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Thermal characterization of oil palm fiber and eucalyptus in torrefaction



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ABSTRACT

Thermal behavior of biomass in torrefaction plays an important role in the operation of pretreatment. To understand the endothermic and/or exothermic characteristics of biomass in the course of torrefaction, an experimental system is conducted and two kinds of biomass (oil palm fiber and eucalyptus) are investigated. The results indicate that the thermal behavior is significantly influenced by the lignocellulosic composition in biomass and the torrefaction temperature. The thermal decomposition of hemicellulose is the dominant mechanism for oil palm fiber torrefied at 200 and 250 °C, whereas the thermal degradation of cellulose is crucial when the biomass is torrefied at 300 °C. Therefore, the heat of reaction of oil palm fiber increases with increasing torrefaction temperature. The torrefaction of eucalyptus is always endothermic, as a consequence of high cellulose contained in the biomass. It is less endothermic when the torrefaction temperature increases, presumably due to the char formation from cellulose thermal degradation and the exothermic lignin decomposition. As a whole, the values of the heat of reaction of the two samples are between -3.50 and 2.23 MJ/kg. The obtained results have provided a useful insight into the control of torrefaction operation and the design of torrefaction reactor.

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1. Introduction

Torrefaction is a promising thermal pretreatment process to upgrade solid biomass where the material is heated at temperatures of 200–300 °C in an inert atmosphere [1]. Torrefaction reduces the moisture in biomass and changes the hygroscopic biomass to the hydrophobic material, rendering the low affinity of water in torrefied biomass [2-5]. As a result, the upgraded materials can be stored for a long time and its utilization efficiency is relatively high. Torrefaction also reduces the costs of biomass transportation and storage [6] and makes the comminution of torrefied biomass easier [3,7–9]. Another important feature accompanied by torrefaction is that the energy density of torrefied biomass is higher than that of its parent biomass [4,10]. It has been reported that torrefaction has a positive effect on combustion [11,12], co-firing [13], co-gasification [4,14], and pelletization [15] of biomass. On account of these advantages, torrefied biomass is a potential alternative to coal consumed in industry.

Over the past several years, numerous studies have been performed on the effects of non-oxidizing torrefaction conditions upon the physical and chemical properties of biomass, such as weight loss, elemental variation, grindability, calorific value, energy yield, and thermal degradation kinetics of biomass [16—19]. Recently, the studies of oxidative torrefaction have also been carried out [20—23] to evaluate to the potential of using air as a carrier gas to upgrade biomass. From these studies, it is recognized that the quality and quantity of solid products are influenced by several operating conditions, such as temperature [17,19], duration [18], feedstock [20], particle geometry and size [16], and atmosphere or oxygen concentration [21—23].

When biomass is torrefied, the thermal behavior of the reaction is of the utmost importance in the pretreatment process. Specifically, the temperature control in the reactor will be disturbed by the endothermic and exothermic reactions in the course of torrefaction, thereby influencing the solid product quality. Up to now, many researchers have studied the heat of reaction of biomass pyrolysis using DTA (differential thermal analysis) or DSC (differential scanning calorimetry). He et al. [24] pointed out that the heat requirements (dry basis) for the pyrolyses of wheat straw, cotton stalk, pine, and peanut in the temperature range of 303–673 K were 523, 459, 646, and 385 kJ/kg, respectively. de Velden et al. [25]

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reported that the heat of reaction (dry basis) for spruce, poplar, eucalyptus, sawdust, sewage sludge, straw, corn, and sunflower in the temperature range of 313–823 K was between 207 and 424 kJ/kg. Fasina and Littlefield [26] discovered that energy required for removing the moisture of pecan shells was obviously higher than that for thermal decomposition, and the effect of heating rate on the energy requirement was slight.

Recently, a few studies concerning the heat of reaction of biomass torrefaction has been published, van der Stelt [27] performed beechwood torrefaction in a fixed bed reactor for 30 min to measure the heat of reaction. Corresponding to the torrefaction temperatures of 230, 250, and 280 °C, the values of heat of reaction for beechwood torrefaction were in the ranges of 425.3 to 1112.9, 21.5 to 1375.4, and -1516.4 to 1159.6 kJ/kg, respectively. They concluded that the thermal behavior during torrefaction became less endothermic or more exothermic with increasing torrefaction temperature. Bates and Ghoniem [28] developed a model using a two-step and first-order mechanism to describe willow torrefaction. They found that the exothermic behavior at the first stage of torrefaction was between 40 and 280 kJ/kg, while the thermal behavior of the second stage depended on temperature. Ohliger et al. [29] studied the torrefaction of beechwood chips at torrefaction temperatures of 270-300 °C and residence time of 15-60 min to evaluate the heat of reaction in a lab-scale reactor, and reported that the heat of reaction was between -199 and 148 kJ/kg.

Biomass is composed of cellulose, hemicellulose, lignin, and small amount of extractives. Therefore, the thermal behavior of biomass in torrefaction is highly related to the endothermic and exothermic reactions of the preceding constituents. The thermal characteristics of the constituents during pyrolysis have been outlined in some studies. For instance, the study of Yang et al. [30] indicated that the pyrolyses of hemicellulose and lignin were exothermic in nature, whereas the pyrolysis of cellulose pertained to endothermic reaction. Gomez et al. [31] pointed out that a higher content of lignin in biomass led to the higher exothermicity in a biomass decomposition process. Haykiri-Acma et al. [32] analyzed the thermal behavior of holocellulose and lignin extracted from hazelnut shells. They concluded that the exothermic extent of lignin in pyrolysis was larger than that of holocellulose, and the endothermic heat flow from cellulose was covered by hemicellulose resulting from the charring phenomenon. Mok and Antal Jr. [33] investigated the effects of pressure and carrier gas flow rate on the heat demand of cellulose pyrolysis, and showed that high pressure and low flow rate increased the exothermic char formation and reduced the heat of pyrolysis. Milosavljevic et al. [34] analyzed the thermochemistry of cellulose pyrolysis in an inert gas at heating rates from 0.1 to 60 K/min. They illustrated that the main cellulose thermal degradation pathway was endothermic; however, cellulose pyrolysis could be driven in the exothermic direction by the charring process which competed with tar formation, especially at low heating rates. Therefore, the char yield was the main factor to change the thermal behavior of cellulose pyrolysis. Cho et al. [35] studied the heat of reaction for cellulose pyrolysis at heating rates of 1-150 K/min, and observed that cellulose decomposition at high temperatures was endothermic. Nevertheless, the pyrolysis became exothermic at low temperatures because of the dominant mechanism of char formation.

In spite of many impressive studied conducted, the information of endothermic and exothermic characteristics in biomass torrefaction remains insufficient. The thermal behavior and net heat flow of biomass torrefaction are important factors in designing torrefaction reactors. Therefore, the objectives of this study are to conduct an experimental system and to investigate the thermal behavior of two types of biomass (i.e. oil palm fiber and eucalyptus) in the course of torrefaction. The thermogravimetric analyses of the

biomass materials will be performed to aid in describing the thermal behavior. The results not only enable us to figure out the thermal degradation characteristics of biomass in different torrefaction environments, but also provide a useful insight into the design of torrefaction reactors.

2. Experimental

2.1. Material preparation and analysis

Oil palm is an important economic crop in some countries, especially in Malaysia, and oil palm fibers are abundant wastes from palm oil fruit harvest and oil extraction processing. On the other hand, eucalyptus is a fast growing plant which is the potential biomass for energy or fuel. Therefore, the two biomass materials were adopted and studied in this work. The eucalyptus was cut into blocks at the dimensions of 14 \times 9 \times 5 mm. The oil palm fiber was preliminarily ground by a shredder and sieved by vibrating screens. Afterward, its size was regulated between 40 and 100 mesh (i.e. 150–385 μm). To provide a basis for experiments, the raw biomass samples were dried in an oven at 105 °C for 24 h. The moisture content in biomass was measured by a moisture analyzer (Ohaus MB45). It suggested that almost all moisture was removed from the drying. Subsequently, the samples were placed in sealed plastic bags and stored in a desiccator at room temperature until experiments were carried out.

The analyses of the raw materials include proximate, elemental (ultimate), fiber, and calorific analyses. The proximate analysis was performed in accordance with the standard procedures of ASTM (American Society for Testing and Materials). The elemental analysis was carried out using an elemental analyzer (Elementar Vario EL III). Hemicellulose, cellulose, and lignin were analyzed following the fiber analysis adopted in a previous study [36]. The HHVs (higher heating values) of the samples were measured by means of a bomb calorimeter (IKA C2000 Basic). The results of the analyses are listed in Table 1.

The TGA (thermogravimetric analysis) was performed by use of a thermogravimetric analyzer (PerkinElmer Diamond TG/DTA). In the TGA, around 5 mg of sample at the sizes below 40 mesh (i.e.

Oil palm fiber

Eucalyptus

Table 1Proximate, elemental, fiber, and calorific analyses of biomass samples.

Biomass

| Photograph | 0 | |
|--------------------------------|-------|-------|
| Proximate analysis (wt%, dry b | asis) | |
| Volatile matter (VM) | 72.46 | 81.07 |
| Fixed carbon (FC) | 20.51 | 18.93 |
| Ash | 7.03 | 0.00 |
| Elemental analysis (wt%) | | |
| C | 51.94 | 50.77 |
| Н | 4.75 | 5.13 |
| N | 2.43 | 0.00 |
| O (by diff.) | 40.88 | 44.10 |
| Fiber analysis (wt%) | | |
| Hemicellulose | 34.00 | 15.35 |
| Cellulose | 26.78 | 48.36 |
| Lignin | 16.08 | 21.26 |
| Other | 23.14 | 15.03 |
| Higher heating value (MJ/kg) | 17.13 | 18.38 |

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