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Org. Process Res. Dev., Just Accepted Manuscript • DOI: 10.1021/acs.oprd.8b00282 • Publication Date (Web): 23 Oct 2018 Downloaded from http://pubs.acs.org on October 24, 2018

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# Spectroscopic Investigation of Thermochemical Depolymerization of Lignin Model Compounds in the presence of Novel Liquid-like Nanoparticle Organic Hybrid Solvents for Efficient Biomass Valorization

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## **Table of Contents**



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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 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 ionic liquid, [EMIM][ESO<sub>4</sub>]. 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 use of NOHM can decompose the C–O and/or C–C bonds of lignin model chemicals more efficiently than the case of [EMIM][ESO<sub>4</sub>].

Keywords: Lignin, NOHMs, 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 level. Among the GHGs, CO<sub>2</sub> 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 CO<sub>2</sub> – first, CO<sub>2</sub> produced from large point sources such as fossil fuel power plants and industrial sites can be captured and stored so not to enter the atmosphere by using carbon capture and storage (CCS) technologies; second, CO<sub>2</sub> emissions can be prevented by fuel switching from fossil fuels to renewable energy resources such 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 CO<sub>2</sub> from the atmosphere with the storing solar energy. Furthermore, the total atmospheric CO2 inventory could become negative when combined with CCS.<sup>1</sup> For this reason, biomasses are expected to replace a significant portion of petroleumbased 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.<sup>5-12</sup> Lignocellulosic biomasses are the most abundant renewable resource in the world. They are generally composed of semi-crystalline cellulose (38–50%), amorphous hemicellulose (23–32%), and amorphous lignin (15–25%).<sup>13-15</sup> 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.<sup>7, 8, 9, 10, 16, 17</sup> Despite the promising potential, however, valorization of lignin via selective conversion has been a challenging problem due to its heterogeneous, non-hydrolysable 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).<sup>18</sup> 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<sup>19,20</sup> and the subunits are linked *via* interunit linkages such as  $\beta$ -O-4,  $\alpha$ -O-4,  $\beta$ -5,  $\beta$ - $\beta$ , 4-O-5, 5-5, and  $\beta$ -1, where the  $\beta$ -O-4 ether linkage is the most common representing 50% of all interunit bonds.<sup>15,21</sup> To break down the complexly integrated subunits to transform it to value-added products, various reactions including hydrolysis.<sup>22, 23</sup> catalytic cracking,<sup>24-26</sup> reduction,<sup>27-30</sup> and oxidation<sup>31-33</sup> can be adopted. As an alternative approach to convert lignin into the value-added aromatic compounds, ionic liquids (ILs) have recently been explored.<sup>15</sup> Because ILs exhibit a low or negligible volatility with the ability to tailor physicochemical properties, various applications including lignin extraction from lignocellulosic biomasses<sup>34-38</sup> as well as catalytic,<sup>39</sup> separations,<sup>40</sup> and biotechnology applications<sup>41</sup> have been investigated.

Here, we report the thermochemical transformation of lignin model compounds with an organic-inorganic hybrid solvent, otherwise known as 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).<sup>42-52</sup> NOHMs exhibit promising potential as a green solvent, particularly for energy and environmental applications, providing environmentally benign and highly tunable properties with a negligible vapor pressure at relatively high working temperatures.<sup>44</sup> Versatile combinations of an organic canopy and inorganic core species offer unique physicochemical properties, and thus, it is potentially applicable to a variety of areas including reaction solvents, CO<sub>2</sub> capture media, thermal management materials, electrolytes, magnetic fluids, and lubricants.<sup>44, 45, 49, 51, 53, 54, 55</sup> As an analog to ILs, we synthesized NOHM with a surface-modified SiO<sub>2</sub> 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, 2phenoxyethanol (99%, Sigma-Aldrich Co., USA), and benzyl phenyl ether (98%, Sigma-Aldrich Co., USA) were used without further purification. As reaction solvents, ethyl alcohol (EtOH, 99.9%) was purchased from Daejung Chemicals & Metals Co., LTD (Republic of Korea), and *tert*butyl alcohol (TBA, 99%) was supplied from Alfa Aesar (USA). A 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][ESO<sub>4</sub>], 95%) was also purchased from Sigma Aldrich Co. (USA).

#### 2.2. Synthesis of the Nanoparticle Organic Hybrid Materials

The NOHM was synthesized based on previously reported methods.<sup>44, 46, 55</sup> Briefly, 3.05 g of a 7 nm silica colloidal suspension (Sigma-Aldrich Co., USA) 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-propane sulfonic acid (Gelest Inc., USA). The acidity of the surface-modified SiO<sub>2</sub> 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, BUCHI Labortechnik AG, Switzerland) for 24 hours to complete the reaction. During the incubation, the mixture was stirred vigorously. After that, the excess silane was removed by dialysis (3.5k MWCO, Pierce Biotechnology Inc., USA) against deionized water for 48 hours. The dialyzed solution was then added to the cation exchange column (Dowex HCR-W2, Sigma-Aldrich Co., USA) 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., USA) was used as a polymeric precursor for the NOHM used in this study. A 20 wt% of the polymer solution was added dropwise to the functionalized silica nanoparticle suspension while monitoring the pH. The addition of the Jeffamine 2070 solution was done until reaching the equivalent point to obtain the highest grafting density. Finally, the NOHM was dried in a vacuum oven at 35 °C for 48 hours. 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 was used (M-Series, REXO Engineering Inc., Republic of Korea) for the thermochemical conversion of lignin model compounds. The reaction temperature was controlled with PID (proportional-integral-derivative) electrical heating and cooling arrangements.

The synthesized NOHM was used as a catalytic solvent for the thermochemical conversion of lignin model compounds. The [EMIM][ESO<sub>4</sub>] was also used as a catalytic solvent for comparison. EtOH and TBA were used as a proton source. The detailed experimental sets are tabulated in Table 1. A 20 ml glass vial was filled with 10 ml of solution included a lignin model chemical, catalytic solvent, and proton source. The vial was inserted into the high-pressure reactor. After tightening the reactor with bolts, the residual air inside the reactor was evacuated by flushing with N<sub>2</sub> several times. Finally, the high-pressure reactor was pressurized up to 20 bar with a syringe pump (500D, Teledyne Isco Inc., USA). After stabilization, the reactor was heated to 473 K for 30 minutes. The thermochemical conversion reaction was carried out at 473 K for 2 hours, followed by cooling for 30 minutes to 293 K for the analyses.

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#### 2.4. Spectroscopic Analyses

A Fourier-transform infrared (FT-IR) spectrometer (Spectrum Two, PerkinElmer Inc., USA) equipped with a deuterated triglycine sulfate (DTGS) detector, and an attenuated total reflectance (ATR) accessory (single reflection ZnSe crystal) was used. All spectra were recorded with a resolution of 2 cm<sup>-1</sup> in the 4000 – 500 cm<sup>-1</sup> wavenumber region with 8 scans at room temperature.

A 400 MHz nuclear magnetic resonance (NMR) spectrometer (AVANCE III HD 400, Bruker Co., Germany) located at Chonnam National University was used. All 2D  $^{1}H^{-1}H$ correlation spectroscopy (COSY) NMR spectra were recorded in the Fourier-Transfrom mode using dimethyl sulfoxide-d<sub>6</sub> (DMSO-d<sub>6</sub>, 99.9 atom% D, Sigma-Aldrich Co., USA) 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 hydrocarbons. 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,<sup>56, 57</sup> hydrolysis,<sup>58, 59</sup> thermochemical depolymerization,<sup>60, 61</sup> and hydrothermolysis.<sup>62, 63</sup> Recently, ILs were used as an effective catalytic solvent, particularly for the cleavage of the C–O ether bond of the  $\beta$ –O–4 linkage.<sup>64, 65</sup> ILs consist of relatively small inorganic anion and large organic cations that can act as a high performance reaction media as a liquid phase under 573 – 673 K.<sup>66</sup> Due to their non-volatile and high thermal stability, ILs could accelerate the cracking of the C–O ether bond of the  $\beta$ –O–4 linkage by thermochemical depolymerization.

Thus, we explored the thermochemical depolymerization of lignin model compounds, 2phenoxyethanol and benzyl phenyl ether, using reaction solvents that were mixtures of proton sources (EtOH or TBA) and catalytic liquids ([EMIM][ESO<sub>4</sub>] or NOHM). To compare the effect of primary and tertiary alcohols as a proton source, EtOH and TBA were chosen. The depolymerization performance of the catalytic solvents was also compared focusing on an IL (([EMIM][ESO<sub>4</sub>]) and the synthesized NOHM. The thermal stability of the NOHM used in this study was previously investigated by Lin et al., and the depolymerization was conducted below its decomposition temperature.<sup>44</sup>

For the preliminary analysis of the depolymerized products by the thermochemical conversion reactions, first, the ATR FT-IR spectra of the products for samples #1 - #6 were

obtained shown in Figure 3. Compared to 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<sup>-1</sup>, which correspond to the vibration of the phenyl C–O stretching, disappeared after the thermochemical depolymerization (Figure 3 (a), (c), (d), (e), and (f)). The intensities of bands in region 800 – 600 cm<sup>-1</sup> were changed, where the vibrations of the aromatic C–H bonds, were also observed shown in Figure 3 (c) – (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 <sup>1</sup>H<sup>-1</sup>H COSY NMR spectroscopy was employed, and the decomposed products were analyzed shown in Figure 4 – 9. Figure 4 and 5 show the 2D COSY NMR spectra of the decomposed products from samples #1and #2, respectively. As shown in Figure 4, most of the products remained as EtOH and 2phenoxyethanol, only a small amount of phenol was observed. In the case of sample #2, similar to sample #1, the benzyl phenyl ether and EtOH were remained, phenol and toluene were additionally observed in Figure 5. The cross peaks ((f1 (ppm), f2 (ppm)))) at (1.06, 3.45) and (3.45, 4.41) identified as EtOH; (3.72, 3.97), (3.72, 4.88) and ( $\sim$  6.83,  $\sim$  6.97) were assigned to 2phenoxyethanol; the cross peaks at ( $\sim$  6.87,  $\sim$  6.95) and ( $\sim$  7.23,  $\sim$  7.30) were assigned as phenol and the cross peaks at ( $\sim$  6.89,  $\sim$  6.93) and ( $\sim$  6.97,  $\sim$  7.03) were identified as toluene which were decomposed from 2-phenoxyethanol or benzyl phenyl ether. The proposed depolymerization reaction scheme is shown in Scheme 1.

To explore the effects of the type of alcohol, TBA, a tertiary alcohol, was selected as a proton source, and the thermochemical decomposition reactions were conducted with [EMIM][ESO<sub>4</sub>]. The 2D COSY NMR spectra of the decomposed products from sample #3 and #4 are given in Figure 6 and 7, respectively. In the case of sample #3, more diverse forms of aromatic hydrocarbons such as phenol (scheme 2), benzene (~ 7.26, ~ 7.42), (~ 7.33, ~ 7.49) (Scheme 3) (a)), and anisole (~ 6.74, ~ 6.79), (~ 7.12, ~ 7.18) (Scheme 4 (a)) were produced from the decomposition of 2-phenoxyethanol. Interestingly, EtOH (Scheme 3(a)) and methanol (3.50, 4.27) were also observed, even though TBA was used as a proton source. The cross peaks at (1.05, 3.32)and (1.12, 4.28) assigned as an [EMIM][ESO<sub>4</sub>] was observed. It is speculated that the formation of phenol, benzene, anisole and methanol can be synthesized at elevated temperature and pressure conditions. In the case of sample #4, the peak patterns, which were assigned to phenol (Scheme 2), and toluene (Scheme 3 (b)), were similar to the case of sample #2 (Figure 5). The [EMIM][ESO<sub>4</sub>] was also observed, however, what was different, EtOH, benzene (Scheme 3 (b)) and phenylmethanol (4.52, 5.24) (Scheme 4 (b)) were produced from the depolymerization of benzyl phenyl ether.

When compared to the cases of EtOH, the use of a 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 that of the primary alcohol, EtOH. As illustrated in Scheme 5, it is speculated that a tertiary carbocation or hydroxide ion generated from TBA could be stabilized by the ionic species of [EMIM][ESO<sub>4</sub>] resulting in more effectively

promoting 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 were adopted as a catalytic solvent, and the thermochemical reactions were carried out for 2-phenoxyethanol and benzyl phenyl ether using TBA as a proton source. The 2D COSY NMR results are shown in Figure. 8 and 9. As seen in Figure 8, the peak patterns were assigned as EtOH (Scheme 3 (a)), phenol (Scheme 2), benzene (Scheme 3 (a)), anisole (Scheme 4 (b)) were similar to the case of sample #4. What was different, however, the amount of aromatic hydrocarbons such as phenol, benzene, and anisole, which were decomposed from 2-phenoxyethanol was relatively larger than sample #4. This phenomenon indicates the NOHM can decompose the ether bond in the aromatic compounds more selectively than the case of [EMIM][ESO4] adaptation.

Figure 9 shows the thermochemical conversion result of sample #6. The result indicates that EtOH, phenol (Scheme 2), benzene (Scheme 3(b)), toluene (Scheme 4 (b)), phenylmethanol (Scheme 4 (b)) were observed. Interestingly, the benzaldehyde (7.59, 7.71), (7.59, (7.91), and (7.59, 8.13) and 2-benzyl phenol (3.72, 7.39) were produced from benzyl phenyl ether. The conversion of benzyl phenyl ether to benzaldehyde<sup>67</sup> and 2-benzyl phenol<sup>68</sup> has been reportedly supported by hydrolysis and/or hydrothermal treatment. It is speculated that the NOHM stabilized tertiary carbocation or hydroxide ion more effectively than [EMIM][ESO<sub>4</sub>] to promote the cleavage of C–O and/or C–C bonds in the lignin model compounds.

#### **4. CONCLUSIONS**

This study examined the thermochemical depolymerizations of 2-phenoxyethanol and benzyl phenyl ether by using proton sources and catalytic solvents. ATR FT-IR and 2D <sup>1</sup>H<sup>-1</sup>H 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 N<sub>2</sub> environment at 473 K. The results revealed that the use of a tertiary alcohol, TBA, enhanced the thermochemical decomposition of the lignin model compounds producing diverse aromatic hydrocarbons compared to the case of the primary alcohol, EtOH. The results also revealed that the synthesized NOHM could be an effective catalytic solvent cracking valuable compounds such as benzaldehyde and 2-benzyl phenol which were not observed in the case of [EMIM][ESO<sub>4</sub>]. Also, the results obviously indicated that the NOHM can decompose the C-O and/or C-C bonds of lignin model chemical more selectively than the case of [EMIM][ESO<sub>4</sub>]. As a designer solvent, the NOHM could be a promising catalytic solvent for lignin valorization by optimal designing 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 NOHM in lignin valorization.



Figure 1. Lignin monolignols: (a) p-Coumaryl alcohol (H), (b) Coniferyl alcohol (G), (c) Sinapyl

alcohol (S).



**Figure 2.** (a) Synthesis and schematic structure of the NOHM with ionically tethered amine terminated polymeric canopy species, and (b) photo image.



**Figure 3.** ATR FT-IR spectra of the thermochemical depolymerization of (a) 2-phenoxyethanol + [EMIM][ESO<sub>4</sub>] + EtOH, (b) benzyl phenyl ether + [EMIM][ESO<sub>4</sub>] + EtOH, (c) 2-phenoxyethanol + [EMIM][ESO<sub>4</sub>] + TBA, (d) benzyl phenyl ether + [EMIM][ESO<sub>4</sub>] + TBA, (e) 2-phenoxyethanol + NOHM + TBA, and (f) benzyl phenyl ether + NOHM + TBA.



**Figure 4.** 2D COSY NMR spectra of the thermochemical conversion of 2-phenoxyethanol + [EMIM][ESO<sub>4</sub>] + EtOH.



**Figure 5.** 2D COSY NMR spectra of the thermochemical conversion of benzyl phenyl ether + [EMIM][ESO<sub>4</sub>] + EtOH.



**Figure 6.** 2D COSY NMR spectra of the thermochemical conversion of 2-phenoxyethanol + [EMIM][ESO<sub>4</sub>] + TBA.

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**Figure 7.** 2D COSY NMR spectra of the thermochemical conversion of benzyl phenyl ether + [EMIM][ESO<sub>4</sub>] + TBA.



**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.



Scheme 1. Proposed ether cleavage mechanism of 2-phenoxyethanol and benzyl phenyl ether using [EMIM][ESO<sub>4</sub>] and EtOH.





**Scheme 2.** Proposed ether cleavage mechanisms of 2-phenoxyethanol and benzyl phenyl ether using [EMIM][ESO<sub>4</sub>] or NOHM with TBA.



**Scheme 3.** (a) Proposed ether cleavage mechanisms of 2-phenoxyethanol for the formation of phenol, benzene, and ethanol. (b) Proposed decomposition mechanism of benzene, toluene, phenol in the [EMIM][ESO<sub>4</sub>] or NOHM with TBA.



**Scheme 4.** Proposed decomposition mechanisms of 2-phenoxyethenaol for the formation of (a) anisole and (b) phenylmethanol reacted with hydroxide ion produced from TBA.



**Scheme 5.** Proposed stabilization mechanisms of the catalytic solvents; the tertiary carbocation and hydroxide ion produced from TBA were induced (a) [EMIM][ESO<sub>4</sub>], and (b) NOHM.

 Table 1. Experimental sets of the thermochemical conversion of lignin model compounds

 examined in this study.

Sample	Lignin model compound (g)	Catalytic solvent (g)	Proton source solvent
#1	2-Phenoxyethanol (0.138 g)	[EMIM][ESO <sub>4</sub> ] (0.236 g)	EtOH (7.89 g)
#2	Benzyl phenyl ether (0.184 g)	[EMIM][ESO <sub>4</sub> ] (0.236 g)	EtOH (7.89 g)
#3	2-Phenoxyethanol (0.138 g)	[EMIM][ESO <sub>4</sub> ] (0.236 g)	TBA (7.81 g)
#4	Benzyl phenyl ether (0.184 g)	[EMIM][ESO <sub>4</sub> ] (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)

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The manuscript was written through contributions of all authors.

#### ACKNOWLEDGMENT

This research was supported by GIST Research Institute (GRI) in 2018. We thank Ms. R. Chang for the help with NOHM synthesis.

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