PYROLYSIS KINETICS OF MOSO BAMBOO

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Abstract.   Pyrolysis processes of moso bamboo (*Phyllostachys pubescens*), bamboo fiber, cellulose, hemicellulose, and lignin were investigated by thermogravimetric analyzer at different heating rates under nitrogen environment. Coatse-Redfern (CR) and Kissinger-Akahira-Sunose model were used to calculate pyrolysis kinetics. The results showed that the thermal degradation occurred during 300-400°C and 200-300°C for cellulose and hemicellulose, respectively. The lignin degraded from 200°C to the end of the process. The pyrolysis process of moso bamboo could be divided into three steps, which all occurred during 130-560°C. The thermal decomposition of bamboo fibers occurred during 232-390°C. As the heating rate increased, the pyrolysis processes of all samples shifted to higher temperatures. The minimum activation energy of each sample was found at different heating rates from the CR model. The results will be helpful to understand the pyrolysis mechanism of moso bamboo to effectively design its thermochemical conversion process.

Keywords: Moso bamboo, pyrolysis, kinetics, thermochemical conversion, model compounds.

INTRODUCTION

Both energy shortage and environmental pollution has accelerated the research on finding alternative energy sources for fossil fuel. As one of the most promising renewable energy sources, biomass is usually used for conversion to value-added biofuels and other biological derivatives. There are many kinds of biomass conversion methods, such as combustion, gasification, liquefaction, etc. (Demirbas 2001). Pyrolysis is one of the thermochemical conversion methods, which can convert biomass to oxygen-containing organic compounds in the inert gas environment (Evans and Milne 1987). The pyrolysis of biomass usually involves char formation, pyroligneous liquid and noncondensable gases, which means the occurrence of various chemical reactions during the pyrolysis process (Collard and Blin 2014). To improve the efficiency of conversion process, it is necessary to investigate the mechanism of biomass pyrolysis. Peters et al (2017) used 149 individual reactions to represent volatilization, decomposition, and recomposition of the pyrolysis process in the Aspen Plus modeling as well as successful validation with pyrolysis experiments in a bench-scale fast pyrolysis rig. In addition, some scholars have used different methods to study the pyrolysis process and analyzed the pyrolysis kinetics

of plants. For example, Tao et al (2017) used a global single component reaction model to investigate the kinetic parameters of the plants. The results showed that the value of the activation energy was closely related to the cellulose content of the sample. Bu et al (2016) investigated the catalytic cracking process of lignin by microwave and conventional heating with activated carbon as a catalyst.

Biomass is mainly a polymer composed of cellulose, hemicellulose, and lignin, and its pyrolysis behavior can be considered as a comprehensive manifestation of pyrolysis behavior of three main components. Cellulose is a large molecular substance which is composed of glucose unit and it is the most widely distributed polysaccharide in nature. Hemicellulose is a heterogeneous polymer, mainly including glucose, xylose, mannose, arabinose, and galactose. The monosaccharide polymers are connected by covalent bonds, hydrogen bonds, ether bonds, and ester bonds. Lignin is an amorphous aromatic polymer and it is the second most natural organic substance after cellulose (Koukios and Valkanas 1982; Pandey 1999; Mohan et al 2006). Table 1 shows the chemical composition of bamboo, wood, and agriculture residue (Yao et al 2008). The variation of structures and chemical compositions of these components resulted in the different pyrolysis

Table 1. Chemical composition of bamboo, wood, and agricultural residue.

Biomass type	Species	Cellulose (%)	Hemicelluloses (%)	Lignin (%)
Wood	Pine	40-45	25-30	26-34
	Maple	45-50	21-36	22-30
Bamboo	Moso bamboo	42-50	24-28	24-26
Agricultural residues	Rice straw	41-57	33	8-19
	Rice husk	35-45	19-25	20
	Bagasse	40-46	25-29	12.5-20
	Cotton stalk	43-44	27	27

characteristics. Zhou et al (2015) investigated the pyrolysis process of three biomass components (cellulose, hemicellulose, and lignin) in both a thermogravimetric analyzer (TGA) and self-designed macro-TGA, and used the peak analysis–least squares method to analyze the kinetics. It has been found that pyrolysis process could be described as a continuous reaction process which has different reactions in different reaction stages, whereas the reaction curve is smooth and each reaction could be represented by the Gaussian peak. At the same time, some people used different methods to study the pyrolysis process of three components; Yang et al (2007) used DSC and FT-IR to investigate pyrolysis of cellulose, hemicellulose, and lignin. It was found that the pyrolysis of cellulose and hemicellulose occurred quickly, but the pyrolysis of lignin was difficult to occur. Stefanidis et al (2014) investigated catalytic pyrolysis of cellulose, hemicellulose, lignin, and their mixtures to analyze the pyrolysis products. It has been found that the limited heat transfer had no significant influence on the pyrolysis curve, but it had a great influence on the product distribution. Lignin is a three-dimensional network of polymers, composed of phenyl propane, which make it more difficult to decompose (Yu et al 2017). Cellulose firstly depolymerizes to produce levoglucan and then reacts to generate furan and other chemicals. The final products are polymerized to form carbon in the pyrolysis process. The pyrolysis of cellulose was divided into two different reaction models which are the first-order kinetic model combining with the thermal hysteresis model and the energy conservation model. However, the kinetic model parameters obtained from the two models are similar, and the pyrolysis activation energy of cellulose is about 198 KJ mol^{-1} (Lin et al 2009).

Given wide ecological amplitudes, high growth rates, and multipurpose use, bamboo species have always been important resources in some parts of the world, such as China, India, Brazil, etc. (Darabant et al 2014). Moso bamboo is the most abundant bamboo species in China. There are about 60,063 km^2 of bamboo resources, among which more than 44,300 km^2 is moso bamboo (*Phyllostachys pubescens*). Moso bamboo has been used to manufacture industrial products. Because of the hollow interior of the bamboo, a lot of waste is produced in the process of utilization, which can be a great potential source to develop biomass energy. Chen et al (2014) investigated the effects of heating rate on slow pyrolysis behavior, kinetic parameters, and product properties of moso bamboo. They found that heating rate had different effects on the pyrolysis products properties, including biochar (element content, proximate analysis, specific surface area, and heating value), bio-oil (water content and chemical composition), and noncondensable gas. Dong and Xiong (2014) studied kinetics comparison of both conventional and microwave pyrolysis for moso bamboo. They found that microwave irradiation had the lower activation energy. Dong et al (2015) used pyrolysis-gas chromatography/mass spectrometry to investigate the influences of four types of dilute acid washing (H_2SO_4, HCl, HF, and HNO_3) on moso bamboo pyrolysis. They found that all acid washings could effectively remove a large portion of inorganics and disrupt the chemical structure to a certain extent. Despite this previous research being very helpful in understanding the thermal decomposition of moso bamboo, to the best of the authors' knowledge, there is a lack of sufficient information investigating the pyrolysis mechanism of moso bamboo through three model compounds. In this article, the pyrolysis characteristics of moso bamboo, bamboo fiber from pulp, and three major

components including cellulose, hemicellulose, and lignin were investigated by TGA at different heating rates of 10, 20, 30, and 40°C min^{-1} under nitrogen environment. The isothermal and non-isothermal models were used to calculate pyrolysis kinetics. The results of this research will be helpful to understand the pyrolysis mechanism of moso bamboo to effectively design its thermochemical conversion process.

<div align="center">MATERIAL AND METHODS</div>

Materials

Moso bamboo (*Phyllostachys heterocycla*), approximately 4 yr old, was taken from a bamboo plantation located in Zejiang Province, China. Bamboo tubes were cut off to 25 mm (longitudinal) by 4 mm (radial). The initial MC was about 10.9%. Bamboo fiber was taken from a paper mill of bamboo in Guizhou Province, China. The initial MC was about 8.7%. They were broken down to particles using a Wiley Mill. The materials were then screened to get 250- to 425-μm particles. Cellulose, hemicellulose, and lignin were manufactured by Fluka Analytical, Sigma Life Science, and Aldrich Chemistry, respectively. All

samples were dried at a temperature of 105°C in the oven until the mass stabilized.

Pyrolysis Characteristics

Pyrolysis characteristics were observed in terms of global mass loss using TA Instrument TGA Q 50 TGA (TA Instrument, New Castle, DE). Firstly, the particles were evenly and loosely distributed in an open sample pan, and the initial sample weight was about 3-6 mg. The temperature change was controlled from room temperature (30 ± 5°C) to 800°C with different heating rates of 10, 20, 30, and 40°C min^{-1}. A nitrogen stream with a flow rate of 40 mL min^{-1} was continuously passed into the furnace to investigate pyrolysis characteristics. Three replicates of each TGA experiment were performed. The experimental data were analyzed by using Origin 8.0 software.

Kinetic Models

The pyrolysis process of samples as a natural polymer is similar to many biomass. In this article, the isothermal model and nonisothermal model were used to analyze the dynamics
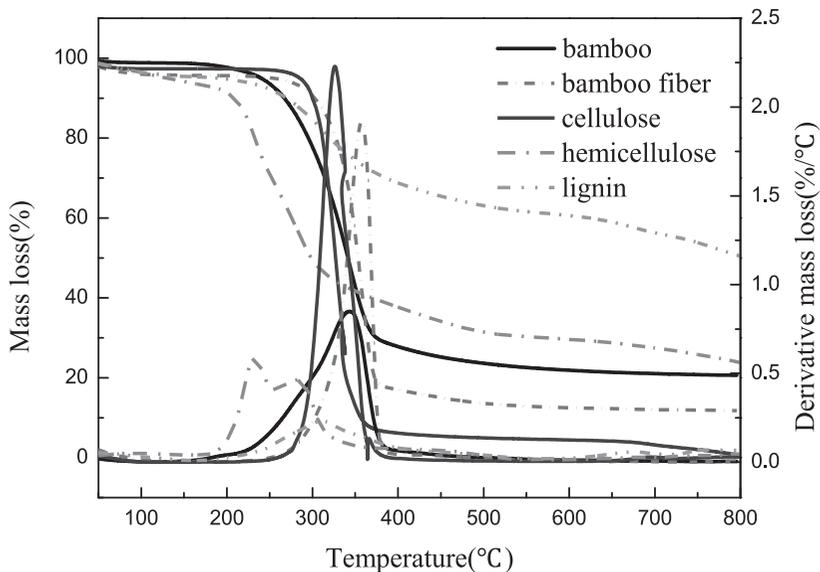
Figure 1.   The pyrolysis process of samples at a heating rate of 10°C min^{-1}.

(Anca-Couce et al 2014). The representative of the isothermal model was the Coatse-Redfern (CR) model (2) (Coats and Redfern 1964). One of the nonisothermal model was Kissinger-Akahira-Sunose (KAS) model (3) (Ozawa 1992). The linear fit of Origin 8.0 software was used to obtain the slope, intercept, and R^2 value of every line and the following kinetic model was used to get activation energy and frequency factor.

The CR model is a kinetic model based on different heating rates. It is suitable for calculating the frequency factor and reaction order by using the activation energy (Yorulmaz and Atimtay 2009).

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (1)$$

$$\ln\left(\frac{-\ln(1-\alpha)}{T^2}\right) = \ln\left[\frac{A \cdot R}{\beta \cdot E_a}\left(1 - \frac{2R \cdot T}{E_a}\right)\right] - \frac{E_a}{R \cdot T}(n = 1). \quad (2)$$

Here, α is the conversion rate, m_t is the mass of samples at any time, m_0 is the initial mass of samples, and m_∞ is the mass of samples at the end;

β is the heating rate, R is the universal gas constant (8.314 KJ mol^{-1}), T is the reaction temperature, and E_a is the activation energy.

The nonisothermal model corresponds to different activation energies at different conversion rates. The KAS model (Eq 3) mainly uses the specific conversion based on the integral reaction model: $G(\alpha) = \alpha/(1 - \alpha)$, where $g(\alpha)$ is usually constant, only consider the first order in this study.

$$\ln\left(\beta/T^2\right) = \ln(A \cdot E_a/R \cdot g(\alpha)) - E_a/R \cdot T. \quad (3)$$

RESULTS AND DISCUSSION

Pyrolysis Characteristics

Biomass materials can release gases and eventually produce carbon during the pyrolysis process. Figure 1 shows the pyrolysis process of all samples at a heating rate of 10°C min^{-1}. Cellulose is an amylose with a certain crystal structure, and the pyrolysis process mainly occurred at 300-400°C. The structure of hemicellulose is not stable because it mainly belongs to amorphous structure and is easy to be pyrolyzed. Lignin is a network structure of polymers
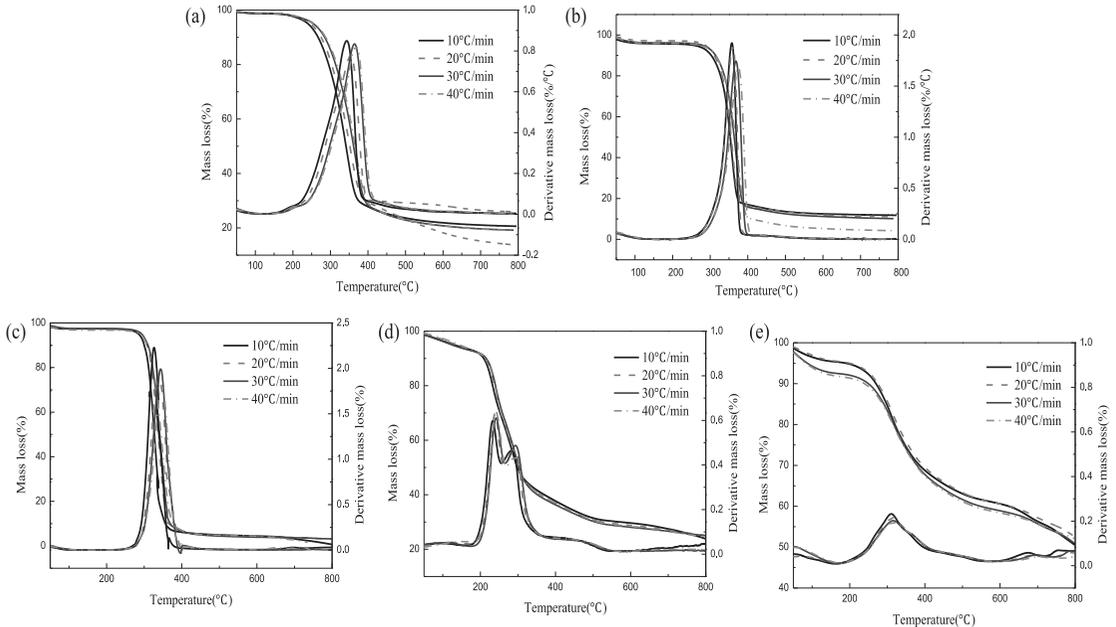
Figure 2. The pyrolysis process of samples with different heating rates. (a) Bamboo; (b) Bamboo fiber; (c) Cellulose; (d-1) First step of hemicellulose; (d-2) Second step of hemicellulose; (e) Lignin.

and has a wide pyrolysis temperature range throughout the whole pyrolysis process. Its thermal decomposition is from 200°C until the end of the pyrolysis process. Compared with the ones of cellulose and lignin, the derivative thermogravimetric (DTG) curve of hemicellulose appeared in the shape of acromion during the pyrolysis process. This was mainly because the side chains of water-soluble hemicellulose glycan were firstly broken down and the molecules underwent depolymerization and recombination, resulting in the production of a small amount of volatile gases, such as CO, CO_2, H_2, etc., by free radicals and functional groups. With the increase in pyrolysis temperature, the glycosidic bond of the glycan chains was broken down and the samples thermally decomposed, resulting in two distinct mass loss peaks (Xiao et al 2001). Cellulose had the highest pyrolysis activity because of the greatest mass loss rate and lignin had the lowest pyrolysis activity. The pyrolysis temperature of moso bamboo was from 130 to 560°C, and the process could be divided into three steps. In the first step, the mass loss was due to removal of moisture and volatiles from the samples at lower pyrolysis temperature. The

second step was the main pyrolysis stage, which occurred at a higher pyrolysis temperature, and the mass loss of sample was the most in this process. In the third step, the degradation of lignin residues from the second step or tar and char from the main components resulted in mass loss of the sample. Bamboo fiber had a similar pyrolysis process with cellulose, but it had a higher peak temperature corresponding to the maximum mass loss rate and a lower pyrolysis activity. Thermal decomposition of bamboo fiber occurred at 232-390°C. Yang et al found that the main pyrolysis of bamboo from pulping occurred during 220-390°C. At this stage, the crystalline region started degrading and the polymer simultaneously decomposed, which evidently resulted in the increase in amorphous structure and the decrease in degree of polymerization (DP). When the temperature increased to 300°C, the crystalline region was degraded and the DP decreased to about 200°C, and abundant amount of l-glucose appeared. As the temperature increased to 370°C, mass loss amounted was 50–70% mainly because of the tar formation, which is mostly composed of l-glucose (Yang et al 2008). With the increase in pyrolysis temperature, the C-C

Table 2.   Pyrolysis characteristics of samples at different heating rates.

Samples	Hr (°C min^{-1})	T_i (°C)	T_p (°C)	R_{max} (mg min^{-1})	T_e (°C)	Mass loss (%)
Moso bamboo	10	130.89	343.16	0.8493	559.88	76.39
	20	136.86	352.53	0.7779	552.24	78.34
	30	151.35	364.71	0.8342	579.61	77.49
	40	145.15	368.67	0.8332	582.23	77.73
Bamboo fiber	10	232.14	358.09	1.9203	390.77	78.02
	20	236.36	359.78	1.9000	392.90	80.40
	30	237.65	368.48	1.7440	405.52	80.40
	40	246.95	374.27	1.6850	411.59	85.69
Cellulose	10	231.71	326.23	2.2289	410.64	91.29
	20	249.29	337.47	1.9721	482.94	92.32
	30	244.08	343.25	1.9931	461.05	92.49
	40	242.47	346.43	1.8324	464.04	87.85
Hemicellulose	10	153.79	232.94	0.5976	556.97	73.80
	20	169.81	238.72	0.6334	553.64	63.95
	30	173.11	241.88	0.6109	572.72	64.46
	40	180.09	241.87	0.6394	571.45	64.22
Lignin	10	163.85	310.57	0.2323	575.01	34.21
	20	166.68	315.35	0.2182	570.99	34.26
	30	170.11	316.38	0.2020	595.62	33.46
	40	172.88	315.53	0.1969	576.96	32.91

T_i = initial temperature; T_p = peak temperature corresponding to maximum mass loss rate; R_{max} = the maximum mass loss rate; T_e = end temperature; Hr = heating rate.
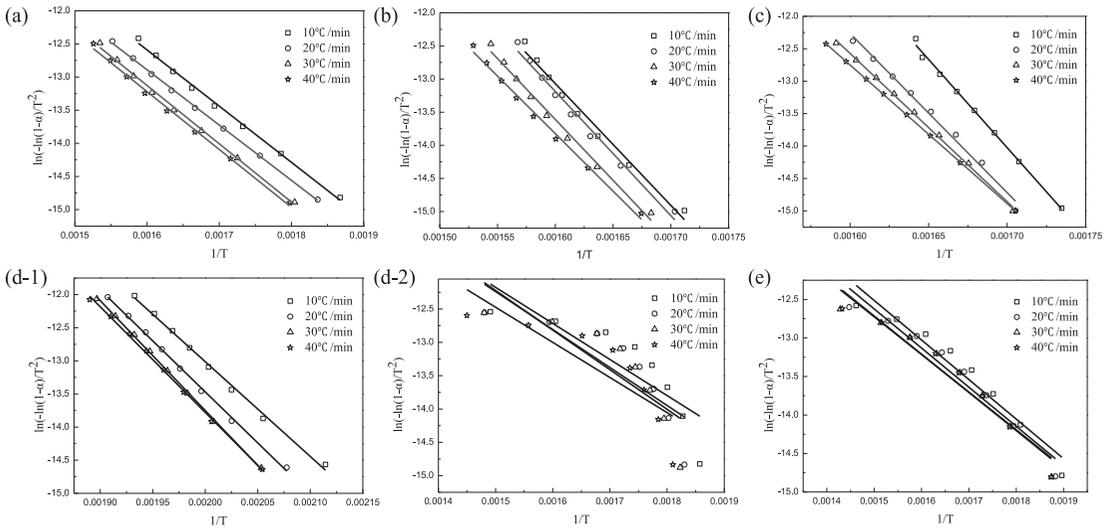
Figure 3. The kinetic process of samples using C-R model. (a) Bamboo; (b) Bamboo fiber; (c) Cellulose; (d-1) First step of hemicellulose; (d-2) Second step of hemicellulose; (e) Lignin.

bond and C-H bond of all samples continued to be broken and the residues gradually thermally decomposed, even though the variation of mass loss of all samples was not significant.

Figure 2 shows the pyrolysis curves of moso bamboo, bamboo fiber, and model compounds at different heating rates. With the increase in heating rate, the pyrolysis process shifted to

Table 3. Kinetic parameters of samples at different heating rates (CR model).

Samples	Hr (°C min^{-1})		Linear function	R^2	E_a (KJ mol^{-1})	A (min^{-1})
Moso bamboo	10		$y = -8487x + 0.990$	0.9964	70.56	2.28E+05
	20		$y = -8347x + 0.465$	0.9993	69.40	2.66E+05
	30		$y = -8800x + 0.952$	0.9970	73.16	6.84E+05
	40		$y = -8730x + 0.749$	0.9960	72.58	7.38E+05
Bamboo fiber	10		$y = -18,378x + 16.335$	0.9820	152.79	2.28E+12
	20		$y = -18,749x + 16.810$	0.9853	155.88	7.49E+12
	30		$y = -18,374x + 15.789$	0.9888	152.76	3.96E+12
	40		$y = -17,358x + 13.948$	0.9926	144.32	7.93E+11
Cellulose	10		$y = -27,201x + 32.216$	0.9962	226.15	2.67E+19
	20		$y = -24,546x + 27.010$	0.9900	204.08	2.64E+17
	30		$y = -22,868x + 24.015$	0.9981	190.12	1.85E+16
	40		$y = -21,370x + 21.443$	0.9999	177.67	1.75E+15
Hemicellulose	First stage	10	$y = -14,308x + 15.604$	0.9954	118.96	8.55E+11
		20	$y = -15,404x + 17.339$	0.9979	128.07	1.04E+13
		30	$y = -16,586x + 19.421$	0.9992	137.89	1.35E+14
		40	$y = -15,952x + 18.124$	0.9981	132.62	4.74E+13
	Second stage	10	$y = -5412x - 4.057$	0.6873	45.00	9.37E+02
		20	$y = -5696x - 3.695$	0.6840	47.35	2.83E+03
		30	$y = -5946x - 3.303$	0.6740	49.43	6.56E+03
		40	$y = -5271x - 4.566$	0.6702	43.83	2.19E+03
Lignin	10		$y = -5137x - 4.807$	0.9397	42.71	4.20E+02
	20		$y = -5081x - 5.001$	0.9454	42.24	6.84E+02
	30		$y = -4891x - 5.389$	0.9388	40.66	6.70E+02
	40		$y = -4962x - 5.272$	0.9445	41.25	1.02E+03

Hr = heating rate; R^2 = correlation coefficient value; E_a = activation energy; A = exponential factor.

higher temperatures, resulting in thermal hysteresis. This also indicated that heating rate was an important factor that affected the pyrolysis process of the sample. The TG curve represented a continuous reaction which changed with the increase in pyrolysis temperature and reflected the pyrolysis characteristics of the samples during the pyrolysis process. Table 2 shows the pyrolysis characteristics of moso bamboo, bamboo fiber, and model compounds at different heating rates. Data certified that the initial and the end temperatures of each sample increased with the increase in heating rate during the pyrolysis process. Bamboo had the lowest initial temperature compared with other samples. Its initial temperature was 130.89, 136.86, 151.35, and 145.15°C, corresponding to the heating rates of 10, 20, 30, and 40°C min^{-1}, respectively. The volatiles have contributed to this phenomena. Liu et al found that bamboo had more than 80% volatiles, which had a lower pyrolysis temperature (Liu et al 2014). The temperature range of bamboo fiber was less than that of moso bamboo during the pyrolysis process, but its maximum mass loss rate was higher than that of moso bamboo. This indicated that the compounds contained in the moso bamboo inhibited its pyrolysis, thereby reducing the pyrolysis activity of moso bamboo (Lou et al

2010). Mass loss is also an important indicator of biomass pyrolysis activity. Table 2 shows that mass loss and the maximum mass loss rate of cellulose was the highest, indicating that the pyrolysis activity of cellulose was the greatest. The mass loss of cellulose was 91.29%, 92.32%, 92.49%, and 87.85% and its maximum mass loss rate was 2.2289, 1.9721, 1.9931, and 1.8324 mg min^{-1}, corresponding to the heating rates of 10, 20, 30, and 40°C min^{-1}, respectively. Among all samples, lignin was the most difficult to thermally decompose, because of the lowest mass loss and minimum mass loss rate during the pyrolysis process.

Kinetic Analysis

Figure 3 shows the kinetic curves of moso bamboo, bamboo fiber, and model compounds obtained at different heating rates using the CR model, whereas Fig 3d-1 and d-2 shows the two main pyrolysis stages of hemicellulose, respectively. The relation between $1/T$ and $\ln(-\ln(1 - \alpha)/T^2)$ is shown in Fig 3, corresponding to the values of X and Y. The CR model relied on simple models to obtain kinetic parameters for complex pyrolysis process at the same temperature. Table 3 shows the kinetic parameters of moso
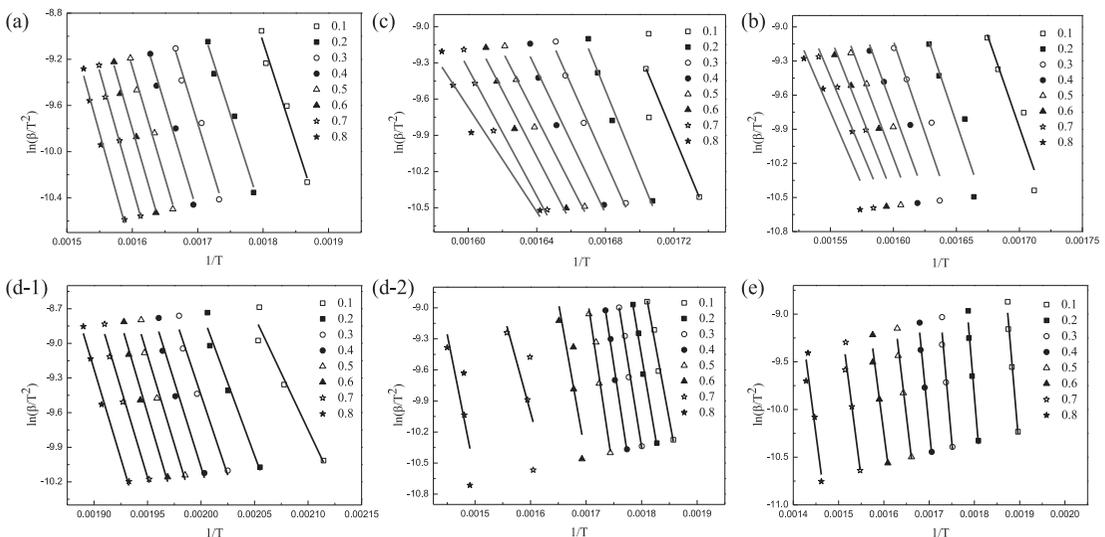
Figure 4.   The kinetic process of samples using KAS model. (a) Bamboo; (b) Bamboo fiber; (c) Cellulose; (d-1) First step of hemicellulose; (d-2) Second step of hemicellulose; (e) Lignin.

Table 4. Kinetic parameters of samples at different conversion rates (KAS model).

Samples	Cr		Linear function	R^2	E_a (KJ mol^{-1})	A (min^{-1})
Moso bamboo	0.1		$y = -17,460x + 22.376$	0.9658	145.16	2.69E+06
	0.2		$y = -17,639x + 21.188$	0.9700	146.65	3.61E+05
	0.3		$y = -18,449x + 21.610$	0.9644	153.39	3.07E+05
	0.4		$y = -18,719x + 21.291$	0.9696	155.63	1.41E+05
	0.5		$y = -19,231x + 21.502$	0.9795	159.89	1.13E+05
	0.6		$y = -19,646x + 21.632$	0.9883	163.34	8.42E+04
	0.7		$y = -20,061x + 21.792$	0.9936	166.79	6.22E+04
	0.8		$y = -20,394x + 21.770$	0.9856	169.55	3.49E+04
Bamboo fiber	0.1		$y = -31,969x + 44.464$	0.8656	265.79	5.75E+15
	0.2		$y = -32,864x + 44.380$	0.8461	273.23	2.29E+15
	0.3		$y = -32,344x + 42.628$	0.8264	268.91	2.35E+14
	0.4		$y = -30,344x + 38.821$	0.7974	252.28	3.58E+12
	0.5		$y = -29,236x + 36.625$	0.7975	243.07	2.76E+11
	0.6		$y = -28,002x + 34.314$	0.7911	232.81	1.90E+10
	0.7		$y = -26,457x + 31.572$	0.7814	219.97	8.34E+08
	0.8		$y = -25,718x + 30.115$	0.7795	213.82	1.17E+08
Cellulose	0.1		$y = -34,269x + 49.033$	0.6546	284.91	5.18E+17
	0.2		$y = -34,846x + 49.013$	0.9696	289.71	2.22E+17
	0.3		$y = -31,825x + 43.348$	0.9789	264.59	4.91E+14
	0.4		$y = -29,549x + 39.097$	0.9584	245.67	4.85E+12
	0.5		$y = -27,726x + 35.712$	0.9686	230.51	1.17E+11
	0.6		$y = -27,376x + 34.819$	0.9612	227.60	3.22E+10
	0.7		$y = -26,347x + 32.805$	0.9600	219.05	2.87E+09
	0.8		$y = -21,670x + 25.006$	0.9244	180.17	8.35E+05
Hemicellulose	First stage	0.1	$y = -19,554x + 31.314$	0.9228	162.57	1.83E+10
		0.2	$y = -25,114x + 41.512$	0.9534	208.80	1.70E+14
		0.3	$y = -27,728x + 46.007$	0.9574	230.53	8.05E+15
		0.4	$y = -29,670x + 49.268$	0.9576	246.68	1.26E+17
		0.5	$y = -30,707x + 50.774$	0.9543	255.30	3.66E+17
		0.6	$y = -31,502x + 51.823$	0.9678	261.91	6.79E+17
		0.7	$y = -30,967x + 50.225$	0.9773	257.46	8.98E+16
		0.8	$y = -30,911x + 49.507$	0.9818	256.99	2.56E+16
	Second stage	0.1	$y = -28,844x + 43.279$	0.9752	239.81	1.95E+15
		0.2	$y = -31,468x + 47.177$	0.9830	261.63	3.91E+16
		0.3	$y = -33,239x + 49.488$	0.9783	276.35	2.18E+17
		0.4	$y = -35,128x + 51.919$	0.9867	292.05	1.51E+18
		0.5	$y = -35,880x + 52.174$	0.9655	298.31	1.27E+18
		0.6	$y = -30,075x + 40.680$	0.6758	250.04	1.03E+13
		0.7	$y = -19,555x + 21.277$	0.6808	192.58	3.81E+04
		0.8	$y = -26,898x + 29.744$	0.5087	223.63	7.69E+07
Lignin	0.1		$y = -55,675x + 95.318$	0.9646	462.88	4.03E+37
	0.2		$y = -56,826x + 92.426$	0.9599	472.45	9.72E+35
	0.3		$y = -53,527x + 83.336$	0.9338	445.03	6.79E+31
	0.4		$y = -47,879x + 71.203$	0.9705	398.07	2.62E+26
	0.5		$y = -39,950x + 55.844$	0.9671	332.14	4.48E+19
	0.6		$y = -36,120x + 47.546$	0.9409	300.30	8.22E+15
	0.7		$y = -36,511x + 45.874$	0.9177	303.56	9.83E+14
	0.8		$y = -35,925x + 41.835$	0.8374	298.68	1.03E+13

Cr = conversion rate; R^2 = correlation coefficient value; E_a = activation energy; A = exponential factor.

bamboo, bamboo fiber, and model compounds obtained by using CR model at different heating rates. The correlation coefficient of the linear relationship (R^2 value) was higher, indicating that CR model could accurately calculate the activation energy of the samples. The activation energy of the pyrolysis process of bamboo fiber, cellulose, and the first stage

of pyrolysis of hemicellulose was higher, in which the maximum activation energy of cellulose was about 200 KJ mol^{-1}. With the increase in heating rate, the activation energy of cellulose decreased gradually. The activation energy was 226.15, 204.08, 190.12, and 177.67 KJ mol^{-1}, corresponding to the heating rates of 10, 20, 30, and 40°C min^{-1}, respectively. However, the activation energy of moso bamboo, lignin, and the second stage of hemicellulose was lower, especially for lignin. The activation energy of lignin was about 42.71, 42.24, 40.66, and 41.25 KJ mol^{-1}, corresponding to the heating rates of 10, 20, 30, and 40°C min^{-1}, respectively. The activation energy of moso bamboo and bamboo fiber varied in the ranges of 69.40-73.16 KJ mol^{-1} and 144.32-155.88 KJ mol^{-1}, respectively. The higher activation energy indicated a higher barrier to the thermochemical conversion of biomass. For different samples, the minimum activation energy was found at different heating rates. For example, the minimum activation energy of moso bamboo corresponded to the heating rate of 20°C min^{-1}. Similarly, the ones of bamboo fiber and cellulose corresponded to the heating rate of 40°C min^{-1}, the one of hemicellulose corresponded to the heating rate of 10°C min^{-1} at the first step and 40°C min^{-1} at the second step, and the one of lignin corresponded to the heating rate of 30°C min^{-1}.

The KAS model was the most accurate one in the nonisothermal model (Slopiecka et al 2012). Figure 4 shows the kinetic curves of moso bamboo, bamboo fiber, and model compounds obtained at different conversion rates using the KAS model. As a nonisothermal model, the KAS model mainly dealt with the activation energy required for the different transition stages of the samples during the pyrolysis process. The relation between the $1/T$ and the $\ln\beta/T^2$ is shown in Fig 4. The kinetic analysis used the integral method and the differential method to study the nonisothermal model. The mechanism of the reaction could be determined if the two methods were consistent (Vyazovkin 2001). Table 4 shows the kinetic parameters of moso bamboo, bamboo fiber, and model compounds obtained by using the KAS model at different conversion rates

from 0.1 to 0.8. The activation energy of moso bamboo, bamboo fiber, cellulose, hemicellulose, and lignin was higher than that of the CR model. The activation energy of lignin was the highest. With the increase in conversion rates, the activation energy gradually decreased. However, the activation energy of moso bamboo was the lowest and its activation energy increased from 145.16 to 169.55 KJ mol^{-1} with the increase in conversion rates. The activation energy of bamboo fiber, cellulose, hemicellulose, and lignin varied in the ranges of 273.23-213.82 KJ mol^{-1} (bamboo fiber), 289.71-180.17 KJ mol^{-1} (cellulose), 208.80-261.91 KJ mol^{-1} (the first stage of hemicellulose), 192.58-298.31 KJ mol^{-1} (the second stage of hemicellulose), and 298.68-472.45 KJ mol^{-1} (lignin).

CONCLUSIONS

Thermal decomposition of cellulose occurred at 300-400°C. The pyrolysis of hemicellulose was during 200-300°C. Lignin pyrolysis was from 200°C until the end of the pyrolysis process. Compared with the ones of cellulose and lignin, the DTG curve of hemicellulose appeared in the shape of acromion during the pyrolysis process. The pyrolysis process of moso bamboo was divided into three stages. The main pyrolysis temperatures of moso bamboo and bamboo fibers were 130-560°C and 232-390°C, respectively. Cellulose and lignin had the highest and lowest pyrolysis activity, respectively. With the increase in heating rate, the pyrolysis process of all samples shifted to higher temperatures. The minimum activation energy of each sample was found at different heating rates. The activation energy of all samples from KAS model was higher than that of CR model.

REFERENCES

Anca-Couce A, Berger A, Zobel N (2014) How to determine consistent biomass pyrolysis kinetics in a parallel reaction scheme. Fuel 123:230-240.

Bu Q, Lei H, Qian M, Yadavalli G (2016) A thermal behavior and kinetics study of the catalytic pyrolysis of lignin. RSC Adv 6:100700-100707.

Chen DY, Zhou JB, Zhang QS (2014) Effects of heating rate on slow pyrolysis behavior, kinetic parameters and products properties of moso bamboo. Biores Technol 169:313-319.

Coats AW, Redfern JP (1964) Kinetic parameters from thermogravimetric data. Nature 201:68-69.

Collard FX, Blin J (2014) A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. Renew Sustain Energy Rev 38:594-608.

Darabant A, Haruthaithanasan M, Atkla W, Phudphong T, Thanavat E, Haruthaithanasan K (2014) Bamboo biomass yield and feedstock characteristics of energy plantations in Thailand. Energy Procedia 59:134-141.

Demirbaş A (2001) Biomass resource facilities and biomass conversion processing for fuels and chemicals. Energy Convers Manage 42:1357-1378.

Dong Q, Xiong YQ (2014) Kinetics study on conventional and microwave pyrolysis of moso bamboo. Biores Technol 171:127-131.

Dong Q, Zhang SP, Zhang L, Ding K, Xiong YQ (2015) Effects of four types of dilute acid washing on moso bamboo pyrolysis using Py-GC/MS. Biores Technol 185:62-69.

Evans RJ, Milne TA (1987) Molecular characterization of the pyrolysis of biomass. Energy Fuels 1:123-137.

Koukios EG, Valkanas GN (1982) Process for chemical separation of the three main components of lignocellulosic biomass. Ind Eng Chem Res 21:309-314.

Lin YC, Cho J, Tompsett GA, Westmoreland PP, Huber GW (2009) Kinetics and mechanism of cellulose pyrolysis. J Phys Chem C 113:20097-20107.

Liu ZJ, Fei BH, Jiang ZH, Liu XE (2014) Combustion characteristics of bamboo-biochars. Biores Technol 167:94-99.

Lou R, Wu SB, Lv GJ (2010) Effect of conditions on fast pyrolysis of bamboo lignin. J Anal Appl Pyrolysis 89:191-196.

Mohan D, Pittman CU, Steele PH (2006) Pyrolysis of wood/biomass for bio-oil: A critical review. Energy Fuels 20:848-889.

Ozawa T (1992) Estimation of activation energy by iso-conversion methods. Thermochim Acta 203:159-165.

Pandey KK (1999) A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy. J Appl Polym Sci 71:1969-1975.

Peters JF, Banks SW, Bridgwater AV, Dufour J (2017) A kinetic reaction model for biomass pyrolysis processes in Aspen Plus. Appl Energy 188:595-603.

Slopiecka K, Bartocci P, Fantozzi F (2012) Thermogravimetric analysis and kinetic study of poplar wood pyrolysis. Appl Energy 97:491-497.

Stefanidis SD, Kalogiannis KG, Iliopoulou EF, Michailof CM, Pilavachi PA, Lappas AA (2014) A study of lignocellulosic biomass pyrolysis via the pyrolysis of cellulose, hemicellulose and lignin. J Anal Appl Pyrolysis 105:143-150.

Tao JJ, Wang HH, Chen S, Zhu F (2017) Reality in the kinetic modelling of pyrolysis of plant fuels. Energy Procedia 107:85-93.

Vyazovkin S (2001) Modification of the integral iso-conversional method to account for variation in the activation energy. J Comput Chem 22:178-183.

Xiao B, Sun XF, Sun RC (2001) Chemical, structural, and thermal characterizations of alkali-soluble lignins and hemicelluloses, and cellulose from maize stems, rye straw, and rice straw. Polym Degrad Stabil 74:307-319.

Yang HP, Yan R, Chen HP, Lee DH, Zheng CG (2007) Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 86:1781-1788.

Yang ZP, Xu SW, Ma XL, Wang SY (2008) Characterization and acetylation behavior of bamboo pulp. Wood Sci Technol 42:621-632.

Yao F, Wu QL, Lei Y, Guo W, Xu Y (2008) Thermal decomposition kinetics of natural fibers: Activation energy with dynamic thermogravimetric analysis. Polym Degrad Stabil 93:90-98.

Yorulmaz SY, Atimtay AT (2009) Investigation of combustion kinetics of treated and untreated waste wood samples with thermogravimetric analysis. Fuel Process Technol 90:939-946.

Yu J, Paterson N, Blamey J, Millan M (2017) Cellulose, xylan and lignin interactions during pyrolysis of lignocellulosic biomass. Fuel 191:140-149.

Zhou H, Long Y, Meng A, Chen S, Li HQ, Zhang YG (2015) A novel method for kinetics analysis of pyrolysis of hemicellulose, cellulose, and lignin in TGA and macro-TGA. RSC Adv 5:26509-26516.