

KINETIC STUDY OF THE THERMAL DECOMPOSITION OF HEMICELLULOSE ISOLATED FROM CORN STALK

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In order to study the thermal decomposition characteristics of hemicellulose, a highly efficient procedure was carried out to extract hemicellulose from corn stalk. Several different sugar units were observed by ^{13}C NMR spectra to show the presence and species of hemicellulose. Following isolation of the hemicellulose, experimental research on its thermal behavior were carried out with a thermogravimetric analyzer under inert atmosphere at heating rates ranging from 10 to 50°C/min, and the kinetic parameters were calculated by the Kissinger and Ozawa methods, respectively. It was found that the thermal degradation of hemicellulose mainly occurred in the temperature range 180-340°C with a final residue yield of 24% at 700°C. An increase of the heating rate could slightly increase both the temperatures at which the peak weight loss rate was observed and the maximum value of weight loss rate. The activation energy (E) and the pre-exponential factor (lnA) obtained by the Kissinger and Ozawa methods were 213.3kJ mol⁻¹, 211.6kJ mol⁻¹ and 46.2min⁻¹, 45.9min⁻¹, respectively. Even though the data showed little difference, the fitting degree of the Ozawa method was better than that of the Kissinger method. The experimental results and kinetic parameters may provide useful data for effective design and improvement of thermochemical conversion units.

Keywords: Kinetics; Thermogravimetry; Pyrolysis; Hemicellulose; Corn stalk

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INTRODUCTION

Due to the urgency of the current world energy supply-and-demand situation and the myriad environmental, economic, and social challenges associated with global climate change, the need for clean sources of energy is receiving increasing attention. In the framework of a future sustainable development, biomass is one of the most often considered sources of renewable energy (Dam et al. 2008). In principle, there are many conversion technologies for utilizing biomass, such as direct combustion processes, thermochemical processes, biochemical processes, and agrochemical processes. Of these, pyrolysis, which can be described as the direct thermal decomposition of the organic materials in the absence of oxygen to obtain an array of solid, liquid, and gas products, forms the focus of this study (Meier and Faix 1999; Demirbas 2001; Bridgewater 2003).

Pyrolysis is an extremely complex process, involving a series of reactions, and subject to the influence of many factors, such as pyrolysis temperature, heating rates, residence time, and raw material compositions. In view of this complexity, researchers have focused on the pyrolysis characteristics of the three main components in plants

(cellulose, hemicellulose, and lignin), hoping to gain an overall understanding or at least for a better understanding of biomass pyrolysis processes (Jakab et al. 1995; Dobele et al. 2001; Yang et al. 2006). Compared with that of cellulose and lignin, the mechanisms and the kinetic data for hemicellulose pyrolysis are still unknown to a large extent because of its complexity and the varying physical and chemical properties. Hemicelluloses, the second most abundant renewable polymers after cellulose, are plant cell wall polysaccharides closely associated with cellulose and lignin. In particular, in contrast to wood hemicelluloses, there are a great variety of linkages and abundance of branching types in graminaceous hemicelluloses, depending on the species and the tissue within a single species, as well as on the age of the tissue (Sun et al. 2005; Xu et al. 2006).

Owing to its structural diversity and the difficulty of its isolation, previous works about hemicellulose have been inclined to use xylan or 4-O-methyl-D-glucurono-D-xylan as a model compound for pyrolysis study. Órfão et al. (1999) studied the pyrolysis kinetics of lignocellulosic materials using xylan as a representative and concluded that the thermal decomposition of xylan could not be modeled with acceptable errors by means of simple reactions. Colomba and Mario (1997) investigated the intrinsic chemical kinetics of xylan pyrolysis in the temperature range 200-340°C and found two consecutive reaction steps emerged in the pyrolysis process. Also 4-O-methyl-D-glucurono-D-xylan was used by Várhegyi et al. (1989) for non-isothermal thermogravimetric experiments in the presence and absence of catalysts (inorganic salts), which helped them to confirm various hypotheses on the catalyzed and uncatalyzed reaction mechanisms of lignocellulose decomposition. In addition to commonly used model substances, there are other methods for the individual evaluation of kinetic parameters of hemicellulose degradation. Müller et al. (2003) considered that the weight loss curve for the hemicellulose can be obtained by subtracting the TG curve of acid-washed wood from the TG curve of water-washed wood, taking into account the weight loss for the acid treatment, and so they used the resulting curve for calculation and reached a relatively wide range of kinetic parameters. However, to the best of our knowledge, there has been little study of pyrolysis mechanisms carried out on real hemicellulose isolated from a particular biomass feedstock.

The purpose of this study is to develop a highly efficient method for isolating pure hemicellulose from gramineous plants, and on this basis to study thermal decomposition characteristics of hemicellulose and provide more reliable kinetic parameters. To this end, the thermogravimetric characteristics of hemicellulose isolated from corn stalk were analyzed, and the dynamic parameters of hemicellulose pyrolysis were calculated by the methods of Kissinger and Ozawa, respectively. Also in order to prove the structural integrity of hemicellulose and the viability of the separation process, the hemicellulose used in present work was characterized by ^{13}C NMR spectroscopy previously.

EXPERIMENTAL

Materials

Corn stalk (with leaves removed) was obtained from Changzhi City, Shanxi Province, China. After being dried in sunlight, it was ground in a Willey mill and

screened to the range 40 to 60 mesh (0.28–0.45mm) for this study. The samples were first extracted with benzene and ethanol (v/v, 2:1) solution for 8h to remove extractives, and then dried in vacuum oven at 50°C. Some characteristics of the corn stalk used are shown in Table 1.

Table 1. Some Characteristics of the Corn Stalk Used (%)

Relative composition of the main components					Ultimate analysis			
Cellulose	Hemicellulose	Lignin	Extractives	Ash	C	H	N	O*
42.4	29.6	21.7	3.4	5.1	42.5	5.9	2.3	49.3
* calculated by difference								

Isolation Methods

The extracted corn stalk was first treated with sodium chlorite in an acidic environment to remove lignin and isolate holocellulose on the basis of National Standards Methods (GB/T2677. 10-1995) and literature data (Shi and He 2003). The holocellulose was then extracted with 5% potassium hydroxide solution (2g holocellulose per 100ml solution) for 8h with magnetic stirring at room temperature. After extraction, the residue was filtered off and washed thoroughly with water until the filtrate was neutral. The combined supernatant fluid was adjusted to pH 5.5 immediately with 6M acetic acid in an ice bath. The solubilized hemicelluloses were then isolated by precipitation of the concentrated filtrates with 3 volumes of 95% ethanol. After filtration, pellets rich in hemicellulose were thoroughly washed with 70% ethanol and then freeze-dried.

¹³C NMR Spectrum

The solution-state ¹³C NMR spectrum was obtained on a Bruker AV 400MHz spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany) operating in the FT mode at 74.5 MHz under total proton decoupled conditions. The sample (100 mg) was dissolved in 1 mL D₂O (99.8% D) with overnight stirring at room temperature. The spectrum was recorded at 25°C after 30,000 scans. A 60° pulse flipping angle, a 3.9μs pulse width, and a 0.85s acquisition time were used.

Thermogravimetric Analysis

Thermogravimetric tests were performed with a Q500 Thermal Gravimetric Analyzer (TA Instruments, USA). High purity nitrogen (99.9995%) was used as the carrier gas and the flow rate was 50mL/min. About 10mg of sample was put in a platinum crucible each time and heated from room temperature to 800°C with heating rates of 10, 20, 30, 40, and 50°C/min, respectively.

Calculated thermogravimetric data were automatically outputted to the Q500 Thermal Gravimetric Analyzer software. Since the thermogravimetric experiment was used to calculate the parameters of chemical dynamics, the impact of the error was excluded as much as possible. Therefore, the average particle size of all samples was less than 60μm and relatively small samples (10mg) were used each time.

RESULTS AND DISCUSSION

Characterization of Hemicellulose

In order to confirm its structural integrity, the structural features of the hemicellulose isolated from holocellulose with 5% potassium hydroxide solution were investigated using the ^{13}C NMR spectroscopy. The assignment of the ^{13}C NMR spectrum (Fig. 1) was based on reported literature data on other non-wood plants (Sun et al. 2005; Xu et al. 2006; Megiatto et al. 2007). As can be seen from the spectrum, the corn stalk hemicellulose is mainly composed of xylopyranose, arabinofuranose, galactopyranose, and glucuronic acid. The main 1, 4-linked β -D-xylopyranose units are characterized by five strong signals at 102.9, 76.9, 75.4, 73.9, and 64.6ppm corresponding to chemical shifts of C-1, C-4, C-3, C-2, and C-5 carbons. The signals at 110.2, 87.2, 81.1, 79.4, and 62.6ppm are attributed to C-1, C-4, C-2, C-3, and C-5 of α -L-arabinofuranosyl residues linked to β -D-xylans, respectively. A weak signal at 102.7ppm originates from galactopyranosyl residues linked to the β -D-xylopyranose chain. The C-1, C-4, C-3, and C-2 of the 4-O-methylglucuronic acid residues in the hemicellulose display signals at 98.5, 83.4, 73.2, and 70.7ppm, respectively. The signals at 177.6 and 58.5ppm are due to the carbonyl and the 4-O-methoxyl group of glucuronic acid residue in xylans. The strong signal at 24.5ppm ascribes to methyl of the acetyl group, and the signal at 181.9ppm belongs to carboxylic groups, revealing that the corn stalk hemicellulose has a considerable content of glucuronic acid. The absence of prominent signals between 110 and 170ppm indicates that the hemicellulose is relatively free from aromatic residues. As supported by ^{13}C -NMR analyses, the isolation process did not affect the macromolecular structure of hemicellulose to any noticeable extent, which suggested that no substantial changes occurred during the treatment.

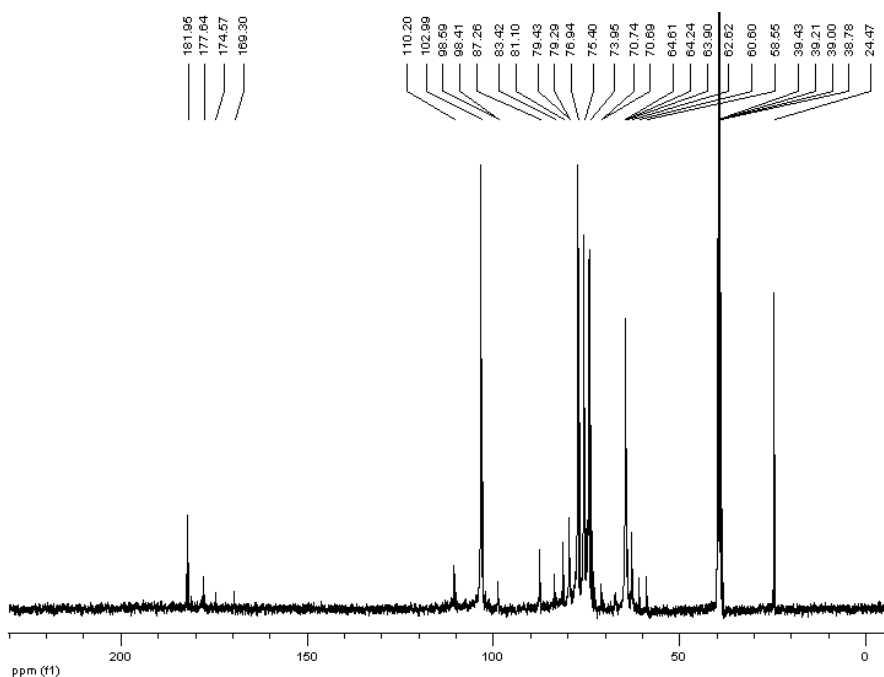


Fig. 1. ^{13}C NMR spectrum of hemicellulose isolated from corn stalk (solvent D_2O)

Thermal Characteristics

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves of corn stalk hemicellulose, obtained at heating rates of 10, 20, 30, 40, and 50°C/min, are plotted in Figs. 2 and 3, respectively. As can be seen from the graphs, the thermal decomposition of hemicellulose started at about 180°C, and its mass loss rate increased greatly with increasing temperature and obtained its maximum value at about 280°C. When the temperature was over 340°C, its weight loss rate became lower until to the final temperature. The amount of solid residue left at 700°C was high (24%), from which it can be concluded the hemicelluloses make a relatively important contribution to the formation of chars in biomass pyrolysis.

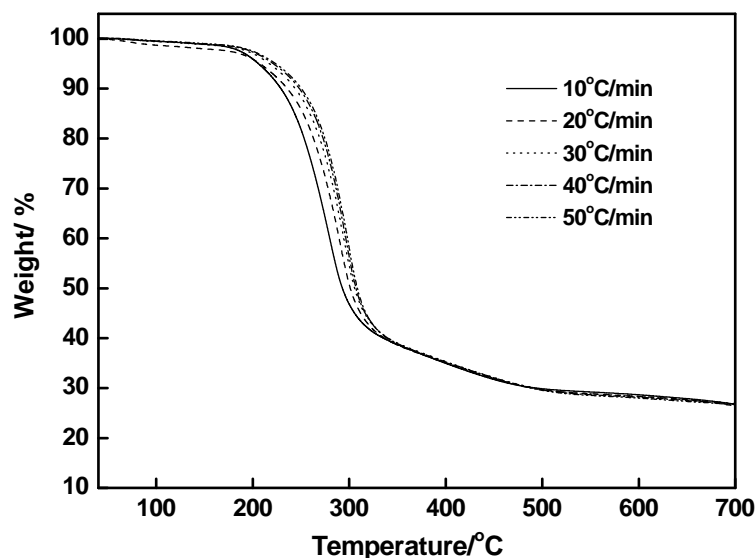


Fig. 2. TG curves of corn stalk hemicellulose at different heating rates

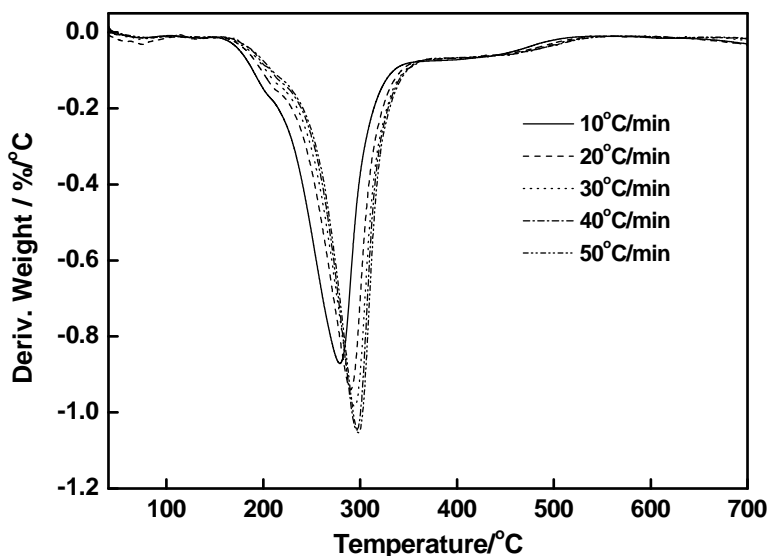


Fig. 3. DTG curves of corn stalk hemicellulose at different heating rates

As the heating rate increased from 10 to 50°C/min, both TG and DTG curves of hemicellulose exhibited a shift in the major weight loss temperature range (180-340°C), towards a little higher temperature zone, and also the maximum value of weight loss rate was increased slightly. According to Bilbao et al.'s viewpoints (1997), this is because the heating rate affects the temperature gradient between the outside and the internal parts of the sample. As the heating rate increases, thermal hysteresis increases, which results in TG and DTG curves moving to higher temperature. However, compared with cellulose and lignin, a variation of heating rates did not have a very significant influence on the degradation of hemicellulose. A barely perceptible shoulder peak was evident at about 205°C on the DTG curve, which indicates that the thermal decomposition process of hemicellulose could be divided into two step reactions. This behavior had been reported by other authors, such as Várhegyi et al. (1997), and they further tried to describe the double peaks observed by models based on successive reactions.

Kinetics

Understanding pyrolysis kinetics is important for the effective design and operation of the thermochemical conversion units and is always a fundamental step for these conversion processes. It had been demonstrated that the activation energy of a solid state reaction can be determined by Kissinger and Ozawa methods, on the premise of not knowing the reaction mechanism (Criado and Ortega 1986). In this work, the kinetic parameters of hemicellulose pyrolysis were calculated by procedures of Ozawa and Kissinger. The following simple equation (Eq. (1)) was used to describe the thermodegradation behavior of corn stalk hemicellulose,

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

where

$$\alpha = \frac{m_o - m}{m_o - m_\infty} \quad k = A \exp\left(-\frac{E}{RT}\right),$$

and where m refers to the sample mass at each monitoring time, and the subscripts o and ∞ represent the initial and terminal sample mass, respectively. The $f(\alpha)$ is a differential form function concerned with kinetic mechanism, and k is the Arrhenius equation, which is a function of the pre-exponential factor (A), apparent activation energy (E), absolute temperature (T), and the gas constant (R).

The temperature-time relation was computed from the following expression (Eq. (2)),

$$T = T_o + \beta t \quad (2)$$

where β is the heating rate, which has units of °C/min, and T_o is the initial absolute temperature.

Thus, Eq. (3) and Eq. (4) were obtained by the integral or differential transformations of Eq. (1) (Kissinger 1957; Ozawa 1965).

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E}{RT_p} + \ln\left(\frac{AR}{E}\right) \quad (3)$$

$$\ln(\beta) = \ln\frac{AE}{Rg(\alpha)} - 5.331 - 1.052\frac{E}{RT} \quad (4)$$

T_p in Eq. (3) refers to the temperature corresponding to the maximum weight loss peaks, and $g(\alpha)$ in Eq. (4) is an integral function of the kinetics mechanism. Equations (3) and (4) provide formulas for calculating the kinetic parameters E and A , which are known as the Kissinger and Ozawa methods, respectively.

Kissinger method

When the temperature reached its maximum value, the effect of the heating rates on the peak temperatures followed Eq. (3). The peak temperatures were obtained from Fig. 3, while the heating rates and other parameters in the Kissinger formula are shown in Table 2. The linear plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ is shown in Fig. 4.

Table 2. Parameter Values in Kissinger Formula

β ($^{\circ}\text{C}/\text{min}$)	T_p (K)	$1/T_p \times 10^{-3}$	$1/T_p^2 \times 10^{-6}$	$\beta/T_p^2 \times 10^{-6}$	$\ln(\beta/T_p^2 \times 10^{-6})$
10	552.9	1.8086	3.2712	32.71	-10.33
20	562.4	1.7783	3.1622	63.24	-9.67
30	567.0	1.7636	3.1104	93.31	-9.28
40	569.6	1.7557	3.0824	123.30	-9.00
50	571.7	1.7492	3.0596	152.98	-8.79

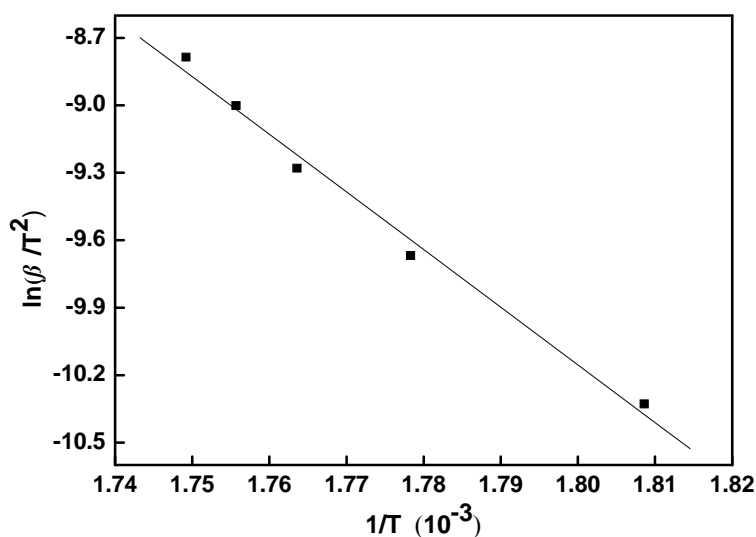


Fig. 4. Linearization curve of Kissinger method

The linear equation in Fig. 4 can be expressed as:

$$y = -25.6555 \times 10^3 x + 36.0256 \quad (5)$$

The linear regression coefficient (R^2) was 0.9896. From the slope (-25.6555×10^3) and intercept (36.0256), the apparent activation energy (E) and the pre-exponential factor ($\ln A$) can be calculated, which were $213.3 \text{ kJ mol}^{-1}$ and 46.2 min^{-1} , respectively.

Ozawa Method

$\ln \beta$ and $1/T_p$ represent the linear relation with a given value of α in the DTG curves at different heating rates. The effect of heating rate on the peak temperatures of the DTG curves was followed in Eq. (4). The relevant parameters in Ozawa formula are shown in Table 3, and the line graph of $\ln \beta$ on $1/T_p$ is plotted in Fig. 5.

Table 3. Parameter Values in Ozawa Formula

β (°C/min)	T_p (K)	$1/T_p \times 10^{-3}$	$\ln \beta$
10	552.9	1.8086	2.3026
20	562.4	1.7783	2.9957
30	567.0	1.7636	3.4012
40	569.6	1.7557	3.6889
50	571.7	1.7492	3.9120

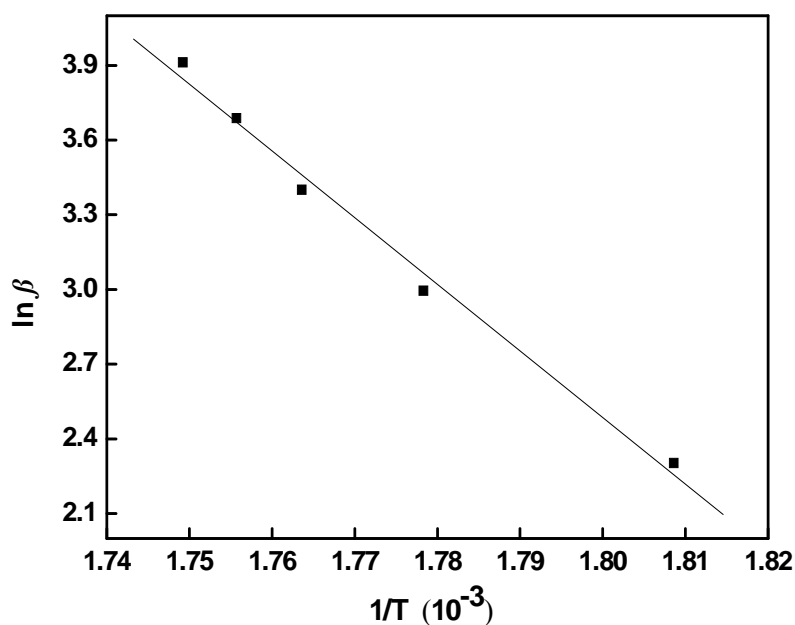


Fig. 5. Linearization curve of Ozawa method

Fitting of the equation in Fig. 5 can be expressed as:

$$y = -26.7797 \times 10^3 x + 50.689 \quad (6)$$

The linear regression coefficient (R^2) was 0.9904, the slope was -26.7797×10^3 , and the intercept was 50.689. As a result, an activation energy of $211.6 \text{ kJ mol}^{-1}$ and pre-exponential factor of 45.9 min^{-1} were obtained.

The Kissinger and Ozawa methods are differential and integral thermal analysis procedures, respectively, and are widely used to determine the activation energy of biomass degradation at different heating rates (Adrianus and Bernd 1983). For pyrolysis of lignocellulosic materials, a wide range of kinetic schemes have been used, including parallel reactions, nucleation models, distributed activation energy models (DAEM), and so on, but only the so-called Kissinger and Ozawa methods do not need information of the reaction mechanism in advance to calculate the kinetic parameters (Criado and Ortega 1986). Due to their simple and fast calculation and broad adaptation of temperature range, both methods were applied in this work for studying the kinetics of hemicellulose pyrolysis.

Many previous kinetic studies of hemicellulose or its model compounds based on different methods show some dissimilarity among the results. Jeguirim and Gwenaelle (2009) proposed that the activation energy and the pre-exponential factor of hemicellulose were 110 kJ mol^{-1} and 20 s^{-1} ($\log A$) by using a global independent reactions model. Várhegyi and Antal (1989) divided the whole thermal decomposition of 4-methyl-D-glucurono-D-xylan into two successive reactions, and reported that its E and $\log A$ values in the first reaction are about 193 kJ mol^{-1} and 16.9 s^{-1} according to the method of least squares. Calculated by DAEM, Wang et al. (2008) obtained the activation energy of xylan in a range of $156.0\text{-}250.1 \text{ kJ mol}^{-1}$ and the pre-exponential factor was in a range of $3.6 \times 10^{11}\text{-}3.4 \times 10^{22} \text{ s}^{-1}$ (A), which happen to cover the present results. Obviously, the differences in kinetic parameters can be attributed mainly to heterogeneous chemical/physical characteristics of hemicellulose used in experimental and various procedures for calculation. It should be noted that the data obtained from the Kissinger and Ozawa methods in this work did not show much difference, but the fitting degree of the Ozawa method was slightly better than that of the Kissinger method.

CONCLUSIONS

1. Based on ^{13}C -NMR analyses, the hemicellulose obtained from corn stalk showed the presence of several typical monosaccharides of graminaceous hemicelluloses, which confirmed that the separation methods did not significantly change the structure of hemicellulose and can be widely used.
2. As regards to TGA experiments, the thermal degradation of hemicellulose mainly occurred in the temperature range $180\text{-}340^\circ\text{C}$ with a final charcoal residue yield of 24% at 700°C . One weight loss peak at about 280°C and a less evident shoulder peak at about 205°C were recorded on the DTG curve, indicating that the thermal

decomposition of hemicellulose can be divided into two step reactions. An increase of the heating rate could slightly delay the decomposition process to higher temperatures and increase the maximum value of weight loss rate.

3. The activation energy (E) and the pre-exponential factor ($\ln A$) calculated by the Kissinger and Ozawa methods were 213.3kJ mol^{-1} , 211.6kJ mol^{-1} and 46.2min^{-1} , 45.9min^{-1} , respectively, which were in agreement with some other works previously reported. Although the data obtained from two methods did not show significant difference, the fitting degree of Ozawa method was better than that of the Kissinger method.

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