อิทธิพลของอุณหภูมิของทอร์รีแฟกชันต่อสมบัติน้ำมันชีวภาพจากไม้กระถินยักษ์

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บทคัดย่อ

ชีวมวลเป็นแหล่งพลังงานหมุนเวียนสำคัญที่ได้มาจากกลไกของสิ่งมีชีวิต เช่น กระบวนการสังเคราะห์แสงของพืช เนื่องจากในชีวมวลมีปริมาณซัลเฟอร์และไนโตรเจนต่ำ กระบวนการไพโรไลซิสเป็นอีกหนึ่งวิธีที่สามารถเปลี่ยนพลังงานที่อยู่ในชีวมวลให้อยู่ในรูปของน้ำมัน ซึ่งง่ายต่อการจัดเก็บและขนส่ง อย่างไรก็ตามมีงานวิจัยก่อนหน้าได้ทำการศึกษาคุณสมบัติของน้ำมันที่ได้จากชีวมวลและรายงานถึงข้อด้อยเมื่อเปรียบเทียบกับน้ำมันเชื้อเพลิงทั่วไป ได้แก่ ค่าความร้อนต่ำ ความเป็นกรดสูง ไม่สามารถผสมกันได้กับน้ำมันเชื้อเพลิงทั่วไป ความหนืดสูง และความไม่เสถียรทางเคมี เป็นต้น ซึ่งคุณสมบัติเหล่านี้เป็นผลจากปริมาณออกซิเจนที่อยู่ในชีวมวลมีปริมาณมาก แต่อย่างไรก็ตาม เป็นที่รู้กันอย่างแพร่หลายว่ากระบวนการทอร์รีแฟกชันที่อุณหภูมิต่ำกว่า 300 องศาเซลเซียส เป็นวิธีที่สามารถช่วยลดปริมาณออกซิเจนในชีวมวลได้ ดังนั้นในงานวิจัยนี้จึงได้ทำการศึกษาอิทธิพลของกระบวนการทอร์รีแฟกชันต่อกระบวนการผลิตน้ำมันชีวภาพจากไม้กระถินยักษ์ (*Leucaena leucocephala*) จากการวิจัยพบว่าปริมาณออกซิเจนในกระถินยักษ์ลดลงจากร้อยละ 46.2 เป็น 37.3 โดยน้ำหนัก เมื่อผ่านกระบวนการทอร์รีแฟกชันที่ 295 องศาเซลเซียส ในขณะที่ผลผลิตของกระถินยักษ์ที่ผ่านกระบวนการทอร์รีแฟกชันมีปริมาณลดลงเมื่ออุณหภูมิของกระบวนการทอร์รีแฟกชันสูงขึ้น หลังจากนั้นกระถินยักษ์ที่ผ่านกระบวนการทอร์รีแฟกชันแล้วจะนำมาผ่านกระบวนการไพโรไลซิสที่อุณหภูมิ 550 องศาเซลเซียส เพื่อผลิตน้ำมันชีวภาพ โดยพบว่า ปริมาณคาร์บอนที่อยู่ในกระถินยักษ์หลังผ่านกระบวนการไพโรไลซิสมีค่ามากขึ้น ในขณะที่ปริมาณออกซิเจนมีค่าลดลง เมื่อนำน้ำมันชีวภาพมาวิเคราะห์ด้วยวิธีการสกัดด้วยตัวทำละลาย (Fractionation) ซึ่งจะแยกน้ำมันชีวภาพเป็นน้ำมันเบา (Light oil) และน้ำมันหนัก (Heavy oil) โดยนำน้ำมันเบามาวิเคราะห์ด้วยเทคนิค GC-MS พบว่าปริมาณกรดอะซิติก (acetic acid) และฟูแรน (furans) ที่อยู่ในน้ำมันเบามีค่าลดลงเมื่ออุณหภูมิของกระบวนการทอร์รีแฟกชันเพิ่มขึ้น และยังพบว่าน้ำมันชีวภาพมีความเป็นกรดลดลง ซึ่งจะสอดคล้องกับการลดลงของปริมาณกรดอะซิติกในน้ำมันเบา จากผลทั้งหมดนี้บ่งชี้ว่า กระบวนการทอร์รีแฟกชันไม่เพียงแต่สามารถปรับปรุงคุณสมบัติของน้ำมันชีวภาพให้ดีขึ้น แต่ยังมีผลต่อคุณสมบัติของชีวมวลหลังผ่านกระบวนการไพโรไลซิสอีกด้วย

คำสำคัญ : กระบวนการทอร์รีแฟกชัน / กระบวนการไพโรไลซิส / กระถินยักษ์ / น้ำมันชีวภาพ

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Effect of Torrefaction Temperatures on Bio-Oil Properties from *Leucaena leucocephala*

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Abstract

Biomass is an important source of renewable energy which is derived from the living mechanism such as photosynthesis of plant due to the lower contents of sulfur and nitrogen in the biomass. Pyrolysis is a technology that can directly produce a liquid fuel from biomass which can be readily stored or transported. However, many researches have reported the negative properties of the bio-oils compare with the conventional fuel oil. The undesirable properties of the bio-oils included low heating value, low pH value, incompatibility with conventional fuels, high viscosity, and chemical instability. These undesirable properties of the bio-oils are mainly brought about by the high oxygen content in the biomass. On the other hand, it is known that the oxygen content in the biomass could be reduced by the torrefaction at the temperatures below 300 °C. So, in this work, the effect of torrefaction at difference conditions on bio-oil production from Leucaena leucocephala was studied. It was found that the oxygen content of leucaena decreased from 46.2 wt% to 37.3 wt% when torrefy at 295 °C whereas the torrefied leucaena yields decreased with the increase in torrefaction temperature. Then, the torrefied leucaena was pyrolysed at 550 °C to produce bio-oils. The bio-oils were then fractionated into light oil and heavy oil fractions. Light oil fraction was analyzed by GC-MS technique to examine the effect of torrefaction on the bio-oils properties. It was found that acetic acid and furans were decreased in light oil fraction with the increase in torrefaction temperature. The decrease in acetic acid in the bio-oils resulted in the increase of the pH value of bio-oils. Moreover, it was found that carbon content in solid char increased while the oxygen content slightly decreased with the increase in torrefaction temperature. These results indicated that not only torrefaction process could improve bio-oils properties prior pyrolysis process but also affected the properties of solid char.

Keywords : Torrefaction / Pyrolysis / *Leucaena leucocephala* / Bio-oils

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1. Introduction

Biomass was the main source of energy in the form of fire wood and charcoal since the 19th century, but was replaced by coal and oil in the 20th century. Fossil fuels that include coal, petroleum, and natural gas are non-renewable energy because they take a long time to form. They have been consumed as industrial fuels. Recently, renewable energy is becoming more important because fossil fuels reserves are gradually being depleted and their use of fossil fuel raises environmental concerns [1]. Biomass can be converted into energy by various ways such as providing heat energy from combustion for use in steam production, fuel gas from gasification for heat in engines and turbines for electricity generation, and liquid fuel from pyrolysis. Pyrolysis is thermal decomposition process that takes place in the absence of oxygen, which aim to produce the liquid fuel or the so-called bio-oil. As a result, biomass decomposes to generate mostly vapors, aerosols and some charcoal. Bio-oil is dark brown liquid which depends on type of feedstock and mode of pyrolysis The liquid product has a heating value about half that of conventional fuel oil [2]. However, many researchers have reported the negative properties of the bio-oil compare with the conventional fuel oil [2, 3]. The undesirable properties of the bio-oils included low heating value, low pH value, incompatibility with conventional fuels, high viscosity, and chemical instability [4, 5]. The oxygen content in the bio-oil is 40-45 wt% on a dry-ash free basis. The high oxygen content leads to a low heating value of 16-19 MJ/kg, which is less than conventional fuels that have a heating value between 40 and 44 MJ/kg.

In this study, *Leucaena leucocephala* was used as sample. Leucaena is considered as a potential energy crop with a very high yield (30 – 35 ton/ha/year). Pretreatment or upgrading of raw biomass before further utilization is an alternative way to increase its energy density and improve the combustion properties. Torrefaction of biomass can be described as a mild treatment at low temperature. This mild temperature pyrolysis process allows moisture to be removed and causes partial endothermic decomposition of the chemical structure of the biomass, causing it to develop more favorable physical, chemical and thermal fuel properties. Although there is much research on the torrefaction of biomass, most of them are aimed to upgrade the solid fuel properties of biomass. So far, little work has been performed to study the effects of torrefaction on the production and the properties of bio-oils. So, this study, the biomass was first upgraded by torrefaction at below 300°C. Then, the torrefied biomass was pyrolyzed to produce the bio-oils. It was expected that the oxygen content in the bio-oils produced from the torrefied biomass would decreased, and the properties of the bio-oils produced would be improved.

2. Procedure

2.1 Materials

Leucaena leucocephala was used in this study as a studied biomass. The raw biomass was cut and milled into fine particles by using cutting mill and ball mill. The particle size is less than 75 μm for the experiments for proximate and ultimate analysis. The particle size range 75-150 μm was used for chemical compositions analysis and pyrolysis experiment. The biomass selected was less than 1 cm for torrefaction process in a fixed-bed reactor. The sized biomass samples are dried in a vacuum oven at 70°C for 24 hours before the experiments and analyses.

2.2 Torrefaction experiments

Fig.1 (A) shows the schematic diagram of torrefaction experiment. The reactor was placed inside a tubular electric furnace with 35 cm in length and 12 cm in internal diameter, connected to a temperature and heating control system. The bed was vertically positioned into the reactor. The sample of raw biomass was packed in a stainless steel mesh (200 µm) holder with a diameter of 10 cm and a height of 25 cm. The sample temperatures were measured by means of four type K thermocouples introduced through the top flange of the reactor. These data were collected by a data collector. Fig.1 (B) shows the detail position of the thermocouples in the sample holder. The temperature controls were achieved by means of a PID controller which regulated the output power of the furnace.

About 200 g of sample was uniformly distributed inside the sample basket and placed in the uniform heated zone of the reactor prior to the experiment. The lid of the reactor was closed and nitrogen flow rate of 5 L NTP/min was set by means of a mass flow controller. The nitrogen flow rate was maintained for 30 min in order to remove the air from the reaction chamber to ensure inert condition. The sample was heated from room temperature to 260°C and 295 °C with a rate of 10 °C min^{-1} under a nitrogen atmosphere. The desired temperature was held for each condition. The gas leaving from the torrefaction reactor was cooled by using two lines of condensers series in ice bath, where most of the tar and water were collected.

2.3 Pyrolysis experiments

The schematic diagram of experimental set-up of pyrolysis process is shown in Fig.2. A quartz tube was used as a reactor which is 3.5×10^{-2} m in diameter and 6×10^{-1} m in length. The temperature of the reactor was controlled by temperature controller which was linked to the thermocouple that was inserted in the same position with the sample bed. In an experiment, about 5 g of oven dried samples with particle size between 75-150 µm was packed in a wire mesh basket. The sample was placed on the middle of the quartz tube and heated from room temperature to 550°C with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. The nitrogen flow rate of 400 mL min^{-1} was maintained 30 min before starting the experiment to ensure inert condition. The gas leaving from the pyrolysis reactor was condensed by using condensing unit; maintaining below -10°C in salt-ice bath, where most of the bio-oil was collected.

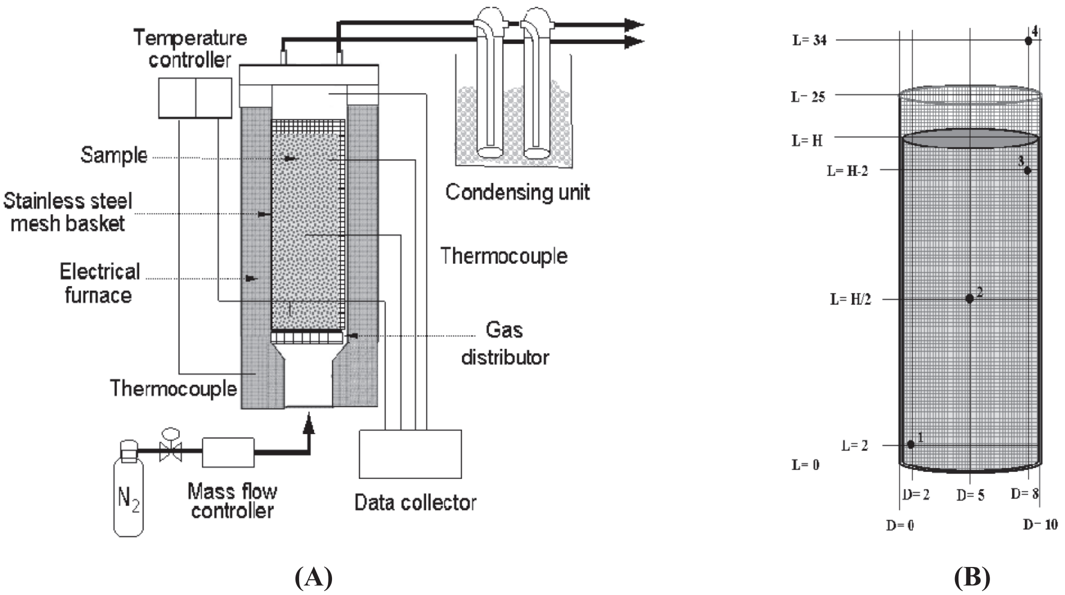


Fig. 1 (A) Experimental system for torrefaction experiments,
(B) Scheme of basket and position of thermocouples inside the sample
(L = height; H = sample height; D = diameter, cm)

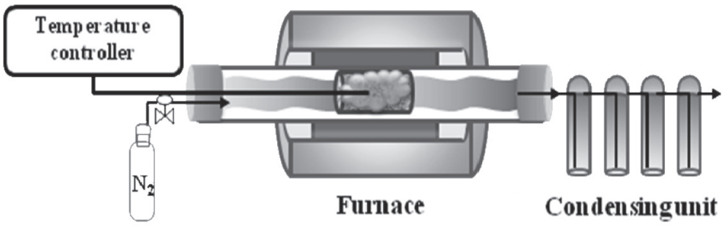


Fig. 2 Schematic diagram of experimental set-up of pyrolysis experiment

2.4 Analyses

Proximate analysis

The thermobalance (Perkin-Elmer, Pyris1 TGA) was used to analyze the proximate analysis. Approximately 5 mg of sample was used for this purpose. The sample was initially heated to 110°C under the flow of nitrogen (99.999% purity) with a rate of 10°C min^{-1} and 50 ml min^{-1} and hold for 10 min. After that the sample was heated to 900°C in order to quantify volatile matter. At 900°C, the N_2 gas was switched to air atmosphere in order to quantify the fixed carbon content and ash content.

Ultimate analysis

The ultimate analysis gives the composition of the biomass in percent by weight (wt %) of carbon (C), hydrogen (H), oxygen (O), sulfur (S), and nitrogen (N). Dried ground biomass was analyzed in the CHONS analyzer (Thermo Finnegan Flash 1112 series). The oxygen content is traditionally determined by subtracting the sum of other chemical element. In this technique, a sample is burned in excess of oxygen, and various traps collect the combustion products.

Fractionation of bio-oils

Bio-oils were fractionated by using of *n*-pentane. About 8 g of bio-oils were fractionated by 400 ml of *n*-pentane. In this study, the *n*-pentane soluble fraction was called light oil and the *n*-pentane insoluble fraction was called heavy oil.

GC/MS Analysis

GC/MS analyses were used to determine the compounds in the pyrolysis liquid. Analyses were carried out in gas chromatograph (Perkin-Elmer, Clarus 500 GC) coupled with quadrupole mass spectrometer (Perkin-Elmer, Clarus 500 MS), using Restek®-1701 column. The separation column was heated from 50 °C to 250 °C with a heating rate of 5 °C min^{-1}. The injector temperature and detector temperature were 250 °C.

3. Results and discussion

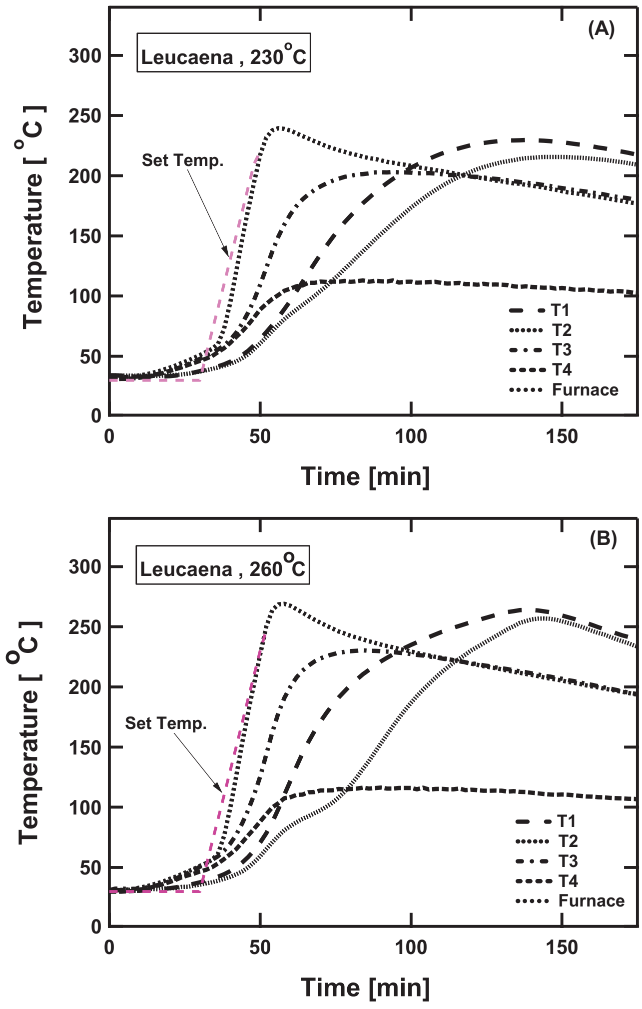
3.1 Examination of torrefaction of leucaena

Table 1 shows ultimate analyses, calorific values, chemical composition and proximate analyses of raw leucaena. From the ultimate analyses, raw leucaena has low carbon and high oxygen content that results in its low calorific value. From the proximate analyses, raw leucaena has very high amount of volatile matter while ash content is quite low.

Table 1 Ultimate analyses, calorific values chemical composition and proximate analyses of raw leucaena

Ultimate analysis (wt%, d.a.f)	
C	46.7
H	6.0
N	1.1
O	46.2
HHV (MJ/kg, d.a.f)	18.66
Chemical compositions (wt%, d.a.f)	
Extractive	8.0
Hemicellulose	31.8
Cellulose	3.1
Lignin	27.2
Proximate analyses (wt%, d.b.)	
Volatile matter	85.9
Fixed carbon	13.7
Ash	0.4

Next, we will examine the torrefaction reaction of leucaena. Fig. 3 shows the temperature profiles inside the reactor during the torrefaction of leucaena. It was found that the different positions provided the different temperatures. The temperature of furnace had the highest heating rate that increased to set temperature while temperature of sample had slightly change. The temperature at T1 (bottom bed) increased to desired torrefaction temperature with heating rate approximately 2 °C min^{-1} and held at desired torrefaction temperature approximately 30 min. Even though the temperature of furnace decreased after it was increased to a set temperature, sample's temperature could increase to desired torrefaction temperature. It was suggested that torrefaction process is an exothermic process which is difficult to control the temperature of the process [6]. However, when torrefaction reactions occur, the heat releasing from reaction could transfer to unreacted biomass and slowly underwent torrefaction reactions.



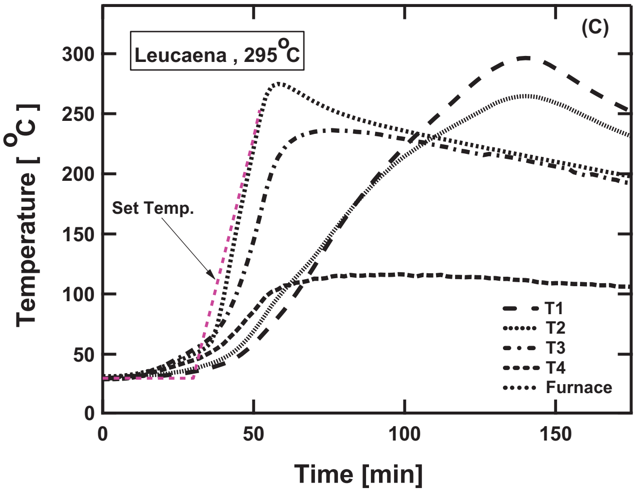


Fig. 3 Temperature profiles during the torrefaction of leucaena at 230°C (A), 260°C (B), and 295°C (C)

Table 2 shows the yields of product during the torrefaction of leucaena at 230°C, 260°C and 295°C. It was found that the yield of torrefied leucaena decreased with the increase in torrefaction temperature: it decreased from 86.5% to 69.6% when increase the torrefaction temperature from 230°C to 295°C. On the other hand, the yield of liquid slightly increased when increased the torrefaction temperature from 230°C to 295°C. The yield of gas during the torrefaction increased monotonously with the increase in torrefaction temperature.

Table 2 Product distribution through the torrefaction of raw leucaena.

Leucaena leucocephala	Yield [wt%]		
	Solid	**Liquid**	**Gas**
230 °C	86.5	5.3	8.2
260 °C	81.4	8.6	10.0
295 °C	69.6	14.9	15.5

3.2 Analyses of products from torrefaction

Analyses of torrefied leucaena

The proximate and ultimate anlyses of the torrefied leucaena at 230°C, 260°C and 295°C are shown in Table 3. It was found that the volatile matter as well as the oxygen content decreased significantly with the increase in torrefaction temperature.

On the other hand, the fixed carbon and the carbon content increased with the increase in torrefaction temperature. For example, the oxygen content of leucaena decreased from 46.2% to 37.3%

when it was torrefied at 295°C resulting in the calorific values of 22.6 MJ/kg. This result indicated that the calorific value of the leucaena could be increased more than 20% when torrefaction at 295°C.

GC-MS analysis of liquid from torrefaction

The liquid products produced from torrefaction were analyzed by GC-MS technique. Fig. 4 show that the GC-MS chromatogram of the liquid produced from torrefaction. The results showed that the acetic acid was the main component in the liquid products for all studied biomass samples. The main peaks were acetic acid and acetic anhydride, which were observed at retention times of 8-10 min and then 2 furan, tetrahydro-5-methanol was also observed at retention time of 14 min.

Table 3 Proximate, ultimate analyses and calorific values of torrefied biomass samples.

Leucaena	Proximate analyses [wt%, d.b.]			Ultimate analyses [wt%, d.a.f.]				O/C	H/C	HHV [MJ/kg, d.a.f.]
	Volatile matter	Fixed carbon	Ash	C	H	N	O			
Raw	85.9	13.7	0.4	46.7	6.0	1.1	46.2	0.74	1.54	18.7
230 °C	84.5	14.2	1.3	49.2	6.1	0.8	43.9	0.67	1.49	19.7
260 °C	75.7	21.8	2.5	50.6	5.9	0.8	42.7	0.63	1.40	20.2
295 °C	69.7	27.5	3.8	56.0	5.8	0.8	37.4	0.50	1.24	22.6

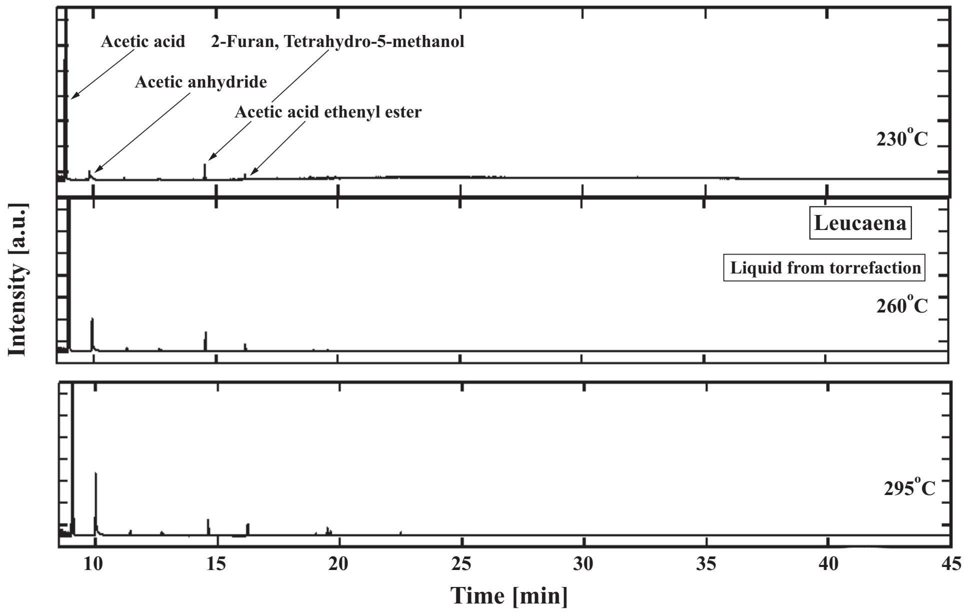


Fig. 4 GC-MS chromatograms of liquid produced from leucaena by torrefaction

3.3 Examination of pyrolysis of raw and torrefied leucaena

Next, we will examine the pyrolysis of raw and torrefied leucaena. Fig. 5 shows the yields of products during the pyrolysis of raw leucaena at temperature 450 °C - 600°C. It was found that the yield of pyrolysis liquid increased with the increase in pyrolysis temperature, had maximum at 550°C and then decreased with the further increase in pyrolysis temperature. The yield of pyrolysis liquid at 550°C was 52.1% for raw leucaena. On the other hand, the yield of solid decreased monotonously with the increase in pyrolysis temperature: it decreased from 29.7% to 26.7% when increase the pyrolysis temperature from 450°C to 600°C. The gas yield increased monotonously with the increase in pyrolysis temperature. The increase in gas yield during this range of temperature may be brought about by the decomposition of liquid product as found from the decrease in liquid yield. These results indicated that the optimum pyrolysis temperature for producing bio-oils from leucaena was 550°C. So the bio-oils were produced by pyrolysis at 550°C. The previous works also reported that the optimum pyrolysis temperature for biomass was 550°C [7-9]

The effects of torrefaction on the pyrolysis of leucaena were then examined. Table 4 shows the yields of pyrolysis products during the pyrolysis of raw and torrefied leucaena at 550°C. It was found that the yield of pyrolysis liquid decreased with the increase in the torrefaction temperature: it decreased from 52.1% for raw leucaena to 36.0% for the leucaena torrefied at 295°C. On the other hand, the solid yields increased with the increase in the torrefaction temperature: it increased from 27.5% for raw leucaena to 42.4% for leucaena torrefied at 295°C. To compare with the raw leucaena, the yield was also calculated as wt% of raw leucaena and was shown in Table 4. The pH of the bio-oils produced from the pyrolysis of raw and torrefied leucaena were also shown in Table 4. The pH of the bio-oils was measured by electronic pH meter (Methrom). It was found that the pH of the bio-oils slightly increased with the increase in torrefaction temperature: it increased from 2.7 for bio-oils produced from raw leucaena to 3.1 for bio-oils produced from leucaena torrefied at 295°C. This result indicated that the bio-oils produced from the torrefied leucaena have less acidity compared with the bio-oils produced from raw leucaena.

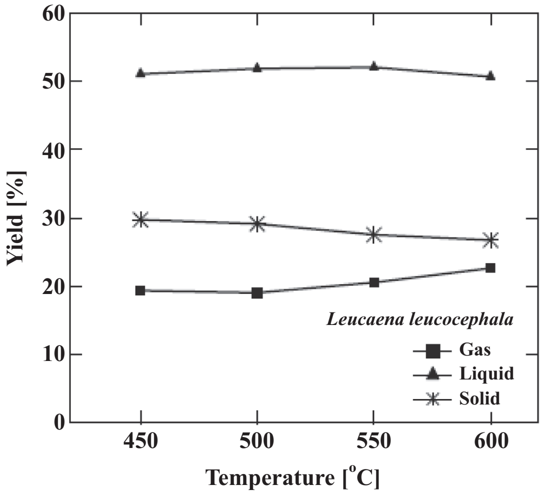


Fig. 5 Yield of products during pyrolysis from raw leucaena at various temperature

Table 4 Yields of pyrolysis products during the pyrolysis of raw and torrefied leucaena at 550°C

Leucaena	Yield [wt%]			Yield [g/100 g raw leucaena]			pH of bio-oil
	Solid	Liquid	Gas	Solid	Liquid	Gas	
Raw	27.5	52.1	20.4	27.5	52.1	20.4	2.7
230 °C	29.8	45.0	25.2	26.1	38.9	21.8	2.7
260 °C	32.4	44.4	23.2	26.7	36.1	18.9	2.8
295 °C	42.4	36.0	21.6	29.9	25.1	15.0	3.1

3.4 Analyses of products from pyrolysis

Analyses of solid char

Solid char was characterized by ultimate analysis as shown in Table 5. It was found that carbon content increased with the increase in torrefaction temperature. On the other hand, the oxygen content slightly decreased with the increase in torrefaction temperature. It was also found that the yield of char (raw leucaena basis) prepared from leucaena torrefied at 295°C was higher than that of the char prepared from raw leucaena.This result can be explained by the cross-linking reaction. It has been reported in the previous study that the structure of leucaena was changed by the torrefaction at temperature below 300°C and the cross-linking reactions occurred during the pyrolysis resulting in increase in char yields [10].

Fractionation of bio-oils produced from torrefied leucaena

The fractionations of bio-oils produced from torrefied leucaena were examined. Table 6 shows the results of fractionation of bio-oils produced from pyrolysis of raw and torrefied leucaena at 550°C. It was found that the yield of light oil increased with the increase in torrefaction temperature: it increased from 17.1% for bio-oil produced from raw leucaena to 25.7% for bio-oil produced from leucaena torrefied at 295°C. On the other hand, the yield of heavy oil decreased with the increase in torrefaction temperature: it decreased from 25.5% for bio-oil produced from raw leucaena to 9.0% for bio-oil produced from leucaena torrefied at 295°C. These results indicated that the light oil fraction in the bio-oils could be increased by the torrefaction of leucaena before the pyrolysis. The yield of water in the bio-oil was slightly increased with the increase in torrefaction temperature.

Table 5 Ultimate analysis of solid char from pyrolysis at 550°C

Leucaena	Ultimate analyses [wt%, d.a.f]				Yield of solid char [wt%, d.a.f]
	C	H	N	O	
Raw	80.4	2.6	1.0	15.9	27.5
230 °C	78.1	2.7	1.1	18.1	26.1
260 °C	80.6	2.7	1.1	15.5	26.7
295 °C	82.2	3.0	1.1	13.7	29.9

Table 6 Fractionation results of bio-oils produced by pyrolysis of raw and torrefied leucaena at 550°C

Leucaena	Fractions of bio-oils [wt%]		
	Light oil	**Heavy oil**	**Water**
Raw	17.1	25.5	57.5
230 °C	19.1	23.0	57.9
260 °C	25.9	13.1	61.0
295 °C	25.7	9.0	65.3

GC/MS analyses of bio-oil produced from torrefied leucaena

The bio-oils produced from torrefied leucaena were analyzed by using GC-MS technique. Fig. 6 shows the GC-MS chromatograms of the bio-oils produced from raw and leucaena torrefied at 230°C, 260°C and 295°C. It was found that the GC-MS chromatogram of the bio-oils was quite complex and the bio-oil consist of many oxygenated compounds such as organic acid, phenols, furans, etc. It is quite difficult to study the effect of torrefaction on the quality of the bio-oils by analyzing the GC-MS chromatograms of the bio-oils. So, we will examine the effect of torrefaction on the quality of bio-oils by analyzing the GC-MS chromatograms of light oil fraction. Fig. 7 shows the GC-MS chromatograms of the light oil fraction of the bio-oils produced from raw and leucaena torrefied at 230°C, 260°C and 295°C. It was found that the amount of acetic acid and 2, 5-dimethyl furan in the light oil fraction of bio-oils produced from the torrefied leucaena was less than that of the light oil fraction of bio-oils produced from raw leucaena. This result was consistent with the increase in pH values of the bio-oils produced with the torrefied leucaena as shown in Table 4. Moreover, the GC-MS chromatogram of the light oil fraction produced from leucaena torrefied at 295°C was less complex than that of the light oil fraction produced from raw leucaena. These results suggested that the properties of bio-oils could be improved by the torrefaction pre-treatment prior to pyrolysis.

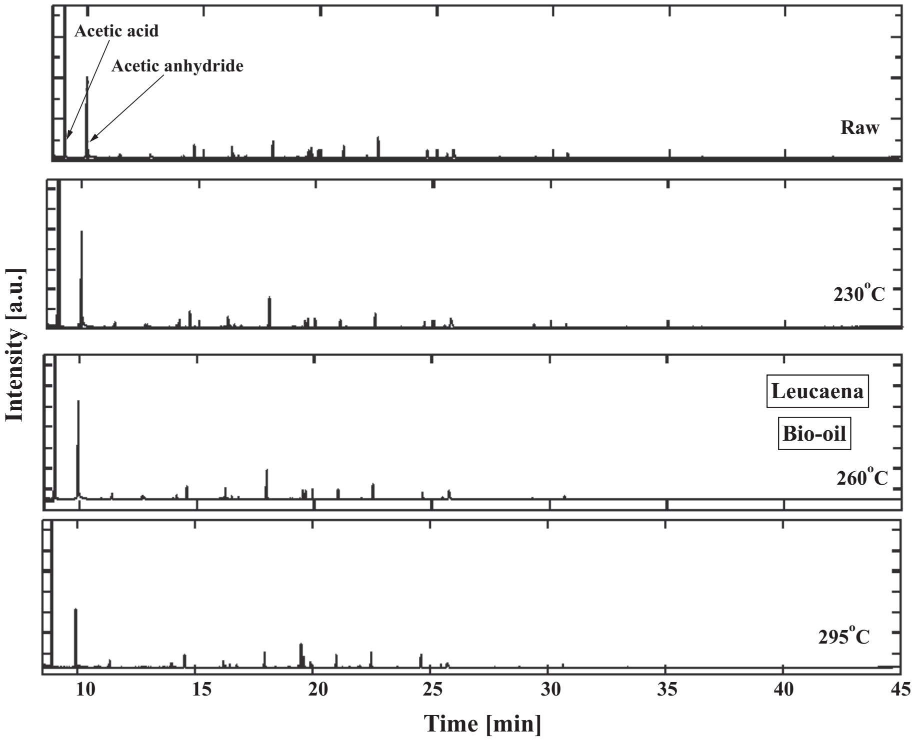


Fig. 6 GC-MS chromatograms of bio-oils produced from raw, torrefied leucaena at 230, 260 and 295°C

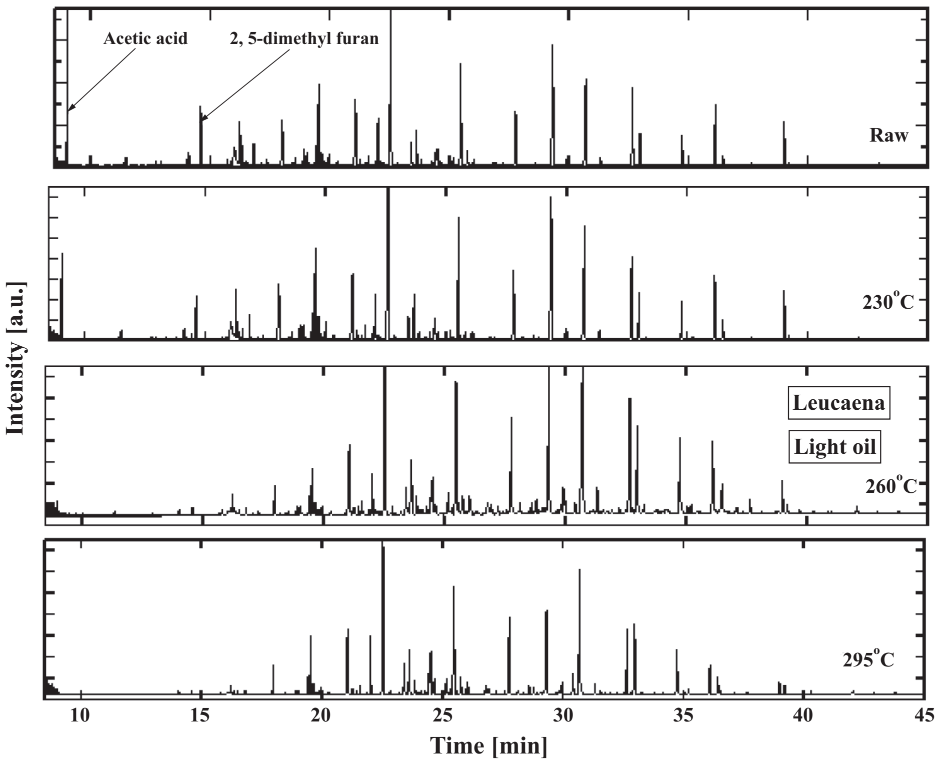


Fig. 7 GC-MS chromatograms of light oil fractions produced from raw, torrefied leucaena at 230°C, 260°C and 295°C.

4. Conclusion

Leucaena was torrefied in nitrogen atmosphere from 230°C to 295°C. Then, the torrefied leucaena was pyrolysed at 550°C to produce bio-oils. It was found that the oxygen content of leucaena decreased from 46.2 wt% to 37.3 wt% when torrefied at 295°C. The yield of torrefied leucaena decreased with the increase in torrefaction temperature: it decreased from 86.5% to 69.6% when increase the torrefaction temperature from 230°C to 295°C. The yield of bio-oil decreased with the increase in the torrefaction temperature: it decreased from 52.1% for raw leucaena to 36.0% for the leucaena torrefied at 295°C. The pH value of the bio-oils slightly increased with the increase in torrefaction temperature: it increased from 2.7 for bio-oils produced from raw leucaena to 3.1 for bio-oils produced from leucaena torrefied at 295°C. This result indicated that the bio-oils produced from the torrefied leucaena have less acidity compared with the bio-oils produced from raw leucaena. From the GC-MS analyses, it was found that the amount of acetic acid and 2, 5-dimethyl furan in the light oil fraction of bio-oils produced from the torrefied leucaena was less than that of the light oil fraction of bio-oils produced from raw leucaena. The carbon content in solid char increased with the increase in torrefaction temperature while the oxygen content slightly decreased with the increase in torrefaction temperature. These results suggested that the properties of bio-oils could be improved by the torrefaction pre-treatment prior to pyrolysis. Torrefaction affected the properties of solid char.

5. Acknowledgement

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6. Reference

1. Zhang, L., C. Xu, and Champagne, P., 2010, "Overview of recent advances in thermo-chemical conversion of biomass", *Energy Conversion and Management*, Vol. 51, No. 5, pp. 969-982.

2. Bridgwater, A.V., Meier, D., and Radlein, D., 1999, "An overview of fast pyrolysis of biomass", *Organic Geochemistry*, Vol. 30, No. 12, pp. 1479-1493.

3. Bridgwater, A.V., 1999, "Principles and practice of biomass fast pyrolysis processes for liquids", *Journal of Analytical and Applied Pyrolysis*, Vol. 51, No. 12, pp. 3-22.

4. Oasmaa, A. and Meier, D., 2005, "Norms and standards for fast pyrolysis liquids: 1. Round robin test", *Journal of Analytical and Applied Pyrolysis*, Vol. 73, No. 2, pp. 323-334.

5. Onay, O. and Kockar, O.M., 2003, "Slow, fast and flash pyrolysis of rapeseed", *Renewable Energy*, Vol. 28, No. 15, pp. 2417-2433.

6. Chen, W.-H. and P.-C. Kuo, 2011, "Torrefaction and co-torrefaction characterization of hemicellulose, cellulose and lignin as well as torrefaction of some basic constituents in biomass", *Energy*, Vol. 36, No. 2, pp. 803-811.

7. Putun, A.E., 2002, "Biomass to bio-oil via fast pyrolysis of cotton straw and stalk", *Energy Sources*, Vol. 24, No. 2, pp. 275-285.

8. Acikgoz, C., Onay, O., and Kockar, O.M., 2004, "Fast pyrolysis of linseed: product yields and compositions", *Journal of Analytical and Applied Pyrolysis*, Vol. 71, No. 4, pp. 417-429.

9. Onay, O., Beis, S.H., and Kockar, O.M., 2001, "Fast pyrolysis of rapeseed in a well-swept fixed-bed reactor", *Journal of Analytical and Applied Pyrolysis*, Vol. 58-59, No. 4, pp. 995-1007.

10. Wannapeera, J., Fungtammasan, B., and Worasuwannarak, N., 2011, "Effects of temperature and holding time during torrefaction on the pyrolysis behaviors of woody biomass", *Journal of Analytical and Applied Pyrolysis*, Vol. 92, No. 1, pp. 99-105.