

Lignin Depolymerization with Phenol via Redistribution Mechanism in Ionic Liquids

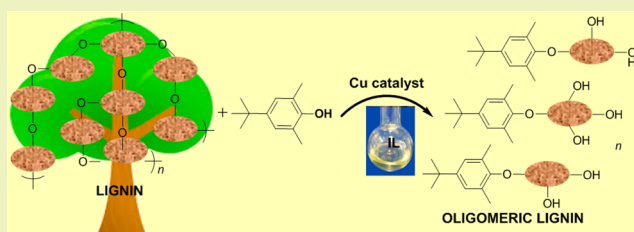
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Supporting Information

ABSTRACT: Nowadays, ionic liquids (ILs) have been recognized as a promising way to fractionate biomass. In this study, we discuss how lignin depolymerization was achieved via the redistribution mechanism with phenols in ionic liquids. Two ionic liquids (1-ethyl-3-methylimidazolium xylenesulfonate [emim][ABS] and 1-butyl-3-methylimidazolium methylsulfate [bmim][MeSO₄]) were selected as a solvent for lignin depolymerization. Before embarking on lignin depolymerization, two selected lignins (organosolv lignin and Klason lignin) were characterized based on their chemical structure and molecular weight. The depolymerized results show that the two lignins (organosolv lignin and Klason lignin) can be extensively depolymerized under oxidative conditions using a Cu/EDTA complex in the presence of a monomeric phenol (4-*tert*-butyl-2,6-dimethylphenol) that is blocked from oxidative coupling in the *ortho* and *para* positions at temperatures of 180 °C.

KEYWORDS: Lignin, Ionic liquids, Depolymerization, Redistribution, Biomass



INTRODUCTION

Lignins form an essential component of wood tissues in which their amounts range from 15% to 36% and perform multiple functions that are essential to the life of a plant.¹ Despite their unique characteristics as abundant natural products with multiple chemical and biophysical functionalities, lignins are largely under-exploited chemically because of the lack of practical methods for depolymerizing them in a selective manner. Lignin can be isolated from the lignocellulosic feedstock by various methods, involving different mechanical and chemical processes.^{2–8} However, it is difficult to depolymerize lignin to valuable small molecules such as phenolic compounds because of its cross-linked macromolecular structure.^{6–8} A suitable depolymerization method is required to obtain polyphenolic compounds from lignin.

Recently, we have reported the chemical depolymerization of lignin using the redistribution mechanism with phenols.⁹ The redistribution mechanism is one of the pathways in oxidative polymerization and depolymerization of polyphenols in which the carbon–oxygen bond (aryl ether bond) formed between phenols can dissociate under oxidative conditions.^{10,11} This unique technique can depolymerize lignin at mild conditions such as at 80 °C and atmospheric pressure. By using this technique, lignin was able to successfully depolymerize in water by addition of 4-*tert*-butyl-2,6-dimethylphenol in the presence of a Cu catalyst to form oligomers. The average molecular weight of the oligomeric lignin products from depolymerization was around 1000. We have used water as a reaction solvent and NaOH as a base for the reaction; however, it is very important to search for alternative solvents such as ionic liquids (ILs) that can dissolve lignin without addition of a base for the

depolymerization reactions. In addition, ILs have several advantages when used for depolymerization of lignin, including enabling reactions to be done at atmospheric pressure, minimal emissions of organic vapor, and the ability to recycle the IL. There are many reports that have focused on using ILs for lignin dissolution, isolation, and depolymerization.^{12–21}

Ragauskas et al. examined the application of selected ILs as aprotic green solvents for lignin dissolution.⁷ The data showed that among IL with the same cation and different anions the order of lignin solubility for varying anions was [MeSO₄][−] > Cl[−] ~ Br[−] ≫ [PF₆][−], indicating that the solubility of lignin was principally influenced by the nature of the anions.⁷ The ILs 1-hexyl-3-methylimidazolium trifluoromethanesulfonate [hmim][CF₃SO₃], 1,3-dimethylimidazolium methylsulfate [mmim][MeSO₄], and 1-butyl-3-methylimidazolium methylsulfate [bmim][MeSO₄] have been reported as effective solvents for lignin.¹⁷ Kilpelainen et al. demonstrated that both hardwoods and softwoods readily dissolve in various imidazolium-based ILs under mild conditions.¹⁸ Tan et al. extracted lignin from bagasse using the ionic liquid mixture 1-ethyl-3-methylimidazolium xylenesulfonate [emim][ABS], an ionic liquid that incorporates an effective pulping agent xylenesulfonate anion with 1-ethyl-3-methylimidazolium at atmospheric pressure.¹⁹ Recently, several researchers reported the oxidation of the lignin model compounds in ionic liquids.^{15,16,20–22} However, research based on lignin depolymerization in ionic liquids using

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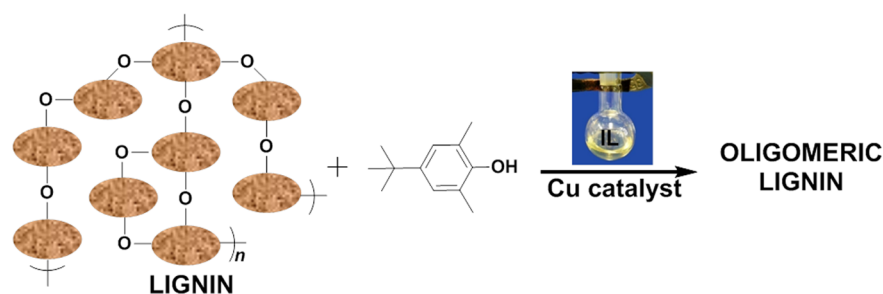


Figure 1. Schematic representation of possible lignin depolymerization involving a redistribution mechanism.

a chemical catalyst is limited, and none of them have used the redistribution with phenol for depolymerization.^{16,23}

In light of this data, the use of ILs as solvents to promote chemical depolymerization of lignin using the redistribution mechanism with phenol is the objective of this study (Figure 1). We selected [emim][ABS] and bmim[MeSO₄] as ILs for the depolymerization reported in this study.

EXPERIMENTAL SECTION

Materials and Measurements. Organosolv lignin, CuCl₂·2H₂O, ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA), 1-butyl-3-methylimidazolium methylsulfate ([bmim][MeSO₄]), 1-ethyl-3-methylimidazolium chloride, and 2,6-dimethylphenol were purchased from Sigma-Aldrich. Sodium xylene sulfonate was purchased from Fluka. Tasmanian blue gum wood chips were provided from CSIRO Forest Biosciences. Hydrochloric acid (32%) was obtained from Ajax Finechem. High purity oxygen purchased from BOC Australia was used for experiments that required oxygen. All reagents were used as purchased from the supplier without any further purification.

Infrared spectra (IR) were obtained using a PerkinElmer RX1 series Fourier transform infrared spectrometer with KBR pellets. ¹H NMR spectra were recorded on a Bruker DRK-400 spectrometer operating at 400 MHz as solutions in CDCl₃ and D₂O. Solid state ¹³C spectra were obtained using a Bruker AM300 instrument equipped with a Bruker 4 mm solid state probe operating at 75.5 MHz for ¹³C 300 MHz for ¹H using 4 mm zirconium oxide rotors with Kel-F end-caps. Molecular weights of lignins and depolymerized lignin were determined by GPC using the GPC apparatus with the UV detection set at 280 nm using Tosoh alpha 4000 and 2000 columns. DMF (with 10 mM LiBr) was used as mobile phase with a flow rate of 1.0 mL/min. Calibration curves were obtained by using polystyrene standards.

Synthesis of 4-*tert*-Butyl-2,6-dimethylphenol (TBDMP). TBDMP was prepared from 2,6-dimethylphenol (DMP) by following the reported literature procedure.²⁴ ¹H NMR (400 MHz, CDCl₃): δ 7.03 (s, 2H, ArH), 2.28 (s, 6H, CH₃), 1.32 (s, 9H, CH₃). ¹³C NMR (400 MHz, CDCl₃): δ 16.3, 31.7, 34.0, 122.5, 125.7, 143.0, 150.0. IR (KBr): ν_{O-H} = 3403 cm⁻¹, ν_{C-H} = 2917 cm⁻¹, ν_{C=C} = 1617 cm⁻¹

Preparation of [emim][ABS]. [emim][ABS] was prepared using the reported procedure.¹⁹ Yield 80%. ¹H NMR (400 MHz, D₂O): δ 8.55–8.45 (s, [C₂mim] ArH), 8.21–8.19 (s, [ABS] ArH), 7.80–6.90 (m, [ABS] ArH), 4.15–4.00 (q, [emim] –CH₂–CH₃), 3.73 (s, [emim] –CH₃), 3.00–2.75 (m, [ABS] –CH₃–CH–CH₃), 2.65–2.55 (q, [ABS] –CH₂–CH₃), 2.53–2.40 (m, [ABS] CH₃–Ar), 2.28 (s, [ABS] –CH₃–Ar), 2.24–2.12 (m, [ABS] –CH₃–Ar), 1.45–1.25 (t, [emim] –CH₂–CH₃), 1.20–1.11 (m, [ABS] –CH₂–CH₃, CH₃–CH–CH₃).

Preparation of Klason Lignin. Klason lignin was prepared from lignocellulose (milled Tasmanian blue gum wood chips, *Eucalyptus globulus*) using the method reported by Browning.²⁵ Yield 25% w/w. Selected IR bands (ATR, cm⁻¹): 3400 w, 2926 w, 2850 s, 1600 s, 1460 s, 1425 s. GPC (10 mM LiBr in DMF) *M*_w = 5.0 × 10³ Da, *M*_w/*M*_n = 1.5.

Depolymerization Reaction. M-lignin, the high molecular weight fraction of methanol insoluble organosolv lignin, and Klason lignin, which were separately extracted from wood chips, were used for the

depolymerization. The typical depolymerization procedure was undertaken as follows: M-Lignin (5.0 mg (1% of [emim][ABS] or [bmim][MeSO₄]), TBDMP (7.0 mg, 0.04 mmol), CuCl₂·2H₂O (0.7 mg, 0.004 mmol), and EDTA (1.2 mg, 0.004 mmol) were added to [emim][ABS] or [bmim][MeSO₄] (0.5 g). The reaction mixture was stirred under oxygen at 180 °C for 3 h. At the end of 3 h, the pH of the mixture was adjusted to 2 by dropwise addition of 1 M HCl. The resulting precipitate was collected and washed by centrifugation with distilled water until the pH of the supernatant reached 7. The washed precipitate was dried under vacuum at room temperature. The acidified supernatant was then extracted with three volumes of dichloromethane, which was subsequently removed under vacuum. The procedure above was repeated twice allowing the depolymerization to proceed for 6 and 9 h. The molecular weight distributions of the depolymerized products were characterized by GPC. Yield (90%). A control reaction was carried out in the absence of TBDMP and catalyst (Cu(II)Cl/EDTA) as described above in order to compare the results.

Control Lignin Depolymerization Reaction without Phenolic Additive (TBDMP). For each reaction, lignin (5.0 mg of 1% of [emim][ABS]) was added to [emim][ABS] (0.5 g). The reaction mixture was stirred under oxygen at 180 °C for 6 h. At the end of 6 h, the pH of the mixture was adjusted to 2 by dropwise addition of 1 M HCl. Further treatment for isolation and characterization of the product was identical to that described above.

RESULTS AND DISCUSSION

Lignin Characterization. The structure and properties of different varieties of lignin vary with extraction method, plant type, environmental factors, and even genotype. Before embarking on lignin depolymerization, it is important to select different types of well-characterized lignin.

We have selected two lignins (organosolv lignin and Klason lignin) for the depolymerization study. Organosolv lignin (Aldrich) has a high polydispersity index (>4) and contains low molecular weight fractions. The method for isolating high molecular weight lignin by removing a low molecular weight lignin fraction from organosolv lignin (Aldrich) was previously reported.⁹ Methanol was used for the separation of the high molecular weight fraction of organosolv lignin by dissolving the low molecular weight lignin fractions into methanol. The high molecular weight fraction obtained was designated as M-lignin and used for the depolymerization. A second variety of lignin chosen for this study was Klason lignin extracted from wood chips.²⁵

Isolation of Klason lignin from Tasmanian blue gum wood chips (*Eucalyptus globules*) was conducted using the well-known Klason method.²⁵ In this method, total hydrolysis of polysaccharides is achieved using 72% sulfuric acid.¹ To obtain complete hydrolysis of the polysaccharides, 72% w/w H₂SO₄ was used because below 65% w/w H₂SO₄ cellulose is not completely hydrolyzed and above 80% w/w H₂SO₄ the polysaccharides can be converted to insoluble products.¹ The

yield of the isolated lignin was 25% w/w, which is typical for wood from this species of tree.¹ The molecular weight of the isolated lignins was analyzed by GPC, and the material was characterized further by FTIR and NMR.

The GPC chromatogram (Figure 2) of the isolated M-lignin and Klason lignin showed one peak in the GPC chromatogram,

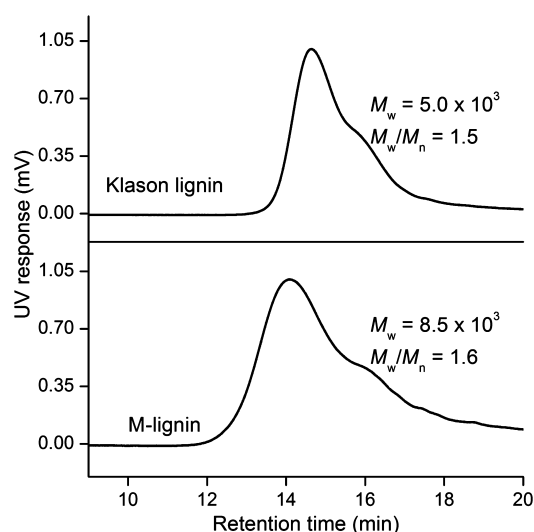


Figure 2. GPC chromatograms of M-lignin and Klason lignin.

and the average molecular weight of M-lignin and Klason lignin was 8.5×10^3 with polydispersity of 1.6 and 5.0×10^3 and with polydispersity of 1.5, respectively.

The FTIR spectra of the two types of lignin (Figure 3) showed characteristic bands typically reported for lignin at 1600

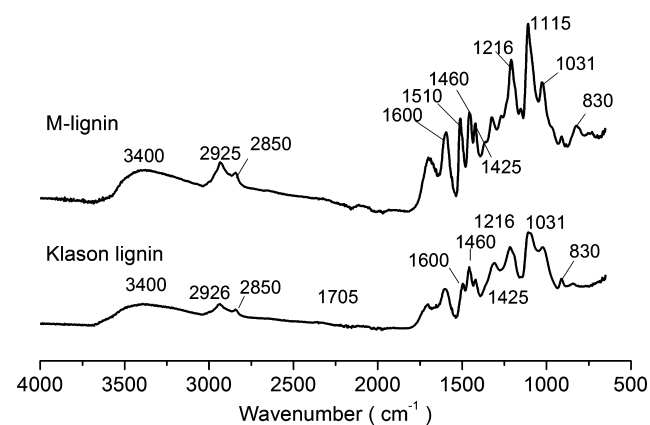


Figure 3. Infrared spectra of M-lignin and Klason lignin.

and 1425 cm^{-1} corresponding to aromatic ring vibrations of the phenylpropane skeleton. A wide band at 3400 cm^{-1} corresponds to the aromatic and aliphatic OH groups. Bands at 2926 and 1460 cm^{-1} arise from C–H vibrations of the CH_2 and CH_3 groups, and a band at 2850 cm^{-1} is attributed to C–H stretching in methoxy groups. In Klason lignin, in particular, there was no evidence of bands characteristic of cellulose, which would appear at 3240 and 750 cm^{-1} , indicating that following treatment with 72% aqueous sulfuric acid there was no residual cellulose present in the insoluble residue.

Solid state ^{13}C NMR is a useful technique for obtaining bulk chemical structural information on lignin.²⁶ Solid state ^{13}C

NMR spectra of the lignins were recorded and showed relatively sharp peaks for methoxy resonances at 55–56 ppm and for aromatic ring carbons at 110–160 ppm. All the spectra obtained did not show evidence of any residual cellulose (Supporting Information).

Depolymerization of Lignin in Ionic Liquid. First, a set of attempted depolymerizations of M-lignin were conducted in an IL mixture containing the 1-ethyl-3-methylimidazolium cation [emim] and a mixture of alkylbenzenesulfonate with the xylene sulfonate anion [ABS] (Figure 4).



Figure 4. (a) Ionic liquid [emim][ABS] and (b) M-lignin in [emim][ABS].

The depolymerization of M-lignin was conducted by adding 4-*tert*-butyl-2,6-dimethyl-phenol (TBDMP) to lignin in the presence of Cu-ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA) as a catalyst under oxygen at $180 \text{ }^\circ\text{C}$. As simple phenol can polymerize under the oxidative condition, TBDMP was selected as it could not polymerize under the condition used because of the methyl group on *ortho* and *tert*-butyl group on *para* positions. The extent of depolymerization was monitored by taking samples after 3, 6, and 9 h (Figure 5). It was found that the average molecular weight of the reaction

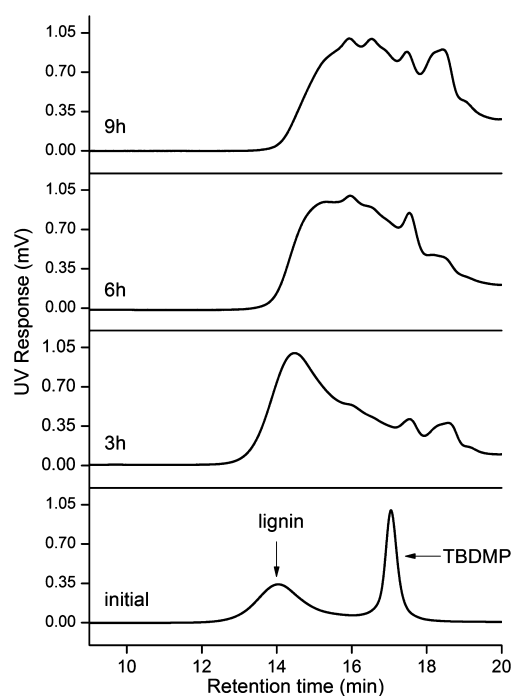


Figure 5. GPC traces of depolymerization of M-lignin in [emim]-[ABS] with TBDMP.

mixture after 3 h reduced from 8.5×10^3 to 4.7×10^3 with a high polydispersity index (PDI) of 5.8 (Table 1), indicating the

Table 1. Molecular Weight Changes of Depolymerized M-Lignin in Ionic Liquid [emim][ABS]

depolymerization time (h)	M_w (g mol ⁻¹)	PDI (M_w/M_n)
0	8500	1.6
3	4700	5.8
6	1900	3.1
9	1300	2.8

start of depolymerization. With time, the average molecular weight and polydispersity of the reaction mixture decreased further. After 9 h of depolymerization time, the average molecular weight of the depolymerized sample had dropped to 1.3×10^3 with PDI of 2.8. The GPC chromatogram shows that the original high molecular weight lignin peak that appeared at 14 min retention time disappeared after 6 h (Figure 5).

The IL [bmim][MeSO₄] has been also reported as an effective solvent for certain lignins. A further attempt at depolymerization of M-lignin was therefore conducted in [bmim][MeSO₄] in order to compare the effectiveness of this reaction medium with the data obtained when using [emim]-[ABS]. The depolymerization was carried out using exactly the same conditions.

The GPC chromatograms (Figure 6) show that the M-lignin peak, which appears at 14 min retention time, disappeared after only 1 h depolymerization. The average molecular weight at that point had reduced to $M_w = 5 \times 10^3$ with PDI = 2.5. A

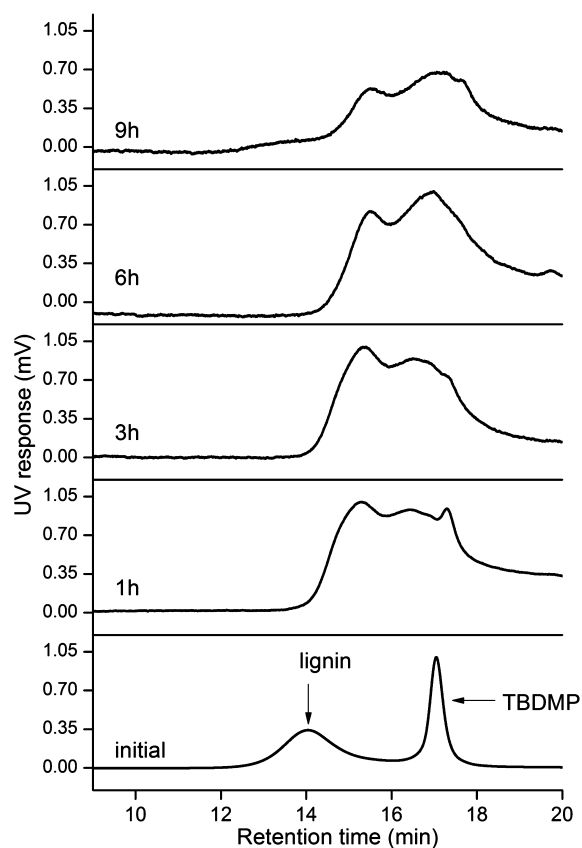


Figure 6. GPC chromatograms of depolymerization of M-lignin in [bmim][MeSO₄] with TBDMP.

summary of how molecular weight decreased with time is presented in Table 2. Continuation of the depolymerization

Table 2. Molecular Weight Changes of Depolymerized M-Lignin in ionic liquid [bmim][MeSO₄]

depolymerization time (h)	M_w (g mol ⁻¹)	PDI (M_w/M_n)
0	8500	1.6
1	5000	2.5
3	3200	2.0
6	2000	1.8
9	1700	1.7

reaction for 9 h afforded a material with an average molecular weight of 1.7×10^3 and PDI of 1.7. We have described in our previous studies that the depolymerization using redistribution proceed first, and the repolymerization of the depolymerized product proceed next.^{10,11} It is important to stop the depolymerization before the repolymerization starts. The repolymerization of depolymerized oligomeric lignin can occur when the reaction is left for a long time. This was verified by the depolymerization of M-lignin carried out in [bmim][MeSO₄] for an extended period of 24 h. The average molecular weight of the product obtained after 24 h reaction time was $M_w = 4.0 \times 10^3$ with PDI = 2.9 (Supporting Information), compared with the result after 9 h, which gave $M_w = 1.7 \times 10^3$ with PDI = 1.7 (Table 2).

After 9 h of depolymerization, depolymerized product from M-lignin in [emim][ABS] showed a higher polydispersity of 2.8 compared with the product in [bmim][MeSO₄] that showed a lower polydispersity of 1.7. Solubility of lignins in both ILs was similar, as the cation of both selected ILs was imidazolium-based, and it was reported to give high lignin solubility with anions [MeSO₄] and [ABS].^{17,19} However, there was a difference in viscosity of both ILs. The viscosity of [emim]-[ABS] was reported to be 694 mPa s at 70 °C, and the viscosity of [bmim][MeSO₄] was reported²⁷ to be 19.1 mPa s at 80 °C.^{19,27} It is known that viscosity of the solvents plays a major role in reaction kinetics.²⁸ The viscosity of both ILs may have affected the polydispersity of the depolymerized product.

Depolymerization of Klason Lignin in [emim][ABS].

Using identical procedures to those described above for M-lignin, Klason lignin was also successfully depolymerized in [emim][ABS]. The GPC traces (Figure 7) showed that after 1 h the original broad high molecular weight lignin between retention times of 14–15 min had shifted toward a lower molecular weight range (retention time = 14.5–16.0 min), indicating that depolymerization had commenced. Extension of the reaction from 3 to 6 h gave GPC results consistent with extensive depolymerization. The Klason lignin and TBDMP are soluble in [emim][ABS]; the solubility of the substrate supports the effective depolymerization in [emim][ABS]. The observed changes in average molecular weight and PDI are summarized in Table 3.

The depolymerization of Klason lignin was also conducted in [bmim][MeSO₄]. The GPC chromatograms (Figure 8) showed that the Klason lignin peak, which appears at 14–15 min retention time, disappeared after 6 h of reaction time. A summary of how the molecular weight decreased with time is presented in Table 4. Continuation of the depolymerization reaction for 6 h afforded a material with an average molecular weight of 1.2×10^3 and PDI of 1.8.

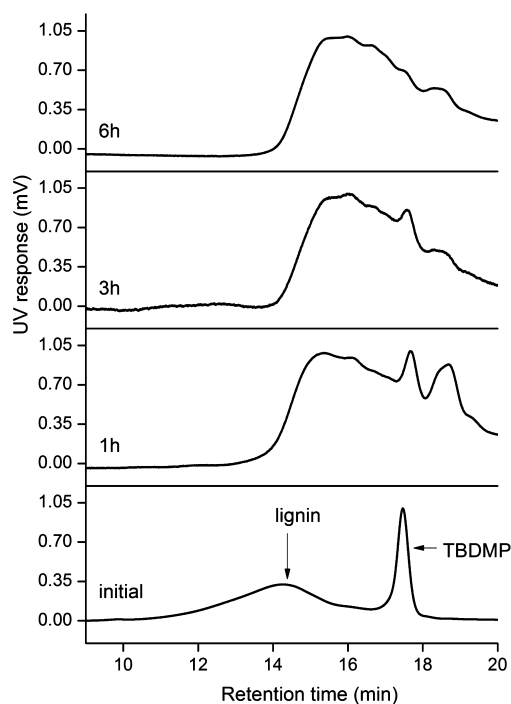


Figure 7. GPC traces of depolymerization of Klason lignin in [emim][ABS] with TBDMP.

Table 3. Molecular Weight Changes of Depolymerized Klason Lignin in [emim][ABS]

depolymerization time (h)	M_w (g mol ⁻¹)	PDI (M_w/M_n)
0	5000	1.5
1	1600	2.6
3	1300	2.0
6	1200	2.0

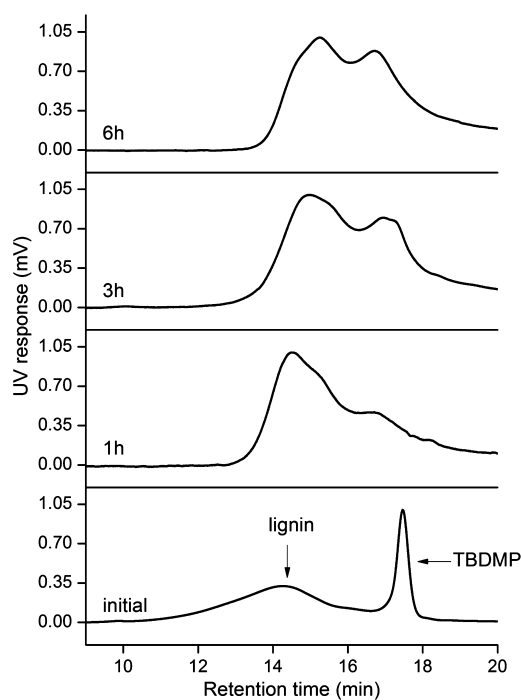


Figure 8. GPC traces of depolymerization of Klason lignin in [bmim][MeSO₄] with TBDMP.

Table 4. Molecular Weight Changes of Depolymerized Klason Lignin in [bmim][MeSO₄]

depolymerization time (h)	M_w (g mol ⁻¹)	PDI (M_w/M_n)
0	5000	1.5
1	4300	3.5
3	2700	2.9
6	1200	1.8

Based on the approximately rate of depolymerization data obtained (Supporting Information), the rate of depolymerization of M-lignin was higher than that of Klason lignin in both ILs. The depolymerizations using the redistribution mechanism can only cleavage aryl ether linkages in lignin. Therefore, the difference observed from both lignins can be attributed to the number of aryl ether linkages present in both lignins. There was no clear difference in depolymerization rates between the two ionic liquids and water.

Characterization of Depolymerized Products. The depolymerized products from all reactions were further analyzed by ¹H NMR and FTIR to characterize their structure. In the ¹H NMR spectrum, there were several unidentified peaks as lignin has a very complicated structure and depolymerized products became a mixture of several phenolic oligomers. However, the resonance attributed to methoxy groups at 3.7 ppm and aromatic protons at 6–8 ppm are the characteristic features of lignin units. The FTIR spectra of the depolymerized lignin showed characteristic bands typically reported for lignin at 1600 and 1425 cm⁻¹ corresponding to aromatic ring vibrations of the phenylpropane skeleton and a wide band at 3400 cm⁻¹ corresponding to aromatic and aliphatic OH groups.

Control Reactions. In order to demonstrate beyond a doubt that the redistribution reaction with TBDMP and Cu catalysts is the key factor in this type of lignin depolymerization, a control reaction using only lignin in both ILs was conducted at 180 °C for 6 h (Supporting Information). The GPC trace obtained from the product of this control reaction indicated an average molecular weight, hence, essentially unchanged from that of the starting material (M-lignin) (M_w = 8500 with PDI = 1.6). These data demonstrate that the redistribution reaction resulting from *ortho/para*-blocked phenol additions under oxidative conditions is an essential factor in the oxidative depolymerization of lignin using a Cu-EDTA complex, and IL itself cannot depolymerize lignin under the reaction conditions employed.

CONCLUSIONS

Molecular weight analysis involving GPC was employed as the main analytical method to monitor molecular weight changes during lignin depolymerization, providing insights into the changes that occurred in the depolymerization experiments. Using two lignins (M-lignin and Klason lignin), it has been demonstrated that lignins can be extensively depolymerized under oxidative conditions using a Cu/EDTA complex catalyst and a monomeric phenol that is blocked from oxidative coupling in the *ortho* and *para* positions (TBDMP). The oligomers formed after depolymerization of M-lignin in [emim][ABS] and [bmim][MeSO₄] gave molecular weights of 1.3×10^3 with PDI of 2.8 and 1.7×10^3 with PDI of 1.7, respectively. The oligomers from Klason lignin in [emim][ABS] and [bmim][MeSO₄] gave molecular weights of 1.2×10^3 with PDI of 2.0 and 1.2×10^3 with PDI of 1.8, respectively. Control reactions were carried out in the absence of TBDMP,

and these indicated strongly that the known redistribution reaction that occurs between phenols of this type under oxidative conditions is an essential factor in successful depolymerization of lignin under oxidative conditions. Ways of further breaking down the oligomeric lignin fragments to obtain valuable monomeric phenolic compounds will be studied in the future.

■ ASSOCIATED CONTENT

■ Supporting Information

Solid-state NMRs of lignins, GPC chromatograms of control reactions done in ILs, and approximate rate of depolymerization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ Author Contributions

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

■ Notes

The authors declare no competing financial interest.

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