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Pyrolysis behavior and kinetics of corn residue pellets and eucalyptus wood chips in a macro thermogravimetric analyzer

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ABSTRACT

Pyrolysis of corn residue in pellet form and eucalyptus wood in chip form was conducted on a continuously weighing fixed bed reactor acting as a macro thermogravimetric (TG) analyzer with 40 ± 1.0 g of sample loading under high purity nitrogen environment. Effect of heating rate (5, 10, and 15 °C/min) was investigated and pyrolysis behaviors of the pellets and wood chips were also compared with those performed on a typical TG analyzer. Experimental results showed that bigger particle size and higher heating rate significantly delayed the pyrolysis reaction, meanwhile the heating rate affected the characteristic temperatures of the pellets and wood chips more than the smaller size. By differential derivative TG technique, the pyrolysis behaviors could be divided into three stages. Within the main stage of pyrolysis process, only a peak could be differentiated clearly in the derivative TG curve, accounted for approximately 67–81% of weight loss. Flynn-Wall-Ozawa method was used to calculate the activation energy against conversion of reaction on the whole temperature domain. It was found that the activation energy values from the macro TG analyzer, which were 60–70 and 59–71 kJ/mol with average values of 64 and 62 kJ/mol for the pellets and wood chips, respectively, were about four times lower than that obtained from the typical TG analyzer.

1. Introduction

Due to depletion of fossil fuel resources and the increasingly serious concern about energy security, environmental sustainability and climate change, biomass is considered as a clean, sustainable, high potential renewable energy source for the future. Currently, biomass was used for renewable energy up to 10% of the global annual energy consumption [1]. Particularly in Thailand, biomass has been widely used for heat production and electrical power generation which will increase to 25% of renewable energy by the year 2036 [2]. Corn is one of the most important agricultural crops in the world which has been planted extensively for food production and animal feeding. After harvesting, a large amount of corn residue including 0.70 kg of stover and 0.15 kg of cobs for every kg of dry corn residue is not usually harnessed but either left as waste or burned openly in its fields. Annually in Thailand, the potential energy of corn residue has been estimated at 65,125 TJ [3]. Consequently, its abundance is such an attractive renewable energy resource. Likewise, eucalyptus, a tree of the high growth rate, is the most widely planted wood in many plantations around the world to support the demand of the paper industry, e.g., paper pulp, timber, and fiber. During the paper production, there are many eucalyptus residues such as leaves, bark, and wood chips. The accumulation and disposal of eucalyptus residues could constitute a source of environmental problems. If corn and eucalyptus residues are used as the valuable feedstock for energy production via

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thermochemical conversion process, not only the residues will be managed effectively, but the environmental pollutions and the energy insecurity will also be lessened.

Main thermochemical processes include pyrolysis, gasification, combustion, hydrothermal liquefaction, and carbonization [4–9]. Among these means, pyrolysis, which is the thermal decomposition of organics at elevated temperatures in an oxygen-free environment, has been developed extensively as a promising platform for biofuels or chemicals production from various types of biomass. By pyrolysis, syngas, oil, and char, the distribution of which strongly depends on the conditions of pyrolysis, are produced and further improved to be transportation fuels and/or chemical materials [10]. For engineering applications, such as designing and optimizing the suitable reactor for these thermochemical processes, predicting the material lifetime, establishing the process conditions, and CFD modeling, knowledge on the thermal behavior of biomass fuels and reliable kinetic data describing their thermal decomposition behavior are important [11]. According to the literature, thermogravimetric analysis (TGA) is one of the most common techniques used to study pyrolysis of biomass [12]. The TGA studies are very useful for understanding about the thermal behavior of small fuel samples and to acquire knowledge about the chemical structure and thermal stability of materials. Many researchers have studied biomass pyrolysis based on its main components, i.e., hemicellulose, cellulose, and lignin [13–16]. It was suggested that biomass pyrolysis on a typical TGA can be considered as the sum of pyrolysis of the three main components [17]. During the typical TGA, a sample of a few milligrams of powdered biomass undergoes the thermal decomposition which heat and mass transfer limitations can be ignored. Therefore, this process is mainly controlled by chemical kinetics. However, for applications at industrial scale, the amount of biomass in real pyrolysis furnaces is much larger and the size of the biomass is commonly up to several centimeters in sizes. Big particle sizes and high sample loading involve heat and mass transfer phenomena which are different significantly from thermal decomposition behavior investigated in the typical TGA. To investigate the thermal decomposition behavior of biomass when also integrating limitations in heat and mass transfer, a specially designed laboratory scale macro-thermogravimetric analyzer (macro-TGA) was considered. So far, there have been only a few studies on pyrolysis of thick biomass in a macro-TGA with high sample loading and big sample size in pellet or chip form.

In the present work, pyrolysis of corn residue pellets and eucalyptus wood chips were carried out in a macro-TGA. Effects of heating rate and particle size were investigated on the overall reaction rate and the thermal decomposition behaviors. Kinetic behaviors of corn residues and eucalyptus wood on the typical TGA and the macro-TGA were evaluated using Flynn-Wall-Ozawa (FWO) method and compared.

2. Materials and methods

2.1. Sample preparation

Corn residue pellets and eucalyptus wood chips were locally obtained from a pelleting factory and a wood industry, respectively. Eucalyptus wood chips were dried naturally in a room at ambient condition. Before the experiments, no other pre-treatment was applied to all samples. All was kept in an air-tight bag to shield from other impurities. The average size was 8 mm in diameter and 25 mm in length for the pellets, and 20 mm in width and 25 mm in length for the wood chips, shown in Fig. 1, respectively.

2.2. Macro-TGA experiments

The biomass samples were tested in a custom-designed and constructed reactor, forming essentially a macro-TGA. The macro-TGA system comprised a carrier gas unit, a furnace unit, and a real-time weighing unit, shown in Fig. 2. The carrier gas from a high-pressure gas cylinder with two-stage pressure-release valves was fed through two volumetric flow control meters to bring out gas products from the reactor in the furnace unit. The reactor was made from cylindrical stainless steel with 50 mm in diameter and 400 mm in height whose exterior was surrounded by 3.5 kW electrical heater and fiber board insulator. The heater was controlled by a digital temperature controller and the temperature was monitored and recorded by a data logger. The maximum heating rate of the heater was 30 °C/min and the maximum temperature was 1100 °C. For the real-time weighing unit, a cylindrical basket with 35 mm in diameter and 80 mm in height was hanged inside the reactor by a stainless steel wire of 1.5 mm diameter to a digital scale which was connected to a computer to allow for continuous weight recording by the data acquisition software. The RADWAG WLC1/A2 digital scale was used with the maximum weight of 1000 g and resolution of 0.01 g. In order to analyze the gas/liquid products, condensation unit and gas/liquid collected unit could be connected to the macro-TGA system.

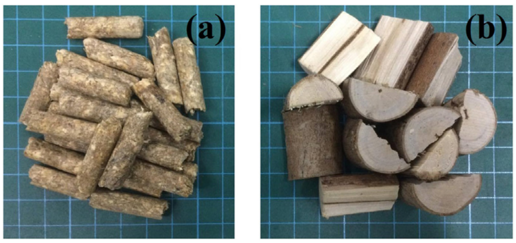

Fig. 1. Biomass samples (a) corn residue pellets (b) eucalyptus wood chips.