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Dynamic Dielectric Properties of a Wood Liquefaction System Using Polyethylene Glycol and Glycerol

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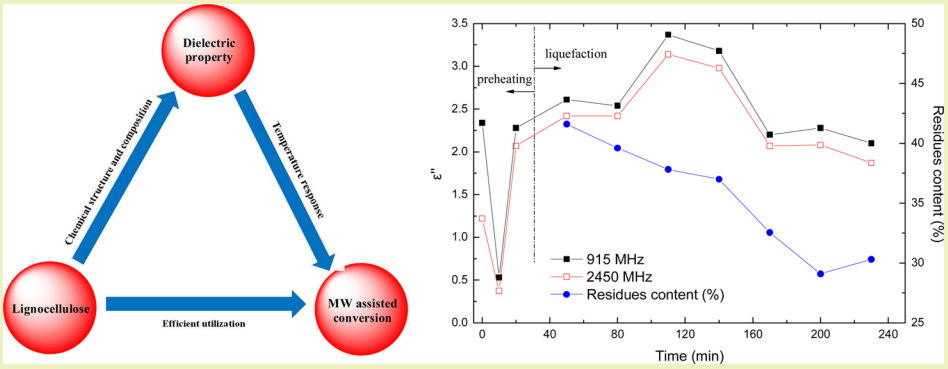
Supporting Information



ABSTRACT: Microwave-assisted liquefaction has shown potential for rapid thermal processing of lignocellulosic biomass. The efficiency of microwave heating depends largely on the dielectric properties of the materials being heated. The objective of this study was to investigate the dynamic interactions between microwave energy and the reaction system during the liquefaction of a woody biomass sample. The dielectric properties of poplar wood particles, model compounds representing the three main chemical components of wood, and individual liquefaction solvent components, along with their mixtures, were measured to evaluate their abilities to convert microwave energy to heat at different frequencies. Dry samples of wood particles, cellulose, xylan, and lignin were all poor microwave energy absorbers as indicated by their low dielectric values relative to the liquefaction solvent components and their mixtures; among the two solvents, polyethylene glycol had lower dielectric values than glycerol, likely due to its larger molecular size. Ionic conduction significantly affected the dielectric loss factor of the liquefaction solvent mixture upon the addition of the sulfuric acid catalyst. During the wood liquefaction reactions, temperature was the main factor that governed the dielectric properties through the preheating stage, and then when the system reached 130 °C, the dielectric properties were governed by changes in chemical composition.

KEYWORDS: *Biomass, Dynamic dielectric properties, Microwave energy, Liquefaction*

INTRODUCTION

Lignocellulosic biomass resources, ranging from dedicated energy crops to forest residues, are considered to be among the most promising and sustainable alternatives to petroleum for the future production of energy, materials, and chemicals.[1,2] Extensive research has been devoted for several decades to develop environmentally friendly and economically feasible technologies for biomass conversions. Liquefaction is one of several thermochemical conversion approaches that can transform lignocellulosic biomass into useful liquid feedstocks; this particular process involves the treatment of the lignocellulosic biomass in the presence of organic solvents at moderate temperatures (100−250 °C). The resulting liquid products can then be used to prepare a variety of polymeric materials depending upon the availability of specific reactive groups.[3] For example, liquefied lignocellulosic biomass, in combination with polyhydric alcohols, could be used as biopolyols for polyurethane production, with the resulting products having improved biodegradability. Binary liquefaction solvent systems, such as one comprised of polyethylene glycol and glycerol, have shown great promise for lignocellulosic biomass liquefaction given the inherent capacity to suppress recondensation reactions, accelerate the liquefaction rate, and reduce the solid residue content of the liquid product.[4]

Microwave heating is of specific interest for thermochemical operations given the potential to reduce processing time, as

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well as to improve the overall production efficiency as compared to traditional heating methods.[5] Microwave heating, also called "dielectric heating," is dependent upon the inherent dielectric properties of the material which are mainly determined by its chemical composition.[6] The dielectric properties can be expressed as $\varepsilon = \varepsilon' - j\varepsilon''$, where ε' is the real part of the complex and is termed as the dielectric constant; $j^2 = -1$ is the imaginary unit, and ε'' is the imaginary part of the complex and termed as the dielectric loss factor. The dielectric constant ε' represents the ability of the substance to be polarized and to store electric energy, while the dielectric loss factor ε'' is related to the ability of the substance to dissipate electric energy or to convert the electric energy to heat.[7] The ratio of ε'' to ε' is called the dielectric loss tangent ($\tan \delta$), and it defines how effective a material can convert electric energy to heat.

Given the unique internal heating ability of microwave energy, it has been studied for applications in food processing,[8] wood drying,[9] organic synthesis,[10] and inorganic nanomaterial synthesis.[11] The use of microwave-based technologies in the thermal treatment of biomass has increased from the midnineties.[5] Recent examples include the liquefaction of wheat straw alkali lignin,[12] gasification of corn stover,[13] and pyrolysis of oil palm biomass.[14] Intuitively, knowledge of the dielectric properties of a given lignocellulosic biomass resource would be useful for understanding its behavior under microwave irradiation and, thus, the ability to convert microwave energy to heat. A limited number of recent studies have investigated the dielectric properties of various lignocellulosic biomass resources, such as oil palm,[15] corn stover,[16] switchgrass,[17] and hay;[18] however, despite these efforts, a fundamental understanding regarding the interactions between microwaves and the reaction system, particularly during the thermochemical conversions, is still lacking.

Lignocellulosic biomass is comprised of three main chemical components (cellulose, hemicellulose, lignin), all having different dielectric properties. As the thermochemical conversion of lignocellulosic biomass proceeds, the chemical composition of the reaction system continuously changes. Accordingly, the dielectric properties of the reaction system are dynamic and are also continuously changing. It is therefore essential to know the dynamic response of the reaction system to microwave irradiation along the thermochemical conversion process and how it affects the resultant liquefaction products. To the best of our knowledge, no detailed study has thus far been conducted on the dynamic dielectric properties of a reaction system during woody biomass liquefaction.

The objectives of this study were to investigate the following: (1) the dielectric properties of wood particles, model compounds representing the three main chemical components of wood (cellulose, hemicellulose, lignin), and the liquefaction solvent itself, with and without the sulfuric acid catalyst, (2) the dynamic dielectric properties of liquefaction mixtures as a function of time and temperature, and (3) the penetration depth of microwaves in the liquefaction system, being important information for the design of larger microwave-based biomass conversion systems.

EXPERIMENTAL SECTION

Materials. Poplar (*Poplar* spp.) wood chips were obtained from a wood processing facility near Nanjing, China, and ground in a Wiley mill. The wood particles used in this work passed through a 80 mesh and lay on a 120 mesh screen. Before using, the wood particles were dried at 105 °C for 24 h in an oven and then stored in a desiccator over a desiccant (calcium sulfate) until further use. Xylan, used as the model compound for hemicelluloses, and microcrystalline cellulose were both purchased from TCI Chemicals Co. Ltd. (Shanghai, China). Kraft lignin was purchased from Zhengzhou Aoyu Chemical Co. (Zhengzhou, China). Sulfuric acid, polyethylene glycol (PEG, M_n = 400) and glycerol were all reagent grade.

Measurement of Dielectric Properties. *Measurement of Dielectric Properties of Solid Samples.* The dielectric properties of the solid samples (e.g., wood particles, cellulose, etc.) were measured with an Agilent E5071C series vector network analyzer (Santa Clara, CA, U.S.A.) equipped with an Agilent 85031B 7 mm calibration kit, using the transmission/reflection method in a 101-point frequency sweep between 300 MHz and 4.5 GHz. The analyzer was in operating mode for at least 30 min before calibration and subsequent data collection.

The solid samples were molded to a ring shape in a coaxial die with 3 mm inner diameter, 7 mm outer diameter, and 2 mm thickness under a pressure of 2 MPa using a hydraulic press. Then, the sample ring was placed in the input unit of the reflection access of the analyzer for measurement. The dielectric constant ε' and dielectric loss factor ε'' were calculated using Agilent 85071 E Material Measurement Software. All measurements were carried out in triplicate.

Measurement of Dielectric Properties of Liquid Samples. The dielectric properties of the liquid samples were measured using the same vector network analyzer but with an Agilent 85070 E dielectric probe kit; the analyzer was first calibrated by a 3-point method (air, 50 Ω short circuit, and deionized water at 25 °C). For each measurement, the liquid sample (30 mL) was placed in a 250 mL three-necked flask equipped with a magnetic stirrer and a thermometer. The flask was heated on a hot plate (Heidolph MR Hei-Tec, Schwabach, Germany) equipped with a heating block and a temperature sensor. The probe was immersed in the liquid throughout the measurement process. The ε'' and ε' values were determined when the desired temperature or time was reached. The probe and the connection cable were fixed with a clamp and remained stationary to ensure the stability and accuracy of the measurements. The dielectric properties (ε' and ε'') of PEG and glycerol, and their different mixtures (including those with the acid catalyst), were conducted at a frequency range from 300 MHz to 4.5 GHz and from 30 to 170 °C in 20 °C increments.

Measurement of Dynamic Dielectric Properties of the Liquefaction System. The dynamic dielectric properties of the liquefaction system were measured using the same method described above for the liquid samples. For a typical measurement, selected ratios of wood particles, liquefaction solvent (PEG/glycerol, 7/3, w/w), and sulfuric acid (if used) were premixed in a beaker and then transferred into a 250 mL three-necked flask. The probe was then immersed in the reaction mixture which was then heated. The dielectric data were collected at designated temperatures or times along the liquefaction process. After liquefaction, the reaction flask was cooled to room temperature, and the liquefaction product was diluted with 100 mL methanol, stirred for 2 h, and vacuum filtered using a filter paper in a Buchner funnel. The solid residue was dried overnight at 105 °C in an oven before weighing. The value for residue content, determined on a dry-weight basis, was calculated as a percentage of the weight of starting wood particles.

Penetration Depth. The penetration depth (D_p) of electromagnetic waves is an important parameter that is often used to design and scale-up microwave heating systems. It is defined as the depth at which the microwave power falls to e^{-1} (e = 2.7183) of its surface value.[15] The penetration depth of a microwave in a mixture can be calculated by the following equation:[19]

$$D_p = \frac{\lambda_0}{2\pi(2\varepsilon')^{1/2}}\left[\left\{1 + \left(\frac{\varepsilon''}{\varepsilon'}\right)^2\right\}^{1/2} - 1\right]^{-1/2} \quad (1)$$

where $\lambda_0 = c/f$ represents the wavelength of microwave in free space, which is related to the speed of light in free space (c = 2.9979 × 10^8 m/s) and the microwave frequency (f).

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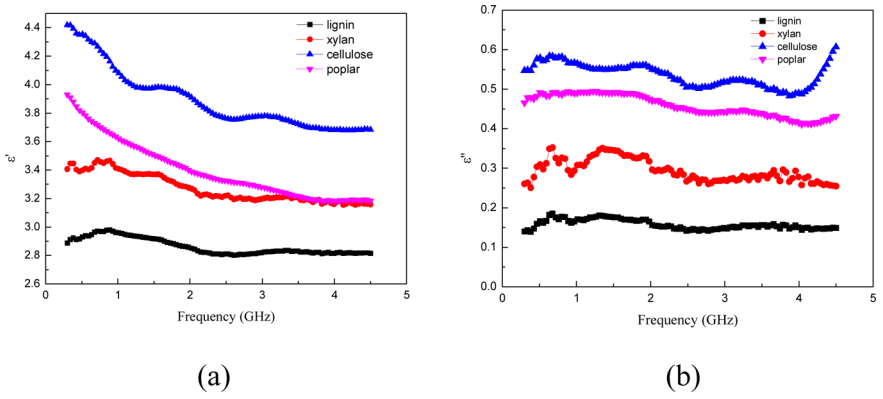

Figure 1. Frequency dependence of (a) dielectric constant ε' and (b) dielectric loss factor ε'' of poplar wood, cellulose, xylan, and lignin at ambient condition.

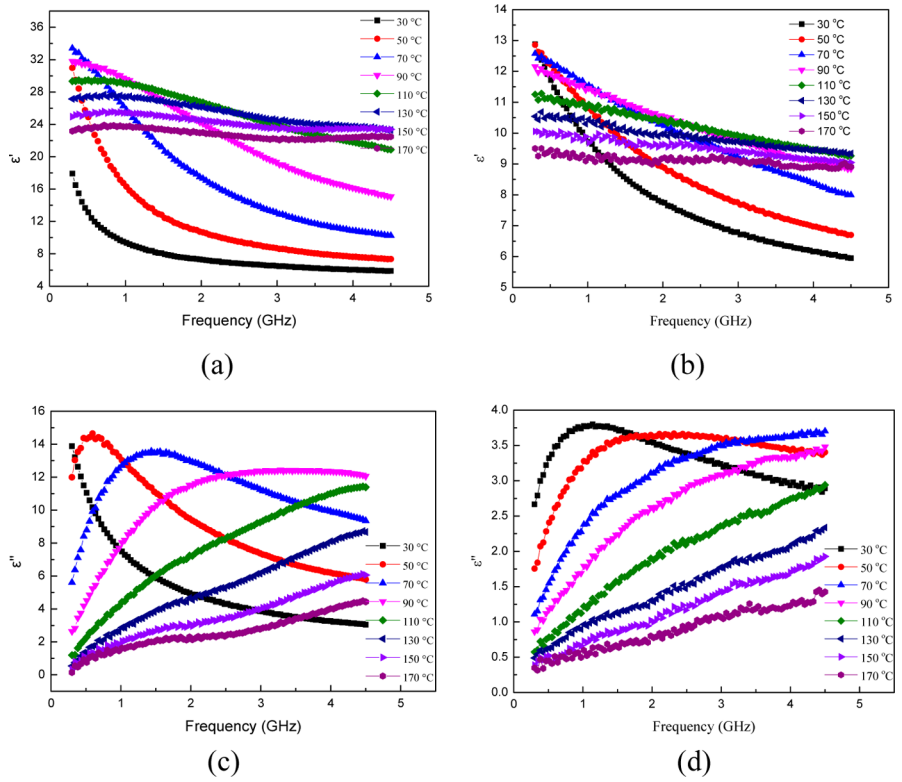

Figure 2. Frequency dependence of dielectric constants ε' of (a) glycerol, (b) PEG, and dielectric loss factors ε'' of (c) glycerol, and (d) PEG at different temperatures.

RESULTS AND DISCUSSION

Dielectric Properties of Poplar Wood and Its Three Main Chemical Components. The dielectric properties of a material are determined by its chemical composition. While the dielectric properties of individual compounds are found in the literature, the dielectric properties of more complex solid and liquid substances, particularly in mixtures with solvents, are not widely reported.[20] Values for the dielectric constant ε' and dielectric loss factor ε'' were thus determined for poplar wood particles, microcrystalline cellulose, xylan, and Kraft lignin; measurements were taken at room temperature over a frequency range from 300 MHz to 4.5 GHz (Figure 1). In general, the dielectric constant ε' and dielectric loss factor ε'' for the wood particles and the above-mentioned model compounds decreased gradually as the frequency increased.

Within the investigated frequency range, the values of both the dielectric constant ε' and dielectric loss factor ε'' were in the following order: cellulose > wood particles > xylan > lignin. This result can be rationalized by the high polarity of cellulose, having the highest number of hydroxyl groups. Specifically, cellulose is a chain polymer of D-glucose linked by β-(1 → 4)-glycosidic bonds. Each glucose monomer has three hydroxyl groups. Unlike cellulose, xylan is a highly branched polysaccharide with a backbone of D-xylose linked by β-(1 → 4)-glyosidic bonds with various substituent groups such as acetyl, glucuronic acid, and hydroxycinnamic acids;[21] with fewer hydroxyl groups, it is less polar than cellulose. Since lignin has a phenolic structure, and is the least polar among the three main chemical components of wood, it exhibits an even lower dielectric constant ε' and dielectric loss factor ε''. Finally, the ε' and ε'' of the wood particles were both intermediate among the

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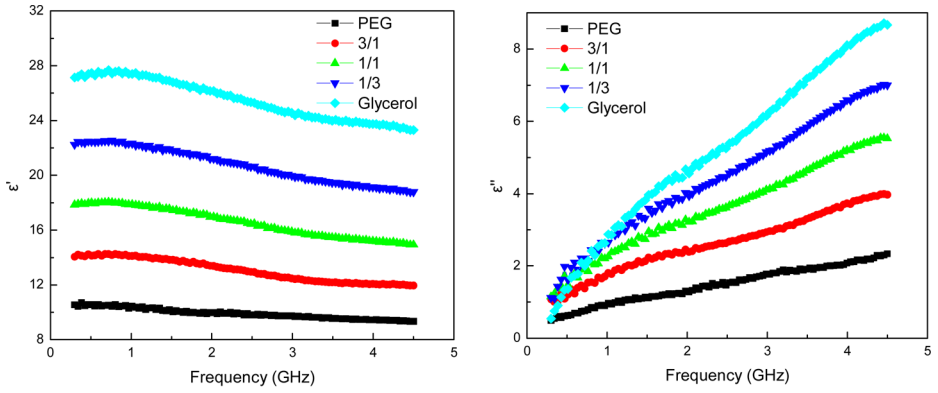

(a) (b)

Figure 3. Frequency dependence of (a) dielectric constant ε' and (b) dielectric loss factors ε'' of liquefaction solvent with different PEG/glycerol ratios at 130 °C.

three wood components but closest to the values of cellulose and xylan due to the polysaccharides comprising the bulk (ca. 70%) of poplar wood. The dielectric properties of the wood particles also confirmed that dry wood absorbs little microwave energy relative to water, having a dielectric constant ε' of 78 at 2.45 GHz under ambient temperature.[22]

Dielectric Properties of the Liquefaction Solvent Components and Mixtures. *Dielectric Properties of Glycerol and PEG.* The dielectric properties of glycerol and PEG are shown in Figure 2. It can be observed that a decreasing dielectric constant ε' for glycerol coincides with increasing frequency at all temperatures investigated (Figure 2a). For organic polar compounds such as glycerol, the dielectric heating mechanism involves dipolar polarization under microwave irradiation. Namely, the dipoles within the polar substance continuously attempt to realign themselves in the oscillating electric field produced by microwave irradiation and heat is then produced through molecular friction.[11] At lower frequency ranges, the dipoles follow the alternating electric field and are effectively polarized. Upon increasing the frequency, the dipoles are no longer able to follow the changing electric field and are not able be polarized to the same extent,[23] thus affording the observed decrease in the dielectric constant ε' with the increase in frequency.

It should also be noted that the decrease in dielectric constant ε' of glycerol, with the increase in frequency, was of a lower magnitude at the higher temperatures (Figure 2a). This could be due to the increase in the kinetic energy of the glycerol molecules at higher temperatures, which caused a faster response to the alternating electrical field. In addition, higher temperatures could force the molecules further apart, thereby reducing the viscosity of the solution and consequently enhancing the realignment process.[24] Similar trends were observed in the corresponding dielectric constant ε' plot for PEG (Figure 2b), although the decreases in ε' (with the increase in frequency) were of a lower magnitude than for glycerol, probably due to the larger molecular size of the PEG.

The dielectric loss factor ε'' of glycerol as a function of frequency, and at various temperatures, is shown in Figure 2c. In general, the dielectric loss factor ε'' increased with the increase in frequency; in some cases, it increased until it reached a maximum value and then gradually decreased. The frequency where the dielectric loss factor ε'' reaches its maximum is also defined as the relaxation frequency, and said relaxation frequency is usually related to a given temperature.[25] As the temperature increased, the relaxation frequency of glycerol moved to a higher frequency range, attributed to the decrease in the relaxation time of the molecule resulting from the faster molecular movement under higher temperatures.[26] When the frequency exceeds the relaxation frequency, the dipole motion no longer keeps in step with alternative electric fields with any further increase in frequency, reducing the dielectric loss factor ε''.[7] Similar trends for the dielectric loss factor of PEG were observed in Figure 2d.

The ε' and ε'' values of glycerol and PEG indicated that they both can be heated well under microwave irradiation. PEG has lower dielectric values than glycerol, which is mainly due to the molecular size differences.[24] Glycerol is a small molecule that enables it to rotate and realign more rapidly in changing electric fields than a much larger PEG molecule. The dielectric analysis results demonstrate that using a polyhydric alcohol (e.g., glycerol) as a liquefaction solvent component not only provides a rich source of hydroxyl groups for incorporation into the liquefied biomass, which is particularly advantageous for polyurethane production,[3] but also serves an important role as a heating medium under microwave irradiation due to its superior dielectric properties.

Dielectric Properties of Liquefaction Solvents with Different PEG/Glycerol Ratios. The liquefaction solvent of interest for the current study was a mixture of glycerol and PEG. The natural extension of determining the dielectric properties of the two solvent components was to then determine the dielectric properties of the two components together, in different ratios, as the liquefaction solvent; the dielectric constants ε' and dielectric loss factors ε'' shown in Figure 3 were determined at 130 °C, a temperature routinely used for woody biomass liquefaction. All solvent mixtures displayed similar trends in ε' and ε''. The dielectric constant ε' decreased with increased frequency due to lower polarizability of the dipoles under high frequency. The dielectric loss factor ε'' increased along with frequency before the relaxation frequency (discussed above) was reached. It is noteworthy that all of the PEG/glycerol ratios that were measured (i.e., 3/1, 1/1, 1/3) had ε' and ε'' values between those of the pure PEG and glycerol.

To further understand the effect of each component on the dielectric properties of the solvent mixtures, the contributions of PEG and glycerol to the dielectric constant ε' of each solvent

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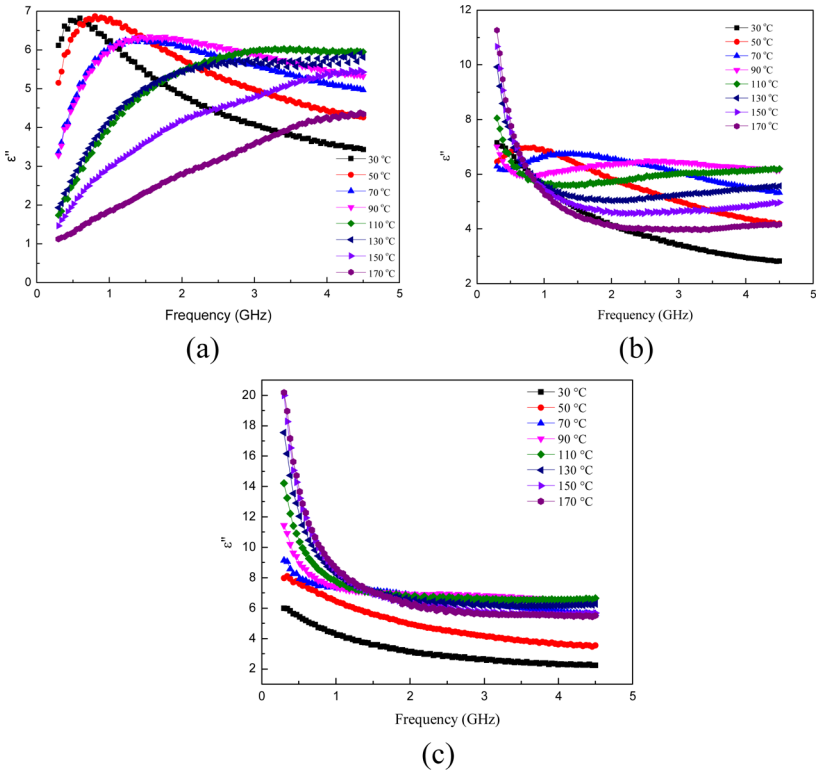

Figure 4. Frequency dependence of dielectric loss factor ε'' of (a) liquefaction solvent, (b) liquefaction solvent with 1.5 wt %, and (c) 3.0 wt % sulfuric acid.

mixture were calculated using equations adapted from those reported in the literature:[7]

$$C'_{\mathrm{PEG}} + C'_{\mathrm{glycerol}} + C'_{\mathrm{interaction}} = 100\% \quad (2)$$

where C'_{PEG} and C'_{glycerol} are the contributions of PEG and glycerol, respectively, and $C'_{\mathrm{interaction}}$ is the contribution of the interaction of PEG and glycerol.

The C'_{PEG} and C'_{glycerol} can be further expressed as

$$C'_{\mathrm{PEG}} = \frac{\varepsilon'_{\mathrm{PEG}}}{\varepsilon'_{\mathrm{solvent}}} \quad (3)$$

$$C'_{\mathrm{glycerol}} = \frac{\varepsilon'_{\mathrm{glycerol}}}{\varepsilon'_{\mathrm{solvent}}} \quad (4)$$

where $\varepsilon'_{\mathrm{PEG}}$, $\varepsilon'_{\mathrm{glycerol}}$, and $\varepsilon'_{\mathrm{solvent}}$ are the measured dielectric constant ε' of PEG, glycerol, and the solvent mixture, respectively.

The contributions of each component on the dielectric loss factor ε'' of the liquefaction solvent can be also expressed by analogous equations as follows:

$$C''_{\mathrm{PEG}} + C''_{\mathrm{glycerol}} + C''_{\mathrm{interaction}} = 100\% \quad (5)$$

$$C''_{\mathrm{PEG}} = \frac{\varepsilon''_{\mathrm{PEG}}}{\varepsilon''_{\mathrm{solvent}}} \quad (6)$$

$$C''_{\mathrm{glycerol}} = \frac{\varepsilon''_{\mathrm{glycerol}}}{\varepsilon''_{\mathrm{solvent}}} \quad (7)$$

where C''_{PEG} and C''_{glycerol} are the contributions of PEG and glycerol, respectively; $C''_{\mathrm{interaction}}$ is the contribution of the interaction of PEG and glycerol; $\varepsilon''_{\mathrm{PEG}}$, $\varepsilon''_{\mathrm{glycerol}}$, and $\varepsilon''_{\mathrm{solvent}}$ are the measured dielectric loss factor ε'' of PEG, glycerol, and the solvent mixture, respectively.

The calculated contributions of each component to the dielectric properties of each liquefaction solvent showed that C'_{glycerol} increased and C'_{PEG} decreased as temperature increased (Figure S1). Moreover, C'_{glycerol} was always higher than C'_{PEG}. This result was consistent with that from Figure 2, which showed that glycerol has a higher dielectric constant ε' than PEG for each applied condition of temperature and frequency. The component contributions to the dielectric loss factor ε'' showed a similar trend as dielectric constant ε' except for that C''_{glycerol} decreased, with both frequencies (915 and 2450 MHz), when the temperature increased above 150 °C (Figure S1). This was due to the decrease in the dielectric loss factor ε'' of glycerol at higher temperature. The above results indicated that for a binary liquid mixing system, the component which has higher ε' and ε'' dominates the dielectric properties of the solvent mixture.

Effect of Sulfuric Acid Catalyst on Dielectric Properties of the Liquefaction Solvent. Dielectric heating involves two heating mechanisms: dipolar polarization and ionic conduction. For dipolar polarization, the dipoles within the polar substance continuously attempt to realign themselves in the oscillating electric field produced by microwave irradiation, with heat then produced through molecular friction; in the case of ionic conduction, charged ions change direction in the oscillating electric field and induce collisions that convert kinetic energy into heat energy.[11] Adding an acid catalyst such as sulfuric acid to the nonconductive PEG/glycerol solvent mixture may therefore affect the dielectric properties of the resulting liquefaction solvent. It is known that ionic conduction does not contribute to the polarization of the nonconductive medium but instead generates energy loss via heating.[7] In

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other words, adding an acid catalyst would mostly affect the dielectric loss factor ε'' other than the dielectric constant ε' of the resulting liquefaction solvent.

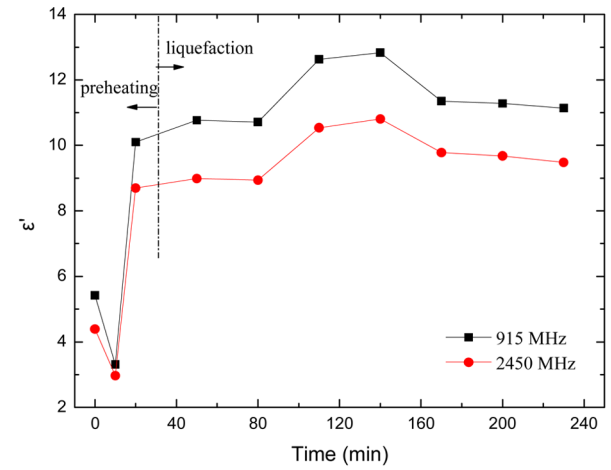
Figure 4 shows the frequency dependence of the dielectric loss factor ε'' for the PEG/glycerol solvent mixture (7/3, w/w) with (Figure 4b and c) or without (Figure 4a) added sulfuric acid (1.5 vs 3.0%, w/w). The liquefaction solvent without sulfuric acid displayed a typical relaxation frequency peak as expected with dipolar polarization alone (see also Figure 2c); however, the dielectric lost factors ε'' of the liquefaction solvents with sulfuric acid exhibited completely different trends.

It should be noted that the dielectric loss factor ε'' for each liquefaction solvent mixture, with acid catalyst, was highly temperature dependent. It seemed plausible that a temperature or viscosity "barrier" limited the movement of the ions, thus the liquefaction solvent mixture displayed a dipolar polarization character at low temperatures, specifically with the lower (1.5%) acid content (see curves measured at 30, 50, and 70 °C in Figure 4b). When the apparent temperature or viscosity "barrier" was surpassed, the acid ions in the solvent mixture could move to a greater extent with the alternating electric field, thus giving higher dielectric loss factors ε''. Similar results were reported in the literature.[26]

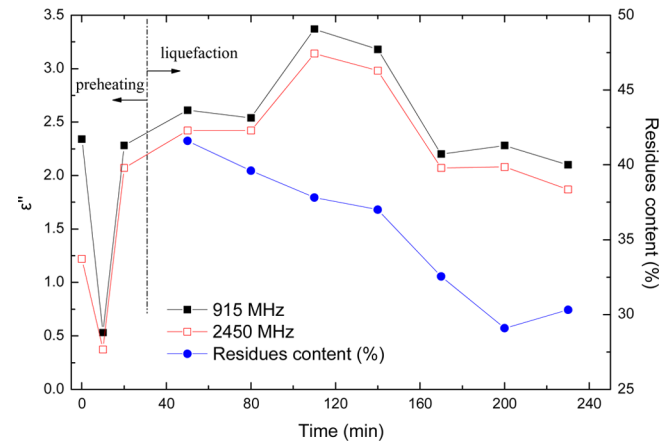
For the dielectric loss factors ε'' measured at higher temperatures, they decreased rapidly within the low frequency range (<2 GHz), and then gradually increased with an increase in the frequency. Such a "twist" pattern in a given dielectric loss factor ε'' curve would likely be due to the presence of both dielectric heating mechanisms in the medium.[7,27] At a low frequency range, ionic conduction is the dominant mechanism,[27] thereby impacting the dielectric loss factor ε'' to a greater extent than any dipolar polarization. For example, a 0.5 M NaCl solution has an ε'' of 269 at 1 GHz, while distilled water has an ε'' of 3.98 at 915 MHz.[27] Therefore, significantly higher ε'' values were observed at a lower frequency range than those at a higher frequency, the latter being governed by dipole polarization mechanism.[7] Comparing the ε'' values of the solvent mixtures with and without sulfuric acid, it would appear that even the addition of a small amount of sulfuric acid could drastically increase the ε'' of the liquefaction solvent due to the greater effect from ionic conduction over any dipolar polarization.

Dynamic Dielectric Properties of the Liquefaction System. The dielectric properties of reaction mixtures are very complicated, especially for heterogeneous systems, and they can be affected by many factors such as temperature, density, frequency, composition, etc.[20] The liquefaction of woody biomass is a particularly complicated reaction that involves the thermochemical degradation of varying amounts of the three main chemical components of wood, being cellulose, hemicellulose, and lignin.[28] As liquefaction progresses, the reaction system might contain numerous reaction intermediates and products, with the reaction mixture composition continuing to change until liquefaction is terminated. A further complication is that the liquefaction of woody biomass involves a phase change starting with solid wood particles that will undergo partial or complete liquefaction; in both cases, this affords increasing amounts of organic derivatives dissolved within the liquefaction solvent. The amount of solid residue in the viscous liquid product depends on the liquefaction conditions and is an indicator of liquefaction completeness. Therefore, in addition to frequency and temperature, the dielectric properties of the liquefaction system is also affected by the phase change and dynamic composition of the reaction system.

Time Dependence of Dielectric Properties for Reaction Mixture during Liquefaction. The dielectric properties of the reaction mixture during the liquefaction of poplar wood particles at 130 °C are shown in Figure 5. The liquefaction process can be divided into two stages, shown by a line on each plot, namely, the preheating (room temperature to 130 °C) and liquefaction stages (130 °C to the end of the reaction). The dielectric properties of the reaction system exhibited similar trends under two frequencies used (915 and 2450 MHz), in which both the dielectric constant ε' and dielectric loss factor ε'' of the reaction system were generally lower during the preheating stage than during the later liquefaction stage. This result reflects the heterogeneous phase of the liquefaction system during the preheating stage. At the onset of the liquefaction reaction, it is unlikely that the liquefaction solvent had significantly penetrated the wood particles because of its high viscosity at near-ambient temperatures. The initial ε' and ε'' values of the liquefaction mixture were therefore similar to those of the liquefaction solvent alone, that being a better



(a)



(b)

Figure 5. Time dependence of (a) dielectric constant ε' and (b) dielectric loss ε'' of liquefaction reaction mixture during the liquefaction process at 915 and 2450 MHz (PEG/glycerol: 7/3, w/w; sulfuric acid content: 1.5 wt %; solvent/wood: 3/1, w/w; reaction temperature: 130 °C).

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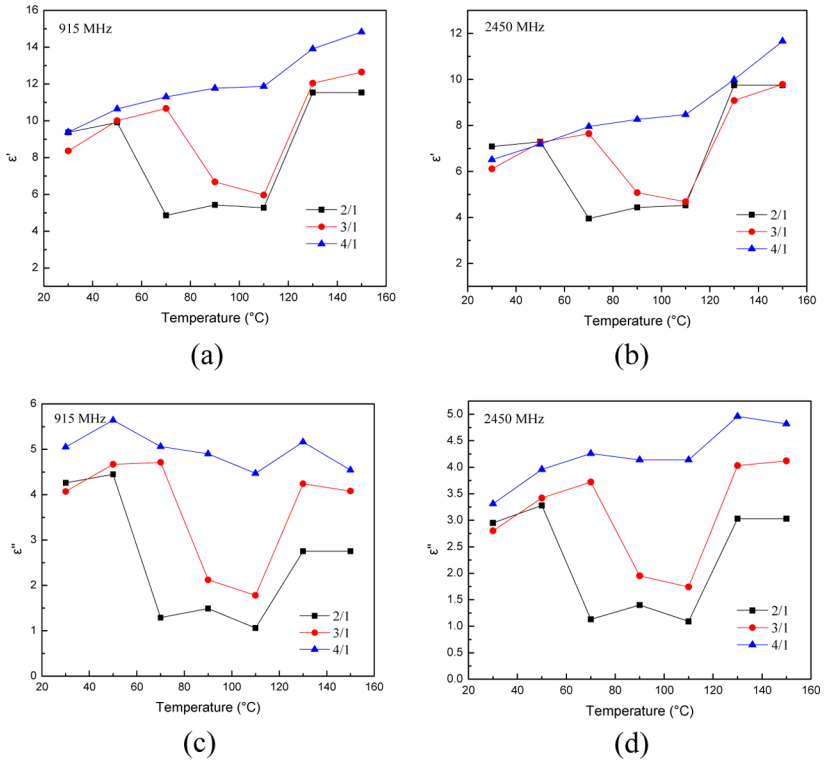

Figure 6. Temperature dependence of (a, b) dielectric constants ε' and (c, d) dielectric loss factors ε'' of liquefaction systems with different solvent/wood ratios at 915 and 2450 MHz (catalyst content: 1.5 wt %).

microwave absorber than the wood particles. As the liquefaction system was heated, liquefaction solvent would have diffused into the wood particles, thereby resulting in a decrease in the dielectric properties. The ε' and ε'' reached the minimum values around 10 min with the temperature of the reaction system being at approximately 110 °C. As the reaction proceeded, and system temperature further increased, the ε' and ε'' rapidly increased. This can be attributed to the higher kinetic energy of the dipoles within the liquefaction system under higher temperature and consequently led better alignment of the dipoles with alternating electric field. In addition, the ionic conduction mechanism may have also played an important role to increase the ε' and ε'' given the fact that the wood particles begin to liquefy when the temperature of the reaction mixture reaches 120 °C. The degradation of woody biomass produces carboxylic acids as well as H_2O,[29,30] which could increase the conductivity of the liquefaction system.

As the temperature of the system became steady (130 °C, 30 min), the ε' and ε'' values reached a plateau in the liquefaction phase except for a transient increase as the reaction time progressed from 80 to 160 min. This transient increase was attributed to the changes in composition of the liquefaction mixture during the reaction. Specifically, it is known that during the early stages of woody biomass liquefaction, depolymerizations of the wood components dominate the reactions. The resultant carboxylic acid, ester, and other polar compounds are likely to increase the polarizability and conductivity of the reaction mixture, leading to increases in the dielectric values. As liquefaction proceeds, condensation and repolymerization of some intermediate products can occur. This would lead to a decline in the presence of polar substances, especially those compounds with hydroxyl groups. Previous research has reported that the hydroxyl number of the reaction mixture decreased during liquefaction, which could be attributed to various alcoholysis, dehydration, esterification, etherification, and condensation reactions occurring during liquefaction.[31] Toward the termination of the liquefaction reaction, the dielectric properties of the liquefaction system became steady except for a slightly decline in ε'', indicating the liquefaction reaction might have reached a relative equilibrium.

Although the dielectric properties varied during the liquefaction process, the residue content, a parameter indicative the extent of the liquefaction reaction, showed a relatively steady decline (Figure 5b). It is well known that thermal decomposition of wood components, and condensation of decomposed fragments, occur simultaneously during the liquefaction process.[32] The decrease in residue content demonstrated continued liquefaction of the wood components until the reaction time reached 200 min. Thereafter, condensation and repolymerization of the liquefied products predominated, as shown by reversal in residue content. The slight decrease in the dielectric properties of the reaction system is attributed to the decrease in polar compounds from the aforementioned condensation and repolymerization reactions.

An understanding of the dynamic nature of the dielectric properties of a reaction system is essential for the safe scale-up of a microwave heating system because abrupt changes of ε' and ε'' may cause erratic variations in temperature in the system, impacting the quality of the reaction products and/or creating conditions that could cause equipment damage. The dynamic dielectric properties of this liquefaction system did vary significantly along the reaction process; however, the ε' and ε'' values of the liquefaction system were lower than those of the liquefaction solvent alone. In addition, at a fixed frequency, the dielectric properties of the liquefaction system

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were affected by two different factors at two stages. During the preheating process, temperature was the main factor that governed the dielectric properties of the liquefaction system, while the composition of the liquefaction system dominated when the system reached 130 °C.

Effects of Mass Ratio of Solvent/Wood on Dielectric Properties. Figure 6 shows the temperature-dependent dielectric properties of the liquefaction system with different solvent/wood ratios (w/w). The liquefaction system with solvent to wood ratios of 2/1 and 3/1 displayed similar trends with the values of ε' and ε'' showing a transient drop within an intermediate temperature range, between 50 to 130 °C (solvent/wood ration = 2/1) or 70 to 130 °C (solvent/wood ration = 3/1). The decreases in ε' and ε'' are likely due to the diffusion of liquefaction solvent into wood particles, with the wood itself having relatively low dielectric properties. The subsequent increase of the ε' and ε'' can be attributed in part to the increasing kinetic energy of the dipoles with increased temperature. Coinciding with this, aforementioned depolymerizations of the wood components would also contribute to the increased dielectric properties of the liquefaction system via ionic conduction under higher temperature.

With the liquefaction system having solvent to wood ratio of 4/1, the dielectric properties showed greater similarity to liquefaction solvent (Figure 2), although the values of ε' and ε'' were still lower than those of the liquefaction solvent alone due to the presence of wood particles. This liquefaction system also showed an increase in ε' and ε'' at a temperature near 110 °C. This can also be attributed to the ionic conduction heating mechanism, occurring with the depolymerizations of wood components, with the liquefaction system changing from solid/liquid mixture to a viscous liquid as liquefaction progressed. In general, the dielectric properties of liquefaction systems with low solvent to wood ratios would be more susceptible to the phase changes than those with high solvent to wood ratio.

Penetration Depth. The penetration depth of microwave energy into the reaction mixture during liquefaction is illustrated in Figure 7. This is an essential factor for the scale-up of the microwave heating system and exploring the distribution of the microwave energy in the material.[15] The penetration depths of the microwave energy at frequencies of 915 and 2450 MHz peaked at temperatures between 70 and 130 °C. The maximum penetration depth was observed at 110 °C (10.2 cm at 915 MHz and 3.5 cm at 2450 MHz). It was observed that the range of temperatures for the higher penetration depths overlapped with the range of temperatures for the phase transition in the liquefaction system, specifically when the liquid/solid mixture transformed into a viscous liquid between 90 to 110 °C. It has been reported that large values of ε' and ε'' will result in surface heating and low penetration depth.[33,34] At the initial liquefaction stage, most liquefaction solvent was not able to penetrate into wood particles and remained "free" in the system. Therefore, the liquefaction system had high ε' and ε'' values close to that of the liquefaction solvent. The penetration depth of the reaction mixture at this stage would be expected to be low. When temperature increased, liquefaction solvent gradually diffused into the wood particles, and the ε' and ε'' values of the liquefaction system decreased and close to that of the wood. The maximum penetration depth for the liquefaction system was observed at the lowest ε' and ε'' values. The significant higher penetration depth at 915 than that at 2450 MHz is due to the longer wavelength of the microwave at 915 MHz. This is also the reason that 915 MHz is always chosen in large-scale industrial treatment.

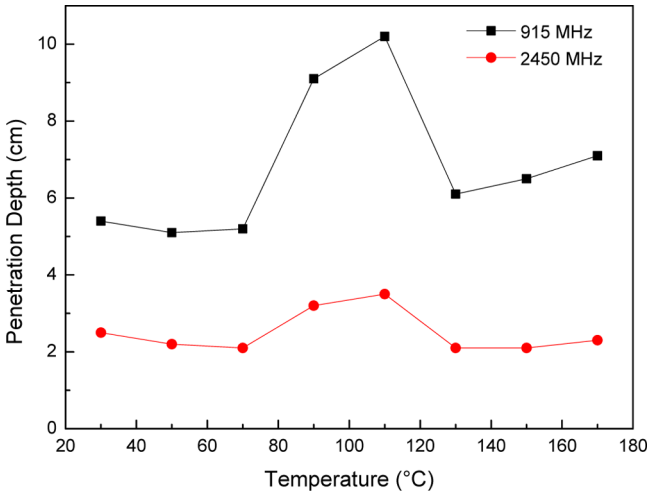

Figure 7. Temperature dependence of microwave penetration depth into the reaction mixture during liquefaction at 915 and 2450 MHz (solvent/wood: 3/1; acid concentration: 1.5 wt %).

CONCLUSIONS

Highly polar polyhydric alcohols can function not only as liquefaction solvents but also as a microwave absorbers due to their excellent dielectric properties. The dielectric properties of a binary liquefaction solvent PEG/glycerol mixture were dominated by those of glycerol, owing to its higher ε' and ε'' values. The addition of sulfuric acid mostly affected the dielectric loss factor ε'' of the liquefaction solvent via the ionic conduction heating mechanism. During the liquefaction process, the dynamic dielectric property of the liquefaction system was mainly affected by the phase change and dynamic compositions of the reaction system.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b02447.

Contribution of the components on dielectric constants ε' and dielectric loss factors ε'' of mixed liquefaction solvent (Figure 1S). (PDF)

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Notes

The authors declare no competing financial interest.

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