



Trade Science Inc.

BioTechnology

An Indian Journal
FULL PAPER

BTALJ, 6(1), 2012 [6-11]

The pyrolysis gas recirculation of biomass fast pyrolysis

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Received: 22nd September, 2011 ; Accepted: 6th January, 2012

ABSTRACT

Fast pyrolysis is suited for conversion of biomass to liquid fuel in the absence of air/oxygen with char and pyrolysis gas as co-products. Nitrogen is usually used as carrier gas and pyrolysis gases include carrier gas and non-condensable gas. To increase its economic potential of the bio-oil production process, a pyrolysis gas recycling unit was proposed in this study. The pyrolysis gas can be recycled and the fresh carrier gas can be added in this unit. The experiment of biomass fast pyrolysis using the pyrolysis gas recycling unit was carried out in a fluidized bed reactor with the wood sawdust as feedstock. The recycling pyrolysis gas fraction compositions were analyzed and compared with the different operating conditions and its effects on the product yields and the bio-oil properties were also investigated. The results show that the operating condition where new N₂ added rate is 12.79v% per hour and the excess pyrolysis gas discharged to balance the system flow rate can obtain the economic and safe operation of bio-oil production. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Biomass;
Pyrolysis;
No-condensable gas;
Pyrolysis gas recycling unit.

INTRODUCTION

Biomass is available in abundance and is cheap and its better utilization is to convert it to energy rich products using suitable processes^[1]. Interest in producing liquid fuels from biomass is increasing worldwide for the reason that bio-oil is easy to transport and store. Biomass can convert directly into bio-oil by thermal decomposition in absence of oxygen with char and pyrolysis gas as co-products^[2-4]. There have been more than 300 compounds identified in different bio-oil derived from biomass fast pyrolysis^[5]. Bio-oil obtained from fast pyrolysis of biomass has the potential to substitute for fossil liquid fuels after it is upgraded by cata-

lytic hydrogenation, catalytic cracking or steam reforming^[6-9].

In recent years, many reactors and processes have been investigated and developed to the point where biomass fast pyrolysis is now an accepted feasible and viable route to renewable liquid fuels, chemicals and derived products. It has been suggested to carry out fast pyrolysis in decentralized plants and to use the produced bio-oils in centralized larger chemical plants, then storage and transport^[10-13]. These advantages have caused greater attention to be paid to fast pyrolysis, leading to significant advances in process development. Four conditions are required in fast pyrolysis including medium temperatures, high heating rates, short vapor

residence times and fast condensation of vapors to obtain a relatively high bio-oil yield. The effects of pyrolysis parameters including pyrolysis temperature, types of biomass and particle size, heating rate and carrier gas flow rate have been well studied^[14-17]. While most of their experiments were conducted using inert atmosphere such as N₂ which continually flowed from bottom to top in order to keep biomass and sand not only bubbling in the bed but also in the absence of oxygen. The pyrolysis gas as co-products would be polluted environment and increased experiment's cost if it was exhausted to the air. In order to increase the economic potential of the process, it has been suggested that the char was burnt to provide the heat for pyrolysis and the pyrolysis gas was recycled as carrier gas in pilot plant-scale and large-scale plants^[18-21].

The main composition of the pyrolysis gas is CO, CO₂, CH₄, H₂ and some other light hydrocarbons. H. Zhang et al.^[22] carried out the experiment using N₂, CO₂, CO, CH₄ and H₂ as carrier gases in the biomass fast pyrolysis in a fluidized bed reactor. The different atmospheres effects on the product yields and the bio-oil fraction compositions were investigated. While, the pyrolysis gas recycled as carrier gas for the biomass fast pyrolysis has not been detail investigated in the past.

In this work, a recycling pyrolysis gas unit was proposed in which the pyrolysis gas can be recycled and the fresh carrier gas can be added. The experiment of biomass fast pyrolysis with the different pyrolysis gas recirculations was carried out in a fluidized bed reactor using wood sawdust as feed stocks. The recycling pyrolysis gas composition was analyzed for different operating conditions, and it effected on the product yields and the bio-oil properties were investigated. The desired pyrolysis gas recycling condition, the recycling flow rate of the pyrolysis gas and the flow rate of fresh N₂ added were also investigated.

EXPERIMENTAL APPARATUS AND PROCEDURES

Experimental set-up

The fluidized bed system for the biomass fast pyrolysis capacity of 10 kg/h was set up. It mainly con-

sisted of the feeding unit including a storage hopper with the automatic shake mechanism which already described in our previous work^[23], and two feeding screws with their motors and frequency controllers, a gas electric heater, a fluidized bed reactor, two cyclone separators, four water condensers, a pyrolysis gas recycling unit and a temperature and pressure control system, as shown in Figure 1.

Pyrolysis gas recycling unit

Figure 2 shows a schematic diagram of the pyrolysis gas recycling unit. It mainly consisted of a recycling gas storage vessel-1 with pressure gauge and safety valve on it, a cycle compressor, an export buffer vessel-2 with pressure gauge and safety valve on it, and the four flow meters for measuring the gas flow rate of inlet, outlet, exhaust and the fresh N₂ added, respectively. The vessel, the connecting pipe and its associated spare parts were made of 316 stainless steel. A pieces of wire netting(200 mesh size) was located at the bottom of the two vessels to separate the condensable liquid which will be discharged by the bottom valve of the vessels. In order to control the operating pressure of the biomass fast pyrolysis system, an interlocking device was set between the recycling gas storage vessel and the cycle compressor. When the recycling gas pressure in the vessel-1 was higher than the operating pressure of the biomass fast pyrolysis system, the cycle compressor started up or stopped running otherwise. The air inlet used in the heating process at the beginning of experiment. While, the N₂ inlet can be used it as added gas when the pyrolysis gas flow rate from the cycle compressor is lower than that need.

Experimental procedure

The biomass used in the experiment was the pine sawdust which was dried at 100°C for 8 hours before experiment; the main properties of the sawdust after drying are shown in Tab. 1. At the beginning of tests, 10kg of the pine sawdust was poured into the hopper. Nitrogen was utilized in the experiments as carrier gas and added gas.

Firstly, the electric heater started to heat the air. The flow rate of air was controlled to 160 l/min. After the desired temperature (550°C) was reached and stabilized, the same flow rate of nitrogen replaced the air

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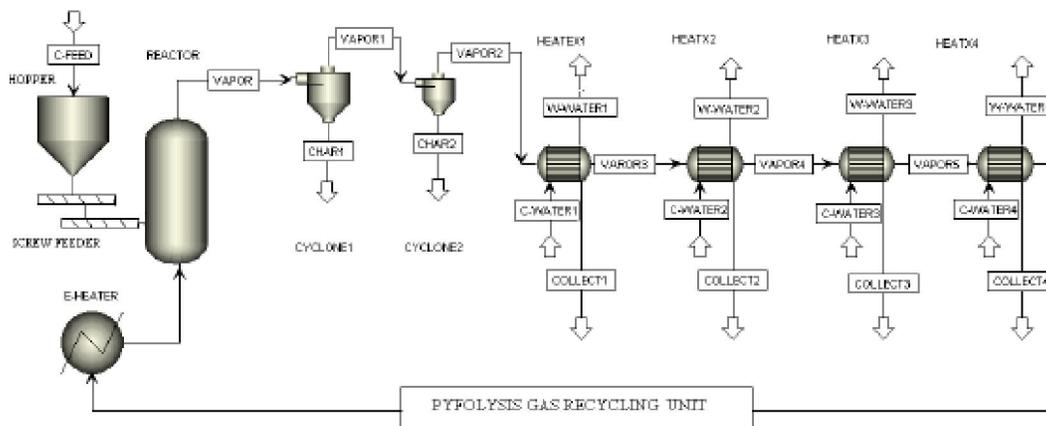


Figure 1 : Schematic diagram of a fluidized bed system for the biomass fast pyrolysis.

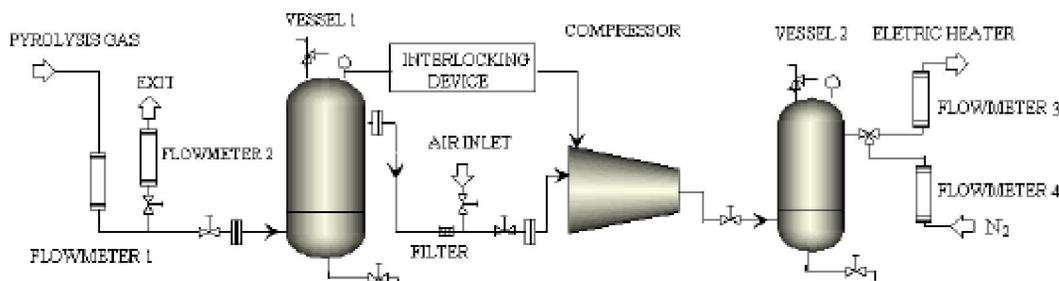


Figure 2 : Schematic diagram of a pyrolysis gas recycling unit.

TABLE 1 : Main characteristics of the biomass

Description	Physical properties			Chemical composition		
	Particle Size (μm)	Moisture (wt.%)	Density (kg m^{-3})	Cellulose (wt.%)	Hemi-cellulose (wt.%)	Lignin (wt.%)
Pine Sawdust	200~300	5.9	188	46.56	35.64	16.45

from the reactor and permitted the pyrolysis reaction under anaerobic condition. The biomass stored in the hopper passing the first and second screw in turn flowed into the fluidized bed reactor, two screw feeders running at the speed of 11rpm, 200rpm separately, which the average feeding rate was 10Kg/h. The biomass decomposed to the vapor products in fluidized bed, and then the vapors were passed through two cyclone separators where the char was separated from the vapor. After that, the vapor through four water condensers was cooled and flowed into the liquid products collectors, as show in Figure 1.

The experiments were conducted in three operating conditions: the first, nitrogen was used as carrier gas and all the pyrolysis gas was exhausted. The second, all the pyrolysis gas was recycled using the pyrolysis gas recycling unit. The third, a part of pyrolysis gas was discharged and the fresh nitrogen was added to need the flow of the operating system. The rate of

the all gases flowing in and out the pyrolysis reaction system was continuously measured by the flow meter. The pyrolysis gas, liquid and char products were collected every 10 minutes under the three experiment conditions.

Products analysis

Analysis of the pyrolysis gas composition was taken using GXH-3011 infrared ray analyzer and gas chromatography CP-3380 made in USA VARIAN at the condition of 5A molecular sieve chromatographic column with TCD detector, at the column temperature of 80°C, detector temperature of 130°C, injection port temperature of 50°C and a constant column flow of 30ml/min of High-purity Argon. The rate of the gas flowing in and out the biomass fast pyrolysis system was to calculate the volume of pyrolysis gas yield by the measurement of the flow meter. The flow rate of the gases was used vortex Flow meter (Type: LUGB-1000. Ac-

curacy range: $\pm 0.5\%$).

The yield of bio-oil and char products was calculated through of products divided by the feedstock weight. The water content of the bio-oil is measured by Karl Fisher analysis with a Radiometer Tim 550^[24]. The viscosity was measured with a rheometer (Type RFS11). The density is calculated from the measurement of the mass of a certain volume of oil at room temperature. The pH is measured by a simple PH meter of PHS-3C.

All the experiments were performed under the same pyrolysis parameters including pyrolysis temperature, types of biomass and particle size, heating rate and carrier gas flow rate. Each experiment was repeated three times to determine the reproducibility.

RESULTS AND ANALYSIS

Nitrogen as carrier gas

This experiment was performed under the condition which the carrier gas used nitrogen and all the pyrolysis gas was exhausted. The exhausted pyrolysis gas temperature which directly measured from the last water condenser was 25°C. Figure 3 shows the pyrolysis gas composition determined by CG in this condition. The main composition of the pyrolysis gas is H₂, O₂, N₂, CH₄, CO, CO₂ and some other light hydrocar-

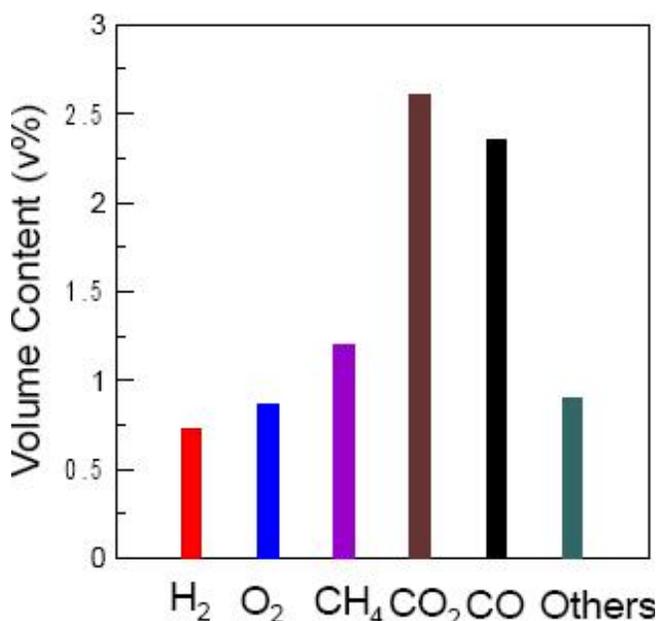


Figure 3 : The pyrolysis gas composition where the carrier gas used nitrogen

bons. From the analysis of all the simple, the average volume content of the main composition is 0.86%, 0.73%, 91.3%, 1.2%, 2.35%, 2.61%, and 0.95%, respectively. The increase rate of the no-condensable gas is 14.4 % per hour from calculating the flow rate of the gas inlet and outlet of the system. There was O₂ existed in the pyrolysis gas in our experiments, it may be from biomass feeding process or produced from pyrolysis reaction process. The total consumption of the N₂ was 9,600 l/h in this process.

The yields weight of the bio-oil and char were calculated. Because the biomass composition is a very complex mixture, the main bio-oil characters was measured for the density, viscosity, pH, and water content. The results shown that wood sawdust fast pyrolysis under this condition gave a total bio-oil yield of 65.6wt%, and the char produced was 20wt%. The density of bio-oil produced was measured by density measurement that was around 1.23g/ml. The viscosity of bio-oil produced was found to be 2.51 cP at 30°C. Karl-Fischer titration method was used for measuring the water content in the bio-oil. The water content was 17.2 wt%. The pH of the bio-oil product in this work was found to be 4.0.

Pyrolysis gas recycled

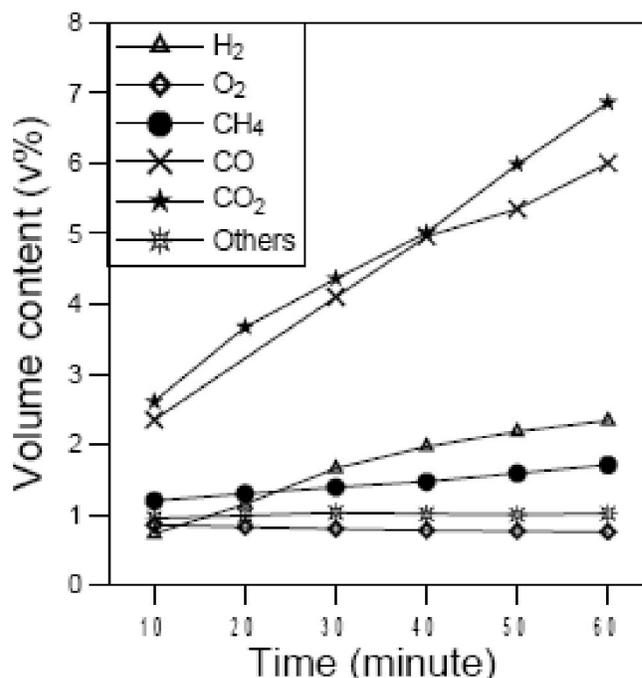


Figure 4 : Fraction compositions volume content of the no-condensable gas with different times under pyrolysis gas recycled

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The second experiment was conducted with the condition that all the pyrolysis gas was recycled. According to first experimental condition, the no-condensable gas increase rate is 14.4% per hour, which must be exhausted to provide steady flow rate for the operating process.

As a comparison with the first experiment, Figure 4 shows the fraction compositions volume content of the no-condensable gas with different times. It shown the main composition of recycling pyrolysis gas was the same as the first condition, but the volume content had changed, and the increase rate of the no-condensable gas is about 16.2% per hour under this experiment condition. This phenomenon can be explained that, with the recycling of pyrolysis gas, H_2 , CO , CO_2 , and CH_4 could take part in the reaction of biomass pyrolysis caused the volume proportion of nitrogen reduced and others composition increased and the more pyrolysis gas yielded in the system. It also shown that CO , CO_2 took great amount in the no-condensable gas. The reason is that there were the reversible reactions occurred; it was easily to get the reactions to produce CO , CO_2 . O_2 composition also existed in the pyrolysis gas. The total consumption of the N_2 was 1,600 l/h in this process.

Biomass fast pyrolysis under all the pyrolysis gas recycling condition gave a total bio-oil yield of 63.8wt%, which is lower compared to N_2 atmosphere. The char produced is also about 20wt%. However, the water content in the bio-oil product was 19.3 wt.% which is bigger changes than the one of the first experiment. This can be explained that the increasing H_2 in the recycling gas could product more water with respect to nitrogen atmosphere. The density, viscosity and pH of bio-oil produced are 1.18 g/ml, 2.45cP, 4.0, respectively, which change is small compared to the first experiment.

A part of pyrolysis gas recycled and the fresh nitrogen added

The recycling pyrolysis gas effected on the liquid product properties and pyrolysis gas compositions were evidence from the above experiment. It was calculated that the volume content reduction rate of N_2 in the recycling gas is 12.79v% per hour from the second experiment condition. Therefore, the experiment was performed with 12.79v% per hour of fresh N_2 added and

the excess volume of pyrolysis gas exhausted to balance the flow of the recycling gas. The results show that the pyrolysis gas exhausted flow rate of 21.32% per hour can keep the N_2 volume content steady in the recycling gas. The experiments are shown that the volume content of N_2 is stabilizing at 89.96% within the operating time. It also shown the increase rate of the no-condensable gas was 14.9 % per hour. CO , CO_2 have a little increasing and the other major components stabilize respect to the first experiment, as show in Figure 5. The total consumption of the N_2 was 1,834 l in this process, the reduction rate of the N_2 consumption is 80.89%.

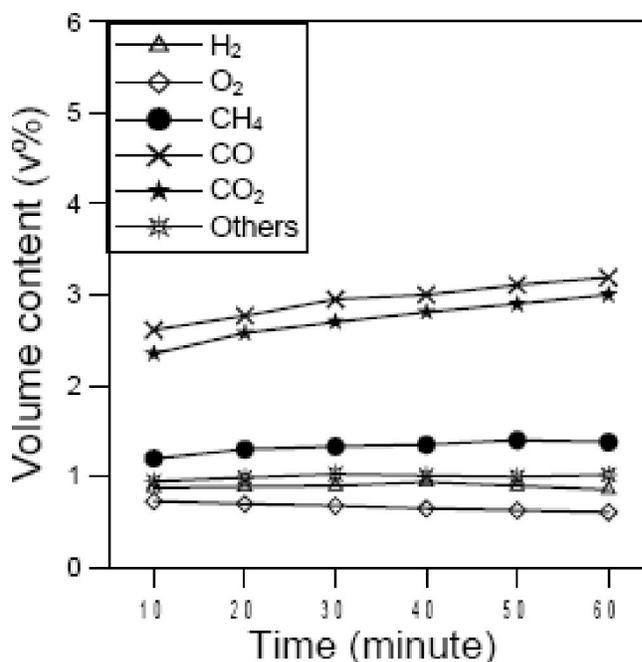


Figure 5 : Fraction compositions volume content of the No condensable gas with different times under the third condition

The bio-oil and the char yields were 65.1wt% and 20wt%, respectively. The water content in the bio-oil product was 17.8 wt%. The density, viscosity and pH of bio-oil produced were 1.22 g/ml, 2.50cP, and 4.0, respectively. The bio-oil characteristics had a little change comparison to the first experiment. It is show that the effect of this condition on the pyrolysis gas composition and the bio-oil properties is lower compared to the second experiment.

H_2 , CO , CH_4 mixed with atmosphere they will be explosive, and the explosion limits are: 4.1%-74.2%, 12.5%-74.2%, and 5.3%-14%, respectively. Whereas,

the little or absence of O₂ and highly presence of N₂ stayed in hermetical ambience got the recycling pyrolysis gas safety in the operating process. The operating pressure control would be the main safety factor to consider.

CONCLUSIONS

The pyrolysis of wood sawdust was performed with three kinds of experiment conditions. The effects of the recycling pyrolysis gas on the product yields, the pyrolysis gas compositions and the bio-oil properties were studied. At the pyrolysis gas recycling condition, the flow rate of the no-condensable gas was increase to 16.2%. The main composition of the recycling pyrolysis gas was the same but the volume content was changed. The water content in the bio-oil product was 19.3 wt% which was the mainly changes of the bio-oil. The experiment was carried out which the pyrolysis gas exhausted rate of 21.32% per hour can keep the N₂ volume content in the recycling gas. The effects under this operating condition on the bio-oil yield and its properties are very small, and this operating condition was safe. The total consumption of the N₂ can reduce 80.89% using the pyrolysis gas recycling unit. The investigating results can provide foundation data for large-scale plant operation.

ACKNOWLEDGEMENTS

This work was supported by the Oil Complementary and alternative Energy Research Team of Henan province; the work was also sponsored by China Postdoctoral Foundation. The authors also wish to thank other team member for their help.

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