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Thermal behavior and kinetic decomposition of sweet potato starch by non-isothermal procedures

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Abstract In this study, X-ray diffraction, thermogravimetric analysis and differential scanning calorimetry (DSC) method were used to analyze the main characteristics of sweet potato starch, and to analyze the thermal degradation process of sweet potato starch. Specifically, X-ray diffraction to study its structure, thermogravimetric analysis to study the thermal degradation kinetics, and differential scanning calorimetry to study the thermogram of sweet potato starch. The thermal decomposition kinetics of sweet potato starch was examined within different heating rates in nitrogen atmosphere. Different models of kinetic analysis were used to calculate the activation energies using thermogravimetric data of the thermal degradation process. Activation energies obtained from Kissinger, Flynn-Wall-Ozawa, and Šatava-Šesták models were 173.85, 174.87 and 174.34 kJ/mol, respectively. The values of activation energy indicated that the thermal degradation of the sweet potato starch was a single reaction mechanism or the combination of multi-reaction mechanisms. The differential scanning calorimetry analysis show that two decomposition stages were presented: the first at a low temperature involves the decomposition of long chain; and

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the second at a high temperature represents the scission of glucose ring. This information was helpful to design the processing process of many natural polymers. Thermogravimetric Fourier transform-infrared (TG–FTIR) analysis showed that the main pyrolysis products included water, methane, carbon dioxide, ammonia, and others.

Keywords: Starch; Kinetic analysis; Thermal degradation; Activation energy; Mechanism

1 Introduction

Starch is one of the most actively investigated biopolymers made from rice, potato, and maize, which is an unusual material with more complicated structure than those of common polymers. This polymer is a mixture of amylopectin, highly branched polysaccharides with a α -1.4 backbone chains linked by α -1.6 bonds, and amylose, a dominant linear structure of α -1.4-linked glucose units [1].

Starch decomposes when heated, and the degradation of starch is a complicated process. In practical applications, it may be enough to consider the basic characteristics of the thermal decomposition process using some simple mechanisms. From the point of view of science and industry, the thermal degradation and stability is a very important problem. The heat treatment of starch has been widely used in the food industry and starch based materials [2,3].

Thermal analysis is a group of techniques for the rapid assessment of thermal stability, decomposition parameters, adsorbed water content, crystal water content, and the thermal degradation dynamics [4]. Thermogravimetric (TG) and differential scanning calorimetry (DSC) methods have been used as a prevalent technique to evaluate the thermal behavior of polymers. The assessment of thermal stability and degradation dynamics of the starch is very important in practical applications. Non-isothermal tests are mostly preferred for the dynamic analysis. To this end, many models, such as Kissinger, Flynn-Wall-Ozawa, Šatava-Šesták, and Broido, were established to study the dynamic parameters of various materials based on the Arrhenius equation [5–8].

There have been some reports about the degradation of raw or processed starches from many different sources using different thermal analysis models [1,2]. Dewatering and pyrolysis were usually deemed as the two main stages related to the decomposition mechanism of starch. The distinctive microstructure of starch and its multiple phase transformation in

the process of heating give an excellent approach to explain the structure-processing-performance relationship. The achievements in the field can increase the knowledge of polymer materials, in particular, that of natural polymer. Thermogravimetric analysis was used to investigate the pyrolysis of corn starches with different amylose/amylopectin ratios in nitrogen [9]. The result showed that the decomposition of starches with a higher amount of amylopectin needed more activation energy. The effect of modification on the thermal property of yellow sorghum starch was investigated [10]. Differential scanning calorimetry testes showed that the gelatinization temperature of modified yellow sorghum starches were lower than those of natural starch. Thermogravimetric analysis was used to study the thermal behavior of mixtures of rice bran and high density polyethylene under nitrogen atmosphere, and the results were compared with those of individual materials [2].

The main purpose of this study was to investigate the thermal behavior of sweet potato starch by TG and DSC. In this study, three methods were used: X-ray diffraction (XRD) to study its structure, TG to investigate the thermal degradation processing, and DSC to survey the thermogram of sweet potato starch. The thermal degradation data were used to analyze the thermal degradation kinetics with different isoconversional models like Kissinger, Šatava-Šesták, Flynn-Wall-Ozawa, and Coast-Redfern models, which were used to evaluate the activation energies of sweet potato starch. The decomposition activation energies got in this study can help to evaluate the thermal stability of sweet potato starch used in food and chemical processing industry.

2 Experimental procedure

2.1 Materials

The sweet potato starches used in this study were purchased from Guiyang Jincheng CO., Ltd. (Guizhou, China), and the moisture content was less than 1%. The dried samples were crushed and sieved using a sieve of 0.15 mm in order to get uniform particles for TG/DSC measurements. The samples were kept in airtight packages.

2.2 X-ray diffraction

The X-ray diffraction was measured using a diffractometer (Siemens D5000) instrument, which was operated at 40 kV and 40 mA, and 2θ range from 5° to 72° with a step size or sampling interval of 0.02° . From the XRD patterns, the interplanar spacings (d) were calculated by Bragg's equation. In order to get the crystallization fraction of sweet potato starch, the software MDI Jade 5.0 [24] was used.

2.3 TG/DSC analysis

A thermal analyzer (STA-625, Reometric Scientific) was used for obtaining TG and DSC curves. The thermal analyses were carried out in alumina crucibles under dry argon atmosphere with a flow rate of 10 ml/min. The starting temperature was 35°C . The rates of heating were 5, 10, 15, and $20^\circ\text{C}/\text{min}$, respectively. Each sample was about 5 mg.

2.4 TG-FTIR test

Thermogravimetry-Fourier transform infrared spectroscopy (TG-FTIR) analysis was obtained by TG 209F3/Tensor 27 (Netzsch/Bruker), heating under N_2 from room temperature to 600°C with a heating rate of $20^\circ\text{C}/\text{min}$.

3 Theoretical background

The thermal degradation speed, $d\alpha/dt$, is the function of degradation temperature, T , and the conversion rate, α ,

$$\frac{d\alpha}{dt} = K(T)f(\alpha), \quad (1)$$

where t is the time, $f(\alpha)$ is the conversion function dependent on the reaction mechanism, K is the rate constant which depends on the temperature and is assumed to follow the Arrhenius equation

$$K = A \exp\left(\frac{E}{RT}\right), \quad (2)$$

where: E – activation energy, A – pre-exponential factor, R – gas constant. Equation (1) is commonly used in the heterogeneous kinetics process [11].

Combination of Eqs. (1) and (2) results in the expression

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha). \quad (3)$$

Thermal degradation speed for $\beta = \frac{dT}{dt} = \text{constant}$, results in the following expression:

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \frac{dT}{dt} = \beta \left(\frac{d\alpha}{dT}\right). \quad (4)$$

Combination of Eqs. (3) and (4) results in the expression

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E}{RT}\right) f(\alpha). \quad (5)$$

This is a prevalent non-isothermal reaction kinetic equation.

3.1 The Kissinger technique

The Kissinger technique is one differential method to research the thermal decomposition behavior. The activation energy, Ea , of thermal degradation is being often determined under linear heating conditions with an equation derived by Kissinger [12]

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) + \ln[n(1 - \alpha_m)]^{n-1} - \frac{Ea}{RT_m}, \quad (6)$$

where T_m and α_m are the temperature and conversion rate at the maximum weight-loss rate, $(d\alpha/dt_m)$, and $n(1 - \alpha_{max})^{n-1}$ is approximatively equal to 1. The Ea value can be calculated from the slope of a plot of $\ln(\beta/T_m^2)$ versus $(1000/T_m)$ at the maximum weight-loss rate. The intercept of the plots of $\ln(\beta/T_m^2)$ vs. $(1000/T_m)$ is

$$I = \ln\left(\frac{AR}{E}\right), \quad (7)$$

and then the $\ln A$ can be calculated using I values.

3.2 Flynn-Wall-Ozawa technique

The kinetic equation obtained by Flynn, Wall and Ozawa on the basis of Arrhenius equation is as follows [13]:

$$\lg \beta = \lg \left[\frac{AE}{RG(\alpha)} \right] - 2.315 - 0.4567 \frac{Ea}{RT}. \quad (8)$$

The Ea value can be calculated from the slope of the plot of $\lg \beta$ vs. $(1000/T)$ for a constant α .

3.3 Šatava-Šesták technique

Šatava-Šesták method is only suitable for the research on solid phase non-fixed-temperature thermal decomposition dynamics [14]. Due to strict mathematical strict illation, the result obtained from this method is quite reasonable. Šatava-Šesták technique equation is as follows:

$$\lg G(\alpha) = \lg \left[\frac{AsEs}{R\beta} \right] - 2.315 - 0.4567 \frac{Es}{RT}, \quad (9)$$

where: Es – the apparent activation energy; As – pre-exponential factor; $G(\alpha)$ – integral mechanism functions. For a fixed heating rate, β_i , the corresponding T and α were substituted into (9), equation obtained is as follows:

$$\lg G(\alpha) = \lg \left[\frac{AsEs}{R\beta_i} \right] - 2.315 - 0.4567 \frac{Es}{RT}, \quad (10)$$

where Es can be obtained according to the slope.

Different kinetic models should be complementary and not competitive.

4 Results and discussion

4.1 Structural analysis of the sweet potato starch

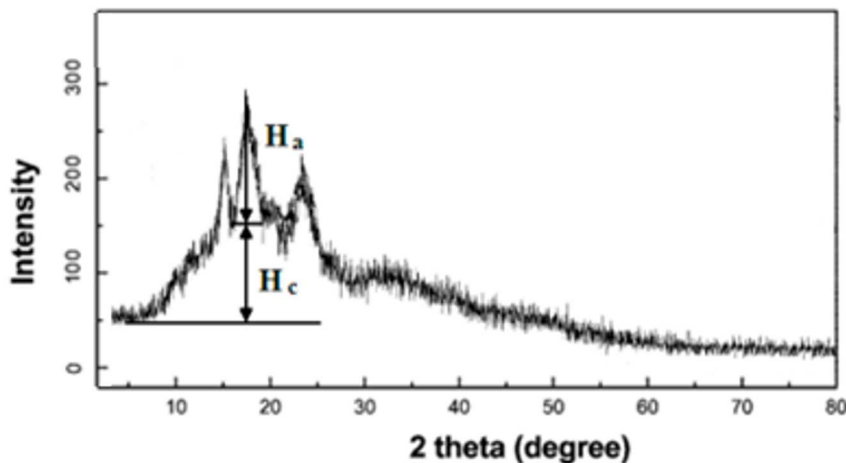


Figure 1: X-ray diffraction patterns of the sweet potato starch sample: H_a and H_c are the crystalline and amorphous profiles, respectively.

The sweet potato starch is mainly composed of amylose and amylopectin whose crystal structure can be researched by XRD. As shown in Fig. 1, the XRD profile of sweet potato starch, the sweet potato starch exhibits three strong peaks at 15.12° , 17.12° , and 23.45° , and three weak peaks at 11.33° , 20.13° , and 26.51° . The crystalline fraction [15] of sweet potato starch was 19%, which is lower than that of banana, cassava and corn starch [1]. The low crystallinity quality of sweet potato starch could be ascribed to the absence of a crystalline amylopectin phase. The contents of amylose and amylopectin were 20.7% and 79.3%, respectively, according to the method reported in the literature [16].

The value of the crystallinity index (X_c) was obtained [15] using the following formula:

$$X_c = \frac{H_c}{(H_c + H_a)}, \quad (11)$$

where H_c and H_a are the intensities for the crystalline and amorphous parts, respectively. The crystallinity index of sweet potato starch is 0.56. Since the crystallinity depends mainly on the crystallization of amylopectin, the H_c value of sweet potato starch is close to amylose content.

4.2 Thermal degradation

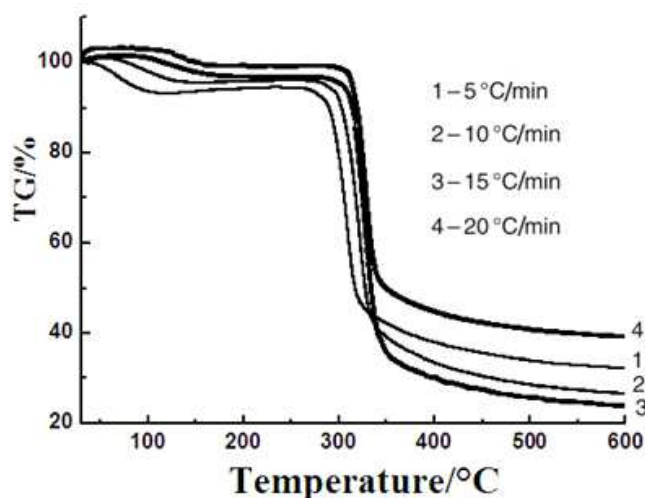


Figure 2: The TG curves of sweet potato starch at different heating rate.

Thermal degradation is a very important part of thermal procedure. Thermogravimetric analysis is a very common method used for research of the thermal degradation process. The thermogravimetric curves of sweet potato starch were measured with different heating rates to study the thermal degradation process with different non-isothermal techniques. Figure 2 shows the thermogravimetric curves of sweet potato starch at different heating rate, respectively. These curves present three primary mass loss parts. The initial temperature of each part was identified as the critical point in the TG curves. The first part is the desiccation which starts instantly when the temperature just rises and ends at about 120 °C. The percentage of mass loss in this part depends on the moisture content of the starch samples. The second part is the main degradation stage, which finishes at around 350 °C. Pyrolysis of starches in this step has been reported to release water, carbon dioxide, carbon monoxide, acetaldehyde, furan and 2-methyl furan [9]. Thermal decomposition has usually been regarded as the important process associated with the degradation mechanisms of starches. The degradation of amylose and amylopectin happened in this step. The last step ends with the formation of carbon black between 350–600 °C. The foremost degradation temperatures were 60, 65, 76, and 80 °C at heating rates of 5, 10, 15, and 20 °C/min, respectively. The TG data of sweet potato starch in Tab. 1 can be obtained from Fig. 2.

Table 1: The TG data of sweet potato starch.

Heating rate	$T_{5\%}/^{\circ}\text{C}$	$T_{10\%}/^{\circ}\text{C}$	$T_{50\%}/^{\circ}\text{C}$	$T_{max}/^{\circ}\text{C}$
5 °C/min	83.07	289.95	316.98	308.37
10 °C/min	286.45	302.84	327.81	321.70
15 °C/min	314.07	318.98	349.88	325.98
20 °C/min	303.49	313.68	333.11	320.32

T_i is the temperature when $\alpha = i$, and T_{max} – the temperature at the maximum decomposition rate

The dehydration process is generally not considered to affect the thermal decomposition of starch, because all water will evaporate before the decomposition of the sample in the open system. Even though the form of the thermogravimetric curves does not change, the starting temperature of decomposition is the same, and the peak temperature increases with the increasing heating rate. This phenomenon is probably ascribed to heat

transfer problem between the sample and equipment [17], and the reason may also be that the rapid heating leads the sample to the given temperature rapidly as a result of the increased thermal lag [18,19]. These curves were used for the calculation of dynamics parameters including activation energy and pre-exponential factor.

4.3 Kinetics of thermal decomposition analysis

In order to get the dynamics parameters and the most probable mechanism of the thermal degradation process, the thermogravimetric curves at different heating rates were dealt with using four kinetic models.

4.3.1 Kissinger model

The Kissinger model was used to analyze the thermogravimetric curves of sweet potato starch. Figure 3 depicts the fitted curve of $\ln(\beta/T_m^2)$ vs. $1000/T_m$ where slopes give $-E/R$, and the correlation coefficient (R^2) is 0.9930. Thus, the Kissinger model can be available applied in sweet potato starch. The Kissinger model can be used to roughly calculate the activation energy of the thermal degradation using the peak value of thermogravimetric curves. Activation energy and pre-exponential factor got from the slope were 173.85 kJ/mol and 27.85/min, respectively. In general, the activation energy value is in the maximum degradation rate or in the largest heat absorption [20].

4.3.2 Flynn-Wall-Ozawa model

The Flynn-Wall-Ozawa model was also employed to process the thermogravimetric curves of sweet potato starch and calculate the corresponding dynamics parameters.

From Fig. 1, the peak temperatures of thermogravimetric curves at different heating rates, T_m , were obtained. Figure 4 illustrated the linear plot of $\lg \beta$ vs. $1000/T_m$ where slopes give a value of $-E/R$. The linear correlation coefficient is 0.9981, and activation energy is 174.87 kJ/mol. Thus, the Flynn-Wall-Ozawa model is also effective for sweet potato starch.

4.3.3 Šatava-Šesták model

The Šatava-Šesták model was also used to process the thermogravimetric curves of sweet potato starch. Mechanism function, $G(\alpha) = -\ln(1 - \alpha)$,

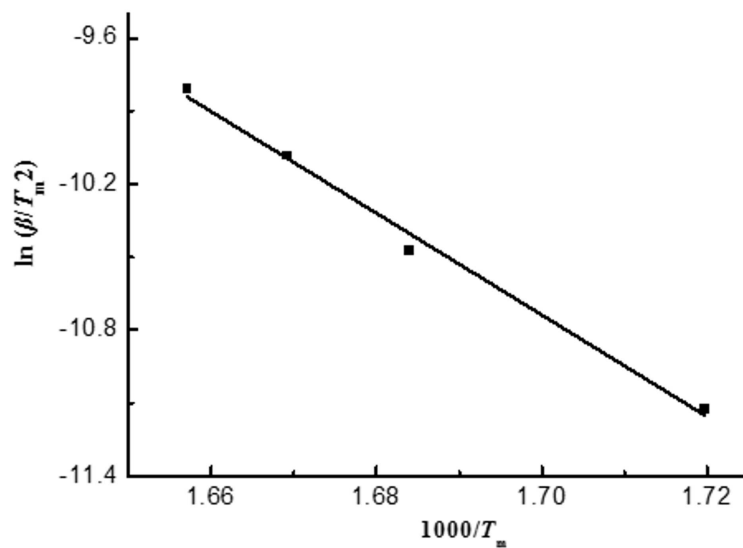


Figure 3: Kissinger plots of sweet potato starch.

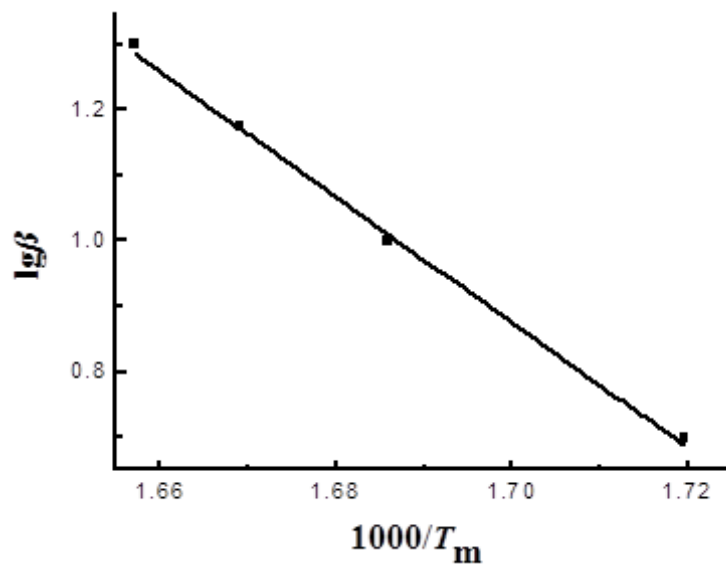


Figure 4: Flynn-Wall-Ozawa plots of sweet potato starch.

was ultimately chosen after comparison with the others. Figure 6 depicts the linear plot of $\lg \beta$ vs. $1000/T_m$ where the slope return a value of $-0.4567E/R$. The fitting curves in Fig. 5 are approximately parallel, and the mean correlation coefficient (R^2) of the fitted curves is 0.9935. Activation energy is usually regarded as the energy barrier to control the bond breaking or bond reapportion step [21]. The activation energies got from the slope ($-0.4567E/R$) were shown in Tab. 2, and the average value is 174.34 kJ/mol.

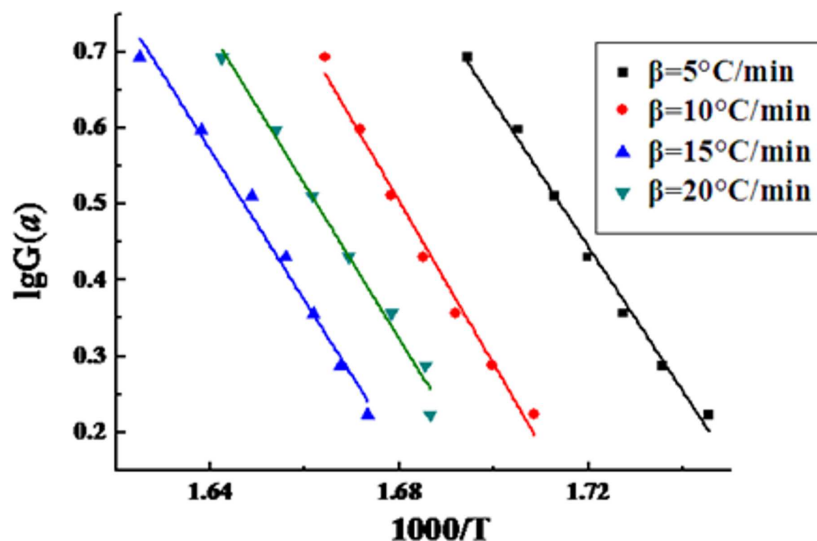


Figure 5: Šatava-Šesták plots of sweet potato starch.

Table 2: The activation energies of sweet potato starch using the Šatava-Šesták model.

$\beta/(\text{°C}/\text{min})$	5	10	15	20
R^2	0.9940	0.9920	0.9990	0.9980
Slope	-9.495	-9.710	-9.549	-9.553
E [kJ/mol]	172.85	176.77	173.84	173.91

Based on the activation energy of sweet potato starch calculated by the three models, the deviation was 5.10%, which indicated that the results

were believable. The high consistency of the values confirmed the reliability of the calculation and also confirmed the predictive ability of dynamics theory [22]. Therefore, the values of activation energies were reasonable. In fact, different kinetic models should be complementary and not competitive [23]. The activation energy alone is insufficient to forecast and simulate the entire process of thermal degradation. The satisfactory degradation model should at least include a set of activation energy and pre-exponential factor. However, since the activation energy can provide important information about the transition energy required to initiate a reaction, in this study the range of activation energy can help to investigate the thermal stability of the sweet potato starch.

4.4 DSC studies

The DSC curve was used to study the thermal transformation occurring in the process of heating under an inert atmosphere. The typical DSC curve of sweet potato starch in a range of 40–580 °C was presented in Fig. 6.

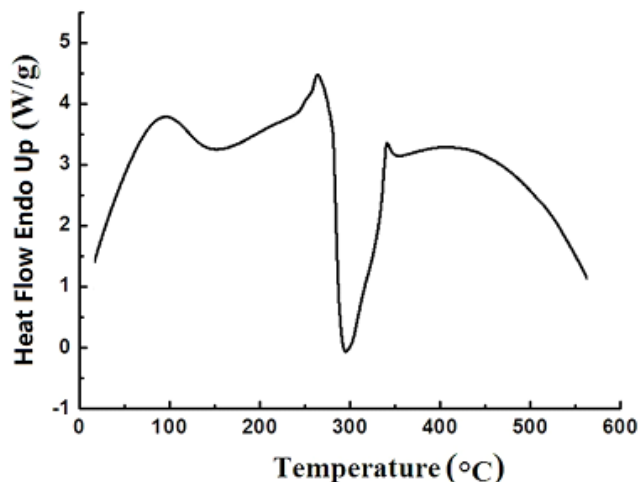


Figure 6: DSC curve of sweet potato starch under heating rate of 15 °C/min.

The peaks at a low temperature (95 °C) are endothermic peaks of gelatinization. Just before this exotherm, there is an endotherm at 270 °C. After opening the DSC pans, the starch sample was yellow to brown. This change is believed to be due to the interruption of long chains. A large exotherm at approximately 280 °C nearly covers all thermogram transition

which represents the decomposition of starch. The result was coincided with those obtained previously from thermogravimetric curves. After opening the DSC pans, the starch sample was carbonized when the temperature was greater than 280 °C. The carbon black directly indicated that the chains of macromolecular had been destroyed, and the rings of small molecular glucose had been destroyed.

4.5 TG–FTIR analysis

The three-dimensional (3D) FTIR diagram of gaseous products from the pyrolysis of sweet potato starch was shown in Fig. 7.

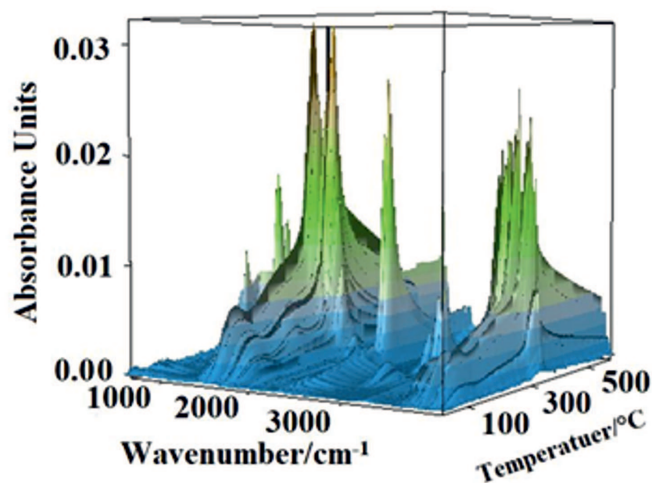


Figure 7: Three-dimensional FTIR diagram of gaseous products from the pyrolysis of sweet potato starch at 20 °C/ min.

By comparison of the standard spectrum of a certain compound, the major products were identified by characteristic absorption bands. Carbon dioxide was released quite strongly, causing the absorption at 2350 1/cm and 667 1/cm. Mainly water vapor was found, which was characterized by peaks at 3736 1/cm. Two narrow bands at about 964 and 927 1/cm indicated the existence of ammonia. The narrow band at 3014 1/cm was the significant peaks of methane. Some other gases could be evolved at the same time, which led to more difficulty to find the peak of gas when testing small quantities.

5 Conclusions

X-ray diffraction, thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) method were applied for studying the main characteristics of sweet potato starch. The crystallinity index of sweet potato starch is 0.56. Thermogravimetric curves were used to study the thermal degradation kinetics of sweet potato starch by non-isothermal process. The activation energy values of sweet potato starch were 173.85, 174.87 and 174.34 kJ/mol based on Kissinger, Flynn-Wall-Ozawa, and Šatava-Šesták models, respectively. The values of activation energies show that the thermal decomposition of sweet potato starch has a single reaction mechanism or a combination of multi-reaction mechanisms. The activation energy values allow developing a simplified approach to generally understand the thermal behavior of sweet potato starch in relation to food processing. The DSC results show that two decomposition temperatures were observed: long chain scission at a low temperature; and the decomposition of glucose ring at a high temperature. The gaseous products from the pyrolysis of sweet potato starch were water, carbon dioxide, ammonia, methane, and others.

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