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Microwave pyrolysis of rice straw: Products, mechanism, and kinetics

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HIGHLIGHTS

- The highest energy densification ratio was achieved at the power level of 300 W.
- The atomic H/C and O/C ratios of rice straw were largely decreased.
- The primary components of gaseous product were CO, H_2, CO_2, and CH_4.
- More gaseous product was obtained at higher microwave power levels.
- Liquid production remained the same and showed a maximum of about 50 wt.%.

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ABSTRACT

Rice straw is an abundant resource for the production of biofuels and bio-based products. How to convert the recalcitrant lignocellulose effectually is a critical issue. The objective of this study was to investigate the products, mechanism, and kinetics of rice straw pyrolysis by using microwave heating. The highest energy densification ratio of solid residues was achieved at the microwave power level of 300 W. The atomic H/C and O/C ratios of solid residues were much lower than those of rice straw. The primary components of gaseous product were CO, H_2, CO_2, and CH_4, whose molecular fractions were 57%, 21%, 14%, and 8%, respectively. The more gaseous product and the less solid residues were obtained at higher microwave power levels, while the liquid production remained the same and showed a maximum of about 50 wt.%. The kinetic parameters of rice straw pyrolysis were increased with increasing microwave power level.

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1. Introduction

Biomass is a resource to produce renewable energy and fuels which are so-called bioenergy and biofuels. Biomass can be produced from various sources, such as wood, crops, agricultural and forestry residues, and biodegradable components of commercial, industrial, and municipal solid waste, which are some of the main renewable energy resources available (Bridgwater, 2006). The first-generation biofuels have caused some controversial issues such as food prices, deforestation, global warming and threats to biodiversity, because they come from the feedstocks of food crops (Luque et al., 2008). The second-generation biofuels, unlike the previous one, are generated from no longer food crops but rather non-food crops and biomass waste. Biomass waste means biological or biodegradable residues left from agricultural, forestry, industrial, and human activities. In the past, most of the biomass waste was not properly utilized or treated but directly burned or discarded on site. This old custom not only wastes the energy inside the biomass waste but causes CO_2 emission as well. The utilization of biomass waste can reduce the impact to the environment and produce useful fuels and chemicals. Besides, compared with other renewable resources giving heat and power, biomass represents the only source of liquid, solid, and gaseous fuels (Bridgwater and Peacocke, 2000).

Microwaves are electromagnetic waves with frequencies between 300 MHz and 300 GHz, and thus the corresponding wavelengths are between 1 mm and 1 m. Microwave heating includes two mechanisms: one is the dipole rotation, and the other is the ion migration. Both of them are able to heat materials quickly and uniformly. Microwave heating is also a selective and energy-saving technology without direct contacts with the heated materials (Jones et al., 2002). Therefore, it is widely used in many applications such as sample pretreatment (Roig, 1995), synthesis (de Andresa et al., 1999), digestion (Bettinelli et al., 2000), extraction (Perez Cid et al., 2001), and sludge stabilization (Chen et al., 2005; Hsieh et al., 2007). The technology of pyrolysis induced by microwave heating has been researched to treat various feedstocks such as oil shale (El harfi et al., 2000), oil-palm stone (Guo and Lua, 2000), paper (Miura et al., 2001), plastic waste (Ludlow-Palafox

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and Chase, 2001), sewage sludge (Menendez et al., 2002), rock phosphate (Bilali et al., 2005), scrap tire (Appleton et al., 2005), coffee hulls (Menendez et al., 2007), wood (Chen et al., 2008), rice straw (Huang et al., 2008), corn stalk bale (Zhao et al., 2010), oil palm biomass (Salema and Ani, 2011), and microalgae (Hu et al., 2012). These researches have shown that, by using the microwave pyrolysis, biomass feedstocks can be converted into various products such as bio-oil, bio-char, fuel gas, and hydrogen. The reaction performance and productivity depends on factors including operating parameters, biomass characteristics, reaction atmosphere, and catalytic effect.

Rice is one of the most important food crops, and its annual worldwide production has been over 700 million metric tons since 2010 (Food and Agricultural Organization of the United Nations (FAO), 2012). Therefore, close to 1 billion metric tons of rice straw can be generated annually, because about 1.35 metric tons of rice straw remains in the field for every metric ton of grain harvested (Kadam et al., 2000). This is really a great quantity of biomass waste or the source of biofuels and bio-based products depending on how to deal with the rice straw. The biochemical treatment of lignocellulosic biomass is difficult due to the natural resistance of plant cell walls to microbial and enzymatic deconstruction (known as biomass recalcitrance), which is largely responsible for the high cost of lignocellulose conversion (Himmel et al., 2007). Thermochemical treatments including pyrolysis and gasification can effectually overcome the biomass recalcitrance by decomposing the crystalline recalcitrant structure of lignocellulose. In order to establish a feasible technology for the treatment of biomass waste like rice straw, this study aims at investigating the products, mechanism, and kinetics of rice straw pyrolysis by using the microwave heating.

2. Methods

2.1. Material

The sample of this study was rice straw provided by Industrial Technology Research Institute (ITRI), Taiwan. The rice straw was stored at room temperature for months to maintain constant moisture content, and then it was shredded and sieved by a 50-mesh (0.297 mm) screen. The basic components and properties of rice straw have been reported in the previous article (Huang et al., 2012). The combustible and ash contents (dry basis) of rice straw were about 90 and 10 wt.%, respectively. The hemicellulose, cellulose, and lignin contents (dry basis) of rice straw were about 20, 42, and 26 wt.%, respectively. The C, H, and O contents (dry and ash-free basis) of rice straw were about 46, 6, and 46 wt.%, respectively. The higher heating value (HHV) of rice straw was about 16 MJ/kg.

2.2. Experimental device and procedure

This study used a single-mode (focused) microwave device with 2.45 GHz frequency. The schematic diagram of overall microwave pyrolysis set-up can be found elsewhere (Wang et al., 2010). The shredded and sieved biomass feedstock was filled in a quartz crucible. Then it was placed inside a quartz tube and precisely in the pathway of microwaves. In order to maintain anoxic circumstances, Nitrogen gas was purged into the system with a flow rate of 50 mL/min. After enough purging to maintain an inert atmosphere, the power supply was turned on and switched to the prescribed microwave power level for the prescribed processing time. Reflection microwave power levels were controlled to be as low as possible during the whole experiment period. When the prescribed processing time was reached, the power supply was turned off and the carrier gas purging was stopped, and then the tar and gas collectors were removed and sealed. After self-cooled down to about 100 °C, solid residues were removed and placed in a desiccator for hours. All the experiments were repeated twice to obtain the results in average values.

2.3. Product analysis

The proximate analysis referred to the standard test method D5142 of American Society for Testing and Materials (ASTM). The elemental analysis was carried out by a Perkin–Elmer 2400 Elemental Analyzer. The heating values of raw rice straw and solid residues were determined by a CAL2K ECO calorimeter. The analysis of gaseous product was carried out by a Perkin–Elmer Auto System XL gas chromatography–thermal conductivity detector (GC–TCD) with a Supelco Carboxen 1010 PLOT column. The temperatures of injector, oven, and detector were 120, 100, and 150 °C, respectively. The flow rate of carrier gas (He/N_2) was 10 mL/min (25:1 split). The liquid product was analyzed by a Perkin–Elmer Turbo Mass Gold gas chromatography–mass spectrometry (GC–MS) with a Supelco Equity–5 capillary column. The initial temperature of oven was 45 °C and held for 3 min, and then it was ramped from 45 °C to 300 °C at the rate of 5 °C/min and held for 5 min. The flow rate of carrier gas (He) was 10 mL/min (20:1 split).

3. Results and discussion

3.1. Performance of microwave heating

The rice straw sample was efficiently heated by the microwave radiation. The temperature was not obviously increased at the first minute, and most of the heating effect occurred at about 1–10 min, as reported in the previous article (Huang et al., 2012). This should be owing to that the rice straw did not absorb enough microwaves yet at the first minute. Once the microwave energy was sufficient, the temperature was effectually increased. The maximum temperature and the maximum heating rate were governed by how much the input energy is (i.e., the microwave power level). The maximum temperature and the maximum heating rate were both increased when increasing the microwave power level, as shown in Fig. 1. The correlation between the maximum temperature and the microwave power level was linear, while the maximum heating rate exponentially increased with increasing microwave power level. Therefore, the maximum heating rate was more sensitive to the microwave power level than the maximum temperature. This means that at higher microwave power levels, the maximum temperatures can be reached more quickly, and thus the processing time can be shorter. Generally, it only took 5–10 min to reach the maximum temperatures at higher microwave power levels (400–500 W), while the temperatures kept climbing very slowly

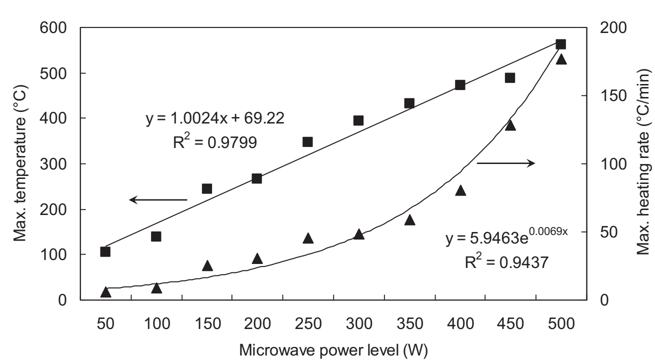

Fig. 1. The maximum temperatures and the maximum heating rates at different microwave power levels.

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