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Examinations of chemical properties and pyrolysis behaviors of torrefied woody biomass prepared at the same torrefaction mass yields

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ABSTRACT

The torrefaction of leucaena at the same torrefaction mass yield, but different torrefaction temperatures and holding times was conducted. Three values of torrefaction mass yields were selected; 60 wt%, 70 wt%, and 80 wt%. For each torrefaction mass yield, three to four torrefaction temperatures and holding times were varied. It was found that the elemental compositions of the torrefied leucaena at the torrefaction mass yield of 80 wt% were not affected by the torrefaction condition. On the other hand, at the torrefaction mass yield of 60 wt% the carbon content of the torrefied leucaena increased, while the oxygen content of the torrefied leucaena decreased with the increase in torrefaction temperature. From the TGA analysis during the pyrolysis, it was found that the weight decreasing profiles were almost the same and they did not depend on the torrefaction conditions for the torrefaction mass yield of 70 wt% and 80 wt%. On the other hand, the significant difference of the pyrolysis behaviors was observed for the torrefied leucaena prepared at the torrefaction mass yield of 60 wt%. The char yield at 800 °C for the torrefied leucaena prepared at 320 °C and 6 min holding time was as high as 27.0%, while it was around 24.0% for the torrefied leucaena prepared at other conditions. Through the results from the gas formation during the pyrolysis of cellulose and the XRD analysis, it may be concluded that the torrefaction of 320 °C and 6 min holding time led to the significant modification of cellulose in the leucaena structure resulting in the different chemical properties when compared to those other torrefaction conditions.

1. Introduction

Due to the environmental problems worldwide by over-excessive usage of fossil fuels, biomass, a renewable energy source, increasingly has then become of more interest. In power generation section, biomass has the significant environmental benefits over fossil fuels such as reducing the CO_2 and sulfur emissions after combustion. Thailand is an agricultural-based country and has abundant biomass resources. Hence, the prospect of converting biomass into power is very attractive and still rising progressively. However, usage of biomass as a fuel always faces several barriers during a thermal conversion process, for example, fouling and slagging problems occurring in combustion process, the relatively high tar production in gasification process, etc. [1–6]. This is due to the naturally negative properties of biomass such as high ash and moisture content, naturally fibrous structure which result in a relatively low heating values and poor grindability compared to coal [7–10]. To deal with these problems, several studies attempted to improve the biomass properties initially before further utilization.

Since the past decades, the upgrading of biomass by a method called torrefaction has been of remarkable interest to several researchers. Torrefaction is a thermal treatment technique performed at relatively low temperature (around 200–300 °C) in the absence of oxygen [11]. During torrefaction, a major hemicellulose, the most reactive component, decomposes evolving H_2O and light acid compounds as a major product, followed by CO_2 and CO [12,13]. Throughout torrefaction, chemical properties and structure of biomass were found to improve attractively, such as a rise in their calorific values including more hydrophobicity [14–17]. Torrefied biomass, in addition, was found to require less energy consumption for size reduction due to the better grindability when compared to its original [10,18]. In the viewpoint of the thermochemical conversion properties, the pyrolysis and combustion behaviors of torrefied biomass were found to differ from the raw biomass. The char combustion rate of torrefied biomass was clearly higher than the char combustion rate of the raw [7,14,19]. The quantity

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Table 1
Ultimate analyses, the higher heating values and yields of leucaenas prepared at the same torrefaction yields.

Sample	Ultimate analysis [%, d.b.]				Yield [%, d.b.]	HHV [MJ/kg, d.b.]
	C	H	N	O[a]		
Leucaena	47.9	6.6	0.7	44.7	–	19.2
At 80 wt% yield						
250 °C, 120 min	53.3	6.0	0.8	40.0	80.4	21.4
280 °C, 5 min	53.2	5.9	0.7	40.2	79.8	21.3
300 °C, 0 min	53.2	5.9	0.8	40.1	80.0	21.3
At 70 wt% yield						
250 °C, 480 min	55.7	5.7	0.8	37.7	70.4	22.4
280 °C, 40 min	55.5	5.8	0.8	37.9	69.4	22.4
300 °C, 5 min	55.4	5.7	0.8	38.1	70.1	22.3
320 °C, 1 min	56.8	5.8	0.8	36.7	69.7	23.0
At 60 wt% yield						
250 °C, 1140 min	59.6	5.7	0.8	33.9	60.6	24.4
280 °C, 105 min	60.0	5.5	0.9	33.6	59.7	24.5
300 °C, 20 min	60.2	5.6	0.9	33.3	60.3	24.7
320 °C, 6 min	62.5	5.3	0.9	31.3	60.6	25.7

[a] Calculated by difference.

of syngas production from gasification of torrefied biomass was slightly higher than that from the raw biomass gasification [20–22]. As shown in the several works mentioned, the obtained benefits through the utilization of torrefied biomass were achieved by the suitable condition conducted during the torrefaction process. In general, there are two main parameters affecting the properties of biomass during torrefaction: temperature and holding time. The higher temperature and longer holding time during torrefaction showed more improvement of torrefied biomass properties [7–10,13,14,17,19,21]. However, normally, the changes in temperature and holding time not only affect the properties of torrefied biomass, but also affect the amount of solid yield inevitably. At rising of temperature and holding time, the mass yield of torrefied product was decreased. The amount of solid product, moreover, was also found to further affect the energy yields of this torrefaction condition.

However, by varying several patterns of temperature and holding time, the possibility to obtain the same mass yield can occur. Then at these similar mass yields, in other words, the obtained chemical properties of torrefied biomasses prepared between high temperature together with short holding time and low temperature together with long holding time could be compared. Recently, indirect comparison of biomass torrefaction process by controlling the energy yield and varying the combination of temperature and holding time was done by Chen et al. [23]. They found that the higher torrefaction temperature and shorter residence time gave high energy utilization of torrefied biomass. So far, however, lack of studies have been investigated on the chemical properties of torrefied biomass which was directly prepared at the same mass yields through the varying temperature and holding time pattern. Further studies on pyrolysis characteristics of torrefied biomass are also rather limited. From the authors' previous work, the intensive study of pyrolysis behaviors of torrefied biomasses was conducted after preparing at several torrefaction conditions [13]. At the same torrefaction temperature, the very long holding time led the significant increase in char formation during subsequent pyrolysis. To extend this knowledge, the chemical properties of biomass were investigated when they are prepared at different torrefaction temperatures and holding times by fixing the final mass yield. Their subsequent pyrolysis characteristics are interesting and they are therefore examined in this paper.

In this study, leucaena (*Leucaena leucocephala*), a woody biomass, was used as sample. In Thailand, leucaena is not only most importantly used as a source of quality animal feed, but also for residual use for charcoal production. This is due to the fact that leucaena is a fast growing tree in which its annual production is around 13.3 t/ha [24]. It is also recognized as a potential energy crop for power generation. In this paper, the investigation on the torrefied leucaena properties after preparing at the same torrefaction yield is preliminarily investigated. Their detailed discussion on their properties was done.

2. Biomass sample

Woody biomass, leucaena collected from Saraburi province, Thailand, was used as a sample in this study. It was cut by a cutting mill and sieved to have a particle size of around 0.5–2 mm. Then, it was dried in vacuum oven at 70 °C for 24 h before the experiments. Leucaena was analyzed for its structural composition. In this study leucaena was extracted for 5–6 h in ethanol in a Soxhlet apparatus, according to TAPPI, T264 om-97 [25]. Then, the chemical analyses of the residue after the extraction were performed. Content of the acid insoluble lignin (known as "Klason lignin") was determined by extracting the residue in a sulfuric acid of 72% (TAPPI T-222) [26]. Content of hemicelluloses and cellulose was determined according to Wise's chlorite method [27] and TAPPI T-203 [28]. Through the analyses, the quantity calculated on dry-ash-free basis are: cellulose = 33.1 wt%, hemicellulose = 31.8 wt%, lignin = 27.1 wt% and extractives = 8.0 wt%. The elemental compositions of leucaena are shown in Table 1. The commercial microcrystalline cellulose and xylan from birch wood purchased from Sigma–Aldrich, Inc. were also used to examine the effect of torrefaction on the pyrolysis behaviors.

3. Experiments

3.1. Torrefaction experiments

Fig. 1 shows the schematic diagram of torrefaction experiment in horizontal quartz tube reactor. About 2.5 g (dry-ash-free basis) of sample was placed in alumina boat located at the middle of the quartz reactor (O.D. 38 mm). Nitrogen (99.999% purity) was then purged through the reactor at the flow rate of 150 ml/min. Then the reactor was heated to the desired temperature (240–320 °C) at the heating rate of 10 °C/min and held at the desired times. When the desired reaction condition was reached, the gas collected in