Fuel xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Modeling and analysis of the pyrolysis of bio-oil aqueous fraction in a fixed-bed reactor

Shaomin Liu [a,*], Lei Chu [a], Mingqiang Chen [b], Wentao Zhang [b], Wenping Xin [a]

[a] School of Earth Science and Environmental Engineering, Anhui University of Science and Technology, Huainan 232001, PR China
[b] School of Chemical Engineering, Anhui University of Science and Technology, Huainan 232001, PR China

HIGHLIGHTS

- The thermodynamic parameters and mass and heat balance equation were estimated.
- A mathematical model on the pyrolysis of bio-oil was established.
- The effects of temperature on the pyrolysis of bio-oil aqueous fraction were studied.
- The comparison of the established model and the experimental results was performed.

ARTICLE INFO

Article history:
Received 31 December 2013
Received in revised form 1 May 2014
Accepted 5 May 2014
Available online xxxx

Keywords:
Bio-oil
Fixed-bed reactor
Pyrolysis
Reaction kinetics
Mathematic model

ABSTRACT

The pyrolysis of bio-oil is important in improving the utilization of biomass energy and the environmental protection. In this study, simulations were conducted in the Aspen Plus environment using the Gibbs reactor to simulate the equilibrium compositions of the bio-oil pyrolysis products at different temperatures. The molar heat capacity at constant pressure of the chemical balance system was calculated through simulation. The thermodynamic parameters of the reactor were determined using the thermodynamic equations and the mass balance principle. Furthermore, the temperature distribution and conversion rate of different catalyst beds were calculated by combining the Runge–Kutta method with the Matlab software. Finally, experiments were performed in a fixed bed reactor, and the experimental results were compared with the simulated results. The calculation result of the established model is in good agreement with the experimental results.

1. Introduction

Bio-oil has much higher energy volume density than solid biomass and poses a great solution to the problem that biomass raw materials are hard to be massively collected, stored, or transported [1–3]. It can be separated into oil phase and aqueous phase by adding water. Due to the lack of fossil fuel resources and the growing greenhouse effect, the utilization of bio-oil as a potential fuel substitute can satisfy the human society's need for energy with wide application prospect [4–6]. Bio-oil can be used directly as low level fuels to provide heat or generate power, or used in internal engine after upgrade.

The pyrolysis of bio-oil is the initial stage of its combustion and gasification, and therefore has a key function in the thermochemical use of bio-oil and the in-depth investigation of pyrolysis characteristics. The kinetics of bio-oil is important [7,8]. Numerous systematic studies on the pyrolysis characteristics and effects of operating conditions on the product distribution have been carried out [9–14]. The main pyrolysis products are water, permanent gases, and char. The yield and the composition of the pyrolysis products depend on the type of reactor, reactor temperature, and catalysis. However, the pyrolysis characteristics of crude bio-oil components have had some issues, such as coke formation and low heating value. Numerous studies have been reported [15,16]; nevertheless, few studies have reported on the comprehensive mass and molar balances at high temperature in a fixed bed [17–19]. The mathematical description relative to the pyrolysis of bio-oil has not been fully understood. A great deal of interest has been addressed to the utilization of bio-oil aqueous fraction; however, the mathematical model of the pyrolysis of bio-oil aqueous fraction has rarely been studied.

This study aims to determine the pyrolysis product yields and the pyrolysis mathematical model to provide significant data for the design and optimization of related gasification and combustion

* Corresponding author. Tel./fax: +86 554 6668742.
E-mail address: shmliu1@163.com (S. Liu).

http://dx.doi.org/10.1016/j.fuel.2014.05.001
0016-2361/

reactors. Moreover, data from this study would provide some theoretical basis for further studies on the use of bio-oil.

In this study, simulations were conducted in the Aspen Plus environment using the Gibbs reactor to simulate the equilibrium compositions of the bio-oil pyrolysis products at different temperatures. The molar heat capacity at constant pressure of the chemical balance system was calculated through simulation. The thermodynamic parameters of the reactor were determined using the thermodynamic equations and the mass balance principle. Finally, the temperature distribution and conversion rate of different catalyst beds were calculated by combining the Runge–Kutta method with the Matlab software.

2. Materials and methods

2.1. Experimental materials

The bio-oil used for thermal analysis was obtained by the pyrolysis of wheat stalk in a small-scale fixed-bed reactor in our laboratory. The sample was prepared by mixing the bio-oil and distilled water. The mass ratio of the distilled water to bio-oil was 4. The water phase of the mixture was used for the thermal analysis.

In this work, acid-activated attapulgite catalyst was used as the support for nickel oxide and molybdenum oxide and simple precipitation was utilized to establish them on the acidized attapulgite. The diameters of the catalyst particles were 1–2 mm; the height of the catalytic bed was 10 cm; the bio-oil feed rate was 2 mL/min to 10 mL/min; the density ρ_B of the bed was 562.39 kg/m^3, the porosity of the catalyst was $\varepsilon = 0.754$; the empty bed mass velocity of the fluid was $G = 76.394$ kg/(m^2 h).

Fig. 1 presents the bio-oil catalytic pyrolysis reactor. The reactor is made of heat-resistant stainless steel tube with a 100 mm diameter and an 800 mm length (including the upper and bottom heads). The reaction temperature is controlled by electronic heating and thermostat. The bio-oil and steam enter the reactor from the upper nozzle. The generated gas is led at different positions on the side face of the reactor for the real-time composition test. The residual product is separated at the bottom of the reactor. The reactor is relatively larger than the catalyst particles, and the height of the bed is over 100 times of the diameters of the particles. The ratio of the diameter of the reactor to that of the catalyst particles is larger than 10. Investigation shows that when the bed height is 100 times over the particles' diameter, the influences of the axial diffusion, thermal conductivity, and radial velocity distribution on the conversion rate are negligible.

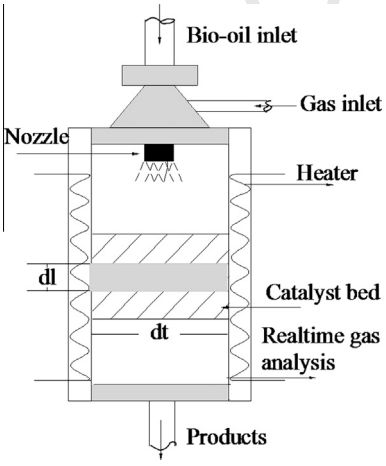

Fig. 1. Catalytic pyrolysis reactor.

2.2. Experimental methods

The catalytic pyrolysis of bio-oil is an endothermic reaction with moderate thermal effect and reaction speed rate. The diameter and bed height of the fixed-bed reactor are significantly larger than that of the catalyst particles, respectively. Therefore, the tubular fixed-bed reactors with thin and long tubes and high flowing rate can be treated as plug-flow or pseudo-homogeneous reactors. In this study, a pseudo-homogeneous, one-dimensional, and plug flow model was selected according to the characteristics of the tubular fixed-bed reactors and the applicable conditions of each model. Combining the features and thermodynamic parameters of bio-oil, the pyrolysis reaction temperatures and the conversion rate distribution of the catalytic bed of the reactor were investigated to determine the key parameters of the reactor.

The bio-oil used for pyrolysis was obtained through fast pyrolysis of pine wood sawdust in a small scale fixed bed at 500 °C. The sample was prepared by mixing the bio-oil and distilled water. The water phase of this mixture was used for thermal analysis. The elemental composition and properties of the bio-oil are shown in Table 1.

Table 1 indicates that the bio-oil aqueous fraction mainly consists of light component organic compounds, which mostly contain carbohydrate-derived compounds. The high viscosity of bio-oil aqueous fraction leads to a bad fluidity low heating value because of the high oxygen content. The basic chemical formula of the water-soluble fractions in bio-oil can be represented by $C_nH_mO_z$. The chemical formula of the bio-oil aqueous fraction can be described by $C_{2.49}H_{9.93}O_{3.73}$, based on the elementary composition.

According to the specific situation of the studied reactor, the establishment of the model is based on the following assumptions:

(1) The property and velocity of the fluid at the cross section perpendicular to the direction of the fluid flow are uniform; velocity, temperature, and concentration gradients do not exist at the radial direction.
(2) The axial thermal and mass transfer is caused by the overall plug flow only.
(3) No radial velocity distribution or axial dispersion of the bed exists at the direction perpendicular to the flow direction.

The outcome of reaction is congealed and separated into the gas and liquid phases. After being dried with non-condensable gas, the gaseous product was determined using GC. The liquid phase was determined using GC–MS. The liquid content was determined using a moisture analyzer, and carbon deposition was determined using TG.

The maximum stoichiometric hydrogen yield can be described by the following reaction stoichiometry (complete pyrolysis of bio-oil aqueous fraction):

$$C_nH_mO_z + (2n - z)H_2O \rightarrow nCO_2 + (2n + m/2 - z)H_2 \quad (1)$$

According to the Eq. (1), the mole ratio of H_2 obtained to stoichiometric H_2 is defined as hydrogen yield, which is calculated as Eq. (2):

$$Y(H_2) = \frac{\text{moles of } H_2 \text{ obtained}}{\text{moles of } H_2 \text{ in stoichiometric potential}} \times 100\% \quad (2)$$

The mole ratio of CH_4 (CO, CO_2) obtained to the carbon in the feed is defined as CH_4 (CO, CO_2) yield and the CH_4 (CO, CO_2) yield is calculated by Eq. (3) [20]:

$$Y(CH_4, CO, CO_2) = \frac{\text{moles of } (CH_4, CO, CO_2) \text{ obtained}}{\text{moles of carbon in the feed}} \times 100\% \quad (3)$$

Please cite this article in press as: Liu S et al. Modeling and analysis of the pyrolysis of bio-oil aqueous fraction in a fixed-bed reactor. Fuel (2014), http://dx.doi.org/10.1016/j.fuel.2014.05.001