Examination of Torrefaction of Woody Biomass under Different Oxygen Concentrations at Temperature Below 300°C

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Abstract

Torrefaction is one of the thermal treatment techniques at relative low temperature range of 200 – 300 °C in an inert atmosphere, which aims to improve the fuel properties attractively for further utilization such as combustion, gasification and/or co-combustion. Many studies have been conducted on the properties of torrefied biomass including woody and non-woody biomass by varying temperature and holding time during torrefaction. It was found that the energy density as well as the higher heating value (HHV) was increased progressively at higher torrefaction temperature and at longer holding time. This is due to the increase in carbon content and decrease in oxygen content in the biomass. The improvement of grindability of torrefied biomass which seems to be the feature for this technique was reported. However, few studies have been conducted to examine the effect of oxygen concentrations at temperature below 300°C. There still remains a need to study the influence of different oxygen concentrations on the thermal reactivity during the torrefaction as well as their effects on the chemical properties of the torrefied biomass. In this study, woody biomass (*Leucaena Leucocephala*) was torrefied at 220, 240, and 260 °C under the oxygen concentration of 2, 5, 10, and 22 %. The gas formation rate during the torrefaction under the different oxygen concentrations was also examined in detail by using TG-MS technique. It was found that the different oxygen concentrations affected significantly the reactivity of biomass during the torrefaction especially at 260 °C. At 260 °C, the high oxygen concentration affected significantly the chemical properties of the torrefied biomass. The results obtained from the study provide the basic information for the design of torrefaction process.

Keywords*:* Biomass, Torrefaction, Pyrolysis, Gasification.

1. Introduction

Biomass is a renewable energy resource which is considered as an environmental friendly fuel by producing less CO_2 emission when compared to that of fossil fuel. Especially in Thailand, there are largely biomass wastes available in several sectors such as agricultural residues, agro-industries by-products including energy crops for using as alternative energy resources. However, due to its variety of species and compositions which depend on its origin, several technical problems are unavoidable experienced during the biomass utilization. Firstly, in particular, biomass has low energy density, which makes the handling and transportation of biomass very difficult. Secondly, due to the fibrous nature of biomass, it is very difficult to reduce the size of biomass into small particle size especially when biomass is to be used in pulverized system such as co-firing with coal in large scale utility boilers. Finally, in most cases, the typical higher moisture content could provide the storage complications such as degradation and also the significant decrease in its heating value. These properties have negative impacts during energy conversion thus resulting in the low gasification/combustion efficiencies and gasifier design limitations.

Several technologies have been proposed to reduce those drawbacks and improve the fuel volumetric energy density. The technologies proposed to address these issues including briquetting/pelletizing which can improve the fuel volumetric energy density and torrefaction. Among these proposed technologies, torrefaction is considered to be very attractive due to its advantage in improve fuel volumetric energy density as well as increase grindability. Torrefaction is usually performed in inert atmosphere at temperature below 300 °C which aims to remove mostly the hemicelluloses content in biomass structure [1]. Recently, the authors have studied the effects of temperature and holding time during torrefaction on the properties of torrefied woody biomass [2]. It was found that the energy density as well as the higher heating value (HHV) was increased progressively at higher torrefaction temperature and at longer holding time. This is due to the increase in carbon content and decrease in oxygen content in the biomass. The improvement of grindability of torrefied biomass which seems to be the feature for this technique was reported [3]. However, few studies have been conducted to examine the effect of oxygen concentrations at temperature below 300°C. There still remains a need to study the influence of different oxygen concentrations on the thermal reactivity during the torrefaction as well as their effects on the chemical properties of the torrefied biomass. In this study, woody biomass (*Leucaena Leucocephala*) was torrefied at 220, 240, and 260 °C under the oxygen concentration of 2, 5, 10, and 22 %. The gas formation rate during the torrefaction under the different oxygen concentrations was also examined in detail by using TG-MS technique. The results obtained from this study provide the basic information for the pyrolyser and/or gasifier design by using torrefied biomass as a fuel.

2. Experimental

2.1 Material

Leucaena Leucocephala from Saraburi province was used as a sample in this study. It was shredded with cutting mill to obtain the sample particle size less than 2 mm. Then, it was dried in vacuo at 70 °C for 24 h before the experiment.

2.2. Torrefaction Experiment

About 30 mg of sample was placed on the quartz wool located at the middle of the reactor (O.D. 10 mm). The gas (helium, 2%, 5%, 10%, and 22% oxygen balanced in helium) was then purge through the reactor at the flow rate of 50 ml/min. Then the reactor was heated to the desired temperature (220, 240, and 260 °C) at the heating rate of 10 °C/min and hold at the desired temperature for 30 min. When the desired reaction condition was reached, the gas collected in a gas bag was immediately injected to the gas chromatography (Shimadzu, GC-14B) to analyze the gaseous products. After cooling down to room temperature, the solid product or torrefied sample was weighed to measure the yield of torrefied sample.

2.3. Evolved Gas Analyses during Torrefaction by TG-MS Technique

The torrefaction experiments were performed in a sensitive thermobalance (Perkin-Elmer, Pyris1 TGA) at a heating rate of 10 °C/min up to a final temperature of 260 °C under the gas (helium, 2%, 5%, 10%, and 22% oxygen balanced in helium) at the flow rate of 50 ml/min. A quadrupole mass spectrometer (Perkin-Elmer, Clarus 500 MS) coupled to the thermobalance (Perkin-Elmer, Pyris1 TGA) was used for the evolved gas analysis. To avoid secondary reactions, a probe was placed very close to the sample pan of the thermobalance in the direction of the gas flow. The transfer lines between the TGA and the MS were heated to 200 °C in order to avoid cold spots and thus prevent the condensation of the gaseous products. The signals for mass numbers of 2, 15, 18, 28, and 44 were continuously detected. Then the mass numbers were converted to the concentrations of H_2, CH_4, H_2O, CO, and CO_2 by referring to the calibration curves constructed using the standard gases. The evolving rates of the gaseous products were estimated from the measurements.

3. Results and Discussion

3.1 Change in Weight During the Torrefaction Under Different Oxygen Concentrations

Fig. 1 shows the change in weight during the torrefaction of leucaena under different oxygen concentration at 220 °C, 240 °C, and 260 °C. It was found that at 220 °C the increase in oxygen concentration slightly increase the weight loss during torrefaction. On the other hand, the oxygen concentration affected significantly the weight loss during torrefaction at 260 °C. The yield of torrefied leucaena at 260 °C and 30 min decreased from 66.5 % to 54.0 % when increase the oxygen concentration from 0% (helium atmosphere) to 22 %. These results indicated that the oxygen concentration affected significantly the yield of torrefied leucaena at 260 °C.

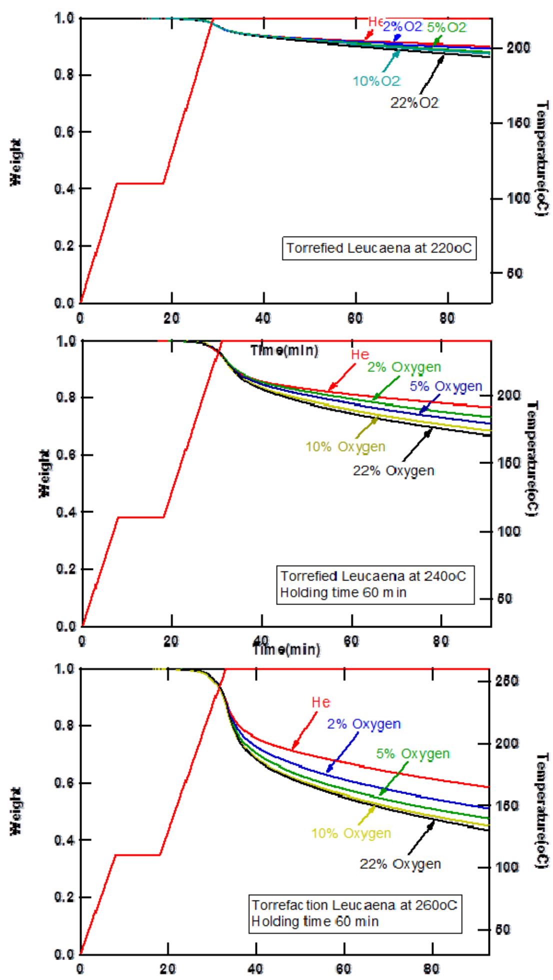

Fig. 1 Changes in weight during the torrefaction of leucaena under different oxygen concentration at 220 °C, 240 °C, and 260 °C.

3.2. Change in Gas Formation Rates During the Torrefaction Under Different Oxygen Concentrations

Next, the effect of oxygen concentration on the gas formation rates during torrefaction was examined in detail by TG-MS technique. The changes in weight and gas formation rates during torrefaction at 260 °C of leucaena under 2% oxygen, 5% oxygen, and 22 % oxygen was shown in Fig. 2. It was found that only H_2O, CO, and CO_2 were formed at this temperature. Water was the main gaseous product for the torrefaction at all oxygen concentrations. It was found that the gas formation rates increased with the increase in oxygen concentration. The amount of gas formed during torrefaction at 260 °C was calculated and was shown in Fig. 3. It was found that the amount of H_2O increased from 13.5 % to 20.1 % when increase the oxygen concentration from 0% (helium atmosphere) to 22 %. The amount of CO_2 increased from 3.5 % to 16.2 % when increase the oxygen concentration from 0% (helium atmosphere) to 22 %. These results clearly indicated that the oxygen concentration enhanced the dehydration and decarboxylation reactions during torrefaction at 260 °C.

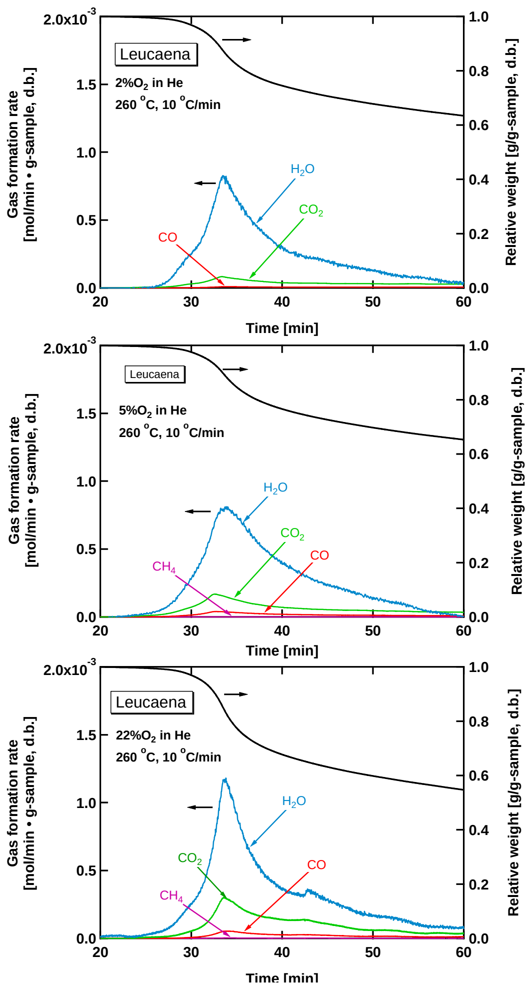

Fig. 2 Changes in gas formation rates during the torrefaction of leucaena under different oxygen concentration at 260 °C.

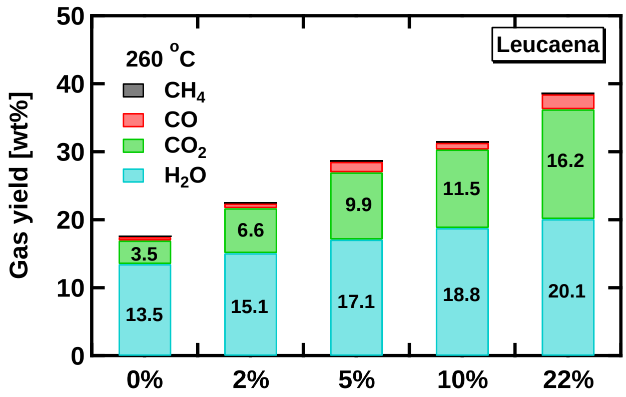

Fig. 3 Amount of gas formed during the torrefaction of leucaena under different oxygen concentration at 260 °C.

3.3 Ultimate Analyses of Torrefied Leucaena Under Different Oxygen Concentrations

The ultimate analyses of the torrefied leucaena at various conditions were shown in table 1. It was found that the carbon content of the torrefied leucaena increased with the increase in temperature and the increase in the oxygen concentration up to 10%. When we increased the oxygen concentration to 22%, the carbon content decreased. On the other hand, the oxygen content of the torrefied leucaena decreased with

Table 1 Ultimate analyses of the torrefied leucaena prepared at various conditions.

Sample		Ultimate Analyses [wt%, d.a.f.]			
		C	H	N	O
Raw		46.9	6.1	0.7	46.3
220 °C	0%	47.7	6.1	0.7	45.5
	2%	48.2	6.2	0.7	44.8
	5%	49.2	6.1	0.7	43.9
	10%	49.7	6.0	0.7	43.6
	22%	48.5	6.0	0.7	44.8
240 °C	0%	49.3	6.0	0.7	44.0
	2%	49.4	6.2	0.7	43.6
	5%	50.4	5.9	0.7	42.9
	10%	51.5	5.9	0.7	41.2
	22%	50.0	5.9	0.7	43.3
260 °C	0%	51.7	6.0	0.7	41.6
	2%	51.3	6.0	0.7	42.0
	5%	53.4	5.8	0.8	40.1
	10%	53.2	5.5	0.8	40.5
	22%	52.4	5.2	0.9	41.6

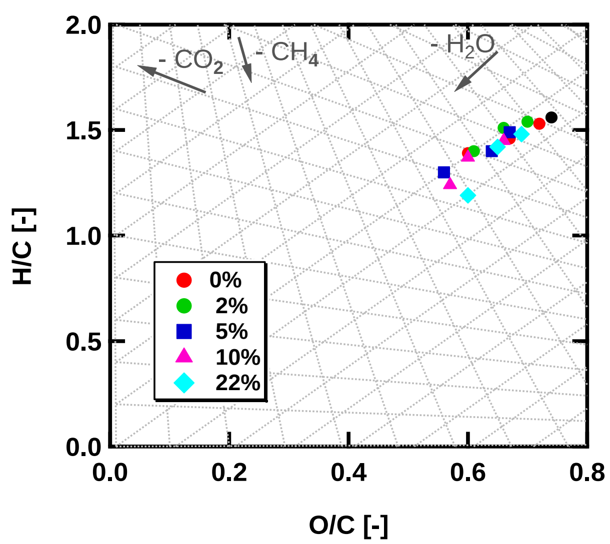

Fig. 4 H/C vs. O/C diagram for raw leucaena and the torrefied leucaena prepared at various conditions.

the increase in temperature and the increase in the oxygen concentration up to 10%. When we increased the oxygen concentration to 22%, the oxygen content decreased.

Next, in order to examine the fuel properties of torrefied leucaena, the elemental composition of leucaena as well as leucaena torrefied at various conditions were also plotted on H/C vs. O/C diagram as shown in Fig. 4. From Fig. 4 raw leucaena was plotted at H/C = 1.56 and O/C = 0.74, while the torrefied leucaena were plotted at lower values, lying along the dehydration reaction line (-H2O). The H/C and O/C values of torrefied leucaena, for example, move from H/C = 1.46 and O/C = 0.67 to H/C = 1.37 and O/C = 0.60 when the oxygen concentration increased from 0% to 10% at 240 °C. This result indicated that the torrefaction of leucaena at 240 °C proceeded through the coalification process even in the present of oxygen resulted in decreasing the values of H/C and O/C. On the other hand, the H/C and O/C values of the torrefied leucaena at 260 °C move from H/C = 1.30 and O/C = 0.56 to H/C = 1.19 and O/C = 0.60 when the oxygen concentration increased from 5% to 22%. This result clearly indicated that the torrefaction at 260 °C under the oxygen atmosphere was different from the torrefaction at 240 °C. It was suggested that the oxidation reaction proceeded at torrefaction at 260 °C under oxygen atmosphere resulted in increase in the values of O/C.

4. Conclusions

Woody biomass (*Leucaena Leucocephala*) was torrefied at 220, 240, and 260 ^{o}C under the oxygen concentration of 2, 5, 10, and 22 %. The gas formation rate during the torrefaction under the different oxygen concentrations was also examined in detail by using TG-MS technique. It was found that only H_2O, CO, and CO_2 were formed during the torrefaction at 260 ^{o}C. At 220 ^{o}C the increase in oxygen concentration slightly increase the weight loss during torrefaction. On the other hand, the oxygen concentration affected significantly the weight loss during torrefaction at 260 ^{o}C. At 260 ^{o}C, the high oxygen concentration affected significantly the chemical properties of the torrefied biomass. From the elemental analyses of the torrefied leucaena, the torrefaction at 260 ^{o}C under the oxygen atmosphere was different from the torrefaction at 240 ^{o}C. It was suggested that the oxidation reaction proceeded at torrefaction at 260 ^{o}C under oxygen atmosphere resulted in increase in the values of O/C. The results obtained from the study provide the basic information for the design of torrefaction process.

References

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