Direct Liquefaction of Bamboo in Ethanol-Phenol Co- Solvent

Yan Ma,[a] Jianchun Jiang,[a,b,]* Weihong Tan,[a] Kui Wang,[a] Hao Ying,[a,b] and Junming Xu [c,]*

Bamboo was converted into bio-oil *via* direct liquefaction with ethanol-phenol as solvent in a 250 mL Parr High-Pressure reactor. The influences of reaction parameters such as reaction time, liquefaction temperature, catalyst content, ratio of solvent/bamboo, and phenol concentration on the liquefaction yield were investigated. The highest liquefaction yield was 98.5 wt.% under the optimal conditions. The elemental analysis of the produced bio-oil revealed that the oil product had a higher heating value (HHV) of 29.5 MJ/kg, which was much higher than that of the raw material (16.4 MJ/kg). Gas chromatography mass spectrometry (GC-MS) and Fourier transform infrared spectrometry (FT-IR) measurements showed that the main volatile compounds in the crude bio-oil were phenolics and esters.

Keywords: Liquefaction; Bamboo; Bio-oil; Ethanol-phenol; Co-solvent

Contact information: a: Institute of Chemical Industry of Forest Products, CAF, National Engineering Lab for Biomass Chemical Utilization, Key and Open Lab of Forest Chemical Engineering; SFA, Key Lab of Biomass Energy Sources and Materials, 16 Suojin five village, Nanjing 210042, China; b: Jiangsu Qianglin Bio-energy and Bio-materials Co., Ltd., 88 Liqiang Road, Liyang 213364, China; c: Research Institute for Forestry New Technology, CAF, Beijing 100091, China;
** Corresponding author: biomass2016@163.com*

INTRODUCTION

The continued use of fossil energies as fuels and raw materials such as coal, oil, and gas results in energy shortages and environmental pollution. The demand for alternative renewable resources has rapidly increased over the past decade. Biomass, as the most abundant and renewable energy source, can be converted into liquid (known as bio-oil). Generally, dry plant biomass is roughly comprised of 40 to 45% cellulose, 25 to 35% hemicelluloses, and 15 to 30 % lignin (Sasaki and Goto 2008). These three compounds can be converted into low molecular weight substances including acids, sugars, phenols, hydroxyacetaldehyde, hydroxyacetone, and alcohols (Shen and Gu 2009; Pedersen and Rosendahl 2015; Li *et al.* 2016). The presence of these compounds can be applied in a wide range of applications as raw materials for production of phenol formaldehyde resins, antioxidants, gasoline additives, polymerization initiators, and bioethanol (Wild *et al.* 2011).

Extensive efforts have been made to liquefy forestry and agricultural residues with various solvents and catalysts. A wide variety of feedstocks have been investigated to increase the yield and quality of the resulting bio-oil, including microalgae (Barreiro *et al.* 2015), spent coffee grounds (Yang *et al.* 2016), and municipal sludge (Lemoine *et al.* 2013). Bamboo is widely distributed across southeast and southwest China, and approximately 1.5×10^9 poles of bamboo are available annually in China (Feng *et al.* 2015). Many researchers have attempted to use bamboo for liquid biofuel production.

Jung *et al.* (2008) used a bubbling fluidized bed equipped with a char separation system to convert bamboo sawdust into bio-oil. The results were very promising, with a maximum bio-oil yield above 70 wt.% of the product. Unfortunately, a relatively high percentage of oxygen (49.55 wt.%) resulted in lower higher heating value (HHV) (17.4 MJ/kg). Other researchers (Liao *et al.* 2014; Xie *et al.* 2014) have focused on bio-oil production *via* liquefaction of bamboo using glycerol-methanol and ethanol solvents. However, the yield of bio-oil and the quality of the liquefied bio-oil has not been satisfactory.

As an efficient pathway for biomass conversion, the direct liquefaction of biomass has been investigated in the presence of various solvents (Zhang *et al.* 2010; Setyaningsih *et al.* 2016) under acid- or base-catalyzed conditions at moderate temperatures (100 to 300 °C) (Zhang *et al.* 2012; Singh *et al.* 2015). Among these used solvents, water is the most widely used liquefaction solvent. However, biomass liquefaction in water is accompanied with many shortcomings, such as challenging operating conditions, low yield of water-insoluble bio-oil, and low-heating values of the resulting bio-oil (Xu *et al.* 2012). As reaction reagent, phenol could react with the degraded small molecules to form compounds with phenolic structure. Phenol was certified to be the optimal solvent for liquefying bamboo (Yip *et al.* 2009). Ethanol was selected as solvents for carbohydrate conversion because it is green derived from biomass conversion and easily recovered. However, very little is known of the ethanol-phenol co-solvent.

In this work, liquefaction of bamboo was studied in the presence of acid catalyst, while using ethanol as solvent and phenol as co-solvent. The effects of the ethanol-phenol co-solvent composition and the reaction temperature were examined with a fixed reaction time. Features of the Gas chromatography mass spectrometry (GC-MS) and gas chromatography (GC) were used to study the composition of liquefied products and extraction compounds, particularly in terms of the elemental composition and energy value of the produced oil.

EXPERIMENTAL

Materials

The bamboo was obtained from saw-mills (Nanjing City, China) as the raw material for liquefaction. The culms were reduced to particles, screened to collect particles that passed through a 40-mesh sieve, and oven-dried at 105 °C for 12 h. The dried particles were stored in polyethylene bags and used without further treatment. The composition (wt.%) of dried bamboo was as follows: cellulose, 38.8 wt.%; hemicellulose, 18.7 wt.%; lignin, 30.2 wt.%; ash, 1.1 wt.%. Chemical reagents such as ethanol, phenol, and sulfuric acid were of analytic grade and purchased from the Aladdin Chemical Reagent Company (Shanghai, China).

Methods

Liquefaction procedure

The influences of reaction parameters on liquefaction yield (LY) were investigated. Bamboo liquefaction experiments were carried out in a 250 mL Parr High-Pressure reactor equipped with a pressure gauge and a stirrer for a certain time. A total of 6.00 g dried bamboo mixed with a certain percentage mass of solvent and sulfuric acid was loaded into the reaction, and the loaded reactors were tightened firmly. The reactor was heated at a heating rate of 3℃/min from room temperature to 140 to 220 °C and kept at the designated temperatures for 30 to 180 min. After the reaction, the autoclave was cooled quickly to room temperature by a water bath. The percentage of LY was calculated by following Eq. 1.

$$\text{Liquefaction yield (\%)} = \left(1 - \frac{\text{mass of solid residue}}{\text{mass of bamboo}}\right) \times 100\% \quad (1)$$

Product separation

The gas was collected, weighed, and subjected to further analysis. The solid and liquid phase mixtures were carefully collected. The solid residue was rinsed with ethanol and dried at 105 °C until the weight remained unchanged; it was then weighed to give the yield of residue. The ethanol in the filtrate was then removed by a rotary evaporator under vacuum at 50 °C, rinsed with 30% (mass ratio) distilled water, and separated by vacuum filtration through a pre-weighed filter paper. The filtrate was designated as water-soluble product containing dissolved organic compounds. The water-insoluble fraction was dried at 30 °C under vacuum for12 h and weighed designated as bio-oil. All experiments were carried out twice to ensure the repeatability of the results and to minimize the experimental errors (< 5%).

Analysis methods

The higher heating value (HHV) of bamboo and bio-oils were calculated based on Eq. 2, the Dulong formula (Liu *et al.* 2013),

$$\text{HHV (MJ/kg)} = [338.2 \times \text{C wt.\%} + 1442.8 \times (\text{H wt.\%} - \text{O wt.\%} / 8)] \times 0.001 \quad (2)$$

where C, H, and O are mass percentages of carbon, hydrogen, and oxygen, respectively.

Elemental analysis (C, H, and N) of the raw material and oil was performed using an elemental analyzer (PerkinElmer, PE-2400, Boston, USA). The oxygen content was calculated by difference and assuming that the sulfur content is negligible using Eq. 3.

$$\text{O (wt.\%)} = 100 - (\text{C} + \text{H} + \text{N})\ \text{(wt.\%)} \quad (3)$$

The functional groups of the raw bamboo and solid residue were investigated by Fourier transform infrared spectrophotometry (FT-IR) (Thermo Nicolet, iS10, Waltham, USA). All measurements were applied directly on the diamond crystal.

The composition of gaseous products was analyzed by gas chromatography (GC) (Shimadzu GC-2010, Tokyo, Japan) using a flame ionization detector. The following gas species were analyzed: H_2, N_2, CO_2, CO, CH_4, C_2H_4, and C_2H_6. The crude bio-oils were analyzed by gas chromatography mass spectrometry (GC-MS) (Agilent 7890N/5975N, Santa Clara, USA) with a 30 m × 0.05 µm × 0.32 nm capillary column (HP-5MS, Santa Clara, USA). Helium (99.999%) was used as the carrier gas with a constant flow of 1.6 mL/min. The oven was programmed to increase at a rate of 5 °C/min until it reached a final temperature of 250 °C and held for 20 min. The injection size was 0.2 µL. Compounds were identified by comparison with the NIST08 library (reference).

RESULTS AND DISCUSSION

Effect of Liquefaction Parameters on Liquefaction Yield

Temperature is an important parameter in ethanol-phenol liquefaction reactions. The experiments were performed between 140 and 220 °C and were held at these temperatures for 30, 60, 90, 120, 150, and 180 min. The pressures inside the reactor at 140, 160, 180, 200, and 220 °C were 0.5, 2.0, 3.0, 4.0, and 5.8 MPa, respectively. As shown in Fig. 1, the liquefaction yield continuously increased from 45.5 wt.% to 55.1 wt.% as the temperature increased from 140 to 160 °C at 60 min. However, when the temperature was increased to 180 °C, the LY was increased remarkably. There was no obvious impact on the LY when the bamboo was liquefied in the range of 180 to 200 °C with the reaction time in the range from 90 min to 180 min. The maximum liquefaction yield (98.5 wt.%) was observed at 180 °C and 60 min reaction time. Interestingly, the LY increased continuously from 38.6 wt.% to 90.3 wt.% as the reaction temperature was increased from 140 °C to 200 °C at the initial stage of liquefaction, whereas LY decreased to 83.2 wt.% at 220 °C, suggesting liquefied products were polymerized at a reaction time of 30 min. Thus, the increased temperature accelerated liquefaction (Ye *et al.* 2012). However, further increases in temperature decreased the LY. The most probable explanation for this is that the process of liquefaction and re-condensation reacted at the same time, while the small molecule polymerization rate increased in the later stage of the reaction (Yamada and Ono 1999).

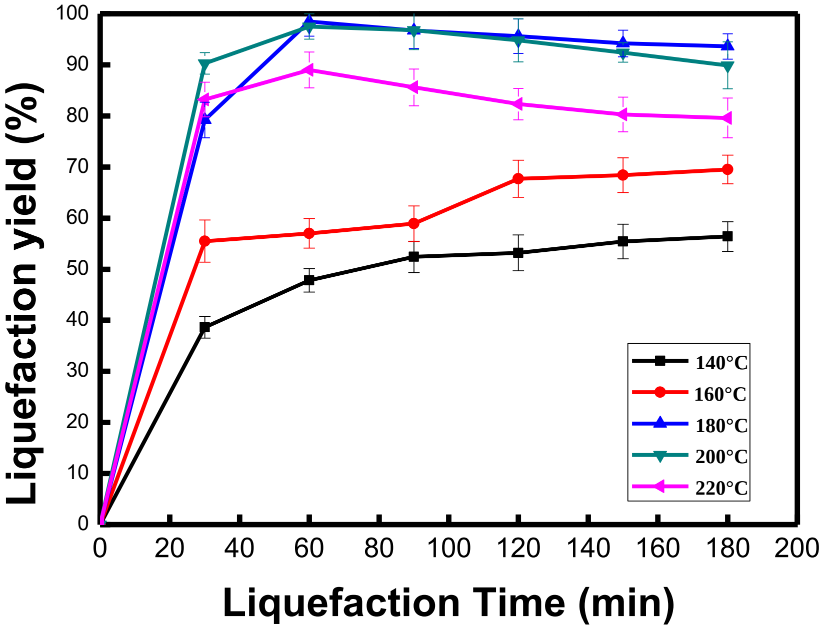


Fig. 1. Effects of reaction temperature on the liquefaction yield of bamboo (bamboo, 6 g; catalyst, 0.18 g; ethanol, 84 g; phenol, 6 g)

Figure 2 shows the influence of various doses of an acid catalyst (H_2SO_4) on LY at 180 °C at different liquefaction time. A low concentration of catalyst had a positive effect on liquefaction. The LY increased dramatically from 65.4 wt.% to 98.5 wt.% as the sulfuric acid loading was increased from 1 wt.% to 3 wt.%, and a dramatic decrease in the LY from 98.5 wt.% to 80.2 wt.% occurred when the acid loading was increased from 5 wt.% to 9 wt.%. This result suggests that an increase of catalyst concentration enhanced the liquefaction reaction and accelerated the re-condensation of the decomposed components, which decreased the LY. The competition among degradation and repolymerization reactions also defined the role of catalyst during the liquefaction process. A lower catalyst (< 5 wt.%) concentration favored the degradation, which rapidly increased the LY, but at the higher catalyst content (> 5 wt.%), condensation was favored. The optimum catalyst concentration for the conversion of bamboo was approximately 3 wt.% (per 6 g bamboo).

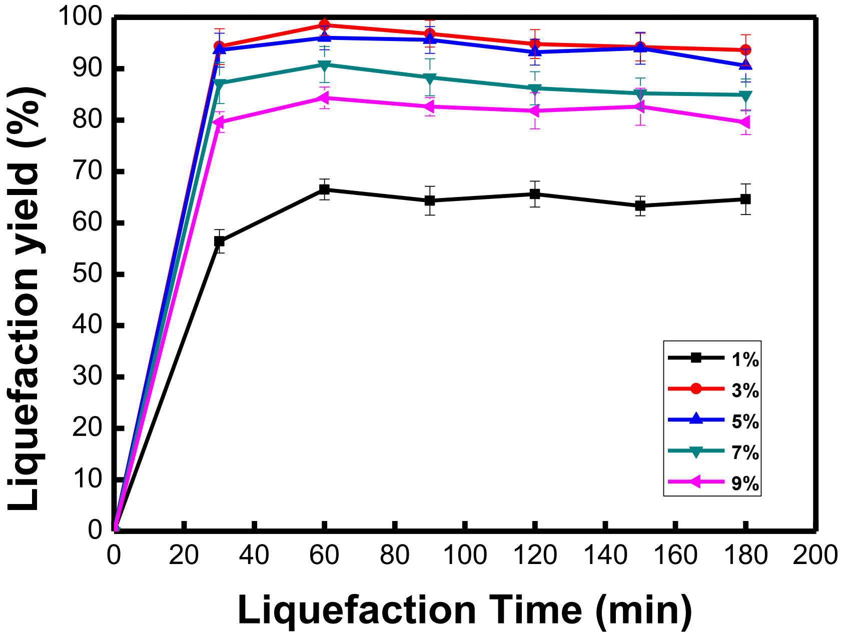


Fig. 2. Effects of catalyst concentration on the liquefaction yield of bamboo (bamboo, 6 g; ethanol, 84 g; phenol, 6 g; temperature, 180 °C)

Figure 3 displays the effect of phenol content at temperatures of 180 °C with different liquefaction times. The effect of phenol content on LY was obvious. The biomass liquefaction yield increased from 70.3 wt.% to 98.5 wt.% as phenol content increased from 1 wt.% to 6 wt.%, respectively, indicating the acceleration of liquefaction reactions with increasing phenol contents. The LY increased to 98.5 wt.% with increasing of the phenol content, and biomass was liquefied completely. With further increase in reaction time, the liquefaction yield was insensitive; it decreased from 98.5 wt.% at 60 min to 96.7 wt.% at 90 min and then leveled off. With ethanol as the pure liquefaction solvent, LY was very low, about 55.2 wt.%. These results can be explained by the fact that the addition of phenol decreases the amount of residue due to its excellent solvolysis of lignocelluloses (Lin *et al.* 2004).

The effect of reaction time on the LY content is also shown in Fig. 3. Compared with reaction temperature, reaction time had a smaller effect on the LY of biomass. The liquefaction yield appeared to first increase sharply then remained approximately constant with increasing reaction time beyond 60 min. This was due mainly to the competition of the two reactions involved in liquefaction: degradation and repolymerization. Initially, the biomass is decomposed and depolymerized to small compounds. These compounds may have rearranged through condensation and repolymerization when the reaction time was further extended (Didem and Filiz 2004). Therefore, 60 min was a desirable reaction time for liquefying bamboo at 180 °C.

The major functions of the solvent included decomposing biomass, dissolving relatively high molecular weight products, diluting the concentration of the products to prevent cross-linked or reversed reactions, and acting as hydrogen-donor during liquefaction (Chen *et al.* 2012).

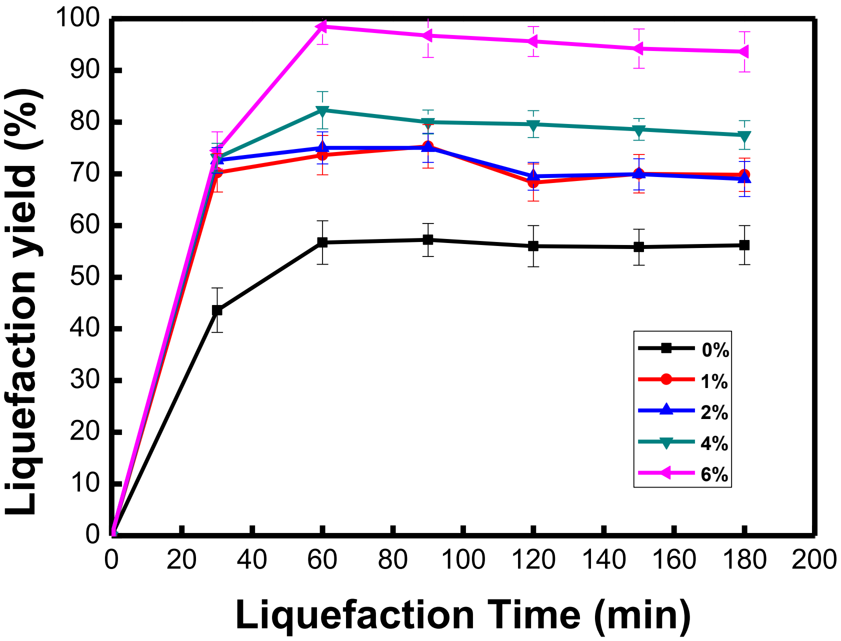


Fig. 3. Effects of phenol concentration on the liquefaction yield of bamboo (bamboo, 6 g; catalyst, 0.18 g; ethanol, 84 g; temperature, 180 °C)

Figure 4 presents the LY from the liquefaction of bamboo in ethanol-phenol mixture at a fixed temperature (180 °C) with different liquefaction times. The liquefaction yields increased when increasing the ratio of liquid to solid, but as the liquid-solid ratio increased to 15, the effect of increasing the ratio of liquid to solid became unapparent. Thus, in the direct liquefaction process, the ethanol and phenol serve both as solvent and reactant in biomass liquefaction. Therefore, the LY decreased when the ratio of liquid to solid was 20, larger solvent loading is unfavorable for the conversion of bamboo. However, a higher LY meant more liquefaction solvent and higher cost is required. Therefore, the mass ratio of liquid-solid of 15 was enough.

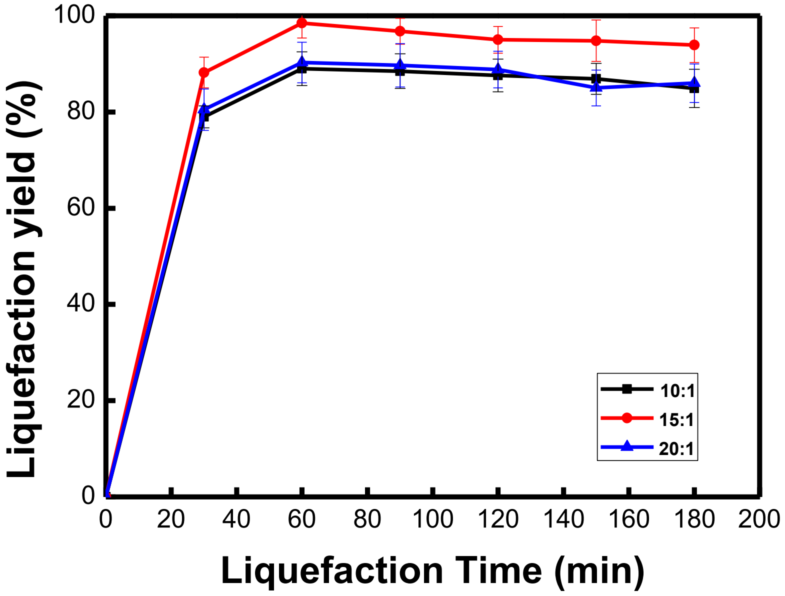


Fig. 4. Effects of mass ratio of solvents/bamboo on the liquefaction yield of bamboo (bamboo, 6 g; catalyst, 0.18 g; phenol, 6 g; ethanol, 54 g, 84 g, 114 g; temperature, 180 °C)

Table 1. Properties of Bamboo and Bio-Oils

Properties	Bamboo	Oil from Different Liquefaction Solvent [a]	
		ethanol-phenol	ethanol
Liquefaction yield (% mass fraction)	—	98.5	55.3
Elemental analysis[b]			
C	50.7	72.3	61.5
H	5.0	6.26	5.65
N	0.1	0.15	0.16
O	44.2	22.3	32.4
H/C molar ratio	1.18	0.87	1.10
O/C molar ratio	0.65	0.23	0.40
HHV(MJ/kg)	16.4	29.5	23.1

[a] Reaction conditions of bamboo, 6 g; catalyst, 0.18 g; phenol, 6 g; ethanol, 84 g; temperature, 180 °C.
[b] On a dry and Ash free basis.

Elemental Analysis

The elemental compositions of the crude bio-oils produced under different conditions are summarized in Table 1. Compared with the elemental composition of the feedstock, the obtained bio-oils had higher contents of carbon and hydrogen but lower concentrations of oxygen. The HHVs of bio-oils were both higher than 20 MJ/kg, while the HHV of the bamboo was only 16.4 MJ/kg. The oxygen content of bamboo was greatly reduced from approximately 44.8 wt.% to 22.5 wt.% mass fraction, and the O:C molar ratio dropped from 0.65 to 0.23. The obvious reduction of oxygen content in the bio-oils was mainly due to the dehydration reactions and the formation of CO/CO_2 during liquefaction (Huang *et al.* 2011). The addition of phenol further increased the carbon and hydrogen contents of bio-oil, compared to the oil from ethanol solvent, but it also reduced the concentration of oxygen. These results reflect the enhanced hydro-cracking and hydrogenation reactions. Therefore, the bio-oil obtained with ethanol-phenol as the medium had a higher caloric value compared with that produced without phenol. Thus, direct liquefaction is a suitable technology to convert bamboo to a more energy-rich bio-oil.

FT-IR Analysis

FT-IR spectra were obtained for the raw bamboo, solid residue, and bio-oil produced at 180 °C with 3 wt.% catalyst concentration and 60 min reaction. An intense broad band between 3300 cm^{-1} and 3600 cm^{-1} was displayed for the feedstock and bio-oil, indicating a high content of carbohydrates (Wang *et al.* 2013). The solid residue showed a significantly lower absorbance in this wave number range, suggesting that the carbohydrates were converted during the liquefaction reaction. The C-H stretching vibrations in aliphatic methylene groups appeared between 2840 cm^{-1} and 3000 cm^{-1}, and weak absorbance in this number range was also observed for solid residue, which indicates the presence of aliphatic structures in raw material (Muradov *et al.* 2012). The intense band at 1703 cm^{-1} suggested the presence of the carbonyl groups in bio-oil, such as the esters identified by GC-MS. The absorbance 1595 cm^{-1} indicated the aromatic skeletal vibrations of the phenolic compounds originated from lignin in the crude bio-oil. The bands from 1350 to 1470 cm^{-1} were ascribed to C-H bending, which indicated alkyl groups in the obtained oil.

Meanwhile, the absorption profiles between 690 cm^{-1} and 930 cm^{-1} implied the presence of phenyl rings and substituted phenyl rings (Cheng *et al.* 2010). The peak at 1050 cm^{-1} appeared in the absorption profile of bamboo and solid residue, which could be C-O connected with hydroxyl groups and were dehydrated after liquefaction.

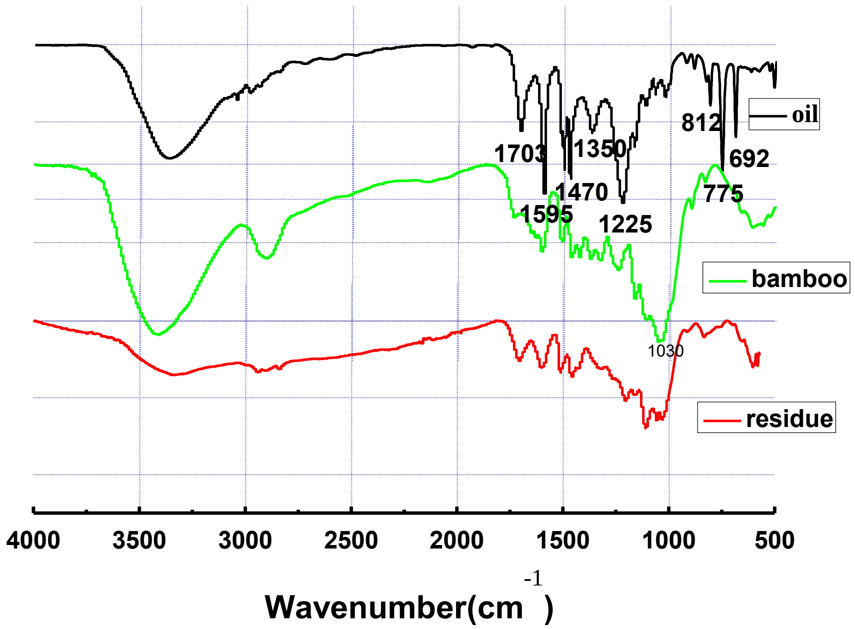


Fig. 5. FT-IR spectra of bamboo, residue, and bio-oil

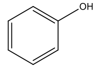
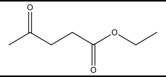
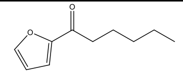
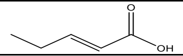
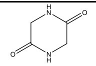
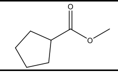
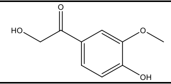
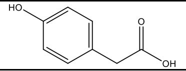
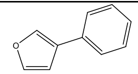
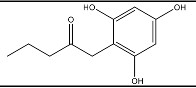
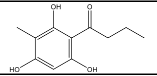
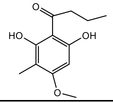
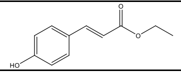
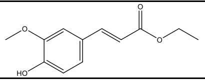
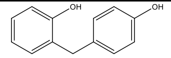
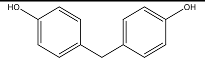
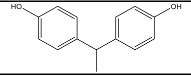
GC-MS Analysis

The organic compounds obtained from the bio-oil were identified by GC-MS analysis. The identification of GC-MS peaks was based, in most cases, on a comparison with the spectra of the NIST 2008 spectrum library (reference). The composition of the major compounds is expressed as percentage peak area (%) based on the total area of selected peaks in the chromatograms, out of more than 50 compounds that were detected in the bio-oil. Only compounds with an area (%) higher than 1% are presented in Table 2.

The content of phenol was 50.44%, and it can be recovered through reduced pressure distillation. Esters (21.06%) were the major compounds identified in the bio-oil, followed by phenolic compounds (in addition to phenol) (12.63%), ketones (6.17%), organic acids (3.56%), and furans (3.13%). Compared with pure ethanol, the ethanol-phenol mixed solvent produced the highest yield of phenolic compounds, which suggested that mixed solvent could promote the formation of phenolic compounds (Liu *et al.* 2013).

Aromatic compounds undoubtedly originated from the deposition of lignin, in which the benzoyl unit was the most common resultant, which were decomposed from the basic unit of lignin-phenyl propane (Xu and Etcheverry 2008). During the liquefaction of phenyl propane, the b-aryl is broken, and a new benzoylether bond is produced (Zhou *et al.* 2010). The reactions between these products led to the formation of phenolic compounds. Most of the minor compounds identified after direct liquefaction were furans and acids. The furan derivatives and the acids were formed primarily from the cellulose and hemicellulose in bamboo. Ketones may have been formed by hydrolysis, dehydration, and cyclization of polysaccharides.

Table 2. Major Compounds in the Bio-Oil Derived from Bamboo Liquefaction

No.	Retention Time (min)	Compounds	Molecular Structure	Area (%)
1	8.785	Phenol		50.44
2	10.845	Ethyl levulinate		9.68
3	15.720	2-Hexanoylfuran		1.31
4	16.120	2-Pentenoic acid		1.10
5	19.102	2,5-Piperazinedione		3.01
6	19.605	Cyclopentanecarboxylic acid, methyl ester		1.20
7	25.968	2,4'-Dihydroxy-3'-methoxyacetophenone		1.38
8	27.673	Benzeneacetic acid, 4-hydroxy-		2.46
9	28.039	Furan, 3-phenyl-		1.82
10	30.013	2-Pentanone, 1-(2,4,6-trihydroxyphenyl)		2.87
11	30.294	1-Butanone, 1-(2,4,6-trihydroxy-3-methylphenyl)-		1.92
12	31.095	Aspidinol		3.63
13	31.461	p-Hydroxycinnamic acid, ethyl ester		1.95
14	32.989	Ethyl (2E)-3- (4-hydroxy-3-methoxyphenyl)-2-propenoate		8.23
15	35.146	Phenol, 2-[(4-hydroxyphenyl)methyl]-		4.41
16	36.697	Phenol, 4,4'-methylenebis-		2.43
17	37.578	4,4'-Ethylidenediphenol		2.16

Note: The reaction conditions were (bamboo, 6 g; catalyst, 0.18 g; phenol, 6 g; ethanol, 84 g; temperature, 180 °C)

CONCLUSIONS

1. The direct liquefaction of bamboo was studied using an ethanol-phenol co-solvent. The optimum operating conditions for liquefaction were 180 °C and with 60 min of reaction time using phenol and ethanol as solvent, which produced a 98.5 wt.% conversion of bamboo.

2. The crude bio-oil was achieved with a higher heating value (HHV) of 29.5 MJ/kg, which was much higher than that of bamboo (16.4 MJ/kg). This result indicated that bamboo can produce high-quality oil *via* direct liquefaction. This oil can be upgraded to become a potentially renewable fuel.

ACKNOWLEDGMENTS

The work was supported by the National Key Technology R&D Program of China (2014BAD02B01), State Key Program of National Natural Science of China (Grant No.31530010), (GrantNo.31422013) and the Research Grant of Jiangsu Province Biomass Energy and Materials Laboratory (JSBEM-S-201502).

REFERENCES CITED

Barreiro, D. L., Gómez, B. R., Hornung, U., Kruse, A., and Prins, W. (2015). "Hydrothermal liquefaction of microalgae in a continuous stirred-tank reactor," *Energy Fuels* 29(10), 6422-6432. DOI: 10.1021/acs.energyfuels.5b02099

Chen, Y., Wu, Y., Zhang, P. L., Hua, D. R., Yang, M. D., Li, C., Chen, Z., and Liu, J. (2012). "Direct liquefaction of *Dunaliella tertiolecta* for bio-oil in sub/supercritical ethanol-water," *Bioresource Technology* 124, 190-198. DOI: 10.1016/j.biortech.2012.08.013

Cheng, S. N., D'cruz, I., Wang, M. C., Leitch, M., and Xu, C. B. (2010). "Highly efficient liquefaction of woody biomass in hot-compressed alcohol-water co-solvents," *Energy Fuels* 24(9), 4659-4667. DOI: 10.1021/ef901218w

Feng, J., Jiang, J., Xu, J., and Yang, Z. (2015). "One-step method to produce methyl-D-glucoside from lignocellulosic biomass," *RSC Advances* 5, 38783-38791. DOI: 10.1039/C5RA04514B

Huang, H. J., Yuan, X. Z., Zeng, G. M., Wang, J. Y., Li, H., Zhou, C. F., Pei, X. K., You, Q., and Cheng, L. (2011). "Thermochemical liquefaction characteristics of microalgae in sub- and supercritical ethanol," *Fuel Processing Technology* 92(1), 147-153. DOI: 10.1016/j.fuproc.2010.09.018

Jung, S. H., Kang, B. S., and Kim, J. S. (2008). "Production of bio-oil from rice straw and bamboo sawdust under various reaction conditions in a fast pyrolysis plant equipped with a fluidized bed and a char separation system," *Journal of Analytical and Applied Pyrolysis* 82, 240-247. DOI:10.1016/j.jaap.2008.04.001

Lemoine, F., Maupin, I., and Lemee, L. (2013). "Alternative fuel production by catalytic hydro- liquefaction of solid municipal wastes, primary sludges and microalgae," *Bioresource Technology* 142, 1-8. DOI: 10.1016/j.biortech. 2013.04.123

Liao, Y., Guo, Y., and Lu, Z. (2014). "Liquefaction of bamboo powder in ethanol and characteristics of liquefaction products," *Journal China Agricultural University* 2, 43-50. DOI: 10.1016/j.fuproc.2010.09.018

Li, J., Zhang, S., Gao, B., Yang, A., Wang, Z., Xia, Y., and Liu, H. (2016). "Characteristics and deoxy- liquefaction of cellulose extracted from cotton stalk," *Fuel* 166,196-202. DOI: 10.1016/j.fuel.2015.10.115

Liu, Y., Yuan, X. Z., Huang, H. J., Wang, X. L., Wang, H., and G. M. (2013). "Thermochemical liquefaction of rice husk for bio-oil production in mixed solvent (ethanol-water)," *Fuel Process Technology* 112, 93-99. DOI: 016/j.fuproc.2013.03.005

Lin, L., Yao, Y., Yoshioka, M., and Shiraishi, N. (2004). "Liquefaction mechanism of cellulose in the presence of phenol under acid catalysis," *Carbohydrate Polymers* 57(2), 123-129. DOI: 10.1016/j.carbpol.2004.01.014

Muradov, N., Fidalgo, B., Gujar, A. C., Garceau, N., and Ali, T. (2012). "Production and characterization of *Lemna minor* bio-char and its catalytic application for biogas reforming," *Biomass and Bioenergy* 42, 123-131. DOI: 10.1016/j.biombioe.2012.03.003

Pedersen, T. H., and Rosendahl, L. A. (2015). "Production of fuel range oxygenates by supercritical hydrothermal liquefaction of lignocellulosic model systems," *Biomass and Bioenergy* 83, 206-215. DOI: 10.1016/j.biombioe.2015.09.014

Sasaki, M., and Goto, M. (2008). "Recovery of phenolic compounds through the decomposition of lignin in near and supercritical water," *Chemical Engineering and Processing* 47(9-10), 1609-1619. DOI: 10.1016/j.cep.2007.09.001

Shen, D. K., and Gu, S. (2009). "The mechanism for thermal decomposition of cellulose and its main products," *Bioresource Technology* 100(24), 6496-6504. DOI: 10.1016/j.biortech.2009.06.095

Setyaningsih, W., Saputro, I. E., Palma, M., and Barroso, C. G. (2016). "Pressurized liquid extraction of phenolic compounds from rice (Oryza sativa) grains," *Food Chemistry* 192, 452-459. DOI: 10.1016/j.foodchem.2015.06.102

Singh, R., Srivastava, V., Chaudhary, K., Gupta, P., Prakash, A., Balagurumurthy, B., and Bhaskar, T. (2015). "Conversion of rice straw to monomeric phenols under supercritical methanol and ethanol," *Bioresource Technology* 188, 280-286. DOI: 10.1016/j.biortech.2015.01.001

Wang, F., Chang, Z., Duan, P., Yan, W., Xu, Y., Zhang, L., Miao, J., and Fan, Y. (2013). "Hydrothermal liquefaction of *Litsea cubeba* seed to produce bio-oils," *Bioresource Technology* 149, 509-515. DOI:10.1016/j.biortech.2013.09.108

Wild, D. P., Reith, H., and Heeres, E. (2011). "Biomass pyrolysis for chemicals," *Biofuels* 2(2), 185-208. DOI: 10.4155/bfs.10.88

Xie, J., Hse, C. Y., and Shupe, T. F. (2014). "Liquefaction behaviors of bamboo residues in a glycerol-based solvent using microwave energy," *Journal of Applied Polymer Science* 131(9), 1-8. DOI: 10.1002/app.40207

Xu, C., and Etcheverry, T. (2008). "Hydro-liquefaction of woody biomass in sub- and super-criticalethanol with iron-based catalysts," *Fuel* 87(3), 335-345. DOI: 10.1016/j.fuel.2007.05.013

Xu, J., Jiang, J. Dai, W., and Xu, Y. (2012). "Liquefaction of sawdust in hot compressed ethanol for the production of bio-oils," *Process Safety and Environmental Protection* 90, 333–338. DOI:10.1016/j.psep.2012.01.001

Yang, L., Nazari, L., Yuan, Z., Corscadden, Y., and Xu, C. (2016). "Hydrothermal liquefaction of spent coffee grounds in water medium for bio-oil production," *Biomass and Bioenergy* 86,191-198. DOI: 10.1016/j.biombioe.2016.02.005

Yip, J., Chen, M., Szeto, Y. S., and Yan, S. (2009). "Comparative study of liquefaction process and liquefied products from bamboo using different organic solvents," *Bioresource Technology* 100, 6674-6678. DOI: 10.1016/j.biortech.2009.07.045

Ye, Y., Fan, J., and Chang, J. (2012). "Effect of reaction conditions on hydrothermal degradation of cornstalk lignin," *Journal of Analytical and Applied Pyrolysis* 94,190-195. DOI: 10.1016/j.jaap.2011.12.005

Yamada, T., and Ono, H. (1999). "Rapid liquefaction of lignocellulosic waste by using ethylene carbonates," *Bioresource Technology* 70(1), 61-67. DOI: 10.1016/S0960-8524(99)00008-5

Zhang, L. H., Xu, C. C., and Champagne, P. (2010). "Overview of recent advances in thermo-chemical conversion of biomass," *Energy Conversion and Management* 51, 969-982. DOI: 10.1016/j.enconman.2009.11.038

Zhang, H., Ding, F., Luo, C., Xiong, L., and Chen, X. (2012). "Liquefaction and characterization of acid hydrolysis residue of corncob in polyhydric alcohols," *Industrial Crops and Products* 39, 47-51. DOI: 10.1016/j.indcrop.2012.02.010

Zhou, D., Zhang, L., Zhang, S., Fu, H., and Chen, J. (2010). "Hydrothermal liquefaction of macroalgae *Enteromorpha prolifera* to bio-oil," *Energy & Fuels* 24, 4054-4061. DOI: 10.1021/efl00151h

Article submitted: June 15, 2016; Peer review completed: August 20, 2016; Revised version received and accepted: September 8, 2016; Published: September 22, 2016.
DOI: 10.15376/biores.11.4.9520-9532