Journal of Analytical and Applied Pyrolysis xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Properties and pyrolysis behavior of moso bamboo sawdust after microwave-assisted acid pretreatment

Yunpu Wang[a,b,c], Dengle Duan[a,b], Yuhuan Liu[a,b,*], Roger Ruan[a,b,d,*], Guiming Fu[a], Leilei Dai[a,b], Yue Zhou[a,b], Zhenting Yu[a,b], Qiuhao Wu[a,b], Zihong Zeng[a,b]

[a] Nanchang University, State Key Laboratory of Food Science and Technology, Nanchang 330047, China
[b] Nanchang University, Engineering Research Center for Biomass Conversion, Ministry of Education, Nanchang 330047, China
[c] Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Guangzhou 510640, China
[d] Center for Biorefining and Department of Bioproducts and Biosystems Engineering University of Minnesota, 1390 Eckles Ave., St. Paul, MN 55108, USA

ARTICLE INFO

Keywords:
Microwave acid pretreatment
Moso bamboo sawdust
Properties
Pyrolysis behavior

ABSTRACT

The effects of microwave-assisted acid pretreatment on the characteristics and pyrolysis behavior of moso bamboo sawdust (BS) were investigated by ultimate, Fourier transform infrared spectroscopy, thermogravimetric (TG), and pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS) analyses in this study. Microwave temperature (100 °C–200 °C), reaction time (30 min–90 min), and acid concentration (0.5 M–1.5 M) were the main influencing factors. Results of ultimate analysis indicated that the properties of the pretreated samples are better than those of the raw BS. Moreover, appropriately reducing the oxygen and ash contents and increasing the microwave temperature promoted decarboxylation and dehydration during pretreatment. Microwave-assisted acid pretreatment decreased the acetyl groups and hydrogen bonds. Of the three main influencing factors affecting the structure of moso BS, microwave temperature was the most important. TG analysis results indicated that the thermostability of the pretreated samples is improved after pretreatment. Moreover, the pyrolysis behavior of moso BS is insensitive to the reaction time and acid concentration under mild conditions. The relative contents of acids, furans, aldehydes, and ketones derived from the pretreated samples decreased according to the results of Py-GC/MS. Meanwhile, the relative glucopyranose and phenol contents of the pretreated samples are higher than those of the raw moso BS and achieve the maximum values of 48.31% and 20.18%, respectively, at 200 °C.

1. Introduction

Growing concerns about global climate change and fossil fuel resource limitations have facilitated the exploitation and utilization of renewable resources for producing next generation green biofuels [1,2]. As one of the most abundant renewable resources on Earth, lignocellulosic biomass (i.e., cellulose, hemicellulose, and lignin) has attracted interest over several years as the only carbon-neutral renewable resource for chemicals and biofuels [3–5]. Lignocellulosic biomass is predicted to account for 35%–40% of the total world energy consumption in the forthcoming 50 years [6]. Currently, various technologies have been developed to convert biomass into chemicals and biofuels [7]; biomass can be converted into bio-oil with yields of approximately 70% in the rapid pyrolysis process [6,8]. However, conversion of lignocellulosic biomass to biofuel is still a challenging process because of the complex structure of plant cell walls; lignocellulose is a major component of plant cell walls [9]. In addition, bio-oil from the direct conversion of lignocellulosic biomass always has undesirable qualities, such as low heating value, high water and oxygen (O) contents, and high acidity or high pH, which negatively affect the utilization and consumption of bio-oil [10,11]. Consequently, a pretreatment step is needed prior to lignocellulosic biomass conversion.

Among the existing pretreatment technologies to improve lignocellulosic biomass for renewable energy production, acid pretreatment is considered one of the most cost-effective and available methods [12]. The main purpose of pretreatment is to remove lignin, disrupt the crystalline structure of cellulose, and reduce biomass recalcitrance [13,14]. Pittman et al. pretreated corn stalks with 2 wt.% aqueous H_2SO_4 solution and determined that acid pretreatment resulted in the removal of Na^+, K^+, Mg^+, and Ca^{2+} salts from the stalks, promoted the formation of anhydrosugar in bio-oil isolated at 400 °C and 450 °C, and improved the cellulose fragmentation in stalks [15]. Wang et al. conducted acid, alkali, and steam explosion pretreatments of pinewood and demonstrated that 1% and 0.5% H_2SO_4 pretreatments resulted in the

* Corresponding authors at: Nanchang University, State Key Laboratory of Food Science and Technology, Nanchang 330047, China.
E-mail addresses: liuyuhuan@ncu.edu.cn (Y. Liu), ruanx001@umn.edu (R. Ruan).

https://doi.org/10.1016/j.jaap.2017.11.024
Received 30 October 2017; Received in revised form 14 November 2017; Accepted 28 November 2017

maximum bio-oil yield. In addition, bio-oil from 1% H_2SO_4 had the most advantageous physical characteristics, such as higher heating value (HHV), higher viscosity, and lower acid value than bio-oil from 0.5% H_2SO_4 [6]. Dong et al. investigated the influences of H_2SO_4, HCl, HF and HNO_3 washing on moso bamboo pyrolysis and determined that HCl washing has the most significant influence on the structure of bamboo, the removal of inorganic components, and the facilitation of the formation of levoglucosan [16].

In recent years, microwave-assisted heating has attracted considerable attention as another effective route to pretreat biomass. In contrast to conventional heating, microwave heating is caused by the transmission of electromagnetic waves, and heat can be generated throughout the volume of the feedstock, which can reduce processing time and save energy [17]. In addition, compared with conventional heating, microwave heating also has many advantages, such as uniform and rapid heating, ease of control, and high selectivity [18–20]. However, the majority of research focused on adopting conventional heating to provide mild temperature for acid pretreatment, and the study of microwave-assisted acid pretreatment biomass was rarely reported.

Moso bamboo is the most abundant plant compared with all other kinds of bamboo and accounts for approximately 60% of the total area of bamboo in China [21]. Currently, moso bamboo has been widely used to produce furniture, flooring, and interior decoration materials, thus leading to the formation of a large amount of bamboo sawdust (BS), which is always burned for heating or discarded without any industrial utilization [21]. Therefore, the effective conversion of BS by pyrolysis is important for the efficient use of renewable energy.

In the present study, the effects of microwave-assisted acid pretreatment on moso BS are investigated. This study aims to understand the effects of microwave temperature, time, and acid concentration on the characteristics (ultimate analysis and FTIR spectra) and pyrolysis behavior (Thermogravimetric analysis and Py-GC/MS) of moso BS. Analyzing the microwave-assisted acid pretreatment of moso BS is significant for providing a cost-effective biomass conversion method and guiding the production of high-quality bio-oil.

2. Materials and methods

2.1. Materials

Moso BS (*Phyllostachys heterocycla* var. *pubescens*) was obtained from a bamboo processing mill in Jiangxi, China. The samples were dried at 105 °C for 12 h in a vacuum oven before use. Hydrochloric acid (analytical grade) was purchased from Xilong Reagent Company, Guangdong, China.

2.2. Microwave-assisted acid pretreatment of bamboo sawdust

Microwave-assisted acid pretreatment of BS was conducted in a microwave digestion device (MDS-6G, Sineo Microwave Chemistry Technology Co., Ltd., Shanghai, China). First, 5 g of BS was dissolved in 50 mL hydrochloric acid solution in five reaction vessels (100 mL; modified Teflon material). Then, these reaction vessels were placed in the microwave digestion device. Microwave power of 600 W was used in the heating process. In addition, microwave temperatures were 100 °C, 150 °C, and 200 °C. The conditions of each experiment are shown in Table 1. Microwave heating times were 30, 60, and 90 min. Hydrochloric acid concentrations were 0.5, 1, and 1.5 M. The pretreated sample was filtered under vacuum to collect solid residue and washed with distilled water until its pH was approximately 7 to avoid residual acid in the feedstock. Thereafter, the sample was dried at 105 °C overnight under vacuum and kept in desiccators at room temperature before use. All experiments were conducted in triplicate.

Table 1
List of reaction conditions.

Run No.	Microwave Temperature (°C)	Microwave Time (min)	Hydrochlori acid Concentration (M)
BS	0	0	0
1-1	100	60	0.5
1-2	150	60	0.5
1-3	200	60	0.5
2-1	100	30	0.5
2-2	100	60	0.5
2-3	100	90	0.5
3-1	100	60	0.5
3-2	100	60	1
3-3	100	60	1.5

2.3. Characterization of bamboo sawdust before and after acid pretreatment

Ultimate analysis to measure the carbon (C), hydrogen (H), and Oxygen (O) contents were performed using an elemental analyzer (Vario EL III, Elementar, Langenselbold, Germany). The ash content was determined according to ASTM E870-82 (2013). Fourier transform infrared (FTIR) analysis was conducted to examine the characterization of the functional groups of BS before and after acid pretreatment using the FTIR spectrometer (Nicolet iS5, Thermo Fisher, Waltham, MA, USA). Each spectrum was recorded in the range of 4000 cm^{-1}–700 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans.

2.4. Thermogravimetric analysis of bamboo sawdust before and after acid pretreatment

Thermogravimetric (TG) analysis was conducted to determine the thermal behavior of BS before and after acid pretreatment using a TG analyzer (TGA 4000, PerkinElmer, Waltham, MA, USA). Before the experiment, all samples were dried at 105 °C overnight in the absence of oxygen. Samples (4 mg) with a particle size of 200 mesh were used to conduct TG and derivative thermogravimetric (DTG) experiments. The corresponding curve was determined by heating the sample from 30 °C to 800 °C at a constant heating rate of 10 °C/min. A high-purity nitrogen gas flow of 100 mL/min was used as the purge gas prior to the experiment.

2.5. Pyrolysis–gas chromatography/mass spectrometry measurement of bamboo sawdust before and after acid pretreatment

Pyrolysis experiments were performed in a pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS) system. The system is composed of a CDS Pyroprobe 5200 pyrolyzer and a GC/MS (Agilent Technologies 7890/5975) equipped with an Agilent HP-5MS (30 m × 0.25 mm × 0.25 μm) capillary column. Approximately 0.5 mg samples were introduced into the pyrolysis tube. In each run, the pyrolysis temperature was 550 °C in the PY-2020i pyrolyzer (Frontier Laboratories, Fukushima, Japan). High-purity helium with a constant flow rate of 1 mL/min was used as the carrier gas to maintain an inert environment. The column temperature was initially maintained at 60 °C for 2 min, programmed to 280 °C at a rate of 10 °C/min, and maintained at 280 °C for 10 min. The inlet temperature was 250 °C, the pressure was 6.704 psi, and the spilt ratio was 20:1. The operating condition of mass spectrometry was electron ionization of 70 eV, and the MS detector scanned from 29 m/z to 500 m/z. The identification of chemical components was conducted according to the National Institute of Standards and Technology database of MS spectra. A semiquantitative method based on the calculation of the percentages of the chromatogram peak was used to determine the relative content of detected compounds.