Journal of Zhejiang University SCIENCE A
ISSN 1673-565X (Print); ISSN 1862-1775 (Online)
www.zju.edu.cn/jzus; www.springerlink.com
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Fluidized-bed pyrolysis of waste bamboo*

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Received Feb. 10, 2007; revision accepted Mar. 24, 2007

Abstract: Bamboo was a popular material substituting for wood, especially for one-off commodity in China. In order to recover energy and materials from waste bamboo, the basic characteristics of bamboo pyrolysis were studied by a thermogravimetric analyzer. It implied that the reaction began at 190~210 °C, and the percentage of solid product deceased from about 25% to 17% when temperature ranged from 400 °C to 700 °C. A lab-scale fluidized-bed furnace was setup to research the detailed properties of gaseous, liquid and solid products respectively. When temperature increased from 400 °C to 700 °C, the mass percent of solid product decreased from 27% to 17% approximately, while that of syngas rose up from 19% to 35%. When temperature was about 500°C, the percentage of tar reached the top, about 31%. The mass balance of these experiments was about 93%~95%. It indicated that three reactions involved in the process: pyrolysis of exterior bamboo, pyrolysis of interior bamboo and secondary pyrolysis of heavy tar.

Key words: Bamboo, Pyrolysis, Fluidized beds, Syngas, Tar
doi:10.1631/jzus.2007.A1495 **Document code:** A **CLC number:** TK229

INTRODUCTION

Bamboo was one of the fastest-growing plants, and it could be harvested in 1~3 years generally. The area of bamboo forests was up to 140000 km^2 in the world, and most was distributed over Southeast Asia, Canada and West Africa. In China, bamboo was the second woody resource, about 50000 km^2 and sharing 1/10 market of woody materials. Researches (Du *et al.*, 2004; Li *et al.*, 2004; Li *et al.*, 2006; Wang *et al.*, 1999; Zhou and Xu, 2004) indicated that cellulose, hemi-cellulose and lignin were the main components in bamboo and their percentages were 35%~45%, 15%~20% and 15%~25% respectively.

Bamboo was a kind of popular materials substituting for wood, especially for one-off commodity. A great deal of waste bamboo was produced every year and it always clustered at specific locations, like furniture plants, noshery, restaurants, etc. It facilitated waste bamboo to be collected and recovered. But by now, few researches were focused on how to make use of it.

Pyrolysis was one of the efficient means with less emission to recover energy from waste biomass (Ayşe *et al.*, 2005; Li *et al.*, 2000; Ni *et al.*, 2006a; 2006b; Xiao *et al.*, 2007; Yan *et al.*, 2006; Zhang *et al.*, 2005; Zhou *et al.*, 2006). This technique could be applied to waste bamboo also. Du *et al.*(2004) studied on bamboo pyrolysis at 300~600 °C in a fixed bed, and researched the main components in the liquid product. The results showed that $C_2H_4O_2$ (acetic acid), C_8H_8O (2,3-dihydro-benzofuran), $C_8H_8O_3$ (2,6-dimethoxyphenol), $C_5H_6O_2$ (2-furanmethanol) were the main components, and the percentages were 15%~35%, 7%~20%, 8%~12%, 3%~8% respectively.

* Project supported by the National Basic Research Program (973) of China (Nos. G199902210534, 2005CB221202 and 2007CB210208), the Hi-Tech Research and Development Program (863) of China (No. 2006AA020101), and the Open Foundation of State Key Laboratory of Clean Energy Utilization of China (No. ZJUCEU2006004)

In order to provide more comprehensive knowledge of waste bamboo pyrolysis, in this paper, experiments were carried out in a thermogravimetric analyzer and a lab-scale fluidized bed. The characteristics of gaseous, liquid and solid products were analyzed in detail. It was looking forward to facilitate the technology for recovering energy and material from waste bamboo.

EXPERIMENTAL METHODOLOGY

One-off chopsticks of bamboo were selected as the feedstock for the experiments. The proximate and ultimate analysis was reported in Table 1. In the experiments of thermogravimetirc analysis bamboo was treated less 0.1 mm, and in the experiments of fluidized-bed pyrolysis, the size was about 5 mm×5 mm×5 mm.

Table 1 Proximate and ultimate analysis of bamboo

Item	Value
Moisture (%)	9.15
Ash (%)	1.63
Volatile (%)	73.92
Fixed carbon (%)	15.30
High heat value (kJ/kg)	17821
C (%)	45.88
H (%)	5.36
N (%)	0.32
S (%)	0.26
O (%)	37.40

The thermogravimetric analysis was made in such procedure: At first, feedstock was put into the analyzer and the beginning temperature was 25 °C; the furnace was heated at 100 °C/min, and when the temperature achieved 100 °C it was kept for 1 min to eliminate moisture in feedstock; then, the furnace was heated at 100 °C/min until the temperature reached 400 °C/500 °C/600 °C/700 °C; at last, the temperature was kept until the total time reached 700 s to make sure the reaction was completed.

The fluidized-bed pyrolysis reactor was equipped with a steel tube of inside diameter of 30 mm and total height of 250 mm, as shown in Fig.1, which was placed in an electrical heater (about 1 kW). A K-type thermocouples was assembled at about 150 mm above the gas distributor. N_2 was acted as fluidized medium and the velocity was about 0.48 m/s. Sand was selected as bed materials and its diameter was 0.250~0.355 mm. The thickness of bed materials was about 80 mm. Feedstock was fed by batch from the top of the reactor, where equipped with a valve. As soon as the feedstock was fed, the valve was closed quickly. The gaseous product came into the cooler firstly; condensable tar was collected in vessels, and after being dried, un-condensable syngas was collected in a gas-bag. This process was going on for about 2 min until the reaction was almost finished. The fluidized bed was airproofed and cooled quickly. Then it was cleaned up and solid product was collected.

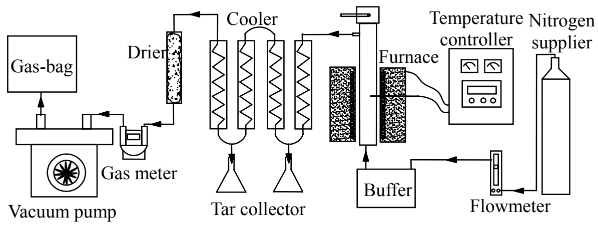

Fig.1 The illustration of fluidized-bed pyrolysis reactor

In experiments, precise flux was measured by a gas meter (G1.6 membrane type, minimal precision: 0.2 L), which was made by Hangzhou Beta Gas Meter Co. Ltd. The un-condensable syngas was detected by Trace 2000 gas chromatography (GC). It was made by Thermo Finnigan in Italy, equipped with Flame Ionization Detector (FID) to detect hydrocarbons ($C_{1\sim8}H_n$) and two Thermal Conductivity Detectors (TCD) to detect CO, CO_2, H_2, N_2, etc. The yields of syngas were calculated by N_2 balance. The heat values of tar and solid product were measured by 5E-1AC/P oxygen bomb calorimeter produced by Kaiyuan Instrument Company in Changsha, China.

RESULTS AND DISCUSSION

The pilot study was carried out in a thermogravimetric analyzer. And the results were reported in Fig.2. At the beginning of 0~300 s, the loss curve was similar; there was a obvious loss at 50~100 s (100 °C), which meant the moisture was moved out from bamboo; the reaction began at 200 s (about 250 °C); the main loss took place during 200~300 s, which meant the main reaction was carried out at 250~400 °C; and after 300 s (about 400 °C), the percentage of solid products reached about 25% and decreased slowly, which meant pyrolysis was almost completed.

If the temperature increased continuously from 400 °C to 700 °C, the percentage of solid products would decrease from 25% to 17%, which indicated there was a further pyrolysis of solid product (Wang *et al.*, 2006).

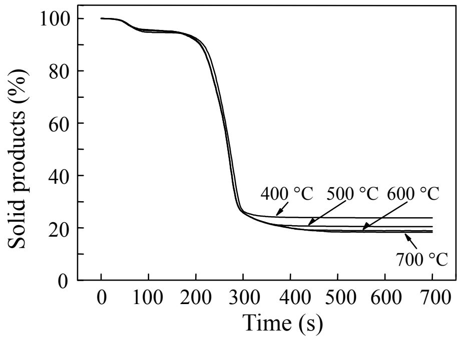

Fig.2 The TG curve of bamboo pyrolysis

Characteristics of solid product from fluidized-bed pyrolysis

The proximate and ultimate analysis of solid product was carried out and reported in Table 2. Generally, the percentage of carbon and fixed carbon rose up respectively with temperature increasing, while that of volatile, hydrogen and oxygen reduced. This meant pyrolysis of solid product was going on with temperature increasing, which was corresponding to the conclusion of TG experiments. The HHV increased from 25000 to 30000 kJ/kg approximately.

It was worthy to report that, when the solid product of 400~500 °C was treated into powder, there was some un-reacted bamboo remained inside it obviously. This indicated that two minutes was not enough for the reaction of pyrolysis at this temperature, or the temperature was not high enough for granule pyrolysis.

Characteristics of tar from fluidized-bed pyrolysis

Different appearance of tar was deserved from various pyrolysis temperatures, as shown in Fig.3. The tar was more liquid and less fuscous with temperature increasing.

Due to the fact that the tar was very hydrophilic and thermo-active, it was difficult to measure the moisture of it. In this paper, silica gel was used to absorb the moisture in it, however there may induce some errors in measuring. HHV of the tar was also detected by oxygen bomb calorimeter. The results were displayed in Table 3. With temperature increasing, percentage of moisture increased, while HHV of tar decreased. It was because more tar was involved in secondary pyrolysis and more H_2O was produced (Chen *et al.*, 2003b; Wang *et al.*, 2006).

Characteristics of syngas

Inorganic gas and hydrocarbon were the main components of syngas, and the yields were displayed in Fig.4. In Fig.4a, steam was free, which would be discussed in Section 3.4. In Fig.4b, C_xH_y meant other hydrocarbons, including C_2H_6, C_3H_8, C_4H_{10}, C_5H_{10}, C_5H_{12}, C_6H_{14}, etc. The main reactions as follows:

$$\text{Exterior bamboo} \rightarrow CO_2+CO+H_2O+\text{heavy tar}+\text{char}, \quad (1)$$

$$\text{Interior bamboo} \rightarrow \text{light tar}+CO+H_2+\text{char}, \quad (2)$$

$$\text{Heavy tar} \rightarrow CO+H_2+H_2O+CH_4+C_2H_4+C_xH_y+\text{light tar}. \quad (3)$$

Table 2 Proximate and ultimate analysis of solid product

Temperature (°C)	Moisture (%)	Ash (%)	Volatile (%)	Fixed carbon (%)	High heat value (kJ/kg)	C (%)	H (%)	N (%)	S (%)	O (%)
400	6.15	5.82	22.82	65.21	25153	67.40	3.46	0.54	0.22	16.41
500	6.70	6.56	20.65	67.09	27660	69.54	3.05	0.80	0.25	13.09
600	5.90	8.49	12.76	72.85	29570	74.64	1.90	0.55	0.27	8.24
700	6.21	8.70	10.91	74.18	30032	76.67	1.69	0.57	0.28	5.87

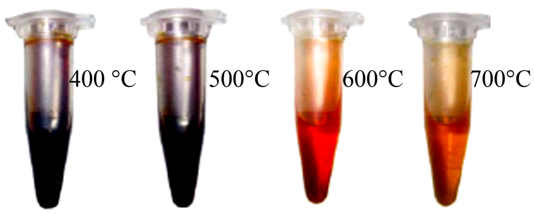

Fig.3 Tar from bamboo pyrolysis at different temperature

Table 3 Characteristics of tar

Temperature (°C)	Moisture (%)	HHV (kJ/kg)
400	13.88	28153
500	14.01	27738
600	15.00	22546
700	20.46	21411

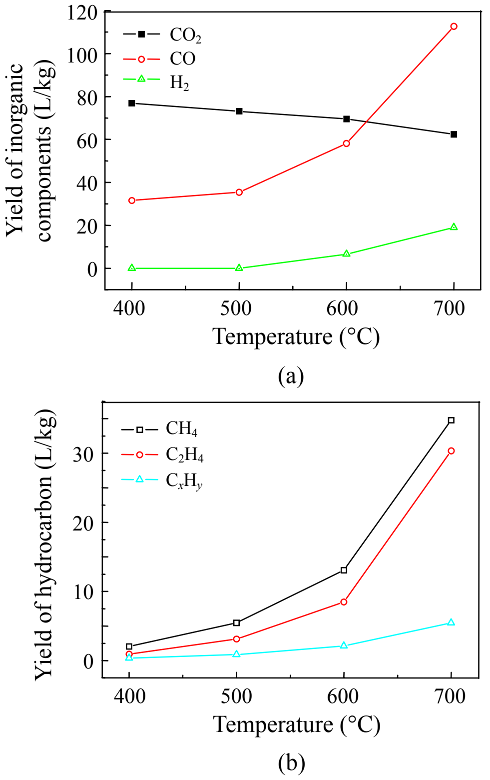

Fig.4 Yield of main components in syngas. (a) Inorganic components; (b) Hydrocarbon

Generally, the yield of inorganic gas was higher than that of hydrocarbon. Excluding CO_2, all yields of the components went up with temperature increasing.

CO_2 and CO was the predominant component in syngas. At 400~500 °C, the total percentage of CO_2 and CO was over 90%, which meant reaction Eq.(1) was the primary reaction. In this reaction, the tar was fuscous and slimy, so it was called heavy tar in this paper, while the liquid tar was called light tar, which was mainly produced at higher temperature. There was still some un-reacted bamboo remained inside the solid products, when temperature was 400~500 °C and reaction time was 2 min. The reacted bamboo was called exterior bamboo in this paper. While at higher temperature, the un-reacted bamboo would pyrolyzed further, it was called interior bamboo.

When temperature was enhanced at over 500 °C and up to 700 °C, the yields of CO_2 decreased tardily, while that of CO, H_2, CH_4 and C_2H_4 increased sharply. Furthermore, with temperature increasing, tar became more lucid and liquid, and less O remained in char. This indicated reactions Eqs.(2) and (3) were taken place during this process. In reaction Eq.(2), due to the exterior char could act as catalysis and reducing agent (Chen *et al.*, 2003a; Tan *et al.*, 2005), light tar and CO were produced rather than heavy tar or CO_2. Higher temperature could enhance the heating ratio and facilitate pyrolysis of heavy tar, which induced reaction Eq.(3).

Mass balance of pyrolysis

In order to verify the accuracy of these experiments, mass balance was fulfilled and the result was displayed in Fig.5. The mass percent of solid product decreased with temperature increasing, which indicated the reaction of pyrolysis was going on with temperature increasing. And reaction Eq.(2) was testified in a certain extent.

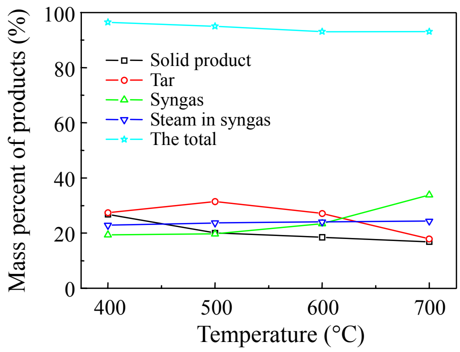

Fig.5 Mass balance of bamboo pyrolysis

The mass percent of tar achieved the highest, about 32%, when temperature was 500 °C. And when temperature increased over 500 °C, the yield of tar reduced, while the yield of syngas increased sharply. This meant reaction Eq.(3) became the principal equation at 500~700 °C.

The mass percent of steam in syngas was stable under the experimental conditions, which implied less steam involved into the secondary reactions.

In spite of carefulness, the mass balance reached 93%~95% due to the limit of collection and measurement. The errors of experiments were analyzed as following: During the cooling process, pyrolysis of the solid product would be going on, although which happened slowly. This would result in some loss of syngas and tar. In the measurement of syngas, only CO_2, CO, H_2 and some hydrocarbons ($C_{1\sim8}H_y$) were detected, but others, such as steam, CH_2O, $C_2H_4O_2$, etc., could not be detected by GC. It also reduced the mass balance.

CONCLUSION

In this paper, bamboo was pyrolyzed in a fluidized bed at 400~700 °C, and the gaseous, liquid and solid products were studied in detail.

(1) With temperature increasing, the mass percentage of solid product decreased from 27% to 17% approximately, while that of syngas increased from about 19% to 35%. When temperature was about 500 °C, the percent of tar reached the highest (about 31%). The mass balance of these experiments was about 93%~95%.

(2) In analysis of solid product, the percent of fixed carbon and carbon rose up with temperature increasing, while that of volatile, hydrogen and oxygen reduced. Its HHV increased from 25000 to 30000 kJ/kg approximately.

(3) The tar was more liquid and less fuscous with temperature increasing. The percent of moisture in tar rose from about 13% to 20% while the HHV of it decreased from 28000 to 21000 kJ/kg roughly, when temperature was increased from 400 °C to 700 °C.

(4) Generally, the yield of inorganic gas was higher than that of hydrocarbon. The yield of CO, H_2, CH_4 and C_2H_4 increased largely with temperature increasing, while that of CO_2 was stable roughly.

(5) The results indicated that the pyrolysis consisted mainly of three reactions: pyrolysis of exterior bamboo, interior bamboo and heavy tar at 400~700 °C. And the pyrolysis of interior bamboo was catalyzed by the char, which was produced from pyrolysis of exterior bamboo.

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