

Spectroscopic Investigation of Thermochemical Depolymerization of Lignin Model Compounds in the Presence of Novel Liquidlike Nanoparticle Organic Hybrid Solvents for Efficient Biomass Valorization

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ABSTRACT: This study reports the thermochemical transformation of lignin model compounds using nanoparticle organic hybrid materials (NOHMs). NOHMs have recently been developed as an emerging class of self-suspended nanoparticle solvent systems created by ionically or covalently grafting organic oligomers or polymers (canopy) onto surface-modified inorganic nanoparticles (core). Because NOHMs exhibit negligible vapor pressure with the ability to tailor physicochemical properties, they could be a promising catalytic solvent for the lignin thermochemical conversion process. The thermochemical conversion of lignin model compounds was achieved with the synthesized NOHM at an elevated temperature of 473 K, and the results were compared with the case of the ionic liquid [EMIM][ESO₄]. The fractured moieties of the lignin model compounds were qualitatively identified by ATR FT-IR and 2D COSY NMR spectroscopies. The results indicated that the NOHM decomposed the C–O and/or C–C bonds of lignin model chemicals more efficiently than [EMIM][ESO₄].

KEYWORDS: lignin, NOHM, thermochemical decomposition, NMR, ionic liquid

1. INTRODUCTION

Significant efforts across the globe have been made up to now to reduce greenhouse gas (GHG) emissions and to mitigate atmospheric GHG levels. Among the GHGs, CO₂ has the most critical role in global warming, and it is mainly caused by the use of fossil fuels such as petroleum-based oil, coal, and natural gas. In this regard, there are two plausible strategies to cope with the climate change triggered by CO₂: first, CO₂ produced from large point sources such as fossil fuel power plants and industrial sites can be captured and stored using carbon capture and storage (CCS) technologies to prevent it from entering the atmosphere; second, CO₂ emissions can be prevented by switching from fossil fuels to renewable energy resources such as biomasses, wind power, solar energy, etc. For most of human history, particularly, biomasses have been used as an important energy resource. Biomasses are considered as an approximately carbon-neutral energy resource because photosynthesis involves the uptake of CO₂ from the atmosphere with the storage of solar energy. Furthermore, the total atmospheric CO₂ inventory could become negative when combined with CCS.¹ For this reason, biomasses are expected to replace a significant portion of petroleum-based energy consumption in the near future in the context of current energy and environmental concerns.^{2–4}

Recently, lignocellulosic biomasses have received considerable attention because they could be a promising alternative to fossil resources for value-added chemical intermediates as well as fuels.^{5–12} Lignocellulosic biomasses are the most

abundant renewable resource in the world. They are generally composed of semicrystalline cellulose (38–50%), amorphous hemicellulose (23–32%), and amorphous lignin (15–25%).^{13–15} Among the components, lignin—a highly branched hydrophobic heteropolymer mainly providing mechanical strength to the plant cell walls and containing up to 40% of the energy content of lignocellulosic biomasses—has significant potential as a renewable feedstock for the production of industrial biofuel and useful aromatic compounds.^{7–10,16,17} Despite the promising potential, however, valorization of lignin via selective conversion has been a challenging problem because of its heterogeneous, nonhydrolyzable cross-linked structure, making it recalcitrant to hydrolysis in lignin valorization. Lignin has complex polymeric structures arising from dehydrogenative polymerization of synapyl alcohol, coniferyl alcohol, and *p*-coumaryl alcohol (Figure 1).¹⁸ The aromatic subunits of the polymeric lignin structure include syringyl type (4-alkyl-2,5-dimethoxyphenol), *p*-hydroxyphenyl type, coniferyl alcohol fragment (4-(3-hydroxy-1-propenyl)-2-methoxyphenol), guaiacyl type (4-alkyl-2-methoxyphenol), and phenylcoumaran,^{19,20} and the subunits are linked via interunit linkages such as β -O-4, α -O-4, β -5, β - β , 4-O-5, 5-5, and β -1, where the β -O-4 ether linkage is the most common, representing 50% of all interunit bonds.^{15,21} To break down the complexly integrated subunits to transform lignin into

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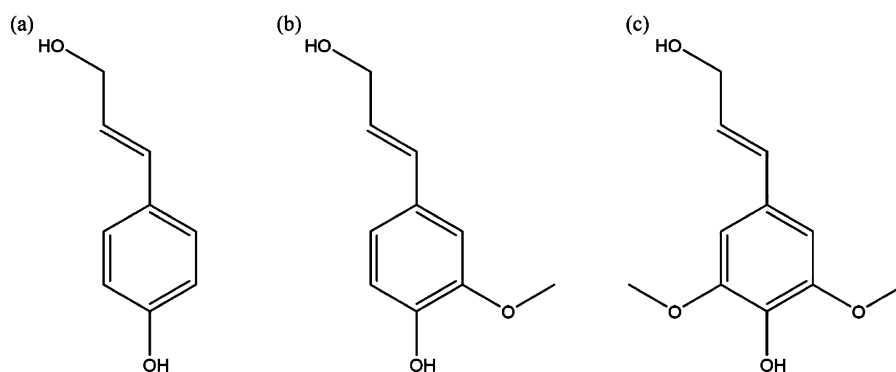


Figure 1. Lignin monolignols: (a) *p*-coumaryl alcohol (H); (b) coniferyl alcohol (G); (c) sinapyl alcohol (S).

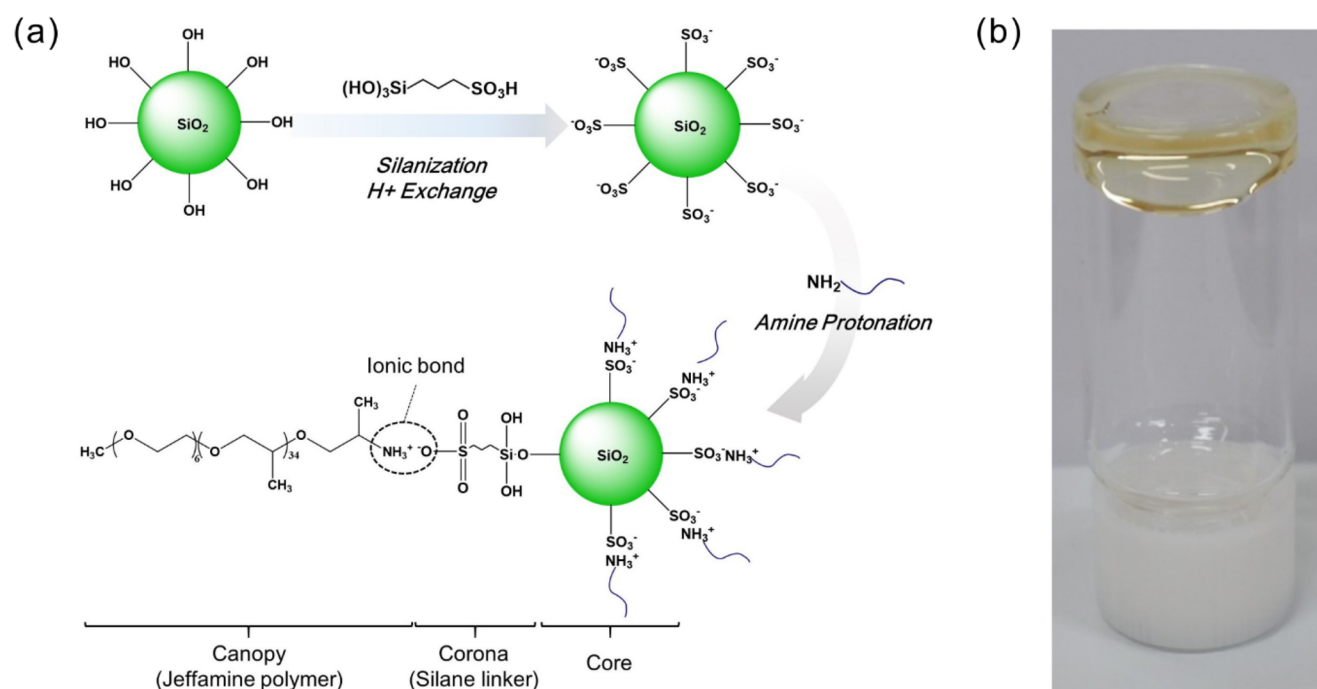


Figure 2. (a) Synthesis and schematic structure and (b) photograph of the NOHM with ionically tethered amine-terminated polymeric canopy species.

value-added products, various reactions including hydrolysis,^{22,23} catalytic cracking,^{24–26} reduction,^{27–30} and oxidation^{31–33} can be adopted. As an alternative approach to convert lignin into value-added aromatic compounds, ionic liquids (ILs) have recently been explored.¹⁵ Because ILs exhibit low or negligible volatility with the ability to tailor physicochemical properties, various applications have been investigated, including lignin extraction from lignocellulosic biomasses^{34–38} as well as catalytic,³⁹ separations,⁴⁰ and biotechnology applications.⁴¹

Here we report the thermochemical transformation of lignin model compounds with an organic–inorganic hybrid solvent, otherwise known as a nanoparticle organic hybrid material (NOHM). NOHMs have recently been developed as an emerging class of self-suspended nanoparticle solvent systems created by ionically or covalently grafting organic oligomers or polymers (canopy) onto surface-modified inorganic nanoparticles (core).^{42–52} NOHMs exhibit promising potential as green solvents, particularly for energy and environmental applications, providing environmentally benign and highly tunable properties with a negligible vapor pressure at relatively

high working temperatures.⁴⁴ Versatile combinations of an organic canopy and inorganic core species offer unique physicochemical properties, and thus, NOHMs are potentially applicable to a variety of areas including reaction solvents, CO₂ capture media, thermal management materials, electrolytes, magnetic fluids, and lubricants.^{44,45,49,51,53–55} As an analogue to ILs, we synthesized a NOHM with a surface-modified SiO₂ nanocore (anion) and a functionalized polyetheramine (cation), and the effects of the NOHM on the thermochemical conversion of lignin model compounds were investigated.

2. EXPERIMENTAL SECTION

2.1. Chemicals. To explore the thermochemical conversion reactions, two lignin model compounds, 2-phenoxyethanol (99%) and benzyl phenyl ether (98%) were obtained from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. As reaction solvents, ethyl alcohol (EtOH) (99.9%) was purchased from Daejung Chemicals & Metals Co., Ltd. (Siheung, Republic of Korea), and *tert*-butyl alcohol (TBA) (99%) was supplied by Alfa Aesar (Haverill, MA,

Table 1. Experimental Sets for the Thermochemical Conversion of Lignin Model Compounds Examined in This Study

sample	lignin model compound (mass)	catalytic solvent (mass)	proton source solvent
1	2-phenoxyethanol (0.138 g)	[EMIM][ESO ₄] (0.236 g)	EtOH (7.89 g)
2	benzyl phenyl ether (0.184 g)	[EMIM][ESO ₄] (0.236 g)	EtOH (7.89 g)
3	2-phenoxyethanol (0.138 g)	[EMIM][ESO ₄] (0.236 g)	TBA (7.81 g)
4	benzyl phenyl ether (0.184 g)	[EMIM][ESO ₄] (0.236 g)	TBA (7.81 g)
5	2-phenoxyethanol (0.138 g)	NOHM (0.75 g)	TBA (7.81 g)
6	benzyl phenyl ether (0.184 g)	NOHM (0.75 g)	TBA (7.81 g)

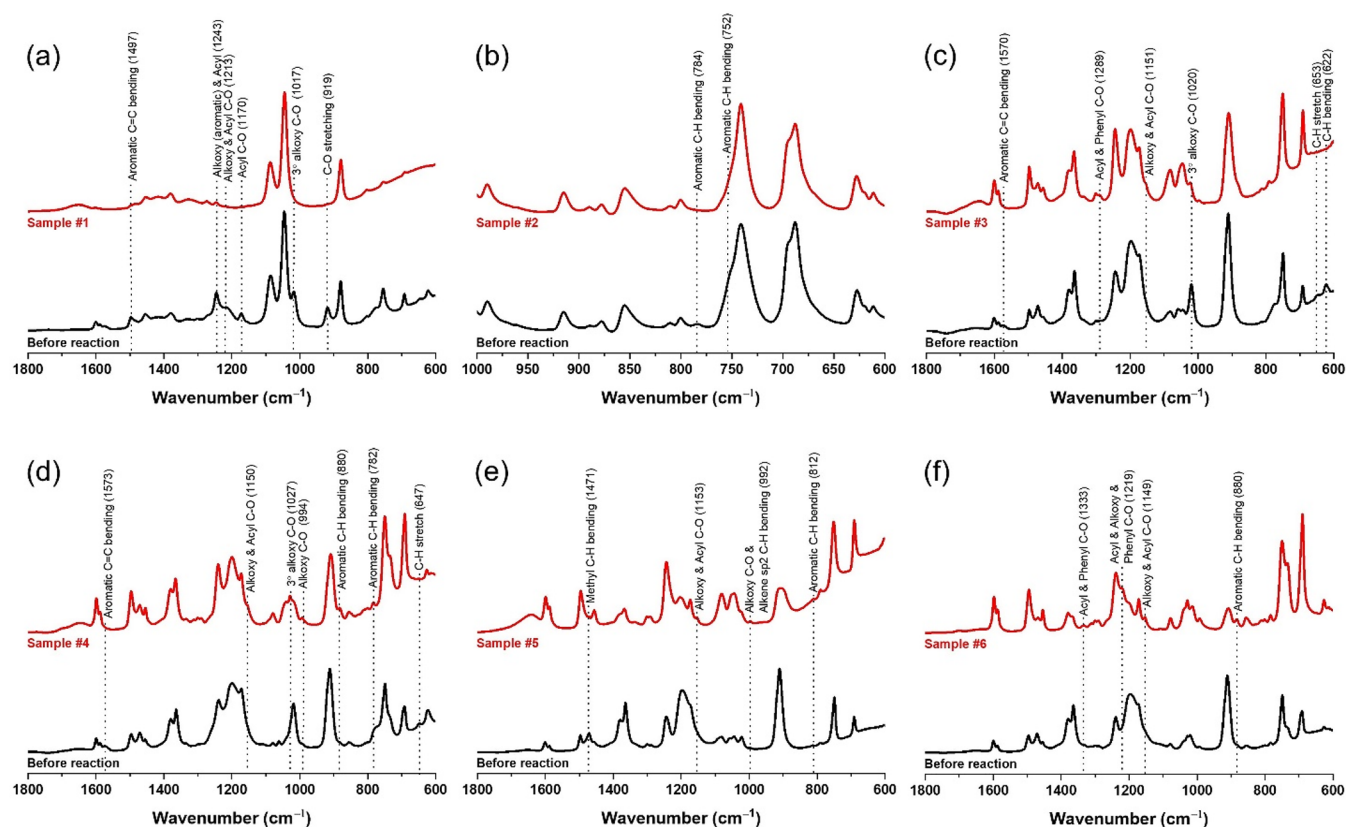


Figure 3. ATR FT-IR spectra of the thermochemical depolymerization of (a) 2-phenoxyethanol + [EMIM][ESO₄] + EtOH, (b) benzyl phenyl ether + [EMIM][ESO₄] + EtOH, (c) 2-phenoxyethanol + [EMIM][ESO₄] + TBA, (d) benzyl phenyl ether + [EMIM][ESO₄] + TBA, (e) 2-phenoxyethanol + NOHM + TBA, and (f) benzyl phenyl ether + NOHM + TBA.

USA). 1-Ethyl-3-methylimidazolium ethylsulfate ([EMIM][ESO₄]) (95%) was also purchased from Sigma-Aldrich.

2.2. Synthesis of the Nanoparticle Organic Hybrid Material. The NOHM was synthesized by previously reported methods.^{44,46,55} Briefly, 3.05 g of a 7 nm silica colloidal suspension (Sigma-Aldrich) was added to deionized water to prepare a 3 wt % silica suspension. The solution was mixed with a 6 wt % solution of 3-(trihydroxysilyl)-1-propanesulfonic acid (Gelest Inc., Morrisville, PA, USA). The acidity of the surface-modified SiO₂ nanoparticle suspension was adjusted to pH 5 with a 1 M NaOH solution. Next, the mixture was heated to 70 °C in a heating bath (B-100, BÜCHI Labortechnik AG, Flawil, Switzerland) for 24 h to complete the reaction. During the incubation, the mixture was stirred vigorously. After that, the excess silane was removed by dialysis (3.5k molecular weight cutoff, Pierce Biotechnology, Rockford, IL, USA) against deionized water for 48 h. The dialyzed solution was then added to the cation exchange column (Dowex HCR-W2, Sigma-Aldrich) to remove the sodium ions and to protonate the sulfonate groups of the functionalized silica nanoparticles.

Next, a polyetheramine (Jeffamine 2070, MW ≈ 2000, Huntsman Co., The Woodlands, TX, USA) was used as a polymeric precursor for the NOHM used in this study. A 20 wt % solution of the polymer was added dropwise to the functionalized silica nanoparticle suspension while the pH was monitored. The addition of the Jeffamine 2070 solution was done until the equivalence point was reached to obtain the highest grafting density. Finally, the NOHM was dried in a vacuum oven at 35 °C for 48 h. Figure 2 shows the schematic structure of the synthesized NOHM.

2.3. Thermochemical Depolymerization of the Lignin Model Compounds. A high-pressure bolted-closure-type magnetic-drive-stirred reactor made of 316 stainless steel with a working internal volume of 300 mL (M-Series, REXO Engineering, Seoul, Republic of Korea) was used for the thermochemical conversion of lignin model compounds. The reaction temperature was controlled with proportional–integral–derivative (PID) electrical heating and cooling arrangements.

The synthesized NOHM was used as a catalytic solvent for the thermochemical conversion of lignin model compounds.

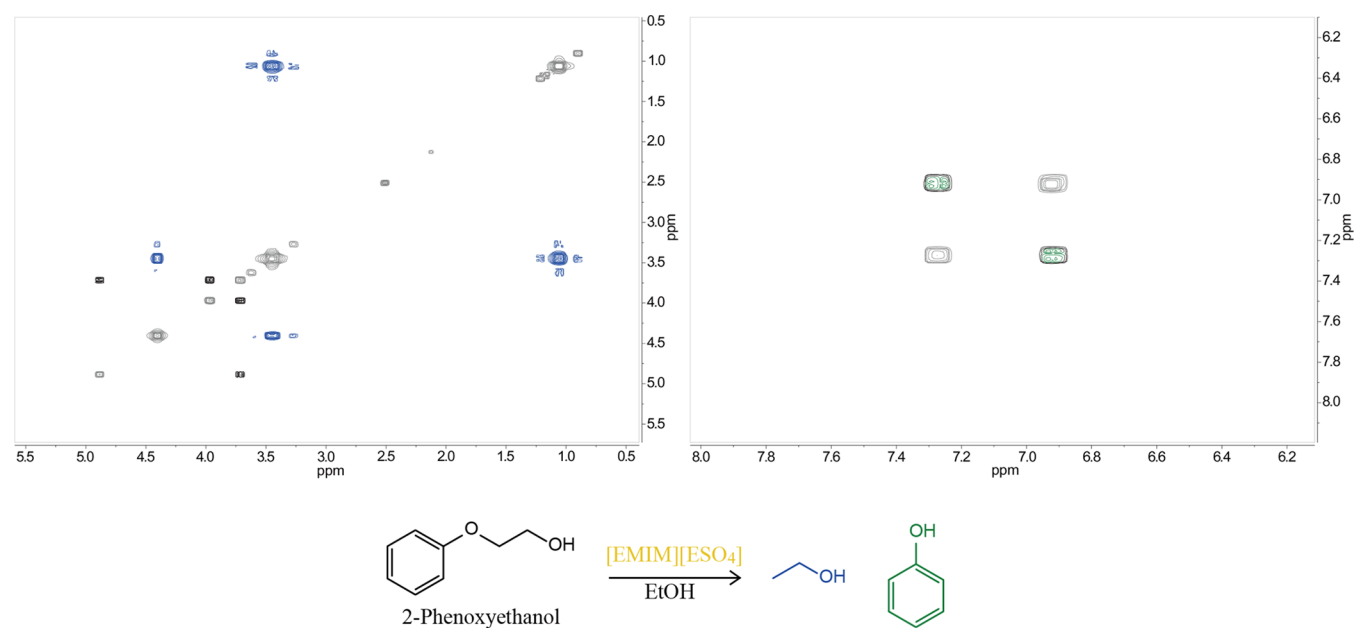


Figure 4. 2D COSY NMR spectra of the thermochemical conversion of 2-phenoxyethanol + [EMIM][ESO₄] + EtOH.

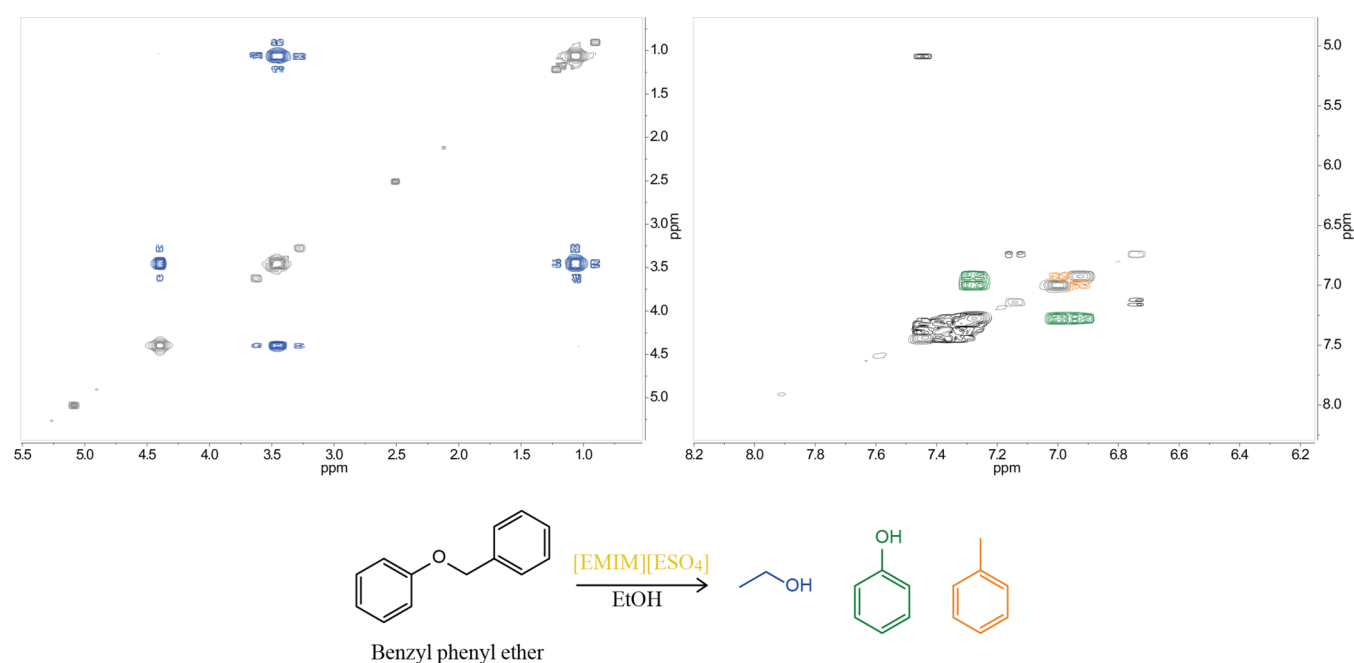


Figure 5. 2D COSY NMR spectra of the thermochemical conversion of benzyl phenyl ether + [EMIM][ESO₄] + EtOH.

[EMIM][ESO₄] was also used as a catalytic solvent for comparison. EtOH and TBA were used as proton sources. The detailed experimental sets are provided in Table 1. A 20 mL glass vial was filled with 10 mL of a solution including a lignin model chemical, catalytic solvent, and proton source. The vial was inserted into the high-pressure reactor. After the reactor was tightened with bolts, the residual air inside the reactor was evacuated by flushing with N₂ several times. Finally, the high-pressure reactor was pressurized to 20 bar with a syringe pump (500D, Teledyne ISCO, Lincoln, NE, USA). After stabilization, the reactor was heated to 473 K for 30 min. The thermochemical conversion reaction was carried out at 473 K for 2 h, followed by cooling for 30 min to 293 K for the analyses.

2.4. Spectroscopic Analyses. A Fourier transform infrared (FT-IR) spectrometer (Spectrum Two, PerkinElmer, Waltham, MA, USA) equipped with a deuterated triglycine sulfate (DTGS) detector and an attenuated total reflectance (ATR) accessory (single-reflection ZnSe crystal) was used. All of the spectra were recorded with a resolution of 2 cm⁻¹ in the 4000–500 cm⁻¹ wavenumber region with eight scans at room temperature.

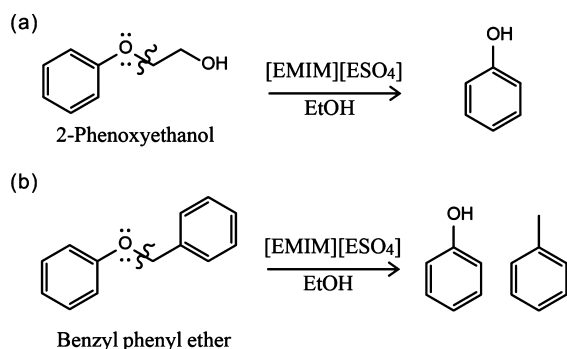
A 400 MHz NMR spectrometer (AVANCE III HD 400, Bruker, Rheinstetten, Germany) located at Chonnam National University was used. All of the two-dimensional (2D) ¹H–¹H correlation spectroscopy (COSY) NMR spectra were recorded in the Fourier transform mode using dimethyl sulfoxide-*d*₆

(DMSO- d_6) (99.9 atom % D, Sigma-Aldrich) as the solvent and tetramethylsilane (TMS) as an internal standard.

3. RESULTS AND DISCUSSION

In general, lignin, a waste woody resource, has a high energy content because its structure is based on aromatic hydro-

Scheme 1. Proposed Ether Cleavage Mechanism of 2-Phenoxyethanol and Benzyl Phenyl Ether Using [EMIM][ESO₄] and EtOH



carbons. Accordingly, it can be converted to useful chemicals by depolymerization into various substituents. However, the structural complexity and diversity make it difficult to use lignin efficiently. For better utilization, several approaches to break down the major linkages such as C–O–C and C=O have been investigated with oxidation,^{56,57} hydrolysis,^{58,59} thermochemical depolymerization,^{60,61} and hydrothermolysis.^{62,63} Recently, ILs were used as effective catalytic solvents, particularly for the cleavage of the C–O ether bond of the β -O-4 linkage.^{64,65} ILs consist of relatively small inorganic anions and large organic cations that can act as high-performance reaction media as liquid phases under 573–673 K.⁶⁶ Because of their nonvolatility and high thermal stability, ILs could accelerate the cracking of the C–O ether bond of the β -O-4 linkage by thermochemical depolymerization.

Thus, we explored the thermochemical depolymerization of the lignin model compounds 2-phenoxyethanol and benzyl phenyl ether using reaction solvents that were mixtures of proton sources (EtOH or TBA) and catalytic liquids ([EMIM][ESO₄] or NOHM). To compare the effects of primary and tertiary alcohols as proton sources, EtOH and TBA were chosen. The depolymerization performances of the catalytic solvents were also compared, focusing on the IL [EMIM][ESO₄] and the synthesized NOHM. The thermal stability of the NOHM used in this study was previously investigated by Lin and Park,⁴⁴ and the depolymerization was conducted below its decomposition temperature.

For the preliminary analysis of the depolymerized products obtained from the thermochemical conversion reactions, first the ATR FT-IR spectra of the products for samples 1–6 were obtained (Figure 3). Compared with the pristine samples (before reaction), the thermochemical conversion reactions caused significant changes over a wide range of the FT-IR spectra. The characteristic bands of 2-phenoxyethanol and benzyl phenyl ether in the range of 1300–1000 cm^{-1} , which correspond to the phenyl C–O stretching vibration, disappeared after the thermochemical depolymerization (Figure 3a,c,d,e,f). Changes in the intensities of the bands in the 800–600 cm^{-1} region, due to the vibrations of the aromatic C–H bonds, were also observed, as shown in Figure 3c–f. Consequently, the ATR FT-IR results clearly show the cleavage of the C–O bonds, and this would be evidence showing the change in the substitution of 2-phenoxyethanol and benzyl phenyl ether in the case of samples 1–6 by the thermochemical depolymerization.

For an in-depth qualitative analysis of samples 1–6, 2D ¹H–¹H COSY NMR spectroscopy was employed, and the decomposed products were analyzed as shown in Figures 4–9. Figures 4 and 5 show the 2D COSY NMR spectra of the decomposed products from samples 1 and 2, respectively. As shown in Figure 4, most of the products remained as EtOH and 2-phenoxyethanol, and only a small amount of phenol was observed. In the case of sample 2, similar to sample 1, the benzyl phenyl ether and EtOH remained, and phenol and

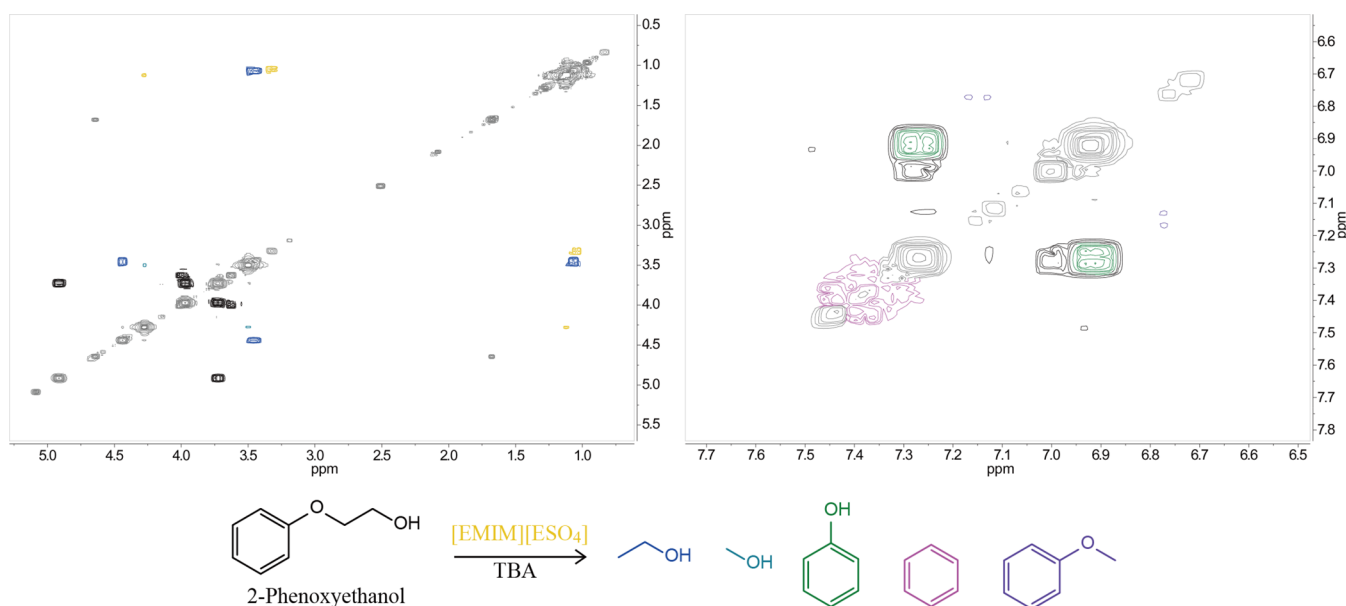


Figure 6. 2D COSY NMR spectra of the thermochemical conversion of 2-phenoxyethanol + [EMIM][ESO₄] + TBA.

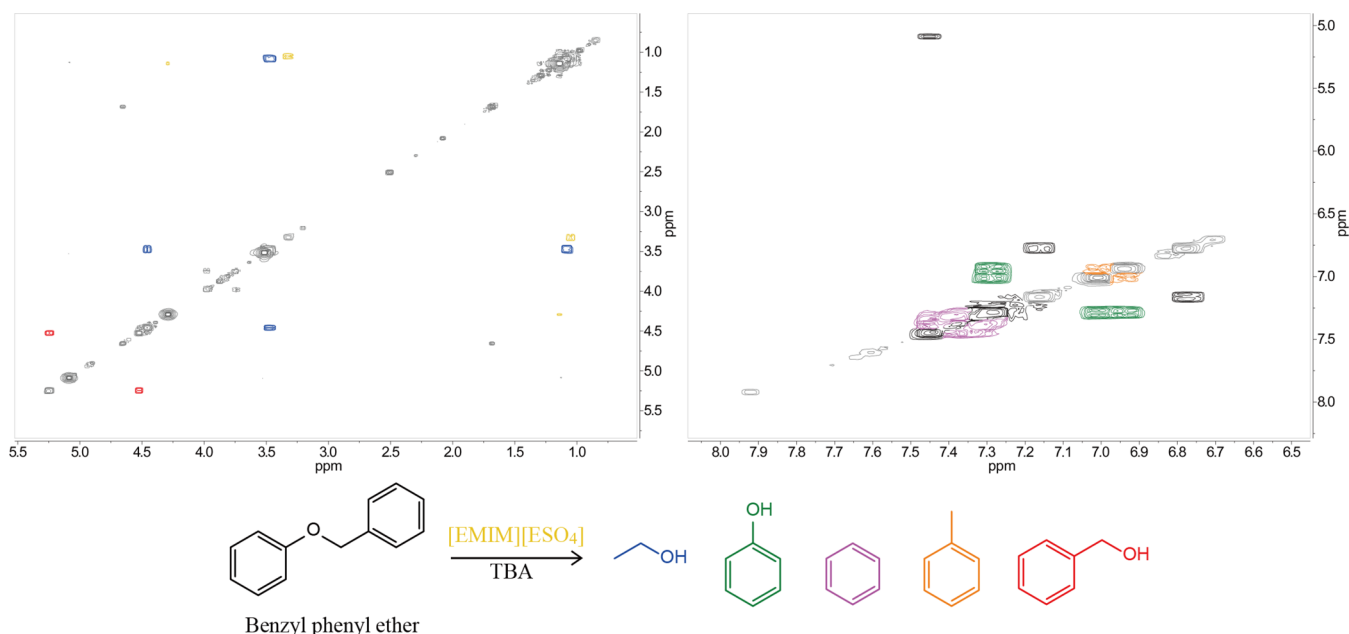
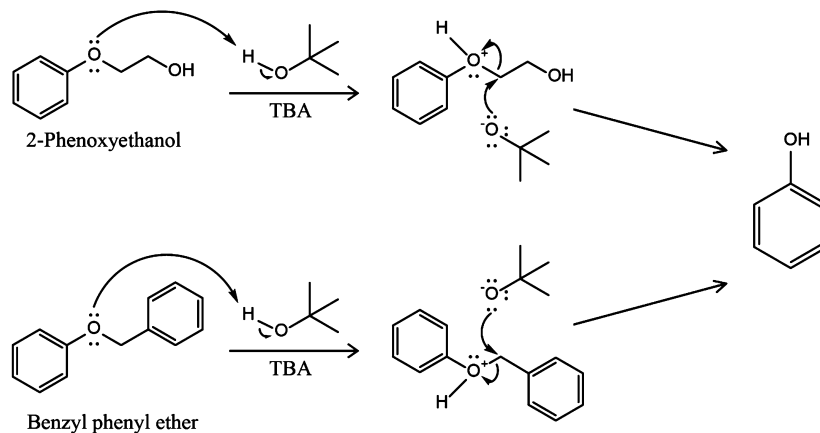
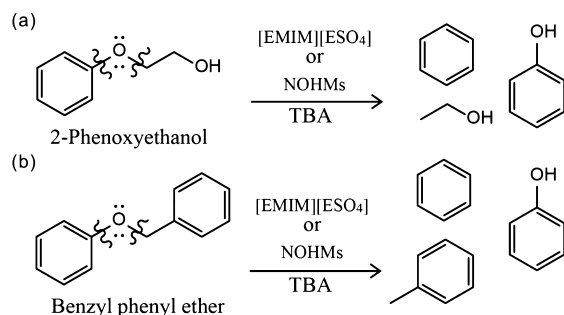


Figure 7. 2D COSY NMR spectra of the thermochemical conversion of benzyl phenyl ether + [EMIM][ESO₄] + TBA.

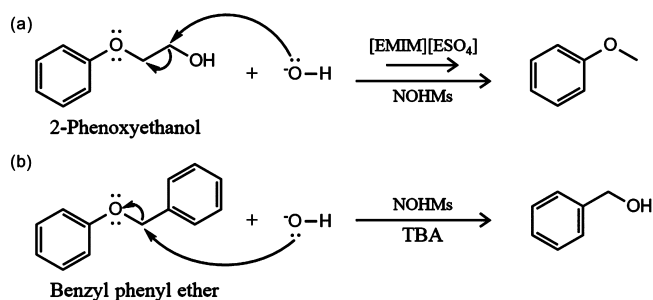
Scheme 2. Proposed Ether Cleavage Mechanisms of 2-Phenoxyethanol and Benzyl Phenyl Ether Using [EMIM][ESO₄] or NOHM with TBA



Scheme 3. Proposed Ether Cleavage Mechanisms of (a) 2-Phenoxyethanol To Form Phenol, Benzene, and Ethanol and (b) Benzyl Phenyl Ether To Form Benzene, Toluene, and Phenol in [EMIM][ESO₄] or NOHM with TBA



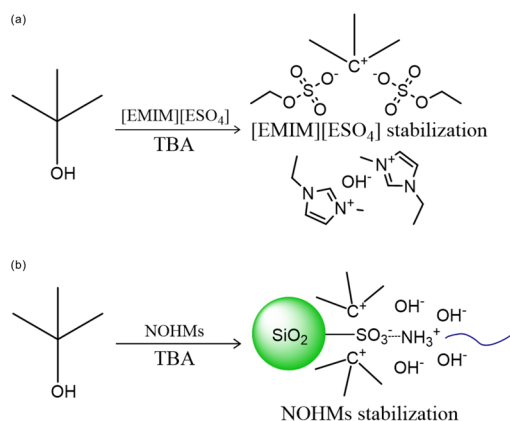
Scheme 4. (a) Proposed Decomposition Mechanism of 2-Phenoxyethanol To Form Anisole and (b) Proposed Reaction of Benzyl Phenyl Ether with Hydroxide Ion Produced from TBA To Form Phenylmethanol



toluene were additionally observed, as shown in Figure 5. The cross-peaks ((f1 (ppm), f2 (ppm))) at (1.06, 3.45) and (3.45, 4.41) were assigned to EtOH, those at (3.72, 3.97), (3.72, 4.88), and (~6.83, ~6.97) to 2-phenoxyethanol, those at

(~6.87, ~6.95) and (~7.23, ~7.30) to phenol, and those at (~6.89, ~6.93) and (~6.97, ~7.03) to toluene, which were produced by decomposition of 2-phenoxyethanol or benzyl phenyl ether. The proposed depolymerization reaction scheme is shown in Scheme 1.

Scheme 5. Proposed Stabilization Mechanisms of the Catalytic Solvents: The Tertiary Carbocation and Hydroxide Ion Produced from TBA Are Stabilized by (a) [EMIM][ESO₄] and (b) NOHM



To explore the effects of the type of alcohol, TBA, a tertiary alcohol, was selected as the proton source, and the thermochemical decomposition reactions were conducted with [EMIM][ESO₄]. The 2D COSY NMR spectra of the decomposed products from samples 3 and 4 are given in Figures 6 and 7, respectively. In the case of sample 3, more diverse forms of aromatic hydrocarbons such as phenol (Scheme 2), benzene (cross-peaks at (~7.26, ~7.42) and (~7.33, ~7.49); Scheme 3a), and anisole (cross-peaks at (~6.74, ~6.79) and (~7.12, ~7.18); Scheme 4a) were produced from the decomposition of 2-phenoxyethanol. Interestingly, EtOH (Scheme 3a) and methanol (cross-peak at (3.50, 4.27)) were also observed, even though TBA was used as the proton source. Cross-peaks at (1.05, 3.32) and (1.12, 4.28) assigned to [EMIM][ESO₄] were observed. It is speculated that phenol, benzene, anisole, and methanol can be synthesized under elevated temperature and pressure conditions. In the case of sample 4, the peak patterns, which were assigned to phenol (Scheme 2) and toluene (Scheme 3b), were

similar to the case of sample 2 (Figure 5). [EMIM][ESO₄] was also observed. The difference was that EtOH, benzene (Scheme 3b), and phenylmethanol (cross-peak at (4.52, 5.24); Scheme 4b) were produced from the depolymerization of benzyl phenyl ether.

Compared with the use of EtOH, the use of the tertiary alcohol TBA seemed to produce more diverse forms of aromatic hydrocarbon compounds. This implies that TBA has a significant role as a proton source in the thermochemical depolymerization of 2-phenoxyethanol and benzyl phenyl ether, exhibiting a better ability than the primary alcohol EtOH. As illustrated in Scheme 5, it is speculated that tertiary carbocations and hydroxide ions generated from TBA could be stabilized by the ionic species of [EMIM][ESO₄], resulting in more effective promotion of the formation of diverse moieties cleaving the C–O and/or C–C bonds of the lignin model compounds.

To examine the potential application of the NOHM for lignin valorization, the synthesized NOHM was adopted as a catalytic solvent, and the thermochemical reactions were carried out for 2-phenoxyethanol and benzyl phenyl ether using TBA as the proton source. The 2D COSY NMR results are shown in Figures 8 and 9. As can be seen in Figure 8, the peak patterns for sample 5 were assigned to EtOH (Scheme 3a), phenol (Scheme 2), benzene (Scheme 3a), and anisole (Scheme 4a), similar to the case of sample 4. The difference was that the amounts of aromatic hydrocarbons such as phenol, benzene, and anisole produced by decomposition of 2-phenoxyethanol were relatively larger than with sample 4. This phenomenon indicates that the NOHM can decompose the ether bond in the aromatic compounds more selectively than [EMIM][ESO₄] can.

Figure 9 shows the results of thermochemical conversion of sample 6, which indicate that EtOH, phenol (Scheme 2), benzene (Scheme 3b), toluene (Scheme 3b), and phenylmethanol (Scheme 4b) were observed. Interestingly, benzaldehyde (cross-peaks at (7.59, 7.71), (7.59, 7.91), and (7.59, 8.13)) and 2-benzylphenol (cross-peak at (3.72, 7.39)) were produced from benzyl phenyl ether. The conversion of benzyl

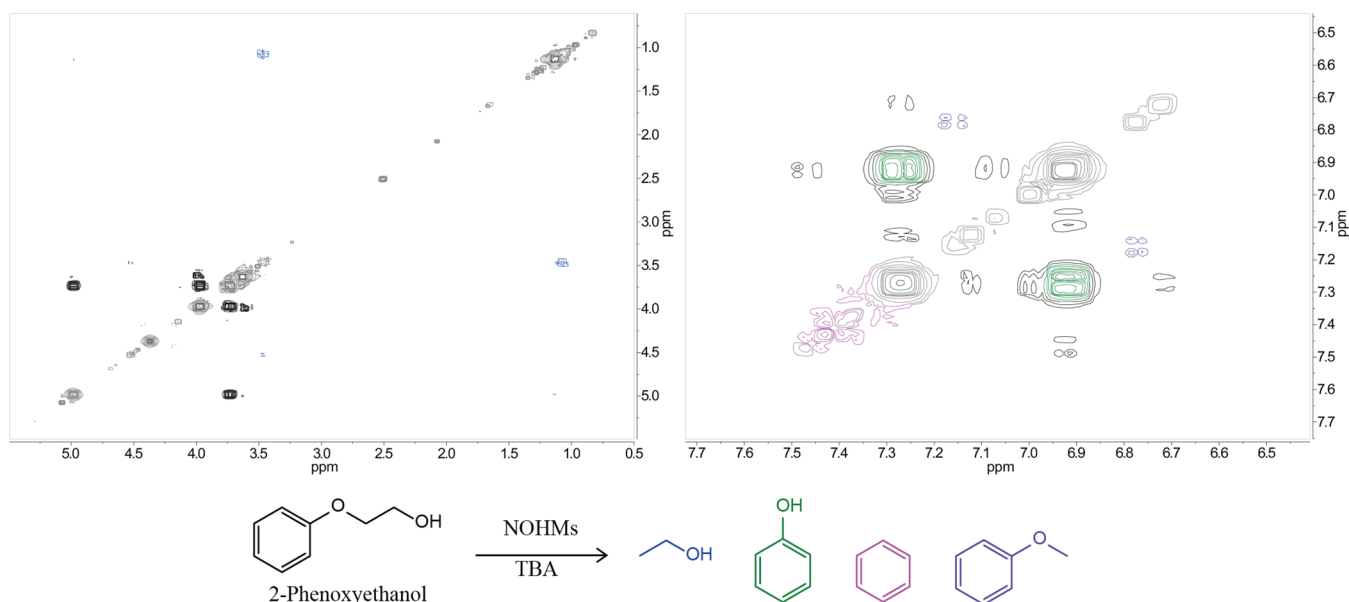


Figure 8. 2D COSY NMR spectra of the thermochemical conversion of 2-phenoxyethanol + NOHM + TBA.

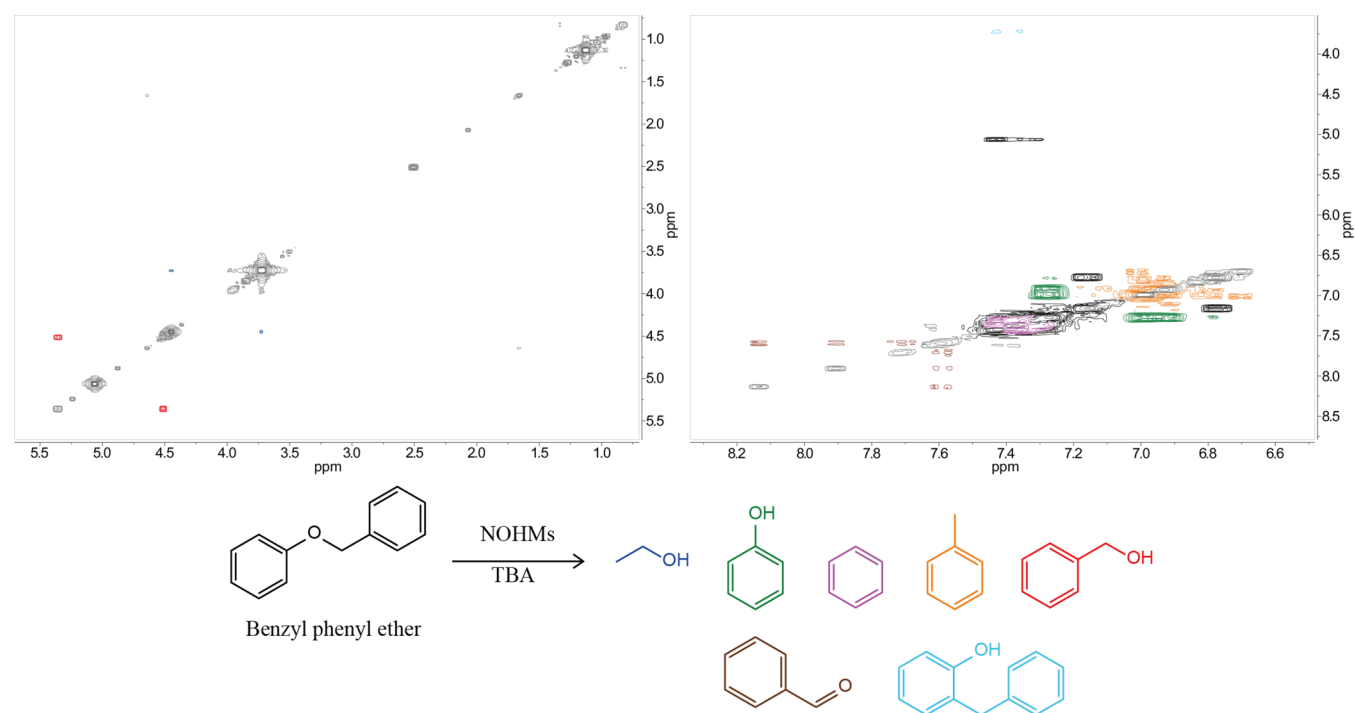


Figure 9. 2D COSY NMR spectra of the thermochemical conversion of benzyl phenyl ether + NOHM + TBA.

phenyl ether to benzaldehyde⁶⁷ and 2-benzylphenol⁶⁸ has been reported to result from hydrolysis and/or hydrothermal treatment. It is speculated that the NOHM-stabilized tertiary carbocations or hydroxide ions are more effective than [EMIM][ESO₄] in promoting the cleavage of C–O and/or C–C bonds in the lignin model compounds.

4. CONCLUSIONS

This study examined the thermochemical depolymerization of 2-phenoxyethanol and benzyl phenyl ether using different proton sources and catalytic solvents. ATR FT-IR and 2D ¹H–¹H COSY NMR spectra revealed that both lignin model compounds were successfully decomposed to aromatic hydrocarbon intermediates such as phenol, benzene, and toluene under the reaction condition of 20 bar in a N₂ environment at 473 K. The results revealed that the use of a tertiary alcohol, TBA, enhanced the thermochemical decomposition of the lignin model compounds and produced a more diverse range of aromatic hydrocarbons compared with the case of the primary alcohol EtOH. The results also revealed that the synthesized NOHM could be an effective catalytic solvent for cracking to form valuable compounds such as benzaldehyde and 2-benzylphenol, which were not observed in the case of [EMIM][ESO₄]. Also, the results obviously indicated that the NOHM can decompose the C–O and/or C–C bonds of the lignin model compounds more selectively than [EMIM][ESO₄] can. As a designer solvent, a NOHM could be a promising catalytic solvent for lignin valorization by optimal design of an organic canopy and inorganic catalytic nanocore species. Because only qualitative analyses were done in this study, further studies that include quantitative approaches are needed to fully utilize the potential applications of NOHMs in lignin valorization.

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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