Journal of Analytical and Applied Pyrolysis 94 (2012) 48–52

Contents lists available at SciVerse ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

The pyrolysis characteristics of moso bamboo

Zehui Jiang[a,*], Zhijia Liu[a], Benhua Fei[a], Zhiyong Cai[b], Yan Yu[a], Xing'e Liu[a]

[a] International Centre for Bamboo and Rattan, Beijing 100102, China
[b] Forest Products Laboratory, USDA Forest Service, Madison, WI 53705-2398, United States

ARTICLE INFO

Article history:
Received 16 August 2011
Accepted 25 October 2011
Available online 4 November 2011

Keywords:
Pyrolysis
Moso bamboo
TG
TG–FTIR
XRD

ABSTRACT

In the research, thermogravimetry (TG), a combination of thermogravimetry and Fourier transform infrared spectrometer (TG–FTIR) and X-ray diffraction (XRD) were used to investigate pyrolysis characteristics of moso bamboo (*Phyllostachys pubescens*). The Flynn–Wall–Ozawa and Coats–Redfern (modified) methods were used to determine the apparent activation energy (E_a). The TG curve indicated that the pyrolysis process of moso bamboo included three steps and the main pyrolysis occurred in the second steps with temperature range from 450 K to 650 K and over 68.69% mass was degraded. TG–FTIR analysis showed that the main pyrolysis products included absorbed water (H_2O), methane gas (CH_4), carbon dioxide (CO_2), acids and aldehydes, ammonia gas (NH_3), etc. XRD analysis expressed that the index and width crystallinity of moso bamboo gradually increased from 273 K to 538 K and cellulose gradually degraded from amorphous region to crystalline region. The E_a values of moso bamboo increased with conversion rate increase from 10 to 70. The E_a values were, respectively 153.37–198.55 kJ/mol and 152.14–197.87 kJ/mol based on Flynn–Wall–Ozawa and Coats–Redfern (modified) methods. The information was very helpful and significant to design manufacturing process of bio-energy, made from moso bamboo, using gasification or pyrolysis methods.

1. Introduction

Bamboo was a kind of biomass material and it owned many advantages such as fast growth and high strength. The bamboo resource was very abundant and had been widely cultivated in the west and south of China. Bamboo had great potential as a biomass material and bio-energy resource of the future. Currently, the area of bamboo was about five million hectares and that of moso bamboo was about 3 million hectares in China [1]. Annual yield of moso bamboo was about eighteen million tons and was greater than all other kinds of bamboo, which was widely used to produce furniture, flooring and interior decoration materials.

As a kind of natural lignocellulose polymer, bamboo would be subjected to thermal decomposition in manufacturing processes of bamboo composites or in the end use of these products. The study on pyrolysis of moso bamboo would be very helpful to better design manufacturing process of bamboo composite or bio-energy, made from bamboo by thermal chemical conversion methods such as gasification and pyrolysis. There had been many researches on pyrolysis of biomass material or lignocellulosic materials. Fu et al. [2] thought that low-temperature pyrolysis could offer a feasible option for wood-waste management and the recovery of a variety of useful chemicals and studied chemical yields from low-temperature pyrolysis of CCA-treated wood. Juhász and Kitahara [3] studied the thermal decomposition of vitamin C using evolved gas analysis–ion attachment mass spectrometry (EGA–IAMS). The experiment results were compared with a previous study employing pyrolysis–gas chromatography–mass spectrometry (Pyr–GC–MS). The observed quantitative and qualitative differences of the pyrolysis products obtained by the two techniques (EGA–IAMS and Pyr–GC–MS) were in part due to the difference in transportation time of the products out of the pyrolysis chamber. Mourant et al. [4] analyzed effects of alkali and alkaline earth metallic species on the yield and composition of bio-oil. The water-washed and acid-washed mallee wood samples were degraded in a fluidised-bed reactor at 500 °C under fast heating rate conditions. The removal of alkali and alkaline earth metallic (AAEM) species did not result in significant changes in the yields of bio-oil and bio-char. However, the bio-oil properties were drastically affected by the removal of AAEM species. Dumroese et al. [5] carried out experimental study on fragmentation of coals during fast pyrolysis at high temperature and pressure. The experimental results showed that primary fragmentation at high heating rate and high temperature could result in the formation of relatively coarse fragments and sometimes in a multitude of fines. The probability of fragmentation and the propensity to form coarse versus small fragments varied. For a given coal fragmentation increased

* Corresponding author.
E-mail address: Jiangzehui@icbr.ac.cn (Z. Jiang).

0165-2370/$ – see front matter.
doi:10.1016/j.jaap.2011.10.010

monotonously with temperature, whereas the effect of pressure was nonmonotonous.

TG, a thermoanalytical technique, was widely used to analyze thermal degradation of lignocellulosic materials. Travis et al. [6] studied pyrolysis behavior and kinetics of biomass derived materials by TG, Mostashari [7] investigated combustion pathway of cotton fabrics though TG method, Anker and Kim [8] analyzed the influence of potassium chloride on wheat straw pyrolysis by TG–FTIR, Bradbury et al. [9] and Koufopanos et al. [10] studied kinetic models for pyrolysis of cellulose materials. Elder [11] studied pyrolysis reactions of lignin model compounds. The most common 'model-free' methods included Fridman method [12], Kissinger method [13], Flynn–Wall–Ozawa method [14,15], Coats–Redfern (modified) method [16] and Doyle method [17], etc.

Despite this previous research was very helpful in understanding the thermal decomposition kinetics of cellulosic materials, bamboo was a different material. Jin and Zou [18] studied the kinetic of bamboo pyrolysis, Li et al. [19] analyzed the factors influencing the characteristics of bamboo pyrolysis. The pyrolysis characteristics of moso bamboo were studied by TG method in the research. TG–FTIR and XRD were, respectively used to investigate moso bamboo pyrolysis products and residues. The Flynn–Wall–Ozawa and Coats–Redfern (modified) methods were used to determine E_a value. The aim of this research was to better design manufacturing processes of bio-energy, made from moso bamboo by thermal chemical conversion methods such as gasification and pyrolysis.

2. Theoretical approach

The fundamental rate equation used in all kinetics studies was generally described as:

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

where k was the rate constant and $f(\alpha)$ was the reaction model, a function depending on the actual reaction mechanism. Eq. (1) expresses the rate of conversion, $d\alpha/dt$ at a constant temperature as a function of the reactant conversion loss and rate constant. In this study, the conversion rate (α) was defined as:

$$\alpha = \frac{w_0 - w_t}{w_0 - w_f} \tag{2}$$

where w_t, w_0 and w_f were time t, initial and final weight of the sample, respectively. The rate constant (k) was generally given by the Arrhenius equation:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \tag{3}$$

where E_a was the apparent activation energy (kJ/mol), R was the gas constant (8.314 J/K mol), A was the pre-exponential factor (min^{-1}), T was the absolute temperature (K). The combination of Eqs. (1) and (3) gives the following relationship:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \tag{4}$$

For a dynamic TGA process, including the heating rate, $\beta = dT/dt$, into Eq. (4), Eq. (5) was obtained as:

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \tag{5}$$

Eqs. (4) and (5) are the fundamental expressions of analytical methods to calculate kinetic parameters on the basis of TGA data.

3. Materials and methods

3.1. Materials

Moso Bamboo was used in the study. The moisture content of samples was about 8.0%. Bamboo materials were cut off to sample size 40 mm (longitudinal) by 20–30 mm (radial) by 3–8 mm (tangential). Then, they were broken down to particles with a Wiley mill and the size of bamboo particles used in the test was about 250–425 μm. Finally, the particles were dried 4 h at 105 °C.

3.2. Test procedures of thermal decomposition

Thermal decomposition was observed in terms of global mass loss though TA Instrument TGA Q 500 thermogravimetic analyzer (TA Instrument, USA). The bamboo powders 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 (300 ± 5 K) to 1000 K with a heating rate of 10 K/min. A high purity nitrogen stream (flow rate of 60 mL/min and 40 mL/min, respectively) was continuously passed into the furnace before thermal decomposition was carried out in order to prevent any unwanted oxidative decomposition. The experimental data could be directly obtained though TGA Q 500 thermogravimetic analyzer, but they were analyzed by using Universal Analysis software from TA Instruments and Origin 8.0 software. E_a values were calculated using a custom program designed within Microsoft Office Excel 2007.

3.3. TG–FTIR test

The experimental setup consisted of a combination of thermogravimetry (TA Instrument, USA) and Fourier transform infrared spectrometer (Bruker IFS 66/S, Bruker Optics, Billerrica, MA). A helium sweep gas flow of 500 mL/min was used to bring the evolved pyrolysis gases from the TGA directly to the gas cell which was heated to 423 K. The system collected FTIR spectra every 30 s and the sample temperature and mass were logged every 3 s. The sample pan was placed close to the end of the furnace, where a steeply decreasing temperature profile existed. This, combined with the high gas flow, minimized the residence time of the evolved gases in the hot zone. In the experiment, sample masses were about 20 mg and they were heated from 323 K to 823 K at heating rate 10 K/min.

3.4. XRD test

XRD test of moso bamboo, treated in different temperatures for 30 min, was carried out using an X-ray diffractometer (Diffraktometer D5000, Siemens, Germany) with an X-ray generator and a Co target (λ = 0.1729 nm) at a scanning speed of 3°/min, and the data were recorded every 0.02° (2θ) for the angle range of 2θ = 5–45°. The crystallinity index (CrI) and the width of crystals (t) were, respectively calculated according to formulas (6) and (7):

$$\mathrm{CrI} = \frac{I_{002} - I_{am}}{I_{002}} \tag{6}$$

where I_{002} was the overall intensity of the peak at 2θ about 22° and I_{am} was the intensity of the baseline at 2θ about 18°.

$$t = \frac{k \times \lambda}{(B \cos\theta)(\dot{A})} \tag{7}$$

where k was the Scherrer constant (0.9), λ was the wavelength of the X-ray, B was the half-bandwidth in radians and θ was the Bragg angle.

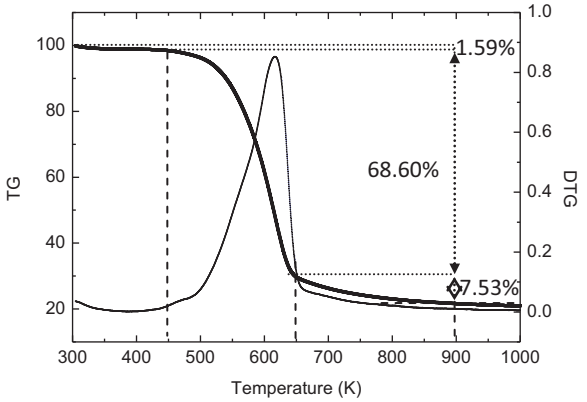

Fig. 1. Pyrolysis process of moso bamboo at a heating rate of 10 K/min.

4. Results and discussion

4.1. Pyrolysis process of moso bamboo

Fig. 1 presents the pyrolysis process of moso bamboo at a heating rate of 10 K/min. As shown in Fig. 1, the pyrolysis process of moso bamboo included three steps. The initial temperature of every step was defined as the critical point of weight change in the TG curve. The initial temperature of thermal decomposition for subsequent steps was the same as the final temperature of thermal decomposition for the previous step. In the third step, the final temperature was defined as the critical point where the sample weight had not changed. In the first step, the degradation temperature was from 300 K to 450 K and weight loss was about 1.59% due to removal of absorbed water from the samples. In the second step, the degradation temperature was from 450 K to 650 K and the weight loss was about 68.69%. The degradation of cellulose, hemicelluloses and partial lignin happened in this step. The critical temperature of maximum weight loss was 620 K for moso bamboo in the pyrolysis process. In the third step, the degradation temperature was from 650 K to 900 K and the weight loss was about 7.53%. The degradation of lignin residues from the second step or tar and char from the main components resulted in weight loss of the sample in the step. The pyrolysis characteristics of moso bamboo from TG are shown in Table 1.

4.2. E_a of moso bamboo

The Flynn–Wall–Ozawa and Coats–Redfern (modified) methods were used to determine the E_a value of moso bamboo in the research. Both methods were the most 'mold-free' methods in E_a determination of biomass materials. The Flynn–Wall–Ozawa method was the integral method, which led to $-E_a/R$ from the slope of the line determined by plotting $\log(\beta)$ against $1/T$ at any certain

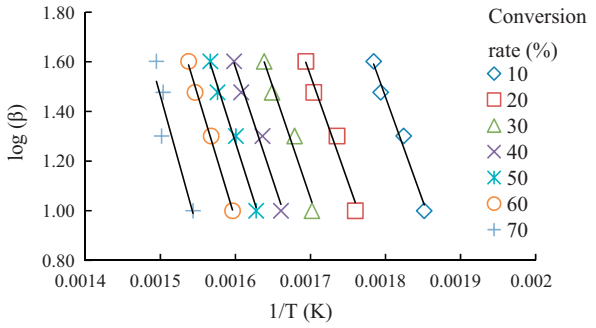

Fig. 2. The typical plot of Flynn–Wall–Ozawa for moso bamboo.

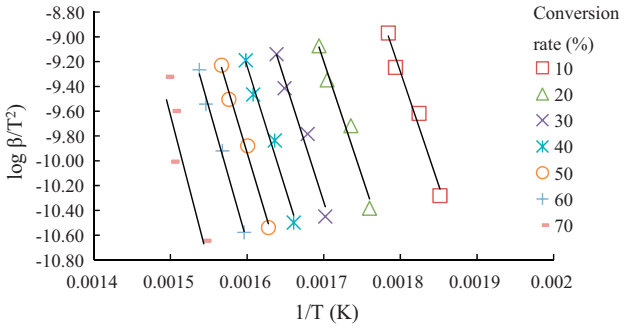

Fig. 3. The typical plot of Coats–Redfern (modified) for moso bamboo.

conversion rate. The modified Coats–Redfern method was a multi-heating rate application of the Coats–Redfern equation. Plotting the left hand side for each heating rate versus $1/T$ at that heating rate gave a family of straight lines of slope $-E_a/R$. The full solution was to be done iteratively by first assuming E_a value and then recalculating the left hand side until convergence occurs. Here, a quick solution, however, was also available by moving $(1 - 2RT/E_a)$ into the intercept and assuming that it was a constant [20]. Both the methods are shown in Table 2.

The typical plots of Flynn–Wall–Ozawa (Fig. 2) and Coats–Redfern (modified) (Fig. 3) showed a general trend of E_a values for moso bamboo. It is shown in Figs. 2 and 3 that the fitted lines were nearly parallel at conversion rate from 10 to 70, which indicated approximate E_a values at different conversions and consequently implied the possibility of single reaction mechanism. Table 3 summarizes the E_a values of moso bamboo calculated according to the conversion rate range from 10 to 70 using Flynn–Wall–Ozawa and Coats–Redfern (modified) methods. As shown in Table 3, the E_a values of moso bamboo were around 153.37–198.55 kJ/mol at conversion rate from 10 to 70 for Flynn–Wall–Ozawa method. The similar results of Coats–Redfern (modified) method were also confirmed this observation, where the E_a values were around 152.14–197.87 kJ/mol. The E_a values

Table 1
Pyrolysis characteristics of moso bamboo from TG.

Pyrolysis characteristics	The first step			The second step			The third step		
	Start (K)	End (K)	Weight loss (%)	Start (K)	End (K)	Weight loss (%)	Start (K)	End (K)	Weight loss (%)
Moso bamboo	300	450	1.59	450	650	68.69	650	900	7.53

Table 2
Flynn–Wall–Ozawa and Coats–Redfern (modified) model-free method.

Method	Expression	Plots
Flynn–Wall–Ozawa	$\log(\beta) = \log(AE_a/RG(\alpha)) - 2.315 - 0.4567E_a/RT$	$\log\beta$ against $1/T$
Coats–Redfern (modified)	$\ln[\beta/(T^2(1 - 2RT/E_a))] = \ln[-AR/(E_a \ln(1-\alpha))] - E_a/RT$	$\ln(\beta/T^2)$ against $1/T$

Table 3
The E_a value of moso bamboo by Flynn–Wall–Ozawa and Coats–Redfern (modified) method.

Conversion rate (%)	Average apparent activation energy of moso bamboo (kJ/mol)	
	Flynn–Wall–Ozawa method	Coats–Redfern (modified) method
10	153.37	152.14
20	156.06	154.49
30	161.99	160.41
40	165.89	164.25
50	172.51	171.02
60	181.61	180.39
70	198.55	197.87

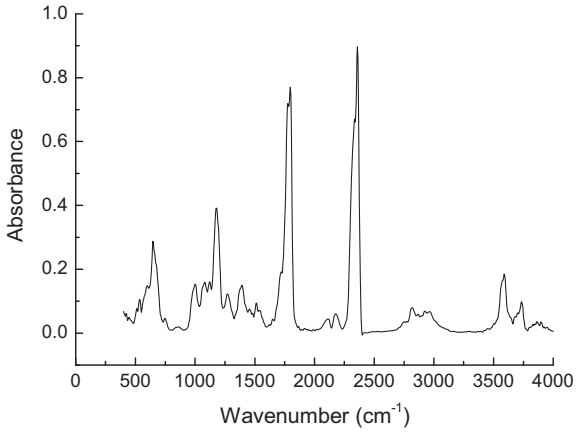

Fig. 4. The absorbance spectra stack plot of moso bamboo pyrolysis at heating rate 10 K/min.

of moso bamboo were gradually increased with the conversion rate increase from 10 to 70. The higher E_a values indicated that thermal decomposition of bamboo was more difficult. The information was very helpful and significant to design manufacturing process of bio-energy, made from moso bamboo, using the thermal decomposition methods such as gasification or pyrolysis.

4.3. TG–FTIR analysis

In the experiment, approximately 20 mg samples were heated to 323 K for 4 min, and then to 823 K at heating rate 10 K/min. When temperature reached 823 K and was steady for 4 min, the samples were immediately cooled to 323 K. The typical absorbance peaks of pyrolysis products of moso bamboo are shown in Fig. 4. According to Fig. 4, the typical absorbance peaks and pyrolysis products of moso bamboo are shown in Table 4 and listed as follows: the peak of 3435 cm^{-1} was O–H stretching vibration and pyrolysis products were mainly absorbed water (H_2O), the peak of 2927 cm^{-1} was C–H stretching vibration and pyrolysis products were methane gas (CH_4), the pyrolysis products of peak (2345 and 650 cm^{-1}) were carbon dioxide (CO_2). The peak of 1718 cm^{-1} was C=O stretching vibration and that of 1617 cm^{-1} was C=C stretching vibration which probably came from pyrolysis products of acids and aldehydes, the peak of 1511 cm^{-1} and 1388 cm^{-1} appeared when nitrogen dioxide (NO_2) was released, the peak of 860 cm^{-1} expressed ammonia gas (NH_3). Bamboo was a kind of biomass material which was composed of several compounds. Some pyrolysis gases could be evolved at the same time, which led to more difficultly find the peak of gas when testing small quantities.

Table 4
The typical absorbance peaks and pyrolysis products of moso bamboo.

Typical absorbance peaks (cm^{-1})	The main pyrolysis products
3535 cm^{-1}	Absorbed water (H_2O)
2927 cm^{-1}	Methane gas (CH_4)
2345 and 650 cm^{-1}	Carbon dioxide (CO_2)
2175 and 2117 cm^{-1}	Carbon monoxide (CO)
1795 cm^{-1}	Nitric oxide (NO)
1718 and 1617 cm^{-1}	Acids and aldehydes
1511 and 1388 cm^{-1}	Nitrogen dioxide (NO_2)
860 cm^{-1}	Ammonia gas (NH_3)

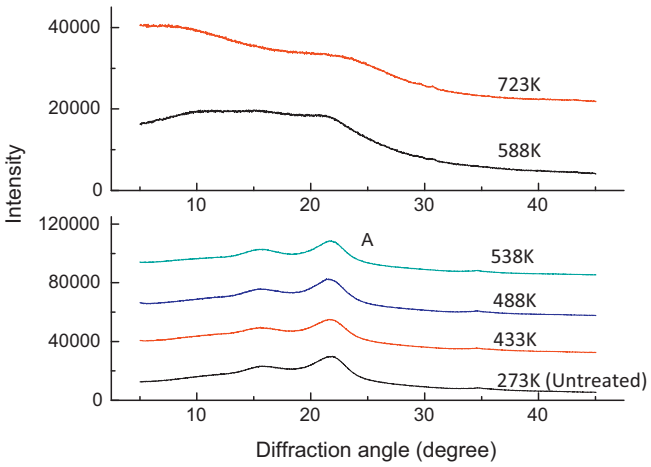

Fig. 5. XRD curve of moso bamboo treated in different temperatures for 30 min.

4.4. XRD analysis

The moso bamboo powders used in this study were also treated in the heat-treating furnaces using different temperatures for 30 min. The heat-treating temperatures were selected basis on the pyrolysis temperature of moso bamboo. For example, the temperature point of 433 K was located in the scope of pyrolysis temperature of absorbed water. The temperature point of 488 K was located in the scope of pyrolysis temperature of hemicelluloses. The temperature points of 538 K and 588 K were located in the scope of pyrolysis temperature of cellulose. The two temperature points (538 K and 588 K) were selected because cellulose was composed of amorphous region and crystalline region. Temperature point of 723 K was located in the scope of pyrolysis temperature of lignin. XRD testing of temperature treated bamboo powder was carried out with an X-ray generator. The XRD test results are shown in Fig. 5.

The crystallinity index (CrI) and the width of crystals (t) were calculated according to formulas (6) and (7), respectively. The crystallinity index (CrI) and the width of crystals (t) of moso bamboo treated at different temperatures are shown in Table 5. As shown in Table 5, the index and width crystallinity of moso bamboo were 28.28% and 3.1488 nm, 28.29% and 3.1974 nm, 30.38% and 3.2667 nm, 32.76% and 3.3441 nm, 3.88% and 2.6069 nm, 0% and 0 nm at the temperature of 273 K,

Table 5
The index and width of crystallinity of moso bamboo treated in different temperatures.

Treated temperature	Crystallinity index (%)	Crystallinity width (nm)
273 K (untreated)	28.28	3.1488
433 K	28.29	3.1974
488 K	30.38	3.2667
538 K	32.76	3.3441
588 K	3.88	2.6069
723 K	0	0

433 K, 488 K, 538 K, 588 K and 723 K, respectively. The experimental results indicated that index and width crystallinity of moso bamboo gradually increased from 273 K to 538 K. The main reason was that crystalline region of cellulose was not degraded, but absorbed water, small molecule hemicelluloses and amorphous region of cellulose had been gradually degraded at the temperature scope.

Biomass materials exhibited two kinds of index and width crystallinity of cellulose: absolute and relative index and width crystallinity. The relative index and width crystallinity were used in this research. Thus, when some matter was degraded except for the crystalline region of cellulose, the relative index and width crystallinity of moso bamboo gradually increased. In the pyrolysis temperature scope of cellulose, temperature points of 538 K and 588 K were selected in this research. The index and width crystallinity of 588 K were lower than that of 538 K, which indicated that cellulose pyrolysis moved from amorphous region to crystalline region. When temperature was near 723 K, the crystalline region of cellulose was completely destroyed and the index and width crystallinity of moso bamboo were 0% and 0 nm.

5. Conclusions

TG was used to investigate the pyrolysis process of moso bamboo. The Flynn–Wall–Ozawa and Coats–Redfern (modified) methods were used to determine E_a value. TG–FTIR and XRD were, respectively used to analyze the pyrolysis products and residues of moso bamboo.

The TG curve indicated that the pyrolysis process of moso bamboo included three steps and the main decomposition occurred in the second step with temperature range from 450 K to 650 K and over 68.69% mass was degraded. The temperature of 620 K was the critical point where maximum mass loss occurred in the pyrolysis process of moso bamboo. The main degradation compositions were hemicelluloses, cellulose and partial lignin of moso bamboo in this step.

The E_a values of moso bamboo increased with conversion rate increase from 10 to 70. The E_a values were, respectively 153.37–198.55 kJ/mol and 152.14–197.87 kJ/mol according to Flynn–Wall–Ozawa and Coats–Redfern (modified) methods. The information was very helpful and significant to design manufacturing process of bio-energy, made from moso bamboo, using the gasification or pyrolysis methods.

TG–FTIR analysis showed that the main pyrolysis products included absorbed water (H_2O), methane gas (CH_4), carbon dioxide (CO_2), carbon monoxide (CO), acids and aldehydes, nitrogen dioxide (NO_2), nitric oxide (NO), and ammonia gas (NH_3).

XRD analysis expressed that the index and width crystallinity of moso bamboo gradually increased from 273 K to 538 K. In the pyrolysis process of cellulose, its pyrolysis gradually occurred from amorphous region to crystalline region. When temperature was close to 723 K, the crystalline region of cellulose was completely destroyed.

Acknowledgement

This research was financially supported by 'Development and demonstration of bamboo/wood composite LVL and wallboard' (Grant No. [2008] 16).

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