Pyrolysis Characteristics and Kinetics Analysis of Moso Bamboo

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In order to investigate the pyrolysis characteristics and mechanism of moso bamboo, its pyrolysis behaviour has been investigated by thermo-gravimetric analysis (TGA), which can be described as four steps: dehydration, hemicellulose pyrolysis, pyrolysis of cellulose and lignin, and residue decomposition. The decomposition of hemicellulose, cellulose and lignin are the main contributions for pyrolysis weight loss. Furthermore, the pyrolysis mechanism has been clarified based on pyrolysis kinetics model fitting. Detailedly, the pyrolysis kinetics of hemicellulose agrees with first order chemical reaction, whereas the pyrolysis kinetic equation of cellulose and lignin accords with the 1D-diffusion parabolic curve. And the apparent activation energy of them is 124.62 and 232.64 KJ/mol, respectively.

Keywords: Moso bamboo, pyrolysis characteristics, pyrolysis kinetics, thermo-gravimetric analysis

Bamboo, one of the well-known fast-growing plants, is also a preference for reforestation in tropical and sub-tropical regions. Currently, Asia, America, Africa etc. are the main bamboo habitats. Especially, China, India, Japan, Myanmar and other countries have numerous bamboo plantations of up to 20 million h with an annual output of 18 million t. In China, there are more than 130 counties (cities) having bamboo planting area of over 10,000 h, with a sum of 7 million hectares, among which is mostly moso bamboo[1, 17]. Development and utilization of bamboo resources have become a major issue in the sustainable development of forestry[13]. Bamboo charcoal and bamboo vinegar are the most valuable pyrolysis products in the field of bamboo processing, which have broad market prospects [14]. However, components of the pyrolysis product are very complicated, which is dominated by the pyrolysis kinetics, so thorough understanding of bamboo pyrolysis characteristics and kinetics is the key theoretical basis for the application of bamboo [15]. The current research on the pyrolysis of bamboo mainly concerns component analysis and practical application of bamboo charcoal and vinegar, while little research on bamboo pyrolysis process and dynamics has been reported. [3] have reported the main chemical components of bamboo and liquid product composition manufatured from slow pyrolysis, and in their work the impact of pyrolysis temperature on product composition was discussed. [5] carried out both routine and fast pyrolysis of Bambusa multiplex and have studied the difference between compositions and yields of liquid, solid and vapour phase product under varied pyrolysis conditions. In [9] it is investigated pyrolysis behaviour of moso bamboo and Bambusa multiplex, and figured out that the pyrolysis is a first order reaction in terms of kinetics with calculated average activation energy. In [4] it was studied the weightlessness kinetics of moso bamboo from different habitats by non-model kinetic method and model simulation, and it was concluded that varied moso bamboo habitats induce different pyrolysis behaviours. However, aforementioned literatures can hardly reveal the mechanism of bamboo pyrolysis, and consequently pyrolysis behaviour cannot be scientifically regulated for the purpose of desired products. Thermo-gravimetric analysis (TGA) is a conventional method to characterize pyrolysis process [10, 11]. Therefore, based on experimental TGA curves of bamboo, with the aid of mathematics, we have obtained kinetic parameters of the pyrolysis to further reveal the mechanism of bamboo pyrolysis and the influencial factors, which can provide theoretical basis for scientifically adjusting pyrolysis conditions to control performance and structure of products and could guide bamboo pyrolysis carbonization and bamboo-based materials research and development.

Experimental part

Materials and methods

5-year-old moso bamboo, which lived in Xiangtan City, Hunan Province, China, was provided by Hengdun Ltd., Hunan.

The bamboo was pulverized and then sieved with a 100-mesh (0.15 mm) AS200 Sieving Instrument (USA). The powder was dried at 353 K for 8 h and then was placed in a desiccator.

TGA was conducted by the Forestry Biotechnology Laboratory of Hunan Province, Forestry and Technology of Central South University, with a Leco thermo-gravimetric analyzer (TGA701, USA) at a heating rate of 10 K/min in temperature range of 303-873 K. Highly pure N_2 served as the balance carrier gas (40 ml/min) and sample protection gas (30 mL/min).

Results and discussions

Pyrolysis Characteristics

The thermogravimetry (TG) and differential thermogravimetry (DTG) curve of moso bamboo are given in figure 1 and 2, respectively.

Pyrolysis process of moso bamboo is a complex physical and chemical process including moisture vaporization, hemicellulose pyrolysis, thermal decomposition of cellulose and lignin, and volatilization and secondary reaction of pyrolysis residues. As shown in figure 1 and 2, the pyrolysis process of moso bamboo could be divided into four phases: dehydration, hemicellulose pyrolysis, decomposition of cellulose and lignin, and residue volatilization.

The dehydration occurred at <440 K. Initially, only moisture was lost. Afterwards, the content of pentosan decreased and consequently the physical and mechanical properties were changed. Slight weight loss at this stage accounts for 8% of the total weight loss and a small weight

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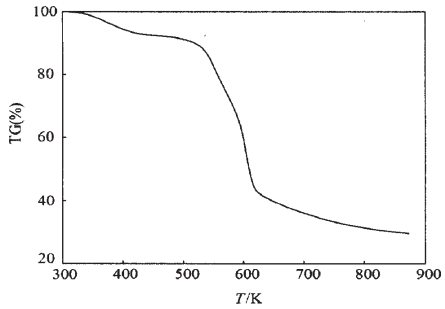

Fig. 1. TG curve of moso bamboo

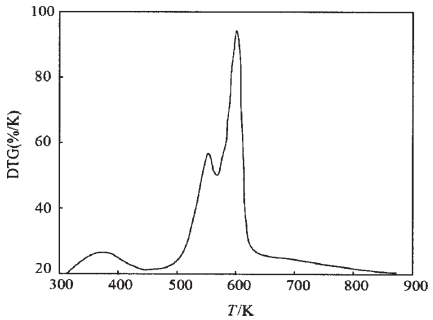

Fig. 2. DTG curve of moso bamboo

loss peak at this stage can be observed in DTG curve, which was mainly caused by dehydration. The stage of hemicellulose pyrolysis corresponds to the temperature range of 440-560 K. In this stage, thermal decomposition of more unstable hemicellulose was enhanced to produce H_2, CO, CO_2, a small amount of acetic acid, etc. Weight loss at this stage accounts for 15% of the total weight loss and a large weight loss peak is observed in the DTG plot.

The phase of cellulose and lignin pyrolysis took place at 560-650 K. In this stage, the simultaneous pyrolysis of cellulose and lignin intensifies thermal decomposition, along with a large number of gaseous high-temperature thermal decomposition products. Owing to the secondary reaction of thermal decomposition products, the amount of H_2 and CO decreased in gaseous product, while hydrocarbons such as methane, ethylene, olefin, and a variety of highly active hydrogen radicals and hydroxyl increased. And the liquid product mainly embraces acetic acid, methanol, acetone and wood tar. Weight loss at this stage accounts for 67% of the total weight loss and a pronounced weight loss peak that arises from the themal decomposition of cellulose and lignin is observed in the DTG curve. At temperatures >650 K, the residue decomposed. In this stage, residual volatile substances in charcoal were distilled off under high temperature.

Kinetic Model of Pyrolysis

Pyrolysis kinetic models can be divided into the following: chemical reaction, diffusion-controlled, phase boundary reaction and nucleation-growth [7]. Relevant research results show that the pyrolysis of biomass generally consist of succesive processes of dehydration, pyrolysis of hemicellulose, and pyrolysis of cellulose and lignin[16]. Therefore, the hemicellulose pyrolysis is easy to carry out than the thermal decomposition of cellulose and lignin. In the DTG curve of moso bamboo, there are two marked peaks of which the weight loss accounts for 82% of the entire weight loss, and complex chemical reactions occur at each stage. On the other hand, the apparent pyrolysis kinetics does not focus on elementary reactions but view the entire pyrolysis process as the combination of a number of "pseudo-components", i.e. apparent pyrolysis behaviours [6]. Therefore, the pyrolysis characteristics of moso bamboo have proven that the pyrolysis process under highly pure N_2 atmosphere could be composed of two steps of reactions to simulate its pyrolysis kinetics.

Seeing that particle size of the moso bamboo powder is small, heat transfer and diffusion phenomenon within internal particles could be ignored. Furthermore, the highly pure N_2 would dissipate the volatiles instantly, so the moso bamboo pyrolysis process could be considered as an irreversible reaction and the first order parallel reaction model should be fitted. Therefore, the Coats-Redfern integral method of pyrolysis kinetics [12, 2] can be used here.

Supposing that initial weight of the bamboo sample was w_0, the pyrolysis reaction processed under programmed-temperature, and the weight became w after a period of t. Hence, the pyrolysis rate could be expressed as follows:

$$\frac{da}{dt} = kf(a) \qquad (1)$$

where $a = \frac{w_0 - w}{w_0 - w_\infty} \times 100\%$ (w_∞ is the weight of refractory residue); k is the Arrhenius rate constant which could be expressed as $k = A \times \exp(-\frac{E}{RT})$;
E is the activation energy; A is the frequency factor; R is the molar gas constant; $f(a)$ is the kinetic model function which depends on the type and mechanism of reaction, and for simple reaction, the $f(a)$ could be given as $f(a) = (1 - a)^n$, where n is the order of reaction. Moreover, in this experiment, the constant heating rate $\varphi = \frac{dT}{dt}$ where T is the thermodynamic temperature, K. Therefore, eq 1 could be expressed as the following:

$$\frac{da}{dT} = \frac{A}{\varphi} \times \exp(-\frac{E}{RT}) \times (1-a)^n \qquad (2)$$

After variables separation, integration and approximation, eq 2 can be changed into the follows:

If n = 1,

$$\ln\left[\frac{-\ln(1-a)}{T^2}\right] = \ln\left[\frac{AR}{\varphi E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad (3)$$

If n ≠ 1

$$\ln\left[\frac{1-(1-a)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{\varphi E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad (4)$$

With regard to most of the E of common reactions, $\frac{2RT}{E}$ is much smaller than 1, so $\ln\left[\frac{AR}{\varphi E}\left(1 - \frac{2RT}{E}\right)\right]$ could be viewed as a constant. Therefore, if n=1, the plot of $\ln\left[\frac{-\ln(1-a)}{T^2}\right]$ against 1 / T would be described. If n≠1, the plot of $\ln\left[\frac{1-(1-a)^{1-n}}{T^2(1-n)}\right]$ against 1/ T would be depicted. For an appropriate n, a straight line could be obtained, and the value of E and A could be calculated from the slope $-\frac{E}{R}$ and intercept $\ln\left[\frac{AR}{\varphi E}\left(1 - \frac{2RT}{E}\right)\right]$

The TG curve of moso bamboo has two major weight loss stages: hemicellulose pyrolysis and pyrolysis of cellulose and lignin. The former is carried out in range of 440-560 K. In this stage, Coats-Redfern integral method could be applied for the pyrolysis kinetics. If n=1, the plot $\ln\left[\frac{-\ln(1-a)}{T^2}\right]$ of against 1 / T is shown in figure 3.

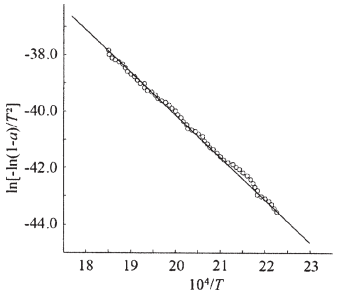

Fig. 3. Plot of $\ln[-\ln(1-a)/T^2]$ against $10^4/T$

The plot could be a first-order chemical reaction, which is attributed to the thermal decomposition of hemicellulose. If $Y = \ln\left[\frac{-\ln(1-a)}{T^2}\right]$ and $X = \frac{1}{T}$ it can be fitted into a straight line as follows with the goodness of fit of 0.996:

$$Y = -10.205 - 1.499X \quad (5)$$

According to the slope of $-\frac{E}{R}$ and intercept of $\ln\left[\frac{AR}{\varphi E}\left(1-\frac{2RT}{E}\right)\right]$ the calculated activation energy E in this stage is 124.62 KJ/mol and the pre-exponential factor A is $6.75 \cdot 10^9\ s^{-1}$.

The other major weight loss of moso bamboo pyrolysis corresponds to 560-650 K. In this stage, a 1D-diffusion equation [8] could be used to characterize the pyrolysis kinetics:

$$\ln\frac{G(a)}{T^2} = \ln\frac{AR}{\varphi E} - \frac{E}{RT} \quad (6)$$

$$G(a) = a^2 \quad (7)$$

The plot of $\ln\frac{a^2}{T^2}$ against 1 / T is shown in figure 4, and the reaction kinetics could be modeled by one-dimensional diffusion parabolic curve, which is primarily attributed to the thermal decomposition reactions of both cellulose and lignin. If $Y = \ln\frac{a^2}{T^2}$ and $X = \frac{1}{T}$, a fitting straight line could be obtained as follows with the goodness of fit of 0.993:

$$Y = -6.532 - 2.798X \quad (8)$$

According to the slope of $-\frac{E}{R}$ and intercept of $\frac{AR}{\varphi E}$ the calculated activation energy E in this stage could be 232.64 KJ/mol and pre-exponential factor A is $8.96 \cdot 10^9\ s^{-1}$.

Conclusions

The pyrolysis behaviour of moso bamboo in temperature range of 303-873 K can be divided into four stages: dehydration, pyrolysis of hemicellulose, pyrolysis of cellulose and lignin and volatilization of residue.

Moreover, at temperatures from 440 to 560 K, the Coats-Redfern integral method can be applied to explore the pyrolysis reaction kinetics, and as a result, the fitting straight line accords with Y = -10.205 - 1.499X with the goodness of fit of 0.996.The results show that the reaction mechanism of hemicellulose pyrolysis is essentially a first-order chemical reaction, and its pyrolysis kinetic parameters are as follows: the activation energy E is 124.62 KJ/mol and pre-exponential factor A is $6.75 \cdot 10^9\ s^{-1}$.

Thirdly, in the range of 560-650 K, a one-dimensional diffusion parabolic curve can be employed to characterize the reaction kinetics, and the fitting straight line corresponds to the following function: with the goodness of fit of 0.993. It is demonstrated that the reaction mechanism of cellulose and lignin pyrolysis is intrinsically one-dimensional diffusion control, and the calculated pyrolysis kinetic parameters are as follows: activation energy E is 232.64 KJ/mol, and pre-exponential factor A is $8.96 \cdot 10^9\ s^{-1}$.

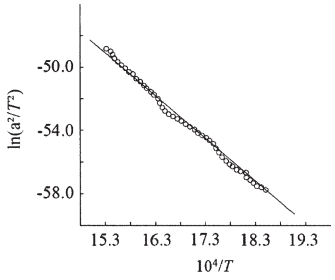

Fig. 4. Plot of $\ln(a^2/T^2)$ against $10^4/T$

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