

Liquefaction of Torrefied Wood using Microwave Irradiation

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ABSTRACT: Torrefaction is an effective pretreatment method to improve the uniformity and quality of lignocellulosic biomass before further thermal processing (e.g., gasification, combustion). The objective of this study was to determine the impacts of torrefaction as a pretreatment before liquefaction. Wood chips were torrefied for 2 h at three different temperatures (230, 260, 290 °C) and then subjected to microwave-assisted liquefaction, as was the untreated wood control. The dielectric properties of liquefaction materials, including the biomass samples and liquefaction reagent, were measured to evaluate their abilities to convert electromagnetic energy to heat. The effects of liquefaction time, temperature, and catalyst concentration on the liquefaction efficiency were also investigated. It showed that torrefaction temperature had significant influence on the liquefaction behavior of wood materials. Wood treated at the lowest torrefaction temperature (230 °C) retained the most structural/compositional characteristics of untreated wood and therefore they both exhibited similar liquefaction behaviors. The higher treatment temperature (290 °C) led to higher liquefaction residue contents, attributed to the increase in carbon content and hydrophobicity from torrefaction.

1. INTRODUCTION

The depletion of fossil energy resources and global environmental concerns have driven current research interests in alternative fuel and chemical sources.¹ Biomass is a renewable resource, and its utilization in biofuels is seen as a carbon-neutral source of energy with lesser impacts on climate change. Lignocellulosic biomass is one of the most abundant sources of biomass in nature, comprised primarily of cellulose, hemicellulose, and lignin.² Its liquefaction in organic solvents, either with or without a catalyst under moderate temperatures (100–250 °C),³ has been used to produce useful chemical products⁴ including raw materials for various applications, such as resins,⁵ foams,⁶ and biofuels.⁷ In particular, biomass is naturally rich in hydroxyl groups, and liquefied products with polyhydric alcohols could be used as polyols for polyurethane production and improve the biodegradability of the resulting product.³

Biomass liquefaction using conventional heating methods (e.g., electrical furnace, oil bath) often present limitations of low rates of heat transfer, high energy consumption, and uneven heating,⁸ the thermal transmission of these methods occurs by means of conduction and convection from the surface of the vessel toward the center of the material within.⁹ In recent years, microwave liquefaction technology has shown potential as an efficient method for rapid thermal processing of biomass. Compared with conventional heating, microwave heating by electromagnetic induction improves the efficiency of heating and temperature controls, therefore enhancing the quality of the final product in biomass liquefaction.¹⁰ Microwave heating has been widely implemented, including the liquefaction of wood,¹¹ corn stover, wheat straw, cotton straw, rice straw,¹² pine sawdust,¹³ and poplar sawdust.¹⁴

Liquefaction is one of several thermochemical processes used to obtain biobased chemicals and biofuels. Gasification converts lignocellulosic biomass primarily into producer gas (targeting carbon monoxide and hydrogen) while pyrolysis affords fuel-

quality liquids (bio-oil) and gases along with biochar comprising 15–25% of the original feedstock as a byproduct.¹⁵ Torrefaction is yet another thermochemical process; however, it is used primarily as a pretreatment to improve biofuel performance by increasing energy density, uniformity, grindability, and reducing moisture uptake, the latter of these augmenting storage by making microbial degradation less favorable.^{16–19} Torrefaction conditions are typically anaerobic with atmospheric pressure and temperatures from 200 to 300 °C.²⁰ Briefly, chemical changes include the softening of the hemicelluloses at 200 °C and their deacetylation, dehydration, and depolymerization as the temperature increases;^{21,22} below 250 °C the lignin and cellulose are largely unchanged.²³

To date, most research on the liquefaction of biomass has been concentrated on transformations from its native state. The above-mentioned benefits of torrefaction for other thermochemical operations presents the possibility of torrefied biomass being diverted to liquefaction operations. Alterations in the chemical composition, particularly in the hemicelluloses, have the potential to generate liquefaction products having different compositions/properties. Illustrating this possibility, during thermochemical processing by pyrolysis, torrefaction has been used to improve the thermal and storage stability of resultant bio-oils.^{24–26} Improved grindability afforded by torrefaction also has the potential to benefit liquefaction operations since smaller particle sizes are preferable; however, since torrefaction had yet to be investigated as a pretreatment for the liquefaction of lignocellulosics, the possibility remained that the benefits observed for other thermochemical processes (e.g., gasification, pyrolysis) may not extend to liquefaction,

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with the distinct possibility of a thermally degraded lignocellulosic being resistant to liquefaction.

Accordingly, the objective of the present study was to investigate the liquefaction of torrefied pine wood using microwave heating. The liquefaction behavior of pine wood treated at different torrefaction conditions were explored. Moreover, the liquefaction residues, and acid insoluble contents of those residues, were compared. Dielectric properties and element analyses of the torrefied wood samples were also discussed, which partly explained the differences between the liquefaction residue yields from different feedstocks. Further, the liquefaction residues were characterized using Fourier transform infrared spectroscopy (FTIR).

2. EXPERIMENTAL SECTION

2.1. Materials. Pulp-grade pine wood chips (mostly *Pinus taeda* L.) were obtained from a commercial supplier and torrefied at three different temperatures (230, 260, and 290 °C) for 2 h as previously described.²⁰ Untreated and torrefied wood chips were ground in Wiley mills and screened to obtain samples with a particle size range of 60–80 mesh; samples were dried in an oven (105 °C) overnight, and then stored in a desiccator over desiccant (Drierite) until needed. Carbon, hydrogen, and nitrogen contents were determined by dry combustion at contract laboratories. Polyethylene glycol (PEG, Mn = 400) and glycerin were obtained from Sinopharm Chemical Reagent Co., Ltd. All other chemicals were analytical grade. Untreated and torrefied wood samples at three different temperatures (230, 260, and 290 °C) were labeled as UW, TW-230, TW-260, and TW-290, respectively.

2.2. Wood Liquefaction. The liquefaction of untreated wood and torrefied wood particles was carried out in a Milestone (Shelton, CT) Ethos A microwave digestion system equipped with 100 mL sealed Teflon reaction vessels and an internal fiber optic temperature sensor. The sample temperature was controlled at desired temperature with the preset microwave power. Polyethylene glycol and glycerin were used as the liquefaction reagent at the ratio of 70/30 (w/w) with a solvent to wood (torrefied wood) ratio of 3/1 (w/w). Sulfuric acid was used as the catalyst at 1.5% and 3% (w/w of liquefaction reagent). A typical liquefaction reaction was as follows: 2.0 g of wood particles, 6.0 g of liquefaction agent, premixed with sulfuric acid catalyst. Each mixture was transferred into a Teflon reaction vessel containing a magnetic stir bar. Liquefaction then proceeded under the preset temperature and time. After liquefaction, the reaction vessel was cooled to room temperature before opening. The liquefied product was transferred into a 400 mL beaker with 100 mL methanol and stirred for 2 h followed by vacuum filtration. The solid residues were dried at 105 °C for 12 h in an oven and weighed.

The yield of liquefaction residue was calculated as a percentage of the weight of the starting wood. The solid residues obtained from the liquefaction of untreated and torrefied woods at three different temperatures (230, 260, and 290 °C) were labeled as RUW, RTW-230, RTW-260, and RTW-290, respectively.

2.3. Measurement of Acid Insoluble (Klason) Contents of Liquefaction Residues. The acid insoluble contents of the liquefaction residues was determined by the Klason lignin method.²⁷ In brief, 0.3 g of oven-dried liquefaction residue was digested by 3 mL of sulfuric acid (72%) at 30 °C for 1 h. Then the mixture was diluted to 100 mL with distilled water and hydrolyzed at 121 °C for 1 h. The hydrolyzed mixture was filtered. The acid insoluble residue (retentate) was oven-dried at 105 °C overnight and weighed. Subsequent combustion at 575 °C in the muffle furnace for 5 h was carried out to determine the ash content of the acid insolubles.

The acid insoluble content of liquefaction residue was calculated by the following:

$$R = \frac{W_1 - W_2}{W_0} \times 100$$

Where R is the percentage of acid insoluble content (%), W_1 is the weight of acid insolubles, W_2 is the weight of the ash determined for

the acid insolubles, and W_0 is the weight of oven-dried liquefaction residue. The acid insoluble content (i.e., Klason lignin) of untreated wood (UW) was also determined using the same method.

2.4. Measurements of Dielectric Properties. Dielectric properties of the wood materials were measured in the frequency range of 300 MHz to 4.5 GHz, according to the transmission/reflection method using an Agilent E5071C series vector network analyzer and an Agilent 85031B 7 mm calibration kit. Before measuring, the vector network analyzer was in operating mode for at least 30 min. The wood materials were molded in a coaxial die with inner diameter of 3 mm and outer diameter of 7 mm before testing.

The dielectric measurement of liquid (mixtures) was carried out using the same analyzer but with an Agilent 85070 E dielectric probe kit. Before the measurement, the analyzer was calibrated by a three-point method (air, 50 Ω short circuit and deionized water at 25 °C).

2.5. FTIR Spectroscopy. The dry liquefaction residues were analyzed by using a Thermo Scientific Nicolet 380 FTIR spectrophotometer. In each case, a small amount of liquefaction residue was homogenized with KBr and then pressed to prepare pellets. The spectra were collected in the absorbance range from 4000 to 400 cm^{-1} over 32 scans with a 4 cm^{-1} spectral resolution.

3. RESULTS AND DISCUSSION

3.1. Chemical and Physical Properties of Raw

Materials. **3.1.1. Elemental Analysis.** The result from elemental analysis of untreated and torrefied wood samples is shown in Table 1. Compared to untreated wood sample,

Table 1. Elemental Analysis for Untreated and Torrefied Wood Samples

sample	weight [%]			H/C
	nitrogen	carbon	hydrogen	
UW	0.05	47.64	6.29	0.13
TW-230	0.08	49.57	5.64	0.11
TW-260	0.09	53.28	5.55	0.10
TW-290	0.08	57.57	5.39	0.09

torrefied woods have higher carbon contents and lower hydrogen contents; the carbon content of the torrefied wood increased while the hydrogen content slightly decreased with the increasing torrefaction temperature. All these changes indicated an alteration in chemical composition among the three main components of woody biomass during torrefaction.

During torrefaction, dehydration, deoxygenation, and dehydrogenation reactions occur as major components decomposed, leading to a general carbonization and devolatilisation of the biomass substrate.^{28,29} Oxygen was removed via reactions releasing it as water vapor, CO, and CO₂.³⁰ Decreasing hydrogen contents in torrefied wood resulted from the removal of hydroxyl groups in the form of water.²⁴ Loss of organic volatiles could also contribute to the decrease of oxygen and hydrogen contents in torrefied wood.³¹ Thus, the increase of carbon coincided with decreases in oxygen and hydrogen contents, undoubtedly impacting both the integrity and proportions of the wood polymer constituents, cellulose, hemicellulose, and lignin. The contents of nitrogen in wood were very small and thus the trends may have been obscured by the limits of the analytical technique. Altogether, the release of volatile matter, and the decomposition of the wood chemical components were increased with the severity of torrefaction, herein with higher temperatures given that the torrefaction time remained constant.

The ratio of hydrogen to carbon (H/C) of a compound determined by elemental analysis can be used to describe the

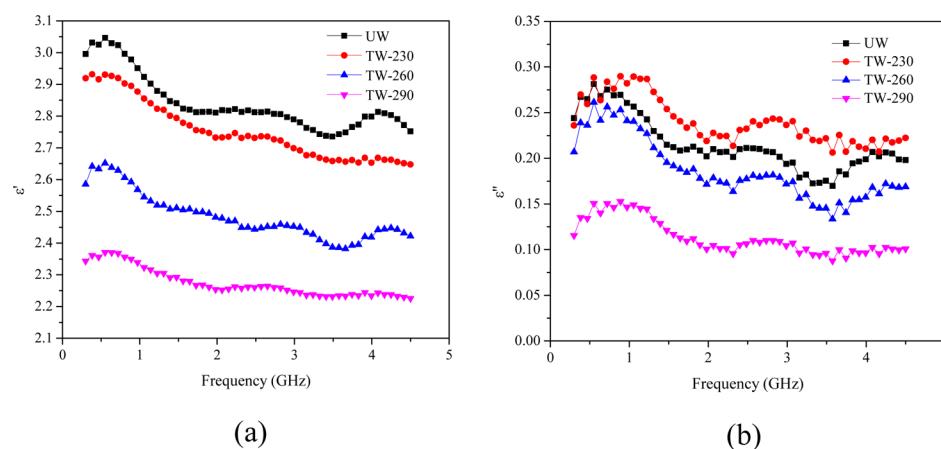


Figure 1. Frequency dependence of dielectric constant (a) and dielectric loss factor (b) of untreated and torrefied wood samples at room temperature (UW untreated wood; TW-230, TW-260, and TW-290 torrefied wood treated at 230, 260, and 290 °C, respectively).

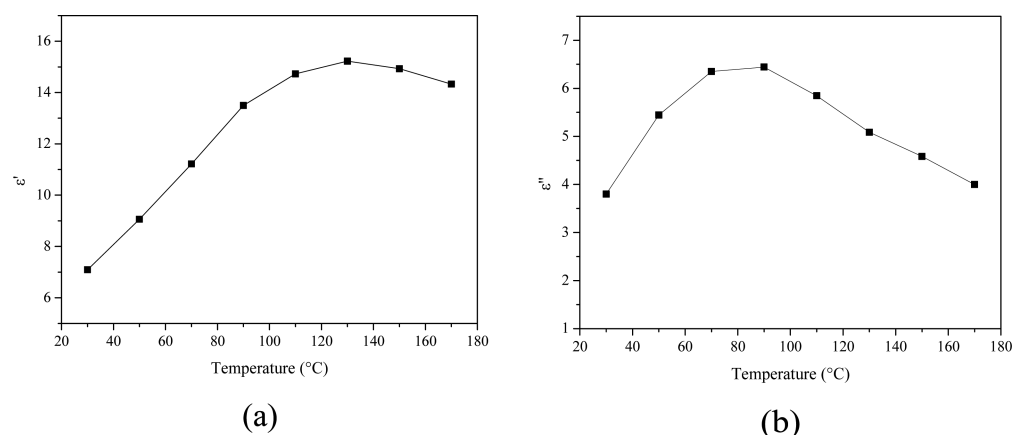


Figure 2. Dielectric constant (a) and dielectric loss factor (b) of liquefaction solvent (PEG/glycerol, 7/3,w/w) as a function of temperature at 2.45 GHz (acid catalyst content: 1.5 wt % of liquefaction solvent).

degree of unsaturation/aromaticity.³² The H/C ratio of natural woody materials, such as lignin or cellulose is around 1.5. The H/C ratio of black carbon is less than 0.2.³³ During torrefaction, the loss of volatile matter and bound water resulted in the decrease of hydrogen content and oxygen content, while the relative carbon content increased. The decreasing H/C ratio with increasing temperature of treatment, although subtle, would appear to coincide with a limited increase in the degree of aromaticity of the torrefied wood samples, which would improve the chemical stability of wood materials.³⁴

3.1.2. Dielectric Properties. Microwave heating depends largely on the dielectric properties of the materials to be heated. The dielectric property of a material is usually expressed as a complex permittivity (ϵ), which can be defined as $\epsilon = \epsilon' - j\epsilon''$, where ϵ' is the real part and termed as dielectric constant and ϵ'' is the imaginary part and as dielectric loss. The dielectric constant (ϵ') signifies the ability of the material to store electric energy, while the dielectric loss (ϵ'') signifies the ability of the material to convert electric energy to heat.³⁵ The ratio of ϵ'' to ϵ' is called the dielectric loss tangent ($\tan \delta$) and it defines the efficiency of a material to convert the electric energy to heat. The dielectric properties of a material is mainly determined by its chemical composition.³⁶ Figure 1 shows the dielectric properties of untreated and torrefied wood samples at the frequency range from 300 MHz to 4.5 GHz under room

temperature. In general, the dielectric constant (ϵ') and dielectric loss factor (ϵ'') of all samples decreased with the increase of frequency. The untreated wood has higher ϵ' and ϵ'' than torrefied wood. And the value of ϵ' and ϵ'' decreased as the torrefaction temperature increased. Lignocellulose is mainly composed of cellulose, hemicellulose, lignin, and fewer amounts of bound water and volatile and semivolatile matter (i.e., extractives). Both the water and many of these volatile materials are highly polar substances which greatly contribute to the high ϵ' and ϵ'' of untreated wood. For instance, the dielectric constant and dielectric loss factor of water are 78.22 and 9.9, respectively, at 2.45 GHz under ambient temperature. It is expected that the ϵ' and ϵ'' of torrefied wood decreased after the release of the bound water and volatile materials during the torrefaction process. As discussed previously, the three main components in lignocellulosic biomass undergo different chemical conversions during torrefaction process. Torrefaction can be classified as light (200–235 °C), mild (235–275 °C), and severe (275–300 °C) in terms of the degree of torrefaction.³⁷ Hemicellulose undergoes significant thermal degradation even under light torrefaction. The decomposition of cellulose begins under conditions of mild torrefaction; however, it is not significant without more severe torrefaction conditions. Lignin is the most thermally stable of the lignocellulosic polymers, decomposing only slightly within the temperature range of torrefaction.³⁸ With losses of hydroxyl

groups during the decomposition of hemicellulose and cellulose, the torrefied wood increases in hydrophobicity.³⁹

Therefore, the decrease of the ϵ' and ϵ'' values of torrefied wood with increasing torrefaction temperature could be well explained by the following factors: (1) the loss of polar hydroxyl groups in hemicellulose and cellulose and (2) the decomposition of hemicellulose and cellulose and with an increasing proportion of less polar lignin. The values of ϵ' and ϵ'' for untreated wood and wood treated at 230 °C were relatively close, indicating that wood treated under light torrefaction conditions retained the most structural/compositional characteristic of untreated wood material.

Liquefaction solvent generally took up to 75% of the liquefaction reaction system. The dielectric properties of the liquefaction solvent therefore contributed greatly to the heating behavior of the liquefaction system under microwave irradiation. Figure 2 shows the dielectric constant and dielectric loss factor of the PEG/glycerol (7/3, w/w) at 2.45 GHz frequency as a function of liquefaction temperature. As the liquefaction temperature increased from 30 to 130 °C, the dielectric constant of liquefaction solvent increased and then decreased when the temperature increased beyond that range. The dielectric loss factor also increased and then decreased with temperature, reaching its highest value at around 90 °C. Given the fact that the dielectric loss tangent is the ratio of ϵ'' to ϵ' , it can be expected that the ability of the PEG/glycerol mixed solvent at this ratio to convert microwave energy to heat gradually increased and then reached the maximum at 50 °C.

3.2. Liquefaction of Torrefied Wood. **3.2.1. Effects of the Reaction Time.** The three main components of wood, namely cellulose, hemicellulose, and lignin, all had the potential for thermal degradation, albeit at different levels, during the torrefaction.⁴⁰ It was therefore expected the torrefied wood would possess different liquefaction behaviors than untreated wood due to changes in their physical and chemical properties. Figure 3 shows the influence of reaction time on the amounts of solid residue remaining after liquefaction for untreated and torrefied wood samples. The beginning point was defined as the time when the reaction system reached the desired liquefaction temperature. It can be seen from Figure 3 that the residue

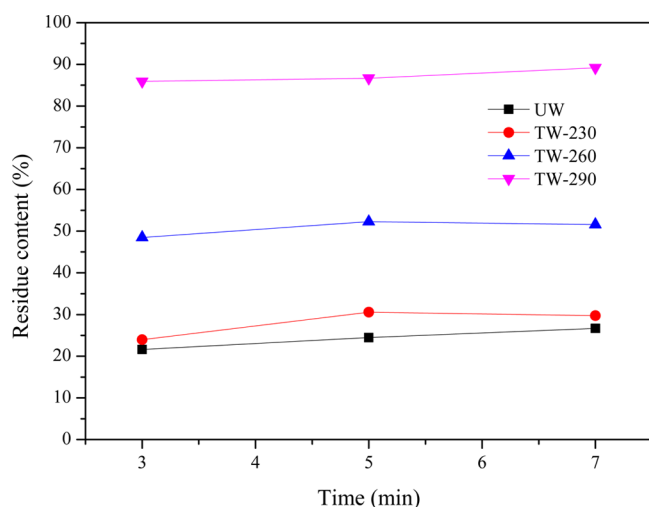


Figure 3. Residue contents of untreated and torrefied wood samples as a function of liquefaction time (liquefaction temperature 130 °C; catalyst content 1.5%; UW untreated wood; TW-230, TW-260, and TW-290 torrefied wood treated at 230, 260, and 290 °C, respectively).

contents of all wood samples increased slightly when reaction time increased from 3 to 7 min. It is known that thermochemical decomposition of wood components and recondensation of decomposed wood fragments are the two major types of reactions occurring simultaneously during the liquefaction process.⁴¹ The decomposition of wood components generally dominates the initial stage of the process. With prolonged reaction times, the recondensation of degraded products becomes profound and results in increased residue contents.

Microwave heating also substantially enhanced the liquefaction rate with a high conversion level in a very short time, likely staying at a relatively stable equilibrium stage. Therefore, the residue content did not change greatly with prolonged reaction time as that typical of liquefaction with convection heating. Results showed that higher torrefaction temperatures led to a dramatic increase in residue contents compared to untreated wood liquefied under the same reaction condition. These different liquefaction behaviors were ascribed to alterations in the physical and chemical properties of wood materials after torrefaction. First, most thermally unstable components in woody biomass underwent degradation, releasing gases and volatile liquids during torrefaction and leaving behind a biochar that was more thermal-resistant. This was particularly true for wood samples treated at the most severe torrefaction condition (i.e., 290 °C). In addition, woody biomass was transformed into hydrophobic materials due to the loss of hydroxyl groups, as well as the carbohydrate fractions via the dehydration, deoxygenation and dehydrogenation reactions.²⁹ The increasing hydrophobicity of the wood samples treated at high torrefaction temperatures could have excluded the polar liquefaction solvent from the lignocellulosic polymer components comprising the wood cell walls. Therefore, much higher liquefaction residue contents were expected for the torrefied woods, especially those treated under mild to severe torrefaction conditions, than untreated wood. Torrefied wood treated under the light condition exhibited similar liquefaction behavior as untreated wood, indicating that light torrefaction preserved most physical and chemical properties of wood sample. This result was in good agreement with that from the elemental analysis.

3.2.2. Effects of the Reaction Temperature. Reaction temperature plays a key role in the liquefaction of woody biomass. Figure 4 shows the effect of liquefaction temperature on the residue contents of the untreated and torrefied wood samples. The residue contents obtained with torrefied wood treated at 230 °C displayed a parallel trend as that of the untreated wood, except with slightly higher values for residue content at each liquefaction temperature. This result was attributed to the limited physical and chemical property changes for the torrefied wood treated at this torrefaction temperature. The residue contents of both samples decreased slightly as the temperature increased from 130 to 150 °C, indicative of a degradation rate being slightly higher than the recondensation rate. When the temperature further increased to 170 °C, the collisions between degraded small molecules likely increased in intensity, promoting the recondensation of these degradation products into insoluble residues.

In the case of torrefied wood samples TW-260 and TW-290, liquefaction temperature did not have significant effects on the residue contents of these two samples. They only slightly increased as the liquefaction temperature increased from 130 to 170 °C, most likely due to the aforementioned recondensation

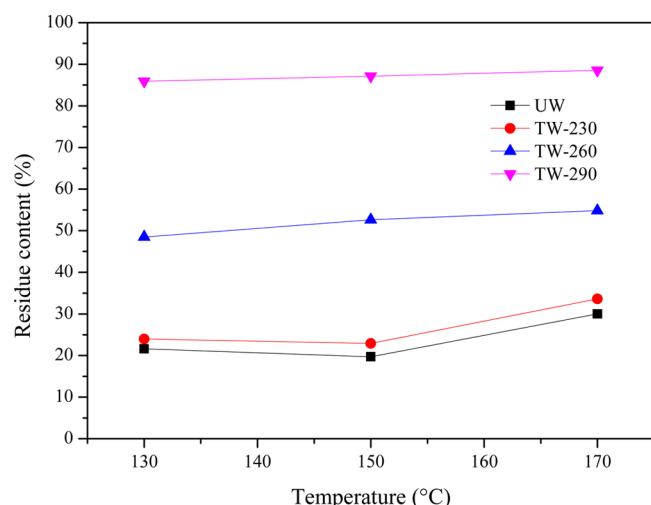


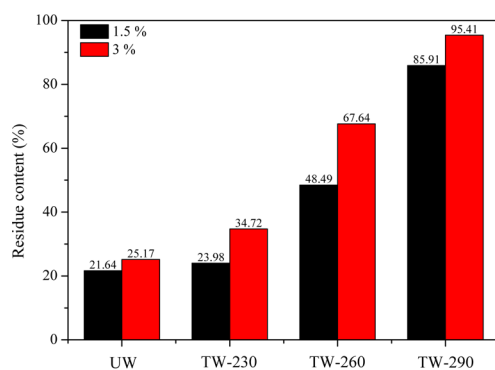
Figure 4. Residue contents of untreated and torrefied wood samples as a function of liquefaction temperature (liquefaction time 3 min; catalyst content 1.5%; UW untreated wood; TW-230, TW-260, and TW-290 torrefied wood treated at 230, 260, and 290 °C, respectively).

of degraded wood components. Nevertheless, they were much higher than those of TW-230 and untreated wood samples. This result was similar to the effect of liquefaction time, suggesting that higher torrefaction temperature transformed woody biomass to a more thermochemically stable material.

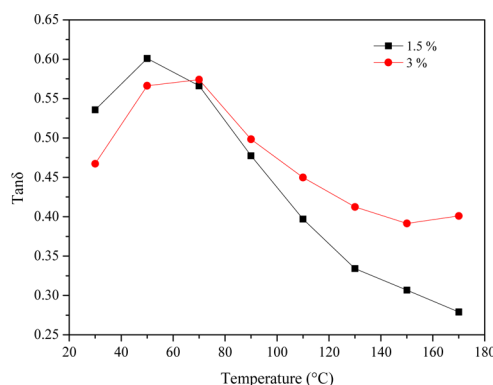
3.2.3. Effects of the Catalyst Concentrations. Acid catalyst is one of the critical factors in the liquefaction of woody biomass. The influence of acid catalyst content on the liquefaction residue content is presented in Figure 5a that the higher amount of acid catalyst (3% vs 1.5%) led to higher recoveries liquefaction residues for both untreated wood and torrefied wood. This result was the opposite of that from the liquefaction of wood biomass using conventional heating⁴² whereby higher amounts of acid catalyst enhanced the cleavage of the glycosidic bonds in carbohydrates, as well as other C–O bonds in woody biomass, promoting the decomposition of wood components during the liquefaction reaction.⁴³ To investigate this anomaly, the dielectric loss tangent ($\tan \delta$) of the liquefaction solvent with the two different acid catalyst contents were determined (Figure 5b). Although the $\tan \delta$ of

the two solvent systems followed the similar trend along the temperature range, the solvent system with higher acid catalyst content exhibited significant higher $\tan \delta$ than that with lower acid catalyst, when temperature was higher than 70 °C; this difference increased dramatically with increased temperature. As discussed previously, the ability of a material or solvent to convert microwave energy is determined by its dielectric loss tangent ($\tan \delta$). In general, woody materials have much lower $\tan \delta$ values than organic solvents. Liquefaction solvent with higher acid catalyst (i.e., high $\tan \delta$), under microwave irradiation, could have generated locally high temperatures (i.e., hot-spots) in the reaction system as much as 50 °C higher than the bulk temperature.⁴⁴ Locally high temperatures might promote the recondensation reactions of degraded products from wood components, leading to the formation of insoluble humins/chars and consequently, higher residue contents.⁴⁵

3.2.4. Characterization of Solid Residues after Liquefaction. Compositional analysis of liquefaction residues can provide some useful information on the liquefaction behavior of the main components (cellulose, hemicelluloses, lignin) comprising lignocellulosic biomass. The acid-insoluble fraction of wood is obtained by acid hydrolysis as a measure of lignin content, so-called Klason lignin. Results in Figure 6 show again that sample RUW and RTW-230 shared similar trend in the changes of the amounts of acid insoluble fractions under different liquefaction temperatures. At lower liquefaction temperature, the acid insoluble fraction of RUW and RTW-230 were higher than the Klason lignin content of UW (29%), suggested that a few condensed products formed during the liquefaction reaction. The higher value of RTW-230 than RUW can be attributed to the formation of acid insolubles during torrefaction. At the higher liquefaction temperatures, more than 70% of RUW and RTW-230 were collected in the acid insoluble fraction, indicating that the recondensation reaction dominated the liquefaction process under high liquefaction temperature.⁴¹ Compared to RUW and RTW-230, the acid insolubles of RTW-260 and RTW-290 were consistently high at all liquefaction temperatures. It was worth noting that TW-260 yielded a residue content around 50% after liquefaction (Figure 4), yet RTW-260 yielded acid insolubles as high as 80%, which was comparable to that of RTW-290. This suggested that mild torrefaction temperature (260 °C) might decompose most



(a)



(b)

Figure 5. Residue contents of untreated and torrefied wood samples (a) and dielectric loss tangent of liquefaction solvent (b) at two acid catalyst contents (liquefaction time 3 min; liquefaction temperature 130 °C; UW untreated wood; TW-230, TW-260, and TW-290 torrefied wood treated at 230, 260, and 290 °C, respectively).

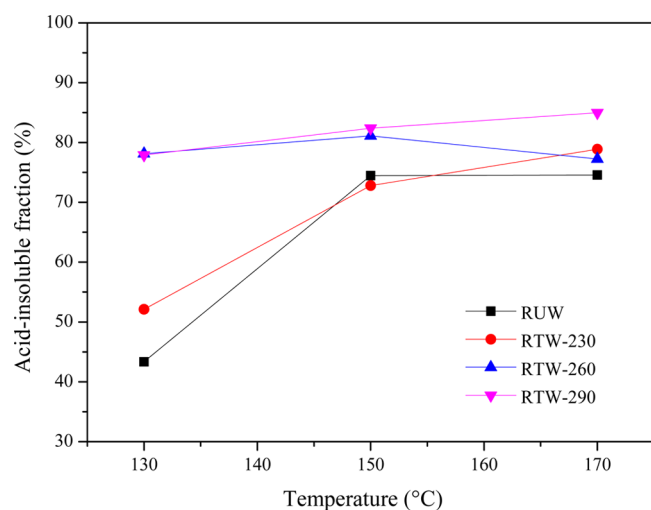
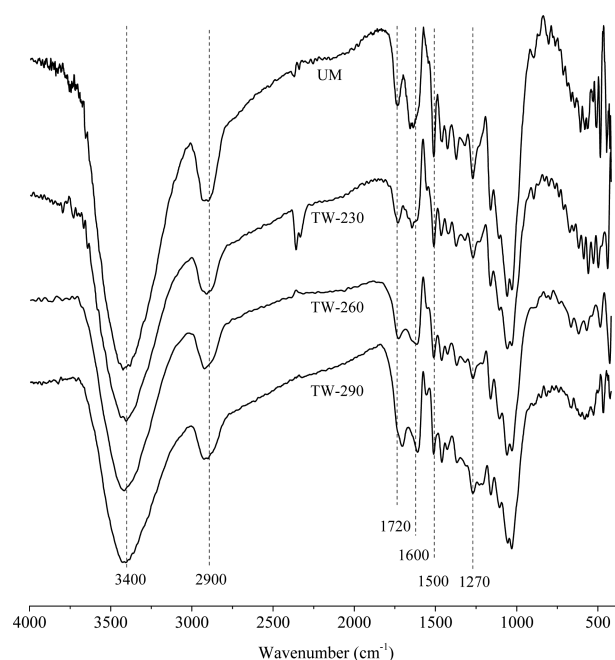


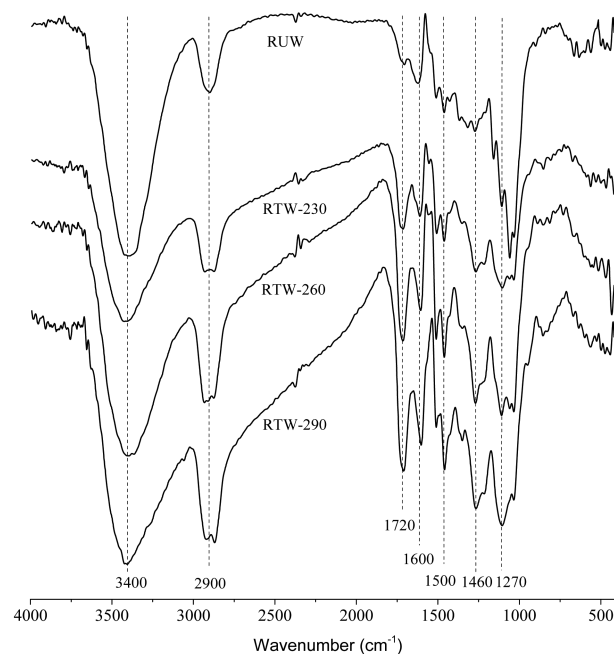
Figure 6. Acid-insoluble contents of the liquefaction residues of untreated and torrefied wood samples as a function of liquefaction temperature (reaction time 3 min; catalyst concentration 1.5%; RUW liquefaction residue of untreated wood; RTW-230, RTW-260, and RTW-290 liquefaction residue of torrefied wood treated at 230, 260, and 290 °C, respectively).

hemicellulose and some cellulose, transforming some of the carbohydrates into condensed products. However, about half of the torrefied sample was still susceptible to liquefaction reaction, while in the case of TW-290, the high torrefaction temperature completely turned the wood into thermal- and acid-resistant substances. This change in torrefied wood could increase its storage time but also decrease its accessibility by liquefied solvent and resulted in less extent of liquefaction. Ku et al.⁴⁶ reported that torrefaction reduced both H_2 production and carbon conversion when subjected to gasification compared to its raw parent biomass. Therefore, the benefit of torrefaction as a pretreatment for later thermal conversion of biomass varied largely in different case scenario.

To assess the changes in chemical functionality by both torrefaction and liquefaction conditions, samples before torrefaction and the liquefaction residues were analyzed by FTIR. Figure 7a and b shows the FTIR spectra of the untreated wood and torrefied wood samples and the corresponding liquefaction residues, respectively. A broad peak at around 3400 cm^{-1} was assigned to $-OH$ groups either from carbohydrates (cellulose and hemicellulose) or lignin,⁴⁷ and the peak at around 2900 cm^{-1} was assigned to the $C-H$ stretch in methyl and methylene groups.⁴⁸ These intense absorbance peaks appeared in both spectra of untreated and torrefied wood. The intensities of the $-OH$ group in torrefied wood samples were lower than that of the untreated wood, confirming the loss of some hydroxyl groups in torrefied wood, most likely from the hemicelluloses. Both spectra provided bands at around 1720 cm^{-1} , caused by the stretching of the carbonyl ($C=O$) groups in hemicellulose.⁴⁹ As was shown in Figure 7a, the intensity at peak 1720 cm^{-1} was lower in torrefied wood samples than that of the untreated wood, consistent with the thermal degradation of hemicellulose during torrefaction process. However, the intensity of this peak in the liquefaction residues became stronger at higher torrefaction temperature (Figure 7b). Providing most hemicellulose has already decomposed during torrefaction, the peak at 1720 cm^{-1} in residues should not belong to the carbonyl groups in hemicellulose. Therefore, it was inferred that the band at 1720 cm^{-1} was assigned to



(a)



(b)

Figure 7. IR spectra of untreated wood and torrefied wood samples (a) and liquefaction residues of untreated and torrefied wood samples (b) (liquefaction temperature 130 °C; liquefaction time 3 min; acid catalyst content 1.5%; UW untreated wood; TW-230, TW-260, and TW-290 torrefied wood treated at 230, 260, and 290 °C, respectively; RUW liquefaction residue of untreated wood; RTW-230, RTW-260, and RTW-290 liquefaction residue of torrefied wood treated at 230, 260, and 290 °C, respectively).

derivatives of cellulose⁵⁰ and esterification products; it has been reported that during the liquefaction process, the hydroxyls

were most likely to be oxidized partly and then reacted with alcohol to form esterification products.⁵¹

The intense peaks at 1600 and 1500 cm^{-1} were assigned to the aromatic skeletal (lignin) vibrations.⁴⁷ The band at 1460 cm^{-1} was derived from C–H deformation combined with aromatic ring vibration, and the peak at 1270 cm^{-1} was due to the methoxyl groups of lignin.⁵² All the peaks that characterized for aromatic compounds (lignin) were strong in the spectra of untreated and torrefied wood samples, indicating that torrefaction process preserved most of the structure of lignin. In addition, the intensities of these peaks increased as the torrefaction temperature increased (Figure 7b), suggesting that the degree of aromaticity of torrefied wood increased significantly with the increase of torrefaction temperature due to the loss of most hemicellulose and part of the cellulose at mild and severe torrefaction conditions. This result was in good agreement with the elemental analysis.

By comparing the spectra of the untreated wood sample, the torrefied wood samples, and the corresponding liquefaction residues, polysaccharide (hemicelluloses) decomposition occurred during the torrefaction process, with the aromatic nature of the torrefied wood increasing after subsequent liquefaction reactions. This result might suggest that (1) polysaccharides remaining in the torrefied wood underwent further decomposition during liquefaction reaction and/or (2) the lignin was the most stable component during both the torrefaction pretreatment and subsequent liquefaction.

5. CONCLUSION

The liquefaction of torrefied wood was carried out at different liquefaction conditions (time, temperature, catalyst concentration) with microwave irradiation. The dielectric properties of liquefaction materials, including the woody biomass and liquefaction reagent, were measured to evaluate their abilities to convert electromagnetic energy to heat. The ϵ' and ϵ'' value of torrefied wood decreased with increasing torrefaction temperature due to the loss of polar hydroxyl groups, the decomposition of hemicellulose and cellulose, and with an increasing proportion of less polar lignin. It was also found that wood treated at the mildest torrefaction condition retained the most compositional characteristics of untreated wood material and therefore exhibited similar liquefaction behavior. As the torrefaction temperature was increased from 230 to 290 $^{\circ}\text{C}$, the wood was more carbonized; reduced reactivity during liquefaction resulted in the significantly amounts of material being collected as insoluble liquefaction residues. The FTIR analysis on torrefied wood and their liquefaction residues confirmed the increase in the aromaticity of woody biomass after torrefaction process. The results suggest that benefits of torrefaction for preprocessing of lignocellulosics for further thermochemical processing are largely offset with liquefaction because of hydrophobic torrefied wood recalcitrance, particularly at the higher torrefaction temperatures.

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Notes

The authors declare no competing financial interest.

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