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ARTICLE *in* JOURNAL- ENERGY INSTITUTE · AUGUST 2014

Impact Factor: 0.62 · DOI: 10.1016/j.joei.2014.03.019

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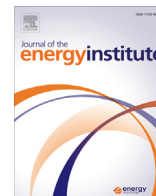


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Isothermal kinetic predictions from nonisothermal data by using the iterative linear integral isoconversional method



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ARTICLE INFO

Article history:

Received 15 January 2013

Accepted 29 July 2013

Available online 29 March 2014

Keywords:

Isoconversional method

Nonisothermal kinetics

Solid-state reactions

Isothermal prediction

ABSTRACT

A key issue in kinetic analysis is the prediction of the evolution of a thermally stimulated solid-state reaction for a given isothermal temperature from nonisothermal kinetic parameters. However, the conventional methods neglect the dependence of the activation energy on the conversion degree during the isothermal process; therefore, they may lead to some important errors in the isothermal kinetic predictions when the kinetic parameters vary significantly with the conversion degree. A new method for the determination of the isothermal conversion-time data from the nonisothermal kinetic parameters determined by the iterative linear integral isoconversional method has been developed. Two theoretically simulated data sets have been analyzed. And the analysis results have shown that the new method can give accurate isothermal kinetic predictions.

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1. Introduction

The thermal decomposition of solid fuels (i.e. coal, oil shale, and biomass) belongs to thermally stimulated solid-state reactions. It is important to study the kinetic analysis of those reactions for the development of energy usage of solid fuels. Some kinetic computations can be used to make predictions of the solid-state reaction, which are widely used to evaluate the kinetic behavior of materials beyond the temperature regions of experimental measurements [1]. One of the most commonly used predictions is called “isothermal kinetic predictions” which means that the nonisothermal kinetic parameters can be used to predict the variation of the conversion degree versus time for a given temperature [2].

Isothermal kinetic predictions can be made directly from the E_α and $[A_\alpha f(\alpha)]$ (E_α is the activation energy E at the conversion degree α , A_α is the frequency factor A at the conversion degree α , $f(\alpha)$ is the differential form of reaction model) values determined by means of the Friedman differential isoconversional method [3]. However, the Friedman differential isoconversional method is numerically unstable and noise sensitive, especially when the reaction rate is estimated by numerical differentiate of experimental data [4]. Vyazovkin [5] proposed a method for isothermal kinetic predictions based on the E_α dependence obtained from the integral isoconversional methods. However, in the derivation process of the Vyazovkin method, the dependence of the activation energy on the conversion degree during the isothermal process is neglected.

The aim of this work is to investigate a new method for isothermal kinetic predictions from the nonisothermal kinetic parameters obtained by the iterative linear integral isoconversional method. Before proceeding to the development of such a method, it is necessary to introduce the conventional methods for isothermal kinetic predictions.

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2. Conventional methods

The overall rate of a thermally induced reaction in solids is commonly described by the following equation: [6]

$$\frac{d\alpha}{dt} = Ae^{-E/RT}f(\alpha) \quad (1)$$

where α is the conversion degree, t is the time, $d\alpha/dt$ is the reaction rate, A is the frequency factor, E is the activation energy, R is the gas constant, T is the temperature, and $f(\alpha)$ is the differential form of the reaction model (the commonly used reaction models can be found in the literature [7]).

Under isothermal conditions, Equation (1) becomes:

$$dt = \frac{1}{Ae^{-E/RT_{iso}}} \frac{d\alpha}{f(\alpha)} \quad (2)$$

where T_{iso} is the isothermal temperature.

The integration of Equation (2) leads to

$$t_\alpha = \int_0^{t_\alpha} dt = \frac{1}{Ae^{-E_\alpha/RT_{iso}}} \int_0^\alpha \frac{d\alpha}{f(\alpha)} \quad (3)$$

After rearranging, the above equation becomes

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = t_\alpha Ae^{-E_\alpha/RT_{iso}} \quad (4)$$

If the reaction is studied under nonisothermal conditions at a linear heating rate, Equation (1) becomes:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha) \quad (5)$$

where β is the heating rate.

The integration of Equation (4), after rearranging, leads to

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T_\alpha} e^{-E_\alpha/RT} dT \quad (6)$$

where T_α is the temperature corresponding to the conversion degree α at the heating rate β .

Equations (4) and (6) hold true on the assumption that the kinetic parameters remain the same when changing temperature.

$$t_\alpha = \frac{1}{\beta e^{-E_\alpha/RT_{iso}}} \int_0^{T_\alpha} e^{-E_\alpha/RT} dT \quad (7)$$

The OFW and KAS methods, the most popular linear integral isoconversional methods, are based on Equation (6) [8]. The OFW method uses the Doyle approximation for the temperature integral, and the KAS method uses the Coats-Redfern approximation [9]. Therefore, the isothermal kinetic predictions appropriate for the kinetic parameters obtained from the OFW and KAS methods are

$$t_\alpha = \frac{E_\alpha}{R\beta} e^{E_\alpha/RT_{iso}-1.0518E_\alpha/RT_\alpha-5.3305} \quad (\text{for kinetics from the OFW method}) \quad (8)$$

$$t_\alpha = \frac{RT_\alpha^2 e^{E_\alpha/RT_{iso}-E_\alpha/RT_\alpha}}{\beta E_\alpha} \quad (\text{for kinetics from the KAS method}) \quad (9)$$

The integration assuming a constant value of E_α in Equation (7) smoothes the dependence of E_α on α [10]. To solve this problem, Vyazovkin proposed an advanced nonlinear isoconversional method, which is based on the integration over low ranges of variables [11], and modified the equation of the corresponding isothermal kinetic predictions [12].

$$t_\alpha = \frac{1}{\beta e^{-E_\alpha/RT_{iso}}} \sum_0^\alpha \int_{T_{\alpha-\Delta\alpha}}^{T_\alpha} e^{-E_\alpha/RT} dT \quad (10)$$

(for kinetics from the Vyazovkin advanced method)

The above methods for isothermal kinetic predictions neglect the variation of the activation energy with the conversion degree during the isothermal process [13], so the use of the above methods may give rise to some errors in the isothermal kinetic predictions for the complex varying activation energy processes.

3. Theoretical part

The iterative linear integral isoconversional method [14] is based on the following equation

$$\ln \left\{ \frac{\beta_i}{T_{\alpha,i}^2 \left[h(x_{\alpha,i}) - \frac{x_{\alpha,i}^2 e^{x_{\alpha,i}}}{x_{\alpha-\Delta\alpha,i}^2 e^{x_{\alpha-\Delta\alpha,i}}} h(x_{\alpha-\Delta\alpha,i}) \right]} \right\} = \ln \left[\frac{R}{E_\alpha \int_{\alpha-\Delta\alpha}^{\alpha} \frac{d\alpha}{A_\alpha f(\alpha)}} \right] - \frac{E_\alpha}{RT_{\alpha,i}} \quad (11)$$

which is obtained from Equation (5). In the above equation, the subscript i denotes the ordinal number of a nonisothermal experiment conducted at the heating rate β_i , $x_{\alpha,i} = E_\alpha/RT_{\alpha,i}$, $x_{\alpha-\Delta\alpha,i} = E_\alpha/RT_{\alpha-\Delta\alpha,i}$, $h(x) = x^2 e^x \int_x^\infty x^{-2} e^{-x} dx$. If we assume the isoconversional assumption that the reaction model remains unchanged, from the slope, S_α , and the intercept, I_α , of the linear relationship (11), we obtain

$$S_\alpha = -\frac{E_\alpha}{R} \quad (12)$$

$$I_\alpha = \ln \left[\frac{R}{E_\alpha \int_{\alpha-\Delta\alpha}^{\alpha} \frac{d\alpha}{A_\alpha f(\alpha)}} \right] \quad (13)$$

Equations (12) and (13) allow ones to arrive at the following two equations:

$$E_\alpha = -RS_\alpha \quad (14)$$

$$\int_{\alpha-\Delta\alpha}^{\alpha} \frac{d\alpha}{A_\alpha f(\alpha)} = -S_\alpha^{-1} e^{-I_\alpha} \quad (15)$$

From Equation (2), we can obtain

$$\int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} dt = \int_{\alpha-\Delta\alpha}^{\alpha} \frac{d\alpha}{[A_\alpha f(\alpha)] e^{-E(\alpha)/RT_{iso}}} \approx \frac{\int_{\alpha-\Delta\alpha}^{\alpha} \frac{d\alpha}{A_\alpha f(\alpha)}}{e^{-E_\alpha/RT_{iso}}} \quad (16)$$

Equation (16) allows ones to arrive at Equation (17)

$$t_\alpha - t_{\alpha-\Delta\alpha} = \frac{\int_{\alpha-\Delta\alpha}^{\alpha} \frac{d\alpha}{\{A(\alpha) \cdot f(\alpha)\}}}{e^{-E_\alpha/RT_{iso}}} \quad (17)$$

From Equation (17), we can obtain

$$t_\alpha = \sum_0^{\alpha} \frac{\int_{\alpha-\Delta\alpha}^{\alpha} \frac{d\alpha}{\{A(\alpha) \cdot f(\alpha)\}}}{e^{-E_\alpha/RT_{iso}}} \quad (18)$$

(for kinetics from the iterative linear integral isoconversional method)

In the above equation, E_α and $\int_{\alpha-\Delta\alpha}^{\alpha} d\alpha/A_\alpha f(\alpha)$ can be calculated from Equations (14) and (15). Then, based on Equation (18), the isothermal predicted conversion-time ($\alpha-t_\alpha$) data can be obtained. From the above analysis, variation of the activation energy with the conversion degree during the isothermal process is taken into account.

4. Applications

4.1. A single step reaction with constant activation energy

To check the accuracy of the newly proposed method, we have applied them to two different data sets: a theoretically simulated data set from a single-step reaction with a constant activation energy, and a theoretically simulated data set from a complex reaction with a real dependence of the activation energy on the conversion degree.

The nonisothermal simulated data have been analyzed. The kinetic parameters for the simulated process are $f(\alpha) = 4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$, $E = 180 \text{ kJ mol}^{-1}$, and $A = 1.6 \times 10^{14} \text{ s}^{-1}$. The T_α values for a set of the α values of 0.005–0.99 (step 0.005) required for isoconversional method are calculated through numerical integration of the nonisothermal kinetic rate equation, using the classical fourth-order Runge–Kutta method.

Fig. 1(a) shows that the isothermal predicted conversion – time ($\alpha-t_\alpha$) data with various methods and comparison with the isothermally simulated data. Fig. 1(b) shows the corresponding relative error of $t_\alpha - \alpha$. According to the results included in Fig. 1, the $\alpha-t_\alpha$ data using various methods has been predicted with acceptable accuracy. Furthermore, it can be seen a better agreement between the simulated isothermal data and the $\alpha-t_\alpha$ data predicted with the Vyazovkin advanced method and the iterative linear integral isoconversional method which is due to the approximations used for the temperature integral in the OFW and KAS methods.

4.2. Numerical data: a complex reaction with the dependence of the kinetic parameters on the conversion degree

We consider the following complex reaction with a variation of the kinetic parameters with the conversion degree: $f(\alpha) = 1 - \alpha$; $E_\alpha = 250 + 56 \ln(1 - \alpha)$; $\ln A_\alpha = 0.2E_\alpha - 5$ (where E_α is expressed in kJ mol^{-1} , A_α is expressed in min^{-1}), which was also analyzed by the literature [15]. The above complex reaction is based on the assumptions suggested by Budrugeac and Segal [16].

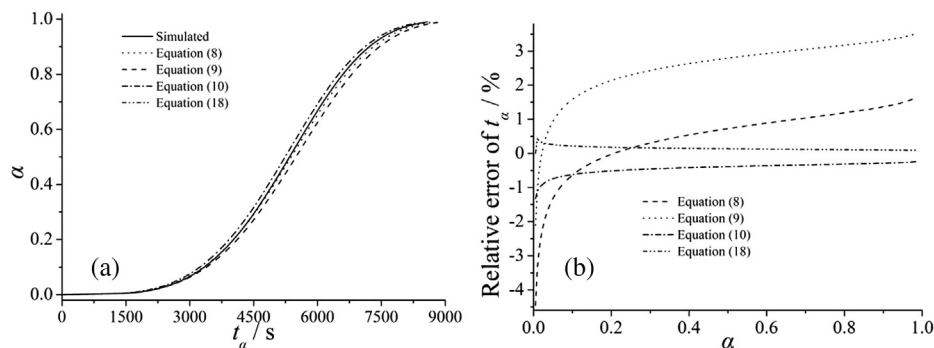


Fig. 1. Isothermal kinetic predictions with various methods and comparison with the isothermally simulated curve for a KJMA reaction ($f(\alpha) = 4(1 - \alpha)[-\ln(1 - \alpha)]^{3/4}$, Parameters: $E = 180 \text{ kJ mol}^{-1}$, $A = 1.6 \times 10^{14} \text{ s}^{-1}$) and constant temperature (523.15 K) (a) $\alpha - t_\alpha$ data; (b) relative error of $t_\alpha - \alpha$ data.

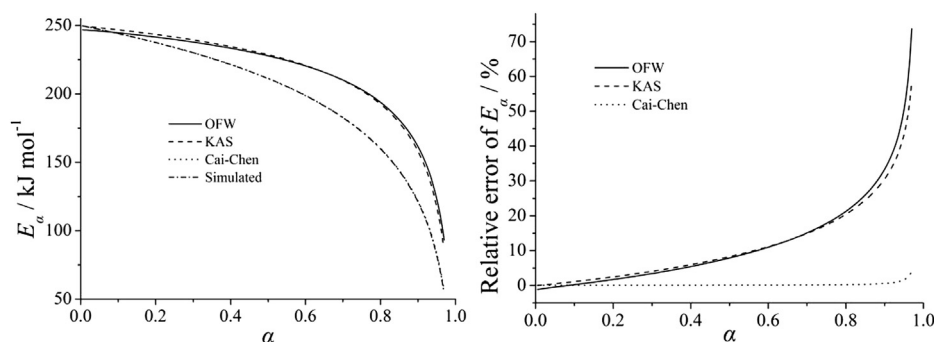


Fig. 2. Dependence of the effect activation energy on the conversion degree determined by various isoconversional methods for the theoretically simulated complex reaction [$f(\alpha) = 1 - \alpha$, $E_\alpha = 250 + 56 \ln(1 - \alpha)$, $\ln A_\alpha = 0.2E_\alpha - 5$ (E_α is in kJ mol^{-1} , A_α is in min^{-1})].

Fig. 2 shows the E_α - α curves obtained from various methods. The E_α values obtained from the iterative linear integral isoconversional method are in excellent agreement with those expected from $E_\alpha = 250 + 56 \ln(1 - \alpha)$. The relative errors of E_α obtained from the OFW and KAS methods are significant and largely increase as far as the conversion degree increases. This phenomenon is due to the fact that the OFW and KAS methods were originally derived by assuming that the activation energy remains constant all over the reaction. The iterative linear integral isoconversional method performs integration over small temperature segments that eliminates a system error produced by the OFW and KAS methods when the activation energy varies significantly with the conversion degree.

Fig. 3(a) shows the isothermal predicted conversion - time ($\alpha - t_\alpha$) data with various methods and comparison with the isothermally simulated data. Fig. 3(b) shows the corresponding relative error of $t_\alpha - \alpha$. From Fig. 3, it can be observed that there are great discrepancies between the simulated $\alpha - t_\alpha$ data and the predicted $\alpha - t_\alpha$ data obtained from the OFW, KAS and Vyazovkin advanced methods. The agreement between the simulated $\alpha - t_\alpha$ data and the calculated data obtained from the iterative linear integral isoconversional method is satisfactory. There are three causes that lead to important errors in the isothermal kinetic prediction with the OFW and KAS methods for complex reactions with varying kinetic parameters. These are: (1) the OFW and KAS methods use the approximations for the temperature integral, (2) the OFW and KAS methods were originally derived for processes with constant kinetic parameters, and (3) the dependence of E_α on α during the isothermal process is neglected. The Vyazovkin advanced method can't give accurate isothermal kinetic prediction is due to the third cause.

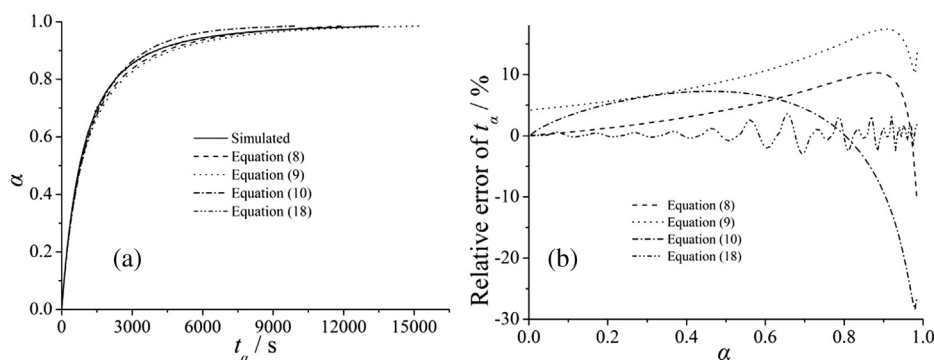


Fig. 3. Isothermal kinetic predictions with various methods and comparison with the isothermally simulated curve for a complex reaction [$f(\alpha) = 1 - \alpha$, $E_\alpha = 250 + 56 \ln(1 - \alpha)$, $\ln A_\alpha = 0.2E_\alpha - 5$ (E_α is in kJ mol^{-1} , A_α is in min^{-1})] and constant temperature (630 K) (a) $\alpha - t_\alpha$ data; (b) relative error of $t_\alpha - \alpha$ data.

5. Conclusions

- The conventional methods for isothermal kinetic predictions neglect the dependence of the activation energy on the conversion degree. Therefore, for complex reactions with varying kinetic parameters, the conventional methods may give rise to some important errors in the isothermal kinetic predictions.
- A new method for isothermal kinetic predictions from the nonisothermal kinetic parameters determined by the iterative linear integral isoconversional method has been developed.
- Two theoretically simulated data sets have been analyzed. The results have shown that the newly developed method can give more accurate predictions than the conventional methods.

Acknowledgments

The authors would like to acknowledge financial support from State Key Laboratory of Heavy Oil Processing, China University of Petroleum (Grant number: 2012-1-02), and School of Agriculture and Biology, Shanghai Jiao Tong University (Grant number: NRC201101).

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