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KINETIC STUDY OF PINE SAWDUST PYROLYSIS *VIA* TG/DTG ANALYSIS

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The pyrolysis of pine sawdust was investigated by thermogravimetric techniques (TG/DTG) in the temperature range from room temperature (20 °C) to 1000 °C under dynamic heating conditions (10, 20, 40 and 80 K min^{-1} heating rates). Little differences in the weight loss as a function of heating rates were observed. Total weight losses of 83%, 78%, 79% and 83% at heating rates of 10 K/min, 20 K/min, 40 K/min and 80 K/min were observed, respectively. From the thermogravimetric analysis, it was established that the thermal decomposition pine sawdust consisted of three main stages: water evaporation (<200 °C), devolatilization of organic volatiles (200~500 °C) and char formation (>500 °C). The kinetic processing of non-isothermal TG data was performed by model-free methods, such as the Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sonuse (KAS) methods. The average activation energy calculated by the FWO and KAS methods was 96.38 and 91.72 kJ mol^{-1}, respectively. Experimental results showed that the values of kinetic parameters obtained by both methods were in good agreement and could be successfully applied to understand the complex degradation mechanism of the solid-state reaction. With a further increase of the conversion degree, a complicated relation between activation energy (Ea) and conversion (α) was evident, as the thermal degradation process of pine sawdust underwent a multi-step reaction. The findings of this study contribute to better understanding of the devolatilization process of different types of biomass.

Keywords: pine sawdust, pyrolysis, reaction kinetics, TG/DTG

INTRODUCTION

As one of the most promising thermal approaches to utilizing biomass, pyrolysis plays a major role in the thermochemical conversion of biomass to bioenergy.[1] The pyrolysis process is highly complex and mainly influenced by several factors, such as biomass composition and heating rate.[2] Little detailed information on pyrolysis kinetics of pine sawdust has been found in the available literature. The lack of data leads to difficulties in comprehensively understanding the thermal decomposition behavior of pine sawdust.

Thermogravimetric (TG) analysis has been proved to be an effective tool to investigate the thermal degradation behavior of biomass,[3-5] polymers[6-8] and even wastes.[9,10] Most thermal decomposition characteristics could be clearly confirmed by TG/DTG analysis. In addition, kinetic parameters could be calculated without considering complicated chemical reactions during thermal decomposition. Recent pyrolytic research has been conducted in the field of biomass, such as rice hull,[11] pine trees,[12] birch wood,[13] bagasse or sawdust,[14-16] *etc*.

Currently, most methods for analyzing non-isothermal solid substrate pyrolytic kinetics by TG/DTG analysis[17,18] can be divided into model-fitting and model-free (iso-conversional) methods.[19] Model-fitting methods, including the Freeman-Carroll method, Coats-Redfern method *etc*., consist in fitting different models to the data for the purpose of optimizing the best statistical model from which the kinetic parameters could be calculated. Model-free methods, including the Kissinger method, Ozawa method, Kissinger-Akahira-Sonuse method, Flynn-Wall-Ozawa method *etc*., require different kinetic curves at different heating rates to calculate kinetic parameters for the same value of conversion.

The purpose of this work is to investigate the kinetics of thermal decomposition of pine sawdust. The pyrolysis process was performed by TG/DTG analysis at several linear heating rates. The TG curves (mass loss curves) were observed and the derivative thermogravimetry (DTG) results were obtained for four heating rates. Two traditional model-free non-isothermal methods, such as Kissinger-Akahira-Sonuse (KAS) and Flynn-Wall-Ozawa (FWO), were used to calculate the activation energy (Ea) and the pre-exponential factor (A). The effect of heating rate on decomposition was also studied. To our knowledge, this is the most detailed thermal and kinetic characterization of pine sawdust pyrolysis to date.

EXPERIMENTAL

Materials

The pine sawdust sample was supplied by a timber mill in Nanjing, China. Proximate, ultimate and component analysis results are listed in Table 1 with the standard operation procedures.[20] Prior to experiments, the sample was 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.[21]

TG/DTG quantitative analysis

TG/DTG analysis equipment and operational conditions are the same as reported previously.[20] Nitrogen of purity >99.99% was used as carrier gas to provide an inert atmosphere. During the experiment, the cell of TG was flushed with 100 ml/min nitrogen to avoid thermal decomposition of the sample. A certain heating rate (10-80 K/min) was applied, with a final temperature of 1000 °C. We repeated the experiment three times for each heating rate within an error range of about ±3% in order to obtain representative experiment results. The sample was loaded into an Al_2O_3 container with the volume of 70 µl for each run. Without considering the change of temperature for this exothermic reaction, the local temperature could be equivalent with the real temperature recorded by the instrument.

Kinetic theory

The kinetics of reaction in solid-state is described by the following equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

Conversion, α, is the normalized form of weight loss data of the decomposed sample and is defined as follows:

$$\alpha = 1 - \frac{m_{(t)} - m_f}{m_0 - m_f} \tag{2}$$

where $m_{(t)}$ is the experimental mass at each monitoring time, m_f is the final mass, and m_0 is the initial dry mass.

According to the Arrhenius equation, the temperature dependence of the rate constant k is given by:

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

where Ea is the activation energy (kJ mol^{-1}), T is the absolute temperature (K), R is the gas constant (8.314 J K^{-1} mol^{-1}) and A is the pre-exponential factor (min^{-1}). The combination of two equations, *i.e.* (1) and (3), gives the fundamental expression (4) of analytical methods to calculate kinetic parameters, on the basis of TGA results.

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot \exp(-\frac{E}{RT}) \tag{4}$$

Table 1

Proximate and ultimate analyses of pine sawdust

	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

The expression of the function $f(\alpha)$ and its derivative $f'(\alpha)=-1$ are used for describing solid-state first order reaction, and the mathematical function $f(\alpha)$ could be restricted to the following expression:

$$f(\alpha) = (1 - \alpha)^n \tag{5}$$

where n is the reaction order. According to the classical theory for the kinetics of chain reaction,[22] biomass thermal decomposition has an order of reaction of 1.0. Substituting expression (5) into equation (4) gives the expression of reaction rate in the form:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{6}$$

For non-isothermal TGA experiments at linear heating rate $\beta=dT/dt$, equation (6) can be written as:

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right)\exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{7}$$

This equation expresses the fraction of material consumed over time.

In this work, the activation energy was obtained from non-isothermal TGA. The methods used to calculate kinetic parameters are called model-free non-isothermal methods and require a set of experimental results at different heating rates.

Model-free methods

Flynn-Wall-Ozawa method

The FWO method[23,24] is an integral technique, expressed in 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 was calculated from the slope of linear relationships. By this method the apparent activation energy (Ea_α) could be obtained from the plot of a natural logarithm of heating rates, $\ln\beta$, versus $1000/T_{\alpha i}$, which represents the linear relation with a given value of conversion at different heating rates. $T_{\alpha i}$ is the corresponding temperature of the DTG curve at a given conversion (shown in Fig. 1).

$$\ln(\beta_i) = \ln\frac{A_\alpha E_\alpha}{Rg(\alpha)} - 5.331 - 1.052\frac{E_\alpha}{RT_{\alpha i}} \tag{8}$$

where $g(\alpha)$ is constant at a given value of conversion, *e.g.*, $g(\alpha) = -\ln(1-\alpha)$ when n = 1.0. The subscripts *i* and α denote a given value of heating rate and a given value of conversion, respectively. The activation energy E_α is calculated form the slope $-1.052\ E_\alpha/R$.

Kissing-Akahira-Sunose method

Similarly, the KAS method[25] could also provide the value of activation energy from a plot of $\ln(\beta/T_{\alpha i}^2)$ against $1000/T_{\alpha i}$ for a series of experiments at different heating rates (β), where $T_{\alpha i}$ is the corresponding temperature of the DTG curve at a given conversion. The subscripts *i* and α denote a given value of heating rate and a given value of conversion, respectively. The equation is based on the following expression:

$$\ln\left(\frac{\beta}{T_{\alpha i}^2}\right) = -\frac{E_\alpha}{RT_{\alpha i}} + \ln\left(\frac{A_\alpha R}{E_\alpha g(\alpha)}\right) \tag{9}$$

The apparent activation energy can be obtained from the plot of $\ln(\beta_i/T_{\alpha i}^2)$ versus $1000/T_{\alpha i}$ for a given value of conversion, α, where the slope is equal to $-E_\alpha/R$.

RESULTS AND DISCUSSION

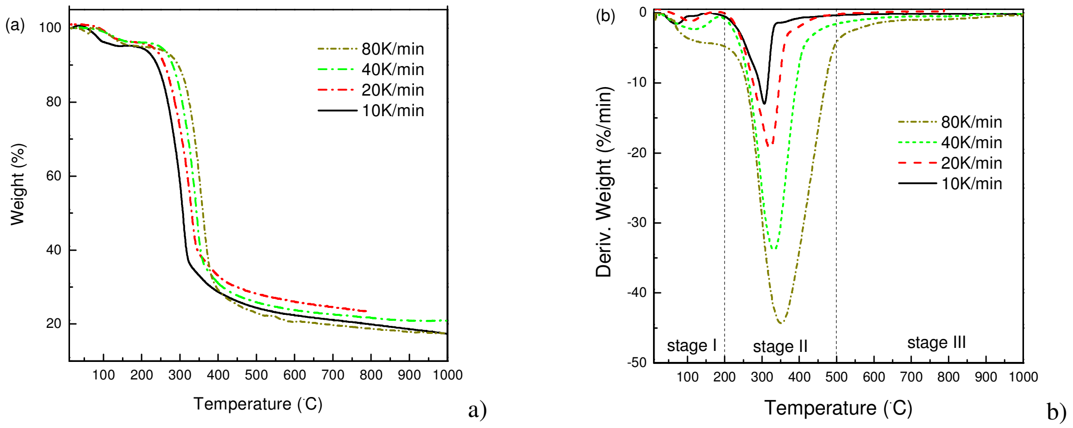
Thermal behavior analysis

The TG and DTG curves of the substrate, obtained at heating rates of 10, 20, 40 and 80 K/min, separately, are plotted in Figure 1 (a and b, respectively). The pyrolysis of the pine sawdust substrate could be divided into three stages, which correspond to water evaporation (stage I), devolatilization of organic volatiles (stage II) and char formation (stage III). In detail, the initial decrease in weight is due to water release when the temperature is below 200 °C, which is related to the extraction of moisture and adsorbed water in the wood substrate[26] (see stage I). The second stage is the primary pyrolysis of pine sawdust, as the temperature increases from 200 to 500 °C, the weight decreases sharply with the maximum weight loss rate of -13.0 %/min at the heating rate of 10 K/min. The temperature corresponding to the maximum weight loss rate of the sample is about 310 °C. A large amount of gas species, such as CO_2, CO, CH_4 and H_2O, are released in this stage, which indicate that they mainly come from this primary pyrolysis stage (see stage II). As the temperature continues to increase, the weight variation is very small, with a lower amount of gas species being released, and char is formed (see stage III).

Effect of heating rate on thermal behavior

Figure 1 (a) and (b) also shows the mass loss curves of pine sawdust at the fixed heating rates from the TG experiments. TG experiments were carried out at the heating rates of 10-80 K/min. It was shown that pine sawdust started to decompose at 200 °C and significant decomposition continued until the temperature reached 500 °C, where the mass yield dropped to 25-30%. After that, pyrolysis progressed at a slower rate as the temperature increased to 1000 °C, where the final yield reached about 20% (see Fig. 1a).

Figure 1 also indicates that there was nearly no change of mass yield in the temperature range of 500-1000 °C. The residue left mostly consisted in fixed carbon and a trace amount of ash. The fixed carbon yields were of about 0.20 g/g pine sawdust. On the other hand, volatile yields were of about 80%.



a) b)

Figure 1: Curves of TG (a) and DTG (b) for pine sawdust at different heating rates

Table 2
Parameter values in FWO formula and KAS formula

Conversion, α	β(min^{-1})	Tα(K)	1/T$_\alpha$×10^{-3}(K^{-1})	Lnβ	Ln(β/T$_\alpha^2$×10^{-6})
0.1	10	513.82	1.95	2.30	-10.18
	20	530.09	1.89	3.00	-9.55
	40	555.85	1.80	3.69	-8.95
	80	570.09	1.75	4.38	-8.31
0.15	10	530.22	1.89	2.30	-10.24
	20	546.52	1.83	3.00	-9.61
	40	569.95	1.75	3.69	-9.00
	80	588.75	1.70	4.38	-8.37
0.2	10	541.45	1.85	2.30	-10.29
	20	558.75	1.79	3.00	-9.66
	40	580.25	1.72	3.69	-9.04
	80	599.12	1.67	4.38	-8.41
0.25	10	550.28	1.82	2.30	-10.32
	20	568.75	1.76	3.00	-9.69
	40	588.65	1.70	3.69	-9.07
	80	607.29	1.65	4.38	-8.44
0.3	10	558.05	1.79	2.30	-10.35
	20	577.57	1.73	3.00	-9.72
	40	596.12	1.68	3.69	-9.09
	80	613.65	1.63	4.38	-8.46
0.35	10	565.05	1.77	2.30	-10.37
	20	585.42	1.71	3.00	-9.75
	40	602.48	1.66	3.69	-9.11
	80	619.87	1.61	4.38	-8.48
0.4	10	571.18	1.75	2.30	-10.39
	20	592.52	1.69	3.00	-9.77
	40	608.3	1.64	3.69	-9.13
	80	625.32	1.60	4.38	-8.49
0.45	10	576.28	1.74	2.30	-10.41
	20	598.56	1.67	3.00	-9.79
	40	613.43	1.63	3.69	-9.15
	80	630.42	1.59	4.38	-8.51
0.5	10	580.6	1.72	2.30	-10.43

	20	603.72	1.66	3.00	-9.81
	40	617.75	1.62	3.69	-9.16
	80	634.85	1.58	4.38	-8.52
0.55	10	584.85	1.71	2.30	-10.44
	20	608.92	1.64	3.00	-9.83
	40	622.37	1.61	3.69	-9.18
	80	639.22	1.56	4.38	-8.54
0.6	10	589.98	1.69	2.30	-10.46
	20	616.49	1.62	3.00	-9.85
	40	628.3	1.59	3.69	-9.20
	80	645.42	1.55	4.38	-8.56

Figure 1(b) shows the derivative thermogravimetry (DTG) corresponding to mass loss data shown in Figure 1(a). For pine sawdust, some trends have been noted: (1) four peaks for four heating rates; (2) a larger peak at higher heating rates; (3) a peak located in a narrow temperature range; (4) a higher peak temperature at higher heating rates. These thermogravimetric curves of the pyrolysis of the pine sawdust substrate were found comparable to those reported in similar pyrolysis studies of other biomass.[12,27]

In addition, the studies conducted on the influence of heating rate indicated that an increase in thermal lag occurs on the pyrolysis of biomass as the heating rate increases.[28] It is obvious that, with an increase in temperature, the pyrolysis process of pine sawdust is greatly influenced by the heating rate, and differences can be seen from the details of the primary pyrolysis ranging from 200 °C to 500 °C (corresponding to stage II in Fig. 1), which indicates that the heating rate mainly influences the primary pyrolysis stage. For pine sawdust, the curves of weight loss rate versus temperature shift to the right as the heating rate increases. The DTG curves for different heating rates (Fig. 1b) show that the rate of decomposition shifted to a higher magnitude and the main peak became broader as the heating rate increased. For example, the maximum mass loss rate (%/min) occurs at about 306 °C at a heating rate of 10 K/min, whereas that at 80 K/min occurs at about 352 °C for pine sawdust. These data are coherent with the literature[29] on woods with similar cellulose and hemicellulose contents to those of pine sawdust. This could be attributed to heat transfer limitation and initiation of secondary cracking reaction effects. The reason for these changes is that higher instantaneous thermal energy is provided in the system and enough time may be required to heat uniformly and reach equilibrium at a low heating rate. On the other hand, a higher heating rate has a short reaction time and the temperature needed for the sample to decompose is also higher, which means enough heat could initiate multiple complex parallel and series reactions for hydrocarbon evolution from the sample.[30] This phenomenon causes the maximum rate curve to shift to the right,[31] which means the thermal diffusion barrier contributes greatly to the pyrolytic apparent activation energy.

Kinetic analysis

The results obtained from thermogravimetric analysis were elaborated according to the model-free methods to calculate the kinetic parameters (see Table 2). The activation energy (*Ea*) and pre-exponential factor (*A*) were obtained by the FWO and KAS methods.

FWO method

The kinetic parameters obtained by the FWO method were calculated according to Eq. (8), for a given value of conversion, α. To determine the kinetic parameters, we chose the same value of α from the range from 0.1 to 0.6 for all the curves at different heating rates. The FWO plots of $\ln(\beta_i)$ versus $1000/T_{\alpha i}$ K^{-1} for different values of conversion are shown in Figure 2. The apparent activation energies were obtained from the slope and pre-exponential factors from the intercept of the regression line and are given in Table 3. The calculated squares of the correlation coefficients, R^2, corresponding to linear fittings in Figure 2, were in the range from 0.94 to 0.99.

KAS method

The kinetic parameters for pine sawdust were calculated using the KAS method according to Eq. (9), for a given value of conversion, α. Similarly, we chose the same value of α from the range from

0.1 to 0.6 for all the curves at different heating rates and we found the corresponding temperature. The KAS plots of $\ln(\beta_i/T_{\alpha i}^2)$ versus $1000/T_{\alpha i}$ K^{-1} for different values of conversion are shown in Figure 3.

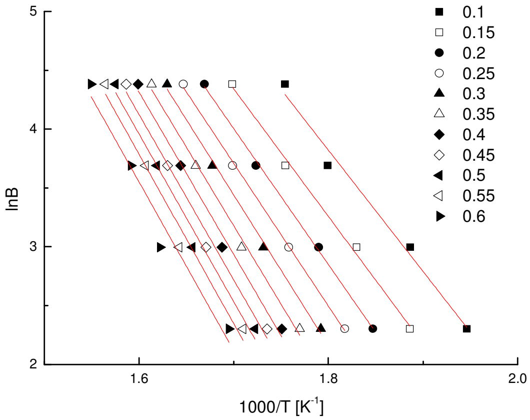


Figure 2: Linearization curves by FWO method

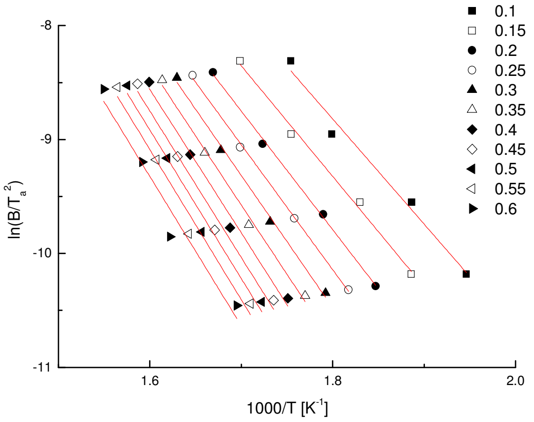


Figure 3: Linearization curves by KAS method

Table 3
Values of Ea and A for pine sawdust pyrolysis obtained by FWO and KAS methods

Conversion, α	FWO			KAS		
	E/(kJ/mol)	A/min^{-1}	R^2	E/(kJ/mol)	A/min^{-1}	R^2
0.1	81.42	7.01E+05	0.97978	76.66	2.82E-02	0.97503
0.15	85.59	1.14E+10	0.99465	80.65	2.32E+03	0.99217
0.2	91.23	2.47E+10	0.99796	86.51	5.38E+03	0.99754
0.25	95.81	7.65E+10	0.99864	91.19	1.77E+04	0.99847
0.3	100.99	1.88E+11	0.99591	96.52	4.66E+04	0.99529
0.35	105.28	5.11E+11	0.993	100.92	1.39E+05	0.99187
0.4	108.97	1.15E+12	0.98752	104.71	3.31E+05	0.98542
0.45	111.00	2.29E+12	0.98197	106.76	6.94E+05	0.9789
0.5	112.52	3.28E+12	0.97635	108.29	1.01E+06	0.97229
0.55	113.71	4.34E+12	0.96897	109.47	1.36E+06	0.96361
0.6	113.27	5.31E+12	0.94934	108.92	1.67E+06	0.9404
Average value	96.38	1.35E+11		91.72	3.03E+04	

R^2 corresponds to linear fittings in Figures 1 and 2

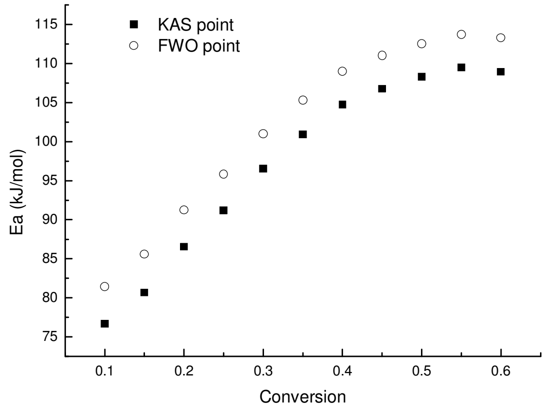


Figure 4: Activation energy as a function of conversion

The apparent activation energies were obtained from the slope and pre-exponential factors from the intercept of the regression line and are given in Table 3. The calculated squares of the correlation coefficients, R^2, corresponding to linear fittings in Figure 3, were in the range from 0.94 to 0.99.

In Figure 4, we can observe that the apparent activation energy for the pyrolysis of pine sawdust was not similar for all conversions, which indicates the existence of a complex multistep mechanism that occurs in the solid state. The apparent value of the activation energy is about 81.42-113.27 kJ mol^{-1} and 76.66-108.92 kJ mol^{-1} for FWO and KAS, respectively. This means that the reaction mechanism is not the same in the whole decomposition process and that the activation energy is dependent on conversion.

The model-free methods allow to estimate the activation energy as a function of conversion without any assumption on the reaction model and allows detecting multi-step kinetics as a dependence of activation energy on conversion, unlike single model-free methods, such as the Kissinger or Ozawa method, which produce a single value of the Ea for the whole process.[32] In addition, the difference in kinetic parameters could be attributed to the complex nature of wood, which comprises a mixture of cellulose, hemicellulose, lignin and extractives, and where the proportion, reactivity and chemistry are affected by variety. Moreover, different experimental conditions and procedures used for calculations could also cause differences in derived kinetic parameters for the same type of biomass.

CONCLUSION

In this work, a comprehensive pyrolysis kinetics study of pine sawdust is presented. Thermogravimetric analysis was performed under nitrogen atmosphere at different heating rates of 10, 20, 40 and 80 K min^{-1}. Thermal decomposition of pine sawdust proceeded in three stages: water evaporation, devolatilization of organic volatiles and char formation. It was found that the main pyrolysis process occurred at about 200-500 °C. The effect of heating rate on the TG and DTG curves was also studied. The activation energy and the pre-exponential factor were calculated by the FWO and KAS methods, as a function of conversion due to the complex mechanism of reaction that occurs during the pyrolysis process. The values of the activation energy obtained by the two methods are in good agreement, *i.e.*, 96.38 and 91.72 kJ mol^{-1}, respectively. Experimental results showed that the model-free methods could describe the complexity of the thermal decomposition process of pine sawdust. However, more work is needed to effectively utilize the rich information obtained from this analysis and to quantitatively investigate the pyrolytic mechanism for practical applications.

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REFERENCES

[1] H. Yang, R. Yan, T. Chin, D. L. Liang, H. Chen *et al.*, *Energ. Fuels*, **18**, 1814 (2004).

[2] R. T. Rao and A. Sharma, *Energy*, **23**, 973 (1998).

[3] R. Bassilakis, R. M. Carangelo and M. A. Wojtowicz, *Fuel*, **80**, 1765 (2001).

[4] N. Gao, A. Li, C. Quan, L. Du and Y. Duan, *J. Anal. Appl. Pyrol.*, **100**, 26 (2013).

[5] J. E. White, W. J. Catallo and B. L. Legendre, *J. Anal. Appl. Pyrol.*, **91**, 1 (2011).

[6] M. Herrera, M. Wilhelm, G. Matuschek and A. Kettrup, *J. Anal. Appl. Pyrol.*, **58**, 173 (2001).

[7] A. Marcilla, A. Gomez and S. Menargues, *J. Anal. Appl. Pyrol.*, **74**, 224 (2005).

[8] X. Chen, L. Huo, C. Jiao and S. Li, *J. Anal. Appl. Pyrol.*, **100**, 186 (2013).

[9] L. Tao, G. B. Zhao, J. Qian and Y. K. Qin, *J. Hazard. Mater.*, **175**, 754 (2010).

[10] H. M. Zhu, J. H. Yan, X. G. Jiang, Y. E. Lai and K.F. Cen, *J. Hazard. Mater.*, **153**, 670 (2008).

[11] H. S. Teng, H. C. Lin and J. A. Ho, *Ind. Eng. Chem. Res.*, **36**, 3974 (1997).

[12] S. S. Kim, J. Kim and Y. H. Park, *Bioresour. Technol.*, **101**, 9797 (2010).

[13] A. Zhurinsh, G. Dobele, J. Rizhikovs, J. Zandersons and K. Grigus, *J. Anal. Appl. Pyrol.*, **103**, 227 (2013).

[14] T. Y. Lin and C. P. Kuo, *J. Anal. Appl. Pyrol.*, **96**, 203 (2012).

[15] X. Gu, X. Ma, L. Li, C. Liu, K. Cheng *et al.*,

Cellulose Chem. Technol., **48**, 275 (2014).
[16] N. Gao, B. Liu, A. Li and J. Li, *J. Anal. Appl. Pyrol.*, **114**, 155 (2015)
[17] P. Simon, *J. Therm. Anal. Calorim.*, **76**, 123 (2004).
[18] N. Sbirrazzuoli, L. Vincent, A. Mija and N. Guio, *Chem. Intell. Lab. Syst.*, **96**, 219 (2009).
[19] K. Slopiecka, P. Bartocci, F. Fantozzi, *Appl. Energ.*, **97**, 491 (2012).
[20] X. Gu, X. Ma, L. Li, C. Liu, K. Cheng *et al.*, *J. Anal. Appl. Pyrol.*, **102**, 16 (2013).
[21] P. L. Rivilli, G. I. Yranzo and J. D. Perez, *Bioresources*, **6**, 2703 (2011).
[22] K. J. Laidler, "Chemical Kinetics", McGraw-Hill Book Company, 1965.
[23] J. Flynn, L. Wall, *J. Polym. Sci.*, *Part B*: *Polym. Phys.*, **4**, 323 (1966).
[24] T. Ozawa, *Bull. Chem. Soc. Jpn.*, **38**, 1881 (1965).
[25] H. Kissinger, *J. Res. Nat. Bur. Stand.*, **57**, 217 (1956).
[26] S. S. Abdullah, S. Yusup, M. M. Ahmad, A. Ramli and L. Ismail, *Int. J. Chem. Biol. Eng.*, **3**, 12 (2010).
[27] Y. Wei, I. Schinthia, J. C. Charles and R. V. Victor, *Environ. Prog. Sus. Energ.*, **31**, 200 (2012).
[28] G. Varhegyi, M. J. Antal, E. Jakab and P. Szabo, *J. Anal. Appl. Pyrol.*, **42**, 73 (1997).
[29] M. Gronli, G. Varhegyi and C. Di Blasi, *Ind. Eng. Chem. Res.*, **41**, 4201 (2002).
[30] T. Mani, P. Murugan, J. Abedi and N. Mahinpey, *Chem. Eng. Res. Des.*, **88**, 952 (2010).
[31] C. Quan, A. Li and N. Gao, *Waste Manage.*, **29**, 2353 (2009).
[32] S. Vyazovkin and C. A. Wight, *Thermochim. Acta*, **340**, 53 (1999).