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Continuous pyrolysis of pine sawdust at different pyrolysis temperatures and solid residence times



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ABSTRACT

In this work, the continuous pyrolysis of pine sawdust is performed with a screw reactor to investigate the influence of pyrolysis temperature and solid residence time on products and energy distribution. Gas chromatograph/mass spectrometer (GC/MS) and Fourier transform infrared spectroscopy (FTIR) were used to confirm the identities of bio-oil. The combustion kinetics of bio-char had analyzed by thermogravimetric (TG). The results of gas chromatograph showed that carbon monoxide is the main component in produced gas, and the maximum gas yield of 54.5% was obtained at the temperature of $900 \,^\circ$ C. Compositional analysis of the oil products showed that phenols were the major components, and its proportion increased at higher temperatures and longer solid residence times. The activation energy of bio-char combustion is $461.10 \,$ kJ mol⁻¹ and $108.45 \,$ kJ mol⁻¹ in the ranges of $290-314\,^\circ$ C and $314-518\,^\circ$ C, respectively. The maximum of energy profit rate is 6.49% obtained at the temperature of $900\,^\circ$ C with the solid residence time of 6 min.

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1. Introduction

Biomass is an extremely abundant, various and inexpensive resource in the world. It is considered as one of the most plentiful and well-utilized sources of renewable energy. Compared to fossil fuels, biomass energy has been paid a great deal of attention in recent years due to the problem of environment pollution and energy shortage. The thermo-chemical conversion of biomass includes combustion, liquefaction, gasification and pyrolysis. Among them, pyrolysis is one of the promising thermochemical conversion routes. Biomass pyrolysis is the degradation of biomass by heat in the absence of oxygen, which produces gas, bio-oil and biochar [1], which have much potential value. As high value energy carrier, pyrolysis gas is suited for heat and electricity generation. Bio-oil can be used as fuel or chemical feedstock due to its higher energy density and abundant chemical compounds [2]. Biochar is utilized as the rough material of active carbon, reductant, adsorbent and soil amendment in industry and agriculture area [3].

In the pyrolysis process, the products of biomass pyrolysis are often influenced by factors such as feed materials, pyrolysis temperature, solid residence time, pyrolysis mode, reactor type, particle size, and so on. These effect factors were extensively investigate on distribution and component of pyrolysis products [4-6]. In general, produced gas yield increases with pyrolysis temperature rising, while the bio-char decreased [7,8]. According to the feeding manner, biomass pyrolysis process can be classified into batch, semi-batch or semi-continuous or continuous processing. Different feeding manners result in the variation of heating rate, thermal history, and residence time, which have deep influence on the distribution of pyrolysis products. Dupont et al. [9] had investigated the continuous pyrolysis of softwoods conducted in an entrained flow reactor under high temperature (800-1000 °C) and fast heating condition (>500 K s⁻¹), they found that biomass pyrolysis was completed for the solid residence time more than about 0.3 s as the temperature greater than 900 °C. Lu et al. [10] studied the influence of temperature, residence time, and catalyst content with a batch type reactor, and their study indicated that high temperature or long residence time leaded to a deeper cracking of chemical bonds.

As pyrolysis is a precursor of other thermochemical processes (gasification and combustion), the mass and energy balance of pyrolysis are essential part to evaluate eventual product yield distribution. Some research papers report experiments of pyrolysis yield analysis [10–12]. The Fourier transform infrared spectroscopy (FTIR) and gas chromatograph/mass spectrometer (GC/MS) analysis are often used to investigated the composition of pyrolysis products. The components of bio-oil from different condenses analyzed by GC/MS shows that the chemical contents in bio-oil varied with the different condensation process based on the dew point of components [13]. FTIR are used to determine the variation of

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function group of bio-oil under different condensations. The mass and energy balances in biomass pyrolysis were studied by different methods. Olaleye et al. [14] have developed a dynamic model for biomass pyrolysis in a two-stage fixed bed reactor and the mass and energy balance were calculated with steam reforming reactor. Imam and Capareda [15] have reported the mass and energy distribution based on the calculation of pyrolysis products from switchgrass pyrolysis. More importantly, little information is known about the analysis of mass and energy distribution during the continuous pyrolysis of pine sawdust, which is a basis to evaluate the economic feasibility of pyrolysis technology. In this works, we quantify analysis the products distribution in pine sawdust pyrolysis, the influences of pyrolysis temperature and solid residence time on product yields were investigated, the product and energy distribution and energy profit rate was carried out in the continuous pyrolysis.

2. Materials and methods

2.1. Raw material

The raw material used in this study is pine sawdust, supplied by a timber mill in Dalian, China. The particle size of pine sawdust varies from 1 to 2 mm, after being crushed and ground. The proximate and ultimate analysis of sawdust samples are given in Table 1, which were carried out in an Elementar analyzer (VarioEL III, Germany) and an automatic proximate analyzer (SDTGA5000, Sundy, China), respectively. Oxygen content is obtained by difference to 100%. The calorific value of pine sawdust is performed by an oxygen bomb calorimeter.

2.2. Experimental equipment and procedure

In this work, the continuous pyrolysis of pine sawdust was carried out in a screw reactor. The schematic diagram of the screw reactor is shown in Fig. 1. This reactor is composed of continuous feeding device, heating device and cooling device. A stirrer installs in feeding hopper to avoid bridging to ensure raw material flow into screw feeder. The heating device consists of a tubular heater, a temperature controller and a *K*-type thermocouple. The temperature of the heater is controlled by temperature controller and is monitored by a *K*-type thermocouple. The cooling device is a spiral glass condenser cooled by tap water. Pine sawdust is feed into the tubular heater reactor for pyrolysis by continuous feeding device. Biomass is decomposed into produced gas, bio-oil and bio-char. Bio-char is directly dropped in ash bucket, bio-oil is trapped in liquid container after a cooling unit, and produced gas is collected in air bags.

The continuous pyrolysis experiments of pine sawdust under different pyrolysis temperature and solid residence time are investigated. The pyrolysis temperature of experiments are conducted at 600–900 °C with the solid residence time of 6 min and feeding rate of 1.47 kg h^{-1} in continuous mode. The frequency of electromotor is modified to control the solid residence time inside the reactor. The solid residence time of 600 °C. Nitrogen with flow rate of 50 ml min⁻¹ serves as both the carrier gas and purging gas for biomass pyrolysis system. When the temperature of reactor reaches at a desired value, the raw materials are fed into the pyrolysis reactor continuously. As the reaction reaches a steady state after 30–40 min at each run, gas samples are collected every 5 min. The liquid and solid products are weighed after the experimental apparatus cooled down to the room temperature.

2.3. Product analysis

The pyrolysis products consist of thermal gas, bio-oil and biochar. Thermal gas is the non-condensable phase of pyrolysis vapors. By contrast, bio-oil is condensable phase, consisting of water and oxygenated compounds. The bio-char is not volatilized in biomass fraction. The composition of gas was analyzed off-line by gas chromatograph (GC-7890, Shanghai, China). The component of bio-oil was detected with GC/MS analysis (HP6890/5973MS, American) and Fourier-transform infrared (FTIR) analysis (EQUINOX55, Germany). The temperature programming of GC/MS analysis was set up as follows: at first, the temperature was increased from normal temperature to 250 °C at 50 °C/min to gasification, and decreased to 170 °C at 5 °C/min. Then, the temperature increased to 240 °C at 10 °C/min, and maintained at 240 °C for 5 min. Bio-oil samples were extracted by organic solvent (CH₂Cl₂) to remove water before performing by FTIR analysis. CH₂Cl₂ in the oil phase was removed by rotary evaporators (RE-2000E). The proximate analysis and calorific value of bio-oil and bio-char were carried out in automatic proximate analyzer (SDTGA5000, Sundy, China) and oxygen bomb calorimeter, respectively.

3. Results and discussion

3.1. Products distribution

The determination of products distribution on continuous pyrolvsis of pine sawdust under different pyrolysis temperature and solid residence time is given in Figs. 2 and 3. From Fig. 2, the bio-oil vield decreases from 51.7 to 18.0% when the pyrolysis temperature increases from 600 to 900 °C, while gas yield increases from 22.6 to 54.5%. It attributed to the secondary cracking of the pyrolysis vapors as well as the decomposition of the long chains macromolecules into smaller fragments at higher pyrolysis temperature. The char yield presents a little fluctuation trend in the range of 21.36–25.11%, appeared a relatively low amount. It might be caused by the more extensive primary decomposition of biomass and the secondary decomposition of the solid product at higher temperature. The similar tendencies of gas and oil yield with the temperature between 500 and 800 °C are reported by Lu et al. and Heidari et al. [10,16]. The variation of product yields demonstrated that higher pyrolysis temperature favors the production of gaseous product.

From Fig. 3, it can be seen that the bio-char yield is gradually decreased with the solid residence time increased from 3 to 7 min. The gas yield slightly decreases from 18.07 to 13.50% in the residence time of 3-4 min, and then increases to 24.48% at 7 min. The bio-oil yield is 28.86% in 3 min. It appeared maximum yield of 51.7% at residence time of 6 min. As solid residence time longer than 6 min, the bio-oil yield decreased to 46.97%. According to the pyrolvsis product yield, pyrolysis process was divided into three stages with solid residence time. In the first stage (3-4 min), the pyrolysis product yields present a stable variation. This can be explained that shorter solid residence time results in incomplete pyrolysis and the secondary reaction is lack with the solid fast removed from the reactor. In the second stage (4-6 min), as the dominating reaction residence time, the bio-oil yield increases from 30.68% in the residence time of 4 min to 51.67% in 6 min; whereas, the char yield decreased from 44.01 to 21.36%. Compared to the first stage, longer pyrolysis time leads to more micro molecule gas produced from the decomposition of cellulose, hemicelluloses and lignin as well as the long chain and macromolecule organic compounds, which increase the yields of bio-oil and gases due to more volatiles release in its second cracking. In the last stage of reaction (greater than 6 min), the main raw materials had been decomposed and the residuals were cracked more thoroughly. The secondary reactions such as Download English Version:

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