THERMOGRAVIMETRIC CHARACTERISTICS
OF WHEAT STRAW LIGNIN

QING YANG and SHUBIN WU

*State Key Laboratory of Pulp and Paper Engineering, South China University of Technology,
Guangzhou, Guangdong 510640, P. R. China*

The thermogravimetric characteristics of wheat straw EMAL (Enzymatic Acidolysis Lignin) were analyzed. The effect of the heating rates on the thermogravimetric characteristics of wheat straw and the wheat straw influence on pyrolysis were investigated. The influence of various heating rates on wheat straw was significant, the pyrolysis rate of wheat straw EMAL increased at temperatures between 200 and 500 °C. At a temperature above 200 °C, the pyrolysis rate of wheat straw EMAL was clearly accelerated, since all DTG curves and the maximum temperature corresponding to pyrolysis shifted to high temperature areas, two maxima being also recorded on the DTG curves. The thermogravimetric dynamics parameters of wheat straw were calculated by the methods of Kissinger and Ozawa, respectively; the activation energy of wheat straw EMAL was of 103.92 and 107.69 KJ·mol^{-1}, respectively, and the frequency factor, *lnA*, of 19.21 and 20.60 min^{-1}. The fitting degree of the Kissinger method was better than that of the Ozawa one. At a pyrolysis temperature over 400 °C, the influence of the lignin present in wheat straw on wheat straw thermal behavior was very clear, lignin pyrolysis dominating over that of wheat straw.

Keywords: wheat straw, thermogravimetry, dynamics, lignin

INTRODUCTION

Knowledge on the kinetics of thermal reactions is vital for predicting the pyrolysis behavior of biomass materials such as lignin. The kinetic study of biomass pyrolysis is of special importance, once it constitutes the initial step of combustion and gasification processes. Knowledge on the thermal decomposition kinetics of lignin is necessary for designing gasifiers and pyrolysis reactors. Thermoanalytical techniques, in particular thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG), provide such information in a simple and straightforward manner.

Due to the complexity of lignin and the difficulty of its extraction, the literature related to the pyrolysis behavior of lignin is scarce. M. Garcìa-Pérez *et al.*[1] proposed an activation energy of 30 KJ·mol^{-1} and a frequency factor of 25 min^{-1} for softwood bark lignin with three-pseudocomponent models. Qian Liu *et al.*[2] studied the kinetics

of fir lignin pyrolysis and put forward a first-order decomposition model for a 149~288 °C temperature range, in which the activation energy and frequency factor were of 72.9 KJ·mol^{-1} and 1.14×10^7 s^{-1}. M. Müller-Hagedorn and H. Bockhorn[3] obtained kinetic parameters for barley straw and Gavott lignins in a TGA based on the Levenberg–Marquardt and improved Runge–Kutta laws. The activation energies and frequency factor for barley straw and Gavott lignins varied from 92 to 102 KJ·mol^{-1} from $10^{7.3}$ to $10^{7.9}$ min^{-1}, and from 84 to 94 KJ·mol^{-1} from $10^{6.7}$ to $10^{7.1}$ min^{-1}, respectively. J. C. Domínguez *et al.*[4] reported that the activation energy of seventeen organosolv lignins, by using the Borchardt–Daniels method, ranged between 17.9 and 42.5 KJ·mol^{-1}. W. Gang *et al.*[5] estimated the activation energy of sawdust lignin to equal 120.7~197.3 KJ·mol^{-1}, according to the distributed active energy model (DAEM). Substantial apparent

differences can be observed in the kinetic parameters reported, which can be due to several factors related to the experimental methods, operating conditions and data analysis, but also to the chemical composition of the raw material examined in each study.

The objective of this work was to investigate the thermal behavior of wheat straw lignin during the pyrolysis process, to study the influence of wheat straw lignin on wheat straw and that of operating conditions on the process characteristics and kinetic parameters, as well as to provide the data and kinetic information necessary for the evaluation of the process, in order to use lignin rationally, by its thermochemical conversion into energy and chemicals.

EXPERIMENTAL
Materials

Material 1: wheat straw from the Baoding region (Hebei province) milled to pass a 120 mesh; material 1 was analyzed as to its chemical composition, according to the National Standard Methods and literature data,[7] with the results presented in Table 1.

Material 2: wheat straw extracted by 5% KOH (some hemicelluloses being removed).[6] The milled wheat straw powder (5 g) was extracted with 100 mL of 5% KOH solution, at room temperature for 8 h, the treated wheat straw powder was washed to neutral with deionized water and dried in a vacuum-oven at room temperature.
Material 3: wheat straw EMAL (enzymatic/acido-lysis lignin).

Cellulase enzymatic hydrolysis

The milled wheat straw powder was dewaxed with acetone in a Soxhlet apparatus for 6 h at 60 °C. The treated sample (10 g) was subjected to an enzymatic treatment, by using industrial cellulase with an activity of about 8000 units/mL carboxyl methyl cellulose (CMCase). Enzymatic hydrolysis was carried out at 40 °C, over 48 h, at pH 4.5 (using acetate buffer solution) and at a content of 5%. After the enzymatic hydrolysis, the impure enzymatic hydrolysis lignin was centrifuged, and washed twice with acidic deionized water at pH 2.0 (HCl), then freeze-dried.

Mild acidolysis

5 g of impure enzymatic hydrolysis lignin were suspended in l00 mL of dioxane/acidified deionized water solution (85:15 v/v, 0.01mol/L HCl) and extracted at 87 °C, by sparging nitrogen gas for 2 h. The obtained mixture solution was filtered and the lignin solution was collected. The solid residue was sequentially washed 2~3 times with a fresh dioxane/deionized water solution (85:15 v/v). The total filtrate solution was neutralized with sodium bicarbonate and stirred for 3 h. The neutralized solution was then rotary-evaporated until a thick solution was obtained. Further on, this thick solution was carefully dropped into a large quantity of acidified deionized water (pH 2.0, HCl) and the precipitated lignin was isolated by centrifugation, washed and freeze-dried. The obtained lignin was finally washed with HPLC grade hexane and dried in a vacuum drying oven, at room temperature.

Material 4: wheat straw holocellulose (containing small amounts of lignin).[7] The milled wheat straw powder was treated with benzene-ethanol (2:1 v/v) in a Soxhlet apparatus for 6 h at 60 °C. 2 g of the treated sample were put into a 250 mL conical flask, and 65 mL deionized water, 0.5 mL glacial acetic acid and 0.6 g sodium chlorite (as 100% available chlorine) were added, followed by shaking, covering with an inverted 25 mL conical flask, and placing in a water bath at 75 °C for 1 h. During heating, the conical flask should be often rotated and shaken, maintaining the temperature of the solution for 1 h, followed by the addition of 5 mL glacial acetic acid and 0.6 g sodium chlorite, shaking up and continuing the heating in a water bath at 75 °C for 1 h. The procedure was repeated four times. The conical flask was taken out of the water bath and cooled in an ice water bath. After suction and filtration on a G2 glass filter of known weight, the filtrate was repeatedly washed with deionized water until the holocellulose residue was neutral. Finally, holocellulose was washed three times with acetone and dried in a vacuum drying oven at room temperature.

Thermogravimetric analysis

Thermogravimetric experiments were performed in a TG209 Integrated Thermal Gravimetric Analyzer from NETZSCH Corporation, Germany, with high purity nitrogen as carrier gas with a flow rate of 40 mL/min. Each time, about 6-12 mg of material were put in a ceramic crucible, and materials 1, 2 and 3 were heated from room temperature to 800 °C, at heating rates of 10, 20, 30, 40 and 50 °C/min, respectively. Material 4 was also tested under the conditions mentioned above, at a heating rate of 30 °C/min. Calculated thermogravimetic rate data were automatically output through the TG209 Integrated Thermal Gravimetric Analyzer system.

The thermogravimetric experiment was applied to obtain the parameters of chemical dynamics, so that the influence of any error should be decreased as much as possible. The average size of all samples was below 0.2 mm, so that the mass loss of the samples was under the control of the kinetic reaction.

RESULTS AND DISCUSSION
Thermal decomposition characteristics of EMAL

The TG and DTG curves of wheat straw EMAL, obtained at heating rates of 10, 20, 30, 40 and 50 °C/min, separately, and plotted in Figures 1 and 2, respectively, show that thermal decomposition occurred over a wide temperature range, starting at approximately 150 °C. A major loss of weight followed, accompanied by devolatilization with charring,[8] which was highly exothermal[9] between 200 and 500 °C, while the char residue at 800 °C varied between 32 and 40%, at different heating rates. However, over 500 °C, this was followed by a slow further mass loss up to the final temperature, the TG curves tending to become flat.

The DTG peaks differed in their position and height, because the heating rate acted as a significant factor on lignin thermal decomposition. With increasing the heating rate from 10 to 50 °C/min, the thermal decomposition rate increased over 200~500 °C, the DTG curves being shifted towards a higher temperature zone, and the temperatures corresponding to the maximum loss of the mass peaks also shifting towards higher values. Moreover, the decomposition rate of wheat straw EMAL evidenced two maxima, presenting the two fast pyrolysis reactions to which wheat straw EMAL was subjected during thermal degradation.

Table 1
Chemical composition of wheat straw, %

| Composition	Content
Ash	3.59
1% NaOH extractives	48.11
Ethanol-benzene extractives	1.89
CH_2Cl_2 extractives	2.35
Nitric acid-ethanol cellulose	41.07
Holocellulose	72.32
Pentosans	23.26
Klason lignin	19.18
Acid soluble lignin	2.82
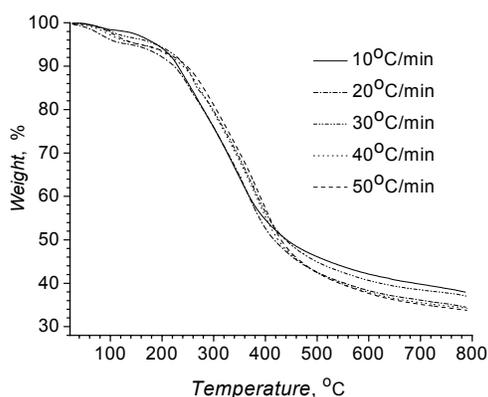
Figure 1: TG curves of wheat straw EMAL at different heating rates
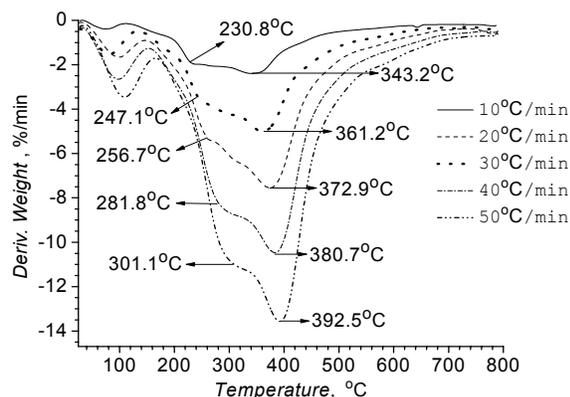
Figure 2: DTG curves of wheat straw EMAL at different heating rates

Kinetics of wheat straw EMAL pyrolysis

The kinetic study of biomass pyrolysis was of special importance, constituting the initial step of the combustion and gasification processes. In the case of lignocellulosic materials, knowledge on the kinetics of their thermal decomposition was useful for designing gasifiers and pyrolysis

reactors. The methods of Kissinger and Ozawa, as two types of non-isothermal kinetics, which benefited from fast measurement, wide temperature range and broad use, were applied in the experiments.

Experimental data were used to fit the kinetic model (eq. 1):

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

where $a = 1 - \dfrac{m_{(t)} - m_f}{m_0 - m_f}$

and $k = A\exp(-E/RT)$

$m_{(t)}$ was the experimental mass at each monitoring time, m_f was the final mass, and m_o was the initial dry mass. $f(\alpha)$ was the differential form of the kinetic mechanism function and k was the kinetic constant which, according to the Arrhenius equation, was a function of the pre-exponential factor (A), apparent activation energy (E), absolute temperature, and constant of ideal gas law (R).

The temperature–time relation was computed from the following expression (eq. 2):

$$T = T_o + \beta t \tag{2}$$

β whose unit was °C/min was the constant heating rate, and T_o – the initial temperature.

The function (eq. 3) and (eq. 4) was deduced *via* eqs. 1 and 2, as follows:

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

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

Equations 3 and 4 provided the formula for calculating the apparent activation energy (E) and the constant of ideal gas law (R) of Kissinger[10] and of Ozawa,[11] respectively. $g(a)$ was the integral form of the kinetics

mechanism function in equation 4.

Kissinger method

While temperature reached its maximum value, the effect of the heating rates on the peak temperature followed equation 3. The peak temperature and the heating rates plotted in Figure 2 are shown in Table 2. The graph of $\ln(\beta/T_p^2)$ depending on $1/T_P$ was plotted in Figure 3.

The fitting of the equation in Figure 3 was expressed as:

$$y = -12.49974 \times 10^3 x + 9.7756 \tag{5}$$

The linear regression coefficient (R^2) was of 0.99. The slope was of -12.49974×10^3, from which the apparent activation energy (E) – 103.92 KJ·mol^{-1} – was deduced; the intercept of the fit equation was of 9.7756, so the pre-exponential factor (lnA) equaled 19.21 min^{-1}.

Ozawa Method

ln β and $1/T_P$ represented the linear relation with a given value of α in the DTG curves of different heating rates. The effect of the heating rate on the peak temperature of the DTG curves was followed in equation 4. The peak temperature and heating rates from Figure 2 are shown in Table 3, while the graph on the dependence of ln β on $1/T_P$ is shown in Figure 4.

The fitting of the equation in Figure 4 was expressed as:

$$y = -13.62676 \times 10^3 x + 24.46324 \tag{6}$$

The linear regression coefficient (R^2) was of 0.98. The slope was of -13.62676×10^3, from which the apparent activation energy (E) – of 107.69 KJ·mol^{-1} – was deduced; the intercept of the fit equation was of 24.46324, so the pre-exponential factor (lnA) equaled 20.60 min^{-1}.

Table 2
Parameter values in Kissinger formula

β/(min^{-1})	T	$1/T \times 10^{-3}$	$ln\beta$
10	616.2	1.62	2.30
20	634.2	1.58	3.00

30	645.9	1.55	3.40
40	653.7	1.53	3.69
50	665.5	1.50	3.91

Table 3
Parameter values in Ozawa formula

$\beta/(\text{min}^{-1})$	T	$1/T \times 10^{-3}$	$1/T^2 \times 10^{-6}$	$\beta/T^2 \times 10^{-6}$	$\ln(\beta/T^2 \times 10^{-6})$
10	616.2	1.62	2.63	26.3	-10.55
20	634.2	1.58	2.45	49.0	-9.92
30	645.9	1.55	2.40	72.0	-9.54
40	653.7	1.53	2.34	93.6	-9.28
50	665.5	1.50	2.26	113.0	-9.09
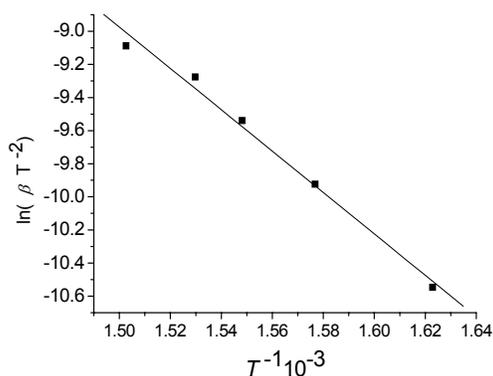
Figure 3: Linearization curves of Kissinger method
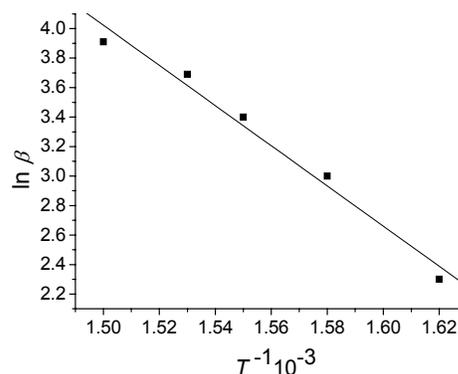
Figure 4: Linearization curves of Ozawa method

Influence of wheat straw EMAL on wheat straw pyrolysis

As the occurrence of any inter-reactions in these three components or the nature of the reaction mechanism acting in the three components (especially lignin) during thermal decomposition are not elucidated yet, various combinations of the main components present in biomass were prepared, for better understanding the thermal and gravimetric characteristics of lignin. To further investigate the influence of wheat straw EMAL on wheat straw pyrolysis, the thermogravimetric analysis of material 1 (cellulose + hemicelluloses + lignin), material 2 (cellulose + lignin), material 3 (lignin) and material 4 (cellulose + hemicelluloses) was performed, and the relation between the conversion of the four materials and temperature being also studied.

The TG and DTG curves of four kinds of materials with heating rates of 30 °C/min are plotted separately in Figures 5 and 6.

Figure 5 shows that the four curves changed slowly, which indicates that cellulose and hemicelluloses are predominantly degraded during wheat straw pyrolysis mostly when the temperature was below 400 °C, which agrees with the literature data,[8] while lignin pyrolysis dominated over wheat straw, when the temperature was above 400 °C. The results suggested that the influence of lignin in wheat straw during wheat straw pyrolysis was obvious at temperatures beyond 400 °C.

As seen in Figure 6, the thermo-gravimetric rate of material 2 and material 1 was quick; however, material 3 reacted slowly, due to its mild DTG curve. Lignin pyrolysis was accelerated as some hemicelluloses were extracted from wheat straw, because the mass loss of material 2 was higher than that of material 1, at the same temperature, when temperature exceeded 400 °C. This might be due to the changes occurring in the remaining lignin, due to the exposure to the KOH used for hemicelluloses extraction. Most decompo-

sition products were volatile, according to the results of the total decomposition of cellulose and hemicelluloses during wheat straw pyrolysis; the main remainder was char due to lignin pyrolysis. The TG curve of material 4 accounted for the easy decomposition of cellulose and hemicelluloses, as reported in literature.[12]

On account of different initial temperatures of the four kinds of materials, the research temperature range was restricted from 250 to 700 °C. The chart of the pyrolysis conversion and the temperature of four kinds of materials with heating rates of 30 °C/min are plotted in Figure 7.
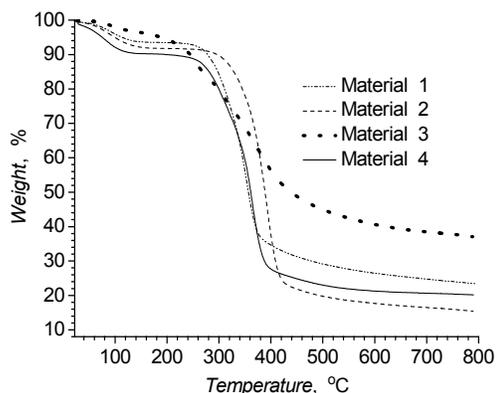
Figure 5: TG curves of the materials
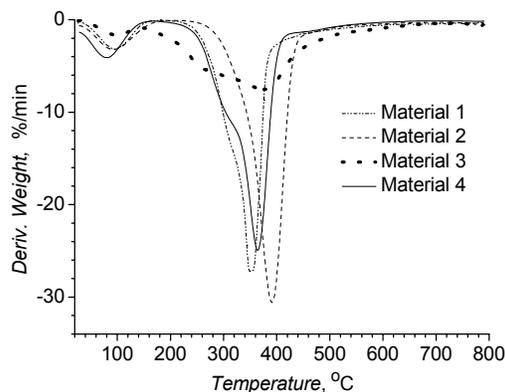
Figure 6: DTG curves of the materials
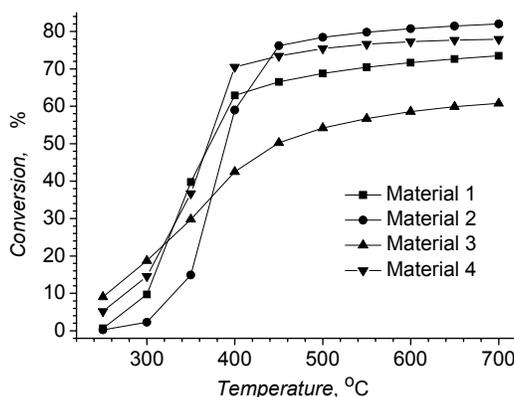
Figure 7: The relationship between conversion and temperature in all materials

The structure and chemical properties of the three main components present in biomass were different, so that the pyrolysis mechanism was not the same. Owing to the large difference in the four materials, the mechanism of biomass pyrolysis benefited from the study of the relationship between pyrolysis conversion rate and temperature for different fractions. The change discrepancy among the four curves was evident at temperatures below 400 °C; the four curves were relatively flat and consistent at temperatures over 400 °C, which agreed with the change of the four TG curves (Fig. 5). Therefore, it was proved that cellulose and hemicellulose pyrolysis occurred mostly at

temperatures under 400 °C. Lignin, as one of the three main components of wheat straw, was an impact factor for the wheat straw converted into volatiles, while its thermal decomposition behavior determined the characteristics of wheat straw pyrolysis at certain temperatures.

CONCLUSIONS
- The influence of various heating rates on wheat straw was significant, the pyrolysis rate of wheat straw EMAL increasing over a temperature range between 200 and 500 °C. At temperatures above 200 °C, the pyrolysis rate of wheat straw EMAL accelerated obviously; all DTG curves and maximum

pyrolysis corresponding temperature shifted towards a high temperature area, two maxima being also recorded on the DTG curves.

- The thermogravimetric dynamics parameters of wheat straw were calculated by the methods of Kissinger and Ozawa, respectively. Although the results of the dynamics parameters were almost equal, the fitting degree of the Kissinger method was higher than that of the Ozawa one.

- At pyrolysis temperatures over 400 °C, the influence of the lignin present in wheat straw on wheat straw was obvious, lignin pyrolysis dominating over that of wheat straw.

REFERENCES
[1] M. Garcìa-Pérez, A. Chaala, H. Pakdel *et al.*, *J. Anal. Appl. Pyrol.*, **78**, 104 (2007).
[2] Q. Liu, S. R. Wang, Z. Yun *et al.*, *J. Anal. Appl. Pyrol.*, **82**, 170 (2008).
[3] M. Müller-Hagedorn and H. Bockhorn, *J. Anal. Appl. Pyrol.*, **79**, 136 (2007).
[4] J. C. Domínguez, M. Oliet, M. V. Alonso *et al.*, *Ind. Crop. Prod.*, **27**, 150 (2008).
[5] G. Wang, W. Li, B. Q. Li *et al.*, *Fuel*, **87**, 552 (2008).
[6] J. X. Chen and J. L. Yu, in "Study Methods on the Chemical Structure in Plant Fibers", South China University of Technology Press, Guangzhou, 1989, p. 43.
[7] S. L. Shi and F. W. He, in "Analysis of Pulp and Papermaking", China Light Industry Press, Beijing, 2003, pp. 25-44.
[8] H. P. Yang, R. Yan, H. P. Chen *et al.*, *Fuel*, **86**, 1781 (2007).
[9] R. Ball, A. C. McIntosh and J. Brindley, *Combust. Theor. Model.*, **8**, 281 (2004).
[10] H. F. Kissinger, *Anal. Chem.*, **29**, 1702 (1957).
[11] T. Ozawa, *J. Thermochem. Acta*, **355**, 35 (2000).
[12] H. P. Yang, R. Yan, H. P. Chen *et al.*, *Energ. Fuel.*, **20**, 383 (2006).