Effects of oxygen concentration on the torrefaction of woody biomass at temperatures below 300°C

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Abstract:
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. However, raw biomass has many drawbacks when compare with fossil fuel such as petroleum oil or coal. Firstly, biomass has low energy density. Secondly, fibrous nature of biomass causes the difficulty in size reduction. So, many techniques have been proposed to reduce those drawbacks and to improve the properties of biomass such as briquetting, biochar, bioslurry 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 a pre-treatment technique, usually preformed in inert atmosphere at temperature below 300°C.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. However, few studies have been conducted to examine the effect of oxygen concentrations at temperature below 300°C. 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. 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.

Keywords: *Biomass; Pyrolysis; Gasification; Torrefaction; Oxygen concentration*

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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, raw biomass has many drawbacks when compare with fossil fuel such as petroleum oil or coal. So, many techniques have been proposed to reduce those drawbacks and to improve the properties of biomass such as briquetting, biochar, bioslurry 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 a pre-treatment technique, usually preformed in inert atmosphere at temperature below 300°C (Stelt et al., 2011). The properties of the torrefied biomass are influenced by several parameters such as types of biomass, torrefaction temperature, holding time, heating rate, pressure, etc. (Wannapeera et al., 2011). Although torrefaction is one of the most promising methods to improve lignocellulosic solid fuels, the procedure requires thermal energy and inert atmosphere. If it is possible to use flue gas from burners, inert gas and a considerable quantity of energy could be saved. So, it is necessary to investigate the torrefaction in the presence of oxygen because flue gas contains varying quantities of oxygen. However, few studies have been conducted to examine the effect of oxygen concentration on the torrefaction at temperature below 300°C. 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 effects of oxygen concentration during the torrefaction on the properties of the torrefied biomass were examined in detail.

2. Experimental

2.1 Material

Leucaena Leucocephala from Saburi province was used as a sample in this study. It was shredded

with cutting mill in order to obtain the desired particle size less than 2 mm. Then, it was dried in vacuum oven at 70°C for 24 hours before the experiment.

2.2 Torrefaction Experiment

The vertical quartz tube reactor was used to torrefaction. About 30 mg of sample was placed on the quartz wool located at middle of reactor (O.D. 10 mm), which the sample particle size is less than 2 mm. The carrier gas (helium, 2%, 5%, 10% and 22% oxygen balance in helium) was then purge through the reactor at the flow rate of 50 ml/min. Then 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 gas bag was injected to the gas chromatography (Shimadzu, GC-14B) to analyze the gaseous products. After cooling down to room temperature, the solid product or torrefied samples were weighed to measure the yield of torrefied sample.

2.3 Gas product analysis by TG-MS technique.

The torrefaction experiment were performed in a sensitive thermobalance (Perkin-Elmer, Pyris1 TGA) at heating rate 10°C/min up to a final temperature of 260°C under the different oxygen concentration as 0% (helium), 2%, 5%, 10% and 22% at the flow rate of 50mi/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. The signal for mass numbers of 2, 15, 18, 28 and 44 were continuously detected. Then the mass numbers were converted to the concentration 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

3.1Weight changes during torrefaction

Fig. 1 shows the TGA curves during the torrefaction of leucaena under different oxygen concentrations at 220 – 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.

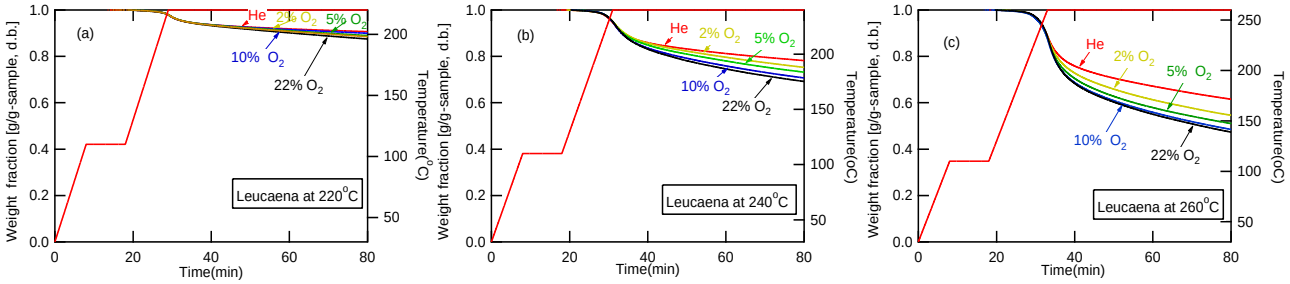

Fig.1 TGA curves of Weight changes of leucaena during torrefaction by varying oxygen concentration (a) 220°C, (b) 240°C and (c) 260°C.

3.2 Ultimate analyses of torrefied leucaena

The ultimate analyses and the higher heating values (HHVs) of the torrefied leucaena at various conditions were shown in Table 1. It was found that the carbon content of torrefied leucaena tend to be increased with oxygen concentration at each temperature except for 22% of oxygen concentration. While, the oxygen content of the torrefied leucaena was slightly decreased with increasing oxygen concentration at 220°C and decreased significantly at higher temperature as 240°C and 260°C. These changing of elemental compositions brought about the obvious increase in the HHV.

Table 1 Ultimate analysis of raw and torrefied leucaena and calorific value

Sample	Oxygen Concentration [%]	Ultimate Analysis [%wt, d.b.f.]				HHV [MJ/kg, d.b.]
		C	H	N	O(diff)	
Raw leucaena		46.9	6.1	0.7	46.3	18.6
Torrefied leucaena 220˚C 30 min	0 (He)	47.7	6.0	0.7	45.6	19.0
	2	48.2	6.0	0.7	45.0	19.2
	5	49.2	6.0	0.7	44.1	19.6
	10	49.7	6.0	0.7	43.6	19.8
	22	48.5	6.0	0.7	44.8	19.3
Torrefied leucaena 240˚C 30 min	0 (He)	49.3	6.0	0.7	44.0	19.6
	2	49.4	6.0	0.7	43.9	19.7
	5	50.4	6.0	0.7	42.9	20.1
	10	51.5	6.0	0.7	41.8	20.1
	22	48.6	6.0	0.7	44.7	19.3
Torrefied leucaena 260˚C 30 min	0 (He)	51.7	6.0	0.7	41.6	20.7
	2	52.4	6.0	0.7	40.9	21.0
	5	53.4	6.0	0.8	39.8	21.5
	10	53.2	5.5	0.8	40.5	21.2
	22	52.4	5.2	0.9	41.6	20.7

3.3 Carbon distribution

Fig. 2 shows the carbon distribution of the torrefaction products under different oxygen concentrations at 220 – 260°C. At 220°C, the oxygen concentration did not affect significantly the carbon distribution: the carbon content in the solid decreased from 92.0% to 89.9% when the oxygen concentration increased from 0% to 22%. On the other hand, at 260°C the carbon content in the solid decreased from 82.7% to 70.1% when the oxygen increased from 0% to 22%. These results clearly show that the oxygen concentration affected significantly the carbon content of torrefied leucaena at 260°C.

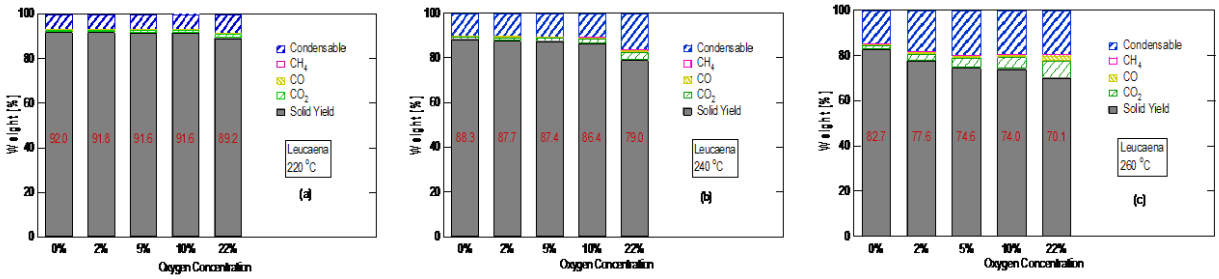

Fig.2 Carbon distribution of torrefaction leucaena (a) 220°C, (b) 240°C, and (c) 260°C.

3.4 Analysis of gas formation rate during torrefaction by TG–MS technique

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 the torrefaction at 260°C of leucaena under He, 5% oxygen, and 22% oxygen were shown in Fig.3. 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. The weight of leucaena started to decrease at temperature above 180°C and decreased rapidly at around 200°C to 260°C. After that, the weight decreased gradually when increasing the holding time for all oxygen concentration. The gas formation rates increased with the increase in oxygen concentration. The amount of H_2O increased from 13.5 g/(100g sample) to 20.1 g/(100g sample) when increase the oxygen concentration from 0% (helium atmosphere) to 22%. The amount of CO_2 increased from 3.5 g/(100g sample) to 16.2 g/(100g sample) 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 the torrefaction at 260°C.

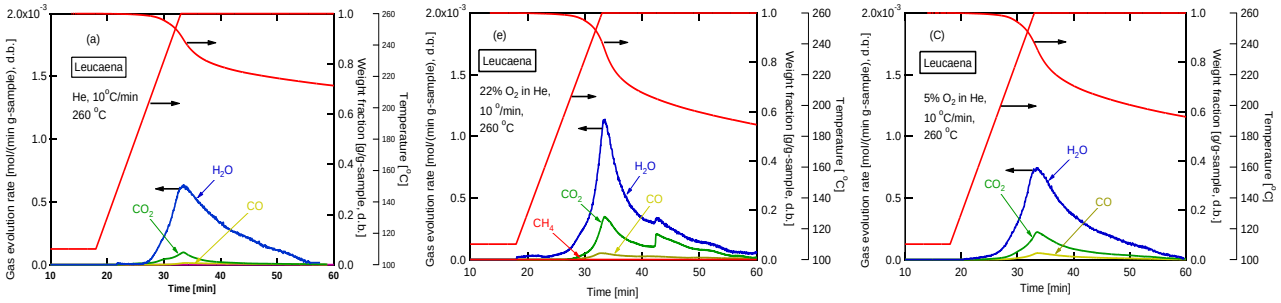

Fig.3 TG-MS curve (x-1) during torrefaction at 260°C of leucaena by varying oxygen concentration: (a) 0%, (b) 5%, and (c) 22%

4. Conclusion

Leucaena was torrefied at 220, 240 and 260°C under the oxygen concentration of 0%(helium), 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. At 220°C the increase in oxygen concentration slightly increases the weight loss during torrefaction. On the other hand, the oxygen concentration affected significantly the weight loss during torrefaction at 260°C.The oxygen concentration did not affect significantly the carbon distribution of the product at 220°C. On the other hand, at 260°C the carbon content in the solid significantly with the increase in oxygen concentration. From the elemental analyses of the torrefied leucaena, 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. The results obtained from the study provide the basic information for the design of torrefaction process.

5. Acknowledgment

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6. References

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