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## Highly Efficient Liquefaction of Woody Biomass in Hot-Compressed Alcohol–Water Co-solvents<sup>†</sup>

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Alcohol (methanol or ethanol) and water showed synergistic effects on biomass direct liquefaction, and the 50 wt % co-solvent of either methanol–water or ethanol–water was found to be the most effective solvent for the liquefaction of eastern white pine sawdust. The 50 wt % aqueous alcohol at 300 °C for 15 min produced a bio-oil yield at approximately 65 wt % and a biomass conversion of >95%. At a temperature higher than 300 °C, conversion of bio-oil to char was significant by repolymerization. The Fourier transform infrared spectroscopy (FTIR) and gas chromatography–mass spectrometry (GC–MS) analyses of the obtained bio-oils confirmed the presence of primarily phenolic compounds and their derivatives (such as benzenes), followed by aldehyde, long-chain (and cyclic) ketone and alcohol, ester, organic acid, and ether compounds. Gel permeation chromatography (GPC) results suggested that hot-compressed ethanol as the liquefaction solvent favored lignin degradation into monomeric phenols. The X-ray diffraction (XRD) patterns of sawdust before and after the liquefaction displayed that the cellulosic structure of the feedstock was completely converted into amorphous carbon at around 300 °C and into crystalline carbon at about 350 °C.

### Introduction

As a potential renewable alternative to petroleum for the world’s energy and chemical production, biomass has attracted increasing interest in recent decades. Woody biomass primarily consists of natural polymers of hemicellulose (20–30%), cellulose (40–50%), and lignin (20–30%).<sup>1</sup> Cellulose as the most abundant constituent of the plant cell wall is a highly crystalline homopolysaccharide of D-glucose, with a degree of polymerization of up to 10 000 or higher. Hemicelluloses are complex heterogeneous polysaccharides composed of D-glucose, D-galactose, D-mannose, D-xylose, L-arabinose, etc.<sup>2,3</sup> The cellulosic components can be depolymerized into monosaccharides by dilute acid hydrolysis and more economically by enzymatic hydrolysis. However, because of the high crystallinity of cellulose and the presence of lignin networks that shield the cellulose from enzymatic attack, hydrolysis of the cellulose and hemicellulose in woody biomass into monosaccharides has been a challenge for the production of second-generation ethanol from forest biomass resources. To hydrolyze cellulose into monosaccharides more efficiently, expensive pretreatment processes are needed to

make biomass accessible by breaking the lignin seal, removing hemicellulose, or disrupting the crystalline structure of cellulose.<sup>4,5</sup> The cellulose/hemicellulose-derived carbohydrates can be refined into various value-added products, such as alcohols, esters, and carboxylic acids, through the so-called “sugar platform” biorefineries.

The lignin component in woody biomass is mainly used for process heat by direct combustion. However, lignin can be a promising source for chemicals, such as phenols and aromatics. Lignin is a complex network polymer of three main lignin building blocks, i.e., *p*-hydroxy-phenyl-propanol, guaiacyl-propanol, and syringyl-propanol, linked mainly by two types of linkages: condensed linkages (e.g., 5-5 and  $\beta$ -1 linkages) and ether linkages (e.g.,  $\beta$ -O-4 and  $\alpha$ -O-4), with the ether linkages being the dominant linkages between the three main lignin building blocks. The phenyl propane units in lignin may be depolymerized into phenolic chemicals by pyrolysis or direct liquefaction. Liquefied woody biomass

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can be used for preparing biofuels,<sup>6</sup> phenolic resins and adhesive,<sup>7–12</sup> polyurethane foams,<sup>13,14</sup> and carbon fiber.<sup>15</sup>

Wood and other lignocellulosic materials can be easily liquefied at a low temperature and atmospheric pressure<sup>16,17</sup> in the presence of phenol with catalysts, such as acids (sulfuric, hydrochloric, phosphoric, and oxalic acids)<sup>12,18–22</sup> and alkali and metal salts [NaOH, Cu(OH)<sub>2</sub>, NaHCO<sub>3</sub>, NH<sub>4</sub>Cl, AlCl<sub>3</sub>, CuSO<sub>4</sub>, FeSO<sub>4</sub>, and NaH<sub>2</sub>PO<sub>4</sub>].<sup>22–24</sup> A strong acid, such as concentrated sulfuric acid, has been used widely as an effective catalyst in the phenolysis liquefaction of woody biomass, and the resulting liquefied products could be used as matrix resins with satisfactory mechanical properties. However, disadvantages of the processes using strong acids include partial carbonization of biomass during liquefaction and corrosion of the equipment. Thus, weaker acids, such as hydrochloric and phosphoric acids, may be more advantageous catalysts for the low-temperature biomass liquefaction by phenolysis. Zhang et al. compared the efficiency of four acid catalysts, hydrochloric acid (37 wt %), sulfuric acid (36 wt %), phosphoric acid (85 wt %), and oxalic acid (99.5 wt %), on the liquefaction of Chinese fir and poplar in the presence of phenol. The results showed that phosphoric acid (85 wt %) and sulfuric acid (36 wt %) were more active catalysts, leading to solid residues as low as 3.2 and 4.0 wt %, respectively, at 150 °C.<sup>22</sup> Maldas and Shiraishi reported the effects of various alkalis and salts on the liquefaction of a birch wood meal in phenol and found that, in comparison to acidic catalysts, alkalis or alkaline salts could produce a lower yield of solid

residues, a lower ratio of combined phenol, and hence, a higher ratio of uncombined phenol.<sup>23</sup>

However, the use of phenol as the liquefaction solvent could yield some problems, such as a high cost of the solvent and recycling of phenol from the liquefied products, as well as some environmental concerns. As a result, other organic solvents, such as alcohols and cyclic carbonates, were tested for low-temperature liquefaction of biomass.<sup>25–27</sup> These solvents could be recycled by evaporation after liquefaction and are much cheaper than phenol. On the other hand, there is growing interest in producing phenol–formaldehyde resole resins and wood adhesives from renewable substances for the engineered wood industry, motivated by the fast climbing phenol price, the depleting fossil fuel resources, and the vast availability of lignin-containing renewable feedstocks. In the past several years, considerable effort was made to replace the petroleum-based phenol partially with lignins, tannins, and liquefied biomass.<sup>22,28,29</sup> In the synthesis of a phenol–formaldehyde resin with an alkaline catalyst, phenols are deprotonated to form phenoxide ions and the electron-rich *ortho* and *para* positions in phenoxide ions are more susceptible to electrophilic aromatic substitution by the hydrated form of formaldehyde (often referred to as an addition reaction).<sup>30</sup> Lignin, tannins, and the liquid products from the above-mentioned low-temperature solvolytic processes using phenol or alcohols are however less effective than phenol in the synthesis of phenolic resins because of their shortage of monophenolic compounds with unoccupied *ortho* and *para* positions.<sup>31</sup> Another explanation might be that the liquid products from the low-temperature solvolytic processes are rich in large molecules of oligomers derived from lignin and cellulosic components, less reactive in the synthesis of phenolic resins. In this regard, liquefaction of lignocellulosic materials for the production of phenol derivatives is preferable at a higher temperature.

Numerous studies have been reported on the liquefaction of biomass at a relatively higher temperatures and under high pressure. Appell et al. reported that a woody biomass could be converted into 40–50% liquid products in the presence of CO with aqueous sodium carbonate as a catalyst under 28 MPa and 350–400 °C.<sup>32</sup> Ogi et al. proved that woody biomass could be converted into bio-oil in a water medium with sodium carbonate as the catalyst under 10 MPa and 300 °C but not in a reductive atmosphere of H<sub>2</sub> or CO.<sup>33</sup> More recently, there has been a surge of interest in using

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hot-compressed and sub-/supercritical fluids for biomass liquefaction. Supercritical fluids have found applications for the chemical conversion of lignocellulosic materials due to their unique properties; e.g., they possess unique transport properties (gas-like diffusivity and liquid-like density), and supercritical fluids also have the ability to dissolve materials not normally soluble in either the liquid or gaseous phase of the solvent and, hence, promote the gasification/liquefaction reactions. Hot-compressed or subcritical water has been used by many researchers for biomass liquefaction,<sup>34–37</sup> while the liquefaction using water solvent normally produced a relatively lower yield of water-insoluble oily products than that using sub-/supercritical alcohols or acetone.<sup>38–42</sup> Another advantage of using alcohols as the solvent for biomass liquefaction is that these alcohols were expected to readily dissolve relatively high-molecular-weight products derived from cellulose, hemicellulose, and lignin because of their lower dielectric constants when compared to that of water.<sup>41</sup> Biomass solvolytic liquefaction was found to be greatly affected by the solvent type.<sup>42</sup> Lignin in woody biomass could be effectively extracted using a co-solvent of ethanol–water at 190 °C (i.e., the organosolv delignification process).<sup>43,44</sup>

Inspired by the above research work on organosolv delignification of biomass, liquefaction of woody biomass in the alcohol–water mixture at a higher temperature will be of interest for the production of bio-oil and phenolic feedstock for the synthesis of bio-based phenolic resins.<sup>44</sup> In the present study, hot-compressed methanol, ethanol, and water and their co-solvents were tested for direct liquefaction of white pine sawdust at 200–350 °C. Effects of the co-solvent with a composition of methanol or ethanol ranging from 0 to 100 wt % and effects of the solvent/biomass ratio (ranging from 5 to 20, w/w) were examined for a fixed reaction time. It was demonstrated that depolymerization/liquefaction reactions of lignin in ethanol or methanol solvent at 290 °C were fast, reaching the maximum conversion within 10–15 min.<sup>38</sup> Thereby, the effect of the reaction time was not investigated and was fixed at 15 min for all of the tests in this work.

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Table 1. Analyses of the Pine Sawdust Used in the Tests

| Proximate Analysis (wt %, db <sup>a</sup> )    |  |       |
|--|--|-------|
| VM <sup>b</sup>                                |  | 84.5  |
| FC <sup>b</sup>                                |  | 15.1  |
| ash  |  | 0.4   |
| Ultimate Analysis (wt %, daf <sup>c</sup> )    |  |       |
| C  |  | 52.5  |
| H  |  | 6.32  |
| N  |  | 0.10  |
| S  |  | <0.05 |
| O <sup>d</sup>                                 |  | 40.6  |
| Structural Composition (wt %, db) <sup>e</sup> |  |       |
| total lignin                                   |  | 28.4  |
| cellulose                                      |  | 40.2  |
| hemicellulose                                  |  | 21.9  |

<sup>a</sup> On a dry basis. <sup>b</sup> Determined by thermogravimetric analysis (TGA) in N<sub>2</sub> at 10 °C/min to 900 °C. <sup>c</sup> On a dry and ash-free basis. <sup>d</sup> By difference. <sup>e</sup> The samples were extracted with acetone for the extractive-free test specimens. Cellulose and hemicellulose were determined according to TAPPI test method T249 cm-85, and the acid-soluble and acid-insoluble lignin were determined according to the TAPPI test method T222 om-88.

## Experimental Section

**Materials.** The biomass used in this study was white pine sawdust sieved to particles less than ca. 20 mesh. The sawdust sample was dried in an oven at 105 °C for 24 h before use. The proximate and ultimate analysis results of the sample and its structural compositions are given in Table 1. The solvents used in the liquefaction tests were distilled water and ACS reagent-grade chemicals (ethanol, methanol, acetone, and ethyl acetate).

**Liquefaction Operation and Product Separation.** The liquefaction of pine sawdust was carried out in a 600 mL stainless-steel autoclave reactor equipped with a stirrer and a water-cooling coil. In a typical run, the reactor was charged with 10 g of pine sawdust and 100 g of mono-solvent (water, methanol, or ethanol) or methanol–water or ethanol–water co-solvent of various alcohol contents. The reactor was sealed, and the air inside the reactor was displaced by high-purity nitrogen. The reactor was subsequently pressurized to 2.0 MPa with nitrogen to prevent the reactive material from boiling in the course of the heating process. The reactor was ramped up to the desired temperature at 10 °C/min and soaked at the temperature for 15 min of reaction before cooling. Once the reactor was cooled to room temperature using the water-cooling coil, the gaseous product inside the reactor was collected into a pre-vacuummed fixed-volume (2800 mL) gas-collecting vessel. In each run, the pressure of the gas vessel was adjusted to 1 atm (abs) using high-purity nitrogen makeup gas and the gas inside the vessel was analyzed using a Micro-GC equipped with thermal conductivity detectors (TCDs). The formation (moles) of gas species (H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>–C<sub>3</sub>) was obtained. The liquid products and solid residue (SR) in the reactor were completely rinsed using acetone, and the resulting suspension was filtered under reduced pressure through a preweighed Whatman No. 5 filter paper. The SR products and filter paper were dried at 105 °C for 4 h before weighing. The acetone in the filtrate was then removed by rotary evaporation under reduced pressure at 40 °C. When co-solvent liquefaction was performed, this step removed the alcohol co-solvent in addition to acetone. The remaining liquid solution was extracted with ethyl acetate using a separatory funnel to separate bio-oil from water and aqueous soluble products. The ethyl-acetate-soluble phase was evaporated under a reduced pressure at 57 °C to remove ethyl acetate and recover liquid oily products, denoted as bio-oil. Yields of bio-oil, SR, and gas (gaseous products) were calculated by the weight percentage of the mass of each product to the mass of the dry pine sawdust loaded into the reactor for each run. The biomass conversion was simply calculated by 100 wt % – SR yield. With the

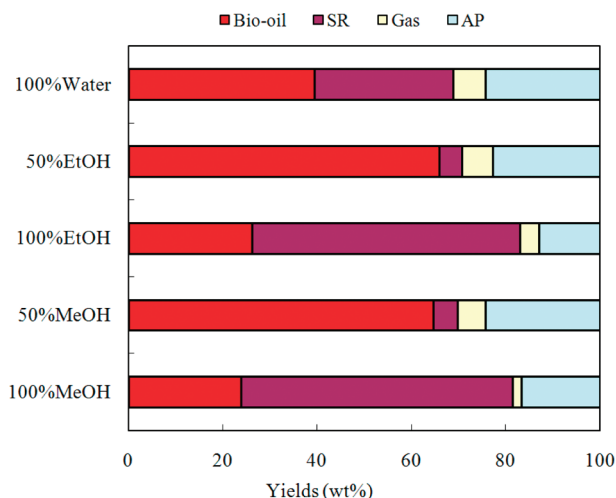


common challenge for the biomass liquefaction studies, quantification of aqueous soluble products (AP) is difficult due to the difficulty in separating the aqueous soluble products from water because of the high boiling point of water and the complexity of the aqueous soluble products (a mixture of carboxylic acids, carbohydrates, aldehydes, etc.). Our major interest of this research was the bio-oil products, therefore the aqueous soluble products were not analyzed. For simplicity, the yield of AP including the pyrolytic water from the biomass was calculated by difference. Two or three duplicate runs were conducted for all of the experimental conditions to minimize the experimental errors, within 5%.

**Characterization of the Liquid and Solid Products.** The function groups in bio-oils was analyzed using a IR2000 spectrometer (PerkinElmer, Waltham, MA). The main volatile compounds were identified by a gas chromatograph–mass spectrometer (GC–MS, Shimadzu QP2010S) with a SHRXI-5MS column (30 m × 0.25 mm × 0.25 μm) and a temperature program of 40 °C (hold for 2 min), 190 °C (12 °C/min), and 330 °C (8 °C/min, hold for 20 min). Admittedly, the GC–MS analysis for the bio-oil products has a limitation in that the less/nonvolatile compounds, such as oligomers of the lignin-degraded products, are not able to be detected because they are unable to pass through the GC column. The molecular weights and their distributions of the bio-oils were analyzed on a Waters Breeze gel permeation chromatograph (GPC) [1525 binary high-performance liquid chromatography (HPLC) pump; UV detector at 270 nm; Waters Styrag HR1 column at 40 °C] using tetrahydrofuran (THF) as the eluant at a flow rate of 1 mL/min, and polystyrene standards were used for calibration. In addition, the crystalline forms of pine sawdust before and after liquefaction at different temperatures were examined by X-ray diffraction (XRD) on a PANalytical X'Pert PRO X-ray diffractometer using Cu Kα radiation with a wavelength of 1.541 87 Å.

## Results and Discussion

**Effects of Solvent Types and Compositions.** Figure 1 shows the yields of bio-oil, SR, gas, and AP from the liquefaction at 300 °C in different solvents, while the solvent/biomass ratio was fixed at 10:1 (w/w). As shown in Figure 1, when a mono-solvent was used, hot-compressed water was more active than the other two alcohol solvents for the liquefaction of pine sawdust. Using water alone, the liquefaction produced 70 wt % biomass conversion and 40 wt % bio-oil yield compared to about 42–43 wt % biomass conversion and 23–26 wt % bio-oil yield from the operations using 100% ethanol or methanol. Ethanol appeared to be slightly more effective than methanol for the conversion of pine sawdust, producing a solid residue at approximately 12 wt %, lower than that of methanol (~23 wt %). Ethanol could reduce the surface tension of the liquefied products and, hence, improve the diffusion of solvent to the lignin matrix. Ethanol is also expected to readily dissolve relatively high-molecular-weight liquid products/intermediates derived from cellulose, hemicellulose, and lignin because of their lower dielectric constants when compared to that of water. A previous study by Miller et al.<sup>38</sup> and a recent study by the authors' research group<sup>45</sup> have proven the effectiveness of supercritical alcohol or hot-compressed water in depolymerization of pure lignin into biophenols (phenolic compounds). Hot-compressed water was demonstrated to be an effective solvent for biomass liquefaction by many previous studies on biomass hydrothermal liquefaction.<sup>34–37</sup> The high activity of a hot-compressed water for liquefying biomass may be ascribed to



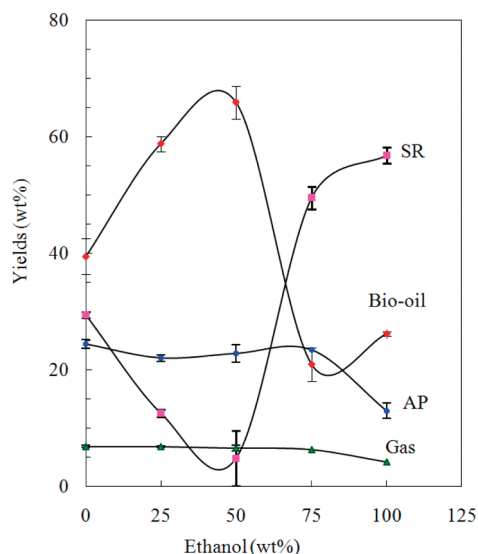
**Figure 1.** Yields of bio-oil, SR, gas, and AP from liquefaction of pine sawdust at 300 °C in different solvents.

its unique roles in the degradation of the polymer structures of the lignocellulosic biomass by hydrolysis reactions. The high activity of a hot-compressed water might also be related to many special properties of water in the hot-compressed or subcritical state; e.g., it has a lower dielectric constant, fewer and weaker hydrogen bonds, a higher isothermal compressibility, and an enhanced solubility for organic compounds than ambient liquid water.<sup>46</sup> Moreover, hot-compressed water has been found very effective for promoting ionic, polar non-ionic, and free-radical reactions,<sup>46</sup> which make it a promising reaction medium for biomass direct liquefaction.

As shown in Figure 1, the biomass conversion in 100% ethanol and 100% methanol at 300 °C is 43 and 42%, respectively, producing a bio-oil yield at approximately 26 and 23 wt %, respectively. The ethanol thus appears to be slightly more reactive than methanol in biomass liquefaction, although these differences are less remarkable. Previous studies, such as Miller et al.,<sup>38</sup> displayed that supercritical ethanol was more reactive than methanol in the degradation of lignin. The higher reactivity of ethanol than methanol might be owing to the slightly lower dielectric constant of ethanol (24.3) than that of methanol (33). As a result, ethanol in particular at its supercritical state may be expected to more readily dissolve and stabilize the relatively high-molecular-weight liquid products/intermediates derived from lignocellulosic biomass during the liquefaction process. Interestingly, as shown from Figure 1, the 50/50% (w/w) co-solvent of either methanol–water (i.e., 50 wt % methanol solution) or ethanol–water (i.e., 50 wt % ethanol solution) was a much more effective solvent than any constituent mono-solvent. The liquefaction in the 50 wt % methanol solution or the 50 wt % ethanol solution led to >95 wt % conversion of biomass and a bio-oil yield of as high as 65 wt % at 300 °C, higher than the arithmetic average of those from the liquefaction in mono-solvents of ethanol or methanol and water. These results thus suggest synergistic effects of alcohol and water on biomass liquefaction. The synergy of water and alcohol has also been provided previously in organosolv delignification of woody biomass at 190 °C, where 50% methanol–water solution or 50% ethanol–water solution was found to be very effective for wood

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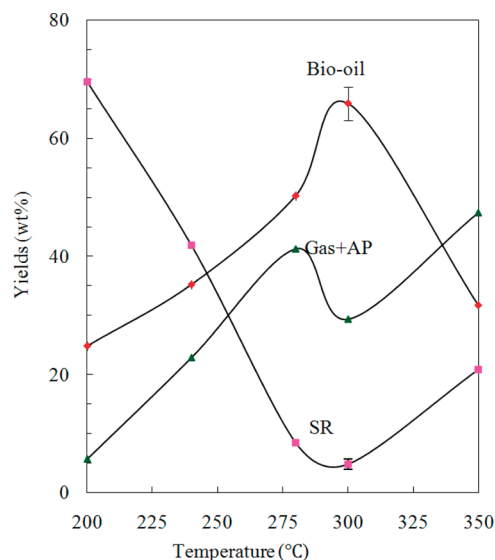


**Figure 2.** Yields of bio-oil, SR, gas, and AP from the liquefaction at 300 °C in a co-solvent of ethanol–water of varying ethanol content.

delignification.<sup>43,44</sup> Although a methanol–water co-solvent is as active as an ethanol–water co-solvent for bio-oil production and biomass conversion, the co-solvent of ethanol–water has attracted more interest, simply because ethanol is a renewable resource, which can be obtained readily by fermentation of sugars. Furthermore, methanol is a poisonous chemical in the synthesis of bio-based phenolic resins using bio-oil to substitute phenol.<sup>47</sup> Consequently, the co-solvent of ethanol–water was selected as the medium of interest in this study, and more tests were carried out on biomass direct liquefaction in the ethanol–water co-solvent.

To determine the optimal composition of the alcohol–water co-solvent for the direct liquefaction, the sawdust sample was liquefied with co-solvents of ethanol–water of different ethanol contents varying from 0 to 100 wt % at 300 °C for 15 min. The yields of bio-oil, SR, gas, and AP are shown in Figure 2. The yields of gaseous products (mainly CO<sub>2</sub> and CH<sub>4</sub>) in almost all runs were approximately 5 wt %; hence, the formation of gaseous products in the process was negligible. As already shown in the previous Figure 1, Figure 2 revealed that mono-solvent of either pure ethanol or pure water was less effective for biomass conversion or bio-oil yields compared to the ethanol–water co-solvent consisting of <50 wt % ethanol. The bio-oil yield and biomass conversion (referring to the SR yield) peaked with the 50 wt % ethanol solution, but interestingly, both the bio-oil yield and biomass conversion were greatly reduced as the ethanol content in the ethanol–water co-solvent increased to 75 wt %. The influence of the ethanol content in the co-solvent system on the yield of gas or AP was not significant, although generally the yields declined slightly as the ethanol content increased from 0 to 100 wt %, likely because of the suppression of the hydrolysis and gasification reactions.

The role of the constituent solvents in the co-solvent system for biomass direct liquefaction will be discussed. For the biomass solvolytic liquefaction process at an elevated temperature in a closed system, ionic and radical reactions, including nucleophilic, electrophilic, hydrolysis,



**Figure 3.** Yields of bio-oil, SR, and gas + AP from the liquefaction with the co-solvent of ethanol–water (50/50%, w/w) at various reaction temperatures.

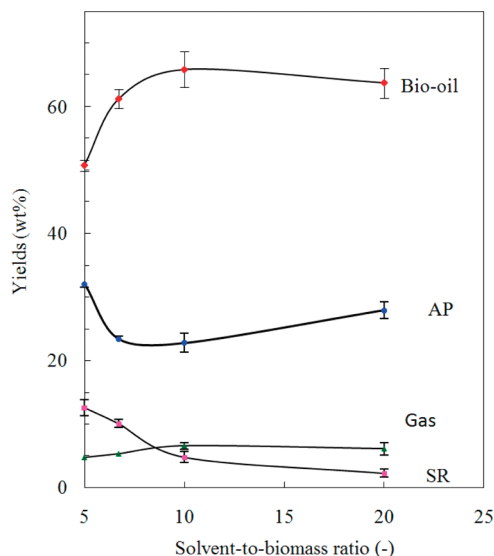
and thermal cracking/pyrolysis reactions, would occur.<sup>48,49</sup> In addition to the special properties<sup>46</sup> of the hot-compressed and subcritical water as described before, alcohols are slightly weaker acids than water. As a result, the lower activity of the 100 wt % ethanol for biomass liquefaction than that of 100% water may be predicted because of the limited hydrolysis reactions in the system with 100% ethanol. The addition of water as a co-solvent into ethanol would thus enhance the solvolytic liquefaction of biomass, as evidenced by the results shown in Figure 2, which was previously observed by Pasquini et al. in organosolv delignification of biomass using ethanol–water co-solvents.<sup>44</sup>

**Effects of the Reaction Temperature.** In this study, slightly higher temperatures from 200 to 350 °C were tested for biomass direct liquefaction for the production of bio-oils. As shown previously in Figures 1 and 2, the gas yields in the process were negligibly low (about 5 wt %), the formation of gaseous products and the aqueous soluble products were lumped into gas + AP. The effects of the reaction temperature (200–350 °C) on the yields of bio-oil, SR, and gas + AP from the liquefaction with the 50 wt % ethanol solution are shown in Figure 3. The results clearly displayed that the yields of bio-oil increased continuously from 25 to 66 wt % as the reaction temperature increased from 200 to 300 °C, while the solid residue decreased greatly from 70 wt % (at 200 °C) to 5 wt % (at 300 °C). However, the oil yield dropped markedly to below 35 wt % if the temperature was further increased to 350 °C, accompanied by significant increases in the yields of SR and gas + AP, suggesting conversion of bio-oil to char and gaseous/aqueous soluble products at a temperature higher than 300 °C. The reaction kinetics reveal chemical reactions are enhanced by elevating temperatures. The enhanced condensations or cracking reactions might transform the bio-oil products/intermediates into gas and coke/char (SR), as shown in Figure 3 (for the results at a

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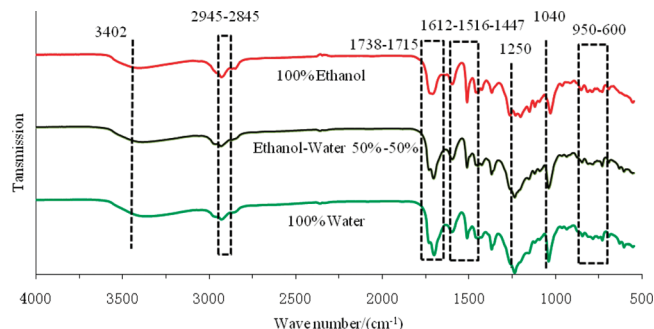
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**Figure 4.** Yields of bio-oil, SR, gas, and AP from the liquefaction with the co-solvent of ethanol–water (50/50%, w/w) at 300 °C at different solvent/biomass ratios.

temperature from 300 to 350 °C). The greatly reduced bio-oil at temperatures >300 °C may be explained by the formation of char through side reactions of the liquid bio-oil products and by the formation of hydrocarbon gases through cracking reactions of the bio-oil. Both types of reactions are thermodynamically favorable at high temperatures. Similar observations were reported previously in direct liquefaction of biomass in hot-compressed water<sup>50</sup> or ethanol.<sup>40</sup> We may thus conclude that 300 °C appeared to be the best temperature for direct liquefaction of pine sawdust to produce bio-oil using the hot-compressed co-solvent of ethanol–water (50/50%, w/w).

**Effects of the Solvent/Biomass Ratio.** Effects of the solvent/biomass ratio were investigated by conducting the liquefaction tests for 15 min at 300 °C using the co-solvent of ethanol–water (50/50%, w/w) at various initial solvent/biomass ratios ranging from 5 to 20. The results of liquefaction product yields are illustrated in Figure 4. The solvent/biomass ratio has been reported as an important factor to influence biomass liquefaction in hot-compressed or supercritical water,<sup>51,52</sup> where interestingly a decreased water/biomass ratio generally led to increased yields of heavy oil and char but a decreased yield of aqueous soluble products. For the operations with a smaller water/biomass ratio, a higher biomass concentration or a lower water concentration prevailed throughout the whole process, which might thus restrict the solvolysis/hydrolysis/hydration of the lignocellulosic solids, leading to a smaller yield of aqueous soluble products and a higher yield of solid residue or char. On the other hand, it is likely that a high biomass concentration or a low water concentration promoted the dehydration reactions of the aqueous intermediates/products, leading to an increased yield of heavy oil. The biomass liquefaction



**Figure 5.** FTIR spectrum of the bio-oil from liquefaction of pine sawdust with the hot-compressed co-solvent of ethanol–water (50/50%, w/w) at 300 °C (solvent/biomass ratio of 10, w/w).

operations in this study employing the co-solvent of ethanol–water, differ from previous work (using water) (see Figure 4). Figure 4 also displayed that an increased solvent/biomass ratio up to 10 (w/w) led to a higher bio-oil yield and a lower SR. The low bio-oil yield at a low solvent/biomass ratio was likely the result of solvent/biomass ratio of 5, biomass not forming a well-mixed suspension in the reactor due to the limited amount of solvent. This would result in unfavorable mass- and heat-transfer conditions inside the reactor, retarding the liquefaction and solvolysis reactions and, hence, reducing the bio-oil yield. Another possible reason could be the formation of char by condensation reactions of bio-oil intermediates/products at a low solvent/biomass ratio.<sup>42</sup> However, the yields of both bio-oil and SR leveled off at the solvent/biomass ratio of 10, suggesting that a solvent/biomass ratio greater than 10 (w/w) negatively affects the direct liquefaction process using the hot-compressed co-solvent of ethanol–water (50/50%, w/w), likely because of the markedly enhanced formation of AP (as shown in Figure 4).

**Characterizations of Liquefaction Products.** The Fourier transform infrared spectroscopy (FTIR) spectra for the bio-oils from the liquefaction using different solvents are illustrated in Figure 5. All bio-oils displayed similar IR adsorption profiles, suggesting similar chemical structures. All displayed the typical hydroxyl group absorption at 3402 cm<sup>-1</sup>, caused by the combination and overlap of aliphatic and aromatic O–H stretching from the phenolic compounds as well as from the moisture inevitably contained in the samples. The adsorption between 1715 and 1738 cm<sup>-1</sup> may be ascribed to the C=O stretching from ketone, aldehyde, and ester groups.<sup>53</sup> The presence of both O–H and C=O stretching vibrations may also indicate the presence of carboxylic acids and their derivatives. Absorption between 2845 and 2945 cm<sup>-1</sup> could be attributed to symmetrical and asymmetrical C–H stretching vibrations of methyl and methylene groups. The band at 1379 cm<sup>-1</sup> was attributed to C–H bending. The C–H stretching vibration and C–H bending indicate alkane groups in the bio-oil. Bands from 1447 to 1612 cm<sup>-1</sup> belonged to the aryl groups, and the adsorption band at 1612 cm<sup>-1</sup> was likely by benzene backbone vibration. The absorption peaks between 1000 and 1300 cm<sup>-1</sup> were attributed to the C–O stretching and O–H deformation vibrations, which described the presence of

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**Table 2.** GC–MS Analysis Results for the Bio-oils from the Liquefaction of Pine Sawdust in the Mono-solvent of Ethanol and Water and the Co-solvent of Ethanol–Water (50/50%, w/w) at 300 °C for 15 min with a Solvent/Biomass Ratio of 10:1 (w/w)

| peak number    | retention time (min) | relative composition by percent area |            |             | compound name   |
|----------------|----------------------|--------------------------------------|------------|-------------|---|
|                |                      | 100% ethanol                         | 100% water | 50% ethanol |   |
| 1              | 3.042                | 4.47                                 | a          | a           | ethyl 2-hydroxypropanoate   |
| 2              | 3.516                | 4.24                                 | a          | a           | 2-furanmethanol   |
| 3              | 4.016                | a                                    | a          | 2.38        | benzene, methyl-  |
| 4              | 4.208                | 2.89                                 | a          | a           | butanoic acid, 2-hydroxy-, ethyl ester  |
| 5              | 4.228                | a                                    | a          | 2.47        | 1-propanol, 2-ethoxy-   |
| 6              | 4.392                | 2.8                                  | a          | a           | ethanol, 2-(ethenylloxy)-   |
| 7              | 4.505                | 2.27                                 | a          | a           | benzene, (1-methylethyl)-   |
| 8              | 4.75                 | a                                    | a          | 13.02       | propanoic acid, 2-hydroxy-, ethyl ester   |
| 9              | 5.047                | a                                    | 15         | 2.21        | 2-furancarboxaldehyde   |
| 10             | 5.231                | 3.02                                 | a          | a           | oxiranemethanol   |
| 11             | 5.725                | 2.77                                 | a          | a           | piperazine  |
| 12             | 6.000                | 2.94                                 | a          | a           | 2-heptanamine, 5-methyl-  |
| 13             | 6.240                | a                                    | a          | 3.65        | 4-[(2-methoxyethoxy)methoxy]-1-cyclopentene   |
| 14             | 6.467                | a                                    | a          | 2.53        | propanoic acid, 2-hydroxy-, methyl ester  |
| 15             | 6.525                | a                                    | a          | 2.05        | benzene, (1-methylethyl)-   |
| 16             | 6.549                | a                                    | 5.77       | a           | 2,5-hexanedione   |
| 17             | 6.586                | 2.2                                  | a          | a           | acetamide, <i>n</i> -(1-methylpropyl)-  |
| 18             | 6.583                | a                                    | a          | 2.34        | 2,5-hexanedione   |
| 19             | 6.656                | 3.06                                 | a          | a           | butanoic anhydride  |
| 20             | 6.828                | 6.79                                 | a          | a           | phenol, 2-methoxy-  |
| 21             | 7.104                | a                                    | 10.74      | 3.26        | 2-furancarboxaldehyde, 5-methyl-  |
| 22             | 7.343                | a                                    | 4.05       | a           | phenol  |
| 23             | 8.209                | 4.79                                 | a          | a           | 1-hydroxy-2-methoxy-4-methylbenzene   |
| 24             | 8.033                | a                                    | 6.27       | 6.64        | 3-methyl-1,2-cyclopentanedione  |
| 25             | 8.191                | a                                    | 2.27       | a           | ethanone, 1-(5-methyl-2-furanyl)-   |
| 26             | 8.516                | a                                    | a          | 6.62        | pentanoic acid, 4-oxo-, ethyl ester   |
| 27             | 8.783                | a                                    | a          | 3.75        | 2-furanmethanol, tetrahydro-  |
| 28             | 8.872                | 3.64                                 | a          | a           | 4-nonanol, 4-methyl-  |
| 29             | 8.947                | a                                    | 17.62      | 9.00        | phenol, 2-methoxy-  |
| 30             | 9.290                | 6.5                                  | a          | a           | guaiacol, 4-ethyl-  |
| 31             | 9.458                | 5.57                                 | a          | a           | formamide, <i>n,n</i> -dimethyl-  |
| 32             | 9.713                | 2.62                                 | a          | a           | 2-methoxy-4-vinylphenol   |
| 34             | 9.842                | 2.92                                 | a          | a           | 2-amino-3-(2-amino-2-carboxy-ethylsulfanyl)-propionic acid  |
| 35             | 10.22                | 4.44                                 | a          | a           | phenol, 2-methoxy-4-(2-propenyl)-   |
| 36             | 10.32                | a                                    | 3.25       | 3.13        | 1-hydroxy-2-methoxy-4-methylbenzene   |
| 37             | 10.33                | 2.97                                 | a          | a           | guaiacol, 4-propyl-   |
| 38             | 10.72                | a                                    | a          | 3.71        | 2-furancarboxaldehyde, 5-(ethoxymethyl)-  |
| 39             | 11.25                | 21.01                                | a          | a           | phenol, 2-methoxy-4-(2-propenyl)-   |
| 40             | 11.39                | a                                    | 3.49       | 5.1         | guaiacol, 4-ethyl-  |
| 41             | 11.76                | a                                    | a          | 2.4         | 2-propyl-tetrahydro-pyran-3-ol  |
| 42             | 12.79                | a                                    | 5.46       | 4.6         | benzaldehyde, 4-hydroxy-3-methoxy-  |
| 43             | 13.18                | a                                    | a          | 2.02        | benzenemethanol, 4-hydroxy- $\alpha$ -[(methylamino)methyl]-  |
| 44             | 13.34                | a                                    | a          | 5.77        | phenol, 2-methoxy-4-(2-propenyl)-   |
| 45             | 13.74                | a                                    | 2.33       | a           | ethanone, 1-(4-hydroxy-3-methoxyphenyl)-  |
| 46             | 14.20                | a                                    | 2.82       | a           | 2-propanone, (4-hydroxy-3-methoxyphenyl)-   |
| 47             | 15.38                | a                                    | 3.18       | a           | 3-benzofuranmethanol, 2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-5-(3-hydroxy-1-propenyl)-7-methoxy-1-(4-isopropylphenyl)-2-methylpropyl acetate |
| 48             | 16.30                | a                                    | 2.55       | a           |   |
| total area (%) |                      | 91.91                                | 84.77      | 86.65       |   |

<sup>a</sup> Not including the small peaks with an area less than 2% of the total area.

primary, secondary, and tertiary alcohols, phenols, ethers, and esters.<sup>54,55</sup> The broad absorption peaks at 1250 cm<sup>−1</sup> were likely attributed to the methoxyl group. Meanwhile, the bands between 690 and 950 cm<sup>−1</sup> indicated the presence of single, polycyclic, and substituted aromatic groups.<sup>53</sup>

However, Figure 5 does show that the bio-oil from 100% ethanol has slightly stronger adsorption signals at 1516 cm<sup>−1</sup>, ascribable to the aromatic rings, than those from 50% aqueous ethanol and 100% water. This result may

further reveal that ethanol because of its lower dielectric constant may be an advantageous liquefaction solvent for the lignin component of the biomass as it can readily dissolve and stabilize the high-molecular-weight liquid products/intermediates derived from lignin. In contrast, there are slightly stronger absorption peaks of ketone, aldehyde, and ester groups between 1738 and 1715 cm<sup>−1</sup> and the primary OH at 1040 cm<sup>−1</sup> observed with the bio-oil derived from the 100% water liquefaction. This might suggest that water contributed more to the cellulose and hemicellulose degradation. Nevertheless, the biomass-derived liquid products are of an extremely complex mixture. Thus, to draw any conclusions based on the FTIR results alone may not be possible. Moreover, the aromatic structures might also derive from cellulose and hemicellulose through secondary

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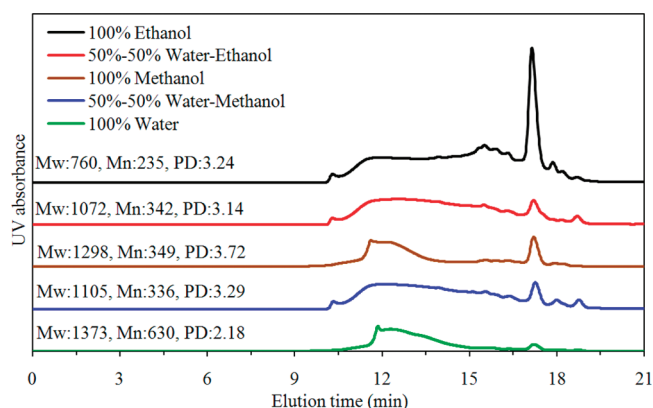


reactions of carbohydrates,<sup>56</sup> and the resulting aromatics could be aromatic structures with side chains of the alcohol, aldehyde, ketone, or alkyl group. Therefore, no marked differences could be observed by FTIR for the liquefied products using different solvents, as shown in Figure 5.

The presence of the phenolic/aromatic compounds, ketones, aldehydes, and carboxylic acids, as revealed by the IR analysis, could be confirmed by the GC–MS analytical results, as provided in Table 2.

Table 2 presents the volatile chemical compounds in the obtained bio-oils from the liquefaction of pine sawdust in the mono-solvent of ethanol and water and the co-solvent of ethanol–water (50/50%, w/w) at 300 °C for 15 min with the solvent/biomass ratio of 10:1 (w/w). The chemical compounds were identified using the WILEY8 library with additional analysis of the retention time and MS spectra of each compound. The relative percent area for each compound identified (defined by the percentage of the chromatographic area of the compound out of the total area) and the total percent area for all of the identified compounds are shown in the table. It should be noted that the percent area values that are presented here show only the relative concentration of each compound in the fraction of the bio-oil that can be vaporized and pass through the GC column. As shown in Table 2, the major compounds identified in the three bio-oil products were phenolic compounds and their derivatives (such as benzene aromatics), aldehyde, long-chain (and cyclic) ketone and alcohol, ester, carboxylic acid, and ether compounds. The lignin in softwood mainly consists of coniferyl alcohol and a small amount of *p*-coumaryl alcohol, which could decompose into guaiacyl- and hydroxyphenyl-type phenolic products in the liquefaction. As shown in Table 2, the detected phenolic compounds were mainly guaiacyl-type phenol derivatives, such as 4-ethyl-guaiacol, 2-methoxy-4-(2-propenyl)-phenol, 2-methoxy-phenol, and 2-methoxy-4-vinyl-phenol formed from the cleavage of guaiacyl-type lignin with varying degrees of alcohol substitution. No monomeric lignin was however identified by the GC–MS. A similar observation was reported by Ohra-aho et al.,<sup>56</sup> where the detectable aromatic products from a pine kraft lignin were composed of 16 guaiacyl-type phenol derivatives and 3 hydroxyphenyl-type phenols. These results may thus suggest that the depolymerized compounds from lignin could undergo substitution reactions to form a variety of phenol derivatives. Another possible reason for not detecting monomeric lignin by GC–MS might be related to the fact that re-polymerization of the monomeric units might take place to form oligomers that were unable to be vaporized and detected in the GC–MS analysis.

The liquefaction in ethanol produced a bio-oil rich in 2-methoxy-4-(2-propenyl)-phenol (21.01%), 2-methoxy-phenol (6.79%), other phenolic compounds (16.5%) and their derivatives, benzenoid aromatic compound (7.1%), alcohol (10.9%), and ester (7.4%). It is also noted from the GC–MS analysis results that a small amount of compounds containing nitrogen and sulfur were detected in some bio-oils. These N/S-containing compounds likely originated from the fuel-bound nitrogen and sulfur in the pine sawdust (although both in a small amount up to 0.1 wt % daf), as shown before in Table 1. In the bio-oil products from the



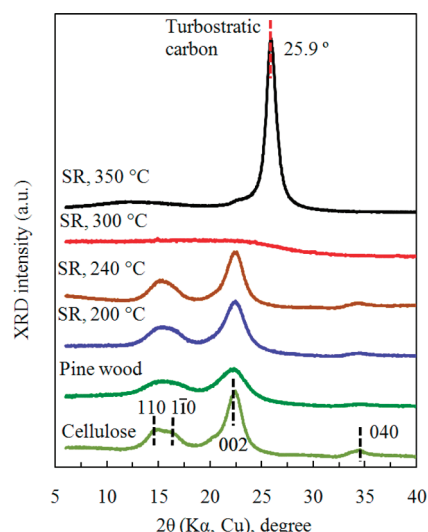
**Figure 6.** GPC results for the bio-oils derived from the pine wood liquefaction in various solvents at 300 °C for 15 min with the solvent/biomass ratio of 10 (w/w). PD (polydispersity) =  $M_w/M_n$ .

liquefaction in water, accordingly, the major compounds identified were various aldehydes (31.2%), such as substituted furfural (25.7%) and benzaldehyde (5.5%). The subsequent detected compounds were phenolic compounds (25.2%) and their derivatives (3.3%) and substituted ketones (13.86%). For the bio-oil produced with the co-solvent of ethanol–water, the detected compounds were mainly phenolic compounds (19.9%) and benzenoid aromatic compounds (7.6%), various esters (22.2%), and substituted aldehydes (13.8%), including furfural and benzaldehyde. The phenolic compounds, in particular the guaiacols, were apparently derived from lignin in the pine sawdust. The bio-oil from the liquefaction in the mono-solvent of ethanol appeared to contain a larger amount of phenolic compounds than that from water or the water–ethanol co-solvent. This suggests that hot-compressed alcohol would facilitate lignin degradation, as also observed in the literature.<sup>38–40</sup>

As mentioned before, GC–MS analysis for bio-oils has a limitation due to less/nonvolatile compounds in the bio-oil, such as oligomers of the lignin-degraded products, were unable to be vaporized; hence, they were not able to be detected by the GC–MS. According to our TGA analysis (30 mL/min  $N_2$  and 10 °C/min from 25 to 700 °C) for the obtained bio-oils, volatile compounds in the bio-oils up to 330 °C (the maximum column temperature employed in our GC–MS tests) were over 60 wt % for the bio-oil from the liquefaction in 100% ethanol and over 40 wt % from the liquefaction in 50% aqueous ethanol and 100% water.

GPC analysis was also performed to examine the molecular-weight distribution of the bio-oils derived from the pine wood liquefaction in different solvents: mono-solvents of ethanol, methanol, or water and co-solvents of ethanol–water or methanol–water (50/50%, w/w). The GPC analytical results are shown in Figure 6. As clearly shown in the figure, all of the obtained bio-oils exhibited a broad molecular-weight distribution and contained a lot of oligomers derived from partial decomposition of lignin, cellulose, or hemicellulose. The bio-oil from the liquefaction in water has the largest  $M_w$  value (1373 g/mol) and  $M_n$  value (630 g/mol) and the lowest polydispersity ( $M_w/M_n = 2.18$ ) compared to the bio-oils obtained with other alcohol-containing solvents. The liquefaction in 100% ethanol led to a bio-oil product with greatly reduced molecular weights ( $M_w = 760$  g/mol and  $M_n = 235$  g/mol). The GPC analysis also showed a sharp peak at a retention time of about 17 min in all of the bio-oil samples. This sharp peak may be attributed to the

(56) Ohra-aho, T.; Tenkanen, M.; Tamminen, T. Direct analysis of lignin and lignin-like components from softwood kraft pulp by Py-GC/MS techniques. *J. Anal. Appl. Pyrolysis* **2005**, *74*, 123–128.



**Figure 7.** XRD patterns of cellulose and white pine wood before and after liquefaction at different temperatures for 15 min.

absorption of phenol or monomeric phenolic compounds. Moreover, the peak was stronger for the bio-oil obtained with 100% ethanol, implying that ethanol might be more effective for the degradation of lignin into monomeric phenols in the liquefaction process.

Figure 7 shows the XRD patterns of cellulose and crude pine sawdust and the SR after the liquefaction at various temperatures (200, 240, 300, and 350 °C) for 15 min in the co-solvent of ethanol–water (50/50%, w/w) and at the solvent/biomass ratio of 10 (w/w). For reference, the XRD profile of pure cellulose (from Sigma-Aldrich) was also obtained and shown in Figure 7. In comparison to that for the crude pine sawdust, no significant evolution in XRD patterns was noticeable in the SR from the liquefaction at a temperature up to 240 °C. Four characteristic peaks at  $2\theta = 14.6^\circ$ ,  $16.5^\circ$ ,  $22.4^\circ$ , and  $34.6^\circ$  from diffraction on the 110,  $1\bar{1}0$ , 002, and 040 planes of cellulose I<sup>57–59</sup> were clearly observable in the pure cellulose sample, as well as the crude pine sawdust and the SR obtained at 200 and 240 °C. In contrast, all four peaks derived from cellulose I disappeared in the SR at 300 °C; instead, broad signals at  $2\theta$  of around  $24^\circ$ , typical of amorphous carbon, were observed. As clearly shown in Figure 7, when the temperature was increasing further to 350 °C, there were strong X-ray diffraction lines at  $2\theta$  between  $24^\circ$  and  $26^\circ$  dominating the spectrum. These XRD signals can be attributed to the C(002) diffraction line of turbostratic carbon ( $2\theta = 25.9^\circ$ ).<sup>60</sup> This suggests the formation of partially crystallized coke/carbon from the pyrolysis of the lignocellulosic matrix or condensation of liquid intermediates/bio-oils, as evidenced by a rapid decrease in the bio-oil yield, when increasing the liquefaction

temperature from 300 to 350 °C (Figure 3). Similar observations on carbon crystallization were reported in previous biomass liquefaction studies with hot-compressed water or methanol.<sup>37,61</sup> The XRD results thus suggest that the cellulosic crystalline structures in the pine sawdust could remain with little change in the co-solvent of ethanol–water at a temperature up to 240 °C, while they would completely decompose to form amorphous carbon at 300 °C.

## Conclusions

In this study, white pine sawdust was effectively liquefied with hot-compressed mono-solvents of water, methanol, and ethanol and co-solvents of alcohol (methanol or ethanol) and water at a temperature from 200 to 350 °C. Some key conclusions are summarized below: (1) A much higher bio-oil yield (approximately 65 wt %) and a greater biomass conversion (95 wt %) were obtained from biomass liquefaction in the co-solvent of 50 wt % aqueous alcohol (methanol or ethanol) at 300 °C for 15 min than those in a mono-solvent of alcohol or water. These results suggested that alcohol (methanol or ethanol) and water showed synergistic effects on direct liquefaction of pine sawdust. (2) The yields of bio-oil increased continuously from 25 to 66 wt % as the reaction temperature increased from 200 to 300 °C, but the oil yield dropped markedly to below 35 wt % if the temperature was increased further to 350 °C, accompanied by a significant increase in SR. These results suggested severe conversion of bio-oil to char by condensation reactions of the liquid bio-oil products at  $>300^\circ\text{C}$ , which was evidenced by the XRD measurements on the solid residues from the liquefaction. (3) The solvent/biomass ratio of 10 (w/w) was found to be an optimal condition for direct liquefaction of pine sawdust to produce bio-oil using the hot-compressed co-solvent of ethanol–water (50/50%, w/w). (4) The FTIR and GC–MS analyses of the obtained bio-oils revealed the presence of high contents of oxygen-containing chemical compounds, such as phenolic compounds, aldehydes, long-chain (and cyclic) alcohols and ketones, ethers, esters, carboxylic acids, etc. (5) All of the obtained bio-oils exhibited a broad molecular-weight distribution and contained a lot of oligomers derived from the lignocellulosic feedstock. The molecular-weight distribution of bio-oil was strongly dependent upon the solvent type. The results of GC–MS and GPC analyses of different bio-oils suggested that ethanol is a more effective solvent for the degradation of lignin into monomeric phenolic compounds. (6) The XRD measurements for solid residues after the liquefaction demonstrated that the cellulosic crystalline structures in the pine sawdust could remain with little change in the co-solvent of ethanol–water at a temperature up to 240 °C, while they would completely decompose to form amorphous carbon at 300 °C.

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