Microwave pyrolysis of lignocellulosic biomass: Heating performance and reaction kinetics

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ABSTRACT

Lignocellulosic biomass is an abundant renewable resource and can be efficiently converted into bioenergy and green materials by using microwave pyrolysis. In this study, microwave pyrolysis of seven biomass feedstocks (corn stover, rice straw, rice husk, sugarcane bagasse, sugarcane peel, coffee grounds, and bamboo) was studied. The maximum temperature of microwave pyrolysis was highly correlated with the combustible content of the feedstocks. The influence of microwave power level on both maximum temperature and heating rate was substantial. Either maximum temperature or heating rate had a linear relationship with microwave power level. However, there was a breakpoint at a power level of 250 W. Compared with conventional pyrolysis, microwave pyrolysis was faster and needed less input energy. Microwave pyrolysis provided higher weight losses than conventional pyrolysis, and this difference was more substantial at lower temperatures. Kinetic parameters of microwave pyrolysis at lower and higher microwave power levels were different. Reaction rates at higher microwave power levels can be higher than those at lower power levels by approximately one order of magnitude. Compared with conventional pyrolysis, the rate constant of microwave pyrolysis was much higher, and its activation energy and pre-exponential factor were much lower.

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1. Introduction

Renewable energy has attracted considerable interest nowadays. The interest in renewable energy primarily comes from the perceived risks of using fossil fuels and CO_2 emissions [1]. Researches and developments of renewable energy that can substitute fossil fuels have been revived in recent years due to high worldwide demand for energy, unstable and uncertain petroleum sources, and concerns over global climate change [2]. Biomass is a promising alternative energy source, because it is an inexpensive, renewable, and abundant source of carbon [3]. Renewable bioenergy and green materials can be derived from biomass [4]. The production of bioenergy includes numerous combinations of resources, conversion processes and end products [5]. Biomass feedstocks should be utilized with lower greenhouse-gas emissions than fossil fuels and with little or no competition with food production, so they may include, but not limited to, the following:

agricultural residues, perennial plants grown on degraded lands abandoned from agricultural use, harvested wood and forest residues, and municipal and industrial wastes [6]. Biomass materials with high energy potential include agricultural residues (straw, husks, and bagasse) and forestry residues (wood chips, sawdust, and bark) [7]. To mitigate climate change and to enhance energy security, the utilization of agricultural and forestry residues is a promising choice to replace fossil resources for the production of energy and chemicals [8].

Agricultural and forestry residues can be regarded as lignocellulosic biomass, because their major chemical components are cellulose, hemicellulose, and lignin. Both cellulose and hemicellulose are polysaccharides. Lignin is an amorphous polymer with no exact structure and consists of an irregular array of variously bonded phenylpropane units [9]. Generally, the percentages of cellulose, hemicellulose, and lignin content are 35–50, 25–30, and 15–30 wt.%, respectively [4]. Therefore, lignocellulosic biomass consists of approximately 60–80 wt.% polysaccharides and thus it can be attractive as feedstocks for fermentation to produce large amounts of free sugars [10]. However, due to the natural resistance of plant cell walls against microbial and enzymatic deconstructions

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(biomass recalcitrance), the cost of lignocellulose conversion would be high [2]. In addition, it is difficult to ferment the lignin, so thermochemical methods are usually proposed for its conversion [10]. The production cost of biofuel is primarily determined by raw material cost, plant capacity, capital investment, operation cost, conversion efficiency, etc. From this point of view, the cost via biological conversion pathway can be lower than thermochemical pathway. However, thermochemical pathway does have higher conversion efficiency than biological pathway. Therefore, thermochemical methods, such as combustion, pyrolysis, and gasification, would be more favorable to convert lignocellulosic biomass into bioenergy and green materials more quickly and more completely.

Microwaves are electromagnetic waves with frequencies between 300 MHz and 300 GHz, and thus the corresponding wavelengths are between 1 m and 1 mm, respectively [11]. Microwave heating includes two mechanisms: dipole rotation and ionic conduction. Both of them are able to heat materials quickly and uniformly. Microwave pyrolysis of lignocellulosic biomass is a promising technology for the production of value-added products. Compared with conventional heating, microwave heating can be more efficient due to its rapid, selective, volumetric, and uniform heating [11–14]. Microwave pyrolysis is a promising attempt to improve the yield and quality of the products and to increase the energy efficiency of the whole process [15]. The difference between microwave and conventional heating can be owing to different heating mechanisms (dielectric heating versus convective and conductive heating) and the occurrence of a hot spot (spark) generated by microwave heating [16]. Microwave heating has been used for the pyrolysis or torrefaction (mild pyrolysis) of various biomass feedstocks, such as scrap tire [14], wood [17], sewage sludge [18], coffee hulls [19], oil palm biomass [20], microalgae [21], sugarcane bagasse [22], wheat straw [23], and corn stover [24]. Microwave pyrolysis of biomass can produce three-phase products: solid (biochar), liquid (biooil), and gas (syngas). Biochar [22], biooil [15], or syngas [25] yield can be highest depending on operational parameters (microwave power level and processing time), biomass characteristics, and the effects of catalysts or microwave absorbers [26].

Although it is generally thought that one of the primary disadvantages of microwave applications is energy consumption, this study tried to investigate and challenge this from the viewpoint of heating performance. The heating rate and weight loss of microwave pyrolysis were compared with those of conventional pyrolysis. Another goal of this study was to investigate the reaction kinetics of microwave pyrolysis since it has been seldom researched. Besides, for the purpose of obtaining convincible and reliable experimental results, various biomass feedstocks were tested at various power levels.

2. Materials and methods

2.1. Materials

The samples of this study were seven different biomass feedstocks including bamboo leaves, rice straw, rice husk, corn stover, sugarcane bagasse, sugarcane peel, and waste coffee grounds, which were collected on farms or in factories or markets. All the biomass feedstocks were naturally air-dried, shredded, and sieved by a 50-mesh (0.297 mm) screen. The proximate analyses of the biomass feedstocks were carried out according to the standard test method D7582-12 of the ASTM (American Society for Testing and Materials). The elemental analyses were performed in accordance with the ASTM standard test method D5291 by using a Perkin–Elmer 2400 Elemental Analyzer. The gross calorific values of the biomass feedstocks were determined by using a CAL2K ECO calorimeter.

2.2. Experimental device

This study used a single-mode (focused) microwave device with a 2.45 GHz frequency. The schematic diagram of the overall microwave pyrolysis set-up can be found elsewhere [27]. Both reaction tube (40 cm length, 5 cm outer diameter) and sample holder (3 cm height, 4 cm outer diameter) were made of quartz. Conventional pyrolysis was carried out by using a TA Instruments SDT Q600 Simultaneous DSC–TGA (Differential Scanning Calorimetry–Thermogravimetric Analyzer) with a nitrogen flow rate of 100 mL/min.

2.3. Experimental procedure

The shredded and sieved biomass feedstock (3–5 g) was added to the quartz crucible and then placed inside the quartz tube that was located in the pathway of microwaves propagation. A thermocouple sensor was placed at the bottom of the quartz crucible to measure the temperature of the biomass sample. To maintain anoxic conditions, nitrogen gas was purged into the system at a flow rate of 50 mL/min. After sufficient purging was performed to maintain an inert atmosphere, the power supply was turned on and switched to a designated microwave power level for 30 min. The reflection microwave power levels were controlled to be as low as possible during the entire experimental period. When the designated processing time was reached, the power supply was turned off, and the carrier gas purging was stopped. The vapor produced during the experiment was immediately cooled by a condenser whose temperature was controlled at 4 °C by a thermostat. The condensable and incondensable parts of the vapor were regarded as liquid product and gaseous product, respectively. After self-cooling to approximately 100 °C, the solid product was moved to a desiccator for several hours. The tests of conventional pyrolysis were carried out at various heating rates and maximum temperatures to observe weight loss and energy consumption. All of the experiments were performed in triplicate at least to obtain average values for the results.

3. Results and discussion

3.1. Compositions of biomass feedstocks

The proximate, elemental, and lignocellulosic compositions of BL (bamboo leaves), RS (rice straw), RH (rice husk), CS (corn stover), SB (sugarcane bagasse), SP (sugarcane peel), and waste CG (coffee grounds) are listed in Table 1. The moisture content of the biomass feedstocks was approximately 5–10 wt.%, and the volatile, fixed carbon, and ash contents (dry basis) were approximately 72–86, 9–17, and 4–12 wt.%, respectively. The combustible (volatile + fixed carbon) content of sugarcane bagasse, sugarcane peel, and corn stover was up to 96 wt.%, whereas the combustible content of bamboo was only approximately 88 wt.%. The carbon, hydrogen, oxygen, and nitrogen contents (dry and ash-free basis) of the biomass feedstocks were approximately 40–49, 6–7, 44–53, and 0.3–1.1 wt.%, respectively. It should be noted that the oxygen content was calculated by difference. The atomic H/C and O/C ratios of the biomass feedstocks were 1.58–1.74 and 0.66–1.00, respectively. The lignocellulosic compositions of the seven biomass feedstocks were very different. Rice straw had the highest hemicellulose content (31.12 wt.%) whereas bamboo leaves had the lowest (25.55 wt.%). Sugarcane bagasse had the highest cellulose content (46.55 wt.%) whereas rice husk had the lowest (30.42 wt.%).