Liquefaction Behaviors of Bamboo Residues in a Glycerol-Based Solvent Using Microwave Energy

Jiulong Xie,[1] Chung-Yun Hse,[2] Todd F. Shupe,[3] Jinqiu Qi,[1] Hui Pan[4]

[1]College of Forestry, Sichuan Agricultural University, Yaan, Sichuan 625014, China
[2]Southern Research Station, USDA Forest Service, Pineville, Louisiana, 71360
[3]School of Renewable Natural Resource, Louisiana State University Agricultural Center, Baton Rouge, Louisiana, 70803
[4]Calhoun Research Station, Louisiana State University Agricultural Center, Calhoun, Louisiana, 71225
Correspondence to: J. Qi (E-mail: qijinqiu2005@aliyun.com)

ABSTRACT: Liquefaction of bamboo was performed in glycerol–methanol as co-solvent using microwave energy and was evaluated by characterizing the liquefied residues. High efficiency conversion of bamboo was achieved under mild reaction conditions. Liquefaction temperature and time interacted to affect the liquefaction reaction. Fourier transform infrared analyzes of the residues indicated that hemicellulose and lignin could easily undergo recondensation. Thermogravimetric analysis results showed that residues obtained at higher temperature/longer reaction time displayed a superior thermal stability as compared to those obtained from mild conditions. Moreover, significant differences were observed in the morphology and structures of residues from different liquefaction conditions according to scanning electron microscopy images. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40207.

INTRODUCTION

Liquefaction of biomass has long been of interest in the conversion of biomass waste into value-added polymeric products for the preparation of polyurethane films, polyurethane foams, phenolic resins, and liquid fuels.[1–4] As an important thermochemical method, liquefaction of forest and agricultural crop wastes have been performed with various liquefaction solvents for different end products.[5–9] However, the most commonly explored solvents for liquefaction are phenol and polyalcohol. These solvents are effective, but require large quantities and are costly. Phenol is derived from petroleum and as such is generally not considered as an environmentally green chemical. A by-product of the transesterification process to manufacture bio-diesel is the production of glycerol. For each kilogram of bio-diesel produced, about 0.1 kg of a crude glycerol accompanies.[10] Therefore, successful replacement of petroleum-based solvents, such as phenol by glycerol in a liquefaction process should have potential to improve the economics of the process.

Bamboo has been widely used for a variety of products such as flooring, furniture, panels, and paper. However, bamboo processing residues such as branches, epidermis, wax, and bamboo pulping by-products have been considered as a waste due to the limited processing technologies for these materials. Although bamboo residues have previously been used in liquefaction reactions to provide bio-based products,[11,12] an economically viable bamboo waste conversion technology is yet to be realized because of the high cost of the liquefaction process. Microwave energy has recently been applied in the liquefaction of lignocellulosic biomass.[13–16] Since microwave energy penetrates and produces a volumetrically distributed heat source, heat is generated throughout the material and leads to faster heating rate and improved kinetics as compared to conventional heating; the development of a liquefaction process combining the greater microwave heating efficiency and the by-product glycerol from the bio-diesel production to replace petroleum-based solvents is a promising method to enhance economic viability of the process and benefit agricultural producers, bio-based processing industries, and the environment. In this study, liquefaction of bamboo with a glycerol-based solvent using microwave energy was systematically investigated. The physical and chemical properties of the liquefied bamboo residues from different reaction conditions were comparatively analyzed. The objective of the study was to optimize the liquefaction reaction with glycerol as a major solvent component.

EXPERIMENTAL

Materials and Chemicals

Three-year-old bamboos (*Phyllostachys pubescens*) were harvested from the Kisatchie National Forest near Pineville,

Louisiana. The bamboo culms were reduced to particles. The particles were screened to collect particle that passed through a 40-mesh sieve and retained on a 100-mesh sieve and then dried to a constant weight in an oven at 80°C. The dried particles were stored in polyethylene bags and used without further treatment. All acids, glycerol, and methanol used were of reagent grade and obtained from commercial sources.

Liquefaction Reaction
Liquefaction of bamboo was performed in a Milestone (Shelton, CT) MEGA laboratory microwave oven. A mixed glycerol and methanol ratio of 2/1 (w/w) was used as the solvent at a solvent to bamboo ratio of 4/1 (w/w). Sulfuric acid content of 1.75% of solvent weight was used as the catalyst. A typical reaction mixture consisting of 2 g of bamboo particles, 8 g of solvent, and 0.14 g of sulfuric acid was loaded in the teflon vessels with a magnetic stirring bar. The teflon vessels were then placed on the rotor tray inside the microwave cavity. The temperature was monitored using an ATC-400FO automatic fiber optic temperature control system. On the basis of monitored temperature, the output power was auto-adjusted during liquefaction. In this study, the temperature was increased from room temperature to 150°C at a heating rate of 37.5°C min^{-1} and then was kept constant for 3 min unless otherwise noted. After a cooling period of 30 min at the end of the reaction, the material was dissolved in 150 mL of methanol under constant stirring for 4 h. The liquefied solutions were then vacuum-filtered through Whatman No. 4 filter paper. The solid bamboo residue retained on the filter paper was oven-dried at 105°C and the conversion yield was calculated as follows:

$$\text{Conversion yield (\%)} = \left(1 - \frac{\text{weight of residue}}{\text{weight of raw material}}\right) \times 100$$

Scanning Electron Microscopy
The structure and the surface morphology of the liquefied bamboo residues were observed using scanning electron microscopy (SEM, JSM-6610). Test samples were coated with gold using a vacuum sputter coater before subjected to the SEM analysis.

Fourier Transform-Infrared Spectroscopy
The FT-IR analysis of the liquefied bamboo residues was performed by a Nicolet Nexus 670 spectrometer equipped with a Thermo Nicolet Golden Gate MKII Single Reflection ATR accessory. A small amount of residue was applied directly on the diamond crystal. Data collection was performed with a 4 cm^{-1} spectral resolution and 32 scans were taken per sample.

Chemical Analysis
The Klason lignin and alcohol–toluene solubility of the liquefied bamboo residues were determined in accordance with ASTM D1105-96 (ASTM 1996) and D1106-96 (ASTM 1996).[17,18] Each sample was performed in duplicate.

Thermogravimetry Analysis
Thermogravimetry/derivative thermogravimetric analysis (TG/DTG) of the original bamboo and liquefied bamboo residues was conducted on a thermal analyzer, TGA Q50, to simultaneously obtain thermogravimetric data. About 2 mg of sample was used in the analysis of TG/DTG. Pyrolysis was terminated
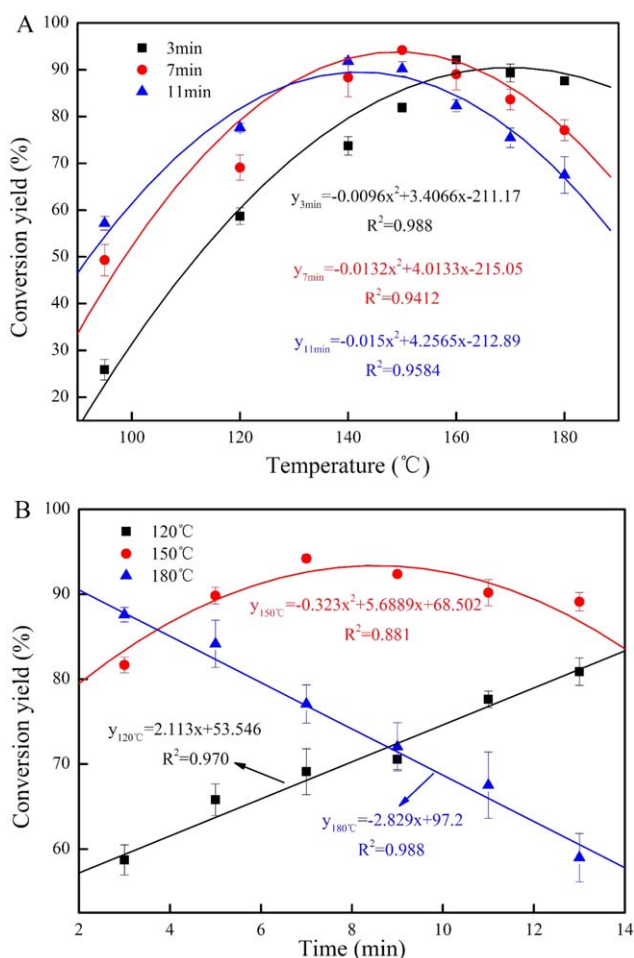

Figure 1. Conversion yield as a function of (A) temperature, (B) time. Other conditions: glycerol/methanol, 2/1; microwave power, 550 W; sulfuric acid, 1.75%; solvent/bamboo, 4/1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

at 800°C with a heating rate of 20°C/min under a flow of 60 mL/min of nitrogen gas.

RESULTS AND DISCUSSION
Liquefaction Reaction Process
The effect of liquefaction temperature on the conversion yield at three reaction times is shown in Figure 1(A). The conversion yield increased rapidly and consistently to the maximum as the liquefaction temperature increased; and thereafter, the conversion yield decreased slightly with further increase in the reaction temperature, indicating a possible curvilinear correlation between temperature and conversion yield. It is generally recognized that liquefaction of lignocellulosic biomass in an organic solvent with an acid catalyst at high temperature is a complex solvolysis processes involving simultaneous reactions of chemical degradation/decomposition, de-polymerization, and re-condensation depending on the process parameters.[19] Several previous studies on liquefaction with conventional heating have shown that low residue content (i.e., increasing conversion yield) was mainly due to the decomposition of hemicellulose,

lignin, and amorphous cellulose[20] and the increasing residue content was attributed to the self-polymerization of the decomposed lignin compounds and/or condensation of lignin fragment with reagents.[21] Similar decomposition and condensation reactions are involved for liquefaction with microwave heating but with remarkable enhancement of the reaction kinetics for microwave energy as compared to conventional heating. A good curvilinear correlation was found between the liquefaction temperature and conversion yield with R^2 values of 0.988, 0.941, and 0.958, respectively, for reaction times of 3, 7, and 11 min [Figure 1(A)]. Furthermore, by taking the first derivative of the curvilinear correlation equation, the optimum temperature for the maximum conversion yields (i.e., maximum yield/optimum temperature) can be determined. The maximum values were 89%/161°C, 90%/151°C, and 89%/142°C, respectively, for reaction times of 3, 7, and 11 min, respectively. It is interesting to note that the values of the maximum conversion yield showed little difference, indicating that the different combinations of temperature and time contribute to almost the same maximum conversion yield. Nevertheless, at high operating temperature, liquefaction can lead to co-condensation reaction of the decomposed (depolymerized) compounds or lignin fragments, which is mostly insoluble and these products are of little economic value unless they are subsequently up-graded. However, low temperature is a preferable operating parameter, but with the significant disadvantage of prolonging the reaction time for optimum conversion. Thus, considering reaction efficiency and cost, the reaction condition of 150°C/7 min seems to be promising.

The significant effect of reaction time on the conversion yield at three temperatures is shown in Figure 1(B). The results showed clearly the interactions between reaction time and temperature to affect the conversion yield. At a low temperature of 120°C, the conversion yield increased from 58.71 to 80.90% as reaction time increased from 3 to 13 min, indicating liquefaction was controlled mainly by a decomposition reaction; while under a high reaction temperature (180°C), the conversion yield showed a decreasing trend, indicating the maximum yield was attained rapidly before 3 min, and the decreasing yield indicated that liquefaction was controlled mainly by a re-condensation reaction.

Rapid liquefaction of bamboo with microwave energy under rather low reaction temperatures (i.e., 120°C) is one of the most interesting results of the study. The prevailing reaction time and temperature with conventional heating in wood liquefaction is 60 min at 150–160°C.[22,23] One possible explanation to the rapid liquefaction is the physical effect of the microwave treatment on lignocellulosic properties. Studies have shown that microwave pretreatment can open water pathways in wood, dramatically increase permeability, and accelerate moisture migration in wood.[24,25] The physical changes in wood properties with microwave energy facilitate favorable conditions for the liquefaction solvents to react. Furthermore, the changes in wood properties combined with the faster heating rates through the volumetrically distributed heat of microwave energy enhance each other to create a heating system, which is significantly superior to that of conventional heating. It should be noted

that the faster heating rates and shorter process times with microwave energy, as compared to that of conventional heating, can provide enormous process development potential for economically viable liquefaction processes such as a continuous reactor, which could greatly advance the commercialization of the process.

Microscopic Analysis of Residue

The SEM images of original bamboo and liquefied residues are shown in Figure 2. The original bamboo [Figure 2(a)] showed uneven-sized bundles with many small fragments on the rough surfaces. As can be seen in the image of the residue at 120°C, the large bundles were reduced into smaller fiber bundles with smooth surfaces indicating that the small fragments attached on the surface of the original bamboo were almost completely removed during the liquefaction reaction. Moreover, broken single fibers or parenchyma cells were also observed from the SEM image [Figure 2(b)] of the decomposed residue. It is apparent that the lignin component was removed, leaving the retained tissue cells in an untidy order.

The significant temperature effect on liquefaction was most evident with reaction at 150°C. The SEM image at 3 min reaction time displayed similar individual fiber morphology to that at 120°C reacted for 13 min, which was with a reaction time of more than four times longer; indicating the significant effect of liquefaction temperature [Figure 2(e)]. Furthermore, it is interesting to note, at a reaction time of 5 min, the fiber and parenchyma cells were broken and a large surface area was created and resulted in a relatively homogeneous texture [Figure 2(f)]. As reaction time increased to 9 min, the liquefied residues turned into small spherical granule substances on the surface (~0.1–0.2 μm in diameter) [Figure 2(g)]; and finally, the granules fused and carbonized into a conglomerate mass as reaction time increased to 13 min [Figure 2(h)]. It should be noted that at 180°C, the formation of carbonized conglomerate mass was the main substance produced early in the liquefaction [Figure 2(i)].

FT-IR Spectroscopy

The transmittance spectra of the residues from different liquefaction conditions are shown in Figure 3. Significant differences for the spectra were found between the original bamboo (spectra a) and liquefied residues (spectra b, c, d) [see Figure 3(A)]. A broad peak at around 3320 cm^{-1}, which was assigned to –OH groups and the peak at around 2880 cm^{-1} related to methyl and methylene stretching[26,27] were stronger in the original bamboo than those in the liquefied residues.

The absorbance peak at 1735 cm^{-1} assigned to C=O stretching vibration of the carboxyl and acetyl groups in hemicellulose[23] was weakened in the spectra of residues from 95 to 120°C, and then was reduced to a shoulder in the spectra of residue from 140°C. However, the peak was intensified in the spectra of residue at 180°C. It can be concluded that hemicellulose could be decomposed at lower temperature and then undergo repolymerization at higher temperature. The absorbance at 1596 and 1506 cm^{-1} arising from the aromatic skeletal vibration, the absorbance at 1456 cm^{-1} assigned to C—H deformation combined with aromatic ring vibration, and the band at 1230 cm^{-1}
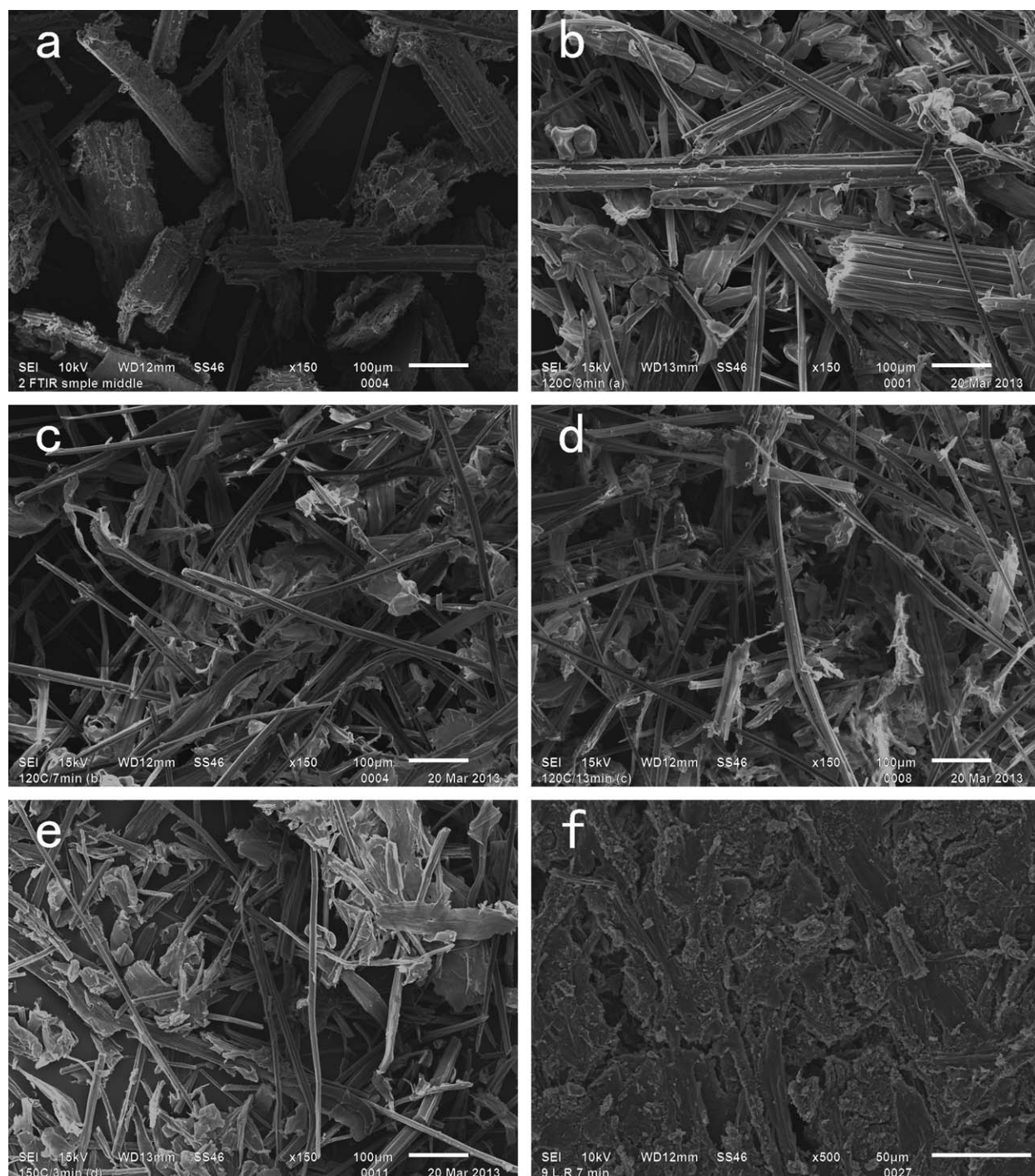
Figure 2. SEM images of liquefied residues obtained from different conditions: (a) raw material; (b) 120°C, 3 min; (c) 120°C, 7 min; (d) 120°C, 13 min; (e) 150°C, 3 min; (f) 150°C, 7 min (g) 150°C, 9 min; (h) 150°C, 13 min; (i) 180°C, 3 min.

corresponding to methoxyl groups of lignin[5] were all shown to be strong peaks in the spectra of the original bamboo. These peaks were weakened in the spectra of residue at 95°C. As the temperature increased to 140°C, the absorbance bands at 1506, 1456, and 1230 cm^{-1} disappeared and the band at 1596 cm^{-1} became a small shoulder. It appears that the lignin was almost completely decomposed at 140°C within 7 min. However, with further increase in reaction temperature, these peaks intensified again; indicating that the decomposed compounds such as aro-

matic ketone groups interact with the aromatic hydroxyl group to form an aromatic network.

The bands for different functional groups of cellulose such as the methylene groups at 1420 and 1365 cm^{-1}; CH_2 rocking vibration at 1320 cm^{-1}, and C—O band at 1162 and 1108 cm^{-1} and CH deformation at 899 cm^{-1} were weakened in the spectra of residues from low liquefaction temperatures and then disappeared in the spectra of residue at 180°C. According to
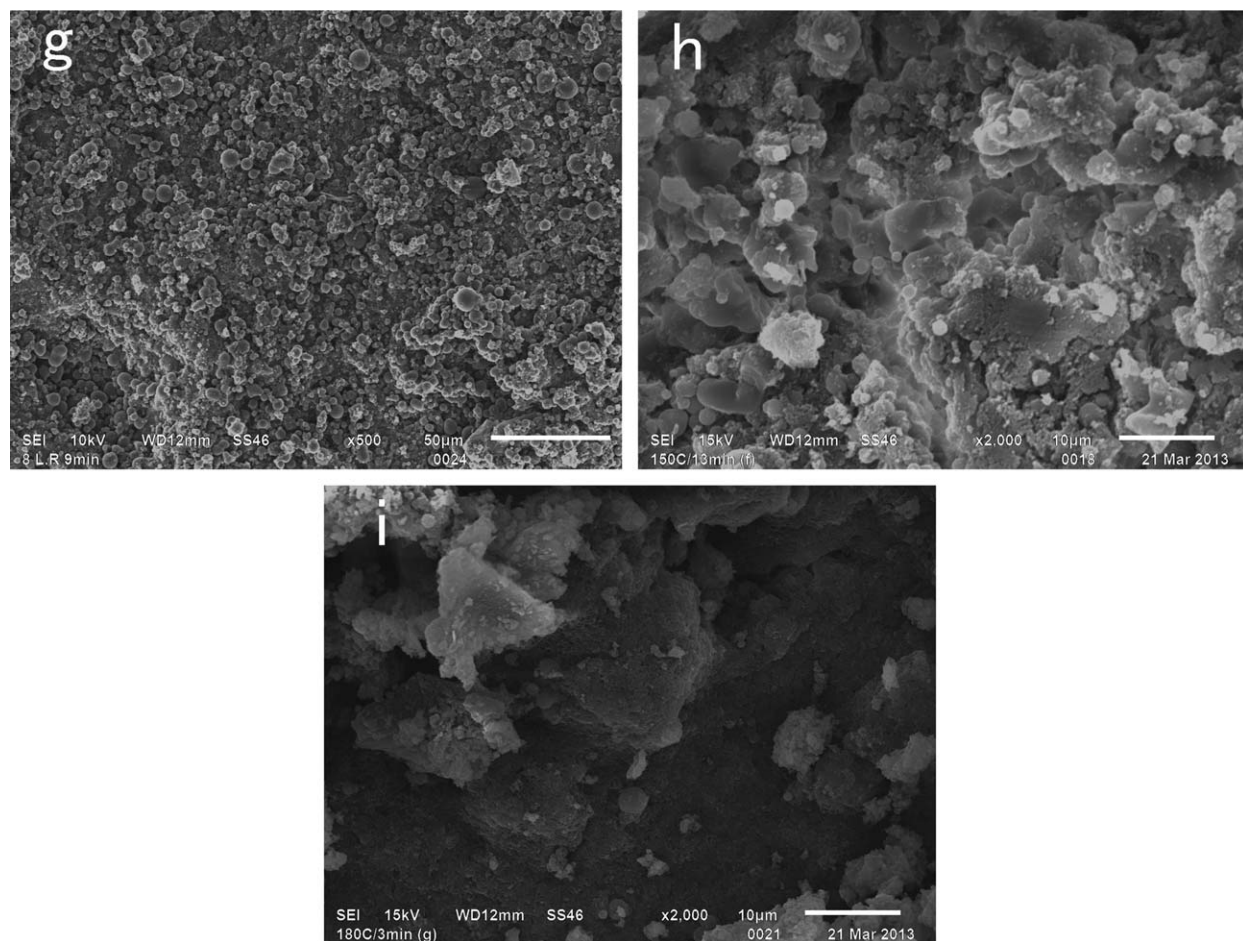
Figure 2. (Continued)

Akerholm et al.,[28] the band at around 1420 cm^{-1} is associated with the amount of crystalline structure of the cellulose. As shown in the spectra of residue from 180°C [Figure 3(A)], the band at 1420 cm^{-1} disappeared, indicating that cellulose, even the crystalline cellulose, could be liquefied with a glycerol/methanol co-solvent using microwave energy. This was consistent with our previous results that microwave heating could provide favorable conditions for fast and complete liquefaction of bamboo. Though microwave irradiation could promote the decomposition of cellulose, it also caused lignin/hemicellulose recondensation. Hence, liquefaction conditions should be properly optimized for the specific functional applications.

The spectra of the liquefied residues as a function of reaction time are shown in Figure 3(B). It was obvious that absorbance bands that characterized functional groups of hemicellulose and lignin have disappeared, leaving the weakened bands assigned to cellulose, which is visible in the spectra of residue liquefied for 5 min at 150°C. This was in good agreement with the conversion yield result, which showed that about 90% of the solid bamboo was converted into the liquid phase. By further prolonging the reaction time to 9 min the retained cellulose was decomposed along with the recondensation of lignin or hemicellulose.

The disappearing bands assigned to the functional groups of cellulose and the intensive bands for those of the hemicellulose and lignin in the FT-IR spectra of the residues obtained from higher temperature/longer reaction time suggested that liquefaction under critical conditions induced by microwave heating was a complex reaction involving the lignin/hemicellulose repolymerization and cellulose decomposition reactions.

Chemical Analysis

The lignin content and the relative intensities of its typical bands for original bamboo and liquefied residues were determined. As shown in Figure 4, the Klason lignin content and alcohol–toluene extractive for original bamboo were 20.91 and 7.24%, respectively. After liquefaction, the lignin content was reduced to 11.54 and 1.85% for the residues from 95 to 120°C, respectively. The negligible alcohol–toluene extractive content for the residues from lower temperatures indicated that the alcohol–toluene soluble substances in bamboo such as waxes, fats, resins, and gums were transferred into liquid with the liquefaction process. The lignin content for the residues from 180°C was 51.1% and the alcohol–toluene extractive content was 40.3%, which was inconsistent with the average Klason lignin content and alcohol–toluene extractives for woody materials. Therefore, the classical chemical method was not suitable
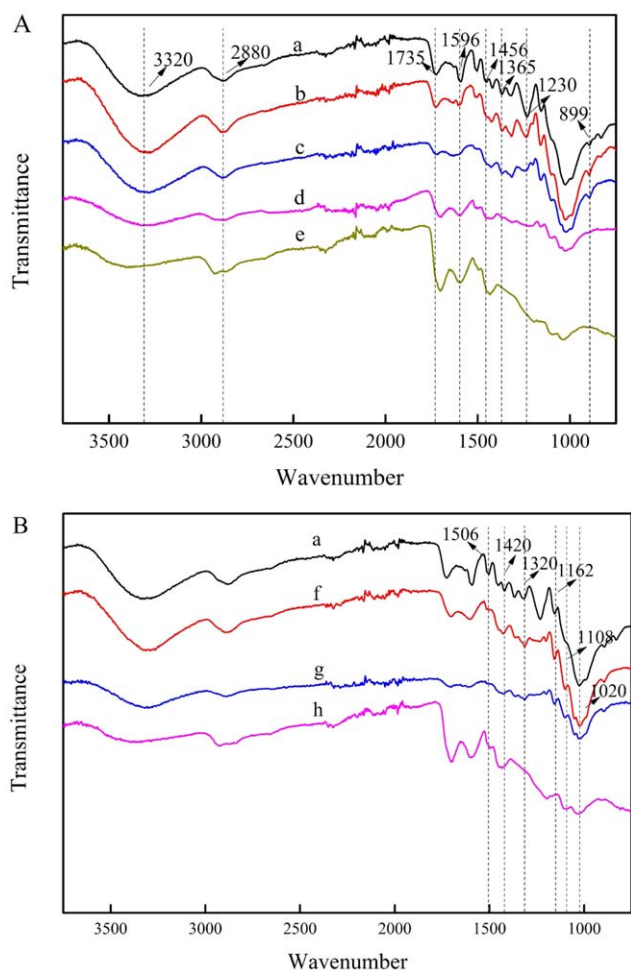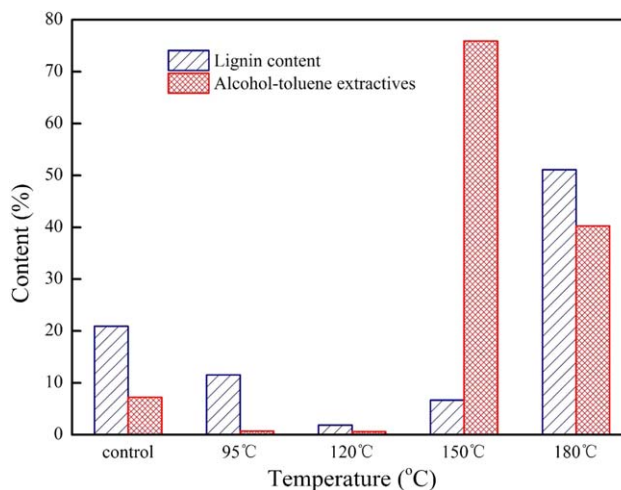
Figure 4. Effect of temperature on the lignin and alcohol–toluene extractive contents of liquefied residues. Other conditions: time, 7 min; microwave power, 550 W; sulfuric acid, 1.75%; solvent/bamboo, 4/1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the functional groups of lignin could be used to estimate the decomposed degree of lignin in bamboo. The absorbance intensities for the residues from 180°C are as strong as that in the original bamboo. The higher intensities were attributed to the functional groups of the insoluble intermediate compounds of lignin and not from lignin. Thus, the intensities could also be used to indicate the recondensation degree of lignin fragments in the liquefaction reactions.

Thermogravimetric Analysis

The TG and DTG curves of the original bamboo and residues are shown in Figure 5. The weight loss process for all the samples could be divided into three stages: the mild weight loss stage, the main pyrolysis stage, and the charring stage. As shown in Figure 5(A), initial weight loss was found in the mild weight loss stage for the original bamboo and the residue at 140°C (curve a, b), while the TG curve for residues at 150°C/9min or 180°C/7min (curve d, e) showed no apparent weight loss in this stage. The initial weight loss for the original bamboo was attributed to the evaporation of lower molecular weight compounds. The initial weight loss for the residue at 140°C may be attributed to the volatilization of retained fragments of decomposition from the major bamboo components with the liquefaction process; however, these fragments were resolved when liquefaction was conducted at 150°C as can be seen in Figure 5(A) (curve c). The TG curves also showed that the

Figure 3. FT-IR transmittances of (a) original bamboo and residues: (b) 95°C, 7 min, (c) 120°C, 7 min, (d) 140°C, 7 min, (e) 180°C, 7 min, (f) 150°C, 3 min, (g) 150°C, 5 min, (h) 150°C, 9 min. Other conditions: glycerol/methanol, 2/1; microwave power, 550 W; sulfuric acid, 1.75%; solvent/bamboo, 4/1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

for the quantitative analysis of major components of the residues from multiple solvolysis reactions.

As listed in Table I, the relative intensities of absorbance bands showed a decreasing trend as the liquefaction temperature increased from 95 to 140°C. It was interesting to note that the trend of relative intensities with the liquefaction temperatures was in accordance with that for the lignin content as shown in Figure 4. It made sense that the intensities of bands assigned to

Table I. FT-IR Absorbance Bands Assigned to Functional Groups of Lignin Retained in Liquefied Residues

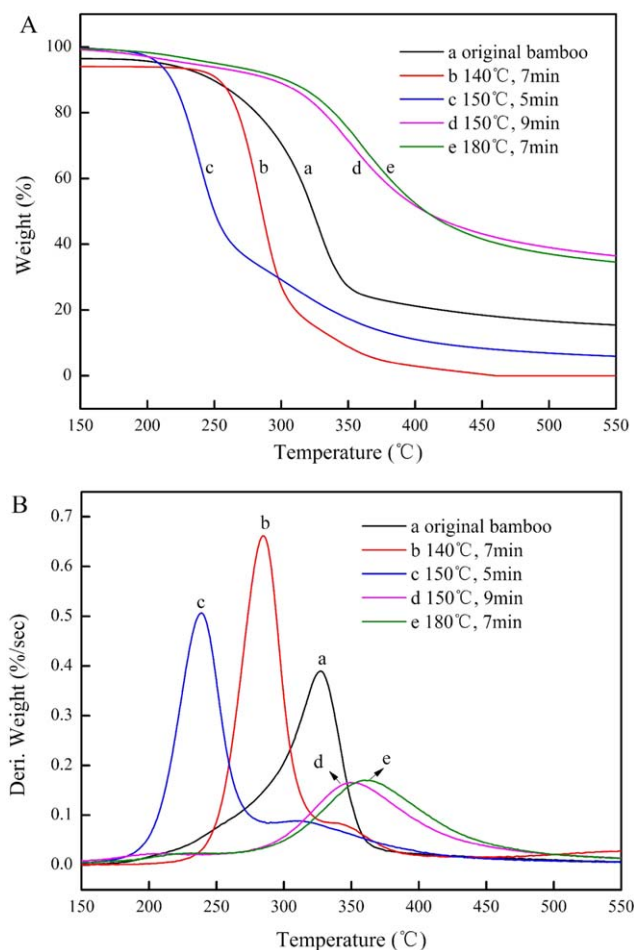| Wave Number (cm)	Assignment	Control	95°C	120°C	140°C	180°C
1596	Aromatic skeleton	0.17	0.12	0.09	0.08	0.16
1506		0.15	0.10	0.08	–[a]	0.15
1456	C—H stretching	0.18	0.14	0.10	–	0.19
1230	Methoxyl groups	0.25	0.18	0.11	–	0.24

[a] Indicates no peaks generated.

Figure 5. TG (A) and DTG (B) curves for (a) original bamboo, decomposed residues (b) 140°C, 7 min, (c) 150°C, 5 min, recondensed residues (d) 150°C, 9 min, (e) 180°C, 7 min. Other conditions: glycerol/methanol, 2/1; microwave power, 550 W; sulfuric acid, 1.75%; solvent/bamboo, 4/1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

weight loss percent of the residues at 140°C/7min, 150°C /5min was the highest in the main pyrolysis stage, and the pyrolysis char yield was the lowest. Compared to the original bamboo, the residue at 140°C/7min, and the residue at 150°C /5min, the residue at 180°C/7 showed wider pyrolysis temperature, less weight loss percent, and higher pyrolysis char. It is clear that this was correlated with acid-insoluble substances with polyphenolic structures such as an aromatic skeleton as indicated by the FT-IR spectra. The higher thermal stability of these structures contributed to its recondensed substances. This could be well evidenced by the findings of Niu et al.[29] who found that the thermal stability of the recondensed residue was mainly from the substances with higher molecular weight formed by polyphenolic structure compounds.

Significant differences were also found for the sharp peaks corresponding to the maximum degradation rate in the DTG curves between all the samples as shown in Figure 5(B). The DTG curves for the residues obtained under mild conditions (140°C/7min, 150°C/5min) showed higher degradation rate and

lower maximum degradation rate temperature compared to those obtained from higher temperature/longer reaction time. The maximum degradation rate and temperature for the original bamboo were intermediate. These differences in degradation rate are largely related to the differences in chemical components between the original bamboo and residue samples. As for the three components of woody materials, hemicellulose was the easiest to be pyrolyzed, cellulose, then lignin in TG analysis.[30] However, when lignocellulose was applied in a liquefied process using organic solvents, lignin was the most reactive component and easily underwent recondensation.[31] On the basis of these reasons, the removal of lignin by liquefaction under mild reaction conditions contributed to the lower weight loss temperature and higher weight loss rate for the residue. The recondensed substances from reactions of decomposed lignin fragments resulted in the lowest maximum weight loss rate and highest maximum weight loss rate temperature for the residues.

CONCLUSIONS

Conversion of bamboo at about 94.33% was achieved by liquefaction with glycerol/methanol using microwave energy. Liquefaction temperature and time had a mutual effect on the liquefaction process. The liquefaction was complex solvolysis chemical reactions under critical conditions according to the residue characteristics. Peaks attributed to the functional groups in hemicellulose and lignin were weak or absent in the FT-IR spectra of residues from low liquefaction temperature, while those in the FT-IR spectra for recondensed residues were intensive. The FT-IR spectra could be selected as a simple method to evaluate the liquefied degree of bamboo and its three main components. Liquefaction behaviors under different conditions were also distinguished by the SEM images. Individual fiber or parenchyma cells were observed in the SEM images of residues from mild reaction conditions, while small spherical granule substances or conglomerate mass were observed with the increasing of temperature or the prolongation of time. The thermal stabilities of the residues obtained from higher temperature or longer reaction time were higher than that of the residues obtained from mild liquefaction conditions (low temperature) and original bamboo.

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