Thermal Decomposition Properties of Materials from Different Parts of Corn Stalk

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To help better utilize corn stalk (CS), pyrolysis behavior of materials from different parts of the CS including corn stalk without pith, corn root, and corn leaf were analyzed using thermogravimetric analysis (TGA) at heating rates of 5, 10, 20, and 25 °C/min. The apparent activation energies determined by the Friedman method for corn stalk without pith, corn root, and corn leaf were in the range of 26.4 to 103.6 kJ/mol, 37.6 to 69.5 kJ/mol, and 35.0 to 103.9 kJ/mol, respectively, depending on the conversion. The main thermal decomposition occurred within a temperature range of 200 to 350 °C (±10 °C). Most of the volatile materials decomposed at less than a 0.8 conversion rate. At greater than a 0.8 conversion rate, the remaining material was mainly char, and the decomposition of char proceeded at higher conversion rates. Different pyrolysis characteristics in the CS indicated that different treatments should be chosen according to different parts for achieving the optimum conversion rate in practical applications.

Keywords: Corn stalk; Different parts; Pyrolysis; Apparent activation energy; TGA

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Project Supported: A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions

INTRODUCTION

Biomass as a degradable and renewable energy resource has gained the attention of more and more researchers. Pyrolysis is the first process of the conversion of biomass materials into gas, oil, (Caballero *et al.* 1997a), chemicals, and char products. The pyrolysis process of biomass materials is complex and affected by many factors such as composition, size, and heating rate (Caballero *et al.* 1997b, Granada *et al.* 2013). Therefore, a kinetic study of the process becomes a very important aspect for utilizing biomass materials.

In China, the annual production of corn stalk (CS) reaches 400 million tons. The problem of making full use of CS has attracted much attention in the last decade (Kim and Agblevor 2007; Lv and Wu 2012; Granada *et al.* 2013; Li *et al.* 2014). Corn stalk is considered a sustainable resource and a replacement for fossil fuel and chemicals. Pyrolysis technology may potentially be used to convert biomass materials to a valuable product, such as pyrolysis oil.

Previous studies indicated that chemical inhomogeneity and structure in different corn stalk fractions were the main reasons for the different processing behaviors (Maiti *et al.* 2007; Lv *et al.* 2013). Hemicellulose, cellulose, and lignin are the three main components of biomass and their thermal decompositions occur at 220 to 315 °C, 315 to 400 °C, and 160 to 900 °C, respectively (Miao and Zhang 2012), to vaporize their extractives (Rao and Sharma 1998).

Ash chemistry is also a key factor that influences the use of biomass materials for direct combustion and gasification (Ross *et al*. 2008). Compositions and structure have been the main factors used in the cited studies to explain pyrolysis behaviors. For example, Wang *et al.* explored the effects of chemical inhomogeneity on pyrolysis behavior and liquefaction reaction of corn stalk fractions at a single rate of temperature rise (Wang *et al.* 2014a,b). In studying sample decomposition kinetics, it is necessary to better understand different reaction mechanisms during the decomposition process.

In this study, we investigated pyrolysis characteristics of materials from the different parts of CS at four different heating rates (*i.e.*, 5, 10, 20, and 25 °C/min) in order to compare their thermal stability properties to guide future chemicals and bio-fuel processing through thermal pyrolysis. The Friedman method was used to determine the apparent activation energy of different parts of CS to better understand the reaction mechanisms and pyrolysis characteristics during the thermal decomposition process.

EXPERIMENTAL

Materials

The CS was collected from an agricultural corn field in Si Yang, Jiang Su Province (China). The CS samples were manually separated into corn stalk without pith, corn root, and corn leaf. All materials were washed with tap water to remove impurities and then dried in an oven at 80 °C for 8 h. Each sample was milled and then screened to obtain particles with sizes between 40 and 60 mesh. Finally, the collected materials were dried in an oven at 103 °C for 4 h before testing.

Methods

The chemical composition analysis of the CS was carried out according to the standard methods ASTM D1107-96 (1996), ASTM D1110-84 (2013), ASTM D1103-60 (1971), and ASTM D1106-96 (2013). The elemental analysis was performed using a Vario EL III elemental analyzer (CHONS-O, Germany). The elemental and chemical composition of the CS samples is shown in Table 1. As shown, the root had the lowest contents of cellulose, hemicellulose, lignin, and ash among the three materials.

Table 1. Elemental and Chemical Composition Analysis of Samples

Sample	Element (%)				Chemical composition (wt%)					
	N	C	S	H	Cellulose	Hemicellulose	Lignin	Ash	Benzene extractive content	Hot water extractive content
CS, no Pith	1.36	45.30	0.14	6.18	32.73	45.53	24.42	8.39	29.78	37.66
Corn Root	0.78	46.87	0.13	6.06	32.26	37.08	16.38	1.74	8.33	9.34
Corn Leaf	1.32	44.88	0.20	6.16	39.43	37.30	24.91	5.22	6.75	14.82

The pyrolysis of samples was conducted with a NETZSCH TG 209F3 thermo-gravimetric analyzer (NETZSCH GmbH, Germany) from 35 °C to 700 °C at four different heating rates of 5, 10, 20, and 25 °C/min under a nitrogen (99.999%) flow rate of 30 mL/min. A 3 to 5 mg sample was placed in the Al_2O_3 ceramic pan of the instrument. Before starting each run, nitrogen was used to purge the furnace for 30 min in order to prevent any unwanted oxidative decomposition.

RESULTS AND DISCUSSION

Thermogravimetric Analysis (TGA)

In this study, the results of thermogravimetric experiments are expressed as a function of conversion α , which is defined in Eq. 1,

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f} \tag{1}$$

where W_o, W_t, and W_f are initial, time t (min), and final mass (g) of the sample, respectively.

The degree of conversion results *versus* temperature for the TGA dynamic experiments at the heating rates of 5, 10, 20, and 25 °C/min of corn stalk with no pith, corn root, and corn leaf are shown in Figs. 1 through 4. The curves of all samples exhibited two weight loss regimes in the region of main decomposition. The early minor weight loss in the samples can be attributed to desorption of moisture as bound water on the surface and the pores of samples (Uzun and Sarioglu 2009). Cellulose, hemicellulose, and lignin are the three main components of biomass materials. Hemicellulose is the easiest to pyrolyze, followed by cellulose and then lignin, the most difficult one (Vafakhah *et al.* 2014). The first stage weight loss of samples between 230 °C and 310 °C can be attributed to the pyrolysis of hemicellulose (Wang *et al.* 2008). The decomposition of cellulose between 310 °C and 600 °C caused the appearance of the second stage. The decomposition of lignin was not obviously observed in this study due to its wide decomposition temperature range between 200 °C and 700 °C. This resulted in an overlap of the weight loss curve of lignin with the curves of the other chemical components (Wang *et al.* 2014a). It was observed that the degradation of CS with no pitch was easier than the other materials at initial reaction stage. This was ascribed to the degradation of higher content of hemicellulose and extractive compounds with poor thermal stability, such as amino acids, fructopyranose, and protein in CS with no pitch (Lv *et al.* 2013). And the degradation of corn leaf was easier than the other two at the second stage due to the higher cellulose in the leaf.

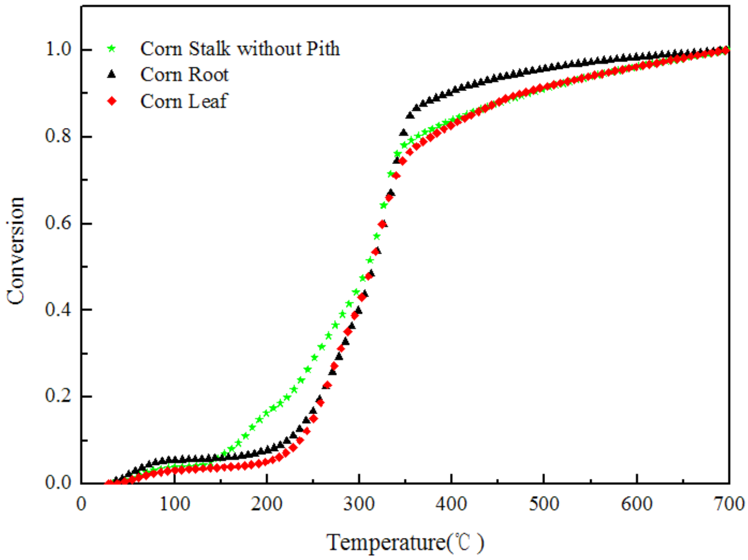

Fig. 1. The effect of pyrolysis rate of corn stalk without pith, corn root, and corn leaf at the heating rate of 5 °C/min

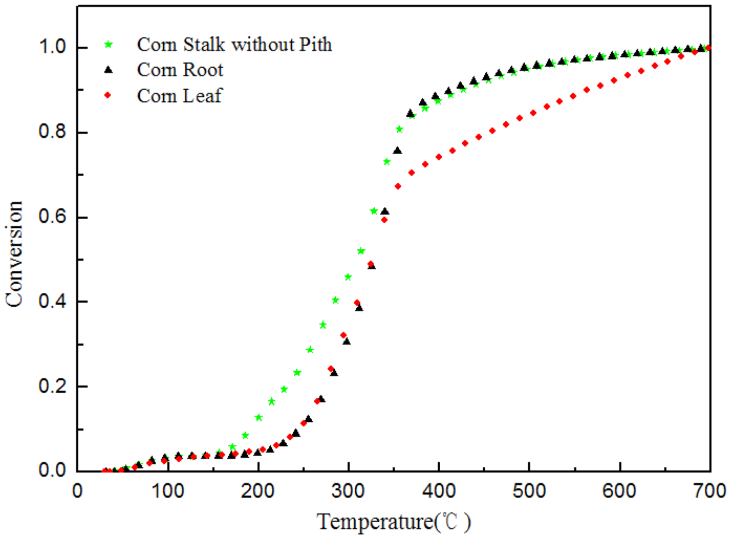

Fig. 2. The effect of pyrolysis rate of corn stalk without pith, corn root, and corn leaf at the heating rate of 10 °C /min

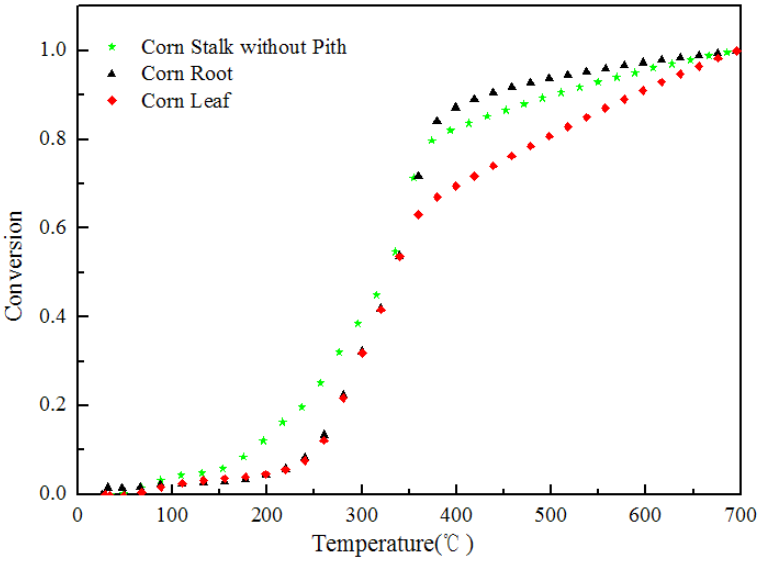

Fig. 3. The effect of pyrolysis rate of corn stalk without pith, corn root, and corn leaf at the heating rate of 20 °C /min

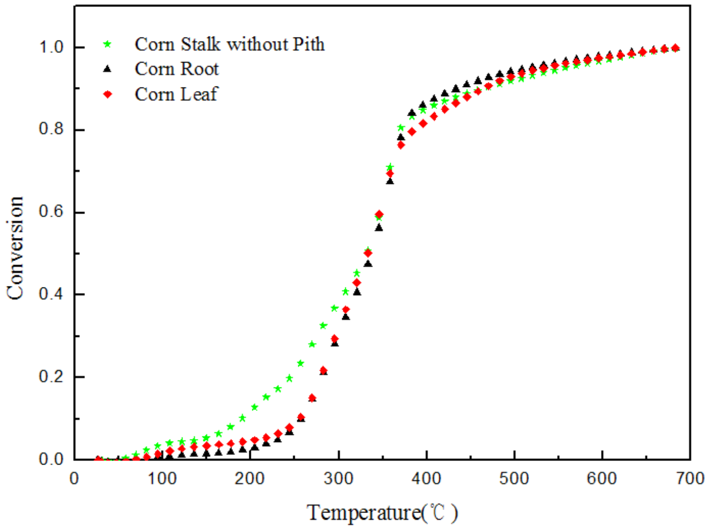

Fig. 4. The effect of pyrolysis rate of corn stalk without pith, corn root, and corn leaf at the heating rate of 25 °C /min

Differential Thermogravimetric Analysis

The differential rate of conversion, *i.e.*, $d\alpha/dt$, was obtained from differential thermogravimetric analysis (DTG) at the different heating rates of 5, 10, 20, and 25 °C/min (Figs. 5 through 8). A large fraction of samples pyrolyzed between 200 °C and 400 °C, which was attributed to hemicellulose and cellulose decomposition. Table 2 shows the characteristic temperatures of the devolatilization reaction of the samples at different heating rates of 5, 10, 20, and 25 °C/min. The maximum value of corn root, corn stalk without pith, and corn leaf at a heating rate 5 °C/min occurred at 338.5, 326.2, and 322.0 °C, respectively. When the heating rate reached 20 °C/min, the maximum value of corn root, corn stalk without pith, and corn leaf occurred at 350, 345, and 330 °C, respectively. The maximum rate of conversion at 5 °C/min was lower than that at 10, 20, and 25 °C/min as shown in Figs. 5 through 8. Corn stalk with no pith had small left shoulders between 120 and 230 °C compared other materials. This was due to the degradation of extractive compounds with poor thermal stability, such as protein, fructopyranose, and amino acids. The appearance of shoulders in the temperature range 230 °C and 300 °C was attributed to the decomposition of hemicellulose. Comparison of the four different heating rates, listed in Table 2, showed that the higher heating rate, the bigger maximum value.

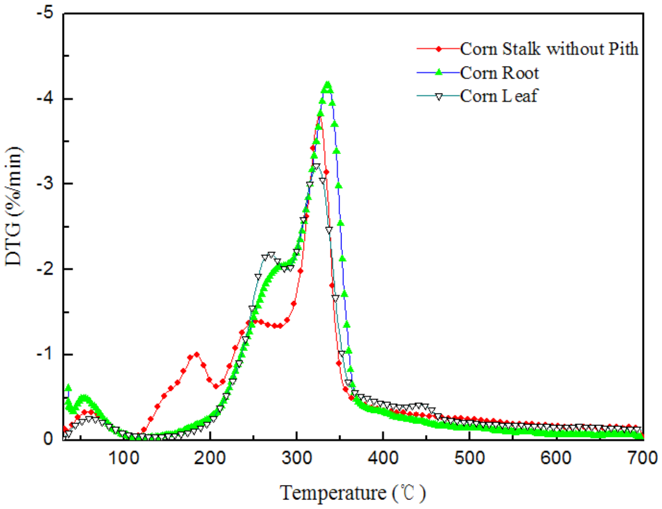

Fig. 5. DTG curves of corn stalk without pith, corn root, and corn leaf at the heating rate of 5 °C/min

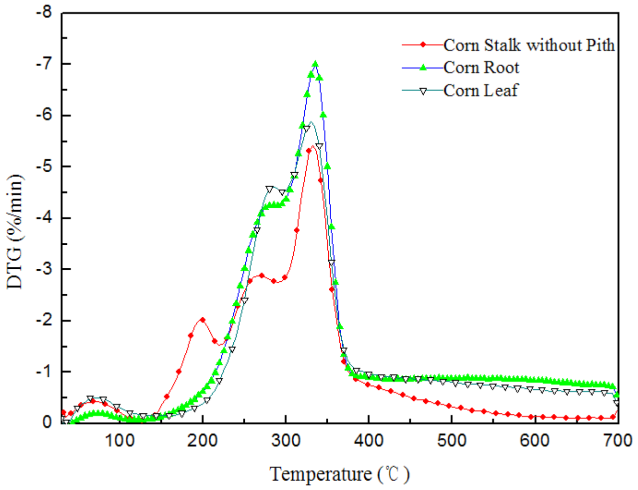

Fig. 6. DTG curves of corn stalk without pith, corn root, and corn leaf at the heating rate of 10 °C/min

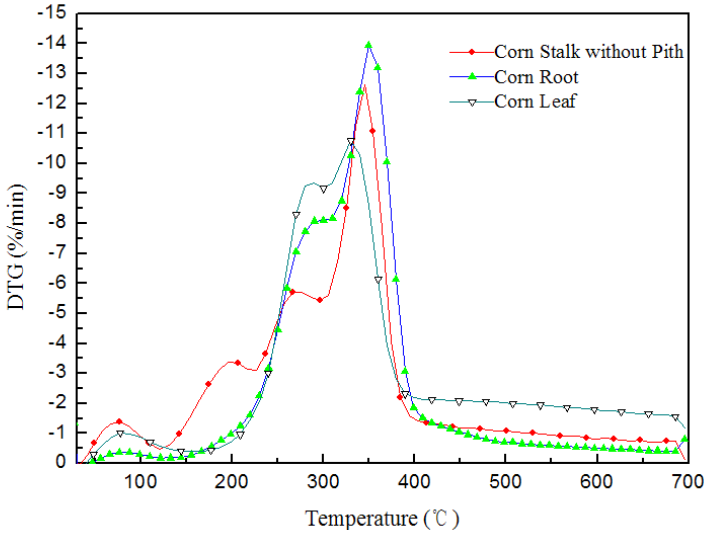

Fig. 7. DTG curves of corn stalk without pith, corn root, and corn leaf at the heating rate of 20 °C/min

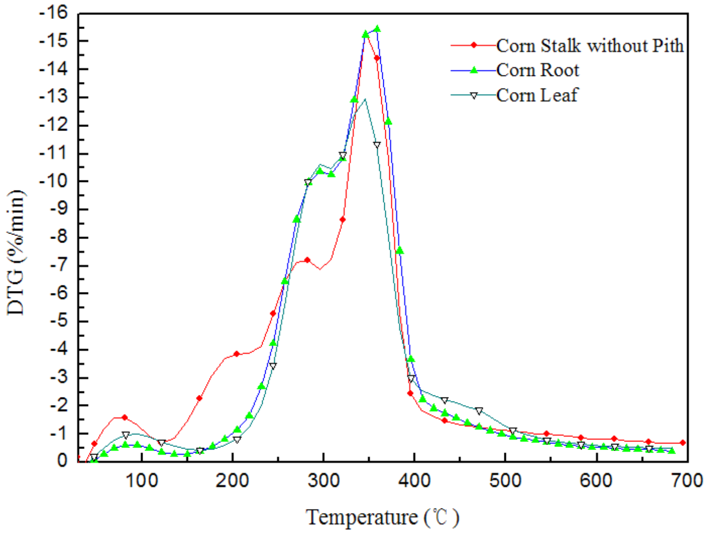

Fig. 8. DTG curves of corn stalk without pith, corn root, and corn leaf at the heating rate of 25 °C/min

Table 2. Characteristic Temperatures of Devolatilization Reaction of the Samples

Heating Rate (°C/min)	Sample	T_o (°C)	T_p (°C)	T_s (°C)	Residue (%)
5	CS, no Pith	204.21	326.20	339.19	19.53
	Corn Root	256.03	338.46	368.77	19.22
	Corn Leaf	241.43	322.04	345.74	23.08
10	CS, no Pith	218.60	332.20	353.45	30.98
	Corn Root	257.03	339.46	369.77	24.15
	Corn Leaf	251.48	329.74	352.41	13.39
20	CS, no Pith	243.39	344.84	365.71	17.90
	Corn Root	258.03	349.70	370.77	18.24
	Corn Leaf	258.09	330.12	361.40	8.51
25	CS, no Pith	231.44	345.49	368.65	18.41
	Corn Root	255.30	358.13	384.12	21.18
	Corn Leaf	255.58	345.56	371.99	26.20

o=onset; p=DTG peak; s=shift

Heating rate tends to affect the peak temperature and the maximum rate of conversion because the amount of thermal energy influences the heat transfer between the surroundings and the interior of the samples (Yang *et al.* 2007; Wang *et al.* 2014b). But the heating rate had no obvious effect on the residue amount.

Kinetic Parameters of Samples

. The kinetic analysis was widely used to assess the thermal stability of biomass materials in the last decades. Many different “model-free” methods have been used to determine the pyrolysis kinetic parameters from the thermogravimetric data (Yao *et al.* 2008; Zhu *et al.* 2012). The Friedman method (Friedman 1964) is one of the most commonly used methods.

The rate of conversion, $d\alpha/dt$, in thermal decomposition is expressed as:

$$\mathrm{d}\alpha / \mathrm{d}t = kf(a) \tag{2}$$

The rate constant k is generally expressed by the Arrhenius equation (Mishra and Bhaskar 2014),

$$k = A \exp(-\frac{E}{RT}) \tag{3}$$

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 temperature independent conversion function, $f(\alpha)$, was expressed as:

$$f(\alpha) = a^n \tag{4}$$

Substituting Eqs. 3 and 4 into Eq. 2 and taking a natural logarithm, the equation 2 yields:

$$\ln(da/dt) = \ln[Af(a)] - E/RT \tag{5}$$

The apparent energy of activation E, based on Eq. 5, can be determined from the relationship between $\ln(d\alpha/dt)$ and $1/T$. Thus, a family of parallel straight lines of slope $-E/R$ can be obtained, from which the apparent energy of activation E

corresponding to the selected conversion can be obtained. The relationship between $\ln(d\alpha/dt)$ and $1/T$ at various conversions from 0.1 to 0.8 is shown in Figs. 9 through 11. For instance, the 0.1 conversion of corn leaf was obtained at the temperatures of 232.56, 243.90, 250.00, and 256.41 °C. At these temperatures, the values of $\ln(d\alpha/dt)$ were -6.026, -5.384, -4.742, and -4.541, respectively. From the slope of $\ln(d\alpha/dt)$ *vs.* $1/T$ at the conversion of 0.1, the activation energy was calculated as 35.041 kJ/mol, and listed in Table 3.

Table 3 shows that the activation energy for the pyrolysis of corn stalk without pith, corn root, and corn leaf was in the range of 26.4 to 103.6 kJ/mol, 37.6 to 69.5 kJ/mol, and 35.0 to 103.9 kJ/mol, respectively, depending on the conversion. This indicated that corn root was converted more cleanly than other materials under the same conversion condition. This was due to the lowest lignin and ash being present in corn root. The activation energy of corn stalk with no pith and corn root increased slowly with increasing the conversion from 0.1 to 0.5. When the conversion increased from 0.6 to 0.8, the activation energy of corn stalk without pith increased sharply (Fig. 12).

Table 3. Calculated Kinetic Parameters for the Pyrolysis of Samples

Conversion								
E (kJ/mol)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
CS, no Pith	26.411	35.891	53.582	58.75	60.663	61.736	75.556	103.615
Corn Root	37.568	42.423	55.912	56.748	62.449	64.174	64.246	69.528
Corn Leaf	35.041	55.542	62.789	64.412	78.601	81.483	82.207	103.897

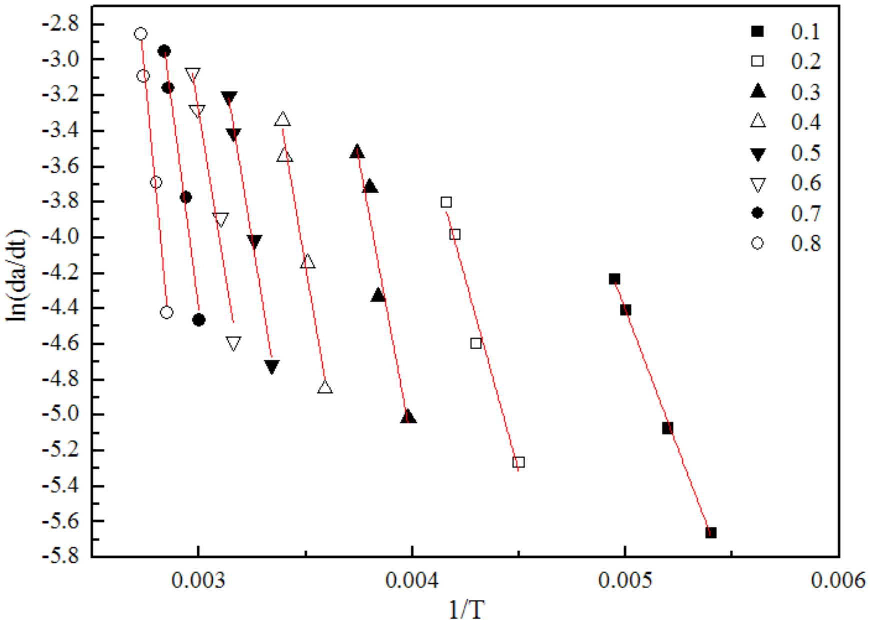

Fig. 9. Typical iso-conversion plot of the Friedman method, corn stalk without pith

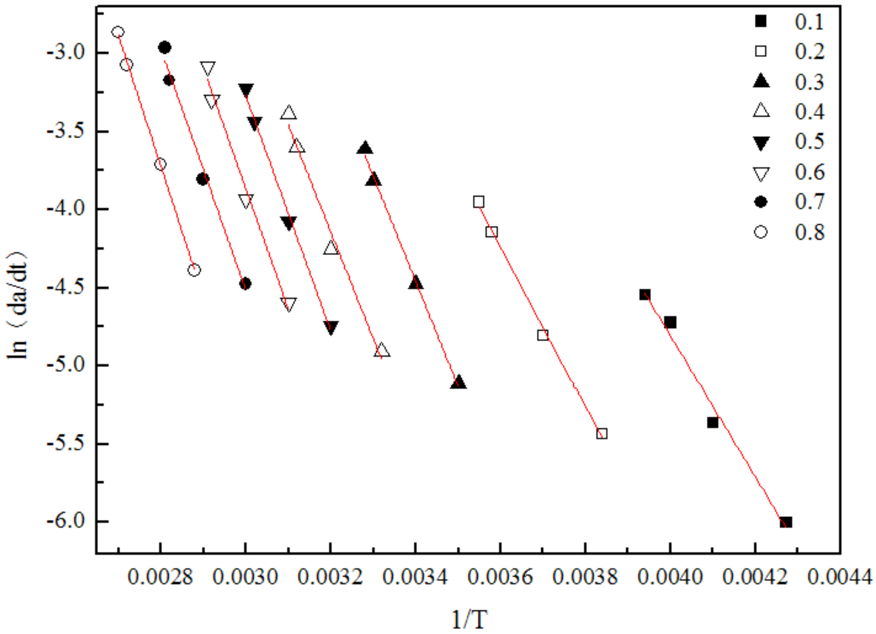

Fig. 10. Typical iso-conversion plot of the Friedman method, corn root

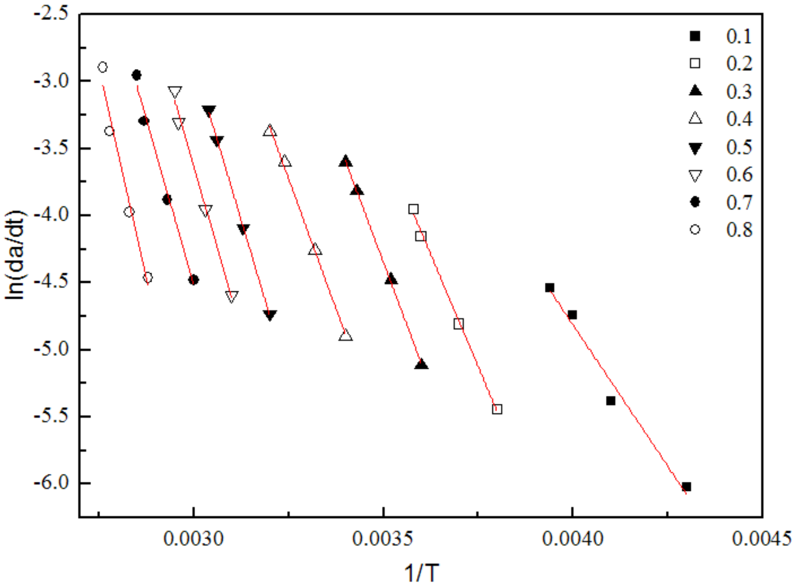

Fig. 11. Typical iso-conversion plot of the Friedman method, corn leaf

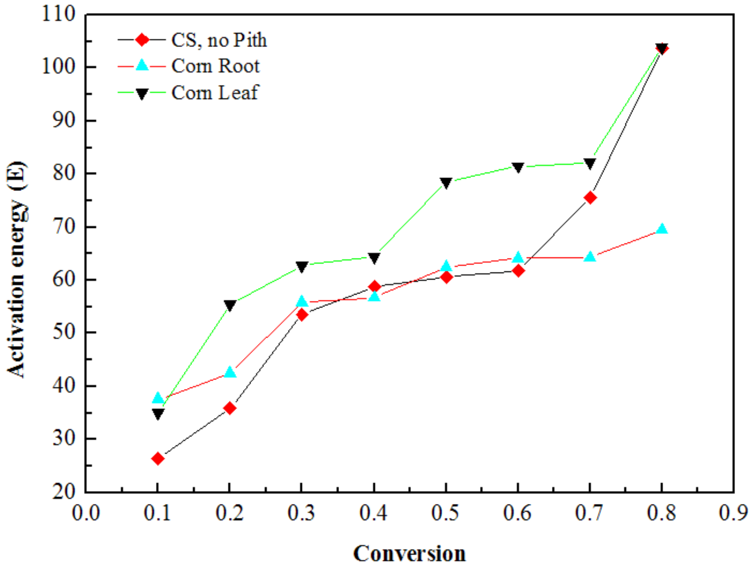

Fig. 12. Iso-conversion plots for activation energy versus conversion

CONCLUSIONS

1. Thermogravimetric analysis of corn stalk without pith, corn root, and corn leaf was carried out to investigate pyrolysis characteristics and to calculate kinetic parameters. The Friedman method was used to determine the apparent activation energy of CS materials. The apparent activation energies determined by the differential method for corn stalk without pith, corn root, and corn leaf were in the range of 26.4 to 103.6 kJ/mol, 37.6 to 69.5 kJ/mol, and 35.0 to 103.9 kJ/mol, respectively, depending on the conversion rate. Corn root converted more cleanly than other materials under the same conversion condition. This was due to the lowest lignin and ash being present in the root.
2. The reaction mechanism of corn with no pith, corn root, and corn leaf of pyrolysis process can be kinetically characterized by two successive reactions.
3. The main thermal decomposition occurred within a temperature range of 200 to 350 °C (±10 °C). Most of the volatile materials decomposed at less than a 0.8 conversion rate. However, the material remaining after a greater than 0.8 conversion was mainly char, and the decomposition of char proceeded at higher conversion rates.
4. The higher the heating rate, the bigger the maximum weight loss rate. The apparent activation energy values of different parts of the CS revealed the difference in pyrolysis behaviors. The result indicated that different treatments should be chosen according to different parts of CS material in order to achieve the most efficient use of the resource.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from the Priority Academic Program Development of Jiang Su Higher Education Institutions (No. 164020890) and by Nanjing Forestry University.

REFERENCES CITED

ASTM D1107-96. (1996). "Standard test method for ethanol-toluene solubility of wood," American Society for Testing and Materials, West Conshohocken, PA.

ASTM D1110-84 (2013). "Standard test methods for water solubility of wood," American Society for Testing and Materials, West Conshohocken, PA.

ASTM D1103-60 (1971). "Standard test method for alpha-cellulose in wood," American Society for Testing and Materials, West Conshohocken, PA.

ASTM D1106-96 (2013). "Standard Test Method for acid-insoluble lignin in wood," American Society for Testing and Materials, West Conshohocken, PA.

Caballero, J. A., Conesa, J. A., Font, R., and Marcilla, A. (1997a). "Pyrolysis kinetics of almond shells and olive stones considering their organic fractions," *Journal of Analytical and Applied Pyrolrolysis* 42(2), 159-175. DOI: 10.1016/S0165-2370(97)00015-6

Caballero, J. A., Font, R., Marcilla, A., and Conesa, J. A. (1997b). "Characterization of sewage sludge by primary and secondary pyrolysis," *Journal of Analytical and Applied Pyrolrolysis* 40-41, 433-450. DOI: 10.1016/S0165-2370(97)00045-4

Friedman, H. L. (1964). "Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to phenolic plastic," *Journal of Polymer Science Part C: Polymer Symposia* 6(1), 183-195. DOI: 10.1002/polc.5070060121

Granada, E., Míguez, J. L., Febrero, L., Collazo, J., and Eguía, P. (2013). "Development of an experimental technique for oil recovery during biomass pyrolysis," *Renewable Energy* 60(12), 179-184. DOI: 10.1016/j.renene.2013.05.010

Kim, S.-S., and Agblevor, F. A. (2007). "Pyrolysis characteristics and kinetics of chicken litter," *Waste Management* 27(1), 135-140. DOI: 10.1016/j.wasman.2006.01.012

Li, G., and Chen, H. (2014). "Synergistic mechanism of steam explosion combined with fungal treatment by *Phellinus baumii* for the pretreatment of corn stalk," *Biomass and Bioenergy* 67(8), 1-7. DOI: 10.1016/j.biombioe.2014.04.011

Lv, G., and Wu, S. (2012). "Analytical pyrolysis studies of corn stalk and its three main components by TG-MS and Py-GC/MS," *Journal of Analytical and Applied Pyrolrolysis* 97(9), 11-18. DOI: 10.1016/j.jaap.2012.04.010

Lv, G., Wu, S., Yang, G., Chen, J., Liu, Y., and Kong, F. (2013). "Comparative study of pyrolysis behaviors of corn stalk and its three components," *Journal of Analytical and Applied Pyrolrolysis* 104(11), 185-193. DOI: 10.1016/j.jaap.2013.08.005

Maiti, S., Purakayastha, S., and Ghosh, B. (2007). "Thermal characterization of mustard straw and stalk in nitrogen at different heating rates," *Fuel* 86(10-11), 1513-1518. DOI: 10.1016/j.fuel.2006.11.016

Miao, Y., and Zhang, G. (2012). "Study about characteristics of FTIR and XRD for corn stalk surface with KH-560 treatment," *Energy Procedia* 16B, 1135-1140. DOI: 10.1016/j.egypro.2012.01.181

Mishra, G., and Bhaskar, T. (2014). "Non-isothermal model free kinetics for pyrolysis of rice straw," *Bioresource Technology* 169(18), 614-621. DOI: 10.1016/j.biortech.2014.07.045

Rao, T. R., and Sharma, A. (1998). "Pyrolysis rates of biomass materials," *Energy* 23(11), 973-978. DOI: 10.1016/S0360-5442(98)00037-1

Ross, A. B., Jones, J. M., Kubacki, M. L., and Bridgeman, T. (2008). "Classification of macroalgae as fuel and its thermochemical behaviour," *Bioresource Technology* 99(14), 6495-6504. DOI: 10.1016/j.biortech.2007.11.036

Uzun, B. B., and Sarioglu, N. (2009). "Rapid and catalytic pyrolysis of CSs," *Fuel Processing Technology* 90(5), 705-716. DOI: 10.1016/j.fuproc.2009.01.012

Vafakhah, S., Bahrololoom, M. E., Bazarganlari, R., and Saeedikhani, M. (2014). "Removal of copper ions from electroplating effluent solutions with native corn cob and corn stalk and chemically modified corn stalk," *Journal of Environmental Chemical Engineering* 2(1), 356-361. DOI: 10.1016/j.jece.2014.01.005

Wang, G., Li, W., Li, B., and Chen, H. (2008). "TG study on pyrolysis of biomass and its three components under syngas," *Fuel* 87(4-5), 552-558. DOI: 10.1016/j.fuel.2007.02.032

Wang, T., Ye, X., Yin, J., Lu, Q., Zheng, Z., and Dong, C. (2014a). "Effects of biopretreatment on pyrolysis behaviors of corn stalk by methanogen," *Bioresource Technology* 164(7), 416-419. DOI: 10.1016/j.biortech.2014.04.062

Wang, T., Yin, J., Liu, Y., Lu, Q., and Zheng, Z. (2014b). "Effects of chemical inhomogeneity on pyrolysis behaviors of corn stalk fractions," *Fuel* 129(8), 111-115. DOI: 10.1016/j.fuel.2014.03.061

Yang, H., Yan, R., Chen, H., Lee, D. H., and Zheng, C. (2007). "Characteristics of hemicellulose, cellulose and lignin pyrolysis," *Fuel* 86(12-13), 1781-1788. DOI: 10.1016/j.fuel.2006.12.013

Yao, F., Wu, Q., Lei, Y., Guo, W., and Xu, Y. (2008). "Thermal decomposition kinetics of natural fibers: Activation energy with dynamic thermogravimetric analysis," *Polymer Degradation and Stability* 93(1), 90-98. DOI: 10.1016/j.polymdegradstab.2007.10.012

Zhu, G., Zhu, X., Xiao, Z., and Yi, F. (2012). "Study of cellulose pyrolysis using an in situ visualization technique and thermogravimetric analyzer," *Journal of Analytical and Applied Pyrolysis* 94(3), 126-130. DOI: 10.1016/j.jaap.2011.11.016

Article submitted: September 24, 2014; Peer review completed: December 11, 2014; Revised version received and accepted: January 29, 2015; Published: February 4, 2015.