

## Optimization for microwave-assisted direct liquefaction of bamboo residue in glycerol/methanol mixtures

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**Abstract** Bamboo residues were liquefied in a mixture of glycerol and methanol in the presence of sulfuric acid using microwave energy. We investigated the effects of liquefaction conditions, including glycerol/methanol ratio, liquefaction temperature, and reaction time on the conversion yield. The optimal liquefaction conditions were under the temperature of 120 °C, the reaction time of 7 min, the glycerol–methanol–bamboo ratio of 8/0/2 (W/W), and the microwave power of 300 W. Maximum conversion yield was 96.7 %. The liquid products were separated into two contents (water soluble part and precipitate part) by addition of a sufficient amount of water. By Fourier transform infrared (FT-IR), the water soluble content mainly contained glycerol and its derivate and carbohydrate degradation products, and the precipitate content was mainly lignin derivatives.

**Keywords** Bamboo residue · Microwave · Liquefaction · Glycerol

### Introduction

As an important thermochemical method, liquefaction of woody materials has been carried out with various solvents for different end products (Mishra and Saka 2013; Xie and Shi 2006; Lin and Hse 2005). However, the most commonly explored solvents for liquefaction are derived from petroleum. These solvents are effective, but require large quantities and are costly. A by-product of the transesterification process to manufacture bio-diesel is the production of glycerol. For each kilogram of biodiesel produced, there is about 0.1 kg of accompanying crude glycerol (Thompson and He 2006). 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.

Compared to conventional heating, microwave energy penetrates and produces a volumetrically distributed heat source, and heat is generated throughout the material and leads to faster heating rate and improved kinetics. Recently, microwave energy has been successfully applied to the liquefaction of lignocellulosic biomass (Krzan and Zagar 2009; Pan et al. 2012; Xu et al. 2012). Therefore, 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.

As one of the most important forest resources, bamboo is widely cultivated in Asia, Africa, and South and Central

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America and has been used as one of the main resources for flooring and furniture manufacturing (Gao et al. 2010). However, because of the limited processing technologies and the special characteristics of bamboo culms, process residues, such as bamboo branches, nodes, epidermis, wax, and pulping by-products, are cast aside as waste. Thus, an economically viable bamboo waste conversion technology is needed to address problems concerning both waste disposal and resource wastage. In the present study, we used microwave heating to investigate the liquefaction of bamboo residues with glycerol-based solvents. The reaction parameters that affect the microwave liquefaction of bamboo were optimized for the yield of liquid product. The liquid product obtained from this liquefaction system was also separated and evaluated.

## Materials and methods

### Materials

Bamboo (*Phyllostachys pubescens*) residue used in the experiments was collected from central Louisiana, USA. The air-dried residues were reduced to particles. The particles were screened to collect particles that passed through a 40-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 process

Microwave liquefaction of bamboo was carried out in a Milestone (Shelton, CT, USA) 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. Based on monitored temperature, the output power was auto-adjusted during liquefaction. Temperature was increased from room temperature to 150 °C at a heating rate of 37.5 °C min<sup>-1</sup> and then was kept constant for 3 min, unless otherwise noted. After a cooling period of 30 min, 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 Eq. 1:

$$\begin{aligned} \text{Conversion yield (\%)} \\ = \left( 1 - \frac{\text{Oven dried weight of residue}}{\text{Oven dried weight of raw material}} \right) \times 100 \end{aligned} \quad (1)$$

### Separation of the liquefied product

The filtrated liquid was evaporated at 45 °C under vacuum to remove methanol, then distilled water (10/1, W/W) was added into the black crude bio-polyols. The mixer was stirred thoroughly with a glass rod. Afterwards, the limous aqueous was centrifuged at 5,000 r min<sup>-1</sup> for 10 min. The water-soluble content was obtained by removal of the water from the supernatant fluid using a rotary evaporator at 70 °C. The precipitate content was dried at 30 °C for 12 h.

### FT-IR analysis

FT-IR analysis of the raw material and liquefied products was performed by a Nicolet Nexus 670 spectrometer equipped with a Thermo Nicolet Golden Gate MKII Single Reflection ATR accessory. A small amount of sample was applied directly on the diamond crystal. Data collection was performed with a 4 cm<sup>-1</sup> spectral resolution and 32 scans were taken per sample.

## Results and discussion

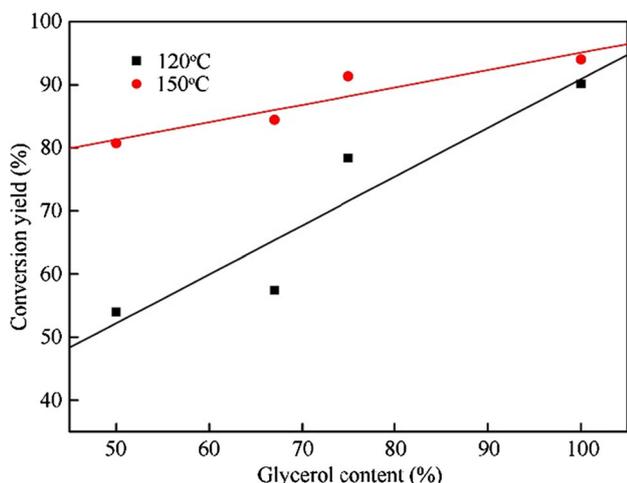
### Effect of glycerol/methanol ratio

The main solvents were glycerol and methanol. The effect of glycerol/methanol ratio on the conversion yield is presented in Fig. 1. At 120 °C, the conversion yield increased significantly with the increasing ratio of glycerol/methanol (Fig. 1). Then the pure glycerol liquefaction of bamboo residues had maximum conversion yield (90.15 and 94.04 % for 120 and 150 °C, respectively). It could be concluded that glycerol was very effective in enhancing the decomposition of bamboo residues at low temperature in this liquefaction system. Similar results showing that the addition of glycerol to PEG accelerated the liquefaction rate were reported for other studies of lignocellulosic liquefaction (Hassan and Shukry 2008). According to the results, glycerol in the liquefaction system reduced the expense of the process.

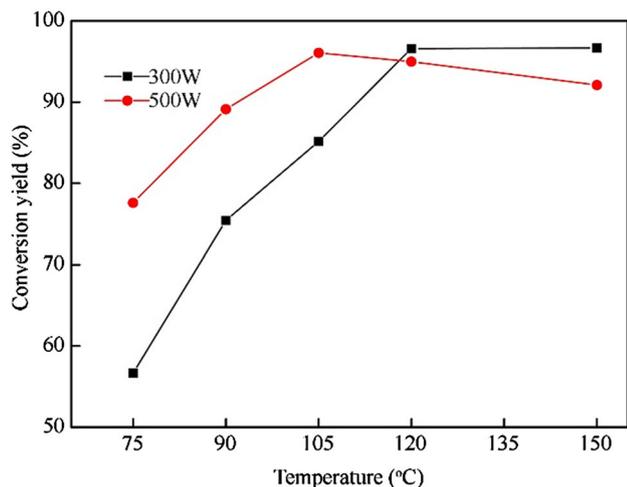
Effect of liquefaction temperature

Figure 2 shows the temperature-dependence of the liquefaction curves for conversion yield at two levels of microwave power (300 and 500 W). At microwave power of 300 W, the conversion yield increased dramatically as the liquefaction temperature increased from 75 to 120 °C (Fig. 2). The bamboo residues were nearly decomposed within 7 min at 120 °C (conversion yield = 96.7 %). Further increase in temperature to 150 °C did not significantly increase conversion yield.

Similar decomposition was observed for liquefaction with microwave power of 500 W at the initial liquefaction



**Fig. 1** Effect of glycerol content on conversion yield. Other conditions: sulfuric acid of 1.75 %, solvent/bamboo of 4/1, reaction time of 3 min, and microwave power of 500 W



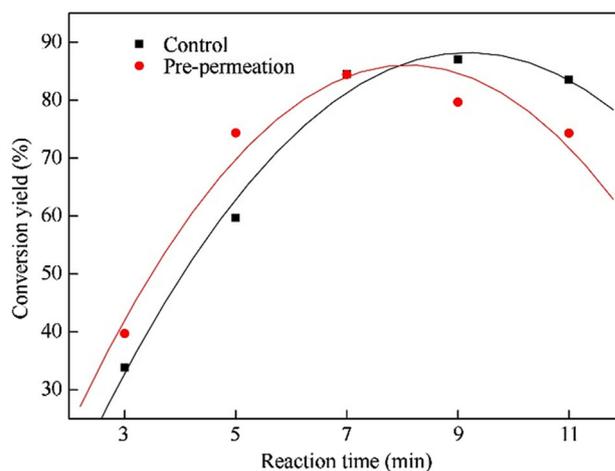
**Fig. 2** Effect of temperature and microwave power on conversion yield. Other conditions: solvent of glycerol, glycerol/bamboo of 4/1, the reaction time of 7 min, and the sulfuric acid of 1.75 %

stage but with remarkable enhancement of reaction kinetics. The conversion yield showed a slight decrease from 105 to 150 °C, which was attributed to the recondensation of the liquefaction intermediates (Lin et al. 2001; Chen and Lu 2009). Accordingly, taking reaction efficiency and energy consumption into consideration, the optimal reaction temperature was 120 °C and optimal microwave power was 300 W.

Effect of reaction time

The effect of reaction time on liquefaction yield is shown in Fig. 3. With increasing reaction time, the liquefaction yield first increased and then decreased. Generally, the liquefaction of lignocellulosic biomass in an organic solvent with an acid catalyst at high temperature is a complex solvolysis process involving simultaneous reactions of chemical degradation/decomposition, de-polymerization, and re-condensation depending on the process parameters. Thus, at shorter times (3–7 min), the increase in conversion yield is mainly due to the fact that degradation/decomposition outweighs repolymerization. Then, with the prolongation of reaction time (9–11 min), degradation gradually decreased and repolymerization played the main role in liquefaction (Balat 2008; Zou et al. 2009; Xie et al. 2014), which attributed to the decrease in conversion yield.

To evaluate the effect of solvent pre-permeation treatment on conversion yield, 2 g bamboo samples measuring 10 × 5 × 1 mm were first treated under 103.5 kPa, full-cell pressure vacuum for 15 min. After the successful adsorption of the solvent (8 g) and catalyst (0.14 g), the pressure was increased to 827.4 kPa for 30 min. Then, the mixture was subjected to the liquefaction system.



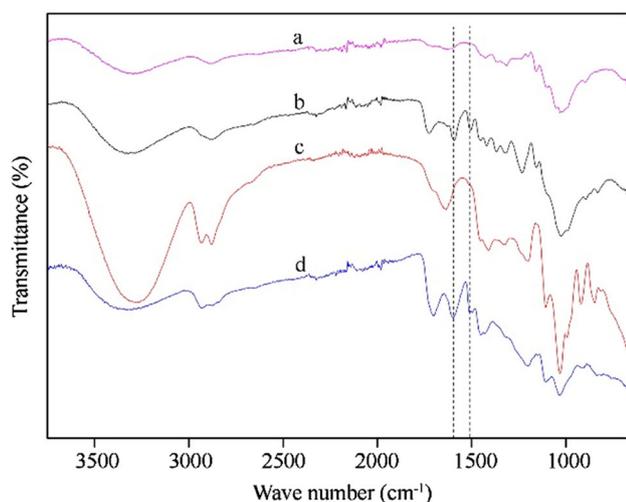
**Fig. 3** Effect of time and pre-permeation on conversion yield. Other conditions: solvent of glycerol, glycerol/bamboo of 4/1, temperature of 150 °C, time of 7 min, sulfuric acid of 1.75 %, and particle size of 10 × 5 × 1 mm

Liquefaction of the pre-permeation bamboo residues showed higher conversion yield than the control samples until 7 min (Fig. 3). However, when liquefaction time was prolonged to 9 min, the conversion yield for pre-treated bamboo was lower than that of the control samples. The pre-permeation treatment made distribution of the reagents within the bamboo much more uniform. Hence, both the uniform distribution of reagents and temperature contributed to the promotion of degradation/repolymerization.

#### FT-IR spectra

FT-IR was conducted to determine the chemical functional groups presented in different contents. The spectra patterns for different content samples were significantly different, indicating that the main chemical groups were diverse (Fig. 4).

From the spectrum of bamboo raw material (Fig. 4, Spectrum b) peaks at 1,735, 1,420, 1,372, 1,320, 1,162, 1,108, 899  $\text{cm}^{-1}$  were related to carbohydrate (cellulose and hemicellulose) bands, and peaks at 1,596, 1,506, 1,456, and 1,230  $\text{cm}^{-1}$  were assigned to lignin. In the spectrum for residue, the lignin/hemicellulose bands at 1,735, 1,596, 1,506, and 1,456  $\text{cm}^{-1}$  were nonexistent, the cellulose bands weakened, and the residue content was mainly cellulose in construction. The water soluble content (Fig. 4, Spectrum c) showed enriched hydroxyl groups as indicated by the band at 3,320, 1,028, 1,108, 920, and 845  $\text{cm}^{-1}$  that assigned to cellulose, glycerol and its derivatives. The lignin bands (1,596, 1,506 and 1,456  $\text{cm}^{-1}$ ) disappeared, indicating that the water soluble content only contained



**Fig. 4** FTIR spectra of (a) liquefied residue, (b) raw material, (c) water soluble content, (d) precipitate content. Liquefaction conditions: solvent glycerol/methanol of 2/1, microwave power of 300 W, sulfuric acid of 1.75 % (w%), solvent/bamboo of 4/1, temperature of 150 °C, and time of 7 min

carbohydrate-degraded fragments and glycerol/methanol blended solvents. The spectrum of the precipitate fraction was significantly different from that of the water soluble content. Characteristic bands of lignin were observed (Fig. 4, Spectrum d), indicating that the precipitate content was comprised of lignin-degraded products.

#### Conclusion

Bamboo residue was almost completely (maximum conversion yield of 96.7 %) converted to liquid phase in glycerol using microwave energy. Addition of methanol into glycerol decreased the conversion yield. Glycerol alone can be recommended as a liquefaction solvent as the maximum conversion yield reached maximum under mild conditions (7 min/120 °C). Increasing liquefaction temperature (to 150 °C) or prolongation of reaction time (9–11 min) led to the condensation reactions in this system. Higher microwave power and pre-permeation treatment could promote the reaction kinetics both in degradation and recondensation. The liquefied products could be successfully separated into two contents by adding water.

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