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Cleaving the β–O–4 Bonds of Lignin Model Compounds in an Acidic Ionic Liquid, 1-H-3-Methylimidazolium Chloride: An Optional Strategy for the Degradation of Lignin

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The hydrolysis of β–O–4 bonds in two lignin model compounds was studied in an acidic ionic liquid, 1-H-3-methylimidazolium chloride. The β–O–4 bonds of both guaiacylglycerol-β-guaiacyl ether and veratrylglycerol-β-guaiacyl ether underwent catalytic hydrolysis to produce guaiacol as the primary product with more than 70% yield at 150 °C. Up to 32 wt% substrate concentration could be treated in the system without a decrease in guaiacol production. The ionic liquid could be reused without loss of activity in guaiacol production from both guaiacylglycerol-β-guaiacyl ether and veratrylglycerol-β-guaiacyl ether. A possible mechanism accounting for the guaiacol production is presented.

Introduction

The use of renewable feedstocks by the chemical industry has the potential to replace petroleum-based feedstocks, possibly extending petroleum reserves and reducing the carbon footprint of a process or product.[1] Second and third generation biofuel production that is based on cellulosic feedstocks will require treating biomass to depolymerize the lignin and release the cellulosic fraction. It is generally accepted that lignin degradation is a rate-limiting step in lignocellulose degradation.[2] Lignin acts as the essential glue that gives plants their structural integrity and is a main constituent of lignocellulosic biomass (15–30% by weight, 40% by energy), together with cellulose and hemicelluloses.[3] However, lignin has received less attention relative to cellulose and hemicelluloses in the biorefinery of biomass. Lignin is rich in benzene rings, therefore, some aromatic chemical compounds, such as vanillin, may be obtained from lignin.[4,5] Moreover, the transformation of lignin has potential to produce fuels.[6]

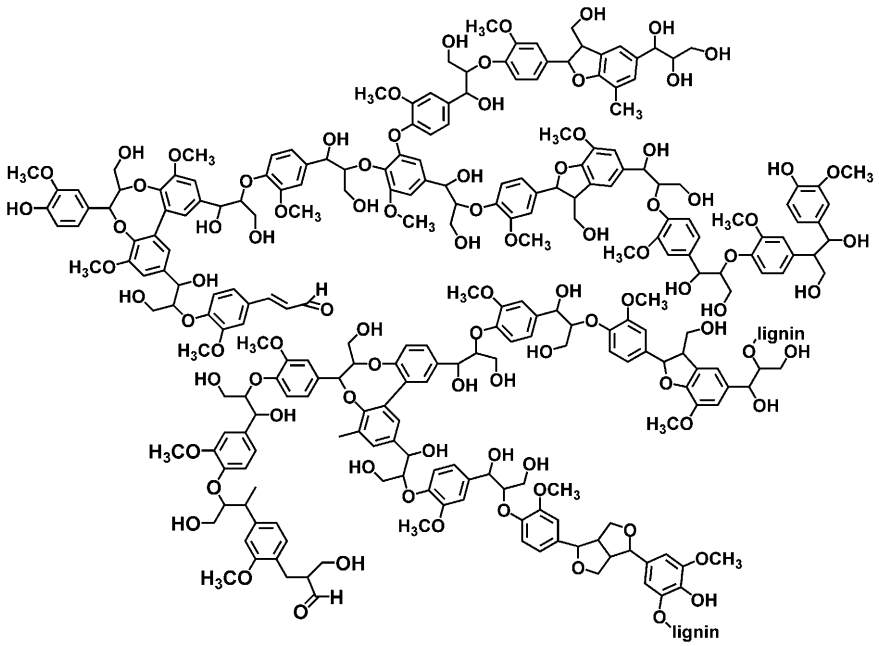

Figure 1. General structure of lignin.[5]

Lignin is a natural amorphous polymer with a very complex structure (Figure 1), which is degraded inefficiently at present and generally burned (energetic utilization) in the course of recovery of chemicals in kraft pulping.[7,8] Lignin is mainly composed of phenylpropane monomers that link together primarily through the C–O linkage of α- and β-ether bonds.[9] The β–O–4 linkage is found to be dominant, representing approximately 50% among all the linkages in lignin;[8,10] therefore, effi-

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ciently cleaving the β–O–4 linkage could be an optional strategy for the degradation of lignin while preserving the aromatic character of the fragments.

Acid and base-catalyzed routes to lignin depolymerization are known; these fundamental processes involve strong acids, caustic alkali, sulfocompounds and volatile toxic solvents that can have negative effects on the environment. Kraft pulping, a common process for the depolymerization of lignin, mainly employs NaOH and NaSH (or anthraquinone) to cleave the β-ether bonds in lignin.[9,11] Acid-catalyzed hydrolysis is another method for cleaving the β-ether bonds of lignin.[12] Studies on the hydrolysis of β-ether bonds in phenylpropane dimer model compounds have been carried out with hydrochloric acid or $AlCl_3$ as the catalyst in dioxane–water or ethanol–water solvents.[13,14]

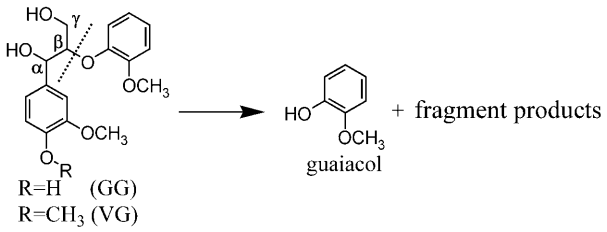
Ionic liquids (ILs) have attracted much attention as a medium for biomass conversion, primarily in the conversion of carbohydrates.[15–17] However, few studies report on the reactivity of lignin in ILs. Recently, ILs have been found to be a direct wood pulp solvent capable of solubilizing lignocelluloses.[18–21] Guaiacylglycerol-β-guaiacyl ether (GG) is commonly employed as a model compound for the phenolic β–O–4 ether linkages in lignin. Recently, Kubo et al. found that an enol ether (EE), 3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxy-phenoxy)-2-propenol, was the primary decomposition product from GG in dialkylimidazolium chloride and acetate ILs.[22] However, EE essentially is a dehydration product from GG, which implies these ILs did not cleave the β–O–4 bond. Binder et al. reported the dealkylation of alkyl substituted 2-methoxyphenols, which served as lignin model compounds, in a variety of ILs and realized up to 11.6% yield of the dealkylation product.[23] However, the high concentration of C–O bonds in lignin suggests cleaving these bonds, especially the β–O–4 bonds, is a more viable degradation strategy. Due to the complex chemical structure of lignin, one has to recognize the limitations of extrapolating results with simple model compounds featuring the β–O–4 bond to lignin. Nonetheless, model compounds, such as employed herein, facilitate understanding lignin chemistry.

Moreau et al. reported 1-H-3-methylimidazolium chloride ([HMIM]Cl) acted as both solvent and catalyst for the dehydration of sugars.[24] Since [HMIM]Cl is an easily synthesized and low-cost acidic IL from the BASIL technology,[25] and a non-volatile IL, we explored its potential as the acid catalyst for the hydrolytic cleavage of β–O–4 linkages common in lignin. Herein, we report initial results on the cleavage of β–O–4 bonds in both phenolic and non-phenolic lignin model compounds in [HMIM]Cl.

Results and Discussion

Cleavage of β–O–4 bonds in lignin model compounds

GG, a common dimeric lignin model compound, is employed for phenolic lignin units featuring the β–O–4 bond. Because guaiacol is liberated after the β–O–4 bond of GG is hydrolyzed (Scheme 1), guaiacol yield was monitored to track β–O–4 bond cleavage. Water is ubiquitous in hydroscopic systems



Scheme 1. The cleavage of β–O–4 bond of lignin model compounds.

and it is needed for the hydrolysis reaction, so a controlled amount of water was added at a level that led to approximately 2 wt% H_2O. The C–2 protons of 1,3-disubstituted imidazolium cations are acidic,[26,27] therefore, two ILs, 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) and 1-butyl-2,3-dimethylimidazolium chloride ([BdMIM]Cl, a C–2 substituted IL) were employed to test the effect of the C–2 proton. After GG (8 mg) and H_2O (2.25 μL) were heated at 130 °C for 120 min in 100 mg of [BMIM]Cl or [BdMIM]Cl, less than 5% GG conversion was observed. No guaiacol was detected by HPLC; a trace amount of EE was detected by HPLC and verified by NMR spectroscopy. Although a controlled amount of H_2O was added into our system, the results are consistent with the low EE yield that was reported in [BMIM]Cl after 180 min at 120 °C,[22] which indicates the C–2 proton has no effect on the GG conversion and hydrolysis of the β–O–4 bond.

Figure 2a presents the results of reacting GG in [HMIM]Cl at various temperatures, in which GG (8 mg) and H_2O (2.25 μL) were added into [HMIM]Cl (100 mg) for each experimental run. GG was effectively cleaved at temperatures as low as 110 °C, producing guaiacol in [HMIM]Cl. The guaiacol yield increased with reaction temperature, reaching 71.5% at 150 °C after 60 min. At the higher temperatures, the guaiacol yield curves displayed a maximum, possibly because guaiacol underwent subsequent reactions.[28] The GG conversion was essentially 100% in all the experimental runs (Figure 2a) except after 15 min at 110 °C, for which the GG conversion was 68.4%, and 6% yield of EE was detected. EE was not detected at longer times or higher temperatures.

In general, lignin consists of more etherified phenylpropane units, so we used veratrylglycerol-β-guaiacyl ether (VG) as a non-phenolic lignin model compound. The phenolic lignin model compound, GG, is considered to be more reactive. As illustrated in Figure 2b, the β–O–4 bond of VG was cleaved as steadily as GG at 150 °C. The guaiacol yield was similar to that from GG and decreased a little after 120 min. The VG conversion also exhibited the same pattern as GG with essentially 100% conversion in all the experimental runs. Both GG and VG were converted rapidly into intermediate products, some of which reacted to guaiacol (see below).

Acid-catalyzed hydrolysis of GG and VG should also produce Hibbert's ketones.[12,29] Figure 3 shows the FTIR spectra of GG, VG, and guaiacol. The absorbance around 3400–3500 cm^{-1} is associated with the hydroxyl group vibrational stretching modes for the three compounds; symmetric and asymmetric

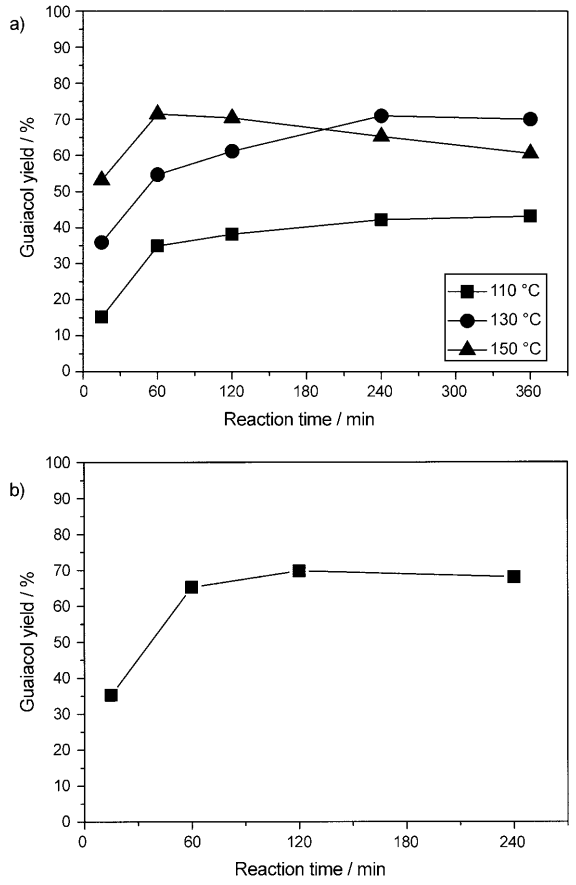


Figure 2. a) The effect of reaction temperature on cleavage of the β–O–4 bond of GG; b) cleavage of the β–O–4 bond of VG at 150 °C.

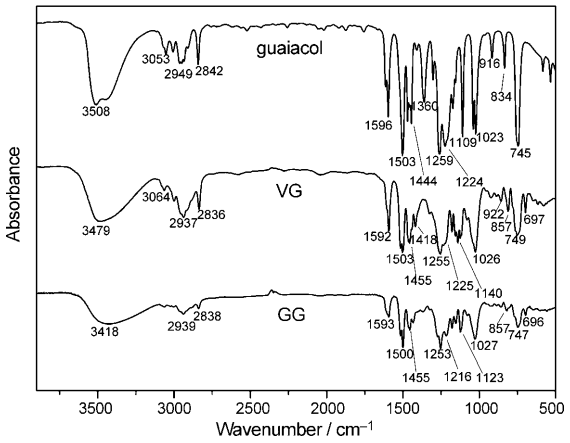


Figure 3. The FTIR spectra of GG, VG, and guaiacol.

C–H modes produce the absorbances between 2800–3000 cm^{-1}; absorbance bands around 1593 cm^{-1} and 1500 cm^{-1} are characteristic of aromatic rings; and absorbances at 1253 (1255 for VG) cm^{-1} and 1027 (1026 for VG) cm^{-1} are the C–O vibrational stretching bands. After the reaction of GG and VG in [HMIM]Cl at 150 °C for 60 min, the product mixtures were extracted by ethyl ether, and ethyl ether was removed before the FTIR test. As illustrated in Figure 4, the FTIR spectra of the product mixtures from GG and VG retained many of the same absorbance features as Figure 3 except for

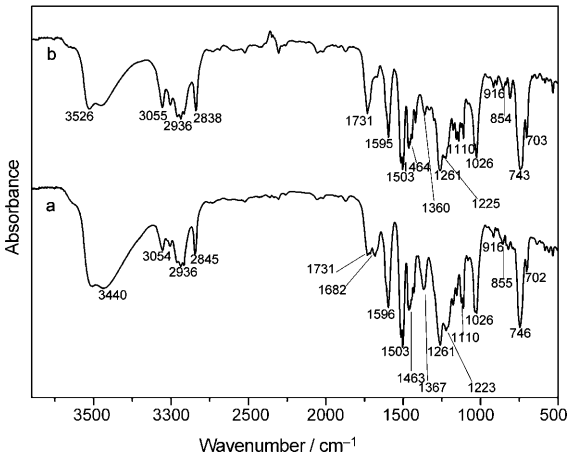


Figure 4. The FTIR spectra of a) product mixture from GG, b) product mixture from VG.

the absorbance around 1731 cm^{-1}, which is the characteristic stretching mode for the C=O bond and implies a ketone or aldehyde was produced. These results are consistent with previous work,[12,29] in which Hibbert's ketones were formed by the acid-catalyzed hydrolysis of GG and VG. The absorbance at 1682 cm^{-1} may result from the conjugate effect between the C=O bond and the benzene ring after the isomerization of Hibbert's ketones.[12,30]

The product mixtures were also monitored by LC–MS. When GG was tested, we found two LC peaks that had a strong $(m+H)^+/z$ of 197 in the MS. (see the Supporting Information, Figure S1). This LC–MS species is associated with Hibbert's ketones,[12,29,30] which are companion products from GG after elimination of guaiacol. When VG was tested, two LC peaks with $(m+H)^+/z$ of 211 were detected in the MS (see the Supporting Information, Figure S2), which are possibly etherified Hibbert's ketones from VG. The Hibbert's ketones were not established quantitatively.

The use of dilute solutions for the conversion of biomass may limit the efficacy of the process. A more desired approach would allow the processing of highly concentrated liquids to minimize the solvent volume and concentration steps associated with solvent removal.[31] In this work, the effect of substrate concentration was also tested by increasing the amount of GG (or VG) from 8 wt% to 32 wt%. As illustrated in Figure 5a, after the system of GG (or VG) and water (molar ratio 5:1 to GG or VG) in 100 mg [HMIM]Cl was heated at 150 °C for 60 min, the guaiacol yield was reasonably constant at about 70% and about 65% for GG and VG, respectively.

Both GG and VG were used in tests to measure the effect of water concentration on the yield. These experiments were run at 150 °C for 60 min with GG (8 mg) or VG (8.4 mg) and [HMIM]Cl (100 mg), with different amounts of water. As illustrated in Figure 5b, at a molar ratio of 5:1, the yield of guaiacol

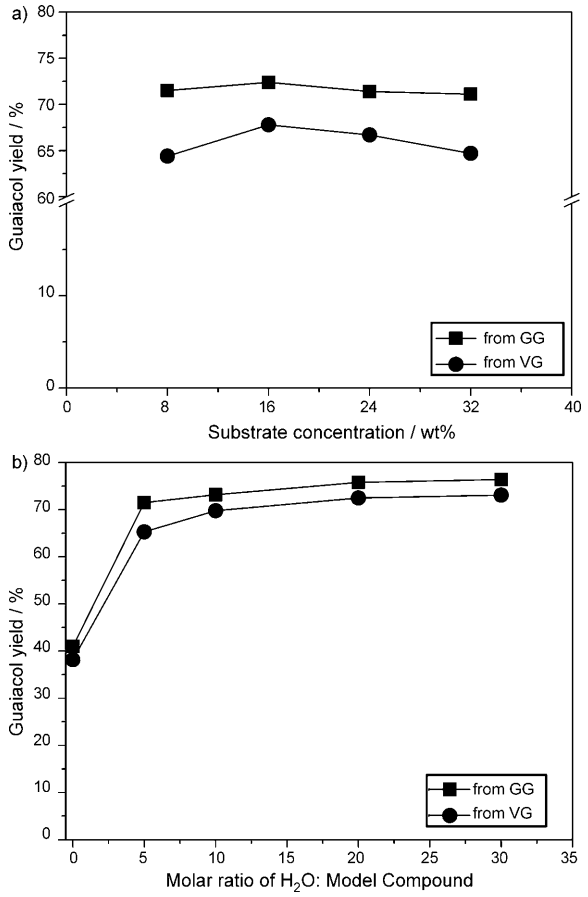


Figure 5. a) The effect of substrate concentration on cleavage of the β–O–4 bonds of GG and VG; b) the effect of water concentration on cleavage of the β–O–4 bonds of GG and VG.

was 71.5 and 65.3% from GG and VG, respectively. When the water was increased to a 30:1 ratio, the guaiacol yield from GG and VG was 76.4 and 73.1%, respectively, while the yield dropped to 41.0 and 38.2% from GG and VG, respectively, when no water was added. A small but significant increase in β–O–4 bond cleavage results from an increase in available water. As the water is removed, the guaiacol yield drops because the hydrolysis does not occur without water present. The reaction is not completely stopped by removal of water, because the possible dehydration of lignin model compounds produces water, which then can hydrolyze the β–O–4 bonds.[12,22]

Figure 6 presents the results of recycling [HMIM]Cl for β–O–4 bond cleavage of GG and VG. After reacting GG (8 mg) or VG (8.4 mg) and H_2O (2.25 μL) in [HMIM]Cl (100 mg) at 150 °C for 60 min, the products were extracted at 100 °C by successively adding methylisobutylketone (MIBK) 10 times, using MIBK (0.6 mL) each time. After the extraction, the appropriate amounts of GG (or VG) and H_2O were added into the [HMIM]Cl directly and without extra treatment. The guaiacol yields changed less than 3% in subsequent runs, which may indicate it is feasible to recycle the IL without loss of activity.

The separation conditions employed for the recycle tests were not optimized and some loss of [HMIM]Cl and cross contamination occurred. In six parallel control experiments,

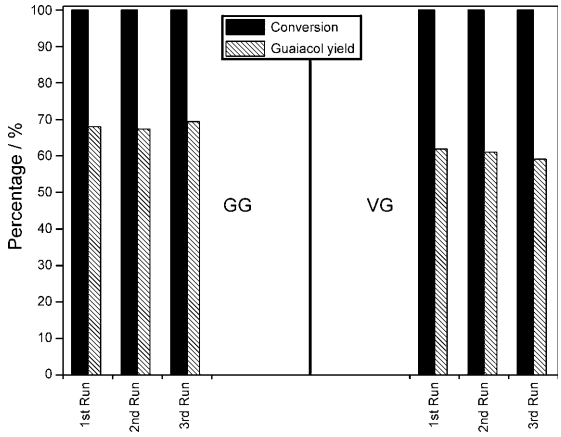


Figure 6. Recycling tests on cleavage of the β–O–4 bonds of GG and VG in [HMIM]Cl.

[HMIM]Cl was contacted with MIBK using the procedure listed above. The average residue of MIBK was 7.3 mg in per 100 mg [HMIM]Cl after the extraction. After removing the solvent by vacuum, the loss of [HMIM]Cl was 1.3 mg per 100 mg. The MIBK was tested by adding an indicator (methyl orange) and did not show to be acidic.

The hydrolysis of the β–O–4 bonds of GG and VG was also carried out in a high boiling solvent, dimethylsulfoxide (DMSO), in combination with HCl. The amount of HCl was chosen at a catalytic amount and was somewhat arbitrary. The hydrolysis of GG and VG was expected.[13,14] As can be seen in Table 1, after heating GG (or VG) and H_2O in DMSO with HCl (10 mol% to GG or VG) as the catalyst at 150 °C for 60 min, 55.2% guaiacol yield was observed from GG with 100% GG conversion while 17.7% guaiacol yield was observed from VG with 61.3% VG conversion. The guaiacol yield from VG increased to 39.1% with 93.8% VG conversion when reaction time was increased to 120 min. Higher HCl concentration (Table 1, entries 2, 4, and 6) appears to have a minor effect on the hydrolysis of GG and VG. The lower guaiacol yield at 100% conversion as compared to that in [HMIM]Cl implies more undesired reactions happened in DMSO under the conditions ex-

Table 1. The results on cleavage of the β–O–4 bonds of GG and VG in DMSO with HCl as the catalyst.

Entry	Lignin model compound	Time [min]	Conversion [%]	Guaiacol yield [%]
1[a]	GG	60	100.0	55.2
2[b]	GG	60	100.0	57.0
3[a]	VG	60	61.3	17.7
4[b]	VG	60	66.2	19.4
5[a]	VG	120	93.8	39.1
6[b]	VG	120	100.0	40.3

[a] Lignin model compound (0.025 mmol) and H_2O (0.125 mmol) were added into DMSO (100 mg) with HCl (10 mol% to lignin model compound) and heated at 150 °C. [b] Lignin model compound (0.025 mmol) and H_2O (0.125 mmol) were added into DMSO (100 mg) with HCl (20 mol% to lignin model compound) and heated at 150 °C.

plored herein. Further, a more complex process is necessary for the separation and purification of products from DMSO, which could increase the production costs. In contrast, an IL approach will likely have advantages in this case, such as distillation or successive extraction by organic solvents from the ionic liquid phase.

Acid catalysis is a common treatment that is widely used in biomass transformation, such as the hydrolysis and depolymerization of cellulose,[32–36] and the conversion of sugars.[15,37–39] The work reported herein employs an acidic IL to treat model compounds that have the β–O–4 bond common in lignin. Additional studies are required to establish the potential for acidic IL as catalysts for lignin depolymerization.

Possible reaction pathways for β–O–4 bond cleavage

The studies reported above revealed essentially 100% conversion of GG and VG at all conditions except the lowest temperature and shortest time. Guaiacol yield was below 100% at all conditions due to consecutive condensation reactions as discussed below. EE was only detected at 6% yield with GG at 15 min and 110 °C. Acidic conditions can lead to the formation of EE from GG,[12,29,30] and EE could undergo a subsequent hydrolysis reaction, leading to the cleavage of the β–O–4 bond of GG to produce guaiacol and a Hibbert's ketone.[12,29,30] EE is also reported to be unstable under acidic conditions,[22] which may explain why EE was not detected in most of the experiments reported herein.

To account for the other products that led to a reduced guaiacol yield, studies were conducted at 110 °C with GG in [HMIM]Cl to determine additional products that could have formed between 0 and 60 min. First, one would expect a condensation reaction involving the hydroxyl groups in GG. In fact, LC–MS showed a peak with $(m+H)^+/z$ of 623 (see the Supporting Information, Figure S3), which is consistent with GG dimers coupled by ether linkages formed from the condensation reaction. Additional products with $(m+H)^+/z$ values of 498 and 303, and some heavier products were also detected (see the Supporting Information, Figures S4–S6) by LC–MS. The UV absorbance cross sections for the GG dimers, and those for the $(m+H)^+/z$ 498 and 303 peaks were assumed equal to GG. As illustrated in Figure 7, EE was the main product detected at the onset of the reaction and showed a maximum after 5 min. The GG dimer products displayed a maximum at 25 min. The subsequent decrease of the dimers most likely resulted from the cleavage of the β–O–4 bond in the dimers to release guaiacol. The unidentified product with a $(m+H)^+/z$ of 498 could be the product formed after one guaiacol was liberated from a GG dimer. In addition, the unknown product with a $(m+H)^+/z$ of 303 and a small amount of other coupling products were all formed in the reaction. However, further study is needed to solve their structural details. Because VG is less reactive than GG, VG was reacted at 130 °C, and we found similar products as GG (see the Supporting Information, Figures S7–S9).

Figure 8 compares the various products after 60 min for the temperatures used herein. At 60 min, the GG conversion was

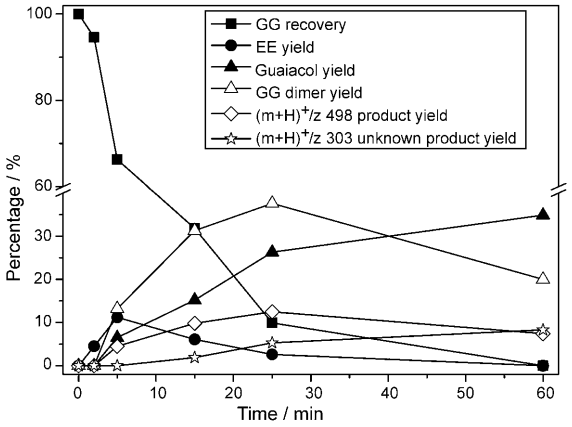


Figure 7. GG recovery and product yields for GG reaction at 110 °C. The response factors of GG dimers, $(m+H)^+/z$ 498 and 303 products are assumed to equal to that of GG.

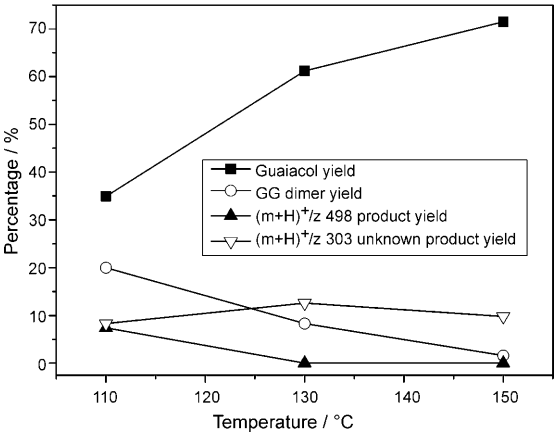
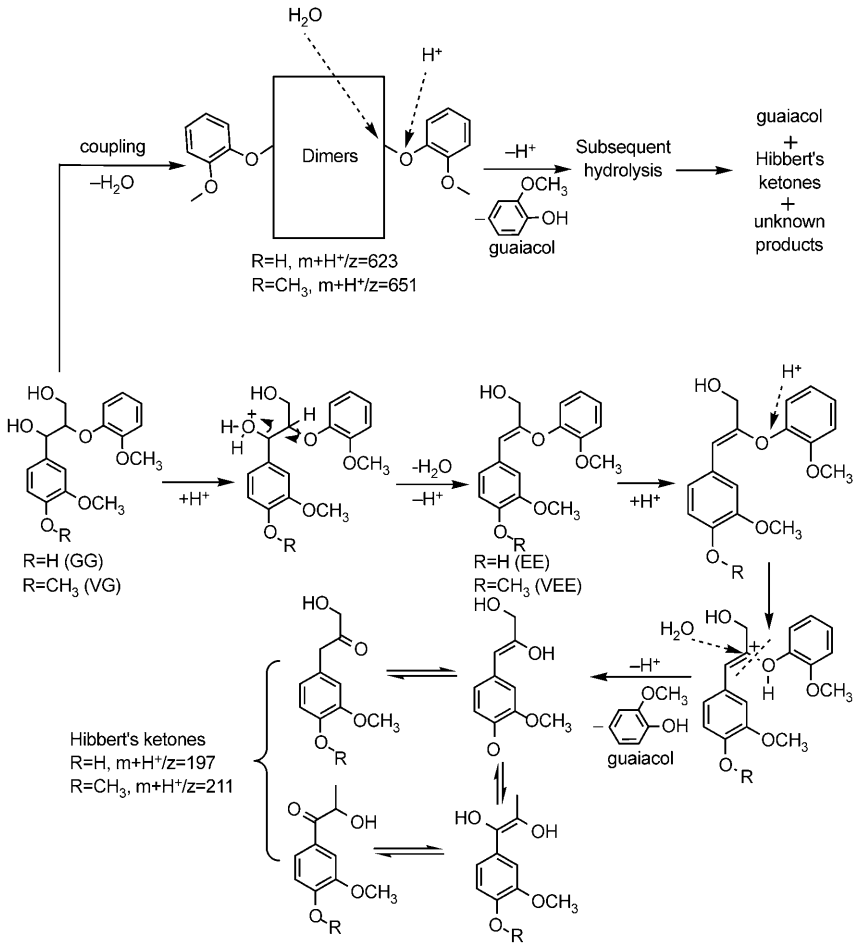


Figure 8. Product yields for GG reaction at different temperatures after 60 min. The response factors of GG dimers, $(m+H)^+/z$ 498 and 303 products are assumed to equal to that of GG.

100%. More of the GG dimers were consumed with increasing temperature. The $(m+H)^+/z$ 498 product yields also decreased with increasing temperature and this could be the result of subsequent reactions of this compound. The unidentified $(m+H)^+/z$ 303 product concentration remained relatively constant, which indicates this product is stable under the reaction conditions and may not lead to the β–O–4 bond cleavage.

Based on the results above, we speculate EE (or the EE analog from VG (VEE)) and GG dimers (or VG dimers) are possible intermediates in the reaction of GG (or VG), leading to the β–O–4 bond cleavage. The $[HMIM]^+$ cation was reported to be Brønsted acidic,[40] which implies H^+ could exist in the system. Based on this, we propose one possible acid-catalyzed mechanism for the hydrolysis of β–O–4 bonds of GG and VG via the possible EE (VEE) and dimer intermediates (Scheme 2). In the proposed pathways, acid-catalyzed dehydration and coupling occur first, which explains why the β–O–4 bonds can be hydrolyzed in [HMIM]Cl without added water. Water could attack the β-carbon of the proposed intermediates, leading to the β–



Scheme 2. Proposed acid-catalyzed mechanism for hydrolysis of the β–O–4 bonds of GG and VG.

O–4 bond cleavage. EE hydrolysis in acids is reported.[12,29] GG and VG dimers could undergo hydrolysis to produce guaiacol and Hibbert's ketones. More added water could increase the rate for the hydrolysis step, which accounts for the slightly higher guaiacol yield (Figure 5b).

Conclusions

We demonstrate an efficient method for the cleavage of β–O–4 bonds of phenolic and non-phenolic lignin model compounds in an acidic ionic liquid, [HMIM]Cl. More than 70% of the β–O–4 bonds of both GG and VG reacted with water to produce guaiacol at 150 °C. There was little change in the reactivity of GG and VG as the substrate concentration increased from 8 wt% to 32 wt%. The ionic liquid solvent/catalyst could be reused without extra treatment or appreciable loss of activity. An increase in available water can lead to more β–O–4 bond cleavage. EE (or VEE) and GG (or VG) dimers also formed, some were further reacted to form guaiacol and Hibbert's ketones. Heavier unidentified products are likely humins. Guaiacol was formed either directly from GG (or VG) monomers, or from the corresponding condensed molecules of GG (or VG). The method described herein may have potential to degrade real lignin (or lignocelluloses).

Experimental Section

Materials: Guaiacylglycerol-β-guaiacyl ether (GG 99%) and 3,4,5-trimethoxybenzaldehyde (TMBA 98%) were purchased from Tokyo Chemical Industry (Japan). Veratryl-glycerol-β-guaiacyl ether (VG 97%) was purchased from Astatech (USA). 1-H-3-methylimidazolium chloride ([HMIM]Cl 95%), 1-butyl-3-methylimidazolium chloride ([BMIM]Cl 95%) and 1-butyl-2,3-dimethylimidazolium chloride ([BdMIM]Cl 97%) were purchased from Sigma–Aldrich (USA). Methylisobutylketone (MIBK 99.5%) was purchased from Acros Organics (Belgium). Dimethylsulfoxide (DMSO 99%), ethyl ether (99.9%), and hydrochloric acid (HCl 36.9 wt%) were purchased from Fisher Scientific (USA).

Typical procedure: [HMIM]Cl was vacuum dried before use. [HMIM]Cl (100 mg) was added into each vial (0.3 mL) with a magnetic stirrer. Then GG (8 mg, 0.025 mmol) and H_2O (2.25 μl, 0.125 mmol) were added into each vial. The vials were sealed, inserted into a Reacti-Therm heating and stirring module (Thermo Scientific, USA) and stirred at 400 rpm at the reaction temperature (110, 130, or 150 °C). Then the vials were cooled in ice water, diluted with H_2O/acetonitrile (1:9 by volume) and analyzed by high pressure liquid chromatography (HPLC).

Analysis method: HPLC was performed on a Dionex Ultimate 3000 series (UV 280 nm) with a Phenomenex Gemini C6-phenyl column (50×4.6 mm, 3 μm). H_2O/acetonitrile was used as the mobile phase. TMBA was added as the internal standard for the quantitative calculations. Liquid chromatography–mass spectroscopy (LC–MS) was performed on an Agilent 6130 single quadrupole mass spectrometer interfaced to an Agilent 1200 Series HPLC with a diode array detector and a Gemini C18 column (50×2.1 mm), H_2O-acetonitrile was used as the mobile phase for LC. NMR spectroscopy was performed on a Varian INOVA 500 MHz series system. FTIR spectra were obtained on a Nicolet Avatar 330 FTIR spectrometer with a Smart Performer ATR attachment.

$$\text{Conversion}(\%) = (1 - \frac{\text{remaining GG or VG detected by HPLC}}{\text{added GG or VG}}) \times 100\% \quad (1)$$

$$\text{Guaiacolyield}(\%) = \frac{\text{produced guaiacol detected by HPLC}}{\text{added GG or VG}} \times 100\% \quad (2)$$

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Keywords: biomass · ethers · hydrolysis · ionic liquids · renewable resources

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