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# Efficient Utilization and Conversion of Whole Components in Waste Biomass with One-Pot-Oriented Liquefaction

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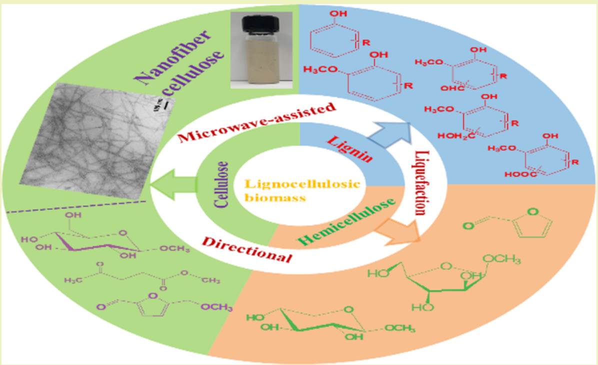
*Supporting Information*



**ABSTRACT:** A simple oriented liquefaction with microwave assistance was introduced to produce phenolic compounds and cellulose nanofibers from the comprehensive utilization of biomass. Effects of process parameters on the yield and composition of liquefied straw products were investigated. Liquefied products was separated into liquid and solid products. The highest phenolics content (72.87%) in liquid products was achieved; the yield of nanofibers from liquefied solid products was 47.43 wt %. With stepwise extraction, phenolics with nice reactivity were largely separated into three fractions. They were mainly composed of phenolic compounds and aromatic derivatives and had good solubility in organic solvents. After a chemical-purified treatment, solid products containing highly crystalline cellulose were converted into nanofibers with good application. These simple processes achieve a comprehensive use of liquefied products to various synthetical directions based on different molecular structures and chemical solubility. Directional liquefaction was significantly effective to produce renewable phenolics and nanofibers and realizes the integrated valorization of whole components in waste biomass.

**KEYWORDS:** *Cellulose nanofibers, Microwave-assisted liquefaction, Phenolic compounds*

## INTRODUCTION

Renewable biomass has attracted widespread attention due to the generation of greenhouse emissions and great focus on environmental protection.[1,2] Biomass wastes, such as agricultural wastes, paper-making residues, forestry wastes, and furniture residues are not fully utilized.[3−5] The three main components in biomass materials are lignin (15%−35%), hemicellulose (20%−30%), and cellulose (40%−50%).[6] The hemicellulose and cellulose consist of C5 and C6 sugar units, and the utilization methods of hemicellulose and cellulose in biomass for producing chemicals and fuels are relatively mature.[7] However, lignin is a complex natural aromatic polymer with a 3D mesh amorphous structure, which consists of methoxylated phenyl-propanoid units. Lignin with recalcitrant biological characteristics, complex structure, and stable thermal properties is relatively intractable and waste in the recent utilization and refining process of biomass.[8−10] Only about 5% of lignin materials were used in relatively low-value commercial exploitation, such as the preparation of lignosulfonate, alkali lignin and kraft lignin, industrial additives, and liquid fuel applications.[11,12] Many different types of feedstocks and fine chemicals, particularly aromatic compounds and hydrocarbon fuels, could be converted from biobased lignin.[13,14] Therefore, many previous efforts have been made to take the place of petroleum-based phenolic compounds in phenolic resin foam with cheap phenolic compounds derived from biomass material.[15] Therefore, an appropriate thermochemical technology for utilizing lignin is needed. It is important to realize the comprehensive utilization and valorization of whole biomass components (cellulose, hemicellulose, and lignin).[16,17]

As an important thermochemical conversion, liquefied biomass under mild conditions can prepare multiple liquid fuels and fine chemicals.[18] The liquefaction processes with alcohols, water, phenols, or apolar−aprotic solvents could lead to the high conversion of biomass materials and yield of target products (70%−85%) with various features (high moisture and oxygen content) that need to be improved.[19,20] As the

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recalcitrant structure of crystalline cellulose, the strong chemical links between lignin and hemicellulose, and the complexity of linking among cellulose, hemicellulose, and lignin, the liquefied products consist of some unstable and unpredictable mixtures with complex structures. Therefore, the liquefaction of biomass to produce high-grade chemicals or good-quality fuels is still a challenging process.[21] Highly crystalline microfibers or nanofibrils celluloses in biomass were the most difficult part for converting into useful chemicals, and most were lost as liquefied residue. With the increasing demand for comprehensive utilization of biomass components, producing cellulose materials or nanofibers from biomass has attracted more and more research in recent years.[22,23] Because of its highly crystalline nature with outstanding thermal stability and strong mechanical performance, nanofiber cellulose as renewable and sustainable feedstocks was widely used for producing future biobased high-performance materials (such as nanostructured biochemicals and biocomposites) with environmentally friendly characteristics.[24−26] The cellulose nanofibers can be produced from traditional raw materials (such as wood, straw, and bamboo) with pretreatment processes and nanofibrillation technologies.[27,28] However, the lignin and hemicellulose in these studies have been removed as waste residues during the preparation process of cellulose nanofibers from biomass. Therefore, an obvious challenge in integrated utilization and conversion technology is the transformation of waste biomass into high-grade fines and chemicals, in particular, to make full use of all of the whole components.

In this study, a simple process involving directional liquefaction of biomass with microwave energy for preparing renewable platform products (glycosides and phenolics) and important materials (cellulose nanofibers) with a one-pot process were investigated in detail. The process suggested that high-purity phenolic compounds from lignin could be extracted from liquefied liquid products with a stepwise process. The cellulose nanofibers were prepared from the liquefied solid product. This one-pot-oriented liquefaction achieves an overall valorization of liquefied liquid and solid products to various directions and applications on the basis of their molecular structures, chemical solubilities, and properties. We determined the most effective liquefaction and chemical treatment parameters on the production of phenolic compounds and cellulose nanofibers. This one-pot directional conversion of waste biomass to high-grade materials and chemicals has great application prospects for integrated utilization of the whole components in waste biomass.

## ■ EXPERIMENTAL SECTION

**Materials and Chemicals.** In this investigation, straw biomass was gathered from a local farm (Shandong, China). The straw particles were 200−300 $\mu$m sieve in size and dried overnight at 110 °C. The dried straw materials were kept in sealed bags before they were used in liquefaction. Other chemicals and feedstocks in our study were analytical grade. The chemical compositions and elemental components of the straw materials are shown in Table S1.

**Analysis Methods.** The compositions and contents of the liquefied liquid products were carried out on a GC-MS (Agilent 7890A-5975C). The GC-MS was equipped with a HP-5 fused capillary column with polydimethylsiloxane with 5% phenyl methyl substitution as a stationary phase. The components in the liquefied products were confirmed and identified by using the pre-established criteria for data analysis and total ion chromatograms and fragmentation pattern. The carrier gas He through the column was at a flow rate of 1.5 mL min$^{-1}$.

The yields of glycosidic byproducts (furfurals and levulinates) were analysis by GC (Shimadzu 2010) equipped with a flame ionization detector. The analysis of glycosides was done on a HPLC instrument (Shimadzu LC-10ATVP) with a column Aminex HPX-87H and RID-20A detector.

The crystallinity analysis of raw straw, liquefied residues, and cellulose fibers were presented with an X'TRA instrument. The XRD instrument is equipped with monochromatic Cu K$\alpha$ radiation.

SEM (NeoScope JCM-5000) was applied to identify the morphology of the straw, liquefied residue, and cellulose fibers to analyze the surface structure of the samples after the reaction and chemical-purified treatment.

The concentrations of nanofiber suspensions from this investigation were diluted from 0.2 to 0.02 wt %. The morphologies of the cellulose microfibers and nanofibers were observed with TEM (JEOL 100CX, MA, USA, 80 kV accelerating voltage). The diameters and size distributions of the nanofibers were calculated by using an image analysis system.

**Oriented Microwave-Assisted Liquefaction.** Directional liquefaction of biomass samples were investigated in Milestone (Shelton, ASM-400 magnetic stirrer, 100 mL sealed Teflon maximum 10 vessels) microwave laboratory equipment. The reactant mixtures in the microwave laboratory system included raw particles, solvent, and catalyst. The reactant mixtures were converted into 100 mL sealed Teflon vessels and heated at a set temperature within designated power, kept for a certain reaction time. Reaction temperature was controlled by an internal temperature probe in sealed Teflon vessels with a fiber optic sensor. After the reaction, the sealed vessels were cooled and moved from the reaction cavity before opening. Then, the liquefied mixtures were vacuum filtered, and solid products from the liquefied mixtures remaining in the filter paper were washed several times and oven-dried at 105 °C for 12 h.

The liquefied solids were bleached and put in a dilute NaClO$_2$ solution (0.15 wt %). The bleaching process of the residue was to eliminate colored polymerizable substances retained in the liquefied residue as well as some oxygenated compounds derived from the holocellulose. Then, the bleached residue was reacted with a sodium hydroxide solution to remove the chemicals from the depolymerized lignin. After the bleached and alkali treatment, the liquefied residues were converted into chemical treatment products named chemical-purified microfibers. The chemical-purified microfibers were immersed in deionized water and put into an ultrasonic-dispersed treatment. The ultrasonic-dispersed process was conducted at 0 °C with an ice water bath throughout the whole treatment process. After the ultrasonic dispersion, the chemical-purified microfibers can be converted into cellulose nanofibers. The yields of cellulose fibers were calculated by the absolute-dried weight of cellulose fibers to the original materials.

Three phenolic compounds fractions were obtained from the liquefied liquid mixtures with an extraction and separation process (Figure S1). The phenolics fractions #1 and #2 were vacuum-dried at room temperature for 12 h, fraction #3 was separated from the organic solvent phase with an evaporated process at 40 °C with a vacuum to recycle the ethyl acetate.

Equation 1 was used to measure the mass conversion of biomass, and eq 2 was used to identify the yield of phenolics from biomass. Equation 3 was used to calculate the mass yield of glycosides (including methyl pentose glycoside and methyl hexose glycoside). Equation 4 was used to identify the mass yield of glycosidic derivatives (include methyl levulinate, furfural, methoxy-2-furanmethanol, 5-methoxymethyl furfural and furan) from biomass.

$$\text{Conversion of biomass (wt\%)} = \frac{m(\text{liquefaction product})}{m(\text{biomass})} \times 100\% \qquad (1)$$

$$\text{Phenolics yield (wt\%)} = \frac{m(\text{liquefaction product}) \times \text{mass yield phenolics (measured by GC)}}{m(\text{biomass})} \times 100\% \tag{2}$$

$$\text{Glycosides yield (wt\%)} = \frac{m(\text{liquefaction product}) \times \text{mass yield glycosides (measured by HPLC)}}{m(\text{bamboo})} \times 100\% \tag{3}$$

$$\text{Glycosidic derivatives yield (wt \%)} = \frac{m(\text{liquefaction product}) \times \text{mass yield glycosidic derivatives (measured by GC)}}{m(\text{bamboo})} \times 100\% \tag{4}$$

## RESULTS AND DISCUSSION

A one-pot-oriented liquefaction process was efficiently promoted with microwave power because of the microwave-assisted process utilizing the magnetic effect of electric current and converting the electromagnetic energy into heat energy at the molecular level of the biomass material. The use of a microwave system provided the advantage of a rapid heat rate throughout the volume of the reaction mixture with an appropriate choice of reagents, and an appropriate reagent also can effectively absorb microwave energy and cause a high acceleration of reaction. With designated conditions, liquefaction under microwave energy can prevent the sugar derivatives from further converting into levulinates and furfurals. The levulinates and furfurals were compatible with phenolics and can reduce the purity of the phenolics. Also, we used the continuous pipeline reactor in the scale-up experiment, and the liquefying agent can be recycled and used in the subsequent experiments, which also can improve the economic viability and ensure the safety of the whole process.

**Effect of Various Parameters on Liquefaction.** *Various Catalysts.* From Table 1, $H_2SO_4$ and $H_3PW_{12}O_{40}$ were the most efficient catalysts with biomass conversions of 83.29 and 81.25 wt %, with phenolic compound yields of 47.29% and 45.86%, respectively. After the microwave-assisted liquefaction, most of the lignin in the straw was decomposed into phenolic compounds with $H_2SO_4$ or $H_3PW_{12}O_{40}$ catalysts under the designated conditions. This result suggests that $H_2SO_4$ and $H_3PW_{12}O_{40}$ could provide sufficient protons for the methanolysis of biomass during the directional liquefaction. This indicated that strong acid catalyst $H_3PW_{12}O_{40}$ contributed to the high liquefaction efficiency with enough acid sites. $H_3PW_{12}O_{40}$ was dissolved in the solvent to form a homogeneous catalytic system, which is also beneficial to converting biomass into target products. It is inevitable that there was a low content of byproducts produced from the further alcoholysis of glycosides in all of the selected catalyzed systems. The byproducts of the glycosides compounds were compatible with phenolics, which could reduce their purity. It is imperative to control the reaction conditions to prevent the glycoside compounds from degrading into furfurals or methyl levulinate and improve the yield of phenolic compounds.

**Table 1. Effect of Various Catalysts on Components of Microwave-Assisted Liquefaction**[a]

| Catalysts | Conv. (wt %) | Liquefied liquid products yield (%) Phenolics | Glycosides | Glycosidic derivatives |
|---|---|---|---|---|
| HCl | 27.29 | 16.31 | 10.42 | 5.78 |
| $HNO_3$ | 22.64 | 12.05 | 6.90 | 7.35 |
| $H_2SO_4$ | 83.29 | 47.29 | 28.75 | 14.51 |
| HCOOH | 7.44 | 6.11 | 4.29 | 0.59 |
| $H_4SiW_{12}O_{40}$ | 79.57 | 23.16 | 27.45 | 11.05 |
| $H_3PW_{12}O_{40}$ | 81.25 | 45.86 | 29.06 | 15.72 |
| $C_7H_7SO_3H$ | 72.89 | 20.16 | 25.44 | 12.76 |
| HZSM-5 | 21.40 | 6.24 | 11.90 | 5.18 |
| Amberlyst 70 | 70.43 | 13.21 | 14.69 | 9.42 |
| $Al_2(SO_4)_3$ | 75.31 | 35.47 | 23.22 | 17.68 |

[a] Reaction conditions: straw, 2 g; methanol, 16 g; acid catalyst, 0.4 g; temperature, 160 °C; 10 min; 800 W.

HCl, HCOOH, and HZSM-5 performed poorer in the yields of phenolic compounds during liquefaction. The results of $C_7H_7SO_3H$, $H_4SiW_{12}O_{40}$, $H_3PW_{12}O_{40}$, and Amberlyst 15 showed that they are also effective to transform most straw components into liquefied products (phenolics and glycosides) under subcritical methanol media with microwave irradiation. These acid catalysts could provide sufficient protons (H+) during one-pot directional microwave-assisted liquefaction with a methanol solvent. The selected metal salt $Al_2(SO_4)_3$ gave a relatively high conversion of biomass (75.31 wt %), with a 35.47% yield of phenolic products. The protons H+ could be probably generated from the methanolysis of the solvent methanol or the hydrolysis of crystalliferous water with a metal ion catalyst.[23] Molecular-sieve solid acid HZSM-5 resulted in a phenolic compound yield of 6.24% and a glycoside (includes methyl pentose and hexose glycoside) yield of 11.90%. Zeolite solid acid HZSM-5 showed lower utility and reactivity; this may because its small pores may be invalid in the methanolysis liquefaction of biomass.

These results demonstrate the fact that some Brønsted acidic sites were generated from catalysts in the reaction mixtures and are effectively responsible for the conversion of biomass with methanol media. $H_2SO_4$ and $H_3PW_{12}O_{40}$ can provide sufficient protons to participate in the microwave-assisted liquefaction. Also, sufficient protons may prevent the formation of dimethyl ether as we did not find dimethyl ether in the liquefied product. The remaining $H_3PW_{12}O_{40}$ was be separated and recycled in subsequent experiments, minimizing the subsequent degradation of the converted glycosides into byproducts. However, the remaining $H_2SO_4$ dissolved in the reaction product cannot be recycled and could only achieve neutralization of the liquefied mixture. At the same time, the strong acid catalyst could offer sufficient hydrogen ions for disrupting the 4-O-5, $\beta$-O-4, $\alpha$-O-4, 5-5, and $\beta$-5 bonds (all the dominant links between the basic phenolic unit of lignin).[29] The highly reactive protons in the catalyst were also able to break the $\beta$-1,4-glycosidic bonds (the dominant interlinkages in single-sugar units of hemicellulose and cellulose). The nucleophile as a hydroxide radical in methanol can attack the C=C (as $\beta$-5, $\beta$-1, and 5-5 link) bonds in lignin. The electrons in the nucleophile moving to the oxonium ion also could break the C−O−C ($\beta$-O-4, $\alpha$-O-4, and 4-O-5 link) bonds; this process can form some neutral hydroxyl groups and good leaving groups. Therefore, using low concentrations of effective $H_3PW_{12}O_{40}$ is a promising process for preparing glycosides and phenolics from the directional liquefaction of biomass.

*Catalyst Loadings.* $H_3PW_{12}O_{40}$ was selected to research the influence of catalyst loadings on the conversion of biomass because it can promote higher phenolic yields and prevent the formation of byproducts. The highly reactive hydrogen protons

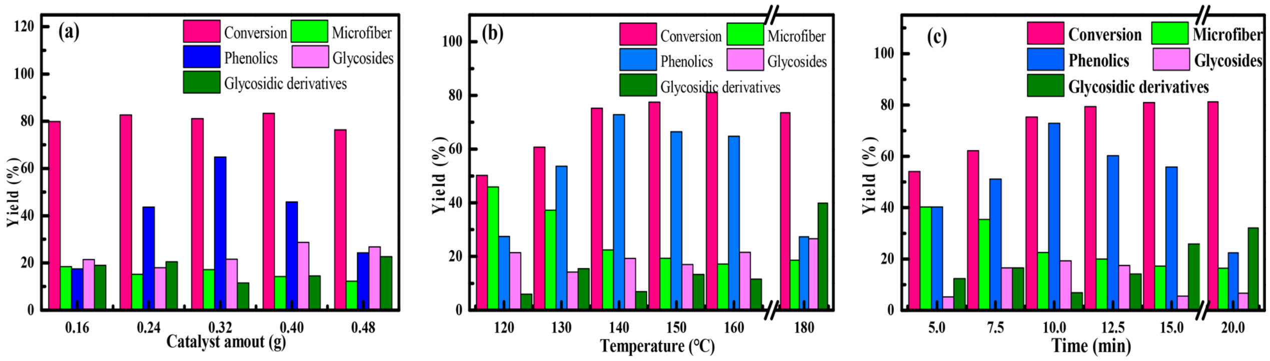

**Figure 1.** Effect of catalyst amounts (a), temperature (b), and time (c) on components of liquefaction.

in $H_3PW_{12}O_{40}$ could efficiently effect and activate the —O— atoms among the linkage bonds of holocellulose (glycosidic bonds link) and lignin (main $\beta$-O-4, $\alpha$-O-4, 5-5, and $\beta$-5 link). The catalyst loadings influenced the selective catalytic reaction by varying the density of H+ in the methanol solvent. With the amounts of catalyst increasing, the yield of phenolics and conversion of biomass initially increased significantly (Figure 1a). This was attributed to the increased concentrations of H+, which may stimulate the methanolysis of straw to a certain degree. The yield of phenolic compounds reached a maximum of 64.80% as the usage of acid was 0.32 g. The color of the residue was light brown.

A further increase in the catalyst loadings can slightly promote the conversion of straw; however, it had a negative effect on the yield of target compounds. The yields of side products (levulinates and furfurals) derived from the alcoholysis of glycosides significantly increased from 11.57% to 22.65% with excessive acid catalyst. These side products were compatible with small-molecule target products and could affect the purity and quality of phenolics. Moreover, the excessive acid catalyst may stimulate conversion of glycoside compounds into humins (the liquefied liquid mixtures became dark brown dark). The conversion decreased with the increased catalyst dosage from 0.40 to 0.48 g; this is likely because more side reactions, such as repolymerization of the liquefied products, took place with increased acid catalyst content. Also, the increased amount of catalyst might contribute to the secondary reactions of cellulose and hemicellulose and forming of black solids such as humins. The repolymerization products and humins were considered as residues, which may be responsible for the decrease in the biomass conversion. Furthermore, with the increase in the catalyst concentrations from 0.40 to 0.48 g, the color of the residue became black, which could increase the difficulty of the bleaching process of the residue for producing nanofibers. Therefore, to achieve controllable methanolysis and good conversion of biomass, an effective catalyst loading of $H_3PW_{12}O_{40}$ of 0.32 g was selected as an optimal amount of catalyst in 16 g of methanol.

*Reaction Temperature.* In general, the increase in temperature promotes the conversion of biomass and accelerates the speed of liquefaction. Temperature inside the reactor influenced desirable product yields. The proper temperature was the key to suppress most side reactions, which could improve the purity and quality of target products. Thus, the methanolysis of straw was investigated with the temperature ranging from 120 to 180 °C (Figure 1b). When the temperature was between 120 and 130 °C, conversion of straw was 50.20 and 60.72 wt %, respectively. Meanwhile, the liquefied products were phenolic compounds, methyl pentose glycoside and furfural, which were derived from lignin and hemicellulose, respectively. According to the contents in the straw (Table S1) and residue (Figure S2), some hemicellulose, lignin, and noncrystalline cellulose were not completely converted into desirable products. A portion of the hemicellulose and lignin were present on the surface of cellulose. At 140 °C, the yield of phenolic compounds reached a maximum of 72.87%, and the conversion of straw was 75.27 wt %. To our surprise, the conversion of straw significantly increased when further increasing the temperature to 160 °C; however, the yield of phenolic compounds slightly decreased. This can be explained because the higher temperature led to the polymerization of phenolic compounds as evidenced by the lignin content of the residue. The higher temperature was the key factor to an increased conversion of straw; however, it also promoted the secondary reactions of cellulose and hemicellulose. The main ingredient of glycosidic derivatives are methyl levulinate, furfural, and 5-methoxymethyl furfural at 160 and 180 °C. The conversion decreased when the reaction temperature was 180 °C or more; this is likely because more side reactions, such as repolymerization of the phenolic compounds that contain some active functional groups such as hydroxyl, carbonyl, and double bonds, took place with higher temperature and formed some high molecular weight byproducts.[30] The repolymerization products adhering to the surface of the liquefied solid product were considered as residues, which may be responsible for the decrease in the biomass conversion.

When the reaction temperature increased, the contents of hemicellulose and lignin in the straw decreased significantly; we could suppose that most hemicellulose and lignin were degraded prior to the degradation of the main cellulose. This is closely bound with the distribution and structure of the three components in the cell wall of the biomass. In the oriented liquefaction, with the help of an acid catalyst, the methanol could first react with hemicellulose and lignin to form C5 sugars and phenolic compounds. With the stripping of the lignin and hemicellulose, the cellulose was exposed in the reaction system with sufficient acid concentration and heat energy. With the methanolysis of noncrystalline cellulose, the content of C6 sugars in the liquefied liquid products was significantly increased (150 and 160 °C, Figure 1b). These glycoside compounds were converted into methyl levulinate, furfural, and 5-methoxymethyl furfural at a higher temperature (180 °C). However, highly crystallized microfibril cellulose is very difficult to convert into small molecular chemicals.[31] In

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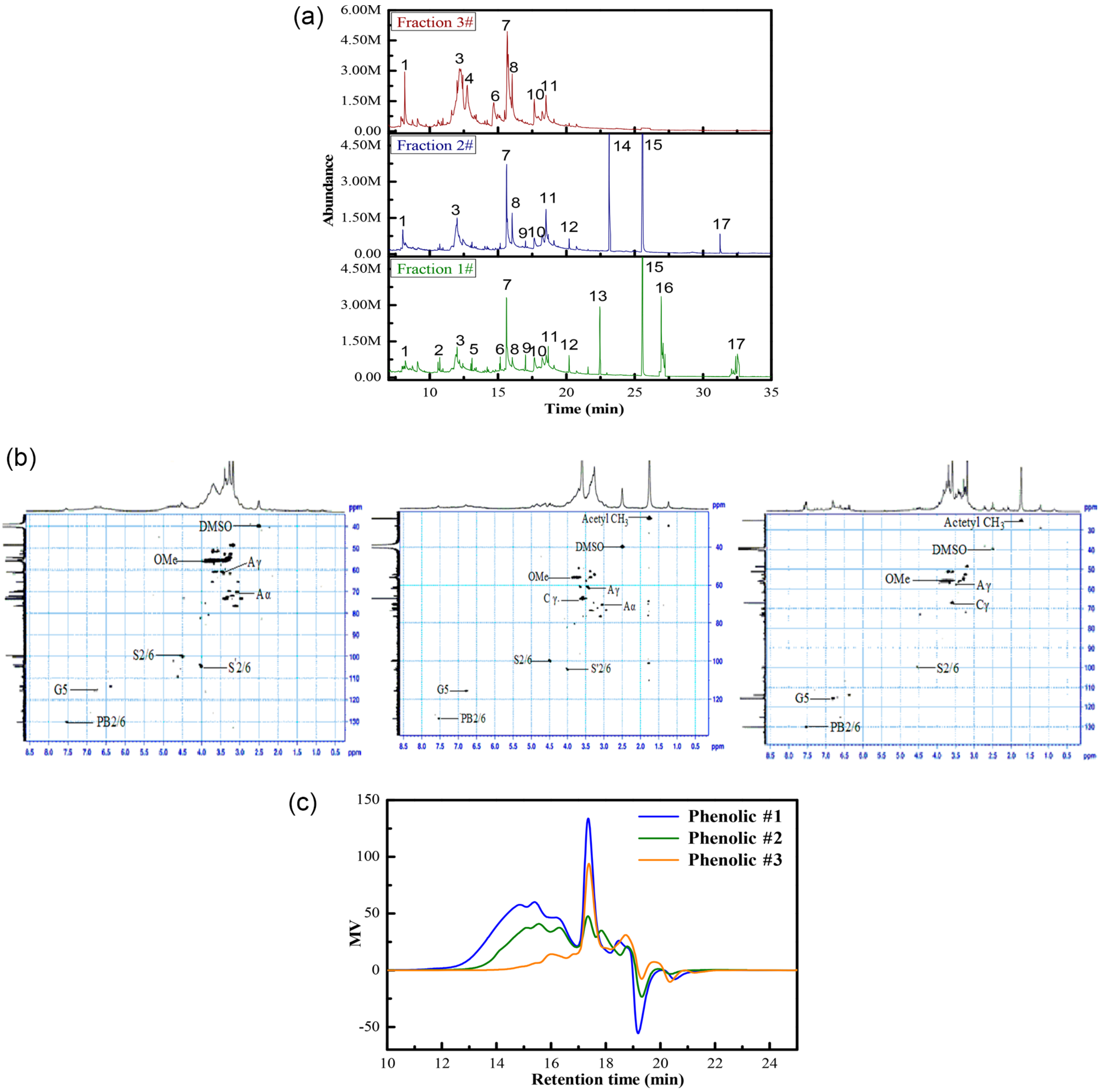

**Figure 2.** (a) GC-MS analysis of three fractions phenolics from straw. (b) HSQC NMR spectra for phenolic compounds in fractions #1, #2, and #3. (c) GPC analysis of three phenolic fractions (#1, #2, #3).

general, the appropriate reaction temperatures could accelerate the reaction rate while avoiding some adverse reactions and promote the upgrading procedure for producing high purity targets. The optimized results showed that a moderate temperature of 140 °C was necessary to allow for both high yield and purity of phenolic compounds.

*Reaction Time.* The influence of reaction time on the conversion of straw and the yields of liquefied products was studied in detail to confirm the optimal conditions for acquiring phenolics and cellulosic fibers. The yield and purity of phenolic compounds were also the reference for determining the optimum parameter. The reaction time was varied in increments of 2.5 or 5 min from 5 to 20 min with temperature of 140 °C. (Figure 1c). When the holding time extend 5 to 10 min, the conversion of straw increased from 54.03 to 75.27 wt %; meanwhile, the yield of phenolics grew from 40.28% to 72.78%. The highest yield of phenolic compounds was achieved in the first 10 min. The yields of phenolics decreased from 60.23% to 22.46% with the holding time extended from 12 to 20 min. The formation of glycosidic derivatives such as methyl levulinate and furfural were favored with longer residence times. At the same time, the yields of other side products such as levulinates and furfurals slightly increased with holding times extended longer than 10 min. As the holding time was extended from 10 to 20 min, the yields of glycosidic compounds grew from 6.89% to 32.11%.

As shown in Figure S3, after the one-pot liquefaction with microwave assistance, the content of lignin in the liquefied residue at 10 min was a lot less than that of 12.5 min. Therefore, we should select the optimal reaction time for producing high purity phenolic compounds. There are two side reactions that can influence the purity of phenolic compounds.

First, the polycondensation or self-polymerization of the activate chemical that produced some chemicals may be compatible with phenolic compounds in liquefied products; as a result, the chemicals and phenolic compounds are mutually soluble. Second, the secondary alcoholysis of glycosides can produce levulinates and furfurals, as they are miscible and with similar physiochemical properties in some organic solvents; the levulinates and furfurals may precipitate in the phenolic products. Also, the influence of microwave instrument power on the liquefaction products was shown in Table S2. In general, a low temperature (140 °C) and a moderate reaction time (10 min), together with a low concentration of the $H_3PW_{12}O_{40}$ catalyst leads to a maximum yield of phenolic compounds (72.87%) and less of a yield of glycosidic derivatives (6.89%). Under these optimal conditions, the purity of phenolic compounds is relative high, and the color of the residue is light brown.

**Characterization of Three Phenolic Compounds Fractions.** *GC-MS Analysis.* The straw was transferred into small molecular weight chemicals from the one-pot liquefaction with microwave assistance. Three fractions of phenolic compounds were isolated from liquefied products using a stepwise separation and fractionation process. Mostly, chief constituents of phenolic compounds from lignin in straw under microwave irradiation are shown in Figure 2a and correspond to Table S3. Various kinds of aromatic derivatives were checked in the phenolic fraction products, such as 4-hydroxy-3-methoxy phenyl acetate and 3,5-dimethoxy-4-methylphenol. This result indicated that the high molecular and polymerized lignin in the biomass was mostly converted into low-molecular phenolics under microwave energy. The composition of the lignin basis structure in the biomass mainly included breaking of the main connections including 4-O-5, $\beta$-O-4, $\alpha$-O-4, 5-5, and $\beta$-5 links and the dibenzodioxin unit of lignin.[32]

The components and distributions of the three phenolic fractions were apparently different with GC-MS results. In detail, the main components of phenolic compounds fraction #1 consisted of relatively high molecular weight compounds with some complex chemical groups and structures, such as 3-methoxy-4-hydroxy benzaldehyde (No. 7, 9.21%), 1-(4-methoxy-3-hydroxy-phenyl) ethanone (No. 13, 12.06%), 4-(1,2,3-trimethoxy propyl)-1,2-dimethoxy benzene (No. 15, 16.17%), methyl-3-(3-methoxy-4-hydroxy-phenyl) acrylate (No. 16, 13.80%), and some phenolic dimer products. The main contents of phenolic compounds fraction #2 were 2,4-dimethoxy phenol (No. 3, 8.32%), 3-methoxy-4-hydroxy benzaldehyde (No. 7, 14.33%), 3-methoxy-4-hydroxybenzoic acid methyl ester (No. 8, 8.62%), 5-methoxy-2-hydroxy-benzoic acid (No. 14, 14.79%), 4-(1,2,3-trimethoxy propyl)-1,2-dimethoxy benzene (No. 15, 19.31%), and part of phenolic dimers. The phenolic compounds fraction #3 mainly consisted of some relatively lower weight aromatic derivatives, such as 2,4-dimethoxy phenol (No. 3, 16.43%), 4-propyl-2-methoxy phenol (No. 4, 8.68%), 3-methoxy-4-hydroxy benzaldehyde (No. 7, 18.48%), 3-methoxy-4-hydroxybenzoic acid methyl ester (No. 8, 11.46%), 3,5-dimethoxy-4-methylphenol (No. 11, 10.21%), and phenolics with simple chemical bonds and molecular structures. The three fractions of phenolic included monomer structures of phenolics with some groups, especially $-OCH_3$, $-OH$, $-C{=}O$, $-CH_3$, and other alkyls. The contents of total phenolics in the three phenolic compounds were 80.34%, 82.48%, and 86.24%, respectively. Therefore, this microwave-assisted methodology used in this study could increase the solubility of depolymerized lignin and enhance the chemical activity of phenolic compounds. The lignin degradation products in the liquefied liquid products were concentrated in all three phenolic fractions with high purity.

The 2D HSQC NMR of three phenolic fractions (#1, #2, and #3) are shown in Figure 2b. In the aromatic region ($\delta_C/\delta_H$ 95−140/5.00−8.00 ppm), the fractions of the three phenolic compounds are diverse, as the interaction of phenolic units and other functional groups derived from the directional liquefaction on the changed branched chain on the PB, G, S, and S′ aromatic rings. The correlation marks at $\delta_C/\delta_H$ 129.9−130.8 and 7.53−7.83 ppm are imputed to the $C_{2,6}/H_{2,6}$-relevant PB units. The prominent related signals shown at $\delta_C/\delta_H$ 116.6/6.60−6.83 and 114.5/6.42 ppm correspond to $C_6/H_6$ and $C_5/H_5$ in the G units. The cross-marks at $\delta_C/\delta_H$ 108.7/7.07 and 105.5−106.5/6.40−6.50 ppm are imputed to $C_{2,6}/H_{2,6}$-relevant S′ and S units. Correlated marks for phenolic #2 are much wider than in phenolic #1 and #3, in compliance with its higher-molecular weights and lower-molecular motion. The regions of the C−O aliphatic side chain ($\delta_C/\delta_H$ 55−87/3.25−6.50 ppm) also provide many important structural evidences about the internal links of the depolymerized lignin. Related marks for $-OCH_3$ ($\delta_C/\delta_H$ 53.3−57.6/3.56−4.02 ppm) and $\beta$-O-4′ links are of the fractions of three phenolic compounds. The $\beta$-O-4 and $\beta$-O-4′ aryl ether links are largely related to the remarkable $\beta$-aryl ether units in the natural lignin from waste biomass. These units have characteristic marks at $\delta_C/\delta_H$ 86.6/5.45 ppm for $C_\alpha/H_\alpha$ and $\delta_C/\delta_H$ 53.3/3.46 and 53.5/3.06 ppm for $C_\beta/H_\beta$. Also, the obvious signals at $\delta_C/\delta_H$ 59.5−59.7/3.40−3.63, 61.4/4.10, and 62.5/3.73 ppm are attributed to $C_\gamma/H_\gamma$. The cross-signals were clearly shown at the spectrum from phenolic fractions #1 and #2 (Figure 2b, #1-B and #2-B), related to characteristic marks from A, B, and C units, and these marks were not found at the fraction #3 spectra. Therefore, it can be speculated that the phenolic fraction #3 is smallest molecular weight phenolic with single benzene, which is consistent with the GC-MS results.

*FT-IR and GPC Analysis.* Figure S5 and Table S4 show an obvious comparison between and three fractions of phenolics. Compared with the FT-IR spectra of the straw material, alkali lignin, and phenolic compounds, the signals are at approximately 3300 $cm^{-1}$ on behalf of the stretching vibration of $-OH$ either. The peaks around 2930 or 2850 $cm^{-1}$ found in all spectra were attributed to the C−H between the symmetric stretching of $-CH_3$ in cellulose, hemicellulose, and lignin. The peaks at 1750 $cm^{-1}$ (attributed to the aldehydes or ketones groups) were weakened in the spectra of straw and lignin. However, these peaks were strong in three phenolic compounds and indicated that some aldehydes or ketone groups were linked to the phenolic group. The bands appearing at 1600 to 1500 $cm^{-1}$ were special C=C vibrations in the aromatic and benzene skeletons of the straw material, alkali lignin, or phenolic compounds, and these spectra of the three phenolic compounds were particularly obvious. This phenomenon indicated that the functional groups in lignin (such as aromatic and benzenes rings) were successfully concentrated in the phenolic compounds with the one-pot directional liquefaction and stepwise extraction process. The peaks at about 1250 $cm^{-1}$ represented the C−O vibration characteristic peaks in Ar−OH among the three fractions of phenolic compounds, which were stronger than in the lignin and straw. The bands appearing at 1050 $cm^{-1}$ represented the $-OCH_3$ skeleton vibration, which is a common group in the unit of lignin and degradation products of lignin (guaiacol). In general, this microwave-assisted liquefaction of straw can decompose highly polymerized phenolic substances of lignin into low-molecular compounds with phenolic hydroxyl, aromatic C═C, Ar−OH, $-OCH_3$, and $-CH_2$ functions.

GPC results of the three phenolic fractions are shown in Figure 2c and Table S5. The results demonstrate that highly polymerized lignin with high molecular weight was solvolytical and liberated from the straw cell walls as fragments with low molecular aromatic derivatives. The depolymerized lignin was further separated from liquefied products according to the molecular size of the products using a stepwise fractionation process. The molecular masses of three phenolic fractions were 802, 545, and 249 corresponding to fractions #1, #2, and 3#. This feature provides the chance for the valorization of lignin by extracting the phenolic compounds into three fractions based on molecular weight ranges. Furthermore, as shown in Figure S6, the fractions of the three phenolic compounds from one-pot directional liquefaction with microwave assistance presented different solubilities in methanol or acetone.

**Characterization of Cellulose Nanofibers.** *Extraction of Cellulose Nanofibers.* To prepare cellulose nanofibers from the microwave-assisted liquefied residues, the solid residues from liquefied conditions of 140 °C and 10 min were treated with both a chemical-purified and ultrasonic-dispersed process. The visual changes in these transformation processes are shown in Figure S7. To prevent the cellulose fibers from generating strong hydrogen bonding, the sample was kept in a water-swelled state throughout whole the treatment. The brown liquefied residue was transformed to white after the bleaching process. The concentration of sodium hydroxide solution and the energy power of the ultrasonic generator used in the chemical-purification and ultrasonic-dispersion process can influence the formation of cellulose fiber.

Table 2 shows the effect of sodium hydroxide concentration and the ultrasonic generator power on the yield of chemical-purified microfibers and ultrasonic-dispersed nanofibers. With the density of sodium hydroxide increased from 0.3 to 4.5 wt %, the yields of chemical-purified microfibers decreased. However, the yields of ultrasonic-dispersed nanofibers relatively increased. This is due to NaOH removing the depolymerized lignin and hydrolyzing the amorphous cellulose. With high density of NaOH, the depolymerized lignin was mostly eliminated, and more crystalline cellulosic fibers were exposed to the ultrasonic-dispersed solvents after the high density of sodium hydroxide treatment. Thus, it may be easily considered that with the density of NaOH increased, the yield of nanofibers increased. After the ultrasonic-dispersion process, there is a continuous increase in the yield of the nanofibers with the ultrasonic outpower increased from 500 to 900 W. With higher ultrasonic outpower, the highly crystalline fibrous structure could be easily split off and resulted in high yields of cellulose nanofibers. The cellulose nanofibers could be homogeneously dispersed in water after the ultrasonic outpower of 700 and 900 W. Moreover, the cellulose nanofibers were transformed into highly viscous suspensions and sufficiently dispersed at 900 W. An obvious improvement was observed in the degree of nanofibrillation in the cellulose nanofibers, and more surface area on the nanofibers cellulose was exposed with the increasing ultrasonic outpower. It is clear that the ultrasonic outpower had a significant impact on the yield of cellulose nanofibers. This could be attributed to the use of ultrasonic-dispersed treatment that can break the hydrogen bonds and disintegrate relatively large particle sizes of microfibers into nanofibers with small particle sizes.

**Table 2. Yield of Chemical-Purified Cellulose Microfiber and Ultrasonic-Dispersed Cellulose Nanofiber**[a]

| Liquefaction condition | Yield of chemical-purified microfibers (wt %) | Yield of ultrasonic-dispersed nanofibers (wt %) |
|---|---|---|
| 0.5 wt % NaOH, 700 W | 80.27 | 21.49 |
| 1.5 wt % NaOH, 700 W | 75.33 | 42.07 |
| 4.5 wt % NaOH, 700 W | 63.19 | 40.14 |
| 1.5 wt % NaOH, 500 W | 75.33 | 31.26 |
| 1.5 wt % NaOH, 900 W | 75.33 | 47.43 |

[a] Yields were on the basis of the weight of residues.

*Morphological Analysis.* The straw, conventional liquefied residues (electronic heating, 180 °C/200 °C, 20 min), directional liquefied residues (microwave energy, 140/160/180 °C, 10 min), and chemical-purified microfibers (140 °C, 10 min) were studied by using SEM, and the results are presented in Figure 3a. The straw showed intact structures and large fiber bundles with an organized structure. Few small fragments were attached on the surface of the straw material (Figure S8a). However, the morphological structures of the liquefied residues were significantly different. After conventional liquefaction, the surface of the residual fibers contained many small fragments, and the surface was irregular (Figure S8b and Figure 3a, 1). It was obviously discovered that original fiber bundles with irregular structures were the main components of the liquefied residue with milder conditions (Figure S8b). With a high liquefied temperature (200 °C), the liquefied product may undergo polymerization and produce some black residues (Figure 3a, 1).

Compared with straw, the main fragments on the surface of the material were removed after the one-pot directional liquefaction. The main components of the residue are bundles of fibers (Figure 3a, 2 and 3). As is well known, lignin filled in the spaces between the cellulose and hemicellulose. Therefore, we can conjecture that alcoholysis reactions occurred on the surface layer of straw materials, mainly on the amorphous hemicellulose and lignin area during the directional liquefaction. This result suggested that the residue was the microfibrils and fibers, and most of the hemicellulose and lignin have been degraded. It was evident that the oriented liquefied process with microwave assistance was efficacious in decrystallization of straw with dissolving or dissociating the stubborn ingredients. The liquefied residue contained much of the crystallized cellulose because it was very hard for the solvent to penetrate this highly crystalline cellulose framework. After the chemical-purified treatment, the cellulose fiber bundles are dispersed to individual individualized microsized fibers (Figure 3a, 4). These microfibers consisted of nanosize fibers with strong hydrogen bonding, and individual nanosize fiber bundles were found on the surface of cellulose microfibers.

Figure 3b shows the TEM image and diameter distributions of the cellulose nanosize fibers, which were obtained after a 40 min ultrasonic-dispersion treatment at 900 W. The cellulose nanosize fibers with a web-like network structure and a relative uniform width were acquired after the ultrasonic dispersion treatment. The TEM observation distribution of nanofibers showed that the supernatant solutions containing nanosize fibers were made up of abundant single fibrils and some

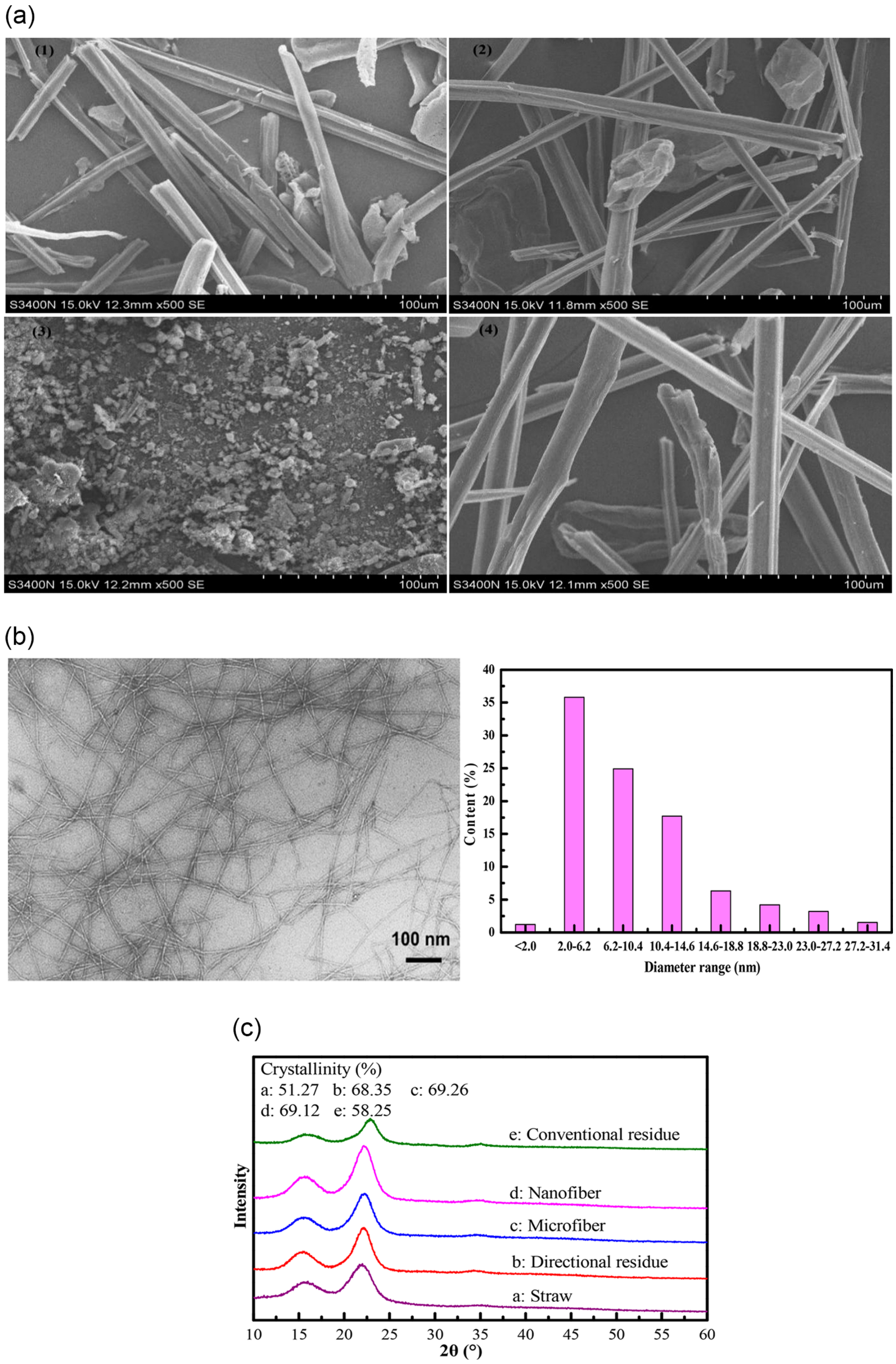

**Figure 3.** (a) SEM pictures of directional residue (140 °C, 1), directional residue (160 °C, 2), directional residue (180 °C, 3), and chemical-purified microfibers (4). (b) TEM image and diameter distributions of the nanosize fibers. (c) XRD analysis of straw, conventional residue, directional residue, microfibers, and cellulose nanofibers.

protofibrils. The TEM image also suggested that the length of most nanosize fibers was a few micrometers. About 62% of the nanofibers had a diameter ranging from 2.0 to 10.4 nm, and 24% of the nanofibers had a diameter within 10.4−18.8 nm. Also, only 9% of the nanofibers had diameters more than 18.8 nm. This ultrasonic way to distribute nanosize fibers from straw microfibers maybe due to the influence of acoustic cavitation of high frequency (20−25 kHz). These results certificated that the oriented force from the ultrasonic reactor was strong enough to vertically fracture the nanosize fibers

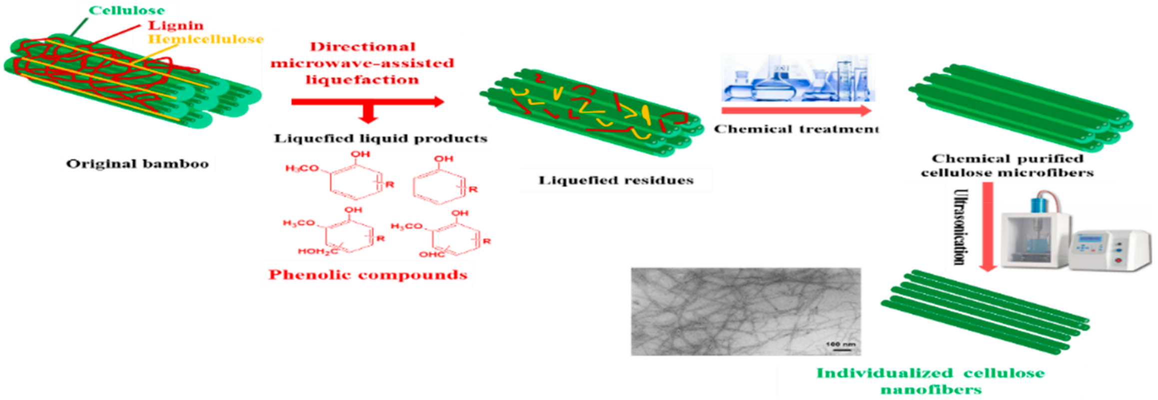

**Figure 4.** Formation process of phenolic compounds and cellulose nanofibers from biomass.

derived from one-pot directional liquefied residues. This was mainly attributed to the strength of ultrasonic dispersion treatment that could destroy the hydrogen bonds in the microsized fibers. The violent collapse promotes shock waves on the surface of the chemical-purified microfibers, which can cause erosion in the surface of the microsized fibers to split along the vertical direction. In general, the ultrasonic-dispersed process can gradually collapse the cellulose microsized fibers into nanosized fibers.

*Crystallinity Analysis.* To investigate the influence of crystallinity on cellulose decomposition, XRD analyses were concluded to study the crystalline behavior of the fibers in the straw material, conventional residue, directional residue, chemical-purified microfibers, and cellulose nanofibers. Three peaks exhibited sharp peaks at the $2\theta$ values at about 16°, 22°, and 35°, which on behalf of 101, 002, and 040, respectively, corresponded to the lattice spacing typical of pure cellulose. These indicated that the crystal structure of cellulose in the straw was not significantly transformed during the liquefaction and subsequent series of treatments. Also, the crystallinity of each material was calculated and is shown in Figure 3c.

A significant increase in crystallinity was observed from 51.27% in the original straw fibers to 68.35% in the directional residues. These results suggest that the oriented liquefaction with microwave assistance increased the relative crystallinity of the residue. This may be because the amount of cellulose in the amorphous section was more decreased than the cellulose in the crystalline section. This change of structure may cause the rearrangement of cellulose molecules and units. Compared with liquefied residues, a slight increase appeared in the crystallinity of chemical-purified treatments. There was no obvious differences of crystallinity observed between chemical-purified microfibers and ultrasonic-dispersed nanofibers. The crystallinity of both sized fibers was about 67%−70%, suggesting that the ultrasonic dispersion had little influence on the crystallinity of the cellulose structure. This is consistent with the FT-IR results of cellulose nanofibers and microfibers (Figure S9). In general, nanosize fibers with high crystallinity were more effective for producing the composite materials in achieving higher reinforcement.

**Transformation Mechanism.** The formation process of phenolic compounds and cellulose nanofibers produced from biomass (Figure 4) was speculated according to the above results. The mass balance of the entire liquefied and extracted process is shown in Table S6. The results demonstrated that all the selected materials were efficiently converted into liquefied liquid products (phenolics and glycosides) and liquefied solid products (cellulose nanofibers). Lignin filled in the spaces between biomass carbohydrates (hemicellulose and cellulose) and acted as a resin to hold the biomass matrix together. Therefore, the ether bonds and acetal bonds between the polysaccharide and lignin were cracking under methanol by microwave liquefaction. With the one-pot directional liquefaction process with microwave energy, the ether bonds between 4-O-5, $\beta$-O-4, cyclic phenyl coumarans, and resinols linked in $\beta$-ethers of lignin were cleaved to some small molecular single phenolics. The high crystallinity cellulose mainly stayed in the liquefied residue. The microwave-assisted liquefied residue had considerable accessibility after a series of chemical treatments, such as producing cellulose nanofibers. The bleaching chemical treatment process was suitable for completely removing the hemicellulose and lignin remaining on the surface of the liquefied residue. With the alkali-washing reaction, the chemical-purified microfibers displayed a relatively irregular morphology, which made it easier to accept external forces. Ultrasonication was used to interrupt the hydrogen bonds between the cellulose fiber bundles. With enough ultrasonic outpower, the highly crystalline fibrous structure could be easily split off and result in cellulose nanofibers. The cellulose nanofibers were transformed into highly viscous suspensions and sufficiently dispersed. This microwave-assisted liquefied process provided an important part in the directional degradation of biomass material in the entire process.

## CONCLUSION

Effective utilization of each fraction of biomass is especially critical for the development of cost-effective chemicals and biofuels. Directional microwave-assisted liquefaction can produce high purity phenolic compounds and cellulose nanofibers and was widely applied in the chemical industry to improve the economic feasibility of entire process. The original biomass can be converted into liquefied liquid products and solid products. The highest phenolic compound content in the liquefied liquid products reached 72.87% at 140 °C for 10 min, and the yield of cellulose nanofibers was 47.43 wt %. Three fractions of phenolic products with high grade and purity were achieved via stepwise separation after the directional liquefied biomass. Three fractions of phenolics had good solubility and reactivity in organic solvents. Highly crystallized cellulose bundles in straw were converted into cellulose nanofibers by directional liquefaction combined with chemical-purification and ultrasonic-dispersion treatment. The generated cellulose nanofibers were in the range of long nanofibrils, and their particle size distributions were nanolevel. This process provided a potential method for the producing high-quality chemicals from liquefied products and makes it possible to realize the valorization of all biomass components.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b05272.

> Chemical compositions of liquefied residues at different temperatures and different times; FT-IR and GPC analysis of three phenolic compound fractions (1#, 2#, 3#), straw, and lignin; images of procedures in the formation of cellulose nanofiber from straw microwave-assisted liquefied residue; FT-IR analysis of cellulose, conventional residue, directional residue, microfiber, and nanofiber. (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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