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Thermal analysis kinetics of Tartary buckwheat flour

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ABSTRACT

This experiment uses a DTA-TG analyzer to perform thermal analysis on Tartary buckwheat flour under static-air condition. The best experimental conditions for the thermal analysis of Tartary buckwheat flour are: sample mass 3.000g, heating rate 10°C/min. This paper studies the thermostabilization of Tartary buckwheat flour and concludes the four stages of thermal decomposition of Tartary buckwheat flour via extrapolated onset temperature of the thermogravimetric curve, as well as the proper processing temperature for Tartary buckwheat flour should be lower than 266.74 °C. By comparing Stava-Sestak method and FWO method, we can get that the apparent activation energy of the thermal decomposition of Tartary buckwheat flour is 235.38 KJ/mol, and the frequency factor is LnA = 44.07. Through comparison between 30 mechanistic function models and kinetic mode function models, it infers the most probable mechanism function for simulating the thermal decomposition of Tartary buckwheat flour. The reaction kinetics model of the decomposition of Tartary buckwheat flour is preliminarily calculated, which has provided a theoretical basis for the temperature control of Tartary buckwheat flour during the processing.

1. INTRODUCTION

Tartary buckwheat is a kind of coarse grain which has been proved by many literatures to have health care function [1]. It is widely cultivated in the western part of China and has great development values as people are paying more attention to the health nowadays. However, in current China, the development of Tartary buckwheat is still in its infancy compared to other developed countries, and there are few studies on the modern process parameters, resulting in the current Tartary buckwheat products have many problems in the R&D and actual production process, such as the change of the properties of active substances due to improper control of processing temperature during processing weakens the health-care functions of the Tartary buckwheat products [2]. At present, the application of Tartary buckwheat in food has involved aspects of processing methods, processing characteristics, influence mechanism and processing technology, and the influence of enzyme chemistry on the quality of processed products. However, the research and application of DTA technology in Tartary buckwheat processing is rare [3].

DTA [4] is a thermobalance technology that uses programs to control the heating rate and sensitivity, by recording the mass and energy change of a substance during heating, it determines the temperature at which the substance begins to lose weight and obtains this substance's thermal stability. Through non-isothermal kinetics, it can calculate the substance's activation energy and frequency factor so as to determine the mechanism function of its thermal decomposition reaction and predict its thermal decomposition reaction model, which provides a reliable theoretical reference for the Tartary buckwheat flour in the processing and storage process. The apparent activation energy, frequency factor and mechanism function obtained are also important theoretical parameters in the in-depth study or processing of Tartary buckwheat flour.

2. MATERIALS AND METHODS

2.1 Test materials and equipment

Tartary buckwheat flour was purchased from Hangfei Tartary buckwheat Co., Ltd., moisture content is less than 10%.

SHMADZU DTG-60 DTA-TG analyzer: Shimadzu Corporation, Japan. The heating range is 20°C~600°C; the atmosphere is static air; the reference material is an empty ceramic crucible.

2.2 Test methods

2.2.1 Method for determining the best thermal analysis image

By comparing different sample masses, the corresponding thermal analysis images are first obtained, then the sharpness and apparent degree of the peak shape are also compared to obtain the best thermal analysis image, and this mass is taken as the best sample mass, again by comparing different heating rates we can obtain different thermal analysis images, and the same standard is used to obtain the best thermal analysis conditions and thermal analysis images.

2.2.2 Determination of reaction critical temperature

The onset temperature of the Tartary buckwheat flour is determined by the best thermal analysis image obtained and the extrapolated onset temperature of the thermogravimetric curve.

2.2.3 Solving thermal analysis kinetic factors

(1) Determination of activation energy E and frequency factor A

The FWO method is used to substitute the temperature of the equal conversion rate under different heating rate conditions in to the FWO equation to solve the activation energy and the frequency factor [5].

(2) Determination of the mechanism function G(α)

Each mechanism function is substituted into the Satava-Sestak equation to solve the activation energies Es and As, and compare them with the activation energy E obtained by the FWO method. Select a kinetic mode function that satisfies the following condition: [6]

$$\left|\frac{E_0 - E_s}{E_0}\right| \leq 0.3 \tag{1}$$

Then, determine the optimal mechanism function by calculating the correlation coefficient.

3. RESULTS AND ANALYSIS

3.1 Determination of the best DTA-TGA image

3.1.1 Influence of Tartary buckwheat flour sample mass on TGA curve

In this paper, a set of five samples were prepared with a gradient of 1.000g between 1.000g and 5.000g, and the heating rate was controlled at 10 °C/min. By selecting the mass with sharp and obvious peak, the best sample mass suitable for the measuring of TGA curve was selected. The mass change has no significant effect on the TGA curve, but has a great influence on the DTA curve, and all curves showed three peaks, among which the peaks of the 3.000g sample are more obvious and easier to analyze. By comparison, 3.000 g was finally selected as the best sample mass for the thermal analysis test of Tartary buckwheat flour.

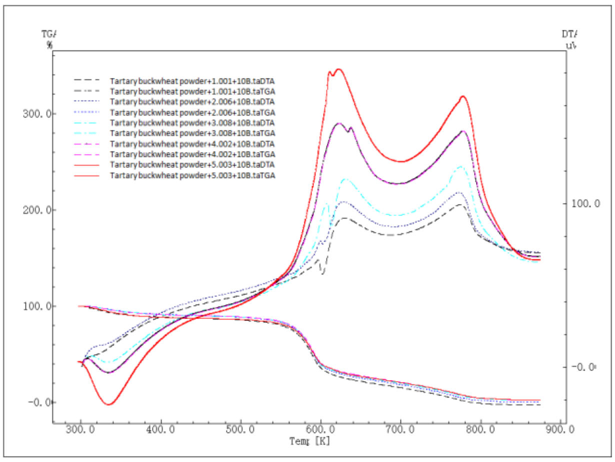

Figure 1. Influence of different sample masses on DTA/TGA curves

3.1.2 Influence of heating rate on thermal analysis image

The faster the heating rate, the more severe the temperature lag, and the initial and end temperature of the weight loss will lag and the information of some intermediate product might lost [7]. In this paper, by comparing the influence of heating rate on Tartary buckwheat flour, the temperature gradients of 5, 10, 15, and 20 °C/min were respectively set at a mass of 3.000g to obtain the most suitable DTA/TGA curve for observation and calculation.

The slower the heating rate, the earlier the energy peak of the DTA curve appears. This is related to the sensitivity of the instrument. The slower the heating rate, the steeper the curve from 300K to 700K. It can be seen from the comparison of the DTA curve that the peak shape at a rate of 10 °C/min is clear and obvious, so the best heating rate for the differential thermal analysis of the Tartary buckwheat flour is 10 °C/min. In summary, the best conditions for the final selection of the Tartary buckwheat flour heat analysis test are: the heating rate is 10 °C/min, and the sample mass is 3.000 g.

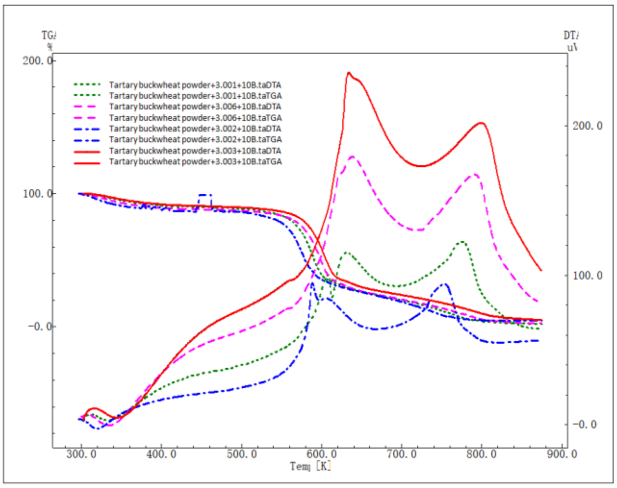

Figure 2. Influence of different heating rates on DTA/TGA curves

3.2 Analysis of the thermal decomposition process of Tartary buckwheat flour

The DTA and TGA curves were drawn by the preliminary experiment, and the extrapolated onset temperature of each reaction was found using TA60 software [8] as shown in the figure below.

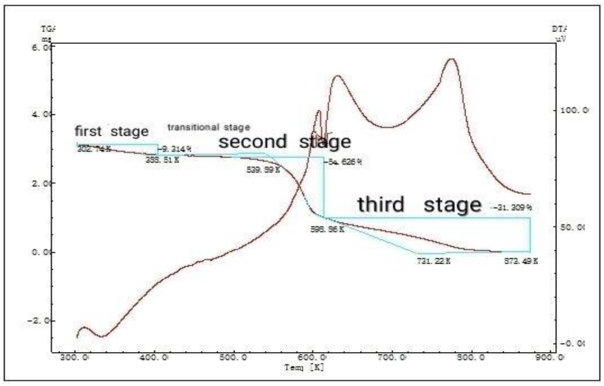

Figure 3. Analytical diagram of thermal analysis image

As the temperature increases, the first stage is the dehydration stage, and the temperature at which the reaction starts is 300K~388.51K, that is, 30°C-115.00°C. The weight loss rate of the Tartary buckwheat flour in this stage is 9.314 %.

The DTA curve in the transition stage is relatively stable, the mass change is not obvious, the reaction temperature is: 388.51K-539.89K, namely 115.00°C-266.74°C. At this stage, there is no significant mass change in the Tartary buckwheat flour, and the temperature range is a suitable for processing.

The second stage is the stage where the weight loss of Tartary buckwheat flour is the largest, and the reaction temperature is 539.89K-593.86K, namely 266.74°C-320.74°C. At this stage, the weight loss rate of Tartary buckwheat flour is the largest in the whole thermal decomposition process, reaching 54.626%. The processing temperature should be lower than this temperature range, and this paper mainly studies the kinetic model of this stage.

In the third stage, the Tartary buckwheat flour undergoes carbonization reaction and other reactions, and the weight loss is 31.309%. The reaction temperature is 593.86K~873.49K, namely 320.74°C~600.34°C. The third stage actually contains two reactions. Because the temperature is too high at this stage, such high temperature processing is generally not used in the actual processing, so we merge these two reactions into the third stage.

In summary, the free water content in the Tartary buckwheat flour can be roughly calculated to be 9.314%, and the temperature at which the Tartary buckwheat flour begins to decompose largely is 539.87 K, namely 266.74 °C. The temperature should be controlled during the processing of Tartary buckwheat flour products so that the processing temperature of Tartary buckwheat flour is lower than this temperature.

3.3 Derivation of thermokinetics parameter solving formula

3.3.1 Derivation of reaction kinetics formula

According to the mass equation, the reaction rate formula can be expressed as:

$$\frac{d\alpha}{dT} = K(T) \times f(\alpha) \times \frac{1}{\beta} \tag{2}$$

$$Try\ out: \alpha\ is\ conversion\ rate$$
$$\mathrm{T}\ is\ temperate,\ the\ unit\ is\ K$$
$$\beta\ is\ heating\ rate,\ the\ unit\ is\ {}^{\circ}C/min$$

According to Arrhenius equation, there is [9]:

$$\mathrm{K(T)} = \mathrm{A}\exp(-\frac{E}{RT}) \tag{3}$$

where: A is the frequency factor; E is the activation energy, the unit is J/mol; R is the molar gas constant; T is the thermokinetic temperature.

Substitute (3) into (2) to get:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp(-\frac{E}{RT}) \times f(\alpha) \tag{4}$$

Separate variables and integrate, then we can get:

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_0^{T} \frac{A}{\beta}\exp(-\frac{E}{RT})dT \tag{5}$$

Unfortunately, the integral on the right side of the equation does not converge in the right domain of T=0, so an accurate analytical solution cannot be obtained, therefore the Stava-Sestak integral formula is used to approximate it.

3.3.2 Kinetics mode function

$$G(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} \quad \text{Order:} \tag{6}$$

$G(\alpha)$ is a kinetics mode function. The correct choice of the mode function has a very important influence on the solving of the kinetic parameters [10]. This paper compares the commonly used 30 [11] kinds of solid-phase non-isothermal kinetics mode functions, as shown in Table 1:

Table 1. Solid phase non-isothermal kinetic mode function table

Function No.	Kinetics mode function
1	α^2
2	$\alpha+(1-\alpha)\ln(1-\alpha)$
3	$(1-2/3\alpha)-(1-\alpha)^{2/3}$
4, 5	$[1-(1-\alpha)^{1/3}]^n$ (n=2,1/2)
6	$[1-(1-\alpha)^{1/2}]^{1/2}$
7	$[(1+\alpha)^{1/3}-1]^2$
8	$[1/(1+\alpha)^{1/3}-1]^2$
9	$-\ln(1-\alpha)$
10, 11, 12, 13, 14, 15, 16	$[-\ln(1-\alpha)]^n$ (n=2/3,1/2,1/3,4,1/4,2,3)
17, 18, 19, 20, 21, 22	$1-(1-\alpha)^n$ (n=1/2,3,2,4,1/3,1/4)
23, 24, 25, 26, 27	α^n (n=1/2,3,2,4,1/3,1/4)
28	$(1-\alpha)^{-1}$
29	$(1-\alpha)^{-1}-1$
30	$(1-\alpha)^{-1/2}$

Firstly, the 30 kinds of kinetic mode functions were respectively substituted into the Stava-Sestak equation to calculate the apparent activation energy and frequency factor respectively. Compared with the FWO method, the kinetic mode functions conforming to the Stava-Sestak method were selected, and then the pattern matching method was adopted to select a set of kinetic mode functions with the best linear fit, and the mechanism function calculated by this kinetic mode function was taken as the most probable mechanism function for the thermal decomposition of Tartary buckwheat flour to establish the thermal decomposition kinetics equation and to give theoretical predictions of the thermal decomposition reaction of Tartary buckwheat flour.

3.3.3 Stava-Sestak method

The Stava-Sestak method [12, 13] calculates the kinetic parameters by substituting various possible kinetic mode functions into the Stava-Sestak equation and calculating the regression equation, then it combines with the kinetic parameters obtained by the FWO method and the linear fit of the regression equation to select the best most approximate mechanism function.

By approximately solving formula (5) we can get formula of the Stava-Sestak method:

$$lg\ G\ (\alpha) = lg\frac{AE}{R\beta} - 2.315 - \frac{0.4567\mathrm{E}}{RT} \tag{7}$$

By substituting the 30 kinds of kinetic mode functions of Table 1 into the $G(\alpha)$ of above formula, a linear regression equation of lg$G(\alpha)$ and 1/T is obtained by using the least squares method:

$$y = ax - b$$

Then according to the linear regression equation there are:

$$\begin{aligned} E &= a \times R \div 0.4567 \\ \lg A &= b + 2.315 + \lg \beta + \lg R - \lg E \end{aligned} \quad (8)$$

3.3.4 FWO method

By approximately solving formula (6) we can get the FWO equation [14]:

$$\lg(\beta) = \lg(\frac{AE}{RG(\alpha)}) - 2.315 - 0.456\frac{E}{RT} \quad (9)$$

where: β is the heating rate; A is the frequency factor; R is the ideal gas constant, takes 8.314 here; E is the activation energy, the unit is KJ/mol; T is the reaction temperature, the unit is K (Kelvin).

By analyzing formula (9) we can find that, lgβ has a linear relationship with 1/T. In the actual calculation, α takes the temperatures of 0.10, 0.20, and 0.30, respectively. The linear regression equation of the two are obtained by the least square method. The activation energy E is obtained from the slope, and the frequency factor A is obtained from the intercept.

An outstanding advantage of the FWO method over other methods is that it is not necessary to determine the kinetic mode function. For complex high molecular substances such as Tartary buckwheat flour, it is often impossible to determine its specific reaction, so it causes great difficulty for the determination of the kinetic mode function [15]. The apparent activation energy of Tartary buckwheat flour can be calculated more accurately using the FWO method. This outstanding advantage of FWO method is also often used to test the correctness of the hypothetical kinetic mode function. The appropriate kinetic mode function was screened by comparing with the results calculated by the Stava-Sestak method.

3.4 Solving thermal analysis kinetic parameters

3.4.1 Selection of kinetic data

Six temperature points are selected starting from 561.68K with a gradient of 4K, and the conversion rate and temperature are read as shown in the following table.

Table 2. Kinetic data T-α table

Conversion rate: α (%)	1.353	3.052	5.255	7.992	11.328
Temperature: T (K)	559	563	567	571	575

According to the Stava-Sestak equation, we can know that lg$G(\alpha)$ and 1/T present a linear relationship, and the linear relationship equation can be obtained via pattern matching and the least squares method, then the activation energy E and the frequency factor A of the reaction can be solved by the slope and intercept of the linear equation.

The results of the calculation are shown in Table 3 below:

Table 3. Solution results of 30 kinds of kinetics mode function

Data points	Data point 1	Data point 2	Data point 3	Data point 4	Data point 5
Conversion rateα	0.013530000	0.030520000	0.052550000	0.079920000	0.113280000
1/T	0.001788909	0.001776199	0.001763668	0.001751313	0.001739130
Function 1	-3.737404407	-3.030830941	-2.558854559	-2.194689050	-1.891693519
Function 2	-4.036466839	-3.327397052	-2.852140208	-2.483827982	-2.175666774
Function 3	-4.689022505	-3.979116468	-3.502755731	-3.133039911	-2.823117122
Function 4	-4.687708807	-3.976130260	-3.497561675	-3.125038467	-2.811591963
Function 5	-1.171927202	-0.994032565	-0.874390419	-0.781259617	-0.702897991
Function 6	-1.084127844	-0.906546609	-0.787317948	-0.694712536	-0.617009761
Function 7	-4.687708807	-3.976130260	-3.497561675	-3.125038467	-2.811591963
Function 8	-4.699434871	-4.002511093	-3.542838431	-3.193643837	-2.908445654
Function 9	-1.865747503	-1.508702282	-1.267758158	-1.079382860	-0.920001539
Function 10	-1.243831668	-1.005801522	-0.845172106	-0.719588573	-0.613334360
Function 11	-0.932873751	-0.754351141	-0.633879079	-0.539691430	-0.460000770
Function 12	-0.621915834	-0.502900761	-0.422586053	-0.359794287	-0.306667180
Function 13	-7.462990010	-6.034809130	-5.071032633	-4.317531440	-3.680006158
Function 14	-0.466436876	-0.377175571	-0.316939540	-0.269845715	-0.230000385
Function 15	-3.731495005	-3.017404565	-2.535516317	-2.158765720	-1.840003079
Function 16	-5.597242508	-4.526106847	-3.803274475	-3.238148580	-2.760004618
Function 17	-2.168255688	-1.813093218	-1.574635897	-1.389425072	-1.234019521
Function 18	-1.397470203	-1.051616295	-0.825327988	-0.655393881	-0.518849042
Function 19	-1.570620193	-1.221063896	-0.989960963	-0.814025201	-0.670139306
Function 20	-1.275466020	-0.933286462	-0.711742216	-0.547664786	-0.418191629
Function 21	-2.343854404	-1.988065130	-1.748780837	-1.562519233	-1.405795982
Function 22	-2.468546799	-2.112443830	-1.872745316	-1.685956806	-1.528571870
Function 23	-1.868702203	-1.515415471	-1.279427280	-1.097344525	-0.945846760
Function 24	-2.803053305	-2.273123206	-1.919140919	-1.646016787	-1.418770139
Function 25	-0.934351102	-0.757707735	-0.639713640	-0.548672262	-0.472923380
Function 26	-0.622900734	-0.505138490	-0.426475760	-0.365781508	-0.315282253
Function 27	-0.467175551	-0.378853868	-0.319856820	-0.274336131	-0.236461690
Function 28	0.005916118	0.013461146	0.023443700	0.036174410	0.052213496
Function 29	-1.862786086	-1.501954325	-1.255983580	-1.061170115	-0.893633264
Function 30	0.002958059	0.006730573	0.011721850	0.018087205	0.026106748

The linear regression equation for each kinetic mode function is obtained by least squares method, y=ax+b.

The results are shown in Table 4:

Table 4. Activation energy results obtained from the 30 kinds of kinetic mode functions

Kinetic mode functions	a	b	R^2	E(kJ/mol)
Function 1	-36432.00	61.578	0.9729	663.22
Function 2	-36734.00	61.818	0.9737	668.72
Function 3	-36836.00	61.348	0.9740	670.58
Function 4	-37040.00	61.714	0.9745	674.29
Function 5	-9260.10	15.428	0.9745	168.57
Function 6	-9221.90	15.448	0.9741	167.88
Function 7	-37040.00	61.714	0.9745	674.29
Function 8	-35335.00	58.656	0.9700	643.25
Function 9	-18674.00	31.609	0.9753	339.95
Function 10	-12449.00	21.073	0.9753	226.62
Function 11	-9336.90	15.805	0.9753	169.97
Function 12	-6224.60	10.536	0.9753	113.31
Function 13	-74695.00	126.440	0.9753	1359.78
Function 14	-4668.50	7.902	0.9753	84.98
Function 15	-37348.00	63.210	0.9753	679.90
Function 16	-56022.00	94.828	0.9753	1019.85
Function 17	-18444.00	30.896	0.9741	335.76
Function 18	-17331.00	29.679	0.9678	315.50
Function 19	-17768.00	30.288	0.9704	323.45
Function 20	-16903.00	29.037	0.9651	307.71
Function 21	-18520.00	30.857	0.9745	337.14
Function 22	-18558.00	30.801	0.9747	337.83
Function 23	-18216.00	30.789	0.9729	331.61
Function 24	-27324.00	46.184	0.9729	497.42
Function 25	-9108.10	15.395	0.9729	165.80
Function 26	-6072.10	10.263	0.9729	110.53
Function 27	-4454.00	7.697	0.9729	81.08
Function 28	-925.42	1.659	0.9770	16.84
Function 29	-19142.00	32.448	0.9775	348.47
Function 30	-462.71	0.830	0.9770	8.42

By comparison, it is found that the 30 kinds of kinetic mode functions have a significant effect on the solving of the activation energy of the Tartary buckwheat flour, correctly determining the kinetic mode function of Tartary buckwheat flour is especially important for the solving of kinetic parameters. As Tartary buckwheat flour is a kind of macromolecular organic matter, its reaction often cannot be directly determined, and its reaction order cannot be directly determined as well, so we can't determine its kinetic mode function by physical or chemical methods. Therefore, for the solving of kinetic mode functions of complex organic matter, the kinetic mode function is often replaced by using the approximate substitution method. This optimal substitution function is the most probable kinetic mode function, and its corresponding mechanism function is called the most probable mechanism function.

According to general experience, the activation energy is a positive number, and substances with an activation energy more than 400 KJ/mol are generally considered to be extremely resistant to chemical reactions at normal temperatures. Therefore, perform a preliminary screening on the obtained results and compare them with the results of the activation energy obtained by the FWO method below, and then solve the most probable kinetic mode function of the thermal decomposition of Tartary buckwheat flour.

3.4.2 Solving activation energy and frequency factor by FWO method

On the thermal analysis images of heating rates of 5°C/min, 10°C/min, 15°C/min, and 20°C/min, respectively select temperature points of a conversion rate of 10%, 20%, and 30%, then the follow table is obtained:

Table 5. Data points calculated by FWO method

Conversion rate	β(°C/min)	T(K)	1/T	Lgβ
10%	5	568.20	0.001760	0.698970004
	10	573.86	0.001743	1.000000000
	15	579.35	0.001726	1.176091259
	20	583.45	0.001714	1.301029996
20%	5	575.51	0.001738	0.698970004
	10	583.00	0.001715	1.000000000
	15	589.94	0.001695	1.176091259
	20	594.55	0.001682	1.301029996
30%	5	583.58	0.001714	0.698970004
	10	589.69	0.001696	1.000000000
	15	597.20	0.001674	1.176091259
	20	602.12	0.001661	1.301029996

Substitute into the FWO equation and draw a diagram:

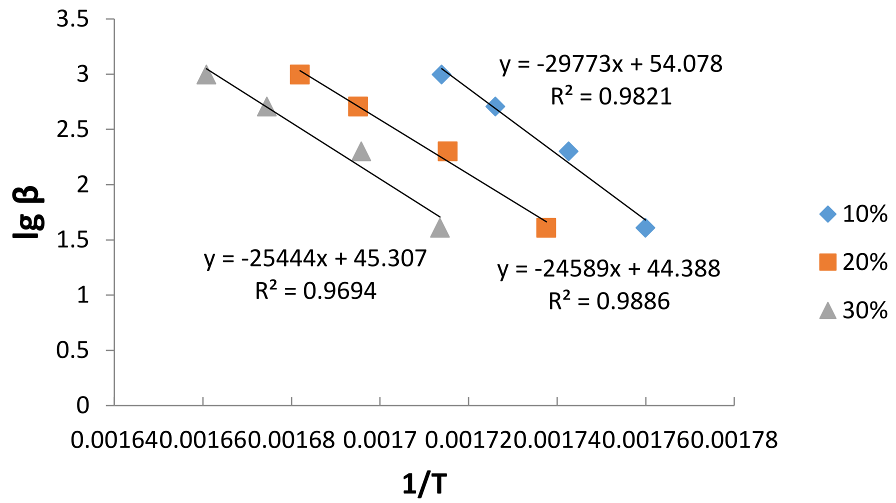

Figure 4. FWO method results

According to FWO equation, there is:

$$\lg(\beta) = \lg(\frac{AE}{RG(\alpha)}) - 2.315 - 0.456\frac{E}{RT}$$

The calculation results are shown in the following table.

Table 6. FWO method calculation results

Conversion rate (%)	Activation energy E(KJ/mol)	LgA	LnA
10%	235.38	19.14	44.07
20%	194.40	19.52	44.95
30%	201.15	19.68	45.32

Comparison of the activation energies of different conversion rates shows that, the activation energies of the three-stage conversion rate are not the same. The activation energy of the first stage is the largest, which is because the complexity of the components of Tartary buckwheat flour and its reactions has led to this reaction not being an elementary reaction, but a result caused by many simultaneous reactions. Since the most concerned issue in food processing should be the temperature at which the Tartary buckwheat flour begins to decompose, so here we select the activation energy of the first stage reaction with a conversion rate of 10% for our research, that is: E = 235.38 KJ/mol, LnA = 44.07.

3.5 Determination of the most probable mechanism function

Compare the 30 kinds of kinetic mode functions and solve their activation energies and errors as shown in Table 7, the allowable range of error is:

$$\left|\frac{E_0 - E_s}{E_0}\right| \le 0.3$$

The activation energies and frequency factors obtained by the 30 kinetic mode functions are compared with the results obtained by the FWO method. It can be seen that the influence of the selection of the kinetic mode function on the activation energy solution is quite significant, and determining an appropriate kinetic mode function is very important for solving the kinetic parameters of the Tartary buckwheat flour.

Table 7. Error of activation energy solved by 30 kinds of kinetic mode functions

Kinetic mode functions	R^2	E (kJ/mol)	E Error
Function 1	0.9729	663.22	1.817634
Function 2	0.9737	668.72	1.840990
Function 3	0.9740	670.58	1.848879
Function 4	0.9745	674.29	1.864656
Function 5	0.9745	168.57	0.283828
Function 6	0.9741	167.88	0.286783
Function 7	0.9745	674.29	1.864656
Function 8	0.9700	643.25	1.732792
Function 9	0.9753	339.95	0.444238
Function 10	0.9753	226.62	0.037200
Function 11	0.9753	169.97	0.277889
Function 12	0.9753	113.31	0.518592
Function 13	0.9753	1359.78	4.776876
Function 14	0.9753	84.98	0.638940
Function 15	0.9753	679.90	1.888477
Function 16	0.9753	1019.85	3.332715
Function 17	0.9741	335.76	0.426450
Function 18	0.9678	315.50	0.340371
Function 19	0.9704	323.45	0.374169
Function 20	0.9651	307.71	0.307270
Function 21	0.9745	337.14	0.432328
Function 22	0.9747	337.83	0.435267
Function 23	0.9729	331.61	0.408817
Function 24	0.9729	497.42	1.113225
Function 25	0.9729	165.80	0.295584
Function 26	0.9729	110.53	0.530387
Function 27	0.9729	81.08	0.655530
Function 28	0.9770	16.84	0.928428
Function 29	0.9775	348.47	0.480433
Function 30	0.9770	8.42	0.964214

By comparison we find that the kinetic mode functions that satisfy the conditions are: No. 4, 6, 10, 11. Then by comparing the linear fits, we find that the No.10 function has the highest linear fit and its activation energy is also significantly closer to that obtained by the FWO method. Therefore, function 10 is selected as the kinetic mode function for the Tartary buckwheat flour, that is:

$$G(\alpha)=[-\ln(1-\alpha)]^{2/3}$$

The most probable mechanism function of the thermal decomposition of Tartary buckwheat flour calculated by above formula is:

$$f(\alpha)=\frac{3}{2}[-\ln(1-\alpha)]^{1/3}\times(1\text{-}\alpha)$$

3.6 Establishment of the kinetic equation of Tartary buckwheat flour

The activation energy calculated by the FWO method is: E=235.38 KJ/mol

The frequency factor is: lnA=44.07.

Using Stava-Sestak method, the activation energies calculated by 30 kinds of kinetic mode functions are compared and then perform logical analysis of its linear fitness to screen out the most probable mechanism function [16].

In summary, the kinetic equation is obtained as follows:

$$\frac{d\alpha}{dt}=\exp\{44.07-\frac{235384.32}{RT}\}\times\frac{3}{2}(1-\alpha)\bullet[-\ln(1-\alpha)]^{1/3}$$

Separate the variable and integrate both sides of the equation simultaneously to get:

$$[-\ln(1-\alpha)]^{\frac{2}{3}}=\exp\{44.07-\frac{235384.32}{RT}\}\times t$$

A thermal analysis kinetic model for the Tartary buckwheat flour is obtained, then predict the kinetic model of the Tartary buckwheat flour.

3.7 Verification of the thermal decomposition kinetic model of the Tartary buckwheat flour

Take the 560 K-570 K temperature range from the TGA diagram and read the derivative of conversion rate with respect to time, and then compare it with the theoretical value calculated by the kinetic model, as shown in the following table:

Table 8. Comparison between model calculation results and actual values

time (sec)	T (K)	Actual results	Model results	Accuracy
1535	560.935706	0.001051424	0.000901308	0.857226
1536	561.081396	0.001052325	0.000917051	0.871452
1537	561.280493	0.001057285	0.000938054	0.887229
1538	561.439795	0.001071713	0.000956029	0.892057
1539	561.599493	0.001075771	0.000974079	0.905471
1540	561.795813	0.001103724	0.000995663	0.902094
1541	561.943396	0.00112717	0.001013561	0.899209
1542	562.12171	0.001160083	0.001034733	0.891947
1543	562.319312	0.001193898	0.001057676	0.885902
1544	562.4578	0.001202915	0.001075896	0.894407
1545	562.653601	0.001203817	0.001100156	0.91389
1546	562.842291	0.001199308	0.001123523	0.936809
1547	562.978888	0.001212384	0.00114199	0.941938
1548	563.179694	0.001217343	0.001167899	0.959383
1549	563.34809	0.001225459	0.001190811	0.971727
1550	563.526709	0.001235378	0.001214422	0.983037
1551	563.695105	0.001249806	0.00123803	0.990578
1552	563.858893	0.001282268	0.001261672	0.983938
1553	564.020514	0.001306615	0.001285007	0.983463
1554	564.221594	0.00133547	0.001313467	0.983524
1555	564.369208	0.001354407	0.001336646	0.986887
1556	564.539496	0.001377852	0.00136268	0.988989
1557	564.735297	0.001377852	0.001391827	0.989857
1558	564.890692	0.001377852	0.001417177	0.971459
1559	565.057104	0.001373794	0.001443886	0.948979
1560	565.250494	0.001368384	0.001474303	0.922596
1561	565.405096	0.00138191	0.001500079	0.914488
1562	565.584509	0.001387771	0.001530108	0.897435
1563	565.761115	0.001411216	0.001559852	0.894675
1564	565.920599	0.001425193	0.001587466	0.88614
1565	566.110999	0.001449089	0.001620617	0.88163
1566	566.273901	0.001467124	0.001650111	0.875275
1567	566.437506	0.001495979	0.001679962	0.877015
1568	566.625098	0.001519875	0.001714005	0.872273
1569	566.788794	0.001528442	0.001745705	0.857853

It can be seen from the data in above table that the solving of kinetic equations has a good simulation of the decomposition of Tartary buckwheat flour. In the temperature range of 560 K~570 K, the reaction rate obtained by TGA images and the values of the model are on the same order of magnitude, the accurate ranges are all above 85%, so the established kinetic mode function is relative reliable. Also, we can see from the table that the accuracy decreases with the increase of temperature, this may be determined by the complex components of the Tartary buckwheat flour itself. This conclusion has also been verified when using FWO method, under a higher temperature, the activation energy, frequency factor and most probable mechanism function have changed [17-21]. However, in food processing, what we concern most is the first stage reaction, so we will not further solve and discuss the reactions in later stages here.

4. DISCUSSION

4.1 Determination of proper processing temperature

By thermal analysis, we can get the temperature at which the Tartary buckwheat flour begins to decompose is 539.89 K or 266.74 °C. In order to reduce the reaction of Tartary buckwheat flour during the actual production and processing, the processing temperature should be lower than this temperature.

4.2 Determination of the best experimental conditions for the kinetic test of Tartary buckwheat flour

By comparing the thermal analysis images obtained by different masses and different heating rate conditions, the best conditions for obtaining the thermal analysis test of the Tartary buckwheat flour by selecting sharp and obvious peak images are: the sample mass is 3.000g, and the heating rate is: 10 °C/min.

4.3 Determination of the thermal decomposition stages of Tartary buckwheat flour

Through the thermal decomposition image of Tartary buckwheat flour, we can get that the decomposition of Tartary buckwheat flour can be divided into four stages: the initial dehydration stage, the transition stage, the first reaction stage, and the second reaction stage. Among them, the Tartary buckwheat flour in the transition stage is the most stable, and it is the optimal temperature range for processing, which is 115.00 °C~266.74 °C. In the first stage, the weight loss of the Tartary buckwheat flour is the most serious, and the onset temperature of the reaction is 266.74 °C, and this temperature should be avoided in order to prevent mass loss during processing. The second stage is the final reaction stage of the Tartary buckwheat flour, in which the Tartary buckwheat flour begins to undergo carbonization and other reactions.

4.4 Establishment of kinetic model for the thermal decomposition of Tartary buckwheat flour

This paper uses the FWO method to calculate the activation energy of the thermal decomposition reaction of Tartary buckwheat flour to be: 235.38 KJ/mol, frequency factor: LnA = 44.07. By comparing the activation energies solved by the 30 kinds of kinetic mode functions and the activation energy solved by the FWO method, and by comparing the linear fits of the 30 kinetic mode functions, we can find that the No.10 kinetic mode function is the most probable kinetic mode function for the thermal decomposition of Tartary buckwheat flour, that is:

$$\mathrm{G}(\alpha) = [-\ln(1-\alpha)]^{2/3}$$

By calculation we can get the most probable mechanism function of the thermal decomposition of Tartary buckwheat flour as:

$$f(\alpha) = \frac{3}{2}[-\ln(1-\alpha)]^{1/3} \times (1\text{-}\alpha)$$

Further, the thermal decomposition kinetic model of Tartary buckwheat flour is obtained as follows:

$$\frac{d\alpha}{dt} = \exp\{44.07 - \frac{235384.32}{RT}\} \times \frac{3}{2}(1-\alpha) \bullet [-\ln(1-\alpha)]^{1/3}$$

Separate the variable from the above formula and integrate to get:

$$[-\ln(1-\alpha)]^{2/3} = \exp\{44.07 - \frac{235384.32}{RT}\} t$$

It is found through verification that this model has a good simulation effect in the temperature range of 560~570K, which has certain guiding significance for the actual production.

REFERENCES

[1] Wang JB. (2013). Development and quality analysis of Tartary buckwheat compound yogurt. Xihua University, 2013

[2] Yin LG, Zhong G, Zeng FK, Min YP. (2002). Buckwheat processing. Cereals & Oils (9): 39-41. http://doi.org/10.3969/j.issn.1008-9578.2002.09.018

[3] Pu YL. (2012). Overview of application of thermal analysis techniques. Guangdong Chemical Industry 39(06): 45, 44. http://doi.org/10.3969/j.issn.1007-1865.2012.06.022

[4] Zhu JP. (2015). Study on thermal analysis for the distinguish of black buckwheat tea and raw buckwheat. Food Research and Development 36(09): 13-16. http://doi.org/ 10.3969/j.issn.1005-6521.2015.09.004

[5] Ren YL, Cheng BW, Xu L, Li ZH, Jiang AB, Lu YC. (2009). Non-isothermal decomposition kinetics of novel fire retarded polyacrylonitrile copolymer in air. Acta Chimica Sinica 67(18): 2127-2132. http://doi.org/10.3321/j.issn:0567-7351.2009.18.012

[6] Kissinger HE. (1956). Variation of peak temperature with heating rate in differential thermal analysis. Journal of Research of the National Bureau of Standards 57(4): 217-221.

[7] Moon C, Sung Y, Ahn S, Kim T, Choi G, Kim D. (2013). Effect of blending ratio on combustion performance in blends of biomass and coals of different ranks. Experimental Thermal and Fluid Science (47): 232-240. http://doi.org/10.1016/j.expthermflusci.2013.01.019

[8] Zhang K, Zhang K, Cao Y, Pan W. (2013). Co-combustion characteristics and blend-ing optimization of

tobacco stem and high-sulfur bituminous coal based o-n thermogravimetric and mass spectrometry analyses. Bioresources Technology 131: 325-332. http://doi.org/10.1016/j.biortech.2012.12.163

[9] Jiang C. (2015). Optimization of coal spontaneous combustion mechanism function by artificial fish swarm algorithm. Liaoning University of Engineering and Technology.

[10] Zou SP, Wu YL, Yang MD, Li C, Tong JM. (2009) Pyrolysis characteristics and kinetics of the marine microalgae Dunaliella tertiolecta using thermogravimetric analyzer. Bioresource Technology 101(1) 359-365. http://doi.org/10.1016/j.biortech.2009.08.020

[11] Wang WW. (2012). biomass characteristics research based on TGA test and BP neural network. North China Electric Power University.

[12] Lai YH, Lu MX, Ma CY, Shi MH. (2001). Research on pyrolysis characteristics of agricultural residues under liner heating temperature. Journal of Combustion Science and Technology 7(3): 245-248. http://doi.org/10.3321/j.issn:1006-8740.2001.03.009

[13] Liu RH, Yuan HR, Xu L. (2007). Kinetic study of maize straw pyrolysis. Acta Energiae Solaris Sinica 28(5): 527-531. http://doi.org/10.3321/j.issn:0254-0096.2007.05.014

[14] Liu ZH, Xu GH, Zhang HL. (2006). Thermal analysis instrument. Beijing: Chemical Industry Press, 2006

[15] Hu RZ, Shi QZ. (2001). Thermal analysis dynamics. Beijing: Science Press.

[16] Wang MF, Jiang EC, Zhou L. (2009). Kinetic analysis of cornstalk pyrolysis. Transactions of The Chinese Society of Agricultural Engineering 25(2): 204-207.

[17] Alonso M, Borrego A G, Alvarez D, Menéndez R. (2001). Reactivity study of chars obtained at different temperatures in relation to their petrographic characteristics. Fuel Processing Technology 69(3): 257-272. http://doi.org/10.1016/S0378-3820(00)00146-6

[18] Zhao M, Wu W, Lu M, Wei XY. (2002). Pyrolysis kinetics of rice straw. Transactions of The Chinese Society of Agricultural Engineering 18(1): 107-110. http://doi.org/ 10.1007/s11769-002-0038-4

[19] Stenseng M, Jensen A, Dam-Johansen K. (2001). Investigation of biomass pyrolysis by thermogravimetric analysis and differential scanning calorimetry. Journal of Analytical and Applied Pyrolysis 58(1): 765-780. http://doi.org/ 10.1016/S0165-2370(00)00200-X

[20] Jiang L, Wang YZ, Yu T, Wu T. (2013). Mechanism of synergistic corrosion of sulfur and chlorine components in biomass mixed coal combustion. Power Station System Engineering (03): 1-4

[21] Liu HX, Cao YB, Li YX. (2009). Application of thermal analysis in the analysis of edible spices and flavors. Food Science 30(17): 349-354. http://doi.org/10.1007/978-3-540-85168-4_52

APPENDIX

Symbol description

E	activation energy, $KJ \cdot mol^{-1}$
G(α)	kinetics mode function
TGA	curve: thermogravimetric analysis curve
DTA	curve: differential thermal analysis curve
K	thermokinetic temperature, unit in K (Kelvin)
α	solid sample mass conversion rate
T	temperature, K
β	differential thermal analysis heating rate: °C/min
f(α)	reaction mechanism function
R	ideal gas constant, 8.314 $KJ \cdot mol^{-1}$
Exp	natural logarithm
E_0	activation energy calculated by the FWO method, $KJ \cdot mol^{-1}$
E_s	activation energy calculated by the Stava-Sestak method, $KJ \cdot mol^{-1}$
t	time, unit: second