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RESEARCH ARTICLE

Kinetics and mechanism of thermal decomposition of cornstarches with different amylose/amylopectin ratios

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Thermal decomposition of cornstarches with different amylose/amylopectin ratios (waxy: 0/100, maize: 23/77, Gelose 50: 50/50, and Gelose 80: 80/20) under nitrogen condition was investigated by thermogravimetric analysis (TGA). Various decomposition models including Friedman, Kissinger, Flynn-Wall-Ozawa, and modified Coast-Redfern methods were used to determine the apparent activation energy of different starches. Fourier transform infrared spectrometry (FTIR) and TGA-FTIR were also used to study the mechanism of thermal decomposition process. The results show a multiple-step mechanism for the thermal decomposition of all cornstarches. The sequence of activation energy for the cornstarches is waxy>maize>G50>G80, which corresponds to amylopectin content. FTIR results confirm that the thermal decomposition of cornstarch is due to the long-chain scission. The higher activation energy for cornstarch with higher amylopectin content can be explained by its higher molecular weight and more α -1,6 bonds.

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Activation energy / Kinetics / Starch / Thermal decomposition

1 Introduction

Starch is a heterogeneous material with more sophisticated microstructures than those of conventional polymers. Most native starches are a mixture of amylose, a linear structure of α -1,4-linked glucose units, and amylopectin, a highly branched structure of short α -1,4 chains linked by α -1,6 bonds. Various properties of starch and starch-based materials strongly depend on the amylose/amylopectin ratio such as gelatinization, retrogradation, and other chemical and physical performances. It has both

scientific and commercial importance to understand the thermal decomposition of starch with different amylose/amylopectin ratios.

Thermogravimetric analysis (TGA) is a useful and widely used tool to characterize thermal decomposition (amount and rate of mass loss), thermal stability, and the lifetime behavior of polymeric materials. Two major weight loss steps of starch have been detected by TGA, *i.e.*, the dehydration and decomposition [1–4]. MS, FTIR (Fourier transform infrared spectrometry), and NMR have also been used to study the mechanism [5–7]. The effect of starch source [4, 8], chemical modification [6, 9, 10], enzyme treatment [1], methylparaben addition [3], *etc.*, on the thermal decomposition of starch have been discussed previously.

On the other hand, the kinetics of thermal decomposition of starch has been studied extensively [2, 3, 6, 8, 10]. Various methods have been developed and evaluated to describe and predict the kinetics of thermal decomposition of starch. Among those methods, model-free methods have shown to be successful in simulating the real data in a multi-step kinetics. By using these methods, the process is detectable in the form of a dependence of activation

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Abbreviations: DTG, derivative thermogravimetry; FTIR, Fourier transform infrared spectrometry; F-W-O, Flynn-Wall-Ozawa; TGA, thermogravimetric analysis.

energy E_α on conversion rate α [11]. The Flynn-Wall-Ozawa (F-W-O) isoconversional method is an example of model-free methods and involves measuring the temperatures corresponding to fixed values of α from experiments at different heating rate and plotting $\ln(\alpha)$ against $1/T$, and then obtain the slope of such plots as $-E_\alpha/R$. If the relationship between E_α and α is not linear, the results indicate a multi-step reaction mechanisms [11, 12]. Kinetic analysis using model-free methods allows evaluating Arrhenius parameters without choosing the reaction model and is sufficient to predict the reaction kinetics over a wide temperature range; thus, similar dependence of the activation energy on the extent of conversion for isothermal and nonisothermal experiments can be obtained. In other words, the model-free isoconversional methods are capable of meeting the above-mentioned justifiable expectations. This is reason for the popularity of various isoconversional techniques in kinetic computations [13].

Although starch has been a popular raw material used in food production and preparation of thermoplastics, where thermal treatment-induced decomposition of starch can occur, there are limited reports dealing with the kinetics of thermal decomposition of starch. Guinesi *et al.* [8] studied nonisothermal kinetics of different starches (corn, cassava, rice, and potato) but little difference were observed. Aggarwal and Dollimore [1] studied the partially hydrolyzed corn, wheat, rice, and potato starches and found their thermal decomposition temperatures were lower than those of original starches. To the best of our knowledge, there is no report about the thermal decomposition of same kind of starches with different amylose/amylopectin ratios detected by TGA. Understanding the effect of amylose/amylopectin ratio on the thermal decomposition of starch as a natural polymer can not only enhance our knowledge of polymer science but also provide important information for the proper control of the thermal processing of starch-based materials. In this work, the thermal decomposition of cornstarches with different amylose/amylopectin ratios (waxy: 0/100, maize: 23/77, G50: 50/50, and G80: 80/20) under nitrogen condition was investigated by TGA. Various decomposition models including Kissinger, F-W-O, and modified Coast-Redfern methods were used to determine the apparent activation energy of these starches. The mechanism of thermal decomposition was also discussed based on the results of FTIR and TGA-FTIR.

2 Materials and methods

2.1 Materials

Cornstarches with different ratios of amylose/amylopectin were used in the experimental work as model materials. All

the starches are commercially available and were kindly supplied by Penford (Australia). The amylose/amylopectin ratios of waxy, maize, Gelose 50, and Gelose 80 are 0/100, 23/77, 50/50, and 80/20, respectively, and the molecular weights of them are about 2.1×10^7 , 1.3×10^7 , 5.1×10^6 , and 6.7×10^5 , respectively (measured by GPC). The raw materials which were used to establish kinetics were dried in an oven at 110°C for 24 h to remove the free moisture.

2.2 Thermogravimetric analysis (TGA)

A Perkin-Elmer Pyris 1-TGA apparatus was used to study the kinetics of thermal decomposition of starch. The temperature was increased from 50 to 800°C at six different heating rates: 2, 3.5, 5, 7.5, 10, and $15^\circ\text{C}/\text{min}$. These moderate heating rates were used in order to keep possible intrusion/mass-induced heat transfer lag at a minimum [14]. A high purity nitrogen stream (99.99% nitrogen) was used continuously purged the furnace at a flow rate of 20 mL/min at room temperature and atmospheric pressure. This nitrogen purge started 30 min before the measurements to establish an inert environment in order to prevent any unwanted oxidative decomposition.

2.3 Fourier transform infrared spectrometry (FTIR)

A Pyris Perkin-Elmer diamond TG/DTA connected with an FTIR (Perkin-Elmer Spectrum 100) was used to analyze the gas products. The sample was heated at $10^\circ\text{C}/\text{min}$ from 50 to 700°C . The gas product was scanned from 4000 to 500 cm^{-1} at resolution of 2 cm^{-1} . All spectra were baseline corrected.

FTIR (Bruker Tensor 37) was used to detect the solid residues. The transmittance spectra were computed between 4000 and 400 cm^{-1} at 4 cm^{-1} resolution with the triangular apodization function in the standard Bruker OPUS 4.2 software. Symmetrical interferograms on 128 scans were co-added for each spectrum. All spectra were baseline corrected and normalized.

2.4 Theoretical approach of kinetics

The fundamental rate equation used in all kinetic studies is generally described as:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where k is the rate constant and $f(\alpha)$ is the reaction model, a function depending on the actual reaction mechanism. Equation (1) expresses the rate of conversion, $d\alpha/dt$, at a constant temperature as a function of the reactant

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concentration loss and rate constant. In this study, the conversion rate α is defined as:

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f} \quad (2)$$

where W_t , W_0 , and W_f are sample weight at time t , initial weight, and final weight, respectively. The rate constant k is generally given by the Arrhenius equation:

$$k = A \exp\left(\frac{-E}{RT}\right) \quad (3)$$

where E is the apparent activation energy (kJ/mol), R is the gas constant (8.314 J/K mol), A is the pre-exponential factor (min^{-1}), and T is the absolute temperature (K). The combination of Eqs. (1) and (3) gives the following relationship:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (4)$$

For a dynamic TGA process, by introducing the heating rate, $\beta = dT/dt$ into Eq. (4), Eq. (5) is obtained as:

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

Equations (4) and (5) are the fundamental expressions of analytical methods to calculate the kinetic parameters based on TGA data. Various models have been developed based on these fundamental equations and the most common model-free methods that are also used in this study are summarized in Table 1.

3 Results and discussion

Figure 1 shows a typical overall process of decomposition of raw maize starch measured by TGA at a heating rate of $10^\circ\text{C}/\text{min}$. It can be seen that there are two steps of weight loss in thermogravimetric (TG) curve: the first one observed up to 150°C is related to the loss of absorbed and bounded water. In the second stage, the weight loss from about 87 to 20% is due to the thermal decomposition. Correspondingly there are two peaks in derivative thermogravimetric (DTG) curves: one is due to dehydration and another one is due to decomposition. Previous studies

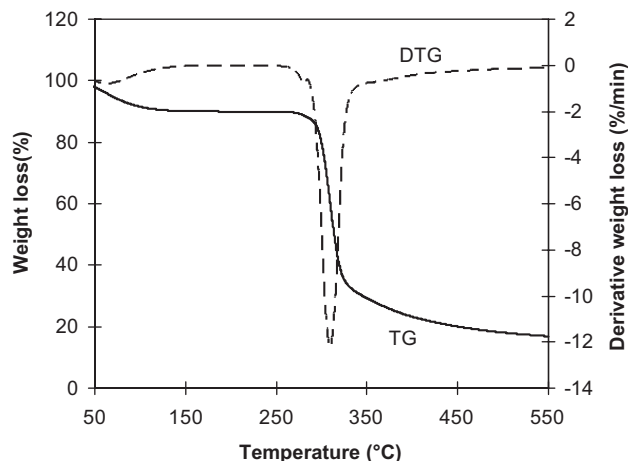


Figure 1. Overall thermal decomposition of maize starch with moisture content 13.55% detected by TGA at a heating rate of $10^\circ\text{C}/\text{min}$.

have shown that dehydration and decomposition have generally been considered as two separate processes associated with the degradation mechanisms of starch [1, 4, 15, 16]. The dehydration is usually not considered for the determination of the kinetic parameters in most of the studies. In the following kinetic study, all the corn-starches were dried in an oven at 110°C for 24 h to remove the free moisture before TGA measurements. Similar curves for other starches (waxy, G50, and G80) were also observed. DTG curve is often used for thermal analysis as it stands for the speed of the weight loss of a sample. In the following discussion, decomposition peak of DTG curve was used to discuss the decomposition temperature and kinetics.

Figure 2 shows the plots of decomposition peak temperature versus heating rates for different starches. As expected, decomposition peak temperature is increased with increasing heating rate. It can also be noted that the sequence of thermal decomposition temperature is waxy > corn > G50 > G80, which in accordance with their amylopectin content.

The most common model-free methods used in this study are summarized in Table 1. The Friedman method is an isoconversional method, which directly leads to $(-E_\alpha/R)$ for a given value of α by plotting $\ln(d\alpha/dt)$ versus

Table 1. Kinetic methods used to evaluate activation energy

Method	Expression	Plots
Friedman	$\ln(d\alpha/dt) = \ln[Af(\alpha)] - E_\alpha/RT$	$\ln(d\alpha/dt)$ versus $1/T$
Kissinger	$\ln(\beta/T_p^2) = \ln(AR/E_\alpha) + (1/T_p)(-E_\alpha/R)$	$\ln(\beta/T_p^2)$ versus $1/T_p$
Flynn-Wall-Ozawa	$\log \beta = \log(AE_\alpha/Rg(\alpha)) - 2.315 - 0.4567E_\alpha/RT$	$\log \beta$ versus $1/T$
Coast-Redfern (modified)	$\ln[\beta/(T^2(1 - 2RT/E_\alpha))] = \ln[-AR/(E_\alpha \ln(1 - \alpha))] - E_\alpha/RT$	$\ln(\beta/T^2)$ versus $1/T$

See Ref. [2,6,14].

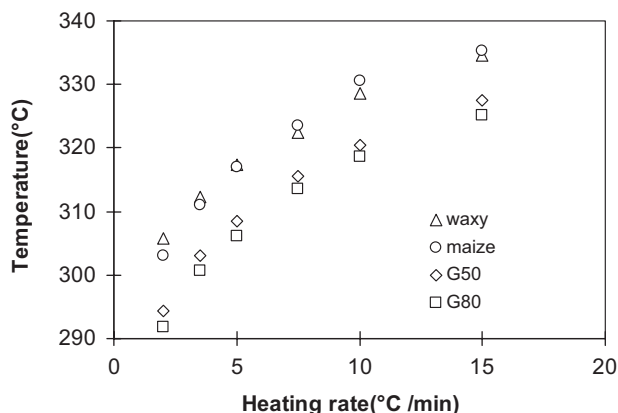


Figure 2. Decomposition temperatures of various starches under different heating rates.

$1/T$. The isoconversional F-W-O method is an integral method, which leads to $(-E_{\alpha}/R)$ from the slope of the line determined by plotting $\log \beta$ versus $1/T$ at specific conversion rate. The modified Coats-Redfern method is a multi-heating rate application of the Coats-Redfern equation. Plotting the left hand side for each heating rate versus $1/T$ at that heating rate gives a series of straight lines of slope $(-E_{\alpha}/R)$. The full solution is to be done iteratively by first assuming a value of E_{α} and then recalculating the left hand side until convergence occurs. A quick solution is also available by moving $(1-2RT/E_{\alpha})$ into the intercept and assuming that it is a constant [14].

Figure 3 represents the typical isoconversional plots based on Friedman, F-W-O, and modified Coats-Redfern methods for maize starch, which show a general trend of activation energy. It is seen that the linear relationship and the fitted lines are nearly parallel when the conversion rate in the range of 0.2–0.6 at corresponding temperature of 318–335°C, which indicates approximate activation energies at different conversions and consequently implies the possibility of single reaction mechanism (or the unification of multiple-reaction mechanisms). The mechanism may relate to the depolymerization of starch in the range of $\alpha = 0.2$ –0.6 [6]. The reaction mechanism, however, could be different in the ranges of lower and higher conversion periods due to unsatisfied parallel line at $\alpha < 0.2$ and $\alpha \geq 0.7$. The change of the reaction mechanism in lower and higher conversion ranges might be caused by the complex reactions in the decomposition process of the cornstarches such as bound water evaporation, carbonization, etc. Figure 3 shows that the thermal decomposition of cornstarches may be a multiple-step mechanism since the relationship between E_{α} and α is not linear. It can also be noticed in Fig. 3 that the curves from F-W-O method and modified Coats-Redfern show the better parallel than those from Friedman. The reason for the relationship between E_{α} and α will be discussed later.

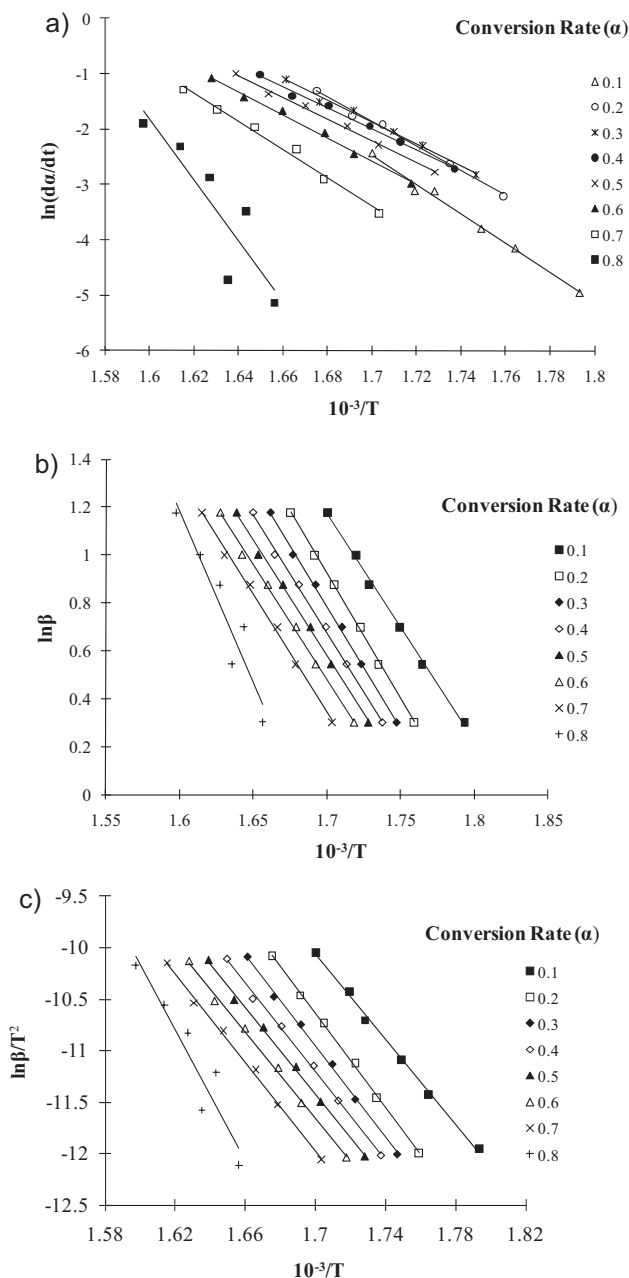


Figure 3. Typical isoconversional plots of (a) Friedman method, (b) F-W-O method, and (c) modified Coats-Redfern method for maize starch.

Activation energy (E_{α}) is generally considered as a measurement of the energy barrier to a controlling (rate limiting) bond rupture or bond redistribution step [17]. Figure 4 shows the plots of activation energy as a function of conversion in the range $\alpha = 0.1$ –0.7 for all the cornstarches. Figure 4a shows the activation energy based on Friedman method, Fig. 4b based on F-W-O method, and Fig. 4c based on modified Coats-Redfern method, respectively. Figure 4b and c clearly show that the sequence of E_{α}

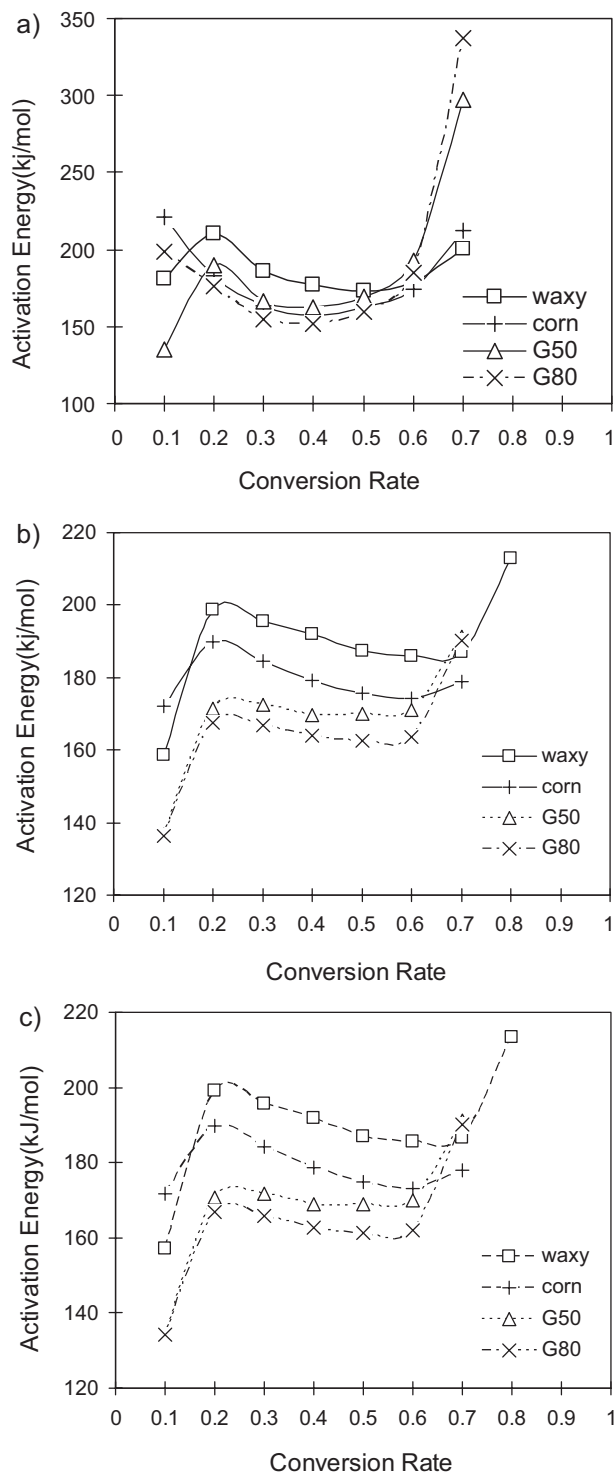


Figure 4. Plots of apparent activation energy as a function of decomposition conversion rate (α) for all selected starches calculated by (a) Friedman, (b) F-W-O method, and (c) modified Coast-Redfern method.

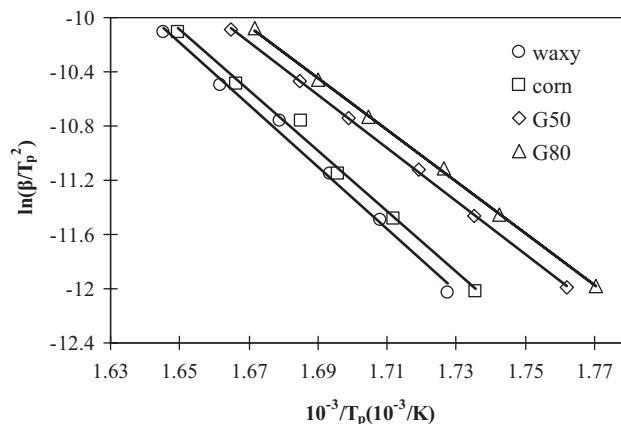


Figure 5. Linear plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ for various starches using Kissinger method.

of the cornstarches is waxy > maize > G50 > G80 in the conversion rate (α) range of 0.2–0.6, though this trend is not apparent in Fig. 4a. The E_a of cornstarch based on F-W-O method and modified Coast-Redfern method is about 160–200 kJ/mol, which is lower than the result from Friedman method.

Figure 5 shows the linear plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ for various cornstarches based on Kissinger method. Although it is not a model-free method to determine the E_a and it may not show the overall trend of E_a due to only some special conversion rate was used [14]. However, the Kissinger is meaningful for determining E_a when the E_a was stable in certain conversion range. In this study, Fig. 5 shows good linearity ($R^2 > 0.99$) for various cornstarches. The activation energy of cornstarches measured is 197, 185, 168, and 164 kJ/mol for waxy, maize, G50, and G80, respectively, which supports the sequence (waxy > maize > G50 > G80) determined by other methods.

Practically, different kinetic analysis methods should be complementary rather than competitive [12]. The F-W-O method and modified Coast-Redfern has shown a better parallel than Friedman in Fig. 4 and constant E_a in Fig. 5. The sequence of activation energy waxy > maize > G50 > G80 for cornstarch has been confirmed by all methods. However, the activation energy alone is not enough to predict and modeling the thermal decomposition process. A satisfied decomposition model must contain at least the whole set of activation energy, pre-exponential factor, and reaction model (*i.e.*, kinetic triplet) [11]. However, as the activation energy (also the energy barrier), can provide the information of critical energy needed to start a reaction, the decomposition activation energy range obtained in this study can help to understand the thermal stability of cornstarches.

In order to understand the effect of amylose/amylopectin ratios on activation energy of decomposition, FTIR was used to study the thermal decomposition mechanism.

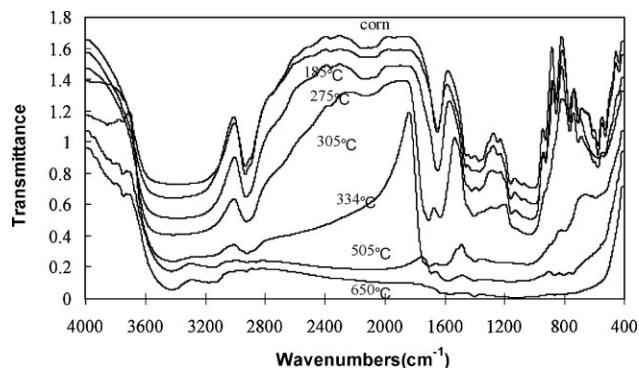


Figure 6. FTIR spectra of decomposition products from maize starch at different temperatures.

Figure 6 shows the FTIR spectra of maize starch after heating in TGA tubular at heating rate of 10°C/min up to different temperatures. The spectra of native sample represents typical pattern of starch [6, 18–21]. A shift of main absorption band at 3399 cm^{-1} to higher values (3405 and 3400 cm^{-1}) at temperature of 185 and 275°C was observed, indicating a decrease of hydrogen bonds with covalent bonds (ether linkages). The sample may show slight yellow color when it was heated to 275°C, indicating the start of decomposition. However, the FTIR spectra at the temperature 185 and 275°C (the onset of decomposition peak) can still be considered to represent the original maize molecules and no polymer decomposition reaction takes place before this temperature. Further heating to 305°C (the maximum decomposition temperature), 334°C (the end of decomposition peak), 505, and 650°C made much difference among the FTIR spectra for maize. When the maize was heated from 305 to 334°C, the broad band at 3399 cm^{-1} shifts to higher wavenumbers (3407 and 3420 cm^{-1}), suggesting the elimination of hydroxyl groups in the glucose ring to form water molecules. The bond at 3000–2800 cm^{-1} decreased markedly, indicating the breaking of the main chain at this temperature. The new peak 1708 cm^{-1} indicates the new formation of new carbonyl compounds, which was probably aldehydes [7]. The bands related to C–C–H bending at 1243 and 1089 cm^{-1} , and those related to C–O and C–C stretching at 1158 and 929 cm^{-1} were also disappeared for samples heating up to this temperature. When the sample was further heated to 505 and 650°C, the sample only show a low absorbance band at about 3430 cm^{-1} , suggesting the carbonization of the sample, when only simple compounds left.

Figure 7 shows FTIR spectra for volatile products from the decomposition of starch heated in TGA at 10°C/min. When the sample was heated to 90, 182, and 261°C, the spectra show little difference comparing with heated to 50°C, except for some slight absorbance at 3400–

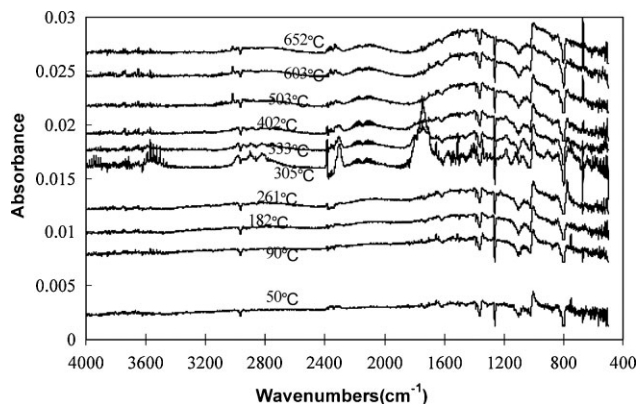


Figure 7. FTIR spectra of volatile products evolved during maize starch decomposition at different temperatures.

3500 cm^{-1} due to the generation of moisture. When the sample was heated to 305 and 333°C, a strong absorbance appeared at ca. 3400–3600 cm^{-1} and ca. 2380, 2262, 1731, 1486, and 1350 cm^{-1} compared with heated to 50°C. At 333°C, the sample had a maximum decomposition rate. Like other polysaccharide, the gaseous productions could include CO, CO₂, H₂O, CH₄, C₂H₄, and CH₂O [4, 6]. Here, the absorbance at 3400–3600 cm^{-1} was due to the moisture gas. The bands located at 2380 and 2262 cm^{-1} indicate the formation of carbon dioxide and carbon monoxide. The fine vibrational structures centered at 1731 cm^{-1} indicate the formation of compounds with carbonyl groups [4]. The presence of CO₂, CO, and carbonyl compounds in the spectra suggests the scission of glycosidic linkages and strong bonds in the backbone of starch. The bands at 1486 cm^{-1} are related to aliphatic structures formed by cleavage of the main chain of starch. When the sample heated to higher than 402°C, there was only weak absorbance, which may due to the little amount of gas generated at this temperature.

In summary, when the starch was heated in TGA under N₂ environment, the starch molecules remained unchanged before 275°C except for the moisture loss. When the temperature arrived 300°C, the decomposition of starch began, with its molecular chain being broken in the range of 300–334°C at the corresponding conversion rate of 0.2–0.6. This may explain the difference of activation energy for different cornstarches. In the study of thermal decomposition of carbohydrate, the mechanism provides a low-energy means of affecting initial carbon–carbon bond breakage at varying positions along the carbon chain, each distinct model leading to a different family of products [22]. In the starch-conversion process, the primary attack is the hydrolysis of α -1,4 glucosidic linkages in the amylose and amylopectin molecules of the starch. In addition, the scission of α -1,6 linkages may occur, and α -1,4 linkages is more susceptible to hydrolysis than α -1,6 linkages [23]. Cornstarches with different amylose have

different molecular weight and number of α -1,6 bonds, which may require different energy to start decomposition reaction. Compared with other cornstarches, waxy has higher molecular weight and more α -1,6 bonds, which results more energy for decomposition. The detailed mechanism, especially C1 and C6 break in the molecular chain, will be studied in the future.

4 Conclusions

TGA was used to investigate the thermal decomposition process of cornstarch with different amylose/amylopectin ratios under N_2 condition. The TGA–FTIR and FTIR was used to determine the gaseous and solid decomposition products, respectively. The various kinetic methods including Kissinger, Friedman, F-W-O, and modified Coast-Redfern were used to determine the apparent activation energy of those cornstarches. The results of activation energy show that the starch thermal decomposition has a multiple-step mechanism. The sequence of activation energy for cornstarches is waxy > corn > G50 > G80, which is corresponding with their amylopectin content. FTIR results confirm that the thermal decomposition is due to the long-chain scission. The higher activation energy for high amylopectin cornstarch could be explained by the higher molecular weight and its more α -1,6 bonds.

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