AV, editor. Progress in thermochemical biomass conversion. Oxford, UK: Blackwell; 2001.
4. Moltó J, Font R, Conesa JA, Martín-Gullón I. Thermogravimetric analysis during the decomposition of cotton fabrics in an inert, air environment. J Anal Appl Pyrol. 2006;76:124–31.
5. Conesa JA, Caballero JA, Marcilla A, Font R. Analysis of different kinetic models in the dynamic pyrolysis of cellulose. Thermochim Acta. 1995;254:175–92.
6. Vyazovkin S, Wight CA. Kinetics in solids. Annu Rev Phys Chem. 1997;48:125–49.
7. Khawam A, Flanagan DR. Complementary use of model-free and modelistic methods in the analysis of solid-state kinetics. J Phys Chem B. 2005;109:10073–80.
8. Vyazovkin S, Wight CA. Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data. Thermochim Acta. 1999;340341:53–68.
9. Zhou D, Grant DJW. Model dependence of the activation energy derived from nonisothermal kinetic data. J Phys Chem A. 2004;108:4239–46.
10. Chen H, Liu N, Fan W. A new method to explain the model dependence of apparent activation energy derived from a single

nonisothermal dynamic curve. Polym Degrad Stab. 2006;91:1726–30.
11. Šimon P. Isoconversional methods: fundamentals, meaning and application. J Therm Anal Cal. 2004;76:123–32.
12. Vyazovkin S, Sbirrazzuoli N. Isoconversional method to explore the mechanism and kinetics of multi-step epoxy cures. Macromol Rapid Commun. 1999;20:387–9.
13. Guigo N, Mija A, Vincent L, Sbirrazzuoli N. Chemorheological analysis and model-free kinetics of acid catalysed furfuryl alcohol polymerization. Phys Chem Chem Phys. 2007;9:5359–66.
14. Pilling MJ, Seakins PW. Reaction kinetics. Oxford, UK, New York: Oxford University Press; 1995.
15. Vyazovkin S, Sbirrazzuoli N. Isoconversional kinetic analysis of thermally stimulated processes in polymers. Macromol Rapid Commun. 2006;27:1515–32.
16. Budrugeac P, Homentcovschi D, Segal E. Critical analysis of the isoconversional methods for evaluating the activation energy. Theoretical background. J Therm Anal Cal. 2001;63:457–63.
17. Flynn JH, Wall LA. A general treatment of the thermogravimetry of polymers. J Res Nat Bur Standard. 1966;70A:487–523.
18. Ozawa T. A new method of analyzing thermogravimetric data. Bull Chem Soc Jpn. 1965;38:1881–6.
19. Doyle CD. Estimating isothermal life from thermogravimetric. J Appl Polym Sci. 1962;6:639–42.
20. Coat AW, Redfern JP. Kinetic parameters from thermogravimetric data. Nature (London). 1964;201:68–9.
21. Vyazovkin S, Dollimore D. Linear and nonlinear procedures in isoconversional computations of the activation energy of nonisothermal reactions in solids. J Chem Inf Comput Sci. 1996;36:42–5.
22. Vyazovkin S, Sbirrazzuoli N. Confidence intervals for the activation energy estimated by few experiments. Anal Chim Acta. 1997;355:175–780.
23. Órfão JJM. Review and evaluation of the approximations to the temperature integral. AIChE J. 2007;53:2905–15.
24. Gao Z, Nakada M, Amasaki I. A consideration of errors and accuracy in the isoconversional methods. Thermochim Acta. 2001;369:137–42.
25. Gao Z, Wang H, Nakada M. Iterative method to improve calculation of the pre-exponential factor for dynamic thermogravimetric analysis measurements. Polymer. 2006;47:1590–6.
26. Kiusalaas J. Numerical methods in engineering with MATLAB. Cambridge, New York: Cambridge University Press; 2005.
27. Vyazovkin S. A unified approach to kinetic processing of nonisothermal data. Int J Chem Kinetics. 1996;28:95–101.
28. Vyazovkin S. Model-free kinetics: staying free of multiplying entities without necessity. J Therm Anal Cal. 2006;1:45–51.
29. Vyazovkin S. Mechanism and kinetics of epoxy-amine cure studied by differential scanning calorimetry. Macromolecules. 1996;29:1867–73.