Research paper

Characterization of Bio-oils from Fast Pyrolysis of Thorny Bamboo (*Bambusa stenostachya*) and Long-branch Bamboo (*B. dolichoclada*)

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【Summary 】

In this study, thorny bamboo (*Bambusa stenostachya*) and long-branch (*B. dolichoclada*) bamboo were integrated as feedstock to produce pyrolysis liquid (bio-oil) using fast pyrolysis technology, and the basic properties of the bio-oils were analyzed. Results showed that the higher heating value (HHV) of both bio-oils were 13.92 MJ/kg for thorny bamboo and 14.87 MJ/kg for long-branch bamboo, and both HHVs were relatively low for use as bioenergy. The bio-oils need to be reprocessed using upgrading technologies to promote the efficiency of energy utilization. However, both bio-oils were analyzed by gas chromatography mass spectrometry (GC-MS) and were shown to contain more than 80 different organic compounds with multifunctional groups. The major compounds in the bio-oil of long-branch bamboo were phenols with the largest proportion of >50%, and those of thorny bamboo included good distributions of phenols, carboxylic acids, and ketones. Both bio-oils are great potential resources beyond just a fossil fuel to provide various chemical compounds.

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Received August 2013, Accepted December 2013. 2013年8月送審 2013年12月通過。

研究報告

刺竹與長枝竹經快速裂解製備生質油之特性研究

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摘　要

本研究以台灣南部之刺竹(*Bambusa stenostachya*)與長枝竹(*B. dolichoclada*)為原料，應用快速熱裂解技術產製生質油，並分析其基本性質，評估其未來作為燃油或其它相關產品應用條件。研究結果顯示，刺竹裂解油之高熱值(HHV)為13.92 MJ/kg，長枝竹裂解油為14.87 MJ/kg，作為替代能源所需熱值略顯偏低，需透過改質技術提昇其應用於能源之效益。然刺竹與長枝竹生質油透過氣相層析質譜分析儀(GC-MS)分析結果，具有超過80餘項豐富之化學組成分，長枝竹生質油以酚類超過50％佔最大比例，刺竹生質油主要成分為酚類、羧酸類與酮類。此結果顯示，兩種竹生質油均具有替代化石燃料，提供生產化學產品之極佳潛力。

關鍵詞：快速熱裂解、生質油、生質材料、刺竹、長枝竹。

林裕仁、何振隆、吳森榮。2013。刺竹與長枝竹經快速裂解製備生質油之特性研究。台灣林業科學 28(4):203-16。

INTRODUCTION

It has become increasingly important to increase bioenergy utilization in the face of 2 crucial issues: fossil fuel over-exploitation which has caused the crisis of resource exhaustion and huge emissions of carbon dioxide derived from fossil fuel combustion which has caused global warming. These must be discussed together and simultaneously taken into consideration with economic development. Among the diverse renewable energy sources, bioenergy has the advantage of low investment costs compared to solar energy and wind power. In addition, bioenergy is a clean renewable energy due to its low emissions of sulfur dioxide and nitrides compared to conventional fossil fuels.

Biomass can be utilized to produce bioenergy, and it generally refers to organic matter produced by plants, including crops and agricultural wastes, such as soybeans, corn, rice husks, rice straw, fruit bars, bagasse, miscanthus, algae, etc. It also includes wastes derived from sawmills and processing plants for woody or bamboo products, such as sawdust, scraps, chips, discarded branches, and tops. However, according to the Taiwanese *Renewable Energy Development Act* promulgated by the Bureau of Energy, Ministry of Economic Affairs, in 2009, biomass is defined as "energy produced by utilizing or processing the agricultural and forest plants, biogas, and domestic organic wastes". Therefore, biomass resources may also include carcasses, biogas from waste water treatment in the livestock sector, organic sludge, waste rubber, waste paper, and black liquor from the industrial sector. According to new statistics of the International Energy Agency, bioenergy currently is the most widely utilized among various renewable energies. Bioenergy supplied approximately 9.8% of the world's total primary energy supply (TPES) and provided

about 35% of the energy in developing countries, where the direct burning of raw woody materials for household energy reached the highest percentage (Wu 2010).

To enhance the efficiency of bioenergy applications, applications of power generation and transportation fuel production need to be expanded from household utilization as energy for cooking and heating to direct combustion, and the rapid development of conversion technologies of biomass energy has become an important issue for energy development strategies for governments around the world. The economic benefits of conversion technologies of biomass energy, that adopt biomass waste as feedstock, will be particularly significant due to the dual function of waste disposal and energy recovery.

Among currently developed global conversion technologies, research and application to the production of pyrolysis oil (called bio-oil as well) by applying fast pyrolysis have been quite skillful, particularly in European countries. Fast pyrolysis can briefly be described as a thermochemical process for converting biomass in the absence of oxygen under a rapid heating process, with immediate quenching to generate bio-oil with two byproducts of bio-char and bio-gas (Wu et al. 2012). Fast pyrolysis possesses high economical benefits for bioenergy applications due to its following advantages: a low threshold of feedstock requirements, lower energy consumption in the process compared to other bioenergy conversion technologies, and a high production efficiency. Bio-oil can become boiler fuel after being blended with heavy oil, or fuel for diesel generators after being blended with diesel fuel. Furthermore, in practice, bio-oil has even been used instead of gasoline or diesel fuel for vehicles through appropriate upgrading technology.

Internationally, there has been much research investigating characteristics of bio-oils from fast pyrolysis from various biomass sources. In addition to woody biomass, various agricultural wastes have also been used for fast pyrolysis, such as rapeseed (Şensöz et al. 2000, Oasmaa et al. 2010), hazelnut shells (Koçkar et al. 2000), sunflower-oil cake (Gerçel 2002), cotton straw and stalks (Pütün 2002), cashew nut shells (Das et al. 2004), rice husks (Tsai et al. 2007), switchgrass (Boateng 2007), rice straw (Jung et al. 2008), palm kernel shells (Kim et al. 2010), etc. Abundant resources of thorny bamboo (*Bambusa stenostachya*) and long-branch bamboo (*B. dolichoclada*) are found in southern Taiwan. In the 1960s~1980s, prosperous bamboo-related industries flourished in the regional economy and greatly contributed to providing jobs and revenue to bamboo farmers, local communities, and the government. However, the industry declined due to soaring labor costs and high competition from cheaper imported products. Consequently, most processing factories shifted to China and Southeast Asia to reduce production costs since the 1980s. This led to quite low resource utilization of these 2 bamboos in the past few decades. It is a very unfortunate reality for large and valuable bamboo resources to be abandoned due to bad circumstances, and bamboo farmers can obtain no benefits from bamboo forest management. To resolve the dilemma of these long-term neglected bamboo resources, in this study, thorny bamboo and long-branch bamboo from southern Taiwan were integrated as feedstock to produce bio-oil using a fast pyrolysis process, and basic properties of the bio-oil were analyzed to determine the important factors to assess the output possibility as a fuel or other relevant products in the future and to develop new ways to increase utilization of thorny bamboo and long-branch bamboo.

MATERIALS AND METHODS

Feedstock preparation

The 2 bamboo species used in this study, thorny bamboo and long-branch bamboo, are of the spreading type that has a running rhizome with sympodial culms. The harvest site was located in Long-Chi District, Tainan City, Taiwan (22°59'N, 120°22'E). The geographic status and climate conditions of the harvest site are described as follows: elevations of 80~100 m, average annual precipitation of ca. 1672 mm, an average annual temperature of ca. 24.1℃, and an average relative humidity of 78%.

Bamboo samples of both species were selected from mature stands aged 4~5 yr. After cutting and simultaneously removing the leaves and branches, only the bamboo culms remained. Culms were first dried in the air outdoors for 1~2 wk, and then were downsized by a chipper to make chips with a mean size of 3~5 cm. The chips were continuously ground by a granulator and sieved to obtain fine particles with a mean size of 2~3 mm. The fine particles were dried in an oven to reduce the moisture content to 10~12% for the experiment.

Composition analyses of the feedstock

Before undergoing conversion to bio-oil, the chemical compositions of the materials were analyzed in accordance with TAPPI T208 om-89. The materials were milled into a powder and screened for the portion that passed a 40-mesh screen and was retained on a 60-mesh screen. Other analyses included holocellulose (the Wise method, as stipulated by the Japan Wood Association, 1985), cellulose and hemicelluloses contents (JIS P9001), lignin (TAPPI T222 om-88), ash content (TAPPI T211 om-93), and alcohol-benzene extractive content (TAPPI T204 os-76).

Thermogravimetric analysis (TGA)

To obtain an approximate pyrolysis temperature before producing the bio-oil, the prepared feedstock was investigated by a TGA using a thermogravimetric analyzer (PYRIS 1 TGA, PerkinElmer, Boston, MA, USA). The TGA operating conditions included a sample amount of ca. 5 mg, a heating rate of 20℃ min^{-1} from room temperature to an appropriate point, and a flow rate of nitrogen of 20 mL min^{-1}. The analytical results showed that the reaction temperature of fast pyrolysis for the 2 bamboos took place in a similar temperature range of 250~400℃, while exhibiting significant weight loss. The turning points, which can be considered the pyrolysis temperatures, were at 343℃ for thorny bamboo and 342℃ for long-branch bamboo (Figs. 1, 2).

However, because only 5 mg of sample was tested in the TGA experiment with a condition of even heating at a fixed test point, the reaction temperature usually appeared to be lower than the actual reaction temperature in practice. It is difficult to reflect the reality of a fast pyrolysis operation in an uneven heating condition (Beall and Eickner 1970). Based on our practical experience and by referring to pyrolytic temperatures of other biomass feedstock, the reaction temperature of fast pyrolysis for the 2 bamboos in this study was raised to 460℃.

Fast pyrolysis procedure

The bio-oils were produced by a fast pyrolysis system, consisting of a screw feeder, a bubbling fluidized bed (BFB) reactor, a char-separation component, a quenching component, a gas-circulation component, and an aerosol filter. Figure 3 shows this fast pyrolysis system (Chang et al. 2010). The system was assembled by the Green Energy & Environment Research Laboratories, Industrial Technology Research Institute (ITRI) in Taiwan.
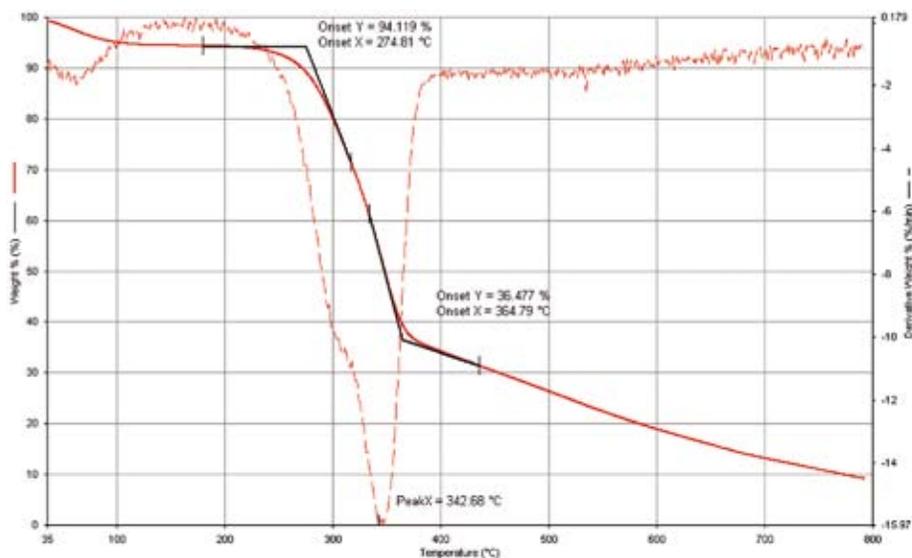
Fig. 1. Thermogravimetric analysis curves of thorny bamboo.
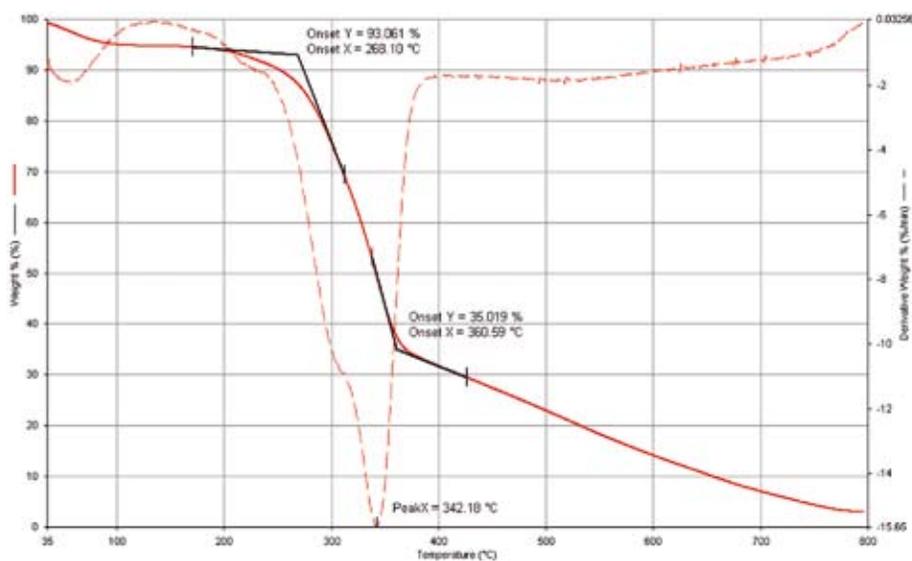
Fig. 2. Thermogravimetric analysis curves of long-branch bamboo.

The BFB reactor was made of a stainless steel tube with an internal diameter of 10 cm and a height of 45 cm, and was indirectly heated by electricity. Besides producing bio-oil in the process, bio-char and combustible pyrolysis gases were also separately yielded. The bio-char was separated from the vapors and gases by 2 cyclonic separators in series, and the vapor and gases were quenched and separated by condensers. The yields of bio-oil and bio-char were calculated using the following equation (1):

Yield (%) = (product weight / dry biomass weight) $\times$ 100 wt.%;   (1)
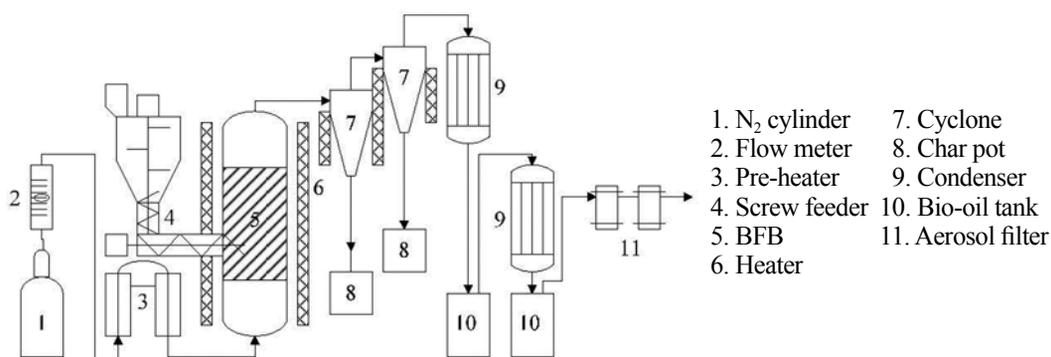
Fig. 3. Diagram of the fast pyrolysis system used in this study.

where the yield was based on the dry bio-mass, and pyrolysis gas was obtained by sub-tracting the bio-oil yield and bio-char yield from 100 wt.%.

To easily compare the properties of the 2 bio-oils from thorny bamboo and long-branch bamboo, the same feed rate of feedstock of 2.6 kg h^{-1}, and the same pyrolytic temperature of 460℃ with a gas flow rate of 65 L min^{-1} were used.

Bio-oil analyses

The moisture contents of the bio-oils were determined using a Karl Fischer titrator (Schott, Mainz, Germany; ASTM D 1744). The specific gravities of the bio-oils were de-termined according to the ASTM D70 meth-od. The pH was measured using a digital pH meter (Thermo, Beverly, MA, USA). Acidity determination entailed weighing 1~2 g of bio-oil in a 250 ml Erlenmeyer flask, then diluting it 100x with distilled water. Afterwards, a few drops of phenolphthalein indicator were add-ed, then titrated using a 0.1 N NaOH solution. A blank titration was also carried out. Acidity was then calculated based on the following equation (2):

Acidity = $(((A - B) \times N \times 6) / S)$ (%);   (2)

where A is the amount of NaOH used in the titration (ml), B is the amount of NaOH used in titrating the blank sample (ml), N is the normality of NaOH solution, and S is the weight of the bio-oil sample (g).

The tar content was determined by weighing 1~2 g of bio-oil in a crucible and heating it with a Bunsen burner until only a dry, black residue was left. The residue was weighed, and the tar yield was determined based on the following equation (3):

Tar content (%) = (mass of black residue/mass of bio-oil) $\times$ 100 (%).   (3)

The ash contents of bio-oils were deter-mined according to the method of ASTM D 482-80 for petroleum products. The viscosi-ties of the bio-oils were determined with a ro-tational viscometer at 25℃ (Brookfield DV-E, Middleboro, MA, USA; ASTM D 445). The higher heating value (HHV, the maximum po-tential energy in dry fuel) in accordance with CNS 10835 (Chinese National Standards) was measured with a Parr 1266 Oxygen Bomb Calorimeter (Parr Instrument Co, Moline, IL, USA).

The chemical compositions of the en-gendered bio-oils were analyzed using gas chromatography-mass spectrophotometry (GC-MS) (HP 6890N GC and 5973N MSD Mass Spectroscopy). The separation column was a BPX-70 capillary column (30 m$\times$250 μm$\times$0.30 μm), and the carrier gas was he-lium at a flow rate 1.0 mL min^{-1}, a split ratio of 1: 10, a temperature of the injection port

of 270℃, an ionizing pressure of 70 eV, and a mass range m/z of 41~400 a.m.u. The starting temperature of the analysis was at 40℃, the heating rate was kept to 1.5℃ min^{-1} to 46℃, and the heating rate was subsequently increased to 4℃ min^{-1}, until the temperature reached 209℃. Compounds were identified by comparing the mass spectra with those of National Institute of Standard and Technology (NIST) and Wiley libraries, and by comparing to known standards.

RESULTS AND DISCUSSION

Feedstock composition

The specific gravities and compositions of the 2 bamboos are given in Table 1. Table 1 shows that both specific gravities were similar at 0.64~0.65. The holocellulose contents of thorny bamboo and long-branch bamboo were 69.45 and 73.36%, respectively. A higher holocellulose content was found in long-branch bamboo. Compared to domestic woods, values of both were higher than for all conifer woods (46.1~54.0%) and major hardwoods in Taiwan (Wang and Ting 1984). However, the specific gravity of thorny bamboo approximated that of rice husks at 69.74% and was slight higher than bagasse at 66.27% (Hsu 1999). A study by Jung et al. (2008) on a kind of bamboo sawdust (*P. bambusoides*) obtained a similar result of 67.5%

compared to thorny bamboo. Lignin contents were 27.43% for thorny bamboo and 23.18% for long-branch bamboo. Both bamboos had lower lignin contents than the average of domestic softwoods (at ca. 30%). The lignin content of thorny bamboo approximated that of major hardwoods in Taiwan, but long-branch bamboo was obviously slightly lower and approximated that of rice straw at 23.3% (Jung et al. 2008). Ash contents of the 2 bamboos were relatively higher than softwoods, but obviously much lower than values of agricultural wastes such as rice husks at 15.44%, bagasse at 4.03% (Hsu 1999), and palm kernel shells at 6.7% (Kim 2010). In addition, thorny bamboo contained more alcohol-benzene extractives at 5.27% than did long-branch bamboo at 3.61%.

Yields of fast pyrolysis products

Besides bio-oil, 2 other byproducts of bio-char and combustible gas were produced during fast pyrolysis. Table 2 shows the yields of the abovementioned 3 products under feed rates of 3.6 kg h^{-1} for thorny bamboo and 3.2 kg h^{-1} for long-branch bamboo at the same pyrolytic temperature of 460℃. Yields of bio-oil of thorny bamboo and long-branch bamboo reached the same level of 55%. Bio-char yield from thorny bamboo at 20% was slightly more than that from long-branch bamboo, but the combustible gas yield from thorny

Table 1. Main composition of thorny bamboo and long-branch bamboo

Composition	Thorny bamboo (*Bambusa stenostachya*)	Long-branch bamboo (*B. dolichoclada*)
Specific gravity	0.64	0.65
Holocellulose (%)	69.45	73.36
α-Cellulose (%)	45.86	48.78
β+γ-Cellulose (%)	23.59	24.58
Lignin (%)	27.43	23.18
Ash (%)	2.45	1.38
Alcohol-benzene extractives (%)	5.27	3.61

Table 2. Yields of bio-oil, bio-char, and combustible gas from thorny bamboo and long-branch bamboo

Species	Feed rate (kg h^{-1})	Product yields (wt.%)		
		Bio-oil	Bio-char	Gas
Thorny bamboo	3.6	55	20	25
Long-branch bamboo	3.2	55	16	29

bamboo at 25% was relatively lower than that from long-branch bamboo. The bio-oil yield is influenced by operating parameters such as the feedstock (Mohan et al. 2006, Zang et al. 2007, Jung et al. 2008), particle size (Koçkar et al. 2000, Şensöz et al. 2000), feed rate (Kim et al. 2010), reactor type (Koçkar et al. 2000), reaction temperature (Pütün 2002, Tsai et al. 2007), heating rate (Pütün 2002, Tsai et al. 2007), holding time and flow rate of the fluidizing medium (Koçkar et al. 2000), etc., and interactive effects among these parameters. The bio-oil yield from woody materials usually reaches rates of 70~80%, which are relatively higher than rates in the range 40~60% for crops and agricultural wastes (Mohan et al. 2006, Zang et al. 2007). Bio-oil yields of both bamboos (55%) in this study at a reaction temperature of around 460℃ were apparently in an acceptable range. However, Jung et al. (2008) obtained a higher bio-oil yield from bamboo sawdust up to a maximum value of about 72% at around 400℃. Nevertheless, the bio-oil yield at around 460℃ was at about 67%. They may have used finer particles with a mean size of 0.6~0.85 mm and operated at a lower reaction temperature. However, based on numerous research results, although yields of bio-oil show big differences in values among various biomass sources, the maximum yield of bio-oil usually occurs in an approximate temperature range of around 400~550℃. An increase in the bio-oil yield with an increasing reaction temperature has not been reported in the literature

so far. Bio-oil yields of most biomasses will relatively drop if the reaction temperature exceeds 600℃ (Koçkar et al. 2000, Şensöz et al. 2000, Gerçel 2002, Pütün 2002, Das et al. 2004). In addition, although the yield of bio-char was reduced with a rise in the reaction temperature, the maximum yield usually appeared at a temperature of < 400℃ (Pütün 2002).

Characteristics of the bio-oils

The basic properties of the bio-oils from thorny bamboo and long-branch bamboo are given in the Table 3. Moisture contents of the bio-oils from thorny bamboo (40.4%) and long-branch bamboo (37.0%) were obviously higher than those from woody biomass, which are generally within the range of 15~30% (Mohan et al. 2006). The moisture content of bio-oil measured by Jung et al. (2008) was also around 40% for bamboo sawdust, but around 60% for rice straw. Specific gravities of the bio-oils were 1.14 for thorny bamboo and 1.13 for long-branch bamboo. Specific gravities of bio-oils from woody biomasses are generally in the range of 0.94~1.21 (Mohan et al. 2006). pH values of bio-oils from thorny bamboo and long-branch bamboo were 2.6 and 3.6, respectively. pH values of bio-oils referenced in the literature are mostly in the range of 2.3~2.9 pH exceeding a value of 3.0 was found only for few biomass feedstocks such as almond shells (5.5) and rice straw (4.2) (Sipilä et al. 1998, Mohan et al. 2006). The pH of bio-oil from long-branch

Table 3. Basic properties of the bio-oils from thorny bamboo and long-branch bamboo

Property	Relative content (%)	
	Thorny bamboo	Long-branch bamboo
Moisture content (wt.%)	40.4	37.0
Specific gravity	1.14	1.13
pH	2.6	3.6
Acidity (%)	4.1	2.0
Tar content (wt.%)	14.58	13.22
Ash (wt.%)	0.52	0.64
Viscosity (cp: at 25°C)	8.72	7.52
Higher heating value (MJ/kg)	13.92	14.87
C (wt.%)	27.41	36.86
H (wt.%)	8.72	8.34
O (wt.%)	63.42	53.99
N (wt.%)	0.45	0.81

bamboo (3.6) was higher than those of most bio-oils. The pH is an important parameter for boiler operations, as boiler corrosion damage can occur if the pH value is too low. The acidity of bio-oil from thorny bamboo (4.1%) was twice than that from long-branch bamboo (2.0%), and the respective tar contents were 14.58 and 13.22% for thorny bamboo and long-branch bamboo. Ash contents of bio-oils from both feedstocks were relatively higher those of other biomass feedstocks, most of which were < 0.1 (Mohan et al. 2006). Bio-oil viscosities (cp; at 25°C) were 8.72 for thorny bamboo and 7.52 for long-branch bamboo, which are relatively lower compared to other biomass sources. It could be that the moisture contents of both bamboos are relatively higher, which could also be the reason causing the relatively low HHVs, that were 13.92 MJ/kg for thorny bamboo and 14.87 MJ/kg for long-branch bamboo. The HHV of bio-oil from bamboo sawdust (*P. bambusoides*) in a study by Jung et al. (2008) was 17.4 MJ/kg, and from other bamboos of *B. nutans* and *B. strictus*, in a study by Mohanty et al. (2011), were also up to 17.8 and 17.4 MJ/kg, respectively. Using technologies such as a transesterifica-tion reaction, hydrodeoxygenation, or emulsification could greatly promote the efficiency in energy utilization of the low HHV through an upgrading process (Zang et al. 2007).

Composition analysis of bio-oils

The compositions of bio-oils from thorny bamboo and long-branch bamboo by the GC-MS analysis are given in Table 4. Totals of 83 and 87 compounds were identified for bio-oils from thorny bamboo and long-branch bamboo, respectively. This means that both oily liquids contain complex mixtures with multifunctional groups. Zang et al. (2007) reviewed most papers studied on the composition of bio-oils and reached similar conclusions.

Table 5 further shows the proportions of individual-compound functional groups of the bio-oils from thorny bamboo and long-branch bamboo. The proportions of alcohols and aromatic hydrocarbons between both bamboos were similar, with alcohols at 1.27 and 1.14%, and aromatic hydrocarbons at 3.60 and 3.36% for thorny bamboo and long-branch bamboo, respectively. Esters and furans showed a little difference between the 2 bio-oils: long-

Table 4. Compounds in the organic composition of bio-oils from thorny bamboo and long-branch bamboo

Compound	Area (%)	
	Thorny bamboo	Long-branch bamboo
Methanol	1.27	1.14
2-Butanone	0.08	0.24
Pentane	0.54	0.24
Methyl vinyl ketone	0.39	0.44
2,3-Butanedione	0.36	1.00
2,3-Pentanedione	0.29	0.30
2-Oxo-butanoic acid	0.28	0.17
2-Butenal	0.16	0.26
3-Ethyl-2-methyl-pentane	0.07	0.04
2,3-Pentanedione	0.10	0.24
Pentanal	0.02	0.04
3-Pentene-2-one	0.02	0.16
1,3-Dioxol-2-one	0.15	0.08
2-Pentanol	-	0.09
Hydroxy-acetaldehyde	-	0.79
Acetic acid	18.61	8.76
1-Hydroxy-2-Propanone	10.84	6.20
Butyric acid, allyester	0.56	0.90
Propanoic acid	1.01	0.52
1-Hydroxy-2-butanone	4.46	1.17
2-Cyclopenten-1-one	2.43	1.84
Furfural	3.08	2.41
1-(2-Furanyl)-ethanone	0.24	0.31
Butanedial	4.18	1.20
Oxirane, (butoxymethyl)	1.42	0.24
Crotonic acid	0.27	0.12
2-Furanmethanol	0.98	0.90
5,9-Dodecadien-2-one, 6,10-dimethyl	0.85	0.34
2-Furancarboxaldehyde, 5-methyl	0.66	0.78
2-Cyclopenten-1-one, 2,3-dimethyl	0.22	0.22
2-Cyclopenten-1-one, 3-methyl	0.44	0.46
2,5-Hexanedione	0.25	0.22
Trans-2-undecenoic acid	0.33	0.20
Undecanal	0.07	0.05
Glutaraldehyde	0.42	0.13
2-Cyclopenten-1-one, 2-hydroxy	1.45	1.14
1,3-Cyclohexanedione, 2-methyl	0.24	0.28
1,3-Dioxolane, 2-ethyl	0.29	0.24
2-Cyclopenten-1-one, 3-ethyl	0.21	0.13
2-Cyclopenten-1-one, 2-hydroxy-3-methyl	2.30	2.60
Phenol, 2-methoxy	2.13	2.57
2(5H)-Furanone, 5-methyl	0.86	0.71

continue

Butyrolactone	1.40	0.59
4-Methyl-5H-furan-2-one	0.49	0.34
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy	0.51	0.61
2(5H)-Furanone	1.83	1.45
O-Creosol	0.26	0.51
Phenol	0.85	1.27
P-Creosol	1.33	2.01
4,5-Diamino-2-hydroxypyrimidine	0.10	0.11
2H-Pyran-2-carboxaldehyde, 3,4-dihydro	0.16	0.27
Phenol, 3-ethyl	0.05	0.13
1,3-Dimethyl-naphthalene	0.03	0.04
P-Xylenol	0.17	0.42
P-Ethylguaiacol	0.50	0.93
P-Cresol	0.46	0.87
M-Creol	0.69	1.00
4-Ethyl-2-methyl-phenol	0.09	0.27
P-Propylguaiacol	0.14	0.30
2,3-Dimethyl-phenol	0.07	0.12
P-Ethylphenol	1.98	3.30
2,3-Dihydro-1H-inden-1-one	0.12	0.16
Trans-m-propenylguaiacol	0.59	1.04
4-Methyl-5H-furan-2-one	0.61	0.32
P-Vinylguaiacol	0.72	3.51
E-Eugenol	0.23	0.58
P-Allylphenol	0.64	0.46
5-Hydroxymethyldihydrofuran-2-one	1.68	1.62
Homovallin	2.95	2.19
Dihydrobenzafuran	0.83	5.24
Syringol	4.18	8.56
2-Hydroxy-gamma-butyrolactone	2.16	1.09
4-Methoxy-3-(methoxymethyl) phenol	0.95	2.54
Dehydroacetic acid	0.79	0.71
4-Allylphenol	0.63	0.52
5-Tert-butylpyrogallol	0.61	0.82
1,4:3,6-Dianhydro-α-d-glucopyranose	1.19	1.20
Cis-2,6-Dimethoxy-4-propenylphenol	1.03	1.75
2,3-Anhydro-d-mannosan	0.10	0.16
2-Furancarboxaldehyde, 5-(hydroxymethyl)	0.56	1.18
2-Mercaptophenol	0.27	0.62
2,6-Dimethoxy-4-vinylphenol	-	2.81
Ferulic acid	1.30	1.22
Homovanillyl alcohol	0.97	0.74
Trans-2,6-dimethoxy-4-propenylphenol	1.19	3.10
Guaiacylactone	2.06	2.17
Disooctyl phthalate	-	1.24

Table 5. Proportions of individual-compound functional groups of the bio-oils from thorny bamboo and long-branch bamboo classified based on the identification by GC-MS

Compound	Relative content (%)	
	Thorny bamboo	Long-branch bamboo
Alcohols	1.27	1.14
Aromatic hydrocarbons	3.60	3.36
Esters	0.56	0.90
Phenols	26.70	50.48
Furans	10.08	8.94
Carboxylic acid	22.59	11.72
Ketones	29.51	19.83
Aldehydes	5.68	3.53

branch bamboo contained a higher proportion of esters (0.90% for long-branch bamboo and 0.56% for thorny bamboo), but thorny bamboo contained a higher proportion of furans (10.08% for thorny bamboo and 8.94% for long-branch bamboo). The greatest differences in contents between the 2 bamboos were in phenols and carboxylic acids. The variations were nearly twice, with phenols at 26.7% for thorny bamboo and 50.48% for long-branch bamboo, and carboxylic acids at 22.59% for thorny bamboo and 11.72% for long-branch bamboo. The difference in the carboxylic acid contents could be the reason why the acidity of the bio-oil from thorny bamboo was up to twice higher than that of long-branch bamboo, as mentioned in the last paragraph. In addition, contents of ketones and aldehydes from thorny bamboo were 29.51 and 5.68%, respectively, both of which were higher than the nearly 30% from long-branch bamboo (ketones at 19.83% and aldehydes at 3.53%). The analytical results showed that the major compounds in the bio-oil from long-branch bamboo were phenols with the largest proportion of functional groups over 50% followed

by ketones and carboxylic acids. The main compounds in the bio-oil from thorny bamboo were phenols, carboxylic acids, and ketones, which were well-distributed, and a few furans.

Bio-oils from *Pinus indicus* were mainly comprised of levoglucosan, furfural, phenol, aldehydes and vanillin (Luo et al. 2004), which were similar to those from spruce (Adam et al. 2005). Also, the major compounds of bio-oils from rice straw were acetic acids, formic acids, ketones, and aldehydes, and those from most hardwoods were aldehydes, ketones, and esters (Sipilä et al. 1998). In conclusion, bio-oils are a complex mixture with all kinds of oxygenated organics, such as esters, ethers, aldehydes, ketones, phenols, carboxylic acids, and alcohols.

CONCLUSIONS

In this study, thorny bamboo and long-branch bamboo from southern Taiwan were pyrolyzed in a bubbling fluidized bed reactor. The bio-oil yields of both bamboos at a pyrolytic temperature of 460℃ were a similar value of 55%. Higher heating values of both bio-oils were < 15 MJ/kg, what is a basic heating value requirement as an alternative bioenergy. To enhance the efficiency of energy utilization, reprocessing is required using feasible upgrading technologies such as a transesterification reaction, hydrodeoxygenation, emulsification, etc. However, both bio-oils were analyzed by GC-MS, and over 80 different organic compounds with multifunctional groups were found. The major compounds in the bio-oil from long-branch bamboo were phenols with a largest proportion of >50%. The main compounds in the bio-oil from thorny bamboo contained phenols, carboxylic acids, and ketones, which were well-distributed. Both bio-oils are a great potential resource instead

of a fossil fuel to provide chemical production through appropriate refinery technologies.

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