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Renewable platform chemicals from directional microwave-assisted liquefaction coupling stepwise extraction of waste biomass

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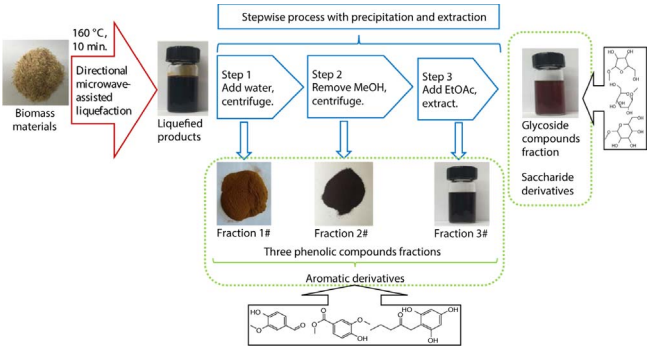
GRAPHICAL ABSTRACT



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ABSTRACT

Directional microwave-assisted liquefaction and stepwise extraction are introduced for producing platform chemicals: aromatics and monosaccharides. When sulfuric acid was used as a catalyst, a 45% monosaccharides yield and a 29% aromatics yield were obtained from bamboo with 0.3 g catalyst per 18 g methanol and 2 g bamboo at 160 °C with 10 min. Approximately 78–86 wt% of the six biomass materials were converted into liquid products. After the stepwise extraction and precipitation process, the yields of monosaccharide derivatives and three phenolic compound fractions were 39–45% and 28–32%, respectively. Monosaccharides from holocellulose collected with a high purity of methyl glycosides were higher than 90%. Aromatic derivatives with different weight-molecular distributions were separated into three fractions with more than 80% phenolics. As their similar chemical properties within each fraction, platform chemicals have great commercial potential for producing high-quality chemicals and biofuels using mild upgrading conditions.

1. Introduction

Lignocellulosic biomass is one of the most promising resources for producing biofuels and chemicals. Waste lignocellulosic biomass, such as furniture manufacturing waste, papermaking waste, and agricultural residues are abundant, renewable, carbon-based and underutilized. Thermochemical conversion (pyrolysis or liquefaction) of lignocellulosic biomass into renewable chemicals has attracted extensive attention because of increasing public attention on environmental protection and growing demand for sustainable biofuels and chemicals

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(Cai et al., 2017; Liu et al., 2014). Converting solid biomass into liquid products can significantly increase the feasibility of transportation and density of energy. Bio-crude from thermochemical conversion of biomass has been identified as a renewable chemical fuel source and energy carrier. However, the structural complexity and chemical instability of such products hinder bio-crudes used as high-quality chemicals and biofuels (Yang et al., 2015). Upgrading and improving the quality of bio-crudes is an effective mean to solve this situation (van Putten et al., 2013).

Conventional thermochemical liquefaction of lignocellulosic biomass produces complex and unpredictable mixtures with unstable structures of liquefied products. This is mainly due to re-decomposition of saccharide derivatives and re-condensation of aromatic products, which causes the subsequent separation and improving processes to become economically impractical (Colmenares and Luque, 2014; Lehtoa et al., 2014). Lignocellulosic biomass is mainly comprised of three components: hemicelluloses, cellulose, and lignin, of which the holocellulose and lignin fractions can account for up to about 60–70% and 15–35%, respectively. The production of high grade liquefied bio-oil is still a challenge because of the strong chemical linkages between hemicelluloses and lignin, the recalcitrant crystalline structure of cellulose, and the complexity of linking between these three components (Besson et al., 2013). The highly complex molecular structure and intrinsic heterogeneity of the lignin macromolecule, such as methoxylated phenyl-propanoid subunits, combined with its highly recalcitrant chemical nature, has so far hampered many efforts to increase its value.

One thermochemical conversion of lignocellulosic biomass is fast pyrolysis, which requires high temperature (around 500 °C) and short reaction time (less than 2 s), and can produce a yield of pyrolytic oil close to 75 wt%. However, the high temperature with fast reaction rate process leads to unpredictable cleavage of complex chemical bonds between hemicelluloses, cellulose, and lignin resulting in low selectivity and complex structure of pyrolytic products. Pyrolytic oil contains complex mixtures of highly oxygen-containing organics (Biswasa et al., 2017; Carpenter et al., 2014). There are hundreds of oxygenated derivatives in pyrolytic oils, however, each product accounts for only a small part of the pyrolytic oils. Currently, there are few efficient solutions to convert fast pyrolysis oils into a high-quality commercial product (Shuai et al., 2016). Liquefaction of lignocellulosic biomass for high quality chemicals using water or organic solvents under mild conditions has attracted extensive interesting. These liquefaction processes can produce a high yield of liquid products (75–90%) with some improved grades, such as low moisture content and acidity (van Rossum et al., 2014; Brand and Kim, 2015). Process development research into converting lignocellulosic biomass into biofuels and chemicals in subcritical or supercritical alcohols (methanol, ethanol, propanol, butanol, etc.) (Huang and Yuan, 2015; Brand et al., 2013) and water (Thangavelu et al., 2014; Zhu et al., 2016) with microwave assistance have been widely investigated. Compared with water, alcohols have better permeability, lower reaction pressures, and more moderate reaction conditions, which can be applied for biomass liquefaction. Another advantage is that alcohols are able to readily dissolve high molecular-weight products derived from biomass. The products formed in alcohols are more stable than the products formed in water, and the alcoholysis of biomass is more efficient than hydrolysis.

Most of the previous studies have focused on the improvement of the liquefied products' yields and properties, such as calorific value, viscosity, and density. These studies may have largely ignored the molecular transformation pathways of the three components in biomass. The molecular structure of chemicals can determine the physical and chemical properties of products. Thereafter, these conventional thermochemical methods, such as fast pyrolysis and solvent liquefaction still lead to the productions with many unpredictable and complex structures (Doassans-Carrère et al., 2014; Li et al., 2014). The upgrading and refining methods reported for fast pyrolysis oil, which are similar to these for liquefied oil (Zhang et al., 2013, 2014; Zhao and Lercher 2012a,b; Yao et al., 2015), provide little economic adaptability and feasibility.

Converting biomass model compounds into high added-value chemicals has already been achieved (Zhao and Lercher, 2012a,b; Chen et al., 2014). High added-value of levulinic acid, levulinates, hydroxyl methyl furfural (HMF), furfurals, and alcohols were achieved from model compounds such as cellulose, starch, fructose, and glucose. These models have great potential for producing liquid fuels and fine chemicals (Song et al., 2016; Saha and Abu-Omar, 2014). These studies mainly concentrated on the molecular change of a single component of cellulose or hemicelluloses in biomass, such as sugars and long chains of sugar units (starch and cellulose). And the process of models indicated the possibility of such high quality chemicals and biofuels to be directly derived from real lignocellulosic biomass. These studies of models are also important for establishing the optimal conditions for converting lignocellulosic biomass into high added-value chemicals and quality biofuels. However, there are many morphological and structural differences between models and real biomass. The transition from the model compounds to actual lignocellulosic biomass requires appropriate modifications to the liquefaction process so that the liquefied products can easily undergo extraction, and can be separated into the desired fractions for further upgrading and refining.

Biomass has a complex lignocellulosic structure of crystallized holocellulose and high-polymerized phenolic lignin, which means that the liquefaction and separation process is more difficult than that of cellulose and starch. Therefore, a new challenge in liquefaction is the valorization of real biomass into high-quality chemicals and biofuels, efficiently utilizing all three components in biomass (Morgan et al., 2017; Luterbacher et al., 2014). Converting cellulose, hemicelluloses, and lignin into platform chemicals such as monosaccharide derivatives (mainly glycoside compounds) and aromatic derivatives (mainly phenolic compounds) with similar physiochemical properties is more desirable. The two platform chemicals can be easily transformed into high added-value biofuels and chemicals. Moreover, there are few reports on effective utilization of the depolymerized lignin derived from biomass (Ragauskas et al., 2014). Substantial current research is primarily focused on the valorization of lignin produced from the pulp and papermaking industry. The physical and chemical properties of lignin can indiscriminately change depending on the process conditions and add further structural complexity to these already heterogeneous polymers. Only approximately 2% of the lignin (available from the pulp and papermaking industry) is utilized for producing commercial chemicals (such as lignosulfonates and kraft lignin) (Guo et al., 2017).

The lignin-derived products (phenolic compounds) have a wide range of applications: raw materials for production of phenol formaldehyde resins, intermediates in the synthesis of pharmaceuticals, gasoline additives, polymerization initiators and colorants, etc. For example, phenolic resins are typically cross-linked polymeric resins which are derived from petroleum. The availability and price of phenols are linked to petroleum, and industrial products using phenols as feedstocks such as phenolic resins or phenol-formaldehyde are relatively expensive. Therefore, attempts have been made to substitute petroleum-based phenol in phenolic resins with cost-effective phenols derived from lignocellulosic material. The phenolic compounds also can be upgraded into high energy hydrocarbons such as alkanes and hydrocarbons with a hydrodeoxygenation process. Glycosidic compound is a high value-added chemical that can be used as a non-ionic surfactant in many aspects of textile medicine, pesticide, building materials, environmental protection, cosmetics, and agriculture. These platform products also have diverse applications, such as the synthesis of high grade furfurals and levulinates, which have been widely used as food or fuel additives. In general, it is important to efficiently extract the phenolic compounds and glycosidic compounds from liquefied products.

Considering all the above limitations, a simple and sustainable process that involves directional microwave-assisted liquefaction of

biomass to produces renewable platform products (monosaccharide and aromatic derivatives) has been designed. This strategy implies that target products derived from holocellulose and lignin in lignocellulosic biomass could be stepwise fractionated according to hydrophobic and hydrophilic properties in the solvent. Therefore, this simple process achieves an integrated utilization of liquefied products to different synthesis directions based on their chemical solubility and molecular structures. Due to the similar physical and chemical properties of platform chemicals components, most side reactions can be avoided in the upgrading and refining process. We determined the effective parameters on the production of two platform chemicals (monosaccharide derivatives and aromatic compounds). The conversion of lignocellulosic biomass to platform chemicals has great promise for predigesting the downstream process.

2. Materials and methods

2.1. Materials and chemicals

For this study, bamboo wastes were collected from the Kisatchie National Forest in Pineville, Louisiana, USA. Five other types of waste lignocellulosic biomass were used in this study: poplar, pine, eucalyptus, bagasse, and straw were collected from a farm (Jiangsu, China). All materials were dried to a constant weight at 105 °C for 24 h, and passed through a 250–425 μm sieve. The materials were then kept in sealed bags until needed. The elemental and compositional properties of six selected raw biomass samples were shown in Table 1. All other chemicals in the study were of analytical grade, commercially available, and used without further purification.

2.2. Analytic methods

The components of liquefied products were conducted on a mass spectrometer (MS, Agilent 5975C VL MSD) and a gas chromatograph (GC, Agilent 7890A) equipped with a fused capillary column (HP-5) with 95% dimethylpolysiloxane and 5% phenyl as the stationary phase. Conditions for analysis: injection mode was split at split rate of 35, the column was kept at 30 °C for 2 min and then at a rate of 10 °C/min heated to 250 °C maintained for 10 min. The carrier gas was helium at a flow rate of 1.5 mL/min. The yields of glycoside derivatives such as furfurals and methyl levulinate (MLA) were quantitatively analyzed by gas chromatography (GC, Shimadzu 2010plus) using a flame ionization detector and their yields were estimated by the internal standard curve method with *n*-octanol as the internal standard.

The quantitative analysis of methyl glycoside compounds fractions were analyzed on a High performance liquid chromatography (HPLC) instrument with an Aminex HPX-87H column (Shimadzu LC-10ATVP), and RID-20A detector. Yields of MLG were estimated using the external standard curve method. The mobile phase was 5 mmol/L dilute sulfuric acid solution (sonication de-aeration) with a flow rate of 0.6 mL/min, and the column temperature was kept at 35 °C.

^{1}H–^{13}C correlation Two-dimensional Nuclear Magnetic Resonance Heteronculear Single Quantum Coherence (2D HSQC NMR) spectra were recorded on a Bruker DRX 500 NMR spectrometer operated at 500 MHz. The specific structures of three phenolic compounds and glycoside compounds fractions were determined by HSQC NMR spectroscopy. The spectral widths for the ^{1}H and ^{13}C dimensions were 8.5 ppm and 120 ppm, respectively. The products were conducted in d_6-dimethyl sulfoxide (DMSO) or D_2O solvent at 30 °C and tetramethylsilane was used as an internal reference.

The molecular weights of three phenolic compounds fractions were measured by gel permeation chromatography (GPC) using a Waters 1515 system (USA) equipped with a Waters 2414 Refractive Index Detector. The column was Styragel HR1, HR2 (300 × 7.8 mm) from Waters. HPLC-grade tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL/min. Analysis was completed in 25 min. GPC was performed using 20 μL injection volume. The column was calibrated by using polystyrene standards with molecular weights in the range between 580 and 1.96×10^4 g/mol.

HPLC results were used to calculate contents of the MLG (include methyl pentose glycoside and methyl hexose glycoside) with an external standard method. GC was used to investigate the absolute contents of levulinates and furfurals in the liquefied product by comparison with an authentic *n*-octanol reference sample. The corresponding peak area ratio of MLA and *n*-octanol reflected the content ratio according to the standard curve ($y = 2.06543x - 0.02107$, coefficient of correlation (R^2) = 0.9999). And the corresponding 5-MMF and *n*-octanol peak area ratio reflected the content ratio according to the standard curve ($y = 1.9657x + 0.0612$, coefficient of correlation (R^2) = 0.9996).

Eq. (1) was used to calculate the conversion of biomass (on a weight basis) in the microwave-assisted liquefaction, and Eq. (2) was used to calculate the MLG (methyl glycoside include methyl pentose glycoside (C5-MLG) and methyl hexose glycoside (C6-MLG) yield from bamboo. Eqs. (3) and (4) was used to measure the main byproducts (5-MMF donates methoxy methyl furfural, MLA donates methyl levulinate) yields.

$$\text{Biomass conversion (wt\%)} = \frac{m\ (\text{liquefaction product})}{m\ (\text{bamboo})} \times 100\% \quad (1)$$

$$\text{MLG yield (\%)} = \frac{m\ (\text{liquefaction product}) \times \text{mass yield of MLG (measured by HPLC)}}{m\ (\text{bamboo})} \times 100\% \quad (2)$$

Table 1
Elemental and compositional properties of waste lignocellulosic biomass.

Materials	Element analysis (wt%)					Composition analysis (wt%)					
	C	H	O[a]	N	S	Ash[b]	Extractives[c]	Cellulose[d]	Lignin[e]	Holocellulose[f]	Pentosan[g]
Bamboo	48.46	4.22	46.95	0.08	0.29	1.18	3.69	43.73	24.45	70.47	25.40
Bagasse	40.10	5.01	54.70	0.07	0.12	2.52	2.57	44.12	22.92	71.79	19.77
Poplar	48.20	4.32	47.24	0.05	0.19	0.64	2.13	39.81	25.73	71.22	25.07
Pine	49.21	4.35	46.20	0.04	0.20	0.29	3.01	40.57	26.67	69.21	14.70
Eucalyptus	48.51	4.20	47.06	0.03	0.20	0.28	2.23	41.68	23.65	73.30	18.73
Straw	45.72	4.87	48.95	0.11	0.35	5.01	2.51	43.64	21.30	71.06	22.56

[a] O content was calculated by mass difference.
[b] Determined in accordance with ASTM D 1102-84.
[c] Determined in accordance with ASTM D 1107-96.
[d] Determined in accordance with ASTM D 1103-60.
[e] Determined in accordance with ASTM D 1106-96.
[f] Determined in accordance with ASTM D 1104-56.
[g] Determined in accordance with ASTM D 1105-96.

$$\text{MLA yield (\%)} = \frac{m\ (\text{liquefaction product}) \times \text{mass yield of MLA (measured by GC)}}{m\ (\text{bamboo})} \times 100\% \quad (3)$$

$$\text{5-MMF yield (\%)} = \frac{m\ (\text{liquefaction product}) \times \text{mass yield of 5-MMF (measured by GC)}}{m\ (\text{bamboo})} \times 100\% \quad (4)$$

2.3. Directional microwave-assisted liquefaction

Liquefaction of biomass with microwave-assistance was conducted in a Milestone (Shelton, CT) microwave laboratory system (ASM-400), and equipped with 100 mL sealed Teflon reaction vessels. This microwave system was especially designed for microwave degradation at 0–1200 W. The automatic temperature in this system was controlled with an internal temperature sensor (fiber optic sensor). The reaction mixtures consisted of 2 g of bamboo, 18 g of methanol, and 0.2–0.6 g of different acid catalysts. Then, the mixtures were transferred into reaction vessels with magnetic stirring during microwave-assisted liquefaction. The mixtures were heated to a set temperature within 5 min under 600 W used as starting microwave power, followed by incubation for a designated period of time (beginning from the moment the set temperature was reached). The sample temperature was controlled at 120–200 °C for 5–20 min with the microwave power at 600 W. After the microwave-assisted liquefaction, the vessels were removed from the microwave cavity and cooled rapidly to room temperature within 2 h before opening. The gaseous products (0.01–0.03 g) were vented because their yields were negligible. Then the liquefaction mixtures were vacuum-filtered through Whatman No. 4 filter paper. The solid retained on the filter paper was washed with methanol and oven-dried at 105 °C overnight. The yield of residue is the percentage of dry weight residue to the original materials and has commonly been used as an index of the liquefaction conversion.

The filtrate mixtures were neutralized using 50 wt% NaOH and then evaporated under vacuum at 45 °C to partly remove and recycle the methanol from the liquefied liquid products. Subsequently, three phenolic compounds fractions and glycoside compounds were successively separated from liquefied filtrate mixtures with stepwise precipitation and extraction. The detail stepwise process of liquefied products was shown in Fig. 1. Firstly, adding water into the liquefaction filtrate (the weight ratio of water to filtrate was 1:5), insoluble pyrolytic lignin with high molecular weight (phenolics fraction 1#) in filtrate mixtures was precipitated with a centrifuge process (5000 r/min, 20 min). Secondly, the liquid mixture was distilled under vacuum to remove methanol. The lower molecular weight fraction of pyrolytic lignin (phenolics fraction 2#) was precipitated from the aqueous solution. The volumetric concentrations of phenolic compounds and glycoside compounds in water were 10%–15% and 20%–35%, respectively. Thirdly, adding ethyl acetate (EtOAc) into the mixture products, the weight ratio of ethyl acetate to mixtures was 1:1. The mixtures were separated into a water soluble phase and an EtOAc soluble phase, and the EtOAc soluble phase was evaporated under vacuum to remove the EtOAc and separate the lowest molecular weight fraction of pyrolytic lignin (phenolics fraction 3#). Fraction 1# and 2# were solid and dried at 30 °C for 24 h. The glycoside compounds were obtained by removal of the water at 60 °C from the aqueous solution using a rotary evaporator.

3. Results and discussion

3.1. Effect of various catalysts on liquefied products

The acid catalyst can provide effective protons for breaking the glycosidic bonds, which are the dominant linkages between the basic monosaccharide units of hemicelluloses and cellulose. Our previous results suggested that most linkages can be degraded with sufficient acid catalysts, and produce monosaccharide derivatives such as methyl pentose glycoside and methyl hexose glycoside (Feng et al., 2015). The −OH functions in methanol as the nucleophile and can attack the electrophilic C adjacent to the glycosidic bonds. With the electrons moving towards the oxonium ion, the nucleophile can cleave the C−O bond, which produces a good leaving group and a neutral hydroxyl group.

We used H_2SO_4 catalyst in our previous studies and found that it had good effects on the conversion of liquefied biomass (Xu et al., 2012). Therefore, we used it again in the present investigation. Several different acidic catalysts including strong acids, heteropolyacids, organic acids, and solid acids were also evaluated as catalysts at a concentration of 2 wt% (basis of methanol and biomass amount) in this liquefaction process. Table 2 showed that H_2SO_4 was the most efficient catalyst with a MLG yield of 32% (C5-MLG and C6-MLG) and a phenolic compounds yield of 27%. With the same weights, HCl and HNO_3 performed poorer than H_2SO_4, HCOOH was the poorest performing catalyst. The H_2SO_4 catalyst also used in other researches about the thermochemical conversion of biomass (Teh et al., 2017), and showed better effects than other acid catalyst, such as HNO_3 and HCl (Szabolcs et al., 2013; Climent et al., 2014), which is consistent with our experimental results. With the same quality of HCl, HNO_3, and H_2SO_4, H_2SO_4 can completely dissolve in methanol and release the most hydrogen ions. This result indicates that H_2SO_4 could provide the strongest acid sites in methanol during microwave-assisted liquefaction. It is probable that the stronger acidity of sulfuric acid contributed to its efficiency. The highly reactive protons in H_2SO_4 can effectively activate the oxygen atoms in the structural bonds of cellulose, hemicelluloses, and lignin. The reactive protons can break the glycosidic bonds in the units of holocellulose and C=O in the units of lignin, and convert cellulose, hemicellulose and lignin into target products. The performance of $C_7H_7SO_3H$, $H_4SiW_{12}O_{40}$, and $H_3PW_{12}O_{40}$ showed that they are also strong enough to degrade cellulose, hemicelluloses, and lignin into target products in subcritical methanol with microwave energy. However, other acids when assessed for the alcoholysis of bamboo performed somewhat worse; mesoporous ZrO_2 resulted in a MLG (includes methyl pentose glycoside (C5-MLG) and methyl hexose glycoside (C6-MLG) yield of 22% and a phenolic compounds yield of 10%. Zeolite HZSM-5 showed lower reactivity and utility possibly because its pores are too small (0.55 nm) to be ineffective in the alcoholysis of bamboo. Using sulfuric acid (H_2SO_4) at low concentration as an acid catalyst is a highly promising strategy for synthesizing target products from methanolysis of bamboo. H_2SO_4 can offer enough hydrogen ions to complete the reaction and generate negligible quantities of dimethyl-ether (an undesirable by-product of the dehydration of methanol). The remaining sulfuric acid in the liquefied mixture was neutralized, thus minimizing the subsequent converted MLG into by-products (MLA) and several furfurals (furfural and 5-MMF).

It was inevitable that small quantities of by-products (MLA and furfurals) were also found in the liquefied products that used $C_7H_7SO_3H$, $H_4SiW_{12}O_{40}$, $H_3PW_{12}O_{40}$, or H_2SO_4 as catalysts, which was probably by subsequent alcoholysis of MLG in the presence of acid catalyst. These acid catalysts could provide enough hydrogen ions during microwave-assisted liquefaction with methanol. Using low concentrations of H_2SO_4 as a cost effective catalyst is a highly promising strategy for producing glycosidic and phenolic compounds from methanolysis of bamboo. Most of the lignin was decomposed with microwave-assisted liquefaction by H_2SO_4, $C_7H_7SO_3H$, and $H_3PW_{12}O_{40}$ catalysts under the designated conditions. The yield of total phenolic compounds derived from lignin reached 19–27% and the conversion of bamboo was approximately 75–84%.

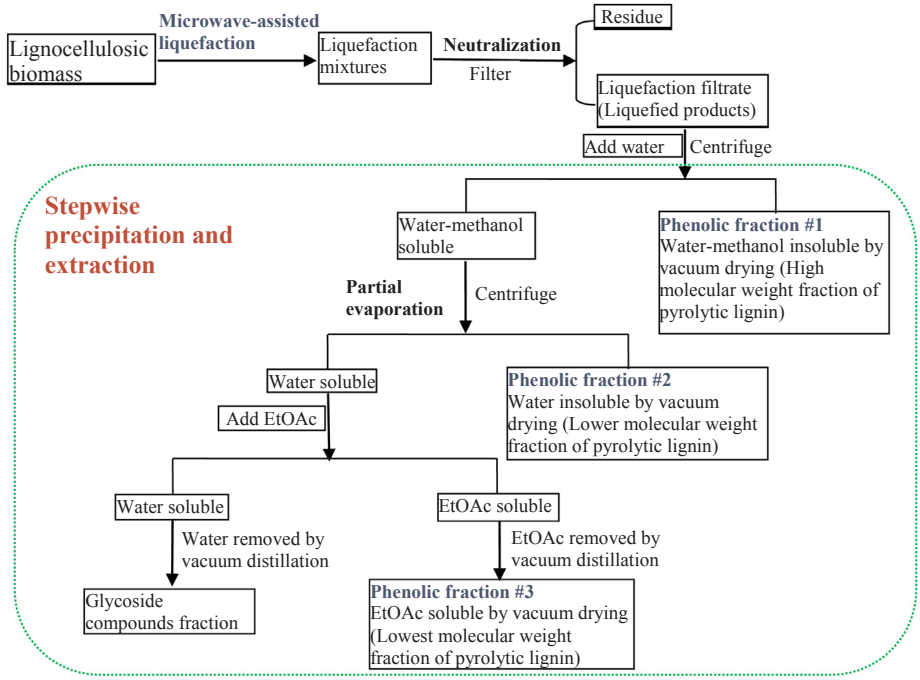

Fig. 1. Schematic of procedures to produce two platform chemicals from biomass.

Table 2
Efficiency of various acid catalysts on microwave-assisted liquefied bamboo.[a]

Catalysts	Conv. (wt%)	Cellulose products yield (%)[b]			Hemicelluloses products yield (%)[c]		Lignin products yield (%)[d]
		C6-MLG	MLA	5-MMF	C5-MLG	Furfural	Total phenolic compounds
Blank	1.54	1	0	0	1	1	0
HNO_3	22.64	2	2	2	5	5	5
HCl	27.29	4	3	1	6	4	11
H_2SO_4	83.29	19	5	8	13	12	27
$H_4SiW_{12}O_{40}$	79.57	13	3	7	14	11	20
$H_3PW_{12}O_{40}$	81.25	16	5	8	15	10	23
HCOOH	7.44	1	0	1	3	1	2
$C_7H_7SO_3H$	75.89	14	8	2	11	4	19
NH_2SO_3H	36.15	7	1	1	14	3	9
HZSM-5	21.40	4	2	1	10	2	4
ZrO_2	40.29	9	1	2	13	4	10

[a] Reaction conditions: bamboo 2.0 g, methanol 18.0 g, acid catalyst 2 wt% (on the basis of biomass and methanol), temperature 160 °C, time 15 min.

[b] Cellulose products: C6-MLG, methyl hexose glycoside; MLA, methyl levulinate; 5-MMF, 5-methoxy methyl furfural. (C6-MLG yields were based on HPLC analysis with external standard method, MLA and 5-MMF yields were based on GC analysis using the internal standard method).

[c] Hemicelluloses products: C5-MLG, methyl pentose glycoside; and furfural. (C5-MLG yields were based on HPLC analysis with external standard method, furfural yield was based on GC analysis using the internal standard method).

[d] The yields of total phenolic compounds were calculated by weight of the phenols on the basis of bamboo.

3.2. Effect of various parameters on microwave-assisted liquefied products

To better understand the liquefaction of bamboo under different acid catalysts to obtain optimal yields of glycosidic and phenolic compounds, processing parameters such as the loading of catalysts, time, and temperature of the reaction need to be further investigated by analysing the liquefied target products and some by-products (e.g. furfurals and MLA).

3.2.1. Catalyst loading

H_2SO_4, $H_4PW_{12}O_{40}$, and $C_7H_7SO_3H$ were selected to study the effect of catalyst amounts on liquefied products yields because they produced the higher glycosides and phenolics yields. As shown in Table 3, the yields of glycosides and phenolic compounds initially increased with the concentration of the acid catalyst increasing. However, further increase of the catalyst loading had a negative effect on the yields of glycosides and phenolics. The glycosides fragments from methanolysis of hemicelluloses and cellulose tended to be further converted into oxygenated by-products such as furfurals and MLA, which is consistent with our previous experimental observations (Feng et al., 2015).

When the amount of H_2SO_4 increased from 0.2 g to 0.4 g, the yield of phenolic compounds increased from 24% to 27%. The optimal catalyst amounts for the synthesis of phenolic compounds were approximately 0.4 g for $H_4PW_{12}O_{40}$ and 0.5 g for $C_7H_7SO_3H$, and the optimum yields of phenolic compounds were 24% and 21%, respectively. After a further increase of the catalyst loading, the conversions of bamboo and yields of phenolic compounds dramatically decreased. The higher acid concentrations not only promoted the polymerization of phenolic compounds but also corroded the reactor equipment.

The optimal catalyst amounts for producing glycosidic compounds from decomposition of bamboo was approximately 0.3 g for H_2SO_4, 0.4 g for $H_4PW_{12}O_{40}$, and 0.5 g for $C_7H_7SO_3H$. The optimal yields of glycosidic compounds (C5-MLG and C6-MLG) were 35% with H_2SO_4, 31% with $H_4SiW_{12}O_{40}$, and 29% with $C_7H_7SO_3H$. However, higher acid concentrations increased the yields of by-products such as furfurals and MLA at the expense of glycosidic compounds. MLA was likely produced from acid-catalysed conversion of the HMF or MMF. The HMF and MMF were formed from the methanolysis of methyl hexose glycoside that were derived from cellulose with acid catalyst. Furfural were mainly formed from the methanolysis of methyl pentose glycoside and to a lesser extent from the decomposition of methyl glycoside.

An increase in the amount of the catalyst might contribute to the methanolysis of glycosidic compounds. These by-products of glycosidic compounds (furfurals and MLA) were miscible with phenolic compounds and may reduce the purity of aromatic derivative products derived from the decomposition of lignin. Higher acid concentration may seriously corrode the reactor equipment. In general, to achieve optimal conversions and controllable methanolysis of bamboo, sulfuric acid was selected at the amount of 0.3 g.

Table 3
Components of microwave-assisted liquefied bamboo by different catalyst loading.[a]

Catalyst	Amount (g)	Conv. (wt%)	Cellulose products yield (%)[b]			Hemicelluloses products yield (%)[c]		Lignin products yield (%)[d]
			C6-MLG	MLA	5-MMF	C5-MLG	Furfural	Total phenolic compounds
H_2SO_4	0.2	75.48	10	3	2	13	4	24
	0.3	84.67	20	4	6	15	9	22
	0.4	83.29	19	5	8	13	12	27
	0.5	84.31	16	13	2	10	13	27
$H_3PW_{12}O_{40}$	0.3	76.71	10	3	5	13	4	20
	0.4	81.25	16	5	8	15	10	24
	0.5	84.26	16	9	7	12	6	23
$C_7H_7SO_3H$	0.4	75.89	14	8	2	11	4	19
	0.5	76.33	16	10	8	13	5	21
	0.6	78.21	12	11	12	4	8	20

[a] Reaction conditions: bamboo 2 g, methanol 18 g, temperature 160 °C, time 15 min.
[b] Cellulose products: C6-MLG, methyl hexose glycoside; MLA, methyl levulinate; 5-MMF, 5-methoxy methyl furfural. (C6-MLG yields were based on HPLC analysis with external standard method, MLA and 5-MMF yields were based on GC analysis using the internal standard method).
[c] Hemicelluloses products: C5-MLG, methyl pentose glycoside; and furfural. (C5-MLG yields were based on HPLC analysis with external standard method, furfural yield was based on GC analysis using the internal standard method).
[d] The yields of total phenolic compounds were calculated by weight of the phenols on the basis of bamboo.

3.2.2. Reaction time and temperature

The typical time profile for the microwave-assisted liquefaction of bamboo using sulfuric acid is shown in Fig. 2(a). As the reaction time increased from 5 to 10 min, the yields of glycosidic compounds (C5-MLG and C6-MLG) and phenolic compounds also increased from 17% to 45% and 24% to 29%, respectively. As the reaction time extended, the yields of other by-products derived from the secondary reactions of cellulose and hemicelluloses (such as furfurals and MLA) slightly increased. However, the yield of monosaccharide derivatives significantly decreased. The yields of phenolic compounds derived from the decomposition of lignin varied from 24% to 30% and continuously increased when the reaction time increased from 5 to 12.5 min. The yields of phenolic compounds and conversion of bamboo decreased from 30% to 20% and 84% to 79%, respectively, when the reaction time prolonged from 12.5 to 20 min.

There are two side reactions that can promote an increase in the yield of aromatic derivative fractions. Firstly, re-polymerization of the activate chemical in liquefied products can produce high molecular-weight compounds, which precipitated in the phenolic compounds. Secondly, further methanolysis of glycosidic compounds could form furfurals and MLA, which also precipitated in the phenolic compounds due to their mutual solubility and similar physiochemical property in the organic solvent. However, the total content of phenolic compounds in the aromatic derivative fraction was unchanged, and the purity of phenolic compounds was reduced. When the reaction time is 12.5 min, the yields of glycosidic compounds (C5-MLG and C6-MLG) can be achieved at 43%. Compared with 10 min, the yield of glycosidic compounds was slightly decreased, however, the yield of phenolic compounds was slightly increased. Therefore, we investigated the specific components of glycoside compounds fraction at 10 min and 12.5 min after the stepwise precipitation and extraction process. The yield of six carbon sugars in glycosidic compounds was apparently higher than five carbon sugars at the reaction time of 10 min. After the microwave-assisted liquefaction for 10 min, the purity of the glycoside compounds fraction was much higher than that of 12.5 min. In general, considering the conversion of bamboo, the yield of target products, and the purity of phenolic fractions, we selected the optimal reaction time to be 10 min. Higher yields of glycosidic compounds (45%) and phenolic compounds (29%) was achieved at the reaction time of 10 min.

Operating temperatures play an important role in the control of thermochemical reactions. Generally, elevated temperature could promote the enhancement of bamboo conversion efficiency and accelerate the rate of the liquefaction process. The reaction temperature effects the conversion of bamboo and the yields of target products. A suitable reaction temperature could prevent most side-reactions, which can promote the fractionation process of high purity products. As shown in Fig. 2(b), the conversion of bamboo and the yields of glycosidic compounds (C5-MLG and C6-MLG) increased as the temperature increased

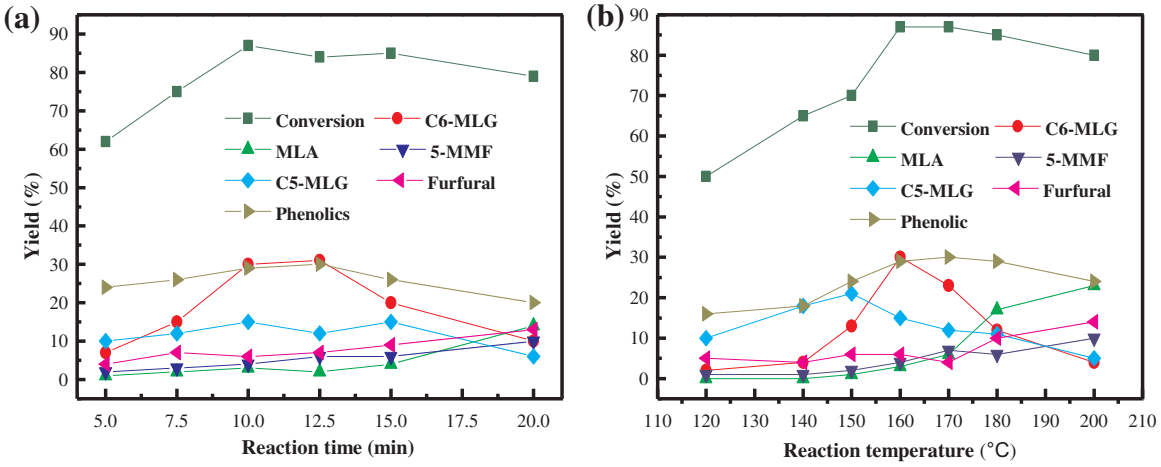

Fig. 2. Chemical changes during the microwave-assisted liquefaction by different time (a) and temperature (b). Reaction conditions: (a) catalyst 0.3 g, bamboo 2 g, methanol 18 g, temperature 160 °C; (b) catalyst 0.3 g, bamboo 2.0 g, methanol 18.0 g, time 10 min. C6-MLG: methyl hexose glycoside, MLA: methyl levulinate, 5-MMF: 5-methoxy methyl furfural, C5-MLG: methyl pentose glycoside.

Table 4
Main components of liquefied bamboo using different liquefaction processes.[a]

R.T (min)	Main products	Percentage (%)	
		Conventional	Microwave-assisted
6.89	Furfural	7.83	1.21
7.03	2,5-dimethylfuran	6.36	–
8.19	Methyl levulinate	4.52	1.52
10.34	Methoxy-2-furanmethanol	3.14	0.23
10.89	4-Methyl guaiacol	1.56	0.63
11.79	5-Methoxy methyl furfural	5.49	3.21
12.43	Methyl-α-xyloside	6.42	13.10
12.67	4-Methoxy guaiacol	1.21	4.25
13.26	Methyl-β-d-arabinopyranoside	2.89	2.23
14.33	Methyl-β-dxylofuranoside	3.37	4.45
13.90	Syringol	3.32	0.89
14.67	4-Hydroxy-3-methoxy benzaldehyde	1.54	1.34
15.62	Vanillin	6.21	9.22
16.05	Methyl-4-hydroxy-3-methoxy benzoate	1.35	5.82
16.63	Methyl-β-dglucopyranoside	2.46	4.69
17.09	Methyl-α-dmannopyranoside	3.30	2.37
17.53	Methyl-α-dglucopyranoside	8.62	18.35
17.95	2-Methoxy-isophthalic acid	4.36	5.21
18.52	1-(3-Hydroxy-4-methoxyphenyl) ethanone	2.08	1.85
19.27	Aspidinol	6.22	2.67
20.83	1,2-Dimethoxy-4-(1,2,3-trimethoxy propyl) benzene	0.83	4.43
21.18	Methyl (methyl-4-O-α-dmannopyranoside) urinate	1.46	2.32
22.05	Methyl-2-(4-hydroxy-3-methoxyphenyl) acetate	1.67	1.08
25.63	Phenolic dimers	5.43	2.69
	Total glycosidic compounds	27.06	45.19
	Total phenolic compounds	37.24	42.40
	Total furfural derivatives	27.34	6.17

[a] Conditions: All experiments used catalyst 0.3 g, bamboo 2 g, methanol 18 g. A conventional liquefaction was carried out at 180 °C for 30 min, and the reaction conditions for directional liquefaction were 160 °C for 10 min.

until 160 °C. At 170 °C, the conversion of bamboo reached a maximum of 87%, and the yields of glycosidic compounds (C5-MLG and C6-MLG) decreased to 35%. The yields of MLA and furfurals (5-MMF and furfural) increased to 6% and 12%, which suggested that MLG would be further converted into furfurals and MLA at temperatures higher than 160 °C. When temperatures beyond 160 °C, few glycoside compounds are formed during the liquefaction process. The yields of phenolic compounds increased from 16% to 30% with increased reaction temperature from 120 °C to 170 °C. The extra amounts of phenolic compounds (compared to the content of lignin in bamboo) suggested that a part of the active liquefied products were re-polymerized and produced high molecular-weight byproducts, which can precipitate together with the phenolic compounds by the stepwise extraction and precipitation process.

The reaction temperature also influenced the chemical distribution and composition of liquefied products. The content of methyl hexose glycoside (C6-MLG, R.T = 15–17 min) at 160 °C was apparently greater that at 150 °C. The yield of phenolic compounds increased with the reaction temperature, indicating the same increasing trend as the methyl pentose glycoside. When the reaction temperature increased, we can speculate that lignin and hemicelluloses were decomposed before the degradation of cellulose. This phenomenon is closely related to the structure of biomass cell walls. During the liquefaction process, the methanol first reacted with both lignin and hemicelluloses to generate aromatic compounds (phenolic compounds) and five carbon sugars (methyl pentose glycoside). After the removal of hemicelluloses and lignin, the highly crystallized micro-fibril cellulose was exposed in the subcritical methanol solvent. Then, the content of six carbon sugars (C6-MLG, methyl hexose glycoside) in the liquefied liquid products was increased with the methanolysis of cellulose. This speculation is in agreement with the content of each component in the liquefied residue at different temperatures. With temperature higher than 170 °C, the by-products (furfurals and MLA) were produced from the methanolysis of methyl glycoside compounds. These by-products furfurals and MLA are miscible with phenolic compounds and can decrease the purity of phenolic products derived from the decomposition of lignin. In order to prevent side reactions, a moderate reaction temperature at 160 °C proved better for higher yield of sugars.

3.3. Directional microwave-assisted liquefaction and conventional liquefaction

Directional microwave-assisted liquefaction focuses on the integrated utilization of all the three major components in lignocellulosic biomass. Compared with other microwave-assisted liquefaction studies (Bu et al., 2015; Chen et al., 2015), the distribution and composition of products were significantly different. There are hundreds of oxygenated derivatives in liquefied products, however, each product accounts for only a small part of the products. These oxygen-containing compounds are mainly derived from the secondary alcoholysis of glycoside compounds, or the polymerization and condensation (side-reactions) of phenolic compounds and glycoside compounds.

In our designated microwave-assisted liquefaction, the distribution of liquefied products was relatively concentrated, mainly the two categories of products (phenolic compounds and glycosidic compounds). In this study, methanol was used as the liquefaction solvent. During the reaction, subcritical methanol could provide good solubility for the liquefied products, which promoted the conversion of solid biomass to liquid products. Methanol was expected to readily dissolve the high molecular-weight products derived from biomass due to their low dielectric constants, which could efficiently prevent re-polymerization and re-condensation of liquefied products. Under these conditions, the diffusion and reactivity of the solvent can be significantly improved.

This study focused on the conversion of biomass and the quality of target products after the liquefaction. With different liquefaction parameters, the conversion of biomass could be increased more than 85% using methanol with an acid catalyst. Many complex mixtures of oxygenated and active compounds were produced at the same time, mainly from decomposition of cellulose and hemicelluloses. During the microwave-assisted liquefaction, hemicelluloses and cellulose were first dehydrated and decomposed into monosaccharide derivatives. The monosaccharide derivatives are instable at high temperatures (such as higher than 160 °C in Fig. 2(b)), and can be further converted into other by-product compounds, such as furfurals and MLA with longer reaction time, higher acid catalyst concentration and reaction temperature. The aromatic derivatives derived from lignin also tend to re-polymerize at increased reaction times and temperatures.

The main components of liquefied bamboo using conventional liquefaction and microwave-assisted liquefaction processes were shown in Table 4. The contents of glycoside compounds after conventional liquefaction and microwave-assisted liquefaction were significantly different, 27.07% and 45.19%, respectively. And the furfurals derivatives (e. g. furfurals and MLA) in the conventional liquefied products were higher than those in microwave-assisted liquefied products. The results indicated that side reactions maybe inevitably occur in the liquefaction process, however, the main liquefied products can be promoted by careful adjusting the reaction conditions. With the appropriate choice of reagents that absorb microwave irradiation, the rapid heating throughout the entire vessel can be achieved, which can facilitate the formation of high purity monosaccharide and aromatic derivatives to provide high added-value platform chemicals and biofuels. In both conventional liquefaction and directional liquefaction processes, there are many oxygenated derivatives in liquefied products. In the

conventional liquefied products, the distribution of each product is dispersed and accounts for only a small part of the liquefied products. The oxygenated compounds such as 5-MMF, HMF, and MLA were mainly products of conventional liquefied products. Although there doesn't seem to be a significant change between conventional liquefaction and directional microwave-assisted liquefaction in the complexity of the liquefied mixtures, the target products from directional liquefaction were concentrated and their yields were significantly improved. It was found that phenolic compounds and monosaccharide derivatives are the major products of directional microwave-assisted liquefaction, while the oxygenated compounds were mainly found in the conventional liquefaction. With microwave assistance, the monosaccharide derivatives were prevented from further decomposition into the furfurals and levulinates derivatives. In the designated microwave-assisted liquefaction, the purities and yields of target products (phenolics and glycosides) were also greatly improved. After directional microwave-assisted liquefaction, the monosaccharide derivatives are insoluble with the aromatic derivatives derived from lignin. This phenomenon can contribute to facilitate a subsequent separation process to obtain two categories of platform chemicals with high purity. The oxygenated by-products (e.g. furfurals and LA) derived from the alcoholysis of MLG in the conventional liquefaction, are soluble with the phenolic compounds, which would reduce the purity and grade of the phenolic compounds products. In the directional microwave-assisted liquefaction, the oxygenated compounds (e. g. furfurals and LA) may be avoided as much as possible by adjusting the reaction conditions. In the designated microwave-assisted liquefaction, the purities and yields of target products (phenolics and glycosides) were also greatly improved. Therefore, the directional microwave-assisted liquefaction can make it possible that the oriented convert the three components of biomass into target products.

3.4. Mass balance of whole directional liquefaction and extraction

The optimal conversion of bamboo and yields of targets products (glycosides and phenolics) were achieved under a shorter reaction time of 10 min, a moderate temperature of 160 °C, and a low concentration of sulfuric acid (1.5 wt% of 2 g of bamboo in 18 g of methanol). As the tests involved repeated data points, average values for the data were obtained by repeating the experiments three times. Several representative biomass feedstocks, including softwood (pine), hardwood (eucalyptus, poplar), gramineous plants (bamboo, and straw), and biomass waste (bagasse) were selected to study the directional microwave-assisted liquefaction of different biomass species under this optimal condition.

The lignin in selected biomass materials has the basic backbone of the phenylpropane structural units, but their aromatic nuclei are different. The basic unit of lignin in softwood (e. g. pine) is mainly guaiacol propane, the basic structure of lignin in hardwood (e. g. eucalyptus and poplar) is guaiacol propane and syringyl propane, the basic structure of lignin in gramineous plants (e. g. bamboo, bagasse, and straw) not only contains guaiacol propane and syringyl propane but also contains *p*-hydroxyphenyl propane units. The types and quantities of hemicelluloses contained in softwood, hardwood, and gramineous plants are significantly different. The contents of hemicelluloses, cellulose, and lignin and the internal structure in the selected biomass materials were also significantly different (Table 1). There are some difference in the content of each component and the internal structure in different biomass, which can affect the composition and structure of the liquefied products. However, in our study, the effect of microwave energy on biomass can break the glycosidic bonds in the units of holocellulose and C=O in the units of lignin, and convert cellulose, hemicellulose and lignin into corresponding compounds with basic unit structure. Therefore, the main product of the alcoholysis of cellulose is methyl hexose glycoside, the main product of hemicelluloses alcoholysis is methyl pentose glycoside, the main products of lignin dissociation is various phenolic compounds. The liquefied results demonstrated that all the materials were efficiently converted into liquid mixture products. Approximately 78–86 wt% of starting biomass materials was converted into liquid products within 10 min. The yields of monosaccharide derivatives (glycosides including C5-MLG and C6-MLG) were 39–45% after stepwise removal of methanol with high purity of glycoside compounds at 160 °C. After the stepwise extraction and precipitation process, the yields of three phenolic compound fractions that were separated from six material liquefied oils were approximately 28–32%. These results indicated that the microwave-assisted liquefaction with designed conditions can be used in a wide range of converting biomass into renewable platform chemicals. In liquefaction and extraction of bamboo process, fraction 1# and fraction 2# were the major fractions of phenolic compounds, their weight yields were accounted for 8.37 wt% and 13.25 wt% of original bamboo weight, respectively. Fraction 3# was extracted by EtOAc solvent accounting for 6.87 wt% of original bamboo weight. Compared with other biomass materials, bamboo and bagasse were better liquefied and the platform products were better separated.

The efficiency of different reaction temperatures on yields of platforms from directional liquefaction using different biomass materials were also investigated. The mass balance of whole liquefaction and extraction from bamboo was shown in Fig. 3. The yield of monosaccharide derivatives from liquefied bamboo including methyl pentose glycosides and methyl hexose glycosides was 56%. The yield of depolymerized lignin from liquefied bamboo including three phenolic compounds fractions was 28%. The results of mass balance of whole liquefaction and extraction indicated that our proposed method can be used in a wide range of biomass because the depolymerized lignin can be completely separated with the stepwise extraction and precipitation process. The findings demonstrated that two groups of platform chemicals could be predictably obtained under carefully controlled conditions. This process can achieve the integrated utilization of liquefied products toward different synthesis directions according to their chemical properties and molecular structures.

3.5. Characterization of fractionated products

3.5.1. Monosaccharide derivatives

The main components in lignocellulosic biomass were converted into liquefied liquid products and miscible in methanol after the directional microwave-assisted liquefaction. The liquefied liquid products

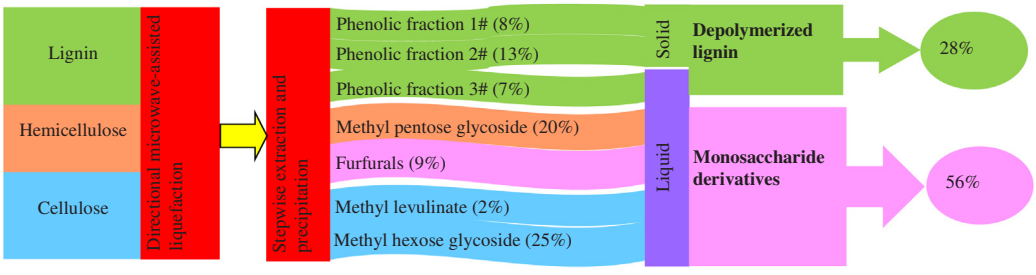

Fig. 3. Mass balance of whole directional liquefaction and extraction. Reaction conditions: bamboo 2 g, catalyst 0.3 g, methanol 18 g, 160 °C, 10 min.

Table 5
The main components of glycoside compounds fraction from liquefied different biomass.

R.T (min)	Compounds	Glycoside compounds percentage (%)		
		Poplar	Bagasse	Bamboo
10.45	Methoxy-2-furanmethanol	0.83	1.57	0.57
11.81	5-Methoxy methyl furfural	1.36	2.14	1.09
12.23	Methyl-α-xyloside	13.14	15.68	17.21
13.06	Methyl-*β*-darabinopyranoside	10.12	20.32	12.28
14.33	Methyl-β-dxylofuranoside	3.45	8.62	1.37
16.63	Methyl-*β*-dglucopyranoside	2.21	1.94	0.68
17.09	Methyl-*α*-dmannopyranoside	16.57	7.48	2.45
17.53	Methyl-*α*-dglucopyranoside	33.33	33.29	55.92
21.18	Methyl (methyl-4-O-α-dmannopyranoside) urinate	8.42	2.28	0.76
	Total glycoside compounds	89.43	93.32	92.33

were further separated by stepwise precipitation and extraction to obtain high purity monosaccharide and aromatic derivatives. The monosaccharide compounds were mainly composed of five and six carbon sugars such as methyl-α-D-mannofuranoside, methyl-α-D-glucopyranoside, methyl-α-xyloside, and methyl-β-D-arabinopyranoside. The total contents of the glycoside compounds were up to 89%–94% in the monosaccharide derivatives fractions from liquefied different biomass including poplar, bagasse, and bamboo (Table 5). Several kinds of oxygenated by-products were also observed in the monosaccharide derivatives fractions, such as furfural and 5-MMF, accounting for approximate 4% of the total peak area.

2D HSQC NMR spectra were also used to analyze the monosaccharide derivatives (glycoside compounds) produced from the conversion of cellulose and hemicelluloses and separated from liquefied bamboo products. The model structures of methyl xyloside and methyl glucopyranoside are representatives for the methyl pentose glycoside and methyl hexose glycoside. The main assignments of $^{13}C-^{1}H$ correlation signals in the HSQC NMR spectrum of glycoside compounds from bamboo are shown in Fig. 4. The spectra showed internal regions at 102.5/5.03 for the linkages (A2) in the methyl hexose glycoside. Methyl pentose glycoside depicted correlations at δ_C/δ_H 107.8–109.5/4.85–4.92. Other observations such as correlation signals at 3.35–3.45/55.5 and 3.52–3.36/57.0 were attributed to the methoxyl units (B1, A1). The obvious cross-signals at 3.85/63.3 and 3.68/63.8 were related to hydroxymethyl groups (A3, B3). The correlations of the H atom and C atom in the methyl glycoside rings were found at the chemical shift between 3.48–3.52/71.5–72.0 (A4, B4).

Our results of HSQC NMR spectra indicated that the (1→4) linkages between monosaccharide units of hemicelluloses and cellulose were broken and replaced by methoxyl groups in the glycoside compounds fraction. These results were also consistent with the FT–IR analysis of the glycoside fraction from liquefied biomass. All the correlations highly coincided with the molecular structures that were identified by GC-MS, which also confirmed the decomposition of hemicelluloses and cellulose, and the formation of low molecular weight glycoside compounds with high purity.

3.5.2. Aromatic derivatives

Degradation of lignin into low molecular weight phenolic compounds might be an alternative method before the valorisation of lignin. The methodologies developed in this investigation could not only increase the solubility of the phenolic compounds but also enhance the chemical activity of depolymerized lignin. Many phenolic and aromatic compounds were identified in the aromatic derivatives products separated from stepwise extraction and precipitation. The GC-MS results of the three phenolic compound fractions showed the formation of aromatic compounds developed after the decomposition of the lignin structure in bamboo by cleaving the dominant linkages such as the 4-O-5, β-O-4, and dibenzodioxin units. The results from the FT-IR analyses of three phenolic compound fractions also confirmed that the depolymerization of the dominant linkages including 4-O-5, β-O-4, and dibenzodioxin units in the natural lignin structure.

The main components of three phenolic compound fractions from liquefied bamboo were investigated and shown in Table 6. Many kinds of phenolic compounds were detected in the products, such as vanillin, 2-methoxy-isophthalic acid, and 1-(2,4,6-trihydroxyphenyl)-2-pentanone. This result indicated that the bamboo was effectively converted into low molecular weight chemicals during the directional microwave-assisted liquefaction. The directional liquefaction of bamboo was not only the degradation of hemicelluloses and cellulose with recalcitrant crystalline structure but also included the depolymerisation of high molecular polymerization lignin with reactive intermediates with carbon-carbon double bonds and hydroxyl and/or carbonyl groups. The decomposition of the lignin structure in the bamboo had a similar mechanism of cleaving the dominant linkages including 4-O-5, β-O-4, and dibenzodioxin unit (Li et al., 2015; Chen et al., 2016).

The three phenolic compound fractions included phenolic monomers, dimers with various functionalities, especially methyl, methoxy, aldehydes, esters, and some complex propyl groups. The distributions and components of the three phenolics fractions were significantly different. Specifically, the main contents of phenolic compounds fraction 1# with high-weight molecular with complex structures and chemical groups, i.e., 1,2-dimethoxy-4-(1,2,3-trimethoxy propyl) benzene, methyl-2-(4-hydroxy-3-methoxyphenyl) acetate, and a part of phenolic dimers. The main components of fraction 2# compounds were vanillin, aspidinol, 1,2-dimethoxy-4-(1,2,3-trimethoxy propyl) benzene, and little phenolic dimer compounds. The fraction 3# compounds mainly consisted of vanillin, 4-methoxy guaiacol, and phenols with simple molecular structure and chemical bonding. Other compounds including 5-MMF and MLA were also identified by GC-MS analysis, and their percentages were 10.21%, 8.72%, and 6.45% in three phenolic compounds fractions, respectively. There were about 8% unknown compounds in the GC-MS spectra of three phenolic compounds fractions, which were supposed to be phenolic trimers, tetramers, and some complex aromatic derivatives. The absolute structural identification of these unknown compounds was not possible because these compounds' authentic standards were not available in the database of GC-MS.

The 2D NMR spectra can provide important structural information of complex compounds and were used to gain a further understanding of the bamboo degradation products. To determine the structures of biomass-derived phenolic compounds, as well as the associated side chain groups and the linkages between phenolic compounds, the three fractions were analyzed by 2D HSQC NMR spectroscopy. The spectra were divided into three regions include aromatic regions, C—O aliphatic side chain regions, and C—C aliphatic side chain regions. HSQC signals for the fractions were compared with published data for lignin or pyrolytic lignin structure (Van den Bosch et al., 2015). The three phenolic compounds fractions contained phenolic monomers and dimers with various functionalities such as methoxy, aldehyde, ether, ester, methyl, and alkyls. The possible substructures and units of the three phenolic fractions are presented in detail. The A, B, C, G, H, I, PB, S, and S′ were on behalf of β-O-4′ ether linkage, resinol units, phenylcoumaran units, guaiacyl units, *p*-hydroxyphenyl units, *p*-hydroxycinnamyl alcohol units, *p*-hydroxybenzoate units, etherified syringyl units, and oxidized syringyl units, respectively.

The main cross peaks of the three phenolic fractions in HSQC NMR spectra are presented in detail. The main correlation signals in the aromatic regions of phenolic compounds in the 2D HSQC spectra are shown in Fig. 5. Due to the decomposition reactions with methanol, the single phenolic correlations were observed in the HSQC spectra. In

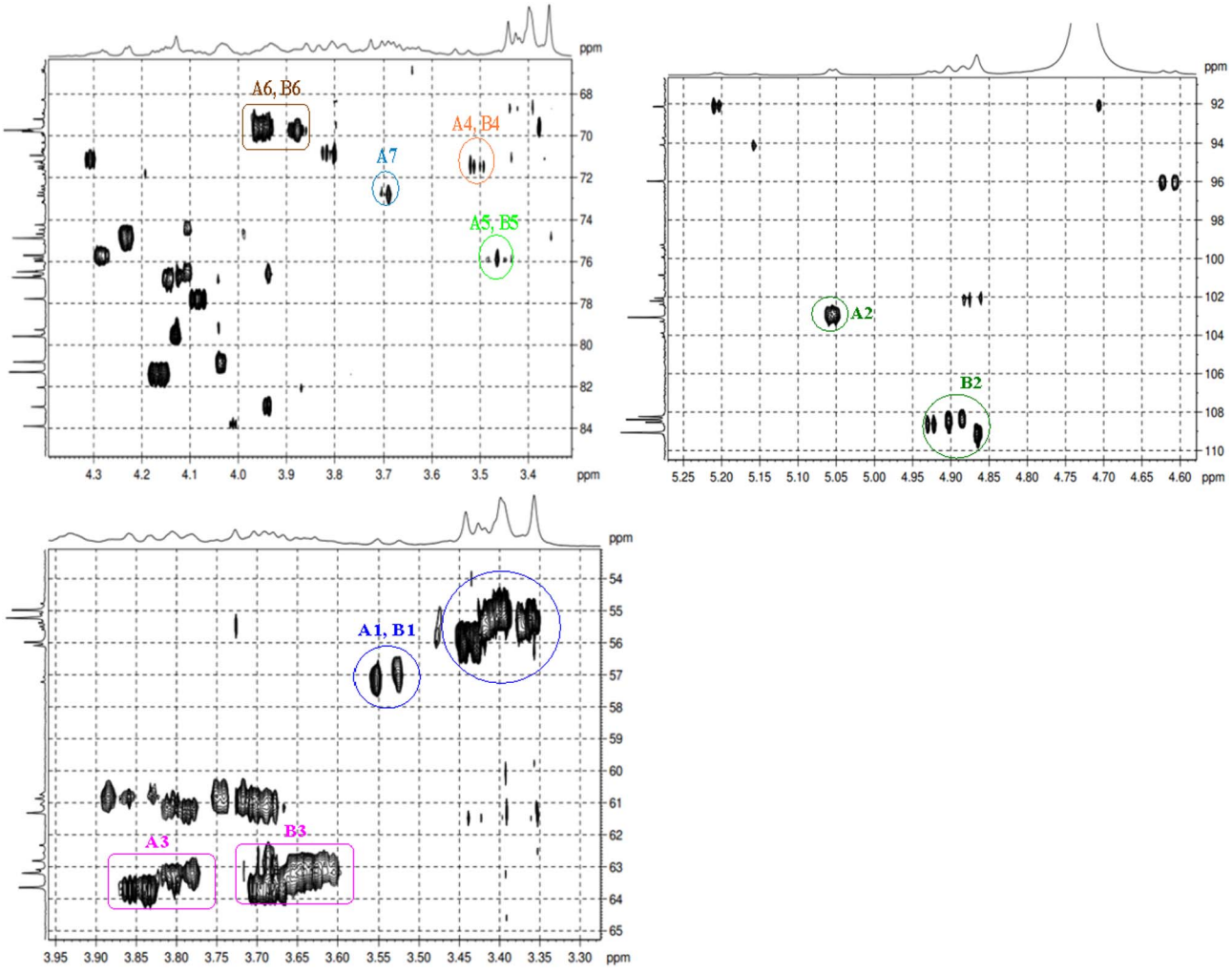

Fig. 4. 2D HSQC NMR spectra of glycoside fraction from liquefied bamboo.

Table 6
Main components of three phenolics fraction from liquefied bamboo.

No.	R.T. (min)	Compounds	Phenolic compounds percentage (%)		
			Fraction 1#	Fraction 2#	Fraction 3#
1	10.75	4-Methyl guaiacol	1.87	–	–
2	12.63	4-Methoxy guaiacol	3.37	9.18	18.35
3	12.98	2-Methoxy-4-propylphenol	–	3.04	9.21
4	13.81	Syringol	2.41	–	1.68
5	14.67	4-Hydroxy-3-methoxy benzaldehyde	1.75	–	6.24
6	15.62	Vanillin	9.05	13.83	20.42
7	16.05	Methyl-4-hydroxy-3-methoxy benzoate	2.39	6.51	12.49
8	17.21	4-(2-Hydroxyethyl)-2-methoxy phenol	2.21	0.57	–
9	17.95	2-Methoxy-isophthalic acid	4.47	3.76	8.06
10	18.51	1-(2,4,6-Trihydroxyphenyl)-2-pentanone	5.82	10.03	9.49
11	20.03	(3,4-Dimethoxyphenyl)(methoxy) methanol	2.54	2.13	–
12	20.52	1-(3-Hydroxy-4-methoxyphenyl) ethanone	11.73	–	–
13	21.06	Aspidinol	–	14.17	–
14	22.57	1,2-Dimethoxy-4-(1,2,3-trimethoxy propyl) benzene	16.93	17.32	–
15	23.03	Methyl-2-(4-hydroxy-3-methoxyphenyl) acetate	13.35	–	–
16	25–27	Phenolic dimers	3.52	2.17	–
		Total phenolics	81.41	82.71	85.94
		Other compounds	10.21	8.72	6.45
		Unknown compounds	8.38	8.57	7.61

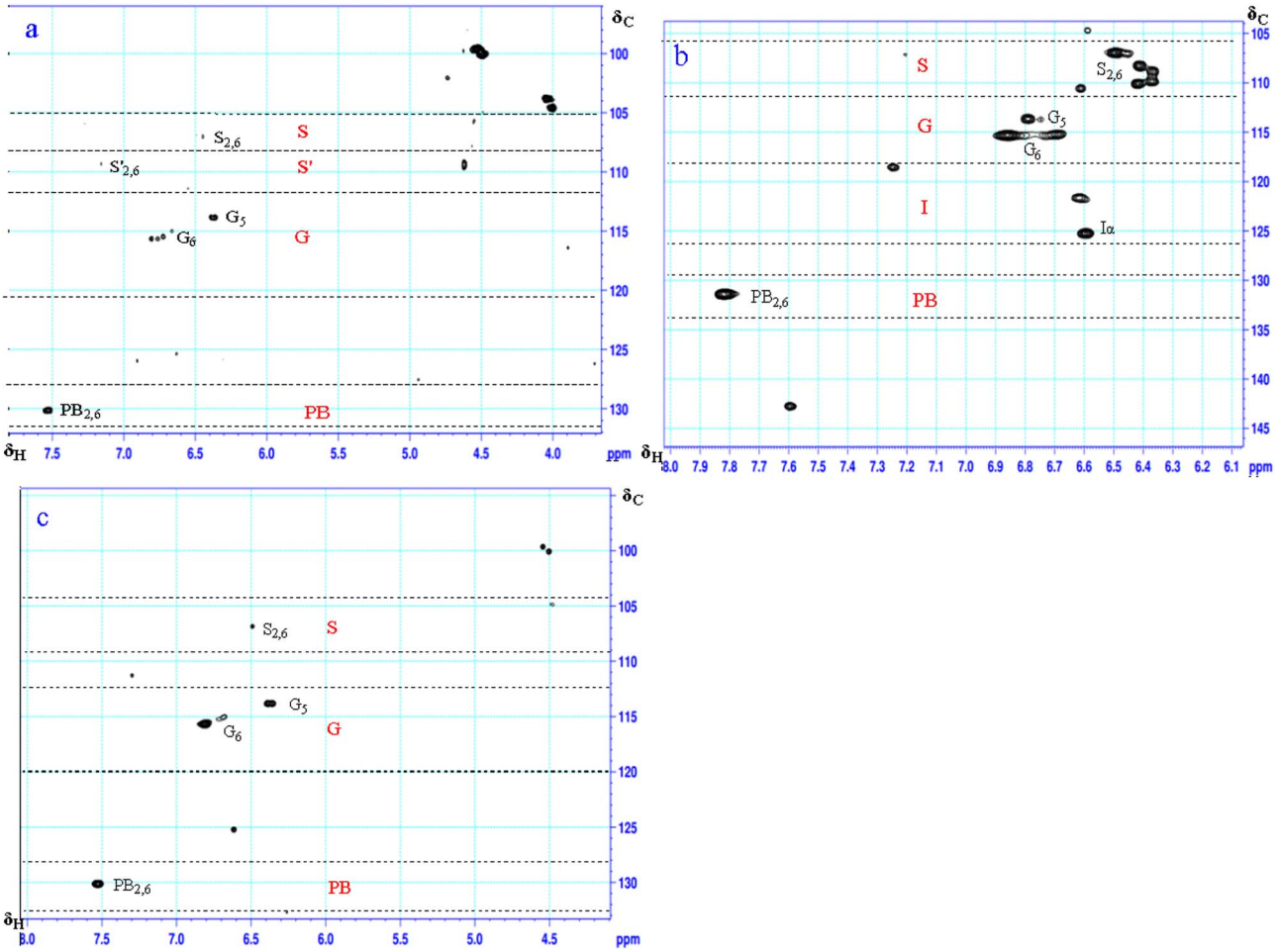

Fig. 5. Aromatic regions of HSQC spectra for phenolic compounds in fractions 1# (a), 2# (b), and 3# (c). Dotted lines represent positions of G, I, PB, S, and S' signals.

detail, the intense correlation signals between δ_C/δ_H 127–135/7.55–7.85 were derived from the protonated aromatic carbons of PB unit. In the previous studies, δ_C/δ_H 105.5/6.40 and 106.2/7.25 were correlated with $C_{2,6}/H_{2,6}$ positions of syringyl units S and S' in depolymerized lignin and natural lignin (Chen et al., 2016). In this study, $C_{2,6}/H_{2,6}$ correlations for the S units were observed at δ_C/δ_H 104.5–107.5/6.35–6.5, and the correlation signals at δ_C/δ_H 108.5/7.20 were attributed to $C_{2,6}/H_{2,6}$ correlations of S' units. Different correlations at δ_C/δ_H 114.5/6.35–6.70 and 116.5/6.65–6.80 were attributed to C_5/H_5 and C_6/H_6 from G unit. The obvious cross-signals at δ_C/δ_H 130.0–131.5 and 7.55–7.80 related to $C_{2,6}/H_{2,6}$ correlations of the PB unit. Minor C_α/H_α aromatic correlation from I units can be found at δ_C/δ_H 126/6.60 in the aromatic region of the fraction 2# HSQC spectra.

Slight changes have been reported in the chemical shifts between the aromatic regions for three phenolics fractions regarding cross-signals of lignin (Chen et al., 2016; Wang et al., 2015). The changes in correlation-signals may be due to the interaction of other functional groups and units that were produced from the microwave-assisted liquefaction process, i.e., the altered side chain of the S, S′, G, and PB aromatic rings. From Fig. 5, we know that the aromatic regions of the three fractions are obviously different. Correlation signals for S′ units are only present in fraction 1#. There are little correlation signals of I units in fraction 2#. Fraction 2# spectra have ratios of G, S, and PB units higher than those in fraction 1#. Only G, PB, and S groups were observed in the aromatic region of all three fractions.

The C—O aliphatic side-chain region provides useful information about the interunit linkages of three phenolics fractions in the 2D HSQC spectra (Fig. 6). Correlation signals for methoxyl groups (δ_C/δ_H 53–57/3.45–3.95) in three phenolic compounds fractions are the most prominent in this region. The methoxyls in the aromatics were connected to the aromatic rings and aliphatic carbons. The methoxyls were connected to aliphatic carbons mainly due to the methanolysis of the dominant units' linkages of β-5, β-β′, and β-O-4; while these were related to the aromatic rings, which were mainly from the structure of the original lignin in biomass, i.e., A-3-OMe, B-3-OMe, A-5-OMe, and B-5-OMe. Lignin is composed of randomly branched units of phenylpropenyls, syringols, and guaiacols units. The phenylpropenyl building blocks, as well as other monomer-derived units (syringols and guaiacols), are connected by several types of either C—C or C—O—C linkages, including 4-O-5, β-O-4, β-β, β-5, and 5-5, forming B unit, C unit, biphenyl, biphenyl ether, and alkyl–aryl ether substructures. The β-O-4 or β-O-4′ linkages are involved in the prominent β-aryl ether units in natural lignin (Chen et al., 2016).

As shown in Fig. 6, the β-aryl ether units have special signals at δ_C/δ_H 52.8/3.52 or 54.5/3.15 for C_β/H_β, and δ_C/δ_H 61.5/3.65 for C_γ/H_γ. These cross-signals corresponding to the characteristic signals from B and C units could be clearly observed in the spectra from fractions 1# and 2#. However, except for the methoxyls, only δ_C/δ_H 51.5/3.65 and 52.5/3.52 were correlated with for C_β/H_β positions from B and C units, and other correlation signals could not be seen at lower contour levels in the spectra of fraction 3#. Therefore, we speculated that the phenolic fraction 3# was composed of single aromatic-ring phenolic compounds with the smallest molecule products. The ether bonds in cyclic phenyl coumarans, resinols, and β-O-4 linkages in β-ethers of natural lignin can break into small molecules through the thermochemical conversion process.

The C—C aliphatic side chain region of 2D HSQC spectra from all kind of phenolic compounds fractions are analyzed. The signal intensity

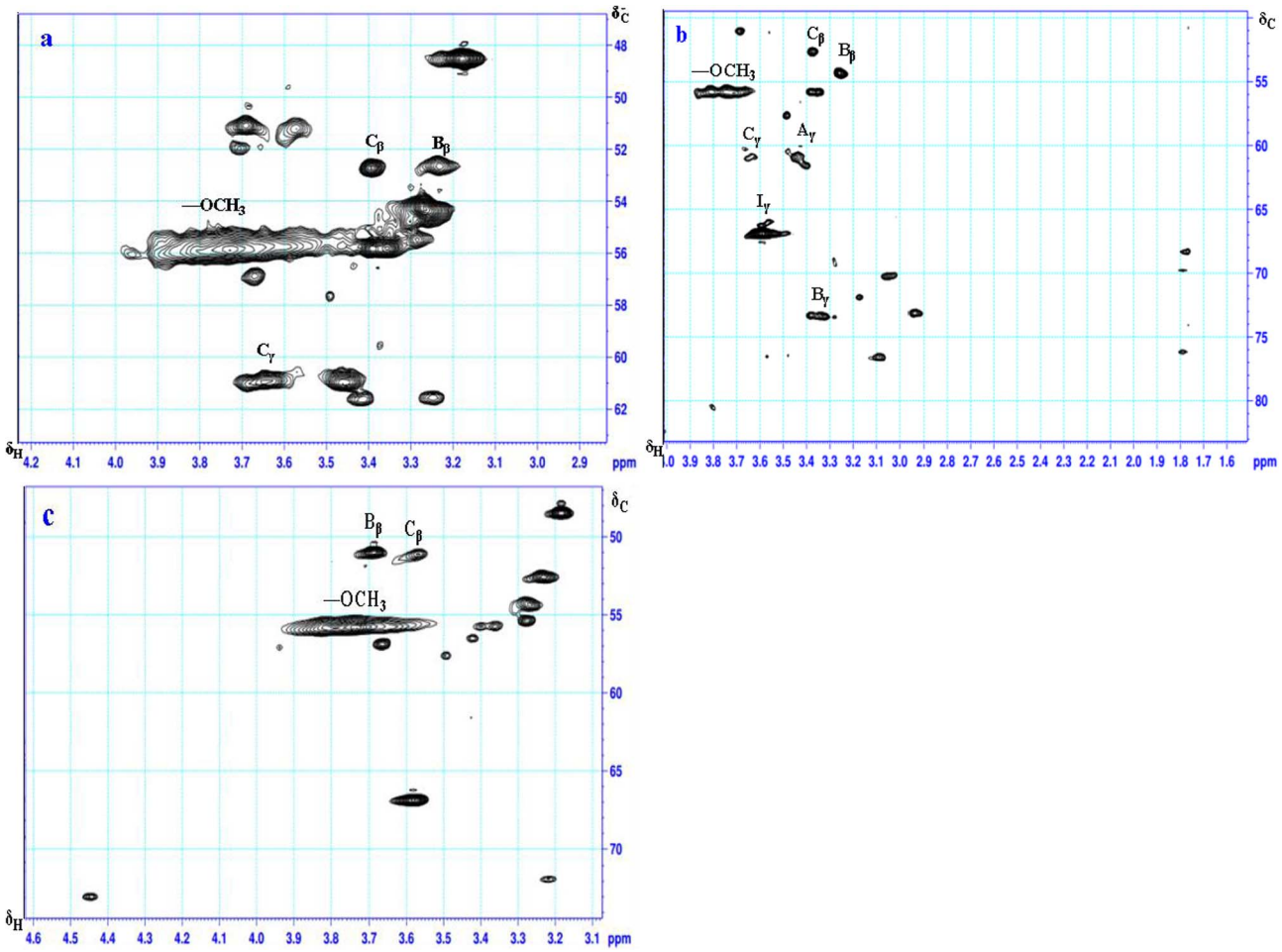

Fig. 6. Aliphatic C—O regions of HSQC spectra for phenolic compounds in fractions 1# (a), 2# (b), and 3# (c).

in the C—C aliphatic side chain region was lower than that in the C—O aliphatic region and aromatic regions. Fractions 1# and 2# showed similar cross-signals spectra in this region. The cross-signals at δ_C/δ_H 28.2/2.06–2.10 correspond to the acetyl CH_3, along with those corresponding to the characteristic signals from phenolic units and were clearly observed in the spectra from fractions 1# and 2#. There was only solvent DMSO-d_6 signal in fraction 3#.

The GPC analysis results of three phenolic compounds fractions and liquefied oil from liquefied bamboo are analyzed. The number-average molecular weight (Mn), weight-average molecular weight (Mw), peak molecular weight (Mp), and z-average molecular weight (Mz) results of three phenolic compounds fractions and liquefied oil were analyzed. The results demonstrate that natural lignin was solvolytically released from the cell wall as fragments of much lower molecular weight than what is currently believed (Guo et al., 2017; Shuai et al., 2016). The depolymerized lignin can be further separated according to the size of molecules from the stepwise fractionation of liquefied products. With the increase of retention time, the molecular weight became lower, but the content became higher, which showed a trend of continuous distribution. This result indicated the polymerized lignin in the bamboo had been effectively depolymerized into small molecules phenolic compounds during the microwave-assisted liquefaction process. The molecular weights (Mw) of fractions 1#, 2#, and 3# and liquefied oil were 797, 542, 249, and 1161, respectively. The Mw of fraction 3# with single aromatic rings was less than 250 Da could be extracted by EtOAc, while phenolic compounds fraction 1# and 2# precipitated as solid products and consisted of some phenolic dimers, tetramers, and other aromatic derivatives of higher molecular weights. The phenolic compounds with different molecular weight distributions have potential for producing downstream products, e.g., carbon materials and phenolic resins. The three phenolic compounds from microwave-assisted liquefaction presented different solubility in different organic solvents. These results suggest that these phenolic compounds from liquefied products should have better chemical reactivity. The phenolic compounds from liquefaction not only had relative low molecular weight, which corresponds to an increasing probability of molecular collision with reactants, but also had lower molecular size providing a potential reaction activity with other reactants because they had only minor steric hindrance compared with pure lignin.

4. Conclusions

Aromatic and monosaccharide derivatives were produced from bamboo with microwave-assisted liquefaction. With stepwise precipitation and extraction, a high concentration (92%) of glycoside compounds was collected in the monosaccharides fraction, and contents of phenolic compounds were approximately 82% in the aromatics fraction. Three phenolics fractions were separated from microwave-assisted liquefied mixtures by partial removal of methanol. Approximately 78–86 wt% of the six biomass materials were converted into liquid products. A 45% monosaccharides yield and 29% aromatics yield were obtained from bamboo with 0.3 g sulfuric acid in 18 g methanol and 2 g bamboo at 160 °C with 10 min.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2017.07.182.

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