



Pyrolysis of biomass components in a TGA and a fixed-bed reactor: Thermochemical behaviors, kinetics, and product characterization



Cui Quan^a, Ningbo Gao^{a,*}, Qingbin Song^b

^a Department of Environmental Science and Engineering, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, Shanxi, China

^b Macau Environmental Research Institute, Macau University of Science and Technology, Macao, China

ARTICLE INFO

Article history:

Received 26 April 2016

Received in revised form 2 July 2016

Accepted 7 July 2016

Available online 8 July 2016

Keywords:

Biomass components

TGA

Fixed-bed reactor

Pyrolysis

ABSTRACT

The pyrolysis characteristics of three main components (hemicellulose, cellulose and lignin) of biomass were investigated using a thermogravimetric analyzer (TGA) and a fixed-bed reactor, respectively. In TGA, the pyrolysis of hemicellulose and cellulose occurred quickly with a weight loss from 210 to 370 °C for hemicellulose and from 260 to 410 °C for cellulose. Lignin decomposed over a wider range of temperature (from 200 to about 600 °C) and generated a high char yield. As the heating rate increased, TG and DTG curves shifted to the higher temperatures. The Flynn-Wall-Ozawa method was introduced to analyze the thermal reaction kinetics, and the activation energy (E) values of hemicellulose, cellulose and lignin pyrolysis are in correspondence with thermostability sequence of these three components. In the fixed-bed reactor, the pyrolysis of lignin generated remarkably high solid residue yield (61%) and very low liquid yield (0.5%) compared with cellulose and hemicellulose. The noncondensable gas mainly consisted of H₂, CH₄, CO₂ and CO. FTIR and GC-MS analysis of liquids showed that liquids from cellulose and hemicellulose pyrolysis included a range of light oxygenated compounds which was indicated that furans, aldehydes and ketones were the most prominent decomposition products. The depolymerization of lignin led to various phenols, including many methoxylated phenols. After pyrolysis, the carbon content in char increased while the hydrogen content decreased. All of the results and findings would help further understanding of thermal behavior of biomass and its thermo-chemical utilization for fuels and chemicals.

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1. Introduction

The prospect of the exhaustion of fossil energy and climate change caused by the excessive use of fossil fuel necessitates shifting energy supply from fossil energy to renewable energy in the near future. Among all renewable energies, biomass energy is receiving increasing interests due to its availability worldwide. In recent decades, special attentions have been paid to the conversion of biomass into biofuels through thermo-chemical conversion processes, such as pyrolysis, gasification and combustion [1]. Among these conversion processes, pyrolysis is a promising technology for biomass utilization, during which biomass can be converted into syngas, bio-oil and biochar [2–4]. Syngas and bio-oil have high heating value and can be used for energy recovery. Bio-oil can also be further upgraded into renewable transportation fuels to replace gasoline, diesel, and chemicals currently derived from nonrenewable sources. Biochar can be used as a fuel, activated carbon, or as

a fertilizer replacement offering an advanced option for biological sequestration of carbon.

Pyrolysis of biomass is a complex process and it includes many different reactions occurring simultaneously, e.g. dehydration, depolymerization, fragmentation, rearrangement, repolymerization, condensation and carbonization. Many researchers have investigated the pyrolysis of different biomass samples, such as miscanthus, olivekernel, almondshell, sawdust, straw, corncob, oreganum stalks, mangaba seed etc [4–7]. The proportion and composition of pyrolysis products are crosswise affected by many factors such as biomass type, feedstock pretreatment, and pyrolysis conditions (e.g., temperature, heating rate, pressure, residence time, and gaseous environment). Gable and Brown [8] found that bio-oil yields increased with biomass heating times in a free fall fast pyrolysis reactor. Kwon et al. [9] investigated the effect of CO₂ on the thermal degradation of lignocellulosic biomass, and their studies revealed that gaseous products including H₂, CH₄, and CO were substantially enhanced in the presence of CO₂ because CO₂ expedited thermal cracking behavior. The study of Zmiewski et al. [10] revealed that the pyrolysis of pinewood using three reactor configurations gave different bio-oil yields, altered the amounts

* Corresponding author.

E-mail address: nbogao@xjtu.edu.cn (N. Gao).

and composition of the non-condensable gases, and gave rise to variations in the amounts and types of chemicals in bio-oil.

Biomass is mainly composed of cellulose, hemicellulose, and lignin, along with smaller amounts of pectin, protein, extractives, and ash. The content of these components in biomass varies depending on the biomass type. Normally, cellulose, hemicellulose, and lignin cover 40–60, 20–40, and 10–25 wt% of biomass materials on dry basis, respectively. Some attempts have been made at correlating the pyrolysis characteristics of biomass with its constituents, i.e., cellulose, hemicellulose, and lignin. Some researchers considered that the pyrolysis of biomass can be represented as a simple superposition of the three main components, and there is no detectable interaction among the components [11]. Qu et al. [12] investigated the relationship between biomass and its three major components, and the results showed that the additivity law can predict the trend of product yields of biomass samples from their composition of hemicelluloses, cellulose, and lignin. However, others indicated that some interactions between cellulose, hemicellulose and lignin exist in biomass pyrolysis [13]. Hosoya et al. [13] found that a significant interaction occurred in cellulose-lignin pyrolysis and a comparatively weak interaction occurred in cellulose-hemicellulose pyrolysis during wood pyrolysis at 800 °C. Cellulose, hemicellulose, and lignin in biomass have very different thermal behaviours. Given the complexity of biomass pyrolysis conversion and the diversity of the obtained products, it may be more convenient to study separately the conversion of each constituent. Knowledge of the pyrolysis characteristics of the three main components is thus essentially important for a better understanding to biomass thermal chemical conversion and further enable the selection of suitable biomass resources for the generation of desired products.

In this paper, a systematic and comparative investigation of pyrolysis behaviours, kinetics, distribution and composition of pyrolysis for three main components (cellulose, hemicellulose and lignin) in biomass was performed in a thermogravimetric analyzer (TGA) and a fixed-bed reactor, respectively. GC, GC-MS, FTIR and elemental analysis were applied to character the pyrolysis products. Studies on the pyrolysis of cellulose, hemicellulose and lignin will promote an understanding of biomass pyrolysis and further enable the selection of suitable biomass resources for the generation of desired products.

2. Methods

2.1. Materials

The main model components of biomass were purchased from Sigma-Aldrich Co., Ltd, including α -cellulose (CAS number: 9004-34-6), hemicellulose (CAS number: 9014-63-5) and lignin (CAS number: 8086-05-1). α -cellulose is in powder fibrous form, and lignin used in this work is alkali lignin in brown powders. Hemicellulose is complex and not commercially available. Xylan from beechwood was used as a hemicellulose model in the study.

2.2. Experimental apparatus and methods

2.2.1. TGA

TGA experiments were carried out in a EXSTAR TG/DTA6300 thermobalanc. In each test about 10 mg sample powder was paved uniformly in a Al_2O_3 ceramic crucible. The temperature of the sample was measured with a K-type thermocouple located under the crucible, and the sample was heated from room temperature to 800 °C under three different heating rates (10, 20 and 40 °C/min). All tests were carried out under N_2 with a flow rate of 60 mL/min.

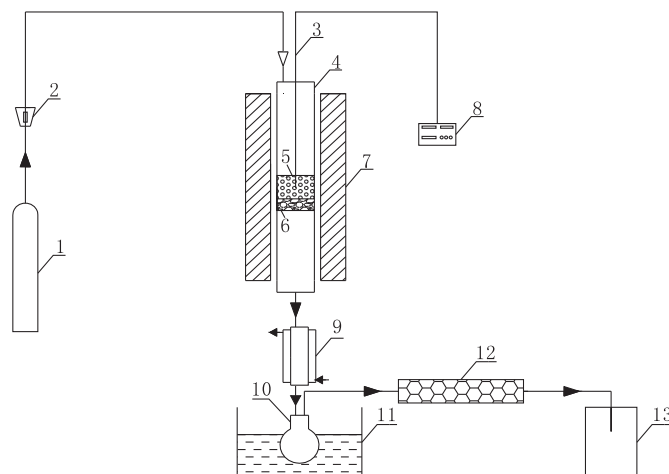


Fig. 1. Schematic diagram of the fixed-bed reactor.

1- N_2 cylinder; 2-Mass flowmeter; 3-Thermocouple; 4-Quartz reactor; 5-Raw material; 6-Quartz wool; 7-Electric furnace; 8-Temperature controller; 9-Condenser; 10-Liquid receiver; 11-Ice-water bath; 12-Cotton filter; 13-Gas collector.

Variation of the sample residual mass with respect to time and temperature change were collected automatically by the equipment.

2.2.2. Fixed-bed reactor

Fast pyrolysis of the samples was conducted in a vertical fixed-bed reactor, as shown in Fig. 1. Tubular quartz reactor has an internal diameter of 26 mm. Nitrogen is used as carrier gas with a flow rate of 100 mL/min. In each trial, 6.0 g of raw material was put inside the reactor which was held by quartz wool placed in the middle of quartz reactor, and then reactor was closed tightly with entry for inert gas connection and output pipe connected to liquid product collecting bottles. Before each experimental run, nitrogen was purged through the reactor for 20 min to ensure the inert atmosphere. The reactor was heated externally by an electric furnace with a length of 400 mm and the temperature was controlled by a K-type thermocouple. When the furnace was heated to the desired pyrolysis temperature (500 °C), the reactor loaded with sample was placed into the furnace and heated for 15 min. And then, the quartz reactor was removed from the furnace but the carrier gas was still maintained until the reactor cooled down to the room temperature.

The volatiles evolved from the reactor were passed through the condenser to collect liquid products. A cotton filter was used to ensure all the condensable vapors were captured. The non-condensable fraction was collected by a gas cabinet using drainage gas collecting method and analyzed by GC. When the reactor was cooled down to room temperature, the remaining solid left behind was taken out, weighed and recorded as char. The liquid products were recovered by washing the liquid collector and connection pipeline with dichloromethane. Then, CH_2Cl_2 was removed by rotary evaporator and the liquid products were obtained. The gas yield was calculated by difference from mass balance.

2.2.3. Product analysis

Chemical compounds of the liquid product were determined by an Agilent 7890A gas chromatograph coupled to a 7000B triple quadrupole mass spectrometer. The capillary column was HP-5MS (30m \times 0.25 mm i.d., 0.25 μ m film thickness). The GC oven was programmed to hold at 40 °C for 2 min, ramped at 8 °C/min to 250 °C, and then held for 10 min. The injector temperature was 300 °C, and the injector split ratio was set to 20:1. Helium was used as a carrier gas. The MS operated in Electronic Impact mode (EI). The mass was set at an ionizing voltage of 70 eV with mass range (m/z) of 40–500. The ion source was kept at 230 °C and the quadrupole at

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