Research paper

Production and Properties of Bio-oils from the Fast Pyrolysis of Ma Bamboo (*Dendrocalamus latiflorus*) and Green Bamboo (*Bambusa oldhamii*) in Taiwan

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【Summary】

Bamboo is viewed as a potential feedstock for the future global energy supply due to the existence of many significantly fast-growing and abundant species. In this study, ma bamboo (*Dendrocalamus latiflorus*) and green bamboo (*Bambusa oldhamii*) were used as feedstock to produce pyrolysis liquid (bio-oil) using a fast pyrolysis technology at a pyrolytic temperature of 460℃, and the basic properties of the bio-oils were analyzed. Results were compared to those of a previous study, which applied the same procedure to produce bio-oils from thorny bamboo (*B. stenostachya*) and long-branch bamboo (*B. dolichoclada* Hayat). Therefore, this study presents an integrated characterization of bio-oils from the 4 bamboo species. Results showed that higher heating values (HHVs) of bio-oils were 5.65 MJ kg^{-1} for ma bamboo at a moisture content of 44.2% and 9.39 MJ kg^{-1} for green bamboo at a moisture content of 43.4%. Both HHVs were relatively lower than those of thorny bamboo and long-branch bamboo for use as a bioenergy source. Analytical results of gas chromatography/mass spectrometry (GC-MS) showed that the main compounds of bio-oils from both ma bamboo and green bamboo consisted of similar proportions to those from thorny bamboo, including a good distribution of phenols, carboxylic acids, and ketones. Only the bio-oil of long-branch bamboo contained a significant proportion of such compounds, the major one of which was phenols with a large proportion of > 50%. Generally, these 4 bamboo bio-oils can be utilized as fuels. The refining technology must be further researched; however, they would be great potential materials instead of fossil fuel resources to provide various chemical compounds. In particular, the bio-oil of long-branch bamboo has the greatest potential.

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研究報告

臺灣麻竹與綠竹經快速熱解生質油之特性研究

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摘　要

由於竹生長快速且種類豐富，被視為全球未來供應能源的潛在來源。本研究以麻竹(*Dendrocalamus latiflorus*)及綠竹(*Bambusa oldhamii*)作為原料，應用快速熱裂解技術並設定熱裂解溫度在460℃，將所產生的熱裂解液(生質油)進行基本性質分析。分析的結果與前人採用相同研究方法所產生的莿竹(*B. stenostachya*) 生質油和長枝竹(*B. dolichoclada* Hayat)生質油相比較。因此，本研究整合四種竹類生質油之特性。研究結果顯示，含水量44.2%的麻竹其生質油高熱值(HHVs)為5.65 MJ kg^{-1}，含水量43.4%的綠竹其生質油高熱值為9.39MJ kg^{-1}。作為生質能源兩者高熱值相對於刺竹及長枝竹略顯偏低。其結果再透過氣相層析質譜分析儀(GC-MS)分析，資料顯示麻竹及綠竹生質油的主要成分與刺竹類似，具有良好的酚類、羧酸類與酮類分佈。只有長枝竹的生質油具豐富的化學成分，其中以酚類超過50%佔最大比例。整體而言，此四種竹類之生質油若欲作為生質能源替代油品，後續勢須透過精煉技術進一步提昇其熱值，然而此四種竹類之生質油均具有替代化石燃料提煉不同化學化合物之高潛力，尤以長枝竹生質油最有潛力。

關鍵詞：生質能、生質油、快速熱裂解、麻竹、綠竹。

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INTRODUCTION

Biomass is any organic matter derived from plants or animals available on a renewable basis. Biomass includes wood and agricultural crops, herbaceous and woody energy crops, municipal organic wastes, and manure (IEA 2012). However, biomass is generally thought to be plant materials derived from the reaction of CO_2 in the air, water, and sunlight, via photosynthesis, to produce carbohydrates that form the building blocks of biomass (Mckendry 2002). Biomass can be used to produce bioenergy, where biomass is directly used as fuel, or is processed into liquids and gases. Biomass-based energy currently accounts for roughly 10% of the world's total primary energy supply (IEA 2012). Most of this is consumed in developing countries for cooking and space heating using very inefficient open fires or simple cook stoves with considerable impacts on health (smoke pollution) and the environment (deforestation).

Bioenergy has increasingly become important to energy utilization because of its renewable significance and environmentally friendly features: low emissions of sulfur dioxide and nitrides, and zero carbon emissions compared to conventional fossil fuels, particularly for mitigating the issue of global climate warming. In addition, compared to other renewable energy sources, such as solar energy and wind power, bioenergy has advantages of low technological requirements and low investment costs. Therefore, in the last 2 decades, some Western developed countries

have intensely focused on bioenergy applications to replace conventional fossil fuel energy supplies. To enhance the efficiency of bioenergy applications, materials that can be utilized for power generation and transportation fuel production need to be expanded from only energy for cooking and heating through direct combustion in household utilization. The rapid development of conversion technologies of biomass energy has become important energy strategies for governments around the world. The economic benefits of conversion technologies of biomass energy, that adopt biomass residues as feedstock, will be particularly significant due to the dual function of waste disposal and energy recovery.

Among currently developed global conversion technologies, related research and applications of pyrolysis oil (also called bio-oil) produced by fast pyrolysis have been quite skillful. Fast pyrolysis can briefly be illustrated as a process that takes biomass as the feedstock, which is placed in a reactor in the absence of oxygen under a rapid heating process to temperatures of 400~600℃, and then quickly quenched to generate bio-oil; solid bio-char and bio-gas are simultaneously produced during this process (Bridgwater et al. 1999, Mohan et al. 2006, Zang et al. 2007, Bridgwater 2012, Isahak et al. 2012). Fast pyrolysis possesses high economic benefits in the field of bioenergy applications due to its following advantages: a low threshold of feedstock requirement, lower energy consumption for the process compared to other bioenergy conversion technologies, and a high production efficiency. Bio-oil can be used as boiler fuel after being blended with heavy oil, or as 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 technologies (Zang et

al. 2007, Bridgwater 2012).

Internationally, there has been much research investigating characteristics of bio-oils produced by fast pyrolysis with various sources of biomass. Besides woody biomass, various agricultural wastes have been utilized, such as rapeseed (Şensöz et al. 2000, Onay et al. 2001, Oasmaa et al. 2010), hazelnut shells (Pütün et al. 1999, 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, bamboo sawdust (Jung et al. 2008), palm kernel shells (Kim et al. 2010), sugarcane bagasse, coconut shells (Tsai et al. 2006), corncobs, straw, and oreganum stalks (Yanik et al. 2007), and even waste furniture sawdust (Heo et al. 2010). However, only a few studies on bamboo bio-oils were reported, such as one that analyzed the bio-oil from bamboo sawdust (*Phyllostachys bambusoides*) (Jung et al. 2008), one that investigated the physical properties of bio-oils from two native bamboo species in India (Mohanty et al. 2011), and one that analyzed the pyrolysis characteristics of moso bamboo (*P. pubescens*) (Jiang et al. 2012), which focused on thermogravimetric analyses. Bamboo is viewed as a potential feedstock in the future global energy supply due to its significant rapid growth, abundant species, and wide distribution (Scurlock et al. 2000). Therefore, besides moso bamboo, more characteristic studies on bio-oils from other bamboo species are necessary, particularly on bamboo residues from processing and species with low economic benefits.

Taiwan has abundant bamboo resources accounting for 7.2% of its total forested area. There are 6 main commercial bamboo species in Taiwan: moso bamboo (*P. pubescens*), Makino bamboo (*P. makinoi*), ma bamboo (*Dendrocalamus latiflorus*), thorny bamboo

(*Bambusa stenostachya*), long-branch bamboo (*B. dolichoclada*), and green bamboo (*B. oldhamii*) (Lin 2011). In the 1960s~1980s, prosperous bamboo-related industries boosted the regional economy and greatly contributed to providing jobs and revenue to bamboo farmers, local communities, and the government. But 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 change led to very low resource utilization of bamboo forests in the past few decades. It is an unfortunate reality that large valuable bamboo resources were abandoned due to bad economic circumstances, and bamboo farmers can obtain no more benefits from bamboo forest management. These circumstances particularly occurred in forests of thorny bamboo and long-branch bamboo of southern Taiwan. To resolve the dilemma of long-term neglected bamboo resources, in 2013, we studied the characteristics of bio-oils from fast pyrolysis of thorny bamboo and long-branch bamboo and initially found the heating values of these two bio-oils to be relatively low (Lin et al. 2013). However, both bio-oils are a great potential resource of chemical production. In particular, long-branch bamboo contains a high proportion, i.e., > 50%, of phenolic compounds. To further investigate this interesting phenomenon in other bamboo species, in this study, ma bamboo and green bamboo were used as feedstocks to produce bio-oils using the same process as in the previous study, and their basic properties were analyzed. Integrated characteristics of the bio-oils from ma bamboo and green bamboo to bio-oils from thorny bamboo and long-branch bamboo were compared, which are important to assess the possibility and efficiency of bamboo bio-oils as fuel and other related products in the future. The study results simultaneously are expected to provide useful information on creating new opportunities to increase utilization of these 4 bamboo species.

MATERIALS AND METHODS

Feedstock preparation

In this study, ma bamboo and green bamboo were pyrolyzed to produce bio-oils, and their properties were analyzed. Both ma bamboo and green bamboo are spreading types that have a running rhizome with sympodial culms which are similar to those of thorny bamboo and long-branch bamboo. The harvest sites of these 2 bamboo species were located in southwestern Taiwan. The ma bamboo site was located in Dapu Township, Chiayi County, and the green bamboo site was located in Longchi Distinct, Tainan City. The geographic status and climatic conditions of the harvest sites are described in Table 1.

To easily compare the results of the previously analyzed thorny bamboo and long-

Table 1. Location, geographic status, and climate conditions of the study sites

Location	Longitude, latitude	Elevation (m)	Average annual precipitation (mm)	Average annual temperature (℃)	Average annual humidity (%)
Da-Pu Township, Chiayi County	23°15′N 120°37′E	640~660	1726	22.8	82
Long-Chi District, Tainan City	22°59′N 120°22′E	80~100	1672	24.1	78

branch bamboo, both bamboo samples in this study were prepared by the same processes: 1) bamboo samples based on species were selected from stands at a mature age of 4~5 yr; 2) after harvesting and simultaneously removing leaves and branches, only the bamboo culms remained; 3) culms were dried outdoors in air for 1~2 wk; 4) they were then processed with a chipper to make chips with a mean size of 3~5 cm; 5) the chips were ground up in a granulator and sieved to obtain fine particles with a mean size of 2~3 mm; and 6) the fine particles were dried in an oven to reduce the moisture content to 10~12% for the following experiments.

Composition analyses of the feedstock

Main compositions of the feedstocks were analyzed in accordance with the analytical procedures of TAPPI T208 om-89 before undergoing pyrolysis to bio-oil. The feedstocks were milled into a powder and screened for the portion passing a 40-mesh screen and retained on a 60-mesh screen. Other analyses and related approaches included holocellulose (the Wise method, as stipulated by the Japan Wood Association, 1985), cellulose and hemicellulose 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)

Although previous study results on thorny bamboo and long-branch bamboo (Lin et al. 2013) provided related experiences on pyrolysis temperature, the feasible reaction temperature of ma bamboo and green bamboo were unknown, because both feedstocks were untested materials for pyrolysis procedures to produce bio-oil. To estimate a rational pyrolysis temperature range before producing the bio-oil, the prepared feedstocks underwent a TGA on a thermogravimetric analyzer (PYRIS 1 TGA, PerkinElmer,

Boston, MA, USA). The TGA operating conditions were 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}.

Fast pyrolysis procedure

Both feedstocks were pyrolyzed to produce bio-oil using the same fast pyrolysis system as that in the previous study (Lin et al. 2013). The fast pyrolysis system consisted 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. The fast pyrolysis structure is illustrated in Fig. 1 (Chang et al. 2010). The system was assembled by the Green Energy & Environment Research Laboratories, Industrial Technology Research Institute (ITRI, Hsinchu, Taiwan).

The BFB reactor was made of a stainless steel tube with an internal diameter of 10 cm and 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 produced; the former was separated from vapors and gases by 2 cyclones in series, and the latter vapor and gases were quenched and separated by condensers using a cool water system, which is low cost and easy to operate. Yields of bio-oil and bio-char were calculated using the following equation (1): Yield (%) = (Product weight / Dry biomass weight)×100;   (1) where the yield is based on the dry biomass, and pyrolysis gas is obtained by subtracting the bio-oil yield and bio-char yield from 100 wt.%.

To easily compare properties of the 4 bio-oils, from ma bamboo, green bamboo, thorny bamboo, and long-branch bamboo, the same feed rate of feedstock of 2.6 kg h^{-1}, a pyrolytic temperature of 460□, and a gas flow rate of 65 L min^{-1} were used.
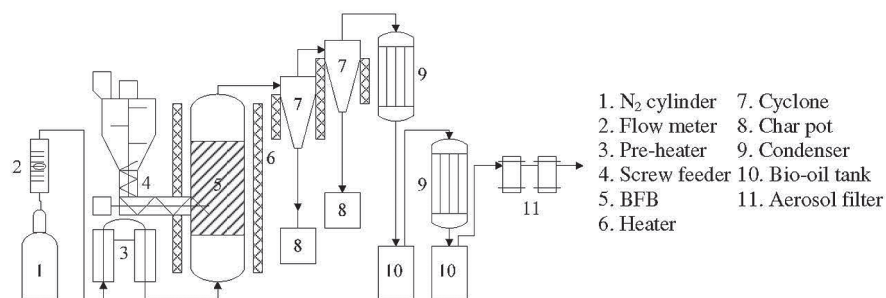
Figure 1: Fast pyrolysis system

Fig. 1. Diagram of the fast pyrolysis system used in this study (Chang et al. 2010). BFD, bubbling fluidized-bed reactor.

Analyses of the bio-oils

　　Basic properties of the bio-oils were analyzed by standard methods shown in Table 2. Besides the analytic standard, the equipment used is briefly described as follows: the moisture content was determined with a Karl Fischer titrator (Schott, Mainz, Germany). The pH was measured using an ORION, 3-STAR digital pH meter (Thermo scientific, Beverly, MA, USA). The viscosity of the bio-oil was determined with a rotational viscometer (Brookfield DV-E, Middleboro, MA, USA). The higher heating value (HHV, the maximum potential energy of the dry fuel) was measured as a calorimetric value with a Parr 1266 Oxygen Bomb Calorimeter (Parr Instrument, Moline, IL, USA). The elemental contents of carbon, hydrogen, nitrogen, and sulfur/oxygen were measured using an elemental analyzer (Elementar Analysensysteme, Hamburg, Germany).

　　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 added, and it was 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):

$$Acidity\ (\%) = ((A-B) \times N \times 6) / S) \times 100; \tag{2}$$

　　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 dry, black residue was left. The residue was weighed to determine the tar yield based on the following equation (3):

$$Tar\ content\ (\%) = (Mass\ of\ black\ residue\ /\ Mass\ of\ bio\text{-}oil) \times 100. \tag{3}$$

　　Chemical compounds of the engendered bio-oils were analyzed using gas chromatography-mass spectrometry (GC-MS) (HP 6890N GC and 5973N MSD mass spectroscopy, Agilent Technologies, city: Santa Clara, CA, USA). The separation column used was a BPX-70 capillary column of 30 m $\times$ 250 μm $\times$ 0.30 μm (SGE Analytical Science, city: Austin, TX, USA), the carrier gas was helium at a flow rate of 1.0 mL min^{-1} and a split ratio of 1:10; the temperature of the injection port was 270□; the ionizing pressure was 70 eV; and the mass range m/z was 41~400 a.m.u. The starting temperature of the analysis was 40□; the heating rate was 1.5□ min-1 to

46□, which was subsequently increased to 4□ min⁻¹, until the temperature reached 209□. Compounds were identified by mass spectra with those obtained from authentic standards and/or the NIST and Wiley libraries spectra, and the literature (Ralph and Ronald 1991)

RESULTS

Composition of the feedstock

Results of the compositional analyses of the 2 bamboo species in this study are shown in Table 3 together with the other 2 bamboo species from a previous study (Lin et al. 2013). The holocellulose contents of ma bamboo, green bamboo, and thorny bamboo were similar at 68.15, 67.83, and 69.45%, respectively, and only long-branch bamboo had a higher value of 73.36%. Lignin contents of ma bamboo, green bamboo, thorny bamboo, and long-branch bamboo were 30.26, 30.10, 27.43, and 23.18%, respectively. Ash contents of ma bamboo, green bamboo, thorny bamboo, and long-branch bamboo were 3.09, 2.61, 2.45, and 1.38, and alcohol-benzene extractives were 1.12, 2.04, 5.27, and 3.61%, respectively. In addition, the specific gravities of ma bamboo, green bamboo, thorny bamboo, and long-branch bamboo were 0.59, 0.73, 0.64, and 0.65, respectively.

Table 2. Analysis items of bio-oil properties and standard methods

Property	Approach
Water content (%)	ASTM D 1744
Specific gravity	ASTM D70
pH	Digital pH meter
Ash (%)	ASTM D 482-80
Viscosity (cp: at 25℃)	ASTM D 445
Higher heating value (HHV) (MJ kg⁻¹)	CNS 10835
C, H, N, S/O	Element analyzer of CHNS/O
Acidity (%)	Described in the text
Tar content (%)	Described in the text
Gas chromatography-mass spectrophotometry (GC-MS)	HP 6890N GC, 5973N MSD mass spectroscopy

Table 3. Main composition of the 4 bamboo species

Composition	M[a]	G[b]	T[c,*]	L[d,*]
Holocellulose (%)	68.15	67.83	69.45	73.36
α-Cellulose (%)	46.77	45.45	45.86	48.78
β+γ-Cellulose (%)	21.38	22.38	23.59	24.58
Lignin (%)	30.26	30.10	27.43	23.18
Ash (%)	3.09	2.61	2.45	1.38
Alcohol-benzene extractives (%)	1.12	2.04	5.27	3.61

[a] Ma bamboo (*Dendrocalamus latiflorus*).
[b] Green bamboo (*Bambusa oldhamii*).
[c] Thorny bamboo (*B. stenostachya*).
[d] Long-branch bamboo (*B. dolichoclada*).
[*] Data taken from Lin et al. (2013).

TGA

Analytical results showed that the main reaction temperature ranges of fast pyrolysis were 250~380 and 250~400℃ for ma bamboo and green bamboo, respectively, while showing significant weight loss (Fig. 2a, b). However, the first weight loss of the feedstock occurred at 100℃, due to moisture evaporation . The turning point, through derivative weight calculations, which could be considered the pyrolysis temperature, was at 343℃ for ma bamboo and 360℃ for green bamboo. Compared to previous study results, the pyrolysis temperature of ma bamboo was at a similar temperature to those of thorny bamboo (at 343℃) and long-branch bamboo (342℃). The pyrolysis temperature of green bamboo was a little higher than those of the other 3 bamboo species (Fig. 2c, d).

However, because only 5 mg of sample was tested in the TGA experiment which operated at a condition of even heating to a fixed test point, the reaction temperature usually appeared lower than the actual reaction temperature in practice. It is difficult to reflect the reality of the fast pyrolysis operation in an uneven heating procedure (Beall and Eickner 1970). Therefore, based on previous practical experience and to allow easy comparisons with previous study results from the other 2 bamboo feedstocks under the same conditions, the reaction temperature of fast pyrolysis for ma bamboo and green bamboo was raised to 460℃ as well.

Yields of fast pyrolysis products

Both of the bio-oils obtained in this study were a free-flowing liquid of a dark-brown to black color with a strong burnt-wood odor, as were the bio-oils obtained from the other feedstocks. Table 4 shows the yields of bio-oil, bio-char, and combustible gases during the procedure of fast pyrolysis from the 4
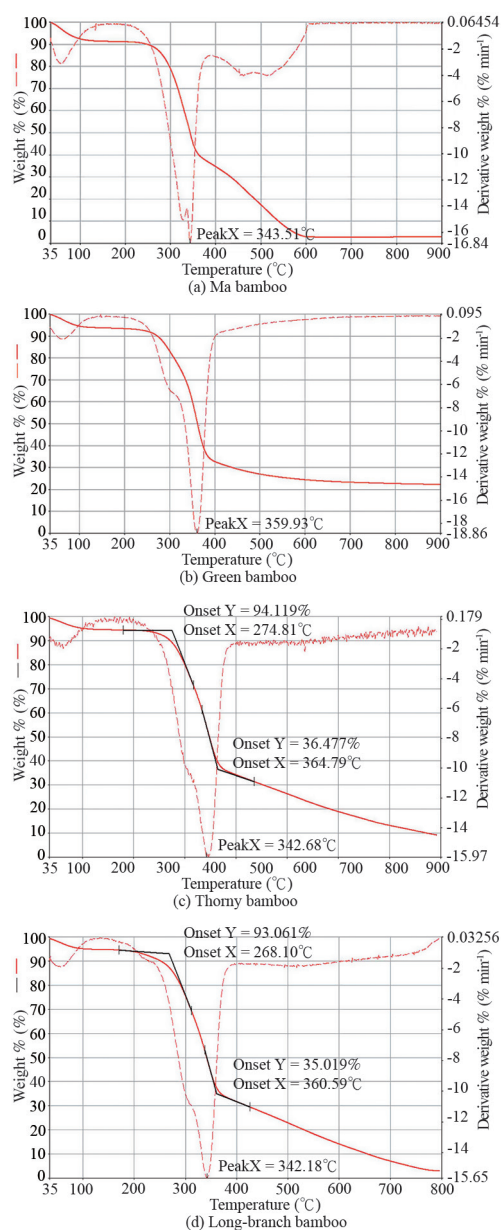
Fig. 2. Thermogravimetric analysis curves of the four bamboo species.

bamboo species at the same pyrolytic temperature of 460℃. Feed rates based on practical conditions were 3.5 kg h^{-1} for ma bamboo and 3.0 kg h^{-1} for green bamboo. The yields of bio-oil of ma bamboo and green bamboo reached the same level of 51%, which was

relatively lower than those of thorny bamboo and long-branch bamboo (both at ca. 55%). Bio-char yields from ma bamboo and green bamboo were almost at same (ca. 20%) and also the same with that of thorny bamboo. Only long-branch bamboo had a lower bio-char yield of 16%. However, thorny bamboo had a relatively lower combustible gas yield of 25%, while the other 3 bamboo species reached the same level of around 30%.

Characteristics of the bio-oils

Likewise, the basic properties of bio-oils from ma the 4 bamboo species are presented in Table 5. Moisture contents of the bio-oils ma bamboo (44.2%) and green bamboo (43.4%) were a little higher than from that from thorny bamboo (40.4%) and much higher than that from long-branch bamboo (37.0%). The specific gravities of the bio-oils were 1.08 for ma bamboo, 1.12 for green bamboo, 1.14 for thorny bamboo, and 1.13 for long-branch bamboo. Specific gravities of bio-oils from woody biomass are generally in the range of 0.94~1.21 (Mohan et al. 2006). pH values of the bio-oils were 3.3 for ma bamboo, 3.6 for green bamboo, 2.6 for thorny bamboo, and 3.6 for long-branch bamboo.

The acidities of bio-oils from ma bamboo and green bamboo were similar at pH7.9 and 7.1, respectively. The acidity of long-branch bamboo was relatively low at only pH2.0 among these 4 bamboo species. Tar contents for ma bamboo and green bamboo were 4.19 and 9.61%, respectively, and were relatively lower than those of thorny bamboo (14.58%) and long-branch bamboo (13.22%). Bio-oil viscosities (cP; at 25℃) were 5.1 for ma bamboo and 5.6 for green bamboo, both of which were lower compared to thorny bamboo and long-branch bamboo. The viscosities of bio-oils in related studies were reported to be in a wide range (0.02~450) based on various feedstocks and different measurement procedures (Mohan et al. 2006). With regard to the elemental composition, among the 4 bamboo species, long-branch bamboo contained higher contents of carbon and nitrogen, and a lower oxygen content.

Composition analysis of bio-oils

Compositions of the bio-oils from ma bamboo and green bamboo by the GC-MS analysis, as well as those from thorny bamboo and long-branch bamboo, are listed in Table 6, and GC-MS spectra of the bio-oils of the 4 bamboo species are given in Fig. 3. The numbers of compounds in the bio-oils from ma bamboo and green bamboo were coincidentally identified to both be 81. The numbers of compounds from thorny bamboo and long-branch bamboo were 83 and 87, respectively. This means that the 4 oily liquids contain complex mixtures with multifunctional groups.

Table 4. Yields of bio-oil, bio-char, and combustible gas from the 4 bamboo species

Species	Feed rate (kg h^{-1})	Product yields (%)		
		Bio-oil	Bio-char	Gas[**]
Ma bamboo	3.5	51	19	30
Green bamboo	3.0	51	20	29
Thorny bamboo[*]	3.6	55	20	25
Long-branch bamboo[*]	3.2	55	16	29

[*] Data taken from Lin et al. (2013).
[**] Gas = 100－(Bio-oil＋Bio-char) by difference.

Table 5. Basic properties of bio-oil from the 4 bamboo species

Property	Relative contents			
	M[a]	G[b]	T[c,*]	L[d,*]
Moisture content (wt.%)	44.2	43.4	40.4	37.0
pH	3.3	3.6	2.6	3.6
Acidity (%)	7.9	7.1	4.1	2.0
Tar content (wt.%)	4.19	9.61	14.58	13.22
Ash (wt.%)	0.97	0.71	0.52	0.64
Viscosity (cP: at 25°C)	5.1	5.6	8.7	7.5
Higher heating value (HHV) (MJ kg^{-1})	5.65	9.39	13.92	14.87
C (wt.%)	15.95	22.19	27.41	36.86
H (wt.%)	3.79	3.88	8.72	8.34
O (wt.%) [**]	79.8	73.18	63.42	53.99
N (wt.%)	0.46	0.75	0.45	0.81

[a] Ma bamboo (*Dendrocalamus latiflorus*).
[b] Green bamboo (*Bambusa oldhamii*).
[c] Thorny bamboo (*B. stenostachya*).
[d] Long-branch bamboo (*B. dolichoclada*).
[*] Data taken from Lin et al. (2013).
[**] O (wt.%) = 100 − (C+H+N) by difference.
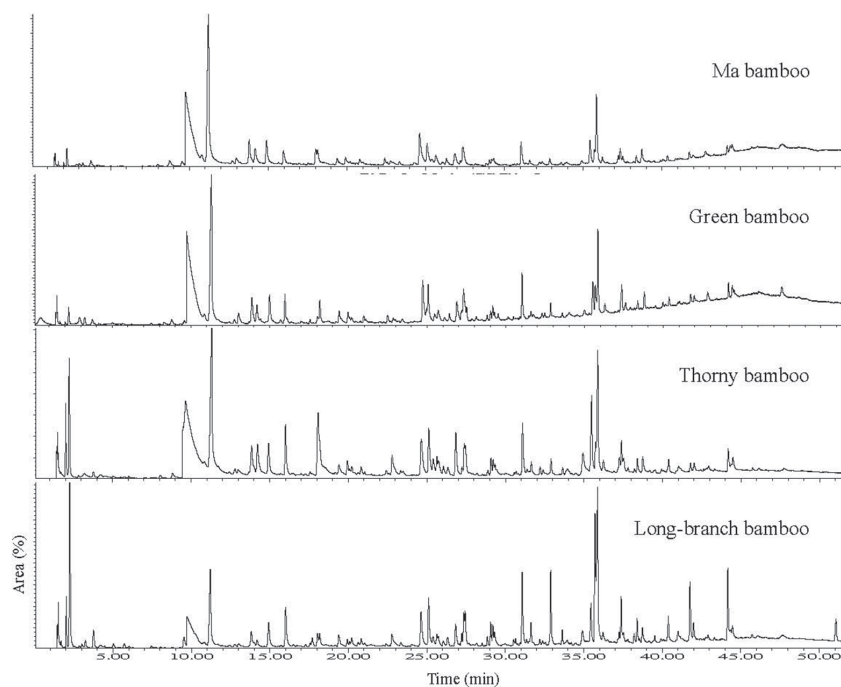
Fig. 3. GC-MS spectra of the bio-oils from the 4 bamboo species.
Note: Peak nos. are described in Table 6.

Table 6. Compounds in the organic composition of bio-oil from the 4 bamboo species

Peak no.	R.T.[a]	Compound	Area (%)				Identification[f]
			M[b]	G[c]	T[d,*]	L[e,*]	
1	2.02	Methanol	1.71	1.19	1.27	1.14	MS, ST
2	3.04	2-Butanone	0.23	0.18	0.08	0.24	MS, ST
3	3.19	Pentane	-[g]	-	0.54	0.24	MS, ST
4	3.24	Methyl vinyl ketone	0.49	0.16	0.39	0.44	MS, ST
5	3.78	2,3-Butanedione	0.56	0.63	0.36	1.00	MS, ST
6	4.24	2,3-Pentanedione	0.34	0.28	0.29	0.3	MS, ST
7	4.53	2-oxo-Butanoic acid	-	-	0.28	0.17	MS, ST
8	5.05	2-Butenal	0.16	0.1	0.16	0.26	MS, ST
9	5.51	2-Methyl-3-ethyl-pentane	-	-	0.07	0.04	MS, ST
10	5.73	2,4-Pentanedione	0.13	0.11	0.1	0.24	MS, ST
11	7.04	Pentanal	0.03	0.06	0.02	0.04	MS, ST
12	7.48	3-Pentene-2-one	0.07	0.08	0.02	0.16	MS, ST
13	8.04	1,3-Dioxol-2-one	0.11	0.1	0.15	0.08	MS, ST
14	8.32	Pyridine	0.24	0.21	-	-	MS, ST
15	8.67	2-Pentanol	0.54	0.71	-	0.09	MS, ST
16	9.46	2-Hydroxyacetaldehyde	0.29	0.63	-	0.79	MS, ST
17	9.66	Acetic acid	25.96	24.58	18.61	8.76	MS, ST
18	11.32	1-Hydroxy-2-propanone	12.66	18.62	10.84	6.2	MS, ST
19	12.80	Butyric acid	0.36	0.31	0.56	0.9	MS, ST
20	12.99	Propanoic acid	1.05	0.68	1.01	0.52	MS, ST
21	13.85	1-Hydroxy-2-butanone	2.3	2.8	4.46	1.17	MS, ST
22	14.93	2-Cyclopenten-1-one	2.49	2.38	2.43	1.84	MS, ST
23	16.01	Furfural	2.13	1.4	3.08	2.41	MS, ST
24	17.57	1,2-Furanyl-ethanone	0.21	0.16	0.24	0.31	MS, ST
25	18.08	Butanedial	0.45	1.18	4.18	1.2	MS, ST
26	18.44	(Butoxymethyl)oxirane	1.49	1.29	1.42	0.24	MS, ST
27	19.17	Crotonic acid	-	-	0.27	0.12	MS, ST
28	19.41	2-Furanmethanol	1.23	0.72	0.98	0.9	MS, ST
29	19.95	6,10-Dimethyl-5,9-dodecadien-2-one	0.91	0.59	0.85	0.34	MS, ST
30	20.23	5-Methyl-2-furancarboxaldehyde	0.46	0.32	0.66	0.78	MS, ST
31	20.63	2,3-Dimethyl-2-cyclopenten-1-one	-	-	0.22	0.22	MS, ST
32	20.82	3-Methyl-2-cyclopenten-1-one	0.45	0.39	0.44	0.46	MS, ST
33	21.05	2,5-Hexanedione	0.23	0.2	0.25	0.22	MS, ST
34	21.48	*trans*-2-Undecenoic acid	-	-	0.33	0.2	MS, RF
35	22.24	Undecanal	-	-	0.07	0.05	MS, ST
36	22.42	Glutaraldehyde	0.53	0.69	0.42	0.13	MS, ST
37	22.79	2-Hydroxy-2-cyclopenten-1-one	0.37	0.12	1.45	1.14	MS, ST
38	23.34	2-Methyl-1,3-cyclohexanedione	0.35	0.05	0.24	0.28	MS, ST
39	23.49	2-Ethyl-1,3-dioxolane	0.07	0.1	0.29	0.24	MS, ST
40	24.03	3-Ethyl-2-hydroxycyclopent-2-en-1-one	0.05	0.13	0.21	0.13	MS, ST
41	24.32	4-Methyl-1,3-dioxane	0.03	0.02	-	-	MS, ST

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42	24.65	2-Hydroxy-3-methyl-2-cyclopenten-1-one	3.44	4.67	2.3	2.6	MS, ST
43	25.13	2-Methoxyphenol	2.67	2.66	2.13	2.57	MS, ST
44	25.41	5-Methyl-2(5H)-furanone	0.74	0.75	0.86	0.71	MS, ST
45	25.65	Butyrolactone	1.14	1.37	1.4	0.59	MS, ST
46	26.05	4-Methyl-5H-furan-2-one	0.37	0.31	0.49	0.34	MS, RF
47	26.35	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	0.63	0.74	0.51	0.61	MS, ST
48	26.85	2(5H)-Furanone	1.76	1.53	1.83	1.45	MS, ST
49	27.24	*o*-Creosol	0.49	0.28	0.26	0.51	MS, ST
50	27.38	Phenol	3.1	2.56	0.85	1.27	MS, ST
51	27.46	*p*-Creosol	1.5	1.4	1.33	2.01	MS, ST
52	27.95	4,5-Diamino-6-hydroxypyrimidine	0.07	0.05	0.1	0.11	MS, ST
53	28.19	3,4-Dihydro-2H-pyran-2-carboxaldehyde	0.2	0.16	0.16	0.27	MS, ST
54	28.54	3-Ethyl-phenol	0.1	0.06	0.05	0.13	MS, ST
55	28.71	1,3-Dimethyl-naphthalene	0.07	0.02	0.03	0.04	MS, ST
56	28.88	*p*-Xylenol	0.32	0.03	0.17	0.42	MS, ST
57	29.09	*p*-Ethylguaiacol	0.49	0.4	0.5	0.93	MS, RF
58	29.23	*p*-Cresol	0.74	0.46	0.46	0.87	MS, ST
59	29.34	*m*-Cresol	0.48	0.89	0.69	1.00	MS, ST
60	30.56	4-Ethyl-2-methyl-phenol	0.14	0.1	0.09	0.27	MS, RF
61	30.68	*p*-Propylguaiacol	0.3	0.12	0.14	0.3	MS, RF
62	30.95	2,3-Dimethylphenol	0.12	0.03	0.07	0.12	MS, ST
63	31.09	*p*-Ethylphenol	2.43	1.91	1.98	3.3	MS, ST
64	31.52	2,3-Dihydro-1H-inden-1-one	0.42	0.2	0.12	0.16	MS, ST
65	31.65	*trans-m*-Propenylguaiacol	0.33	0.3	0.59	1.04	MS, RF
66	32.21	4-Methyl-5H-furan-2-one	0.35	0.3	0.61	0.32	MS, ST
67	32.91	*p*-Vinylguaiacol	0.66	0.44	0.72	3.51	MS, RF
68	33.65	Eugenol	0.2	0.1	0.23	0.58	MS, ST
69	33.96	2-Allylphenol	0.48	0.26	0.64	0.46	MS, ST
70	34.94	5-Hydroxymethyldihydrofuran-2-one	0.46	0.31	1.68	1.62	MS, ST
71	35.49	Homovallin	1.85	2.13	2.95	2.19	MS, RF
72	35.74	Dihydrobenzafuran	1.34	0.82	0.83	5.24	MS, RF
73	35.88	Syringol	4.76	5.69	4.18	8.56	MS, ST
74	36.24	2-Hydroxy-γ-butyrolactone	0.98	0.55	2.16	1.09	MS, ST
75	37.39	4-Methoxy-3-methylphenol	1.83	1.63	0.95	2.54	MS, ST
76	37.53	Dehydroacetic acid	0.65	0.58	0.79	0.71	MS, ST
77	38.22	4-Allylphenol	0.11	0.06	0.63	0.52	MS, RF
78	38.40	5-*tert*-Butylpyrogallol	0.45	0.58	0.61	0.82	MS, ST
79	38.75	Levoglucosan	0.98	1.34	1.19	1.2	MS, ST
80	40.39	*cis*-2,6-Dimethoxy-4-propenylphenol	0.62	0.35	1.03	1.75	MS, RF
81	40.89	1,6-Anhydro-beta-d-glucofuranose	0.19	0.01	0.1	0.16	MS, ST
82	41.03	5-(Hydroxymethyl)-2-furancarboxaldehyde	0.25	0.13	0.56	1.18	MS, ST
83	41.26	2-Mercaptophenol	0.1	0.02	0.27	0.62	MS, ST
84	41.77	2,6-Dimethoxy-4-vinylphenol	0.64	0.5	-	2.81	MS, RF
85	42.01	Ferulic acid	0.22	0.31	1.3	1.22	MS, ST

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86	42.94	Homovanillyl alcohol	0.74	0.49	0.97	0.74	MS, RF
87	44.18	*trans*-2,6-Dimethoxy-4-propenylphenol	0.76	0.39	1.19	3.10	MS, RF
88	44.48	Guaiacylactone	0.67	0.78	2.06	2.17	MS, RF
89	51.07	Disooctyl phthalate	-	-	-	1.24	MS, ST

[a] R.T., retention time (min).

[b] Ma bamboo (*Dendrocalamus latiflorus*).

[c] Green bamboo (*Bambusa oldhamii*).

[d] Thorny bamboo (*B. stenostachya*).

[e] Long-branch bamboo (*B. dolichoclada*).

[*] Data taken from Lin et al. (2013).

[f] MS, NIST, and Wiley library spectra and the literature; ST, authentic standard compounds. RF, Reference: Ralph and Ronald (1991).

[g] - not detected.

Table 7 further shows proportions of individual-compound functional groups of bio-oils from ma bamboo and green bamboo and those from thorny bamboo and long-branch bamboo. The proportions of alcohol among the 4 bamboo species were 1.9, 2.25, 1.27, and 1.14% for ma bamboo, green bamboo, thorny bamboo, and long-branch bamboo, respectively, among which green bamboo contained a higher amount of alcohol. Amounts of aromatic hydrocarbons seemed to be divided into 2 groups, ma bamboo and green bamboo in a group with aromatic hydrocarbons of 2.76% and 2.75%, respectively, and thorny bamboo and long-branch bamboo in the other group at 3.6% and 3.36%, respectively. Esters and furans showed slight differences among the 4 bio-oils: long-branch bamboo had a higher proportion of esters at 0.9%, and thorny bamboo contained a higher proportion of furans at 10.08%. Ma bamboo contained lower proportions of esters and furans.

DISCUSSION

Composition of the feedstock

The holocellulose contents of these 4 bamboo species were all relatively lower than those of hardwoods (at 74~80%), but higher than those of softwoods (at 66~72%) except for long-branch bamboo (Effendi et al. 2008). A study by Jung et al. (2008) on bamboo sawdust (from *P. bambusoides*) obtained a similar result of 67.5% compared to the 3 species of ma bamboo, green bamboo, and thorny bamboo. Regarding the lignin contents of the 4 bamboo species, except for long-branch bamboo, the lignin contents of the other 3 bamboo species were in the range of softwoods (at 25~30%), but higher than the range of hardwoods (at 18~25%). The lignin content of long-branch bamboo was relatively lower than the range of softwoods, but in the range of hardwoods (Effendi et al. 2008) and was approximately that of rice straw at 23.3% (Jung et al. 2008). Ash contents of the 4 bamboo species were relatively higher than those of softwoods and hardwoods, but obviously much lower than agricultural wastes such as rice husks at 15.44%, bagasse at 4.03% (Hsu 1999), oreganum stalks at 4.0%, straw at 4.1% (Yanik et al. 2007), and palm kernel shells at 6.7% (Kim et al. 2010). Thorny bamboo contained more alcohol-benzene extractives at 5.27% than the other 3 bamboo species: ma bamboo at 1.12%, green bamboo at 2.04%, and long-branch bamboo

at 3.61%. Ma bamboo contained a relatively lower value compared to softwoods (at 2~9%) and hardwoods (2~5%).

Yields of fast pyrolysis products

In general, about 40~75% of most agricultural biomass (on a dry-weight basis) is converted into bio-oil in practice (Yanik et al. 2007). Bio-oil yields of the 4 bamboo species (51% and 55%) at a reaction temperature of around 460℃ were apparently in an acceptable range. However, compared to bio-oil yields from woody materials (which usually can reach a range of 72~80%) (Mohan et al. 2006, Bridgwater 2012), the 4 bamboo bio-oil yields were relatively low. Besides the feedstock factor, many related studies reported that bio-oil yields from fast pyrolysis are influenced by operating parameters such as the reaction temperature (Pütün 2002, Tsai et al. 2007, Garcia-Perez et al. 2008, Heo et al. 2010), heating rate (Pütün 2002, Tsai et al. 2007, Heo et al. 2010), particle size (Koçkar et al. 2000, Şensöz et al. 2000, Garcia-Perez et al. 2008, Heo et al. 2010), feed rate (Heo et al. 2010, Kim et al. 2010), reactor type (Koçkar et al. 2000), holding time and flow rate of the fluidizing medium (Heo et al. 2010, Koçkar et al. 2000), ash content of the feedstock (Butler et al. 2011, Isahak et al. 2012), pretreatment and vapor residence times (Bridgwater et al. 1999), etc., and interactive effects among these parameters. However, based on numerous research results, although values of the yield of bio-oil exhibited large differences among various biomass resources, 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 literatures so far. Bio-oil yields of most biomasses will 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).

Table 7. Proportions of individual-compound functional groups of the bio-oil from the 4 bamboo species classified based on GC-MS identification

Compound	Relative contents (%)			
	M[a]	G[b]	T[c,*]	L[d,*]
Alcohols	1.90	2.25	1.27	1.14
Aromatic hydrocarbons	2.76	2.75	3.60	3.36
Esters	0.31	0.36	0.56	0.90
Phenols	25.76	28.78	26.70	50.48
Furans	5.46	7.29	10.08	8.94
Carboxylic acids	26.15	27.88	22.59	11.72
Ketones	34.52	28.55	29.51	19.83
Aldehydes	3.14	2.12	5.68	3.53

[a] Ma bamboo (*Dendrocalamus latiflorus*).

[b] Green bamboo (*Bambusa oldhamii*).

[c] Thorny bamboo (*B. stenostachya*).

[d] Long-branch bamboo (*B. dolichoclada*).

[*] Data taken from Lin et al. (2013).

Characteristics of the bio-oils

Moisture contents of these 4 bio-oils from bamboos were all obviously higher than those of woody biomass, which are generally within the range of 15~30% (Mohan et al. 2006). Moisture contents of bio-oil measured by Jung et al. (2008) were around 40% for bamboo sawdust and around 60% for rice straw. The moisture content is one of the most influential parameters on the HHV of a bio-oil. A higher moisture content can result in a lower HHV of the bio-oil. In this study, the lowest HHV of bio-oil from ma bamboo (of 5.65 MJ kg^{-1}) was found to be connected to a higher moisture content of 44.2%, and the bio-oil from long-branch bamboo had a higher HHV of 14.87 MJ kg^{-1} and possessed a lower moisture content (37.0%). The HHV of bio-oil from bamboo sawdust (*P. bambusoides*) in a study by Jung et al. (2008) was 17.4 MJ kg^{-1}, and those from other bamboo species 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^{-1}, respectively. A typical HHV of bio-oil should reach a minimum value of 17 MJ kg^{-1}. Obviously, the HHVs of bio-oils from all 4 of these bamboo species were much lower. To greatly promote the efficiency of energy utilization of a bio-oil containing a low HHV, it must be subjected to an upgrading process using appropriate technologies such as a transesterification reaction, hydrodeoxygenation, or emulsification (Zang et al. 2007, Butler et al. 2011, Bridgwater 2012).

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 for only a few biomass resources such as oak, maple (3.7), rice straw (4.2), and almond shells (5.5) (Sipilä et al. 1998, González et al. 2005, Mohan et al. 2006). Only the pH of bio-oil from thorny bamboo was < 3.0 among these 4 bamboo species. The pH is an impor-tant parameter for boiler operations, as a low pH value can easily lead to boiler corrosion damage.

A typical ash content of bio-oil from woody feedstock is < 0.1%, and generally not over 0.2% (Mohan et al. 2006). Obviously, ash contents of bio-oils from ma bamboo (0.97%) and green bamboo (0.71%) in this study were much higher than those of other feedstocks. However, ash contents of bio-oils from *B. nutans* at 0.9% and *D. strictus* at 0.8% were also reported in a study by Mohanty et al. (2011).

Compared to the elemental contents of bio-oils from woody biomass, these 4 bamboo species contained lower carbon (15.95~36.86%), higher oxygen (53.99~79.8%), and higher nitrogen levels (0.46~0.81%). Typical elemental composition ranges from woody biomass for carbon, hydrogen, oxygen, and nitrogen are 54~58%, 5.5~7.0%, 35~40%, and 0~0.2%, respectively (Mohan et al. 2006).

Composition analysis of bio-oils

The analytical results showed that the greatest difference in compound contents among the 4 bamboo species was in phenols and carboxylic acids. Variations were nearly 2-fold, with phenols at 50.48% for long-branch bamboo and 25.76, 28.78, and 26.70% for ma bamboo, green bamboo, and thorny bamboo, respectively. But the content of carboxylic acids at 11.72% for long-branch bamboo was only half the amounts for ma bamboo (26.15%), green bamboo (27.88%), and thorny bamboo (22.59%). In addition, contents of ketones were 34.52% for ma bamboo, 28.55% for green bamboo, 29.51% for thorny bamboo, and 19.83% for long-branch bamboo. Ma bamboo contained the greatest amount of ketones, and long-branch bamboo had the smallest proportion. The largest pro-

portion of aldehydes was 5.68% from thorny bamboo, and the smallest proportion was at 2.12% from green bamboo.

The main compounds in the bio-oil from long-branch bamboo were phenols with the largest proportion of functional groups of > 50% followed by ketones and carboxylic acids. As to the other 3 bamboos species, the main compounds of the bio-oils based on content proportions from large to small were ketones, carboxylic acids, and phenols for ma bamboo; phenols, ketones, and carboxylic acid for green bamboo; and ketones, phenols, carboxylic acids, and a few furans for thorny bamboo. Basically, ketones, phenols, and carboxylic acids were well-distributed in the bio-oils of ma bamboo, green bamboo, and thorny bamboo. Compared to other biomass feedstocks, the major compounds from the 4 bamboo species identified in this study were similar to the major compounds of bio-oils from rice straw and bamboo sawdust, which contained phenolics, furfurals, acetic acids, ketones, aldehydes, and some levoglucosan, guaiacol, and alkyl guaiacol (Jung et al. 2008). 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 most hardwoods are aldehydes, ketones, and esters (Sipilä et al. 1998). In conclusion, bio-oils are a complex mixture with all kind of oxygenated organics, such as esters, ethers, aldehydes, ketones, phenols, carboxylic acids, and alcohols (Peng and Wu 2000, Mohan et al. 2006, Zang et al. 2007).

CONCLUSIONS

This study provides a preliminary integrated characterization analysis of bio-oils from 4 bamboo species of Taiwan, among which ma bamboo and green bamboo were analyzed in this study and thorny bamboo and long-branch bamboo were researched in an earlier study. They were pyrolyzed in a bubbling fluidized-bed reactor. The bio-oil yields of the 4 bamboo species at a pyrolytic temperature of 460℃ were 51% for ma bamboo and green bamboo, and 55% for thorny bamboo and long-branch bamboo. Higher heating values of bio-oils from the 4 bamboo specieswere all < 15 MJ kg^{-1}, which is a basic heating value requirement as a bioenergy alternative. In addition, the 4 bamboo species contained relatively higher ash contents compared to most woody biomasses (< 0.1%). To enhance the heating efficiency and reduce the ash contents of these bamboo bio-oils for energy utilization, further research is required. However, the analytical results by GC-MS showed that the 4 bio-oils contained abundant organic compounds with more than 80 different organic compounds with multifunctional groups. In particular, the major compound in the bio-oil of long-branch bamboo was phenols with the largest proportion of > 50%. The main compounds in the bio-oils of the other 3 bamboo species similarly contained phenols, carboxylic acids, and ketones, which were well-distributed. The 4 bio-oils could all be great potential sources instead of fossil fuels to provide chemical compounds through appropriate refinery technologies, in particular, phenolic compounds from the bio-oil of long-branch bamboo.

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