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PAPER

# Renewable chemical feedstocks from integrated liquefaction processing of lignocellulosic materials using microwave energy†

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The objective of this investigation was to find a simple method for the production of phenolic rich products and sugar derivatives (biopolyols) *via* separation of liquefied lignocellulosic materials. Liquefaction of lignocellulosic materials was conducted in methanol at 180 °C for 15 min with the conversion of raw materials at about 75%. After liquefaction, the liquefied products were separated by addition of a sufficient amount of water. It was found that the hydrophobic phenolics could be largely separated from aqueous solutions. The phenolic products that precipitated from the aqueous phase were mainly composed of phenolic derivatives such as 2-methoxy-4-propyl-phenol and 4-hydroxy-3-methoxy-benzoic acid methyl ester. Afterwards, the aqueous solution was distilled under vacuum to remove water and formed a viscous liquid product henceforth termed biopolyol. As evidenced by GC-MS analysis, the biopolyols contained methyl sugar derivatives, including methyl β-D-mannofuranoside, methyl α-D-galactopyranoside, methyl α-D-glucopyranoside, and methyl β-D-glucopyranoside. The effect of glycerol on promotion of the liquefaction reaction was also studied. The yield of residue was significantly decreased from approximately 25 to 12% when a glycerol–methanol mixture was used as solvent rather than methanol. According to the GC-MS analysis, the total content of phenolics and poly-hydroxy compounds (including glycerol and sugar derivatives) in phenolic products and biopolyols was 65.9 and 84.9%, respectively. Therefore, a new method for fractionation of liquefied products was proposed according to the molecular structure of the biomass.

## 1. Introduction

Lignocellulosic biomass from plants is the most abundant form of biomass and does not directly compete with human food uses.<sup>1</sup> The various technologies for the production of platform chemicals and renewable materials have received increasing attention, particularly for non-edible biomass feedstocks. As an efficient pathway for biomass conversion, thermochemical methods such as pyrolysis and liquefaction have great potential to produce biofuels and valuable biochemicals.<sup>2,3</sup>

Lignocellulosic biomass is made up of three main components: cellulose, hemicellulose and lignin, of which the

cellulose fraction and lignin fraction can account for up to 60–70% and 15–30%, respectively.<sup>3,4</sup> The production of poly-hydroxy compounds (biopolyols) from biomass has long been of interest in the polyurethane (PU) industry because of the high content of cellulose and hemicellulose in woody biomass. As an important thermochemical method, liquefaction provides an efficient pathway to convert solid biomass into a liquid product. The liquefied products from biomass provide sufficient hydroxyl functionalities during the reaction with diisocyanate to produce a polyurethane polymer. Generally, the conversion of lignocellulosic biomass to liquid biopolyols can be achieved using petrochemical polyols with appropriate molecular weights as the liquefying agent.<sup>5</sup> The produced biopolyols exhibit promising properties for the production of PU foams, and the produced PU foams show comparable properties with their petroleum analogs.<sup>6–8</sup>

However, all these liquefaction processes require high volumes of petroleum-derived solvents as a liquefying agent, *i.e.*, approximately 100–125 g solvent is required for 20 g of lignocellulosic biomass to obtain high-quality biopolyols.<sup>5,7,9,10</sup> In short, the superior properties of the biopolyols are mainly due to the high amount of petroleum-derived solvents in biopolyol products. The large usage of petroleum-based solvents considerably increases the production cost of biopolyols and consequently hinders future commercialization efforts.

One important reason for the large amount of solvents in the liquefaction process is that considerable lignin derivatives were

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obtained during liquefaction. These undesired products, usually lack hydroxyl functionalities which lead to low activity during the reaction with diisocyanate. Lignin is of particular interest due to its phenolic nature from which a wide variety of phenol derivatives can be derived. Previous reviews have been published on the production of phenolic resins using the liquid products originating from the thermochemical conversion of biomass.<sup>11,12</sup>

However, only partially liquefied products are feasibly used in phenolic resins without significantly degrading the mechanical properties. The reason is mainly due to the many oxygenated derivatives that are degraded from cellulose, such as sugars, acids and other undesirable chemicals, and mix with phenolics in the liquefied liquids. These components act like fillers and may have a negative impact on resin product properties since they can not react with formaldehyde to form crosslinked polymers. In order to resolve this issue, several studies have been reported on how to prepare phenolic rich fractions from biomass and lignin using pyrolysis.<sup>3,13</sup>

Fractionation to remove acids, sugars, and odorous compounds, and to concentrate reactive phenolics, allows increased substitutions for phenolic resins. However, fractionation, especially by pyrolysis and solvent extraction, also tends to be quite costly, and gives lower yields, making the issue of co-product utilization or disposal more significant.

By considering all of the above described limitations, we have designed a simple and sustainable process which involves a degradation reaction of biomass and produces biopolyols and phenolic compounds. This strategy implies that cellulose and lignin derivatives liquefied from biomass could be fractionated conveniently according to their hydrophilic and hydrophobic properties. This simple approach can achieve an integrated utilization of liquefied products toward different synthesis directions based on their molecular structures.

In this study, a new method of liquefaction of woody biomass for the production of chemical products is proposed using solvent mixtures as liquefying agents under microwave energy. We believe that the liquefaction process could be promoted efficiently with microwave energy due to the direct conversion of electromagnetic energy into heat at the molecular level.<sup>14</sup> The successful replacement of petrochemical solvents by glycerol in the liquefaction process has the potential to reduce the production cost of biopolyols. The objective of this study was to investigate the reaction parameters for different yields of solid and liquid products. The mechanism of the liquefaction was also proposed.

## 2. Experimental

### 2.1 Chemicals

For this study, southern pine sawdust was produced from a commercially purchased board which was pulverized to pass through a 60 mesh sieve, followed by oven drying at 105 °C overnight. This ground material was kept in sealed bags until needed, at which time a small sample of the material was dried further in an oven at 105 °C overnight. The elemental analysis for the sawdust was C (46.61%), H (6.63%) and O (46.76%). An inductively coupled plasma optical emission spectrometer (ICP-OES,

PerkinElmer, Optima 7000 DV) was used to analyze the mineral content of the sawdust (Ca: 642 ppm, Fe: 23 ppm, K: 93 ppm, Mg: 127 ppm, Mn: 96 ppm, Na: 21 ppm, P: 17 ppm, Zn: 13 ppm). The weight percentage of ethanol–toluene soluble matter in the raw material was 8.12%, according to the standard test method for ethanol–toluene solubility of wood, ASTM D 1107-96 (ASTM 2007). The weight percentage of lignin in the extracted raw materials was 29.25% according to the standard test method for acid-insoluble lignin in wood, ASTM D 1106-96 (ASTM 2007). All the other reagents used in this work were of analytical grade.

### 2.2 Liquefaction of sawdust by microwave irradiation

Liquefaction of biomass was carried out in a Milestone microwave laboratory system (Ethos EX, 1200 W microwave extraction system, automatic temperature control with fiber optic sensor, ASM-400 magnetic stirrer for homogenous mixing of sample, 100 bar maximum operating pressure, 300 °C maximum operating temperature) equipped with 100 mL sealed teflon reaction vessels and an internal temperature sensor (fiber optic sensor). Samples were irradiated for 5 min under 500 W as starting microwave power. The sample temperature was controlled at 160–185 °C with the microwave power at 700 W. The reaction mixture consisted of 2.0 g of sawdust powder, 4.0 g of liquefying agent (polyhydroxy compounds), 12.0 g of methanol, and 0.10 g of catalyst (sulfuric acid) and was mixed with magnetic stirring during liquefaction. After liquefaction for a preset time (5–20 min), the vessels were allowed to cool to room temperature before opening.

The gaseous products were vented because their yields were negligible. Then, the liquid and solid products were filtered. The solid product was washed with 20 mL methanol three times, dried at 105 °C for 12 h in an oven, and then weighed to give the yield of residue. The residue content was defined as the percentage of dry weight residue to the total raw sawdust charged, and has usually been used as an index of the liquefaction extent.<sup>15</sup>

The filtrate was then evaporated at 70 °C under vacuum to remove the methanol from the liquid product. Subsequently, by adding 10 mL of water into the liquid product, the phenolic compounds were precipitated from the aqueous solution. These products were filtered and dried at 30 °C for 12 h to give the yield of phenolic products. The biopolyol products were obtained by removal of the water from the aqueous solution using a rotary evaporator. The molecular structures of different fractions were characterized by gas chromatography-mass spectrometry (GC-MS), proton nuclear magnetic resonance (<sup>1</sup>H NMR) and Fourier-transform infrared (FT-IR) spectrometry.

### 2.3 Analysis methods

The general profile for the biopolyols and phenolic compounds was obtained using electron ionization mass spectrometry (EI-MS). Analysis of the products was conducted on a mass spectrometer (Agilent 5975C VL MSD) and the products were separated into their components using a gas chromatograph (Agilent 7890A) equipped with a fused capillary column (HP-5,

$l = 30$  m, i.d. 0.32 mm, film thickness 0.25  $\mu\text{m}$ ) with 5% phenyl and 95% dimethylpolysiloxane as the stationary phase. The carrier gas was helium at a flow rate of 1.8  $\text{mL min}^{-1}$ . Condition for analysis: injection mode was split at split rate 35; the column was held at 50  $^{\circ}\text{C}$  for 2 min and then heated to 250  $^{\circ}\text{C}$  at a rate of 10  $\text{K min}^{-1}$  while the injector temperature was 250  $^{\circ}\text{C}$ . The identification of the components of the products was confirmed according to pre-established criteria for data analysis.

FT-IR was used to study the solid and liquid products during the liquefaction process. The filtrate from the residue content was condensed and freeze-dried for FT-IR analysis on a Thermo Nicolet (NEXUS 670) spectrometer. Attenuated total reflection measurements were conducted for the samples.

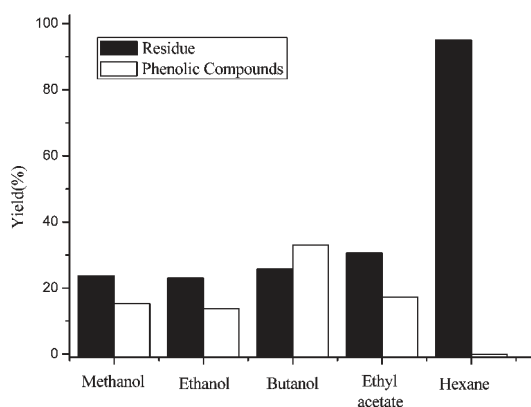
Approximately 80 mg of sample and 0.8 mg of 1,3,5-trioxane used as internal standard were dissolved in 600  $\mu\text{L}$  of acetone (d-6). Quantitative  $^1\text{H}$  NMR spectra were recorded with a Bruker 500 MHz spectrometer at 308 K using an inverse gated decoupling pulse sequence.

A NeoScope JCM-5000 scanning electron microscope (SEM) (5–10 kV accelerated voltage) was used to examine the morphology of the raw samples and liquefied residue in order to compare the effect of different heating treatments. Specimens for SEM inspection were gold-plated prior to analysis.

### 3. Results and discussion

#### 3.1 Mechanism of the lingocellulosic materials in alcohols

To explore the reaction pathway of the alcohols with lingocellulosic materials, solvents with different hydrophilic and hydrophobic properties were used in liquefaction. The reactions were carried out with sulfuric acid (2.5%) as the catalyst for 15 min with magnetic stirring. Fig. 1 shows the results of liquefaction with different solvents. It can be seen that hydrophobic solvents such as hexane have no effect on liquefaction. For hexane, no phenolic compounds were obtained in the separation step after liquefaction. The residue content was 95% and maintained the same appearance as the raw materials before the reaction. This result indicates that the raw materials did not undergo a decomposition reaction. It is apparent that only some organic impurities such as waxes, fatty acids, and rosin acids were



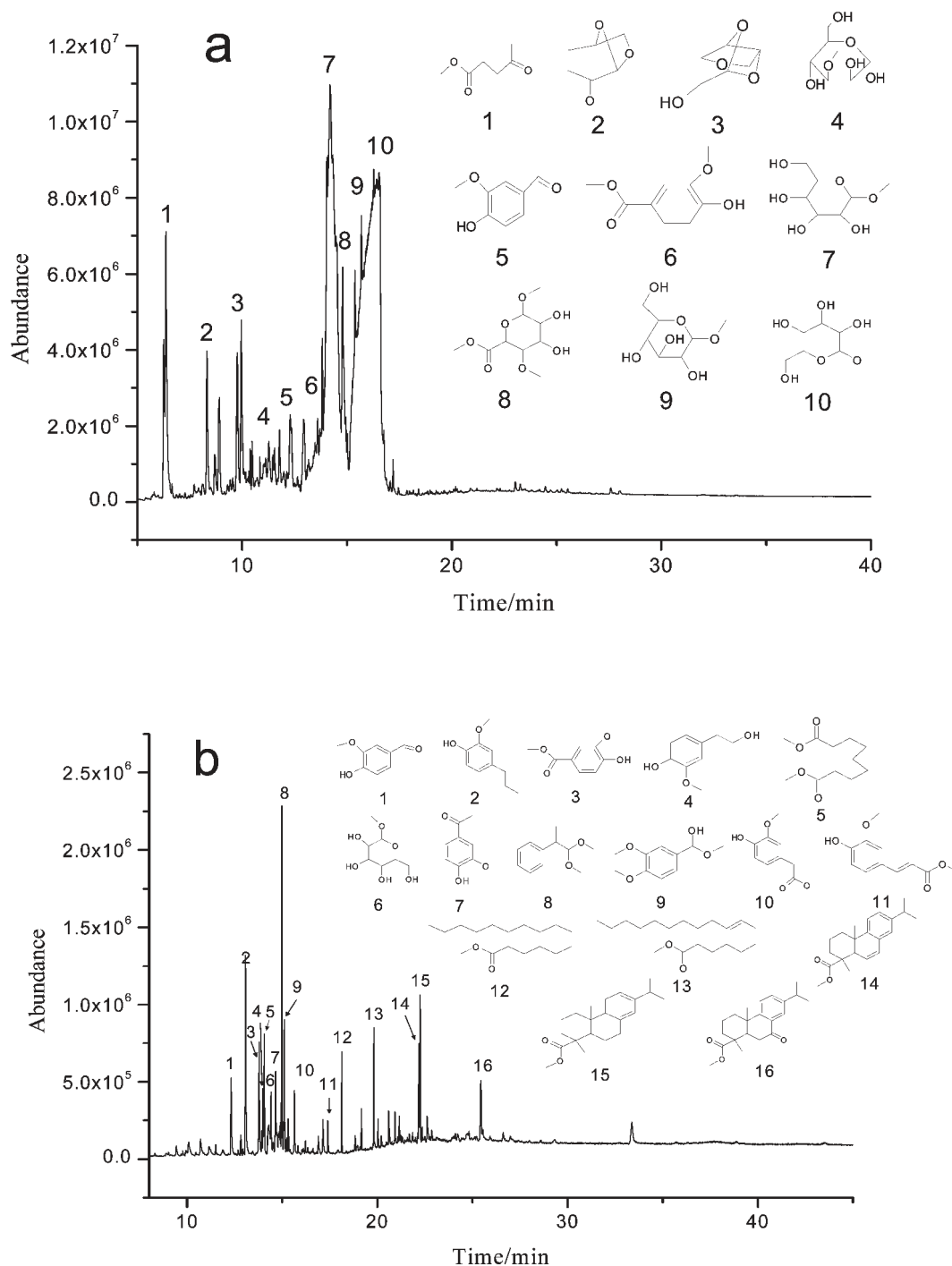
**Fig. 1** Results of liquefaction reaction using various low boiling point solvents. Reaction conditions: sawdust : solvent = 1 : 6, 2.5 wt% sulfuric acid, autogenic pressure, microwave power 700 W, 15 min.

removed. The low reactivity of hexane is due to two main reasons: (1) it has a low ability to interact with microwave radiation, which leads to a low reaction temperature; (2) hexane lacks nucleophilic reactive functionalities, such as  $-\text{OH}$  groups, and so, was consequently unable to split the glycosidic bond and  $\text{C}-\text{O}-\text{C}$  groups in cellulose and lignin.

Conversely, methanol and ethanol showed high reaction activity for decomposition. In general, lower molecular weight alcohols provide favorable permeability and fluidity at higher reaction temperatures, which is beneficial for the conversion of biomass. However, as the length of the carbon chain in the alcohols increased, a serious problem became apparent due to their more hydrophobic nature. As butanol is insoluble in water, the liquefied products had to be extracted with 20 mL water three times to give the biopolyol products. In addition, the solvent could not be completely removed from the phenolic products due to its high boiling point. This is largely the reason that the yield of phenolics using butanol as the solvent was much higher than any other solvents.

Fig. 2 compares the GC-MS chromatograms of the liquefied products from biomass (including biopolyols and phenolic compounds). It was found that the majority of compounds in biopolyols are comprised of six carbon sugars such as methyl  $\beta$ -D-mannofuranoside, methyl  $\alpha$ -D-galactopyranoside, methyl  $\alpha$ -D-glucopyranoside, methyl  $\beta$ -D-glucopyranoside, *etc.* The total content of the sugar derivatives in biopolyols was 73.4% (Fig. 2a). Only 2.1% of phenolics and aromatic compounds were identified. There are also several kinds of oxygenated components generated from cellulose, such as furfural, 4-oxo-pentanoic acid methyl ester, and succinic acid derivatives. The content of these components was 4.7% (Fig. 2a). Thus, we concluded that the sugar derivatives that originated from cellulose and hemicellulose were successfully separated and concentrated. A major advantage of the method proposed in this study is that the operation successfully prevents the sugars from decomposing to furfural derivatives, carboxylic acids, and ketones,<sup>15</sup> indicating that it is perfectly suitable for use as polyols in the polyurethane industry by slight modification using ethylene oxide and propylene oxide. Although there was a small amount of hydrophilic phenolics identified in the biopolyol products, it is not a serious problem for the production of high quality polyol products. A hydroprocessing method can be used to convert these phenolics into saturated cyclohexanolic structures.<sup>16</sup>

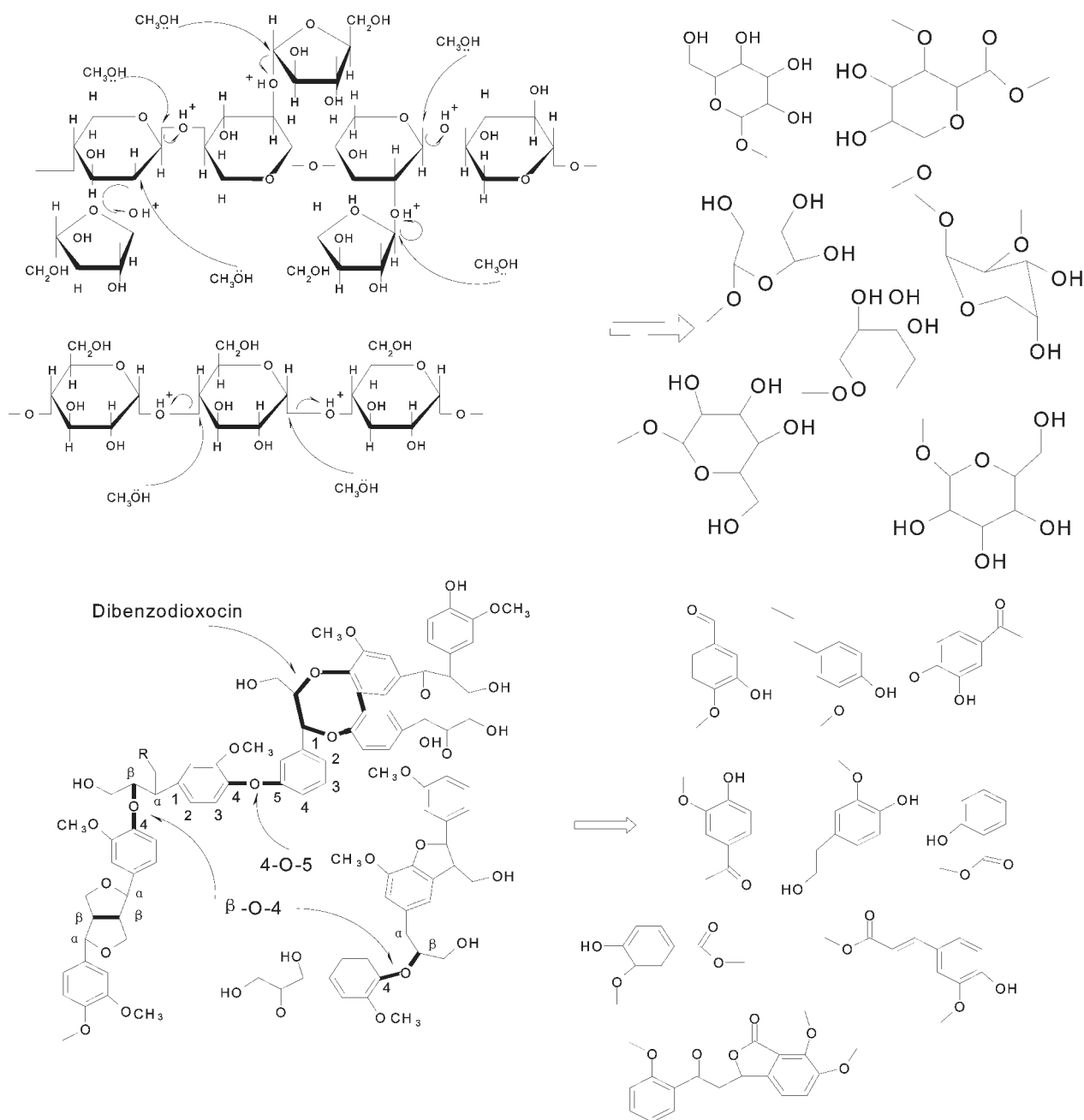
Multiple types of phenolics were identified. This result likely contributed to the cleavage of the  $\beta$ -O-4, 4-O-5, and dibenzodioxocin units, which are dominant groups in lignin structure.<sup>3</sup> The content of these aromatic and phenolic compounds was 48.9% (Fig. 2b). Several types of fatty acid esters and rosin acid esters were also characterized, accounting for 25.9% of the total peak area, and indicating that an extraction pretreatment is necessary in order to obtain phenolic-rich products. Compared with the biopolyol products, there are few oxygen-containing components that could be considered cellulosic derivatives. The total content of residual sugar derivatives in the phenolic products is only 6.8%, indicating that most of the hydrophilic cellulosic derivatives were dissolved in the water phase and separated by filtration. In order to obtain the product with a majority of phenolics, the feedstock was extracted by an ethanol-toluene mixture in the following experiments.



**Fig. 2** GC-MS analysis of the fractionated liquefied products; (a) biopolyols, (b) phenolic compounds. Reaction conditions: sawdust : methanol = 1 : 6, 2.5 wt% sulfuric acid, autogenic pressure, microwave power 700 W, 15 min, 180 °C.

The mechanism for liquefaction using methanol as the solvent was proposed based on the GC-MS analysis. The structure of cellulose and lignin is merely pictorial and does not imply a particular sequence. As shown in Fig. 3, since we only have a weak nucleophile and a poor electrophile, activation of the glycosidic bond is necessary. Protonation of the O atom in the glycosidic bond makes it more electrophilic. This step is very fast and

reversible. Subsequently, the methanol –OH group functions as the nucleophile and attacks the electrophilic C adjacent to the glycosidic bond. As a result, the electrons move towards the oxonium ion, creating a good leaving group and a neutral hydroxyl group, by cleaving the C–O bond. The decomposition of lignin in biomass has a similar mechanism by cleaving the dominant linkages including  $\beta$ -O-4, 4-O-5, and dibenzodioxocin units.<sup>3</sup>

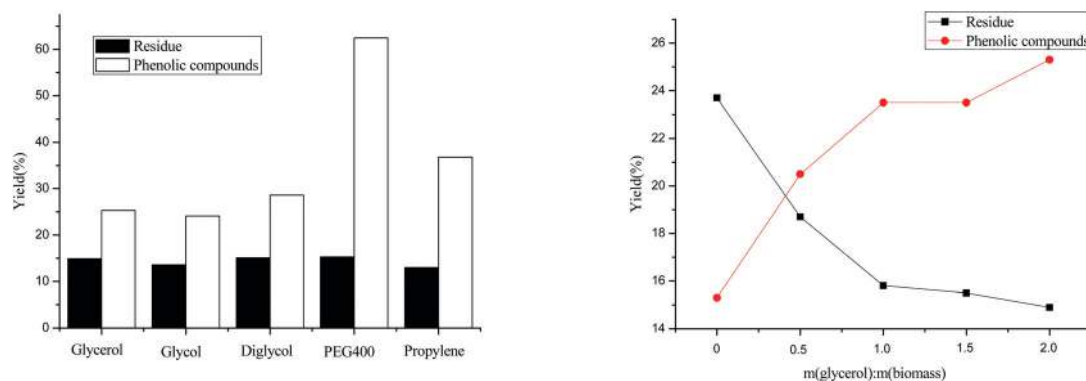


**Fig. 3** Proposed reaction pathway for the liquefaction of sawdust in the presence of sulfuric acid. Reaction conditions: sawdust : methanol = 1 : 6, 2.5 wt% sulfuric acid, autogenic pressure, microwave power 700 W, 15 min, 180 °C.

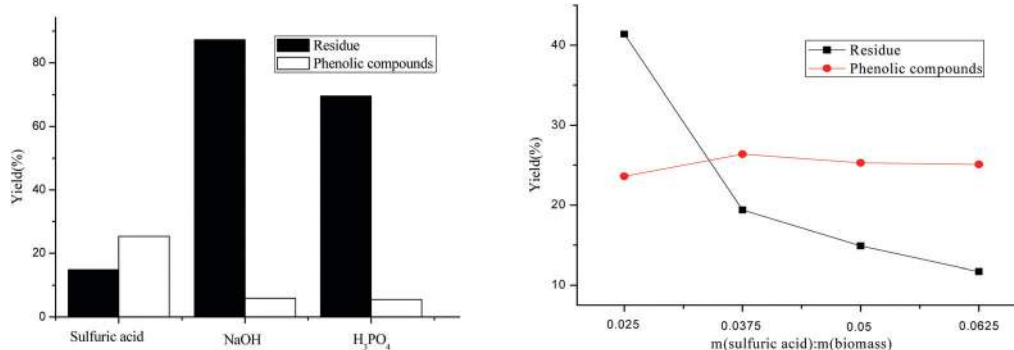
### 3.2 Effect of polyhydroxy compounds on the promotion of liquefaction reaction

Polyhydroxy compounds are usually used as liquefying agents.<sup>9,10</sup> However, there are few reports using these compounds accompanied with low boiling point alcohols such as methanol. We believe that the addition of polyhydroxy compounds in methanol could further increase the conversion of biomass. Compared with those liquefaction processes using high volumes of petroleum-derived solvents, the amount of liquefying agent may decrease markedly because the low boiling point solvents could be easily recovered after liquefaction.

The results of different kinds of polyhydroxyl compounds for liquefaction are shown in Fig. 4. It was found that all liquefying agents can further decrease the yield of residue from 25% to approximately 15% on the basis of methanol. However, only low molecular compounds such as glycol and glycerol can obtain powder phenolic products with reasonable yield. During the separation process after liquefaction, we found that phenolic compounds become a lump of high viscosity gel products when using high molecular liquefying agents. This result can be attributed to the difficulty of removing these liquefying agents by the addition of water. The residual agents were mixed with phenolic products and were prevented from



**Fig. 4** The results of liquefaction reaction using different kinds of poly-hydroxy compounds. Reaction conditions: sawdust : methanol : petrochemical polyols = 1 : 6 : 2, 2.5 wt% sulfuric acid, autogenic pressure, microwave power 700 W, 15 min, 180 °C.



**Fig. 5** Liquefaction reactions under different catalysts. Reaction conditions: sawdust : methanol : glycerol = 1 : 6 : 2, 2.5 wt% catalyst, autogenic pressure, microwave power 700 W, 15 min, 180 °C.

precipitating the phenolics as a solid product from the aqueous solutions.

The effect of glycerol dosage on the reaction was also tested. With an increasing amount of glycerol, the yield of residue decreased while the yield of phenolics gradually increased. This result indicated that polyhydroxy compounds have a beneficial effect on the liquefaction reaction, especially on the promotion of phenolics. This result could be contributed to the synergistic effect of glycerol and methanol.

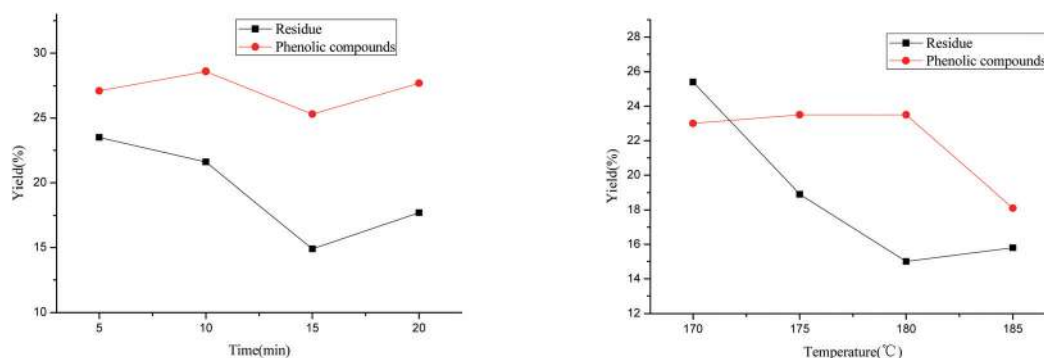
### 3.3 Effect of reaction parameters on the liquefaction reaction

Liquefaction reactions are typically catalyzed by acid and base catalysts.<sup>17,18</sup> In this paper, the activities of different catalysts were investigated. Fig. 5 shows the conversions of sawdust at 180 °C after 15 min with three different catalysts. These reactions used a sawdust/glycerol/methanol ratio of 1 : 6 : 2. It was found that H<sub>2</sub>SO<sub>4</sub> gave the highest conversion of the raw materials while phosphoric acid showed low catalytic activity. This result indicated that sulfuric acid could provide strong acid sites during the reaction. The highly reactive protons in sulfuric acid are able to activate the oxygen atoms in glycosidic bonds. These results are in good agreement with the mechanism analysis in Fig. 3.

It was also found that base catalysts, such as NaOH, gave the lowest conversions of biomass. The biomass feedstock did not

show much difference compared with those prior to reaction. The base catalyst might not be suitable for the liquefaction because it can react with the phenolic hydroxyl group in lignin to form sodium phenolate. Thus, there is no sufficient catalyst to decompose the C–O–C groups in cellulose and lignin. The yield of residue and phenolic compounds changed from 41.4 to 11.7% and 23.6 to 25.1% respectively, when the amount of sulfuric acid was raised from 0.05 to 0.125 (see Fig. 5). These reactions used a sawdust/methanol/glycerol ratio of 1 : 6 : 2 at 180 °C. This result showed that the production of phenolic products can be achieved by using sulfuric acid at a mass ratio of 0.025. Compared with the dosage of sulfuric acid, the amount of glycerol has a dominant effect on the yield of phenolics (see Fig. 4). Fig. 5 also shows the remarkable decrease of residue as a result of using sulfuric acid at a mass ratio of 0.0375. However, the increased amount of catalyst may contribute to the decomposition of cellulose and hemicellulose. To achieve good conversions and controllable decomposition of biomass, a sulfuric acid–biomass ratio of 0.05 : 1.0 was selected as the optimum catalyst amount.

Fig. 6 shows conversions of biomass *versus* time at 180 °C using sulfuric acid. The yield of residue decreased from 23.5 to 14.9% when the reaction time increased from 5 min to 15 min. A further increase in reaction time may cause a recondensation of the liquid products because of the residue increase.<sup>18</sup> The yield of phenolic compounds was kept at a stable value, which



**Fig. 6** Reaction parameters on the liquefaction of biomass. Reaction conditions: sawdust : methanol : glycerol = 1 : 6 : 2, 2.5 wt% sulfuric acid, autogenic pressure, microwave power 700 W, reaction time from 5–20 min (left), reaction temperature from 170 to 185 °C (right).

was approximately 25–27%. This result is in good agreement with the result from lignin analysis. Fig. 6 also shows the effect of reaction temperature. The higher temperature dependence of the yield of residue under this specific set of conditions suggests that 180 °C is a suitable reaction temperature. Further increasing the temperature may cause recondensation of the phenolics since the yield of phenolic products slightly decreased.

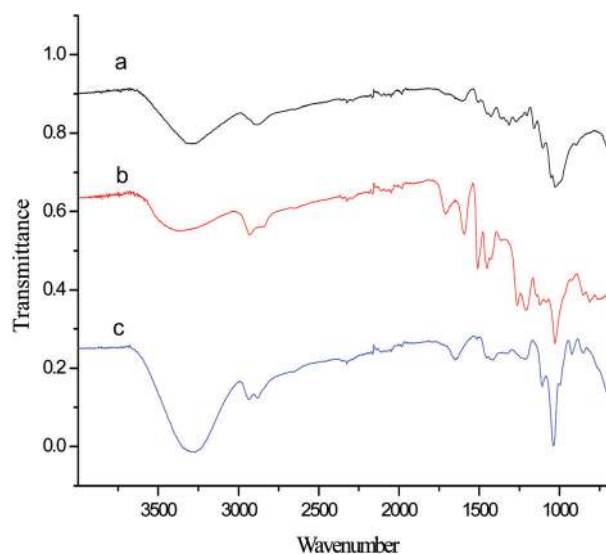
### 3.4 Chemical structure of phenolic compounds and polyhydroxy polyols

GC-MS analysis was used to identify the biopolyols and phenolic compounds in the liquefied product (ESI, Table S1 and Table S2†). After liquefaction, most of the cellulose and hemicellulose was converted into methyl sugar derivatives with polyhydroxyl functionalities. As many as nine monosaccharides were formed, accounting for more than 48% of the total corresponding peak area.

Only one carbonyl compound (pentanoic acid, 4-oxo-methyl ester) was observed after the reactions, accounting for 2.0% of the total peak area. This result showed that the liquefaction process could prevent further degradation of monosaccharides to carbonyl molecules such as furfural and acetic derivatives.<sup>15</sup>

Glycerol and its derivatives such as 1,3-dimethoxy-2-propanol and 3-methoxy-1,2-propanediol were detected. These side products were produced from etherification of methanol with glycerol under sulfuric acid catalyst. Although large quantities of these products were mixed with the sugar derivatives in biopolyol products, they do not have a negative effect on the properties of the polyol products because they can also provide sufficient hydroxyl groups, and form a three-dimensional cross linked framework during the reaction with diisocyanate to form rigid foams. The total content of the polyhydroxy compounds was 84.9%.

Many kinds of phenolic compounds were detected in the products, such as 2-methoxy-4-propyl-phenol, 4-hydroxy-3-methoxy-benzoic acid methyl ester, and 4-hydroxy-3-methoxy benzenoic acid. The content of organic impurities such as fatty acids and rosin acids were significantly decreased to 3.3%. This result is mainly due to the extraction of the raw materials by the ethanol–benzene solvent. Thus, the aromatics and phenolics in solid products can be obtained with the content up to 65.9%. Only trace amounts of sugar derivatives were detected,



**Fig. 7** FT-IR analysis of the fractionated liquefied products from microwave reaction; (a) residue, (b) phenolic products, (c) biopolyols. All the samples were analyzed on a Thermo Nicolet spectrometer. Attenuated total reflection measurements were conducted for the samples. Reaction conditions for the liquefied product: sawdust : methanol : glycerol = 1 : 6 : 1, 2.5 wt% sulfuric acid, autogenic pressure, microwave power 700 W, 15 min, 180 °C.

indicating that the compounds originating from cellulose were separated from the phenolics. There were about 15% unknown compounds in the spectrum, which could potentially be aromatic derivatives. Absolute structural identification of these compounds, however, was not possible since their authentic standards were not available.

It is apparent that the structure of the biomass feedstock was decomposed into smaller units such as sugar derivatives and phenolics. Water was introduced to separate these units according to their hydrophilic and hydrophobic properties. The analysis of the components from GC-MS showed that these fractionation products are promising as platform bio-based chemicals.

We used FT-IR spectroscopy to analyze the solid and liquid products throughout the liquefaction process. Fig. 7 portrays a simple comparison between the biopolyols, phenolic compounds, and liquefied residue. By comparing the FT-IR spectra

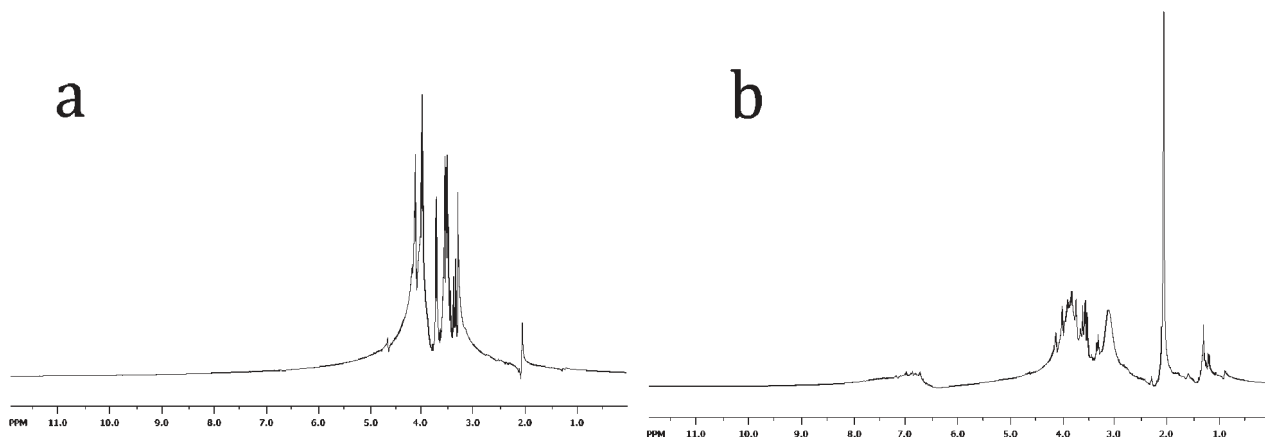
of biopolyols and phenolic compounds, a broad peak at around  $3400\text{ cm}^{-1}$  is seen which represents the  $-\text{OH}$  groups either from cellulose or lignin. The peak at around  $2922\text{ cm}^{-1}$  represents  $\text{C}-\text{H}$  in a symmetric stretching of aliphatic methyl. A band at approximately  $1636\text{ cm}^{-1}$  is characteristic of a  $\text{C}=\text{C}$  stretching vibration in the aromatic skeleton of lignin. This peak is a weak absorption band observed in biopolyols, indicating that the phenolics were concentrated successfully after the separation process. A band appearing at approximately  $1458\text{ cm}^{-1}$  is due to the  $\text{C}-\text{H}$  bending vibration of the methylene groups (scissoring vibration). The residue showed two main bands at  $3400$  and  $1059\text{ cm}^{-1}$ , which have similar absorption bands to biopolyols. This indicated that the residue has a skeleton of cellulose linkages.

Fig. 8 shows the  $^1\text{H}$  NMR spectra of the biopolyols and phenolic compounds. The  $^1\text{H}$  NMR spectrum indicated that a large amount of protons were aliphatic H adjacent to oxygen ( $3.0\text{--}4.5\text{ ppm}$ ) in the biopolyols. There was no peak observed from  $6.0\text{--}8.0\text{ ppm}$ . This result indicated that the biopolyols are mainly composed of saturated oxygenated compounds with plenty of hydroxyl groups. This result is in good agreement with

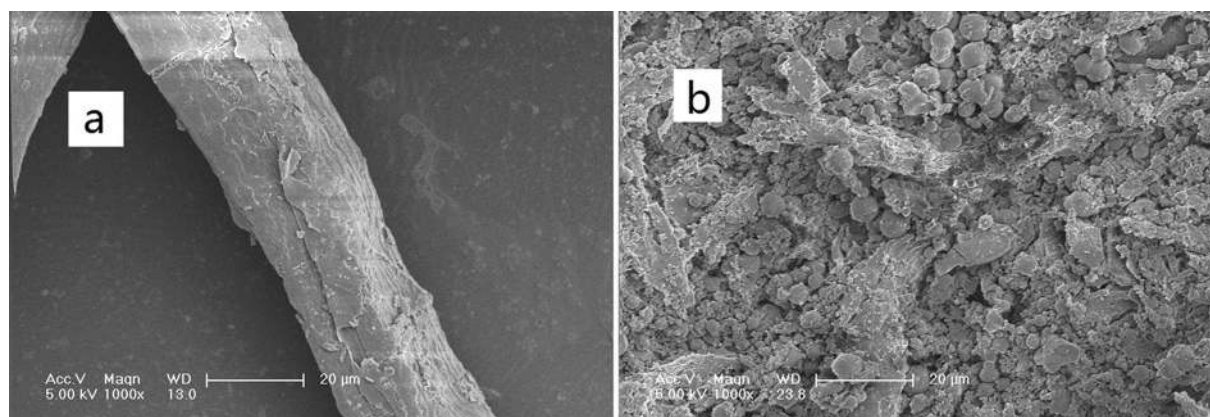
the GC-MS observations. Compared with biopolyols, the NMR spectra of the phenolic compounds showed many peaks within  $3.0\text{--}4.5\text{ ppm}$ . These protons are mainly adjacent to the oxygen atoms in phenolics. Moreover, the protons of aromatic compounds ( $6.0\text{--}8.0\text{ ppm}$ ) were observed in the spectra, which is largely phenolic due to the decomposition of lignin.

### 3.5 Microscopic analysis of residue

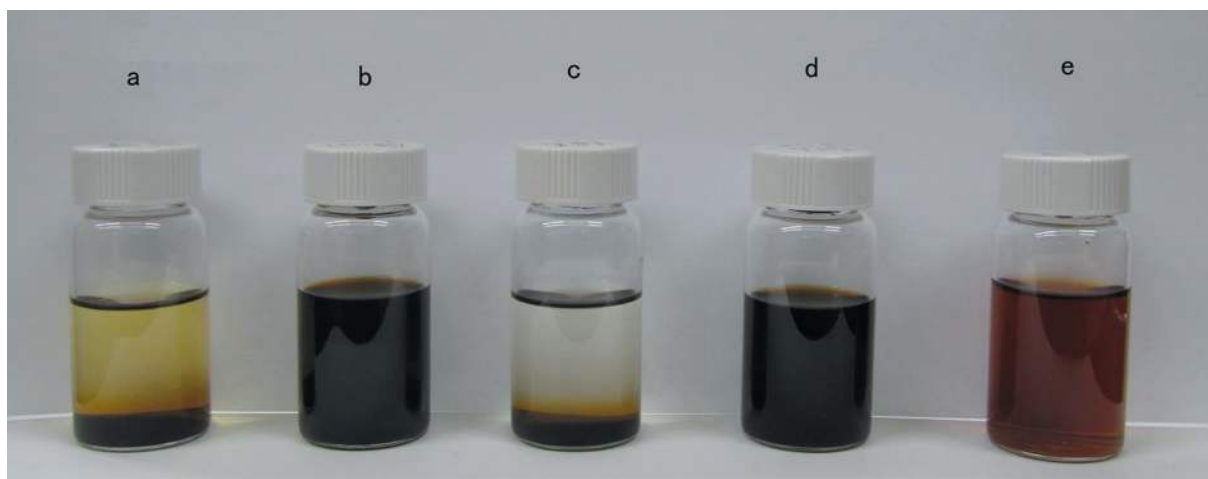
SEM images of the liquefied residue are shown in Fig. 9(b). The surface of the fibers is rough and comprised of many small fragments of cell wall components due to reaction processing. Most small fragments attached on the surface of the residue fibers have been removed, but the liquefied residue mostly remained in its original fiber bundles. This observation indicates that the residue is the cellulose skeleton. It is very difficult for the solvent to penetrate this high density crystallized cellulose framework under the reaction conditions in this study. Although higher amounts of sulfuric acid can increase the conversion of the biomass, we believe the better solution may be to use a



**Fig. 8**  $^1\text{H}$  NMR analysis of the fractionated liquefied products; (a) biopolyols, (b) phenolic compounds. The spectra were recorded with a Bruker 500 MHz spectrometer at 308 K. Reaction conditions for the liquefied product: sawdust : methanol : glycerol = 1 : 6 : 1, 2.5 wt% sulfuric acid, autogenic pressure, microwave power 700 W, 15 min,  $180\text{ }^\circ\text{C}$ .



**Fig. 9** SEM images for raw material (a) and liquefied residue (b) after being dried at  $105\text{ }^\circ\text{C}$  for 12 h.



**Fig. 10** The solubility of biopolyols and phenolic products in different organic solvents at ambient temperature; (a) pure lignin in acetone, (b) phenolic product in acetone, (c) pure lignin in THF, (d) phenolic product in THF, (e) biopolyol product in ethanol.

steam explosion pretreatment to obtain a higher reaction surface area.

### 3.6 Solubility of phenolic compounds and biopolyols in conventional solvents

Lignocellulosic materials usually have poor solubility in conventional organic solvents because of their high degree of polymerization and multi-hydrophilic groups. This difficulty arises because the complicated three-dimensional lignin network in wood is interlinked with other lignocellulosic components and thus binds the entire wood matrix.<sup>3</sup> As a result, the insolubility of lignocellulosic materials in common solvents has severely inhibited efforts to produce value-added platform chemicals due to their poor molecular interactions with other reagents. In this study, the three main components (hemicellulose, cellulose and lignin) in biomass were decomposed into smaller fragments such as sugar derivatives and phenolics. The solubility of these products was significantly promoted due to their small molecular size and low molecular weight. Then, the solubility of the products derived from the liquefied products was tested using several organic solvents. For comparative purposes, the solubility of pure lignin was also tested.

As shown in Fig. 10, the phenolic products can be easily dissolved in organic solvents such as acetone and tetrahydrofuran (b and d), while lignin is completely insoluble in these solvents (a and c). These results suggest that phenolic compounds from liquefaction should have better reaction activity because a homogeneous phase can be formed in many reactions by solvents. These phenolic compounds not only have lower molecular weights, which corresponds to an increasing probability of molecular collision with other reactants, but also provide a potential reaction activity with formaldehyde or other reactants because they have only minor steric hindrance compared with lignin.

On the other hand, Fig. 10(e) shows biopolyols can be dissolved easily in ethanol. Actually, they can be blended with water, methanol and other hydrophilic solvents in any proportion. This property is very important because the preparation of rigid polyurethane foam requires a uniform mixture of

polyols, blowing agent (water), and other additives before the reaction with diisocyanate. A stable and uniform mixture has a close relationship with the quality of the foams.

## 4. Conclusions

This study has presented a simple process for separating liquefied products, which can be obtained from various lignocellulosic biomass, into sugar derivatives (mainly from cellulose and hemicellulose) and phenolic rich products (mainly from lignin) using various solvent mixtures as liquefying agents under microwave irradiation. The process is simple, highly efficient, and uses minimal petroleum-based chemicals. The effect of different organic solvents on the liquefaction reaction was tested. It was found that lower molecular weight alcohols show higher activity for the degradation of biomass due to their nucleophilic groups. It was also demonstrated that the phenolic compounds form a second phase *via* the addition of water in liquefied products, which can be easily separated from the aqueous phase. After the removal of the phenolics from the aqueous solution, a high concentration of polyhydroxy compounds (including glycerol and sugar derivatives) were obtained. The total content of phenolics and polyhydroxy compounds in phenolic products and biopolyols was 65.9 and 84.9%, respectively. The solubility of the fractionated products was also tested. Both of the products have good solubility in conventional organic solvents, indicating these products have a potential ability to react with other reagents.

With an appropriate choice of reagents that absorb microwave radiation, rapid heating throughout the entire reactor can be achieved, which can effectively promote the productivity of the scale-up facilities. On the other hand, liquefaction under microwave irradiation can produce high purity polyhydroxy compounds to provide high-value platform chemicals which can be widely used in the polyurethane industry, which improves the economic viability of the whole process. This process is very stable and provides a potential approach for the preparation of high-quality chemical feedstocks from liquefied products.

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