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TG-FTIR ANALYSIS OF PINE SAWDUST PYROLYTIC KINETICS

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The pyrolysis of certain pine sawdust was studied by thermogravimetric analyzer coupled with Fourier transform infrared spectroscopy (TG-FTIR). Different heating rates were applied to a final temperature of 950 °C. Total loss weights of 78%, 79% and 83% at heating rates of 20 °C/min, 40 °C/min and 80 °C/min, respectively, were observed, and the temperature trend of evolving gaseous products, such as CH_4, H_2O, CO and CO_2, was investigated. The plot of the thermal decomposition rate curve leads to kinetic parameters, which were calculated by Kissinger's and Ozawa's methods; the activation energy of the substrate was of 130.14 and 133.21 $kJ \cdot mol^{-1}$, respectively, and the frequency factor, of 2.594×10^{11} and 3.143×10^{11} min^{-1}. The results show that the above-mentioned methods successfully represent decompositon curves and fit the experimental data very well. Therefore, this study provides a simple way to evaluate the pyrolytic rate of biomass in a real combustor.

Keywords: pine sawdust, pyrolysis, reaction kinetics, TG-FTIR

INTRODUCTION

Pyrolysis is one of the promising thermal approaches that can be used to convert biomass into energy.[1] It plays an important role in the thermochemical conversion of biomass materials to bioenergy. The pyrolysis process is highly complex and depends on several factors, such as biomass composition and heating rate.[2] Little detailed information predicting product specification and yields on pine sawdust pyrolysis was found in the available literature. The lack of data leads to difficulties in understanding the emission behavior of pine sawdust during the thermal treatment process.

In this study, volatile products from TG during TG-FTIR experiment were swept into gas cell immediately by the carrier gas so that secondary reactions were minimized. At the same time, 3D spectra that reflect the effect of time and wavenumber at different heating rates were generated by Nicolet spectrometer. The results on weight loss and composition of the evolved gases obtained in the study provide sufficient information to understand the pyrolysis characteristics of pine sawdust.

EXPERIMENTAL

Proximate analysis (moisture, ash, volatile content and fixed carbon of pine sawdust residue sample) and ultimate analysis of the combustible fraction (in weight-by-weight percentage) are shown in Table 1. After being dried in an oven at 105 °C for 3 h, the original materials were crushed and pulverized to a size of <0.2 mm before they were analyzed.

Table 1
Proximate and ultimate analyses of material

	Proximate analysis				Ultimate analysis			
	Moisture	Ash	Volatile	Fixed carbon	C	H	O	N
Concentration (wt%)	11.26	0.61	75.32	12.81	50.02	5.54	44.40	0.04

A Bruker Vector 22 spectrometer and a Setsys Erolution TG92 thermal analyzer, coupled by a Thermo-Nicolet TGA special connector, were used. The stainless steel transfer pipe and gas cell (20 cm optical path length) were heated at 180 °C. Nitrogen was used as carrier gas with a flow rate of 100 ml/min for both TGA and spectrometer. The resolution in FTIR was set to 1 cm^{-1}, the number of scans per spectrum to 4 times/min and the spectral region to 400-600 cm^{-1}.

A certain heating rate (20-80 °C/min) was applied, with a final temperature of 900 °C. For FTIR, a weight loss of about 10 mg usually gives an adequate signal, so approximately 15 mg of sample was used in this study. A medium-sized crucible of 70 µl made of Al_2O_3 was adopted as sample container.

RESULTS AND DISCUSSION

The TG and DTG curves of the substrate, obtained at heating rates of 10, 20, 40, 60 and 80 °C/min, separately, are plotted in Fig. 1 (a,b), respectively, showing that thermal decomposition occurred over a wide temperature range, starting at approximately 150 °C, and moisture was mainly released at this stage.

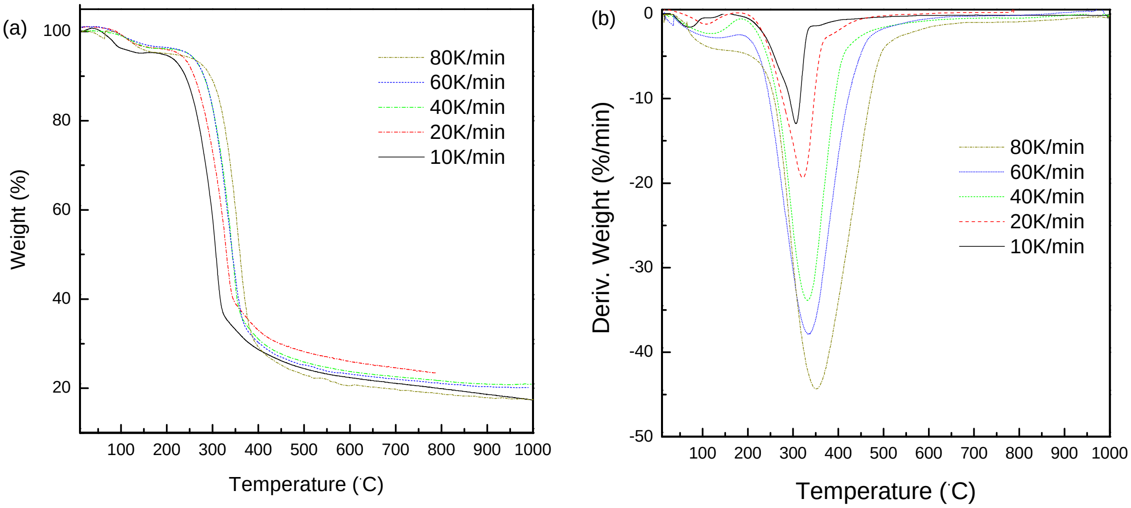

Figure 1: TG (a) and DTG (b) curves for lignin at different heating rates

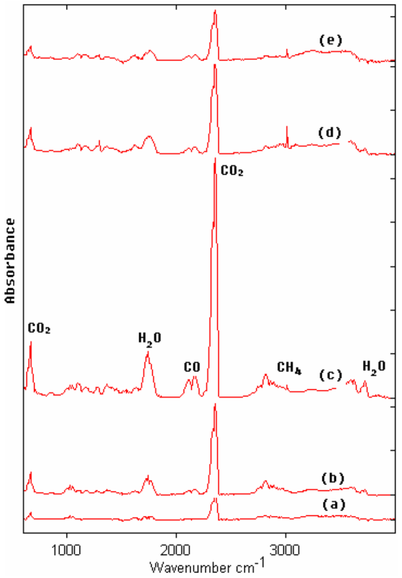

Figure 2: FTIR spectrum for pyrolysis products evolving from the sawdust sample at different temperatures (a) 250 °C, (b) 300 °C, (c) DTG peak Tmax = 321.2 °C, (d) 500 °C, (e) 700 °C

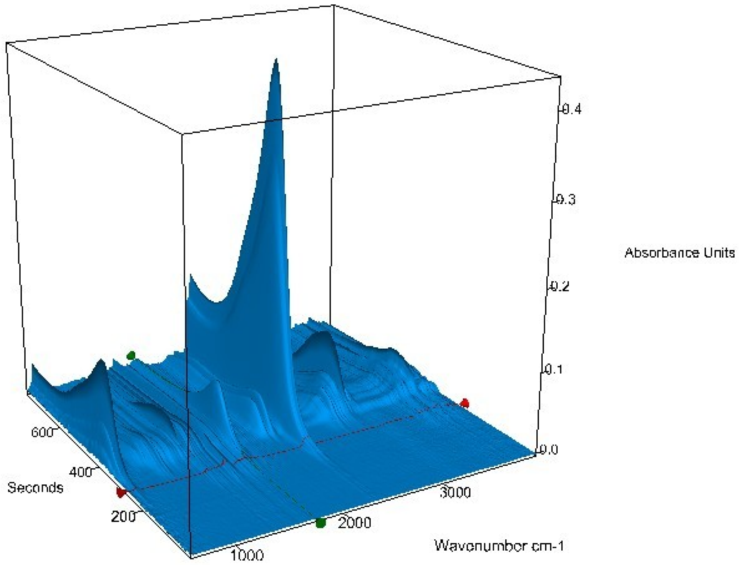

Figure 3: 3D infrared spectrum of evolution gases during the pine sawdust pyrolysis at the heating rate of 20 K/min

The second stage represented fast thermal decomposition between 200 °C and 350 °C, weight loss occurring mainly in this temperature range with the main gas products identified by FTIR as follows: CO_2, CO, H_2O and CH_4 (see Fig. 2). The maximum of the DTG curve (weight loss rate) was attained at about 320 °C. The last stage consisted in high temperature charring of the residue, with a much smaller weight loss. Still, there remained a little residue at 950 °C, i.e. between 17 wt% and 23 wt% of the original weight.

The 3D infrared spectrum of the evolution gases includes information on infrared absorbance, wavenumber and temperature (Figure 3). From the infrared spectrum, the change of spectral intensity along time direction is similar to TG results. But the temperature at the spectral intensity peak is decided by TG because there is a delay of several seconds from TG to FTIR.

The pyrolysis of pine sawdust proceeds according to a free-radical pathway.[3] There is a larger proportion of ether linkages (β-O-4 and α-O-4) in biomass, such as sawdust and lignin, the ether bonds are liable to break due to their lower bond energy, forming large free radicals. These large free radicals undergo uni-molecular decomposition, forming products. According to the classical theory for the kinetics of chain reaction,[4] the uni-molecular decomposition has an order of reaction of 1.0.

Kissinger and Ozawa methods are, respectively, differential and integral thermal analysis methods applied to determine the apparent activation energy of pyrolysis at different heating rates. In non-isothermal kinetics, for the most usual case of a linear heating program corresponding to a constant heating rate, the dependence of the reaction rate on the temperature and the extent of the reaction could be described by the following differential equation (Eq. 1):

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) = k(1-\alpha)^n \qquad (1),$$

where

$$\alpha = 1 - \frac{m_{(t)} - m_f}{m_0 - m_f}, \quad k = A \cdot \exp\left(-\frac{E}{RT}\right) \quad \text{and } n=1.04 \qquad (2)$$

$m_{(t)}$ is the experimental mass at each monitoring time, m_f is the final mass, and m_0 is the initial dry mass; $f(\alpha)$ is the differential form kinetic mechanism function and k is the kinetic constant, which, according to the Arrehenius equation, is a function of the pre-exponential factor (A), apparent activation energy (E), absolute temperature (T) and constant of ideal gas law (R).

The substitution of Eq. (2) in Eq. (1) yields:

$$\frac{d\alpha}{dt}=A\exp(-\frac{E}{RT})(1-\alpha)^n \tag{3}$$

For a linear heating rate, β=dT/dt, Eq. (3) becomes:

$$\frac{d\alpha}{dT}=(\frac{A}{\beta})\exp(-\frac{E}{RT})(1-\alpha)^n \tag{4}$$

The temperature–time relation was computed from the following expression (Eq. (5)):

$$T=T_0+\beta\cdot t \tag{5}$$

where β (°C/min) is the constant heating rate, T_0 is the initial temperature and T_p is the maximum temperature peaks of DTG curves.

The function (Eqs. (6) and (7)) was deduced via Eqs. (1)-(5), as follows:

$$\ln(\frac{\beta}{T_p^2})=-\frac{E}{RT_p}+\ln(\frac{AR}{E}) \tag{6}$$

$$\ln(\beta)=\ln\frac{AE}{Rg(\alpha)}-5.331-1.052\frac{E}{RT_p} \tag{7}$$

where $g(\alpha)=-\ln(1-\alpha)$ when n=1.0 (8)

Eqs. (6) and (7) provided the formula for calculating the apparent activation energy (E) and the constant of ideal gas law (R) of Kissinger[5] and Ozawa,[6] respectively. g(α) is the integral form of the kinetics mechanism function in Eq. (7). Kissinger's method is based on the fact that the reaction rate dα/dt rose to a maximum value with an increase in reaction temperature.[5] Ozawa's method is an integral technique expressing straight lines at different heating rates according to the relationship between the logarithm of the heating rate and reciprocal temperature at constant mass loss, in which the apparent activation energy of degradation is calculated from the slope of linear relationships.[6] The methods of Kissinger and Ozawa, as two types of non-isothermal kinetics benefiting from fast measurement, wide range of temperature and broad use, were applied in the experiments.

Kissinger's method

The kinetic parameters for pine sawdust were calculated using Kissinger's method. While temperature reached its maximum value, the effect of heating rates on peak temperature followed Eq. (6). The peak temperature and the heating rates plotted in Fig. 4 are shown in Table 2. The graph of $\ln(\beta/T_p^2)$ depending on $1/T_p$ is plotted in Fig. 4.

Fitting the equation in Fig. 4 was expressed as:

$$\ln(\frac{\beta}{T_p^2})=-\frac{15.65331\times10^3}{T_p}+16.62308 \tag{9}$$

As can be seen from Table 2, the linear regression coefficient (R^2) was 0.987. The slope was -15.65331×10^3, from which the apparent activation energy (E), 130.14 kJ·mol^{-1}, was deduced; the intercept of the fit equation was 16.62308, so the pre-exponential factor was 2.594×10^{11} min^{-1}.

Table 2
Parameter values in Kissinger's and Ozawa's equations

β(min^{-1})	T_p	$1/T_p\times10^{-3}$	$1/T_p^2\times10^{-6}$	$\beta/T_p^2\times10^{-6}$	$Ln(\beta/T_p^2\times10^{-6})$	Lnβ
10	579.18	1.73	2.98	29.81	-10.42	2.30
20	594.22	1.68	2.83	56.64	-9.78	3.00
40	605.08	1.65	2.73	109.25	-9.12	3.69
60	616.32	1.62	2.63	157.96	-8.75	4.09
80	624.98	1.60	2.56	204.81	-8.49	4.38

Ozawa's method

lnβ and $1/T_p$ represent the linear relation with a given value of α in the DTG curves of different heating rates. The effect of heating rate on the peak temperature of the DTG curves was followed in Eq. (7). The peak temperature and the heating rates from Fig. 5 are given in Table 2, while the graph of lnβ depending on $1/T_p$ iss shown in Fig. 5.

Fitting the equation in Fig. 5 was expressed as:

$$\ln(\beta)=-\frac{16.85612\times10^3}{T_p}+31.42234 \tag{10}$$

The linear regression coefficient (R^2) was 0.989. The slope was -16.85612×10^3, from which the apparent activation energy (E), 133.21 kJ·mol^{-1}, was deduced; the intercept of the fit equation was 31.42234, so the pre-exponential factor was 3.143×10^{11} min^{-1}.

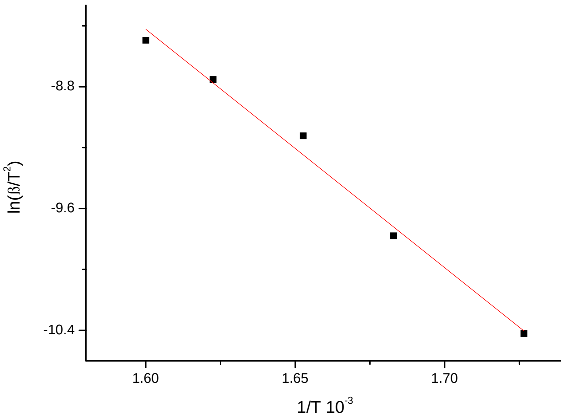

Figure 4: Linearization curves according to Kissinger's method

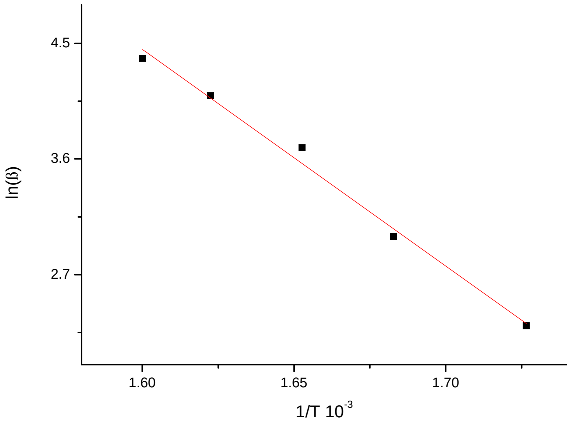

Figure 5: Linearization curves according to Ozawa's method

CONCLUSION

We successfully analyzed the pine sawdust pyrolysis process and evolved gases by using TG-FTIR. The influence of various heating rates on sawdust was significant, the pyrolysis rate of the substrate increasing over a temperature range between 200 and 500 °C. At temperatures above 200 °C, the pyrolysis rate of the substrate accelerated obviously; all DTG curves and corresponding maximum pyrolysis temperature shifted towards a high temperature area, two maxima being also recorded on the DTG curves.

The thermogravimetric kinetic parameters of pine sawdust were calculated by the methods of Kissinger and Ozawa, respectively. The results of the kinetic parameters were almost equal and the fitting degree of the Ozawa method was similar to that of the Kissinger one. In conclusion, TG-FTIR approach has a good potential to provide valuable parameters for the predictive modelling of biomass pyrolysis. However, more work is needed to optimise the experimental technique, to better utilize the rich information obtained from this analysis and to quantitatively validate simple and useful correlations for practical applications.

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REFERENCES

[1] H. Yang, R. Yan, T. Chin, D. L. Liang, H. Chen and C. Zheng, *Energ. Fuels*, **18**, 6 (2004).

[2] R. T. Rao and A. Sharma, *Energy*, **23**, 11 (1998).

[3] P. F. Britt, A. C. Buchanan, K. B. Thomas and S. K. Lee, *J. Anal. Appl. Pyrol.*, **33**, 2 (1995).

[4] K. J. Laidler, "Chemical Kinetics", McGraw-Hill Book Company, 1965.

[5] H. E. Kissinger, *Anal. Chem.*, **29**, 11 (1957).

[6] T. Ozawa, *Bull. Chem. Soc. Jpn.*, **38**, 11 (1965).