Reaction Kinetics, Mechanisms and Catalysis (2024) 137:1987–2001
https://doi.org/10.1007/s11144-024-02629-7

Modified Friedman isoconversional kinetic method for effective activation energies of waste tires rubber pyrolysis

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Received: 18 March 2024 / Accepted: 8 April 2024 / Published online: 13 April 2024

Abstract

A modified Friedman isoconversional method based on the weight-loss data was proposed to determine the kinetics models and parameters. Thermal pyrolysis kinetic characteristics of waste tire rubber (WTR) samples under nitrogen conditions was investigated by measuring the rate of mass loss as a function of time and temperature. The obtained thermal pyrolysis data was applied to analyze the kinetic parameters using the Flynn–Wall–Ozawa (FWO), Kissinger–Akahira–Sunose (KAS) and modified Friedman isoconversional methods. The results showed that the modified Friedman isoconversional method was used to provide the most precise values of activation energy for WTR pyrolysis, which ranged from 130.5 to 177.6 kJ/mol with the conversion range of 0.1–0.9. It can avoid systematic errors in the FWO and KAS methods. These data were in good agreement with the values reported in the related previous studies. Therefore, the modified Friedman method provides an accurate and effective way to explain the pyrolysis parameters and equations of kinetics in WTR.

Keywords Waste tire rubber · Pyrolysis mechanism · Kinetics · Modified Friedman isoconversional method

Introduction

The rapid development of the automobile industry accelerates the usage of tires, and thus a large number of end-of-life tire rubbers are generated and accumulated. Waste tire rubber (WTR) is considered non-environmental solid waste due to its highly complex structure and the diverse composition of raw materials [1, 2]. Several

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conventional methods such as landfilling, reclamation and incineration are employed to handle these solid wastes [3, 4]. Among these methods, the pyrolysis of WTR has been the key research to deal with the most of solid waste and produce value-added chemicals [5]. Pyrolysis of WTR can convert solid waste into pyrolytic gas, oil, pyrolytic carbon black under a non-oxidative atmosphere to produce gaseous, oil and solid product. Therefore, It is essential for understanding the mechanism of thermal pyrolysis process of WTR. [6, 7]

Tire rubbers are mainly composed of rubber (60–65 wt.%) and carbon black (25–35 wt.%), which consist of the majority part of organic materials and thus are valuable sources of hydrocarbon feedstock [8, 9]. To understand the pyrolysis mechanism of WTR, the kinetic analysis of the process is a must by building the kinetics models and parameters on the basis of the non-isothermal thermogravimetric analysis (TGA) [10]. Non-isothermal TGA is the most commonly used analytical technique for performing kinetic analysis of the pyrolysis by measuring the mass change that occurs as the material is heated at a constant rate. TGA can provide featured information that can be used to perform kinetic analysis and then obtain kinetic parameters by applying kinetic methods (model-fitting or isoconversional methods) [11]. In theory, kinetic experiments conducted under nonisothermal conditions can provide kinetic parameters such as reaction models, activation energies and pre-exponential factors [12]. However, kinetic models are sometimes inaccurate and misleading because they originate from the predictions based on fitting data [13]. On the other hand, isoconversional methods yield reasonably consistent and reproducible activation energies, such as model-free methods [14, 15]. The isoconversional kinetic methods can be divided into integral and differential ones [16]. Muhammad Yasin Naz et al. found that sensitivity analyses of rate constants for chemical kinetics of the plastic waste pyrolysis reaction were essential for the efficient valorization of plastic waste into combustible liquids and gases, and the role of individual rate constants provided important information on the process conditions, quality, and quantity of the pyrolysis products. The reaction temperature and time were also reduced through these analyses [17, 18]. Therefore, The obtained activation energy can be used to determine reaction mechanisms [19].

The most common integral isoconversional methods are the Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) methods [20]. The application of the FWO and KAS isoconversional methods would lead to some systematic errors in the calculation of the conversion-dependent activation energies because both methods are derived with the assumption of a constant activation energy and the approximations for the temperature integral [21]. Moreover, when the activation energy drops substantially in the later stages of conversion, both give nonsensical kinetic predictions which violate the sequential reaction assumptions intrinsic to the models. Many shortcomings associated with the integral isocon-versional methods can be overcome by making the integral method piecewise continuous, which in the limit of small steps, makes it equivalent to the differential isoconversional method. The Friedman differential isoconversional method is considered as the most accurate method, it simultaneously uses the conversion and conversion rate data, which are usually obtained by numerical differentiation and would amplify the data noise level. Therefore, the Friedman method is sensitive to data noises [22]. However, the Friedman method highly depends on instantaneous conversion rate values, which is very sensitive to experimental noise and tends to be numerical unstable [9, 23]. Moreover, the pyrolysis process of the heterogeneous WTR contains many complex reactions, which yield products in the different forms [24]. Therefore, It is important and urged that the kinetic parameters, especially the activation energy indirectly reflecting the potential for the thermal conversion of WTR.

To avoid the numerical unstable problems of the Friedman method, a new modified Friedman method was proposed in this work. The pyrolysis kinetic of WTR samples was investigated based on weight-loss data using thermogravimetric analysis. The activation energy was applied to study the pyrolysis mechanism of waste rubber. This method enables us to precisely calculate E_α without any assumption about $f(\alpha)$, in which the conversion rates are not required. The modified Friedman method aim to deal with the numerical unstable situation of the traditional methods.

Material and methods

Characterization of WTR samples

WTR material in this experiment was purchased from a recycling company in China. The steel material for reinforcing with the size of 1–5 mm was removed from the waste tires and thrown. Then the remained samples were mechanically grinding by a blender, until the size of samples was below 20 mesh to increase heat and mass transfer. The density of the obtained sample was 1.13 g/cm^3.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a high-precision tool for the pyrolysis kinetic study of WTR [25]. Thermal pyrolysis behavior of WTR samples under nitrogen conditions was investigated by measuring the rate of mass loss as a function of time and temperature. 15 mg of WTR was placeed into the analyzer, TGA was carrried out at a nitrogen gas flow rate of 60 mL/min and was performed at different heating rates (5, 10, 20 and 40 °C/min) from 50 to 700 °C.

Kinetics

FWO and KAS methods

The reaction rate of the sample in a solid state can be described by the below differential expression [26]:

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

where α was the conversion degree, t was the time, A was the frequency factor, E was the activation energy, T was the temperature, R was the value of the gas constant and $f(\alpha)$ was the function of the reaction mechanism. By non-isothermal conditions at a certain heating rate, Eq. (1) can be described as:

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

Here β stands for the heating rate, and

$$\beta = \frac{dT}{dt} \tag{3}$$

For determining the effective activation energy of a solid state reaction, the isoconversional kinetic methods were widely used, which can be divided into integral and differential isoconversional ones [27].

The most common integral isoconversional technique are the Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) [28]. They are model-free methods focused on the activation energy.

$$\text{FWO}: \ \ln \beta_i = \ln\left(\frac{A_\alpha \cdot E_\alpha}{R \cdot g(\alpha)}\right) - 5.331 - 1.052 \frac{E_\alpha}{RT_{\alpha,i}} \tag{4}$$

$$\text{KAS}: \ \ln\left(\frac{\beta_i}{T^2_{\alpha,i}}\right) = \ln\left(\frac{A_\alpha \cdot R}{E_\alpha \cdot g(\alpha)}\right) - \frac{E_\alpha}{RT_{\alpha,i}} \tag{5}$$

The model-free methods applied three or more series of thermogravimetric data to obtain the activation energy of each conversion according to isoconversional methods [29]. However, these methods ignored kinetic model functions and cannot give an intact model, lacking of pre-exponential parameters and reaction models.

Modified friedman isoconversional method

The Friedman differential method was widely accepted as the most accurate isoconversional method, which was inferred from the basic formula [30]. This method was obtained from Eq. (2).

$$\ln\left[\beta_i \left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = \ln\left[A_\alpha \cdot f(\alpha)\right] - \frac{E_\alpha}{RT_{\alpha,i}} \tag{6}$$

where i stand for the heating rate of ith and the α stand for the value of the conversion degree. During the process, the Friedman method still uses the values of instantaneous conversion rate, which is very susceptible to experimental noise. The experimental data tends to become unstable.

To avoid the unstable value results problems of the Friedman method, this paper put forward a new modified method. By the numerical calculation theory, finite-difference can approximate the derivative:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{T_{\alpha,i}} \approx \left(\frac{\Delta\alpha}{\Delta T}\right)_{T_{\alpha,i}} = \frac{\Delta\alpha}{T_{\alpha+\Delta\alpha/2,i} - T_{\alpha-\Delta\alpha/2,i}} \tag{7}$$

Substituting Eq. (5) into Eq. (4), the equation below can be inferred:

$$\ln\left(\beta_i \frac{\Delta\alpha}{T_{\alpha+\Delta\alpha/2,i} - T_{\alpha-\Delta\alpha/2,i}}\right) = \ln\left[A_\alpha \cdot f(\alpha)\right] - \frac{E_\alpha}{RT_{\alpha,i}} \tag{8}$$

For a certain value of α, the value of $\ln\left[A_\alpha \cdot f(\alpha)\right]$ is a constant. The left equation was linear with the reciprocal of the temperature. A plot of $\ln\left(\beta_i \frac{\Delta\alpha}{T_{\alpha+\Delta\alpha/2,i} - T_{\alpha-\Delta\alpha/2,i}}\right)$ against with $-\frac{1}{RT_{\alpha,i}}$ at different heating rates can give a straight line, and the slope of straight line was the isoconversional value of E_α. The function between effective activation energy and α was obtained by changing the values of α.

During the application of the new modified method, there is no need for the conversion rates and E_α is calculated without any assumption about $f(\alpha)$. And the modified method can effectively lessen the effect of experimental noises by the traditional Friedman method.

Results and discussion

Thermal pyrolysis process of WTR

The precise component analysis (Table 1) showed that the WTR material consisted of a volatile substance content of 55.8 wt%. It indicated that the sample would produce vapors during the pyrolysis process. A relatively rich carbon content (34.8 wt.%) was found in the sample, which demonstrated that the heat value of the WTR material would be high.

Fig. 1a precisely illustrates thermogravimetric (TG) curves of the weight loss with the temperature between 50 and 700 ℃ at different heating rates (5, 10, 20, 40 °C/min) in nitrogen. The samples showed the same total weight loss under the different heating rates, and the final weight of the samples remained the same value, ranging from 29 to 34% under the heating rates of 5, 10, 20, 40 °C/min. It can be seen that the pyrolysis of the WTR underwent a main decomposition step ranging 200 from 500 ℃.

The changes in the derivative mass loss (DTG) with the temperature are shown in Fig. 1b, and there were two main peaks in the DTG figures at the low heating

Table 1 Components analysis of WTR sample (on dry basis)

Matter content	Mass fraction (%)
Volatile substance	55.8 ± 1.3
Carbon black	34.8 ± 0.9
Ash	9.4 ± 0.7

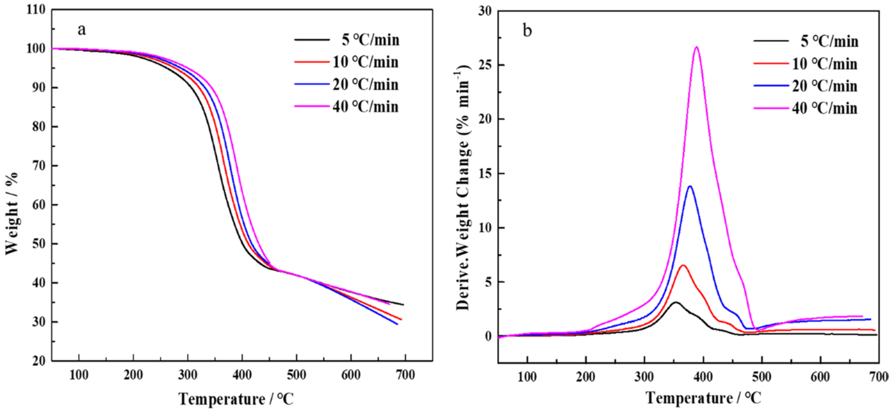

Fig. 1 WTR pyrolysis kinetic data. **a** weight loss and **b** derivative weight loss data by thermogravimetric analysis

rates. According to the temperature of the first peaks observed, it was inferred that the WTR contained various light component including plasticizers and other additives. In the second main decomposition stage, the main components of the WTR samples underwent several complex degradation reactions, such as depolymerization, decarboxylation and cracking. The second stage accounted for about 55% of the total weight loss of the WTR and the remaining sample was attributed to ash and unreacted organics.

Effect of heating rate

As shown in Fig. 1b, there was a delay in the degradation process with the increase of heating rates. The heating rates had a big influence on the temperature range, during which the first stage of the WTR pyrolysis occurred. The reaction of the WTR pyrolysis firstly occurred at a low temperature by using slow heating rates, and as the heating rate increased, the temperature of the decomposition reaction shifted to a higher temperature. These results highly agreed with those of DTG experiments as the literature reported before. From Fig. 1b, one peak was observed in the derivative

Table 2 Characteristics of derivative weight loss curve

Heating rate (°C/min)	Peak temperature (°C)	Derivative weight loss peak value (%/min)
5	353	2.7
10	365	7.1
20	376	14.1
40	393	26.9

weight loss curve. Table 2 lists the information about the derivative weight loss curves.

Some scholars suggested that the heat-transfer of this material was a limited function of heat and mass transfer [31]. The limitations showed more obvious at higher heating rates when the time of pyrolysis decreased. The degree of pyrolysis at higher heating rates was higher than that at lower heating rates. Given that the sample particle size (<250 mm) and weight (10 mg), it seems unlikely that there was a big temperature gradient within the different samples. Besides, staying time at each temperature increased when the heating rate was slow, and meanwhile the weight of WTR particles decreased more at the same temperature. Conversely, higher heating rates enabled the particles have a shorter residence time at each temperature, which explained that the same total mass fraction conversion was reached at different temperature. This also explained the different curve trends in Fig. 1b, where the thermal decomposition rates (dx/dt) climbed with the increasing of heating rates. Furthermore, the biggest heating rate led to only one peak in the smooth DTG curve.

Model-free kinetic results

Among the kinetics parameters, activation energy (E_α) stands for the required energy during the reaction, which determines the reaction paths [32]. Iso-conversional methods is a more accurate method, determining of E_α without supposing the reaction mechanism of the pyrolysis process [33]. The values of E_α at the main pyrolysis process of WTR were calculated by FWO and KAS methods based on weight-loss data at various heating rates. The plot of log β vs. ($-$ 1.052/RT_i) (FWO) and the plot of log [β/T^2] vs. ($-$ 1000/T_i) (KAS) for the given conversion degrees were drawn in straight lines, as shown in Fig. 2. The values E_α for every phase of WTR at different conversion degrees were evaluated by the regression lines and are shown in Table 3. E_α values were nearly the same at a given conversion with these two methods. Actually, the considerable variation of E_α values has been reported in the former literature [34, 35].

Modified Friedman isoconversional method results

The $\alpha - T$ curves at various heating rates can be numerically solved with Eq. (2). Fig. 3 illustrates the $\alpha - T$ curves at different heating rates of 5, 10, 20 and 40 °C/min for the theoretically simulated process.

The T, T and T values at different α and different heating rates for the pyrolysis process of WTR were calculated and are listed in Table 4.

The corresponding values of $\ln\left(\beta_i \frac{\Delta\alpha}{T_{\alpha+\Delta\alpha/2,i} - T_{\alpha-\Delta\alpha/2,i}}\right)$ and $-\frac{1000}{RT_{\alpha,i}}$ were also computed. The linear regression operations of the plots of $\ln\left(\beta_i \frac{\Delta\alpha}{T_{\alpha+\Delta\alpha/2,i} - T_{\alpha-\Delta\alpha/2,i}}\right)$ vs. $-\frac{1000}{RT_{\alpha,i}}$ for various conversions are performed in the Origin Software environment, as

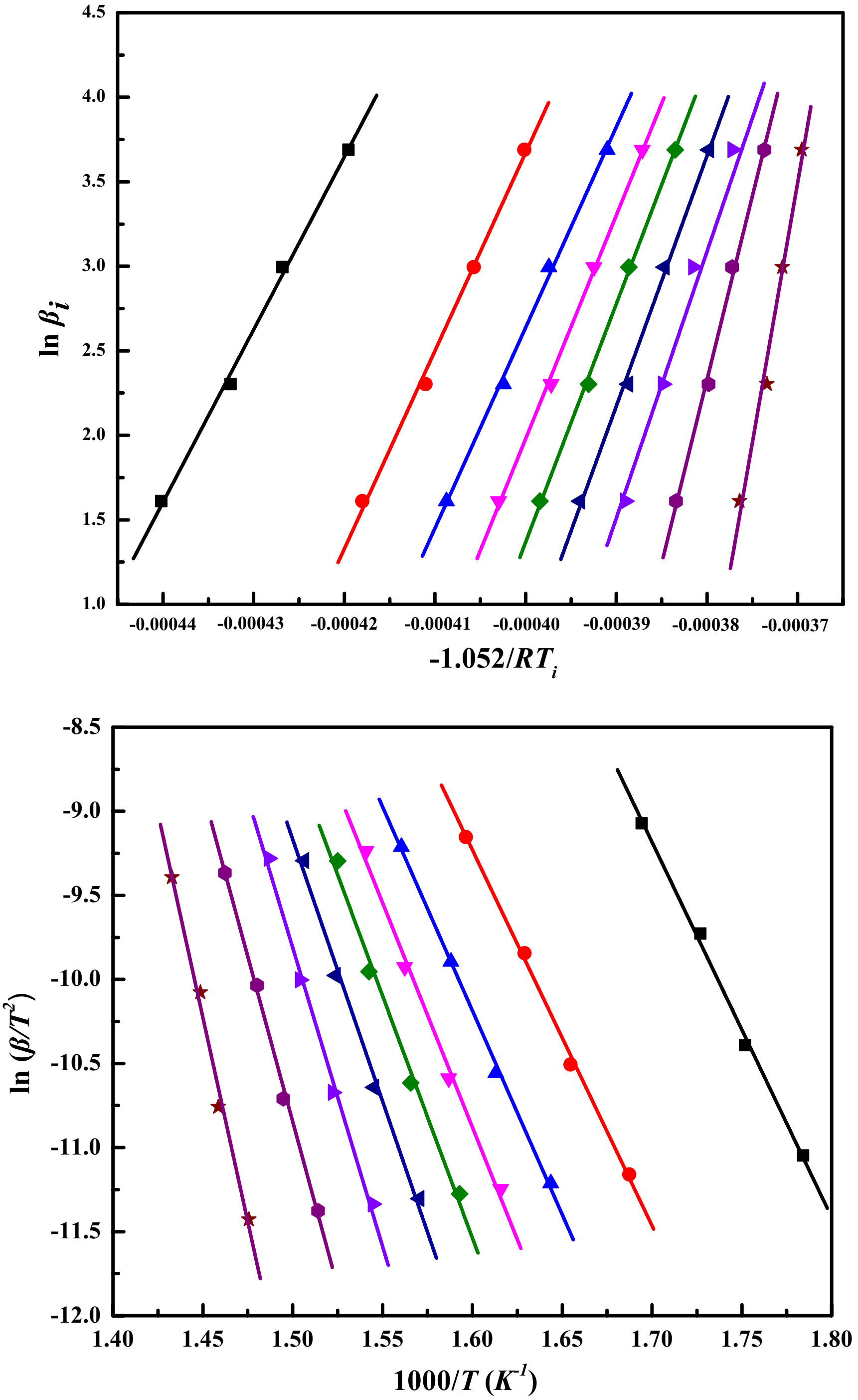

Fig. 2 The plot of log β vs. ($-$ 1.052/RT_i) (FWO) and the plot of log [β/T^2] vs. ($-$ 1000/T_i) (KAS)

Table 3 E_α values for various conversion degrees of WTR calculated by FWO and KAS methods

Conversion (x)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
E_α (FWO)	118.6	121.7	128.8	141.8	152.9	165.4	172.4	178.7	189.2
E_α (KAS)	113.1	117.2	125.7	132.2	144.9	155.9	169.2	175.7	184.2

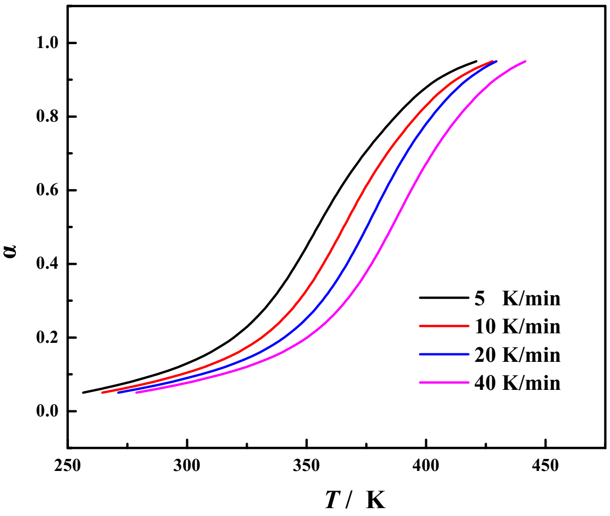

Fig. 3 the $\alpha - T$ curves at different heating rates of 5, 10, 20 and 40 °C/min

Table 4 Values of $\ln\left(\beta_i \frac{\Delta\alpha}{T_{\alpha+\Delta\alpha/2,i}-T_{\alpha-\Delta\alpha/2,i}}\right)$ and $-\frac{1000}{RT_{\alpha,i}}$ for $\Delta\alpha=0.01$

α	5 °C/min		10 °C/min		20 °C/min		40 °C/min	
	YY	XX	YY	XX	YY	XX	YY	XX
0.1	– 5.00201	– 0.4636	– 4.4195	– 0.4586	– 3.75064	– 0.4536	– 3.05064	– 0.4486
0.2	– 4.91559	– 0.45173	– 4.31279	– 0.44673	– 3.66479	– 0.44193	– 2.94787	– 0.43693
0.3	– 4.76405	– 0.43197	– 4.1407	– 0.42697	– 3.50174	– 0.42257	– 2.88174	– 0.41857
0.4	– 4.59717	– 0.41647	– 3.95892	– 0.41147	– 3.30894	– 0.40727	– 2.70894	– 0.40327
0.5	– 4.40245	– 0.40447	– 3.76492	– 0.40138	– 3.15177	– 0.39724	– 2.69177	– 0.39334
0.6	– 4.20134	– 0.39513	– 3.5593	– 0.39093	– 2.89735	– 0.38663	– 2.19735	– 0.38263
0.7	– 4.03898	– 0.38759	– 3.37289	– 0.38289	– 2.70394	– 0.37919	– 2.00394	– 0.37519
0.8	– 3.87915	– 0.3814	– 3.19775	– 0.3769	– 2.5252	– 0.3732	– 1.9252	– 0.3702
0.9	– 3.73371	– 0.37623	– 3.04053	– 0.37283	– 2.36444	– 0.36793	– 1.66444	– 0.36503

YY: $\ln\left(\beta_i \frac{\Delta\alpha}{T_{\alpha+\Delta\alpha/2,i}-T_{\alpha-\Delta\alpha/2,i}}\right)$ XX: $-\frac{1000}{RT_{\alpha,i}}$

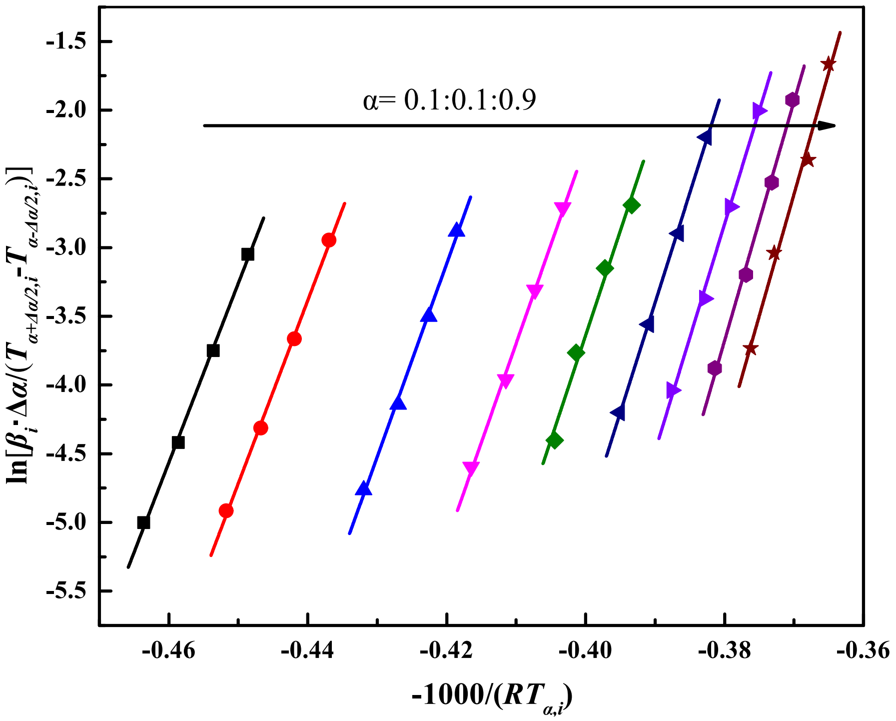

Fig. 4 The linear regression operations of the plots of $\ln\left(\beta_i \frac{\Delta\alpha}{T_{\alpha+\Delta\alpha/2,i}-T_{\alpha-\Delta\alpha/2,i}}\right)$ vs. $-\frac{1000}{RT_{\alpha,i}}$ for various conversions

Table 5 E_α values for each phase of WTR at various conversion degrees by the modified Friedman method

Conversion(x)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
E_α (modified Friedman method)	130.4	133.1	140.5	143.8	152.2	159.5	165.1	174.2	177.0

shown in Fig. 4. From this figure, it can be found that perfect linear relationships between $\ln\left(\beta_i \frac{\Delta\alpha}{T_{\alpha+\Delta\alpha/2,i}-T_{\alpha-\Delta\alpha/2,i}}\right)$ vs. $-\frac{1000}{RT_{\alpha,i}}$ for all conversions considered in this study.

Table 5 shows the values of $E\alpha$ at different conversion degrees of WTR were calculated by the modified Friedman method. To compare the modified Friedman isoconversional method and commonly used integral isoconversional methods (FWO and KAS methods), the values of $E\alpha$ as a function of α obtained from three different methods are shown in Fig. 4. The curves intuitively suggested that the $E\alpha$ calculated by the modified Friedman method shows higher accuracy and reliability than FWO and KAS methods. Besides, the newly proposed method is a linear integral method whose implementation is much easier than the nonlinear isoconversional method

Table 6 The ln[A_α·$f(\alpha)$] values at α values calculated by the modified Friedman method

α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
ln[Aα·f(α)]	55.4471	55.2013	55.9304	55.2807	57.2683	58.8408	59.9347	62.5214	62.9086
R^2	0.9974	0.9977	0.9962	0.9970	0.9793	0.9984	0.9952	0.9940	0.9846

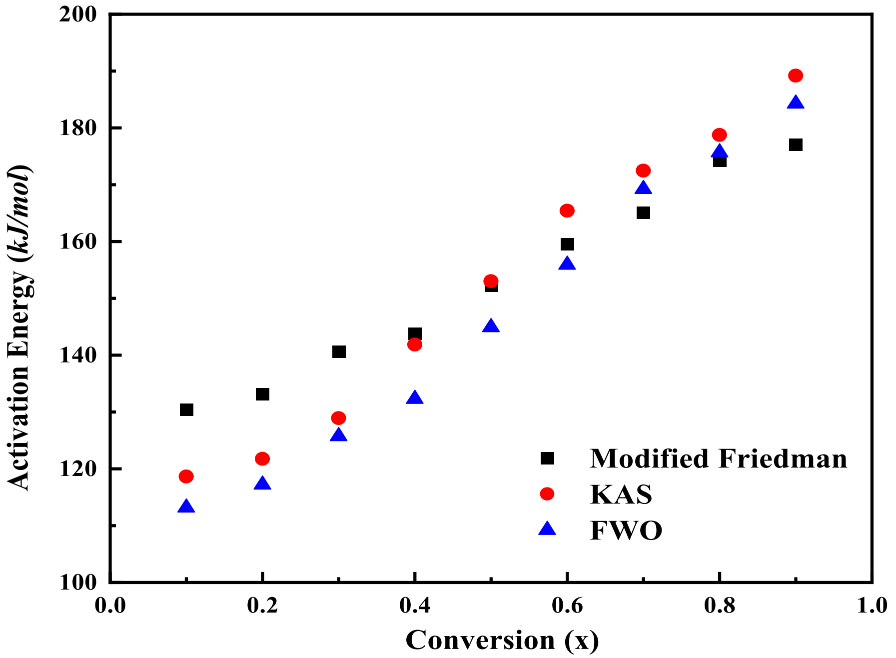

Fig. 5 The relative deviations of the activation energies calculated by the modified Friedman method with different Δα values

proposed by Vyazokin, which requires optimization and has high computation complexities. [36]

Table 6 lists the values of ln[A_α·$f(\alpha)$] at α calculated by the modified Friedman method. Fig. 5 shows the relative deviations of the activation energies calculated according to the different values of Δα in the modified Friedman method. From Fig. 5, it can be obtained that the relative deviations in the determination of the E_α values decrease with the increase of Δα. Based on the previous mentioned theoretical analyses for the simulated process, it can be conferred that the modified Friedman isoconversional method can provide the more accurate values of the activation energies for thermally reactions of the solid-state.

Based on the above result of $E\alpha$ and ln[A_α·$f(\alpha)$] calculated by the modified Friedman method for the pyrolysis of WTR. The linear relationship between $E\alpha$

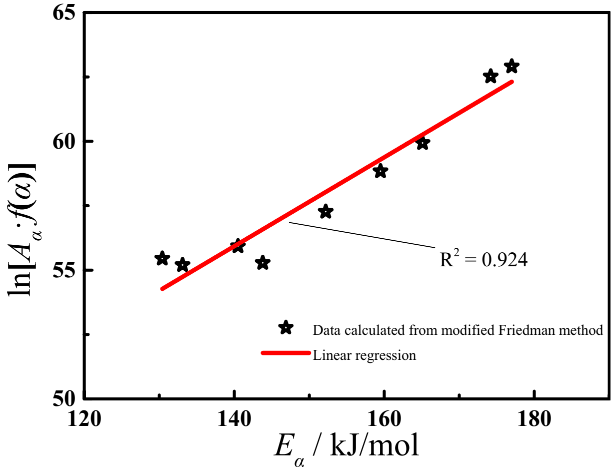

Fig. 6 Relationship between $\ln[A_\alpha \cdot f(\alpha)]$ and $E\alpha$ calculated by the modified Friedman method for the pyrolysis process of WTR

and $\ln[A_\alpha \cdot f(\alpha)]$ is shown in Fig. 6. the following empirical formula thus can be established:

$$\ln\left[A_\alpha \cdot f(\alpha)\right] = \mathrm{a} + \mathrm{b}E\alpha \tag{9}$$

Here a and b are constants. The values of a and b and the coefficient value of determination (R^2) of the WTR pyrolysis are also shown in Fig. 6.

Conclusions

Pyrolysis of waste tire rubber has been previously considered as a promising management for the global waste issue. This paper proposed a modified Friedman method to fully understand the reaction kinetics and mechanisms of the pyrolysis process of the tire rubber.

Through thermogravimetric experiments at heating rates of 5, 10, 20 and 40 °C/min, the thermal degradation of WTR was investigated. We found that the activation energies of pyrolysis ranged from 130.5 kJ/mol to 177.6 kJ/mol, which was calculated by the modified Friedman method. The value of average activation energy is 153.0 kJ/mol. The results were highly consistent with reported literature values. FWO and KAS methods were also applied to calculate the activation energy. The obtained data was compared with the newly proposed method to discuss the applicability of various reaction models to the pyrolysis process of waste tire rubber. According to the activation energies calculated by the modified Friedman isoconversional method, the chemical reaction of waste rubber pyrolysis is a rate-limiting step, which is due to the heterogeneous and strongly bonded characteristic of the WTR.

Acknowledgements The authors gratefully acknowledge the financial support provided by Shanghai Municipal Commission of Science and Technology (No. 23YF1442200) and China Postdoctoral Science Foundation (No. 2023M732329), and the authors also would like to acknowledge manuscript revision by Yuqiong Li.

Author contributions Zhen Zhang: Conceptualization, Methodology, Experiments, Test result analysis, Manuscript drafting, Manuscript revision and editing. Xiaoguang Zheng: Test result analysis, Manuscript revision and editing. Junmeng Cai: Conceptualization, Methodology, Test result analysis, Manuscript revision and editing.

Funding Funding was provided by Natural Science Foundation of Shanghai Municipal Science and Technology Commission (No. 23YF1442200) and Postdoctoral Research Foundation of China (Certificate Number 2023M732329).

Data availability There is no data statement.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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