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

Junmeng Cai [a,b,*], Yong Chen [c], Rongrong Liu [d]

[a] School of Agriculture and Biology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China
[b] State Key Laboratory of Heavy Oil Processing, China University of Petroleum, 18 Fuxue Road, Beijing 102249, People's Republic of China
[c] School of Mechanical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China
[d] School of Biomedical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China

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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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* Corresponding author. School of Agriculture and Biology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China. Tel.: +86 21 34206624; fax: +86 21 34205744.
E-mail address: jmcai@sjtu.edu.cn (J. Cai).

2. Conventional methods

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

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

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:

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

where T_{iso} is the isothermal temperature.

The integration of Equation (2) leads to

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

After rearranging, the above equation becomes

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

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

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

where β is the heating rate.

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

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

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.

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

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

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

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

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].

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

(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