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Kinetic Analysis of Wheat Straw Oxidative Pyrolysis Using Thermogravimetric Analysis: Statistical Description and Isoconversional Kinetic Analysis

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The oxidative pyrolysis kinetics of wheat straw was studied by thermogravimetric analysis (TGA) under oxygen dynamic atmosphere. Nonisothermal TGA data at three heating rates of 5, 10, and 20 K min^{-1} were analyzed. The kinetic conversion data calculated from the TGA data were fitted by the Weibull and logistic mixture models, and the corresponding statistical analyses were performed. The statistical results showed that the Weibull mixture model fitted the experimental data better than the logistic mixture model and can accurately reproduce the kinetic conversion data. Making use of the data predicted by the Weibull mixture model, some data required in the isoconversional kinetic analysis, such as α vs T_α, can be easily obtained. An iterative linear integral isoconversional method was developed and applied to evaluate the activation energy of the oxidative pyrolysis process of wheat straw. The Vyazovkin−Dollimore nonlinear integral isoconversional method was also used to calculate the activation energy. The results have shown that two isoconversional methods are equivalent for the estimation of the activation energy and the obtained activation energy is significantly dependent upon conversion for the oxidative pyrolysis process of wheat straw.

1. Introduction

As the biggest agricultural country in the world, China has an abundant crop straw resource. The annual production of crop straw in China totals about 700 million tons, and the quantity of wheat straw annually generated is about 90 million tons.[1] Thermochemical conversion of crop straw for the production of fuel or heat is one of the most promising non-nuclear forms of future energy. The study of the oxidative pyrolysis kinetics of crop straw is fundamental to optimize its combustion process.[2] Therefore, knowledge of the kinetic parameters, in particular the activation energy of the process, must be known.

The kinetic analysis of the pyrolysis of wheat straw in an inert or oxidizing atmosphere using thermogravimetric analysis (TGA) was investigated in some published papers,[3−6] where the model-fitting methods were used for the determination of the kinetic parameters. The model-fitting methods bring to the problem that usually quite different reaction models can satisfactorily fit the kinetic data at the cost of drastic variations in the Arrhenius parameters, although they allow to directly determine the kinetic triple (the frequency factor, activation energy, and reaction model function).[7] The ambiguity of the kinetic triple caused by the application of the model-fitting methods can be overcome when using the isoconversional methods. These methods allow the activation energy to be evaluated as a function of conversion without previous assumptions on the reaction model.[8] These isoconversional methods can be divided into integral and differential isoconversional methods. The differential isoconversional methods, such as the Friedman method[9] and the Budrugeac method,[10] require employing instantaneous reaction rate values. It is very sensitive to experimental noise and tends to be numerically unstable, especially when the rate is estimated by numerical differentiation of experimental data.[11] Therefore, the integral isoconversional methods are extensively used for estimating the activation energy. Some conventional integral isoconversional methods, i.e.,theFlynn−Wall−Ozawamethod[12,13]andKissinger−Akahira−Sunose method,[14] lead to important errors in the determination of the activation energy[15] due to the fact that some approximations are used for the estimation of the temperature integral in those conventional methods. The nonlinear integral isoconversional method proposed by Vyazovkin and Dollimore[16] were derived without any assumptions. In this method, some nonlinear procedures must be used. In this study, an iterative linear integral isoconversional method will be presented.

The aim of the present study is to investigate the kinetics of the oxidative pyrolysis of wheat straw. The specific objectives of the present study are:

(a) To conduct thermogravimetric analysis on wheat straw at three heating rates in an oxidizing atmosphere.

(b) To use some statistical models for description of experimentally obtained data.

(c) To develop an iterative linear integral isoconversional method to more accurately determine the activation energy.

(d) To determine the activation energy using isoconversional methods.

2. Experimental Section

The wheat straw sample used in this study was obtained from a north village in China. It was ground to be a size range less than 0.2 mm and placed in a sealed box to avoid contamination

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and then dried in a muffle furnace at a temperature of 378 K for 24 h. Its elemental chemical composition obtained in a C−H−N elemental analyzer was: C, 44.96%; H, 5.69%; N, 44.19%.

TGA provides a convenient means to monitor the kinetics of thermally stimulated solid-state processes by measuring the mass loss as a function of time or temperature.[17] A STA 449C thermogravimetric analyzer from NETZSCH Instruments Incorporated was used for the thermal analyses of the wheat straw sample in oxygen dynamic atmosphere (60 mL min^{-1}) at three heating rates of 5, 10, and 20 K min^{-1}. In all cases, about 5 mg of powder wheat straw sample was thermally treated.

The reaction conversion was calculated from the TGA data based on the following equation

$$\alpha = \frac{m_i - m}{m_i - m_f} \tag{1}$$

where α is the extent of conversion, m_i, m, and m_f refer to the initial, actual, and final mass of the sample.

3. Isoconversional Kinetics

The general equation that describes the kinetics of reactions in solids can be written as follows[18]

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

where t is the time, T the temperature, A (the frequency factor) and E (the activation energy) the Arrhenius parameters, R the universal gas constant, and $f(\alpha)$ the differential conversion function.

For nonisothermal conditions, when the temperature varies with time with a constant heating rate, eq 2 is rewritten by

$$\frac{d\alpha}{dT} = \frac{A}{\beta}e^{-E/RT}f(\alpha) \tag{3}$$

where β is the heating rate.

By separation of variables and integration, we get

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T e^{-E/RT}dT = \frac{A}{\beta}I(E,T) \tag{4}$$

where $g(\alpha)$ is the integral conversion function and $I(E,T)$ the temperature integral, which has no exact analytical solution.[19,20]

Let us introduce a notation

$$x = \frac{E}{RT} \tag{5}$$

With regard to eq 5, eq 4 takes the form of eq 6

$$g(\alpha) = \frac{AR}{\beta E}T^2e^{-E/RT}h(x) \tag{6}$$

where

$$h(x) = x^2e^x\int_x^\infty x^{-2}e^{-x}dx \tag{7}$$

After taking logarithms, eq 6 can be rearranged in the following form

$$\ln\frac{\beta}{T^2h(x)} = \ln\frac{AR}{Eg(\alpha)} - \frac{E}{RT} \tag{8}$$

By use of a general assumption that the conversion function is independent of the heating rate, eq 8 can be written for a given extent of conversion and a set of experiments performed under different heating rates β_i ($i = 1,..., n$) as eq 9

$$\ln\frac{\beta i}{T_{\alpha,i}^2h(x_{\alpha,i})} = \ln\frac{A_\alpha R}{E_\alpha g(\alpha)} - \frac{E_a}{RT_{\alpha,i}} \tag{9}$$

where the subscript α indicates the values related to a given extent of conversion and the subscript i indicates the values related to a given heating rate.

In the Kissinger−Akahira−Sunose integral isoconversional method[14] commonly used in the kinetic analysis of thermally stimulated solid-state reactions, eq 9 is an approximate relation with regarding $h(x_{\alpha,i})$ as unity, although $h(x_{\alpha,i})$ is a function of E_α and $T_{\alpha,i}$. To calculate E_α more accurately, an iterative linear integral isoconversional method was developed in the present paper. In this method, except for the first step, $h(x_{\alpha,i})$ is not approximately regarded as unity and is calculated based on the activation energy value obtained at the previous step. The $h(x)$ function does not have an exact analytical function but can be numerically solved by means of Mathematica. In the syntax of Mathematica, the $h(x)$ function can be expressed as $x + x^2e^x$ExpIntegralEi[$-x$] (where ExpIntegralEi is a special function in Mathematica[21]). The iterative procedure for the estimation of the activation energy is given as follows:

Step 1. Supposing $h(x_{\alpha,i}) = 1$ to estimate the initial value of the activation energy, $E_\alpha^{(0)}$ according to the slope of the plot of $\ln(\beta_i/T_{\alpha,i}^2)$ vs $T_{\alpha,i}^{-1}$.

Step 2. By use of $E_\alpha^{(0)}$ to calculate $h(x_{\alpha,i})$, from the slope of the plot of $\ln[\beta_i/T_{\alpha,i}^2/\, h(x_{\alpha,i})]$ vs $T_{\alpha,i}^{-1}$ 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 $|E_\alpha^{(0)} - E_\alpha^{(1)}| < \epsilon$, where ϵ is a defined small quantity such as 0.001 kJ mol^{-1}.

To verify the validity of the iterative linear integral isoconversional method, the nonlinear integral isoconversional method proposed by Vyazovkin and Dollimore[14] is introduced. The nonlinear method is based on minimization of the following function

$$\Phi(E_\alpha) = \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{I(E_\alpha, T_{\alpha,i})\beta_j}{I(E_\alpha, T_{\alpha,j})\beta_i} \tag{10}$$

For each given extent of conversion in eq 10, the E_α value is determined as a value that minimizes $\Phi(E_\alpha)$ and the temperature integral $I(E_\alpha,T_{\alpha,i})$ is numerically solved.

4. Determination of the T_α Values

To apply the isoconversional methods, one has to determine the T_α values. In the paper of Vyazovkin,[8] the T_α values were estimated from the experimental data via a nonlinear interpolation. Admaďević et al.[22] investigated the possibility of applying the normalized Weibull distribution function for describing the dehydration curves at different heating rates and calculated the T_α values at different heating rates according to the fitted Weibull distribution functions. Barbadillo et al.[23] proposed that an overall thermogravimetric analysis curve can be fitted by a logistic mixture model. Then, some further kinetic analyses can be performed using those fitted logistic mixture models. Cai and Liu[24] found that a plot of α vs T related to solid-state reactions can be successfully described by one or the linear combination of few Weibull distribution functions (Weibull mixture model). Then, the T_α values can be obtained from the fitted kinetic conversion data.

In this paper, the Weibull and logistic mixture models were used for the statistical description of the experimental kinetic conversion data of the oxidative pyrolysis process of wheat straw. In the Weibull mixture model, it is assumed that a kinetic

conversion curve may be fitted by one or the linear combination of few Weibull cumulative distribution function

$$\alpha(t) = \sum_{i}^{k} w_i\left(1 - e^{-\left(\frac{t}{\mu_i}\right)^{\gamma_i}}\right) \tag{11}$$

where k is the number of the Weibull mixture model components, w_i stands for the weight of the ith component of Weibull mixture model, γ_i and μ_i are the shape and scale parameters, respectively. Under nonisothermal conditions with the linear heating program, the following relationship is valid

$$t = \frac{T - T_0}{\beta} \tag{12}$$

where T_0 is the initial temperature.

By substitution of eq 12 into eq 11, one can obtain the Weibull mixture model for nonisothermal conditions

$$\alpha(T) = \sum_{i}^{k} w_i\left[1 - e^{-\left(\frac{T - T_0}{\eta_i}\right)^{\gamma_i}}\right] \tag{13}$$

where $\eta_i = \beta\mu_i$.

The expression of the logistic mixture model for nonisothermal conditions is given as follows

$$\alpha(T) = 1 - \sum_{i=1}^{m}\left(c_i\frac{e^{a_i + b_i(T - T_0)}}{1 + e^{a_i + b_i(T - T_0)}}\right) \tag{14}$$

where m is the number of logistic mixture model components and a_i, b_i, and c_i are constants.

In the literature, there are several statistical test methods used to evaluate statistically the performance of a fitting. Among these, the correlation coefficient, the reduced chi-square (χ^2), and the root-mean-square error are the most widely used ones,[25,26] as given below

$$R^2 = \frac{\left(N\sum_{i=1}^{N}\alpha_{\exp,i}\alpha_{\mathrm{pre},i} - \sum_{i=1}^{N}\alpha_{\exp,i}\sum_{i=1}^{N}\alpha_{\mathrm{pre},i}\right)^2}{\left[N\sum_{i=1}^{N}\alpha_{\exp,i}^2 - \left(\sum_{i=1}^{N}\alpha_{\exp,i}\right)^2\right]\left[N\sum_{i=1}^{N}\alpha_{\mathrm{pre},i}^2 - \left(\sum_{i=1}^{N}\alpha_{\mathrm{pre},i}\right)^2\right]} \tag{15}$$

where R is the correlation coefficient which can be used to test the linear relation between experimental and predicted values,[27] $\alpha_{\exp,i}$ the experimental value of α, $\alpha_{\mathrm{pre},i}$ the estimated value of α, and N the number of experimental data points

$$\chi^2 = \frac{\sum_{i=1}^{N}(\alpha_{\exp,i} - \alpha_{\mathrm{est},i})^2}{N - z} \tag{16}$$

where χ^2 is the reduced chi square and z is the number of parameters. The lower are the values of χ^2, the better is the goodness of fit.[28]

$$\mathrm{RMSE} = \left[\frac{1}{N}\sum_{i=1}^{N}(\alpha_{\exp,i} - \alpha_{\mathrm{est},i})^2\right]^{1/2} \tag{17}$$

Table 1. Parameter Values of Logistic Mixture Models for the Statistical Description of the Kinetic Conversion Data of Wheat Straw Oxidative Pyrolysis

	heating rate		
parameter	5 K min^{-1}	10 K min^{-1}	20 K min^{-1}
a_1	13.72600	22.11002	5.80102
a_2	2.91331	21.69070	14.69633
a_3	17.36480	9.50552	13.77044
a_4	29.79713	6.14706	12.66910
b_1/K^{-1}	−0.14604	−0.19036	−0.06368
b_2/K^{-1}	−0.02808	−0.18254	−0.11554
b_3/K^{-1}	−0.07745	−0.04161	−0.10772
b_4/K^{-1}	−0.27115	−0.06124	−0.04973
w_1	0.21934	0.21537	0.17165
w_2	0.36759	0.15223	0.19915
w_3	0.15262	0.24028	0.41281
w_4	0.27776	0.38659	0.21359

Table 2. Parameter Values of Weibull Mixture Models for the Statistical Description of the Kinetic Conversion Data of Wheat Straw Oxidative Pyrolysis

	heating rate		
parameter	5 K min^{-1}	10 K min^{-1}	20 K min^{-1}
γ_1	13.70642	7.49005	2.46501
γ_2	2.05122	2.23203	12.43421
γ_3	15.81984	26.99286	24.22230
γ_4	11.96024	15.89976	8.18269
η_1/K	110.06034	115.51821	152.07178
η_2/K	127.93140	153.81112	275.83112
η_3/K	88.29179	119.16570	131.93443
η_4/K	232.70814	253.13950	127.54494
w_1	0.43033	0.37478	0.27934
w_2	0.36239	0.33063	0.15575
w_3	0.06269	0.16889	0.12693
w_4	0.14460	0.12570	0.43798

where RMSE is the root-mean-square error which provides information on the short-term performance. The value of RMSE is always positive, and the lower are the values of RMSE, the better is the goodness of fit.[29]

The optimal fittings were obtained with four Weibull mixture model components and four logistic mixture model components. The parameter values of logistic and Weibull mixture models are presented in Tables 1 and 2. The statistical results from two models such as the R^2, χ^2, and RMSE values are shown in Table 3.

From the results included in Table 3, the Weibull mixture model has been found to be a better model for reproducing the oxidative pyrolysis kinetic conversion data of wheat straw. The experimental and predicted kinetic conversion data by the Weibull mixture model are presented in Figure 1a. The comparisons between the experimental and predicted data at different heating rates are also shown in parts b, c, and d of Figure 1, and good correlation can be seen. From the results included in Figure 1, it was found that the Weibull mixture model fits the oxidative pyrolysis kinetic conversion data very well.

The T_α values for various α at different heating rates can be determined from eq 13 with proper parameter values. Equation 13 can not be analytically solved, and therefore, it must be

Table 3. Statistical Results from the Weibull and Logistic Mixture Models for Oxidative Pyrolysis Kinetic Conversion Data of Wheat Straw

	heating rate								
	5 K min^{-1}			10 K min^{-1}			20 K min^{-1}		
	R^2	χ^2	RMSE	R^2	χ^2	RMSE	R^2	χ^2	RMSE
Logistic mixture model	0.999831	2.9062×10^{-5}	4.5103×10^{-3}	0.999334	1.1202×10^{-4}	8.8552×10^{-3}	0.999507	9.3358×10^{-5}	8.1661×10^{-3}
Weibull mixture model	0.999856	2.3903×10^{-5}	4.1629×10^{-3}	0.999771	3.7203×10^{-5}	5.1935×10^{-3}	0.999819	3.3105×10^{-5}	4.9431×10^{-3}

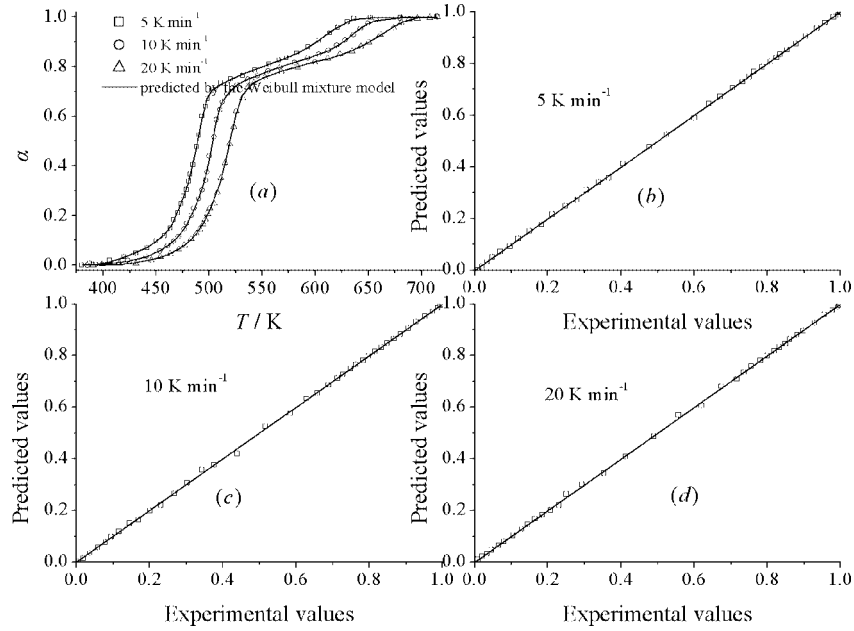

Figure 1. (a) Comparison of the experimental (dots) and predicted (solid lines) kinetic conversion data by the Weibull mixture model. (b−d) Correlation between the experimental and predicted kinetic conversion data by Weibull mixture model at 5,10, and 20 K min^{-1}, respectively.

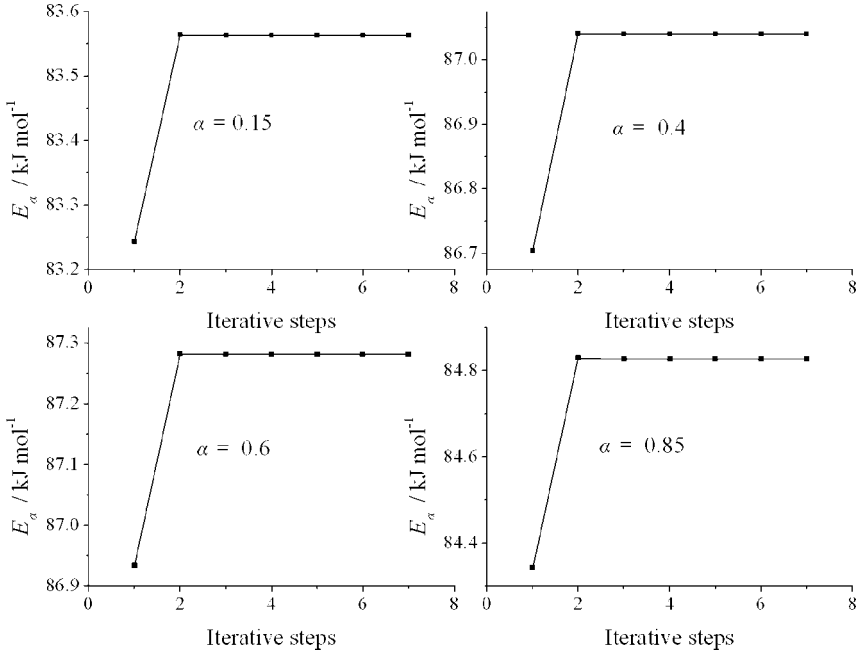

Figure 2. Some iterative calculations of E_α for oxidative pyrolysis of wheat straw at some α values.

solved by means of some numerical techniques. In this study, the Mathematica software system has been used for the numerical solution of eq 13 by using the "FindRoot" function.

5. Results and Discussion

On the basis of the α vs T_α data obtained in the above section, two isoconversional methods mentioned in section 3 were applied to perform the kinetic analysis of the oxidative pyrolysis process of wheat straw. The calculation procedures, results, and some discussion are described as follows.

To illustrate the iterative integral isoconversional method, some iterative calculations of E_α for oxidative pyrolysis of wheat straw at some α values are shown in Figure 2, where it can be seen that the E_α convergence values can be obtained through three or four iterative steps.

It is noted that it is difficult to obtain the derivatives of eq 10. Therefore, a certain algorithm for minimization without derivatives is required. Some numerical calculations of $\Phi(E_\alpha)$ at some values of α were performed by means of Mathematica, and the obtained results are shown in Figure 3. It can be observed that $\Phi(E_\alpha)$ is a unimodal function of E_α. The golden section search method, which can be used to find the minimum of a unimodal continuous function without using derivatives,[30] was employed to determine E_α minimizing $\Phi(E_\alpha)$.

Figure 4 shows the E_α vs α produced from the obtained α vs T_α data by means of the iterative linear integral isoconversional method and the Vyazovkin and Dollimore isoconversional method. The inspection of this figure shows the following:

The E_α values obtained by the nonlinear integral isoconversional method are practically identical to those estimated

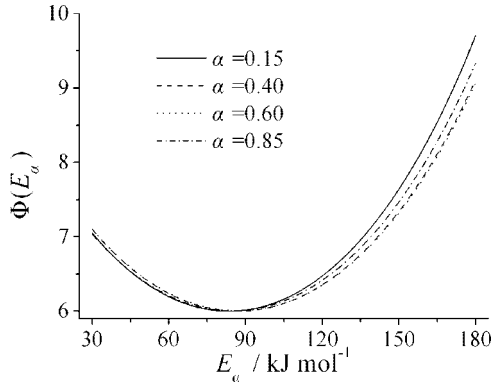

Figure 3. The plots of $\Phi(E_\alpha)$ vs E_α at some α values.

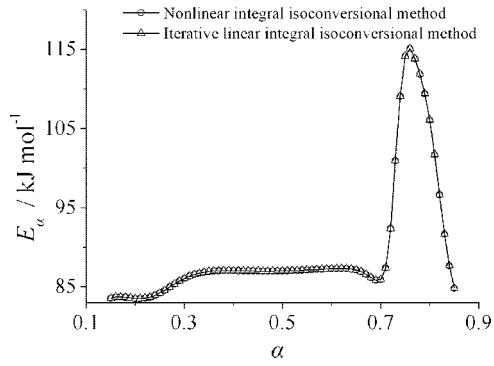

Figure 4. The E_α dependences evaluated for oxidative pyrolysis of wheat straw by means of the iterative linear integral isoconversional method and nonlinear integral isoconversional method.

by the iterative linear integral isoconversional method; this fact suggests that the iterative linear integral isoconversional method is equivalent to the nonlinear integral isoconversional method for the determination of E_α.

A strong variation in E_α with α can be observed, which suggests the oxidative pyrolysis process of wheat straw is a multistep reaction.

In the 0.15−0.70 conversion range, E_α has a value of 86.2 ± 1.3 kJ mol^{-1}; when the conversion is 0.70−0.85, E_α has a value of 93.4 ± 13.1 kJ mol^{-1}.

Ergudenler and Ghaly performed the thermogravimetric analysis of wheat straw in an oxidizing atmosphere at a single heating rate of 20 K min^{-1} and determined the kinetic parameters based on the assumption that the reaction mechanism would follow the *n*th-order model.[3] They obtained the activation energy value of 30−80 kJ mol^{-1}, which is different from the value obtained in this paper due to the fact that the different methods have been used for the determination of the activation energy.

5. Conclusions

Two isoconversional methods (the iterative linear integral isoconversional and nonlinear integral isoconversional method) were used for performing the kinetic analysis of the oxidative pyrolysis process of wheat straw. The iterative linear method and the nonlinear one proposed by Vyazovkin and Dollimore[16] show concurrence in the calculation of E_α. The significant dependence of the activation energy upon conversion was obtained, which indicated that the oxidative pyrolysis of wheat straw is a complex process. The effective activation energy was 86.2 ± 1.3 and 93.4 ± 13.1 kJ mol^{-1} in the conversion range of 0.15−0.70 and 0.70−0.95, respectively.

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