EXPERIMENTAL STUDY ON BIO-OIL PYROLYSIS/GASIFICATION

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This study aims to understand the mechanism of bio-oil gasification and the influence of operating parameters on the properties of the gas products. Firstly, the pyrolysis/gasification of bio-oil was performed using a thermogravimetric analyzer (TGA). The evaporation of gas products from bio-oil were measured on-line with coupled Fourier Transform Infrared Spectroscopy (FTIR). The main gas products were CO, CO_2, CH_4, H_2O, and light hydrocarbons, etc. Organics mainly evolved out at lower temperature (100-200°C), while the cracking of heavy hydrocarbon components took place at higher temperature (>200°C). Simultaneously, the gasification behavior of bio-oil was investigated in a fixed bed gasification reactor under different temperature and residence time. The gas product evolving was checked using micro-gas chromatography. It was observed that the yield of CO and H_2 increased with increasing gasification temperature above 600°C, and the maximum value was obtained at 800°C. Prolonging the residence time was not favorable for the upgrading of syngas quality.

Keywords: Bio-oil; Pyrolysis/gasification; TGA-FTIR; Fixed bed; Syngas

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INTRODUCTION

Biomass is a renewable energy resource that can be derived from essentially all the organic materials produced by human and natural activities. It is a potential source of clean energy and can replace fossil fuels (Yuan et al. 2005; Zhang 2004). There are a number of technological applications to make use of a wide variety of biomass types as a renewable energy source. Biomass can be used to produce liquid fuels such as bio-oil. However, higher viscosity, higher moisture, higher acidity, lower heating value, and heat instability are unfavorable properties relative to high-class applications (Zhu 2006). Therefore, it is one of the important goals to convert bio-oil from the liquid into gases, including H_2, CO, CO_2, CH_4, C2, C3, etc., which can then be used to synthesize high-grade fuels such as methanol, dimethyl ether, etc. (Czernik and Bridgwater 2004).

Bio-oil is the liquid product of fast pyrolysis of biomass. Many researchers have been engaged in its application and further treatment. There have been number of studies which dealt with the pyrolysis of bio-oil. In these studies, the influence of pyrolysis temperature and nitrogen flow rate on the pyrolysis gas products are investigated (Panigrahi 2002). The characteristics of bio-oil gasification in a fixed-bed under oxygen-free conditions were considered by Zhu Xifeng and Venderbosch (2004), while Guo and Yan (2005) have approximated the characteristics of bio-oil pyrolyzed from biomass via catalytic cracking in a fixed-bed reactor. However, the gasification behavior (the release of gaseous products) is rarely studied. In this study, the gasification mechanism and volatile evolving behavior is studied in depth with TGA-FTIR and a fixed-bed reactor, complemented with micro-GC. In the pyrolysis experiment, the influence of pyrolysis temperature, heating rate, and sweeping gas under specified pyrolysis conditions on the product yields were carried out.

EXPERIMENTAL

Materials

The bio-oil investigated in this study was sawdust oil from fast pyrolysis with a fluidized-bed reactor at 500°C (Wang et al. 2008). Its elemental composition (dry basis) was C=49.67%, H=7.378%, N=0.56%, O= 42.26%, and S=0.14%.

Experimental Setup

The pyrolysis of bio-oil was conducted in a thermogravimetric analysis (TGA) device (model NETZSCH STA409C, from Germany). The sample was heated at 10°C/min, first from ambient to 150 °C, and then kept at that temperature for 10 min to remove moisture. It was then heated to 900°C and kept at that temperature for 3 min. To mitigate any problems caused by heat and mass transfer, the sample size was maintained at ~40 mg for every experiment. To remove gaseous and condensable products from the TGA furnace and minimize any secondary vapor-phase interactions, the flow rate of sweeping gas (N_2) was kept at 150 ml/min.

The gases released in the TGA were swept immediately to a gas cell, followed by the FTIR (GASMET Dx4000 Series) analysis using a deuterated triglycine sulfate (DTGS) detector. The transfer line and gas cell were heated to an internal temperature of 180°C, to avoid condensation or adsorption of semi-volatile products. Each IR spectrum was obtained in 20 s, and the IR scanning range was from 4000 to 500 cm^{-1}.

For an in-depth investigation of the influence of heating rate, a bio-oil was pyrolyzed in the TGA at 5, 10, and 20°C/min. The samples were heated up separately from the ambient to 900°C to record any further weight loss.

Pyrolysis Experiments

Pyrolysis of bio-oil materials was conducted in an externally heated fixed bed, as shown in Fig. 1. The system consisted essentially of a quartz tube (ID 16 mm, and 500 mm long; OD 28mm, and 560mm long) with a continuous feeding system containing a peristaltic pump, fixed-bed gasification system containing gasification reactor and electric heating furnace, and a cooling system for the separation of water and condensable organic vapors (tar), as well as various gas measurement devices. Purge gas (N_2) was supplied to the reactor at a certain flow rate, and the furnace was preheated to 600-1000°C.

The bio-oil was passed through by the peristaltic pump into the reactor. The feedstock (bio-oil) entering into the reactor is heated up, dehydrated, devolatilized, and finally decomposed following Eq. (1) to generate solid charcoal, liquid tar, water vapor and H_2-rich gas products (H_2, CO, CO_2,CH_4, etc.). To mitigate the influence of sample feeding on the temperature profile in the reactor, the feeding rate was kept at ~0.46g/min.

$$\text{Bio-oil} \rightarrow \text{Gas } (H_2;CO;CO_2;C_mH_n) + H_2O + \text{tar} + \text{char} \qquad (1)$$

The volatiles and fine particles, carried by purging gas, were passed through a cyclone and quartz wool filter and thereby any fine particles were removed. The condensable components were quenched when gas was passed through a water-cooling tube and two ice-water condensers in series. After every experiment, the non-condensable gases were pre-cleaned through a glass wool filter and dried by silica gel prior to analysis.

The gas products were analyzed using a Four-Channels Micro-Gas Chromatograph (Micro-GC, Agilent 3000). Three columns used were: (1) column A (molecular sieve) for analysis of H_2, O_2, N_2, CH_4, and CO at 95°C; (2) column B (Plot U) for the analysis of CO_2 and some hydrocarbons (C_2H_4, C_2H_2, and C_2H_6) at 100°C; and (3) column C (aluminum oxide) for the analysis of C_3H_8 and C_3H_6 at 140 °C. The carrier gas was helium of high purity.

Because of a high content of the element oxygen in bio-oil, the gasification was carried out in the absence of gaseous O_2 in the experiment. The main purpose of our research was to study the mechanism of bio-oil gasification. The investigation of the effects at 600°C, 700°C, 800°C, 900°C, and 1000°C, and residence time of gas products under different nitrogen flow rate (50ml/min, 75ml/min and 100ml/min) on gasification characteristics allowed us to achieve optimized conditions during bio-oil gasification.

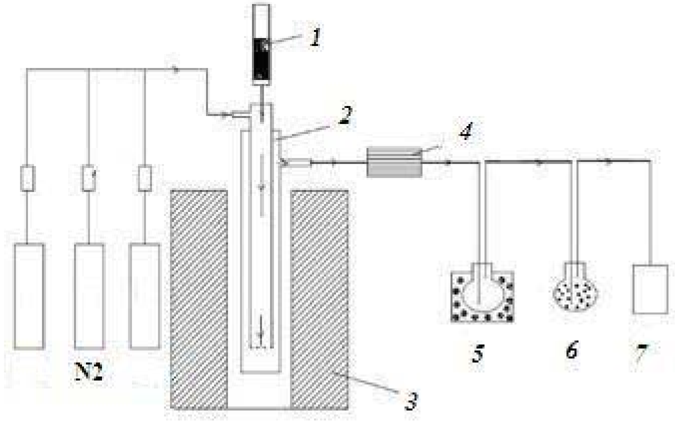

Fig. 1. The flow scheme of bio-oil gasification system. 1. bio-oil, 2. fixed bed, 3. furnace, 4. particle filter, 5. ice-water condenser, 6. gas dryer (silica gel), and 7. gas analyzer (Micro-GC, FTIR).

EXPERIMENTAL RESULTS AND DISCUSSION

Decomposition of bio-oil and product distributions

The TG, derivative thermogravimetric (DTG), and differential scanning calorimetry (DSC) curves of bio-oil pyrolysis/gasification are shown in Fig. 2. The thermal degradation of bio-oil showed two major weight loss ranges. The first quick weight-loss step, which included the removal of moisture content and light hydrocarbons (aldehydes, organic carboxylic acid, and alcohols) in bio-oil, occurred in a temperature range between 50 and 120°C. At temperatures lower than 100°C, the weight loss was 30%. In this stage, the volatilization absorbed a great deal of heat, for which there appeared one big endothermic peak on the DSC curve. The second stage, which consisted of the cracking of phenols, eugenol, and vanillin component in the bio-oil obtained during the first step, occurred at temperatures over 200°C. The breakage of chemical bonds within the heavy components of bio-oil released a large amount of energy, which caused heat release, hence a negative value was shown on DSC curves; this was mainly caused by the volatilization and decomposition.

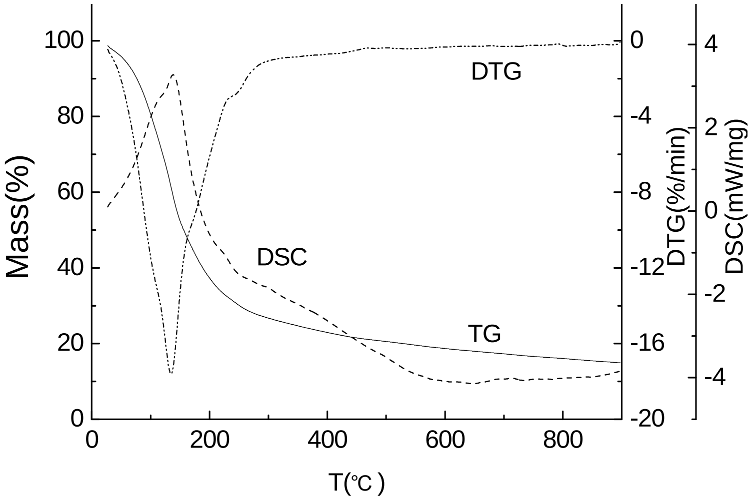

Fig. 2. TG, DTG and DSC curves of bio-oil pyrolysis/gasification (20°C /min).

Effect of Heating Rate

The heating rates in this study were varied as follows: 5, 10, and 20 °C/min. The TG and DTG curves of bio-oil pyrolysis, relative to the change of heating rate, are plotted in Fig. 3. The curves showed that the maximum weight loss occurred in the temperature range from 100 to 150°C. There was no further weight loss from that temperature up to 500°C. With increasing heating rate, the maximum weight loss peak shifted to a higher temperature, and the maximum weight loss rate increased. The temperature increased until the reaction was completed. In this work, by different heating rates at 5°C /min and 20°C /min, the results relative to the patterns of TG/DTG curves were very close. The results corresponding to a heating rate of 10°C /min were different from those obtained at other heating rates. For example, the corresponding DTG curves did not change significantly with the peak at about 150°C, and residues accounted for about 50%. The temperature of maximum mass loss rate was higher than that of other heating rates (5°C /min and 20°C /min).

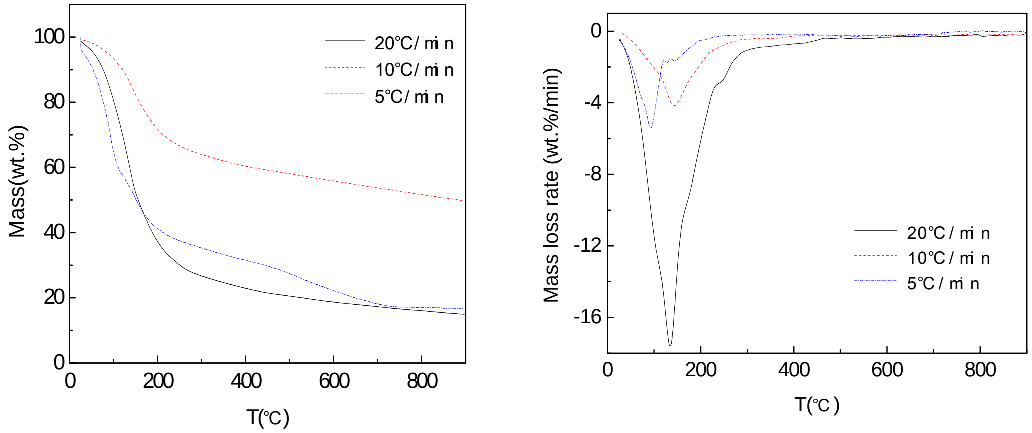

Fig. 3. TG and DTG curves of bio-oil pyrolysis under different heating rates

Data from TG and DTG curves of bio-oil pyrolysis under different heating rates were used to determine the kinetic parameters. Mathematical analysis was performed by the integral method of Coats and Redfern (Coats et al. 1965). From the aspects of the thermal chemical reaction, thirty kinds of typical kinetic mechanism functions were involved (Hu et al. 2001).

The biomass pyrolysis is assumed to be controlled primarily by chemical decomposition, and the kinetic parameters (activation energy, the pre-exponential factor, and the coefficient of correlation) could be calculated, based on the Universal Integral Equation Method and Differential Equation Method (Wang et al. 2003).

Kinetic equations of two types can be written as follows:

Universal Integral Equation: $G(\alpha)=[(1-\alpha)^{-1/3}-1]^2$ (2)

Differential Equation: $f(\alpha)=\frac{3}{2}(1-\alpha)^{4/3}[(1-\alpha)^{-1/3}-1]^{-1}$ (3)

By using $G(\alpha)=\int_0^\alpha \frac{d\alpha}{f(\alpha)}$,

where $f(\alpha)$ is a function, the type of which depends on the reaction mechanism, and α is the degree of conversion.

The results showed that the bio-oil pyrolysis was controlled by the three-dimensional diffusion model. Therefore, the corresponding kinetics parameter of bio-oil pyrolysis are shown in Table 1. The results showed that the molar heat generation of bio-oil pyrolysis was highest at 10°C /min, compared to the other two heating rates.

Table 1. The Kinetics Parameter of Bio-oil Pyrolysis

Heating rate /°C·min^{-1}	Universal Integral Method			Differential Equation Method		
	E/kJ·mol^{-1}	lnA/s^{-1}	r	E/kJ·mol^{-1}	lnA/s^{-1}	r
5	61.30	10.66	0.9856	54.57	8.54	0.9665
10	69.92	11.00	0.9993	73.08	11.89	0.9977
20	57.13	8.60	0.9969	52.60	7.30	0.9931

Analysis of TG-FTIR

The release and formation behaviors of gas products and the sample quality change from TGA were measured on-line, coupled with FTIR measurements. By this procedure it was possible to obtain dynamic information for bio-oil pyrolysis from the lower heating rate. A typical IR spectrum of gas products released from bio-oil pyrolysis at 480°C are shown in Fig. 4. The change in IR peak heights will reflect the tendency of concentration variation of the gas species (Yan et al. 2005; Bassilakis et al. 2001). The specific wave numbers of the IR peak of the main gas species from biomass pyrolysis are listed as the following: the area for CO_2 was calculated from 2400 to 2260 cm^{-1}, CO from 2100 to 2200 cm^{-1}, CH_4 from 2700 to 3200 cm^{-1}, organics from 900 to 1900 cm^{-1}, and H_2O from 3700 to 3500 cm^{-1} (Bassilakis et al. 2001). However, the area obtained between 900 and 1900 cm^{-1} for organics might also include a minor contribution from water, which also absorbs at 1500 cm^{-1}.

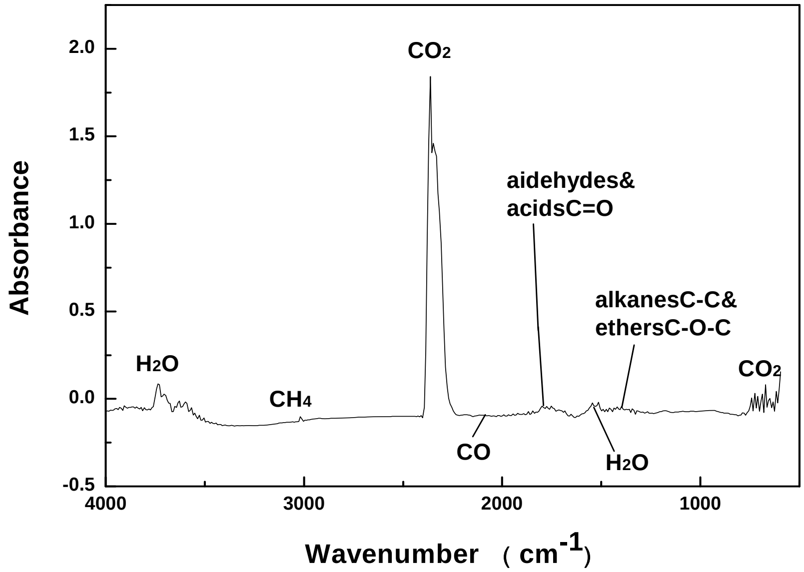

Fig. 4. Typical IR spectrum of gas product released from bio-oil pyrolysis at 480°C

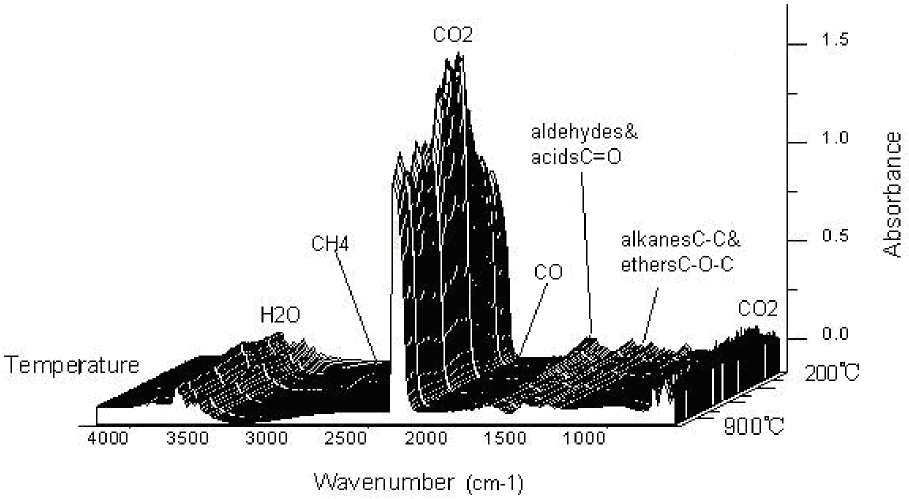

Fig. 5. 3-Dimensional IR spectrum of gas product releasing from bio-oil pyrolysis at 5 °C /min

The IR spectra taken every 12s from 20 to 900°C in the experiment were plotted by placing one on top of the other to form a 3D spectrum. This type of plot reveals how the product distributions of bio-oil changed with the wave number and temperature. From Fig. 5, it can be observed that the main gas products of biomass pyrolysis are: CO_2, CH_4, CO, and some organics (a mixture of acids, aldehydes (C=O), alkanes (C–C), and ethers (C–O–C), etc.) with some H_2O. The release of gaseous products mainly was focused at relatively low temperatures, which corresponded well with the observation of biomass weight loss in Fig. 2, except for some CO_2, CH_4, and CO evolving at a higher temperature. With increasing pyrolysis temperature, the content of the organic compounds decreased gradually, and the content of CO_2, CH_4, and CO increased. This was mainly because of the cracking of heavy hydrocarbon components, which took place at higher temperature (>200°C). The results were consistent with the bio-oil gasification curves of weight loss at the high temperature stage. Carbon dioxide gas showed two absorbance peaks near to 500°C; however it was released at significant levels throughout the heating cycle during the whole process. The release of CH_4 was mainly concentrated within the range 230 to 500°C. Methane evolution reached a maximum at 300°C and then decreased to zero at 500°C.

The release of organic compounds was different from other gas products. It occurred mostly at relatively low temperatures. The rapid weight-losing stage (50 to 200°C) of bio-oil, corresponding to the removal of moisture content and light hydrocarbons in bio-oil, occurred in the temperature range between 50°C and 120°C. Because these volatiles were released at lower temperature (<200°C), they were not able to undergo reactions of gasification or prolysis, so the gaseous product mainly consisted of small molecular organic compounds. It could be concluded from the above analysis that the products of cracking of bio-oil associated with the weight loss was mainly comprised of lower heavy hydrocarbon components (<20wt. %) and higher light hydrocarbon components.

Effect of Temperature in Fixed Bed

The properties of gaseous products from bio-oil gasification at 600, 700, 800, 900 and 1000°C are shown in Fig. 6. The syngas mainly contained CO, H_2, CO_2, CH_4, and the C2 fractions in gas phase were a very minor proportion. It can be seen that the content of syngas changed with increasing temperature. With increasing pyrolysis temperature from 800 to 900°C, the content of hydrogen reached a maximum at about 25% (In syngas). But the H_2 content decreased as the temperature increased to 1000°C. This result was expected, since it could be seen that bio-oil at high temperature would lead to complete decomposition. Hydrogen reacted with oxygen-containing groups, leading to the formation of water.

With increasing temperature, the content of CO decreased, it reached a minimum at 850°C, and then it increased with further increase in temperature. The carbon dioxide increased with increasing temperature. This was mainly because the bio-oil contained a lot of organic carboxylic acids, in which carboxyl decomposition was a main source of CO_2. The content of CH_4 increased, and at 700°C it reached a maximum, and then decreased with increasing in temperature.

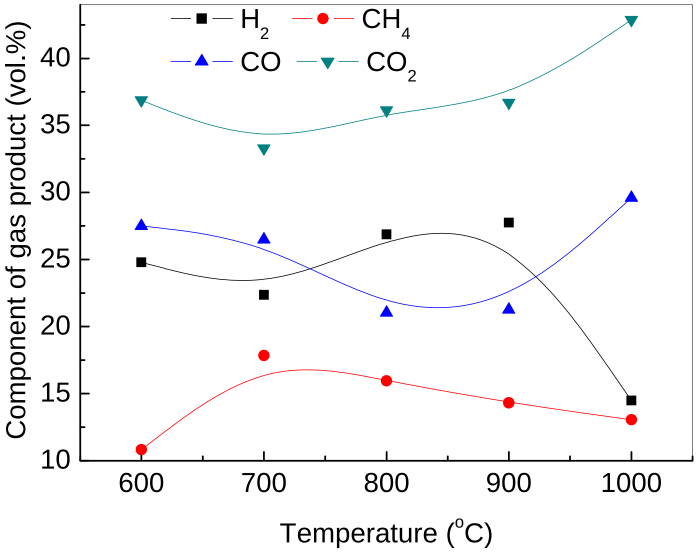

Fig. 6. Properties of gas product from bio-oil gasification at different temperatures

Yields of the main gaseous products are shown in Table 2. In this table a nitrogen balance method was introduced and used to calculate the absolute gas yield and the gasification efficiency. It can be seen that increasing temperature favored improving the yield of syngas. When the temperature was 600°C, the efficiency of gasification was about 20%. The highest gasification efficiency was 80% when temperature was from 600 to 1000°C. However, the evolution of H_2 and CO was mainly associated with high grade fuel through biomass, CO_2 was not utilizable, and CH_4 required reforming to produce more H_2 and CO. When considering these results with respect to maximum H_2 and CO yields, it is clear that the optimum pyrolysis temperature was 800°C under the experimental conditions used. Therefore, in the experiments, the pyrolysis temperature was held at 800°C, and the highest yields and quality of syngas were obtained from bio-oil gasification.

Table 2. Gas Yield of Main Gas Products from Bio-oil Gasification

T(°C)	600	700	800	900	1000
H_2 (wt. %)	0.39	0.70	1.43	1.39	0.78
CH_4 (wt. %)	1.38	4.52	6.81	5.76	5.66
CO (wt. %)	6.09	11.70	15.67	14.93	22.39
CO_2 (wt. %)	12.91	23.25	42.55	40.73	51.27
Efficiency (wt. %)	20.77	40.17	66.45	62.81	80.09
H_2+CO (ml/g)	42.19	78.62	129.99	125.39	121.48

Effect of Sweeping Gas

As reported in the literature, a sweeping gas removes products from the hot zone to minimize secondary reactions such as thermal cracking, repolymerization, and recondensation, and to maximize the liquid yield (Pütün et al. 1999). At the optimum pyrolysis temperature (800°C), a second set of pyrolysis experiments was conducted to determine the effect of sweeping gas (N_2) at different flow rates (50, 75, and 100 ml/min).

Figure 7 reveals the effect of nitrogen flow rate on product yields. The proportion of H_2 increased in directly linear manner with the increase of sweeping gas flow rate, while that of CH_4, CO, and CO_2 gradually decreased. The yields of the main gas products from bio-oil are shown in Table 3. As the flow rate was increased from 50 ml/min to 75 ml/min, the content of gas products increased, while the flow rate increased to 100ml/min, and the content of CO, CH_4, and CO_2 decreased significantly.

In described experiments the nitrogen flow rate was a key factor in determining the gas residence time, which was an important parameter affecting the characteristics during the gasification of biomass. The effect of residence time on gas yield can be examined by changing the flow rate of the sweeping gas while pyrolysis temperature is kept constant. Because long residence time or lower sweeping gas flow rate results in formation of carbon deposits, the gas yield also decreases (Encinar et al. 1997). In contrast, a shorter residence time of the volatiles in the reactor as the sweeping gas velocity increased, caused relatively minor yield of gas products at high temperature. Thus, all the quantities mentioned above decreased with the increase of nitrogen flow rate. In this study, the optimum flow rate of the nitrogen was 75ml/min at a pyrolysis temperature of 800°C.

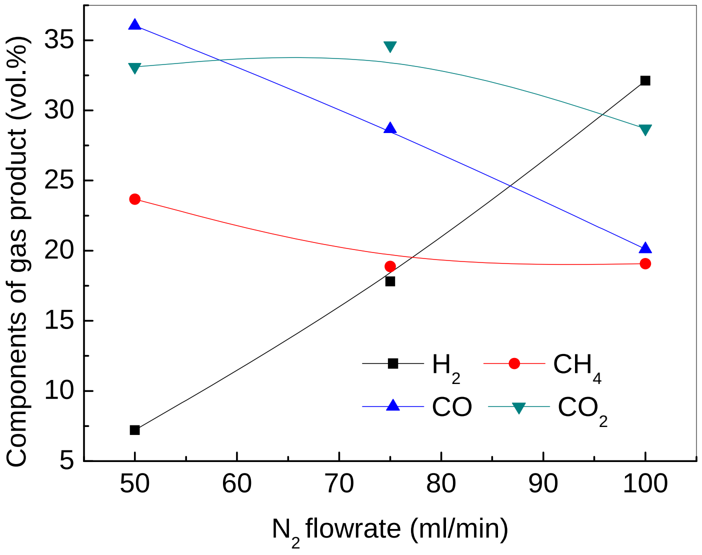

Fig. 7. Main gas component of syngas from bio-oil gasification with different N2 flow rate

Table 3. Yield of Main Gas Product from Bio-oil

N_2 flow rate (ml/min)	50	75	100
H_2 (wt %)	0.24	1.35	1.43
CH_4 (wt %)	6.25	11.50	6.81
CO (wt %)	16.60	29.38	15.67
CO_2 (wt %)	20.93	44.28	42.55
Efficiency (wt. %)	44.01	86.51	66.45
H_2+CO (ml/g)	72.55	176.01	129.99

CONCLUSIONS

1. The pyrolysis of bio-oil can be divided into two stages, devolatilization (200-300°C) and carbonization (>300°C). FTIR results showed that the gas products from bio-oil gasification mainly contained CO, CO_2, CH_4, H_2O, and light hydrocarbons. Organics mainly evolved at relatively low temperature (<200°C), while the cracking of heavy hydrocarbon components took place at higher temperature (>200°C).
2. The gasification behavior of bio-oil was investigated in a fixed bed gasification reactor under different temperature and residence time. The results showed that the yield of CO and H_2 reached their maximum values of 15.67 wt% and 1.43wt%, respectively, at 800°C. With increasing temperature, the efficiency of gasification

increased from 20.77% to 66.45%, while the release of CH_4 was mainly concentrated in the neighborhood of 700°C.

3. The effect of residence time on gas yield can be examined by changing the flow rate of the sweeping gas while the pyrolysis temperature is kept constant. Because long residence time or lower sweeping gas flow rate result in formation of carbon deposits, the gas yield also decreases. Also, the optimum flow rate of the nitrogen was found to be 75ml/min. At the same time, the yield of CO and H_2 reached an optimum, and gasification efficiency was best under this condition.

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