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Pyrolysis products from industrial waste biomass based on a neural network model

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ABSTRACT

Pyrolysis of pine sawdust, a typical industrial biomass waste, was studied. The effects of operating temperature, biomass particle size, and space velocity on the products of biomass pyrolysis were investigated. A three-layer artificial neural network (ANN) model was developed and trained to simulate and predict the selectivity and yield of gas products. Good agreement was achieved between the experimental and simulated results. The major gas products of biomass pyrolysis are CO, CO_2, H_2, and CH_4. The ANN model showed that the major gas products depended mainly on the temperature, and the total selectivity of CO, CO_2, H_2, and CH_4 increased from 2.91% at 300 °C to 34.31% at 900 °C. The selectivity of main gas products increased with increasing space velocity. When the space velocity increased from 45 min^{-1} to 85 min^{-1}, the selectivity of major gas products increased from 29.12% to 34.03%. Within the sample particle size range from 0.1 to 1.7 mm, there was no significant difference in the selectivity of major gas products. The pyrolysis temperature also influenced the composition of the tar in the biomass pyrolysis product. In the temperature range investigated, the benzene composition was favored at lower temperatures, such as 400 °C, however, the light-weight PAHs were preferably generated at higher temperatures above 600 °C.

1. Introduction

Biomass pyrolysis is a type of thermolysis, thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen, which produces char, condensable liquid and non-condensable gas products. Biomass pyrolysis process is usually divided into four stages based on a thermal viewpoint [1,2]. In the drying stage in which the temperature is below 100 °C, the biomass releases moisture and some bound water. In the initial stage, the biomass temperature is between 100 and 200 °C. It releases low-molecular-weight gases, such as CO and CO_2, and small amounts of acetic acid. In the intermediate stage, the temperature is between 200 and 600 °C. Most of the vapor or precursors to bio-oil are produced at this stage. Large molecules of biomass particles decompose into char, condensable gases, and non-condensable gases. The final stage takes place at a temperature between 300 and 900 °C. The final stage of pyrolysis involves secondary cracking of volatiles into char and non-condensable gases. If they stay in the biomass long enough, large molecule condensable gases will also crack, producing additional char (secondary char) and gases. The condensable gases, if removed quickly from the reaction, condense outside in the downstream reactor as tar or bio-oil. A higher pyrolysis temperature also favors the production of hydrogen, which increases quickly above 600 °C [3].

Biomass pyrolysis produces non-condensable gases (including H_2, CO, CH_4, and CO_2), tar, and char [4]. Many factors, such as biomass particle diameter, temperature, heating rate, and residence time can influence the production rate and product properties of biomass pyrolysis [5]. Temperature is the most important factor. Biomass releases different products under different temperature profiles [6–9]. Several researchers [10–13] have investigated the product selectivity and production rate of biomass pyrolysis at different temperatures, ranging from 300 to 1000 °C, in a fluidized bed reactor or revolver. Biomass particle size is also an important factor affecting the pyrolysis reaction rate. Biomass particles with larger diameters have weaker heat transfer capacity, so the internal temperature increases slowly, which affects the selectivity of

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biomass pyrolysis. Researchers have investigated the relationship between biomass particle size and the selectivity of biomass pyrolysis in fluidized and free-fall reactors [5,14]. The results show that biomass with smaller particle diameters releases more gases, and less tar and char, and the fraction of H_2 and CO will increase as the biomass particle diameter becomes even smaller. Cui et al. [15] analyzed biomass pyrolysis via thermogravimetric analysis and a self-designed pressurized thermal gravitational analyzer and concluded that the reaction rate of biomass pyrolysis was higher under higher pressure. Generally, heating rate, flow rate of carrier gas, biomass molecular structure, and reactor pressure all influence the composition of products from biomass pyrolysis.

Tar is a by-product of biomass pyrolysis, the composition of which is very complex. Currently, more than 300 compounds have been detected in tar; despite this, many compounds remain unknown [16,17]. Tar usually comprises mostly benzene derivatives and polycyclic aromatic hydrocarbons (PAHs) [18–22]. The fractions of six compounds in particular are typically each greater than 5%, including benzene, naphthalene, methylbenzene, ethenylbenzene, phenol, and indene. These compounds are liquids at low temperatures and crack into permanent gases with low molecular weights at high temperatures. These small-molecule gases do not condense into liquids when the reactor temperature falls back to the range within which the original compounds are liquids. Recently, many researchers investigated the reactions of tar at different temperatures. Tar starts to condense below 200 °C and starts to react and produce char, pyroligneous acid, additional tar (secondary tar), and gases above 200 °C. Above 600 °C, the secondary tar and pyroligneous acid are evaporated and mixed, producing gases. At a temperature of 500 °C, the production rate of tar from biomass pyrolysis is highest. Biomass pyrolysis produces tar through a series of complicated reactions. They depend on many reaction factors, but especially reaction temperature. Tar in the vapor phase cracks into light hydrocarbons, aromatic hydrocarbons, alkenes, hydrocarbons, and PAHs as the reactor temperature increases.

Chemical kinetic models are one approach to gain insight into a reaction and provide a better understanding of the effect of the processing parameters. The kinetic models reported by Di Blasi [23] is a typical example that investigated the influence of several variables for wood and biomass pyrolysis, such as reaction temperature, residence time, and pressure. Although a dynamic model provides relatively stable and accurate performance in this reaction, a complicated structure is required, especially for a multiple responses system/multi-stage reaction process which contains many processing parameters and mechanisms.

Compared with 'traditional' chemical and physical models, artificial neural networks have the advantages of being able to model complex phenomena rapidly and easily by simply starting with measured values and investigating potentially complex and nonlinear relationships, linking various physical values. Additionally, a neural network has versatility as a black box information processor. All fields including neural network applications use the same symbols. Regardless of the form, neurons represent the same ingredient in different neural networks. This commonality makes it possible to share the same neural network theory and algorithms across various areas. Mikulandrić et al. [24] compared the effects of equilibrium models and neural network model in the biomass gasification process in fixed bed gasifiers. The results derived from different equilibrium modelling approaches (for various operating conditions) could not be compared or explained in some cases. Results from devised equilibrium models were comparable with results derived from literature only for specific operating points. However, neural network models showed good capability to predict biomass gasification process parameters with reasonable accuracy and speed. As a consequence, the effective utilization of the ANN model was beneficial in understanding the complex relationship between the raw materials and pyrolysis products and even the technical management in the actual pyrolysis process [25].

In this study, the distribution of biomass pyrolysis products and the effects of operation conditions on pyrolysis were investigated. We summarized rules on the influences of temperature, biomass particle size, and space velocity on biomass pyrolysis products. Moreover, an ANN model was developed and trained to simulate and predict the selectivity and yields of gas products with different operation parameters in the biomass pyrolysis.

2. Materials and methods

2.1. Raw material

The typical biomass selected for pyrolysis was pine sawdust (without bark, purchased from Porta Pine, Germany). This biomass was milled, sieved, and classified to obtain fractions of uniform particle size, and then dried for at least 12 h at 105 °C. The particle size of the biomass was classified into six groups: 0.14, 0.17, 0.22, 0.34, 0.64, and 1.70 mm. Nitrogen (99.999 vol.%, Beijing Haipu Gas Co. Ltd., China) was used as the carrier gas. Analytical-grade methanol (Beijing Chemical Works, China) was used as the tar absorbent.

2.2. Experimental setup

The configuration of the pyrolysis reactor is shown in Fig. 1. The pyrolysis apparatus consists of a quartz tubular reactor (Length: 1 m and the inner diameter: 50 mm). The reactor was heated by a tube furnace (OTF-1200X, Hefei Kejing Material Technology Co. Ltd., China) in an inert N_2 atmosphere. First, 4 g of pine sawdust was introduced into the furnace. The flow rate of carrier gas (N_2) was controlled by a mass flow controller (D08-4E, Beijing Seven Star Electronics Co. Ltd., China). For each experimental run, the reactor was heated to a set temperature (400, 500, 600, 700, or 800 °C) at a heating rate of 20 °C/min prior to pushing the biomass sample into the heated zone. The reaction time was 30 min. The volatile products passed through two impingers filled with methanol which were cooled in ice-water bath, and the produced tar was remained in the impingers. The remaining aerosol was removed with a filter filled with degreasing cotton. The gas product passed through a wet type gas flowmeter to record the total gas volume. Finally, the gas product was collected in a sampling gas bag (15 L, Dalian Delin Gas Packaging Co. Ltd., China).

2.3. Analytical methods

Produced gases were analyzed by a GC-17A (Shimadzu Corp., Japan) equipped with a thermal conductivity detector (TCD) and a Carboxen-1010 PLOT capillary column (30 m × 0.53-mm I.D., 30-μm average thicknesses, Supelco Corp., USA). The injection (injection volume of 200 μL) was performed at 100 °C in splitless mode. The oven temperature program was 50 °C constantly for 15 min. The temperature of the detector was 200 °C. Argon (99.999 vol.%, Beijing Haipu Gas Co. Ltd., China) was used as the carrier gas, at a constant flow of 10 mL/min.

TG analysis was carried out with a STA449F3 Jupiter (Netzsch-Gerätebau GmbH, Germany). Approximately 40 mg of pine sawdust was heated in argon at 10 °C min^{-1}, from ambient to 800 °C for pyrolysis.

The yield and selectivity of gas product were calculated as follows:

$$\text{The yield of gas product (mmol/g)} = \frac{V_o}{24.4 \times 4} \quad (1)$$

$$\text{The selectivity of gas product (\%)} = \frac{c_j}{c} \times 100\% \quad (2)$$