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Reactions of lignin model compounds in ionic liquids

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ABSTRACT

Lignin, a readily available form of biomass, is a potential source of renewable aromatic chemicals through catalytic conversion. Recent work has demonstrated that ionic liquids are excellent solvents for processing woody biomass and lignin. Seeking to exploit ionic liquids as media for depolymerization of lignin, we investigated reactions of lignin model compounds in these solvents. Using Brønsted acid catalysts in 1-ethyl-3-methylimidazolium triflate at moderate temperatures below 200 °C, we obtained up to 11.6% molar yield of the dealkylation product 2-methoxyphenol from the model compound 2-methoxy-4-(2-propenyl)phenol and cleaved 2-phenylethyl phenyl ether, a model for lignin ethers. Despite these successes, acid catalysis failed in dealkylation of the saturated-chain model compound 4-ethyl-2-methoxyphenol and did not produce monomeric products from organosolv lignin, demonstrating that further work is required to understand the complex chemistry of lignin depolymerization.

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1. Introduction

Lignin is one of the major components of biomass and a potential source for aromatic chemicals. Accounting for 15–30% of woody biomass, it is produced today in large quantities as a byproduct of wood pulping (50 Mt in the US alone in 2000) and is mainly burned for power generation and recovery of pulping chemicals [1–3]. This polyphenolic material, however, could potentially serve as a renewable chemical feedstock if suitable conversion chemistry is developed. As indicated by the generalized structure of lignin which is shown in Fig. 1, native lignin consists of aryl ether units connected by an array of ether and alkyl linkages, and

cleavage of these linkages would yield monomeric phenols and methoxyphenols. Organosolv lignin, which has relatively low molecular weight and is sulfur-free, is a particularly attractive target for catalytic conversion. This form of lignin results from cleavage of most α -aryl ethers and some β -aryl ethers in the native lignin through a pulping process using an aqueous–organic solvent at low pH [4–8]. The intent of this study was to develop catalytic depolymerization of organosolv lignin to monomeric aromatics via acid-catalyzed dealkylation chemistry in ionic liquids at moderate temperatures.

Acid catalysis, commonly used for dealkylation of aromatics, is one of the several options for depolymerizing lignin. Hydrocracking of lignin using metal catalysts has been studied

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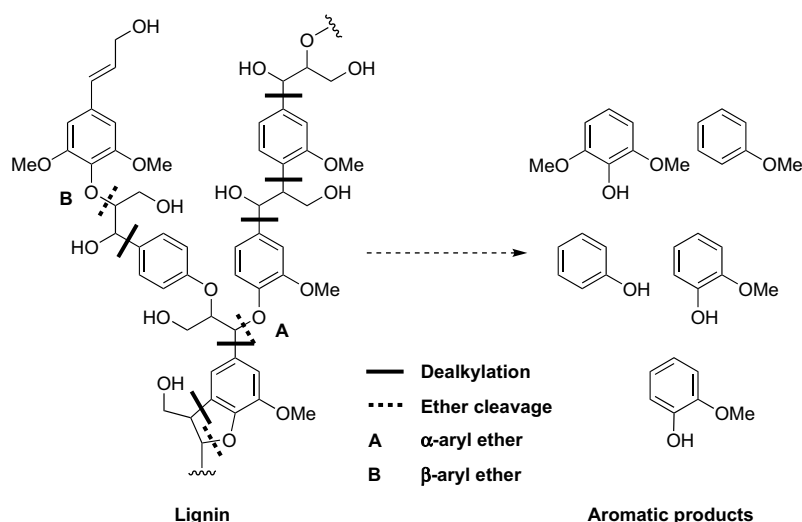


Fig. 1 – Generalized chemical structure of lignin and schematic for its conversion into monomeric aromatic products. Reactions which cleave aryl ethers and aryl-alkyl linkages would enable conversion of lignin into valuable aromatic chemicals.

extensively [9–12]. For instance, Alen and coworkers reported up to 71 wt% yield of acetone-soluble products from a variety of lignins treated with hydrogen and nickel-molybdenum or chromium oxide catalysts at 400 °C [10]. Nevertheless, such hydrocracking processes typically produce less than 10 wt% of monocyclic aromatics [10]. Schultz and coworkers used alkaline hydrolysis of lignin at 250 °C to produce monomeric phenols in 16–18 wt% yield [13]. In this case concurrent treatment with hydrogenolysis catalysts did not affect the yield. Lewis acid catalysts such as ZnCl_2 , FeCl_3 , and AlCl_3 have been used to depolymerize lignin and produce phenols in low yields, typically at temperatures in excess of 300 °C [14–19]. For instance, by treating organosolv lignin with 10 wt% FeCl_3 in water at 305 °C, Thring and coworker obtained 14.1 wt% ether-soluble products including 3.0 wt% identifiable phenolic compounds [17]. Using temperatures over 500 °C and Brønsted acidic zeolite catalysts, Thring and coworkers produced liquid and gaseous hydrocarbons from a lignin-acetone stream in up to 85% combined yield [20]. In contrast to other depolymerization processes, no phenolic products were observed, suggesting that lignin is cracked into alkene intermediates which undergo further reactions to form the ultimate hydrocarbon products. Coal also possesses chemical linkages similar to those in lignin, and Lewis and Brønsted acid catalysis has been utilized to produce liquid products from coal [21–24].

Ionic liquid solvents may be advantageous media for this acid-catalyzed lignin chemistry because they favor carbocation-forming reactions [25,26] and, unlike typical organic solvents, readily dissolve lignin [27,28]. Despite these potential benefits, ionic liquids have been primarily studied in the conversion of carbohydrates [29–31], and there are few studies of lignin reactivity in ionic liquids. This investigation fills the gap by examining lignin chemistry in dialkylimidazolium ionic liquid solvents, primarily 1-ethyl-3-methylimidazolium triflate and chloride ([EMIM]OTf and [EMIM]Cl, Fig. 2). Butyl (BMIM) and octyl (OMIM) derivatives as well as ionic liquids of other anions were used to a lesser extent.

Ionic liquids also have limitations as reaction media. They may present challenges for the separation of reaction products, and their expense necessitates highly efficient solvent recycling. In the case of successful lignin depolymerization, volatile aromatic products might be distilled from the ionic liquid reaction medium, and polymeric lignin-based byproducts might be precipitated with water or be separated by selective membrane technologies to prepare the ionic liquid for re-use. Nonetheless, these separation issues would require significant process engineering. In addition, the physicochemical characteristics of ionic liquids limit the range of temperatures which may be explored for lignin conversion chemistry. [EMIM]Cl has a relatively high melting temperature of 89 °C, and many chloride and triflate ionic liquids decompose at temperatures above 200 °C [32,33], creating a useful temperature range of 100–200 °C. In the presence of reactive species, the actual stability of these solvents may be even lower.

Given the above constraints, this investigation focused on depolymerization of organosolv lignin at moderate temperatures using acid catalysts under reductive conditions. The experimental plan employed high-throughput screening of a wide range of Lewis and Brønsted acid catalysts in combination with reduction catalysts in a variety of ionic liquids (Tables 1 and 2). For simplicity of analysis, conditions were first tested with the model compound eugenol before experiments were performed with alternative models and organosolv lignin. Reactions were evaluated based on the generation

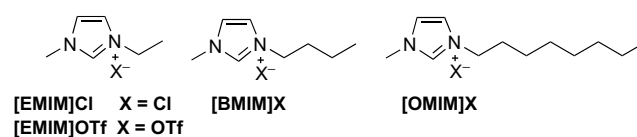


Fig. 2 – Dialkylimidazolium ionic liquids. These low-melting salts are promising solvents for lignin and, in the case of the chloride salts, lignocellulosic biomass.

Table 1 – Conversion of eugenol in ionic liquids using supported metal, Lewis acid, and Brønsted acid catalysts.

Catalyst	Ionic liquid	Conversion (%)	Guaiacol yield (%)	4-Propylguaiacol yield (%)	Isoeugenol yield (%)
–	[EMIM]OTf	19.6	–	–	–
Co-0179T (Co/silica)	[EMIM]OTf	100.0	–	64.5	–
Cu-1186T (Cu/alumina)	[EMIM]OTf	99.8	–	48.8	–
Cr-0211T (chromia/alumina)	[EMIM]OTf	50.0	–	2.9	–
0.5% Pd/alumina (C3677)	[EMIM]OTf	99.6	–	77.5	–
5% Pd/5% Re/carbon	[EMIM]OTf	100.0	–	48.0	–
G-99B (Copper chromite)	[EMIM]OTf	97.9	–	59.2	–
NISAT H RS (Ni)	[EMIM]OTf	99.3	–	71.3	–
Ti-0720 T (High surface area titania)	[EMIM]OTf	33.5	–	1.2	–
Nb ₂ O ₅ Hydrate (6518-43-11)	[EMIM]OTf	40.6	–	2.1	–
Silica/alumina T-869	[EMIM]OTf	21.5	–	0.3	–
Montmorillonite K10	[EMIM]OTf	37.0	–	–	–
Sulfated ZrO ₂	[EMIM]OTf	44.9	–	2.9	–
PtO ₂	[EMIM]OTf	99.4	–	68.3	–
–	[EMIM]Cl	55.3	–	1.3	1.0
CrCl ₂ ·2 H ₂ O	[EMIM]Cl	82.9	–	–	–
FeCl ₂	[EMIM]Cl	91.0	–	–	0.2
FeCl ₃ ·6 H ₂ O ^a	[EMIM]Cl	73.8	–	–	0.7
CoCl ₂	[EMIM]Cl	37.1	–	0.4	1.7
NiCl ₂	[EMIM]Cl	37.9	–	0.3	2.5
PdCl ₂	[EMIM]Cl	99.6	–	43.9	–
CuCl ₂	[EMIM]Cl	60.8	–	0.9	–
ZnCl ₂	[EMIM]Cl	34.1	–	0.2	2.9
InCl ₃	[EMIM]Cl	38.6	–	0.3	3.3
SnCl ₄	[EMIM]Cl	44.9	–	–	1.9
CeCl ₃	[EMIM]Cl	29.9	–	0.5	3.3
SmCl ₃	[EMIM]Cl	34.4	–	0.2	3.3
AlCl ₃	[EMIM]Cl	95.1	–	–	4.7
RuCl ₃ × H ₂ O ^a	[EMIM]Cl	100.0	–	66.0	–
RhCl ₃ ^a	[EMIM]Cl	100.0	–	74.5	–
MnCl ₂ ^a	[EMIM]Cl	56.0	–	2.2	0.7
La(OTf) ₃	[EMIM]OTf	25.8	–	–	–
Sc(OTf) ₃	[EMIM]OTf	71.8	–	16.5	1.2
Zn(OTf) ₂	[EMIM]OTf	30.2	–	–	0.6
HCl ^b	[EMIM]Cl	99.6	–	–	–
H ₂ SO ₄ ^b	[EMIM]Cl	100.0	–	–	–
H ₂ SO ₄ ^c	[EMIM]OTf	100.0	7.8	–	–

Conditions: 10 wt% substrate in ionic liquid, 100 wt% supported catalyst or 10 mol% homogeneous catalyst, 180 °C, 2 h, 6.9 MPa H₂. Conversions and yields assessed by GC.

a 20 wt% catalyst.

b 40 wt% catalyst.

c 3.4 MPa H₂.

of volatile aromatic products. Model compounds which bear the chemical functionality of lignin are commonly used for exploratory and mechanistic studies [34–37] because of the complex chemical structure of lignin. For this study, lignin-like model compounds decorated with alkyl groups were chosen to focus on dealkylation chemistry. Eugenol (2-methoxy-4-(2-propenyl)phenol, **1**, Fig. 3) was chosen as the primary model compound in this study because it contains the guaiacyl aromatic moiety common in lignin, has a functionalized alkyl chain as a target for dealkylation reactions, has been used previously in lignin model studies, and is easily obtained. As a secondary model compound, 4-ethyl-2-methoxyphenol (4-ethylguaiacol, **2**) presents a more challenging unfunctionalized alkyl substituent. On the other hand, 2-phenylethyl phenyl ether (**3**) mimics the β-aryl ethers

common in lignin, providing a test of dealkylation conditions against ether linkages. Herein we report the reactivity of these model compounds and organosolv lignin itself in ionic liquids in the presence of a range of catalysts.

2. Experimental

2.1. General considerations

Commercial chemicals were of reagent grade or better, and were used without further purification. Cryoground Nafion NR-50 resin (perfluoro(3,6-dioxo-4-methyl-7-octenesulfonyl fluoride)-tetrafluoroethylene copolymer), Co-0179T, Cu-1186T, Cr-0211T, 5% Pd/5% Re/carbon, 0.5% Pd/Al₂O₃ (C3677),

Table 2 – Conversion of eugenol to guaiacol using Brønsted acid catalysts in [EMIM]OTf.

Catalyst	Temperature (°C)	Conversion (%)	Guaiacol yield (%)	4-Propylguaiacol yield (%)	Isoeugenol yield (%)
HOTs	180	95.5	1.6	1.3	0.5
H ₃ PMo ₁₂ O ₄₀	180	100.0	8.6	1.3	–
H ₄ SiW ₁₂ O ₄₀	180	100.0	7.5	1.7	–
Amberlyst 35	180	75.9	0.4	0.6	1.4
Dowex Monosphere M-31	180	45.8	–	–	1.8
Nafion	180	99.3	6.7	1.9	–
Nafion ^a	180	100.0	11.6	–	–
–	200	52.0	0.4	3.0	1.1
Nafion ^b	200	99.2	1.3	2.7	–
ZSM-5	200	53.0	0.2	3.0	3.9
USY	200	99.4	7.4	3.7	–
Y	200	97.7	2.2	4.4	0.5
LZY-82	200	99.7	6.7	3.5	–
X-4835	200	72.7	0.7	3.1	2.7
HFZ-33	200	97.8	2.5	5.7	0.5
Mordenite	200	98.2	2.4	4.2	0.5
Ferrierite	200	63.7	0.5	3.4	3.2
0.1% Pt/ZSM-5	200	99.5	0.2	50.4	–
0.1% Pt/USY	200	99.6	0.5	51.9	–
0.1% Pt/Y	200	100.0	0.9	49.0	–
0.1% Pt/LZY-82	200	100.0	1.3	42.5	–
0.1% Pt/X-4835	200	94.2	0.7	24.2	2.0
0.1% Pt/HFZ-33	200	99.8	0.5	49.6	–
0.1% Pt/mordenite	200	100.0	4.3	32.3	–
0.1% Pt/ferrierite	200	100.0	4.1	13.8	–

Conditions: 10 wt% substrate in [EMIM]OTf, 100 wt% supported catalyst or 5 mol% homogeneous catalyst, 180 °C, 2 h, 6.9 MPa psi H₂.

Conversions and yields assessed by GC.

a 10 mol% catalyst, 3.4 MPa H₂.

b 10 mol% catalyst.

Ti-0720T, Nb₂O₅ Hydrate (6518-43-11), zeolite USY (H⁺ form), zeolite X-4835 (H⁺ form), and zeolite HFZ-33 (H⁺ form) were obtained from Engelhard (now BASF, Iselin, NJ). Zeolites ZSM-5 (H⁺ form), Y (H⁺ form), mordenite (NH₄⁺ form), and ferrierite (NH₄⁺ form) were obtained from Zeolyst International (Valley Forge, PA). Zeolite LZY-82 (H⁺ form) was obtained from Union Carbide (now Dow Chemical, Midland, MI). G99-B, NISAT H RS, and T-869 SiO₂/Al₂O₃ were obtained from Sud-Chemie (Louisville, KY). Amberlyst 35 was obtained from Rohm and Haas (Philadelphia, PA). 2-Methoxy-4-(2-propenyl)phenol (eugenol, CAS # 97-53-0), 2-methoxyphenol (guaiacol, CAS # 90-05-1), 4-ethyl-2-methoxyphenol (4-ethylguaiacol, CAS # 2785-89-9), montmorillonite K10, sulfated zirconia, Dowex Monosphere M-31, and organosolv lignin (AlCell[®] lignin from mixed hardwoods [8], product number 371017) were obtained from Aldrich (Milwaukee, WI). [EMIM]OTf, [EMIM]Cl, 1-ethyl-3-methylimidazolium bromide, 1-ethyl-3-methylimidazolium methane

sulfonate, 1-ethyl-3-methylimidazolium dicyanamide, triethylsulfonium triflimide, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate, and 1-butyl-1-methylpyrrolidinium triflimide were obtained from Solvent Innovations (Cologne, Germany). 1-Ethyl-3-methylimidazolium acetate, 1-butyl-3-methylimidazolium trifluoroacetate, 1-octyl-3-methylimidazolium chloride, 1-octyl-3-methylimidazolium tetrafluoroborate were obtained from Fluka (Buchs, Switzerland). Chloroaluminate ionic liquid [EMIM]AlCl₄-AlCl₃ was prepared from 1 equivalent of [EMIM]Cl and 2 equivalents of AlCl₃ [38]. 2-Phenylethyl phenyl ether (CAS # 40515-89-7) was obtained from Frinton Laboratories (Vineland, NJ). All commercial catalysts were used as received.

All reactions were performed in glass vials sealed with Teflon gaskets in a steel High Pressure Reactor (HPR) on a Heated Orbital Shaker Station (HOSS) from Symyx (Santa Clara, CA). Gas chromatography was performed on an Agilent 6890 using a DB-1 column (Agilent J&W, 15 m × 0.25 mm × 0.25 μm).

2.2. Preparation of zeolite catalysts

For each zeolite (see General Considerations), 25 mg of the zeolite powder was placed in a glass vial in a calcination reactor. For Pt-doped zeolites, the zeolite powder was then treated with the appropriate concentration of chloroplatinic

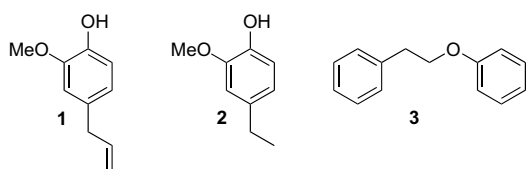


Fig. 3 – Lignin model compounds. Eugenol (1), 4-ethylguaiacol (2), and 2-phenylethyl phenyl ether (3).

acid solution to achieve 0.1% Pt by incipient wetness impregnation. Next, the zeolites in the calcination reactor were heated to 300 °C under N₂(g) (10 cm³ min⁻¹). After 2 h, the reactor was cooled to 150 °C, and the catalysts were reduced under H₂(g) (50 cm³ min⁻¹) for 2 h. Upon cooling, the calcination reactor was sealed and taken into a nitrogen-filled glove box.

2.3. Representative procedure

In an HPR 24-well plate, glass vials 1, 4, 7, 10, 13, and 16 were charged with sulfuric acid (10 mol % with respect to substrate). Vials 2, 5, 8, 11, 14, and 17 were charged with 4-toluenesulfonic acid (10 mol % with respect to substrate). Vials 3, 6, 9, 12, 15, and 18 were charged with Nafion (10 mol % with respect to substrate). Next, [EMIM]OTf (225 mg) was added to each vial, followed by substrate: eugenol (25 mg, 152 μmol) in vials 1–3, organosolv lignin (25 mg) in vials 4–6, 2-phenylethyl phenyl ether (25 mg, 126 μmol) in vials 7–9 and 13–15, and 4-ethylguaiacol (25 mg, 164 μmol) in vials 10–12 and 16–18. The vials were then capped with a gas-permeable Teflon gasket, sealed in the HPR, purged with N₂ gas followed by H₂ gas, and heated to 180 °C on the HOSS while shaking at 600 rpm. Once at reaction temperature, the HPR was pressurized to 6.9 MPa with H₂ gas. After 2 h, the HPR was cooled to ambient temperature and vented. The reaction mixtures were diluted with a known mass of CH₂Cl₂ (~2 g), mixed vigorously, and centrifuged. The supernatant solution was analyzed by GC (Injection port: 270 °C, 200:1 Split; Column Flow: 2.0 cm³ min⁻¹; Oven: 40 °C for 1.6 min min⁻¹, ramp 15 °C min⁻¹ to 160 °C, ramp 25 °C min⁻¹ to 280 °C, hold for 1.4 min; Detection: FID, 300 °C).

In the case of reactions performed using zeolite catalysts, [EMIM]OTf was dried over molecular sieves, and solvent, catalyst, and substrate were added to the reaction vials in a nitrogen-filled glove box. The HPR was sealed before being removed from the glove box and placed on the HOSS.

3. Results and discussion

3.1. Catalyst screening

The study began with a screen of a wide range of heterogeneous and homogeneous catalysts for conversion of the lignin model compound eugenol in [EMIM]OTf and [EMIM]Cl, two ionic liquids with distinct anion properties (Table 1). At 180 °C under 6.7 MPa H₂, low to moderate conversion of eugenol was observed in the two solvents in the absence of catalyst; alkene isomerization to isoeugenol (4, Fig. 4) was observed in

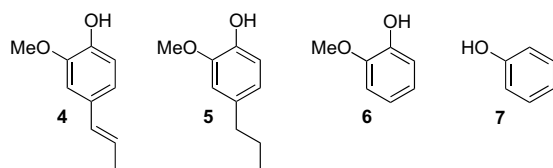


Fig. 4 – Reaction products of lignin model compounds. Isoeugenol (4), 4-propylguaiacol (5), guaiacol (6), and phenol (7).

[EMIM]Cl. The alkene isomerization reaction may be catalyzed by trace amounts of hydrochloric acid which can add to the terminal alkene before eliminating to form the isomerized alkene [39]. The majority of supported metal catalysts in [EMIM]OTf hydrogenated the alkene functionality of eugenol to form 4-propylguaiacol (2-methoxy-4-(2-propyl)phenol, 5), as did palladium(II), rhodium(III), and ruthenium(III) chlorides in [EMIM]Cl (the active catalysts in these cases are probably formed by reduction of the metal chlorides by hydrogen). While dealkylation activity might be expected from the chromia/alumina catalyst (Cr-0211), the reaction temperature, which was much lower than the 350–500 °C typically used with this catalyst, was perhaps too low to observe this reactivity [40,41]. A range of Lewis acidic heterogeneous and homogeneous catalysts including metal chlorides and triflates produced only low yields of identifiable products from eugenol, mainly isoeugenol. On the other hand, heterogeneous and homogeneous Brønsted acid catalysts such as Nafion (perfluorinated sulfonic acid resin), H⁺-exchanged zeolites, sulfuric acid, and heteropoly acids (H₃PMo₁₂O₄₀ and H₄SiW₁₂O₄₀) produced guaiacol (6) in up to 11.6% yield from eugenol in [EMIM]OTf (Table 2). Notably, Pt/zeolite catalysts, traditionally utilized for dealkylation of aromatics [42], were less effective than zeolites without Pt. Additionally, guaiacol production by Brønsted acid catalysts was accompanied by very high conversion of eugenol, likely resulting in the formation of undetected oligomeric products (*vide infra*).

With traditional bifunctional hydrocracking catalysts on acidic supports, such as Pt/zeolites, nickel-molybdenum/alumina, or chromia/alumina, dealkylation occurs through loss of an alkene followed by hydrogenation of the alkene into an alkane as shown in Fig. 5A [43]. Similarly, for eugenol with Brønsted acid catalysts, the dealkylation reaction may occur by a retro-Friedel–Crafts alkylation, producing a stabilized allyl cation as well as guaiacol [39,44]. The allyl cation may be scavenged by chloride ion to form allyl chloride or react with other nucleophiles (Fig. 5B).

3.2. Effect of conditions on acid-catalyzed eugenol dealkylation

In general, stronger acid catalysts such as H₂SO₄, heteropoly acids, and Nafion increased the yield of guaiacol from eugenol.

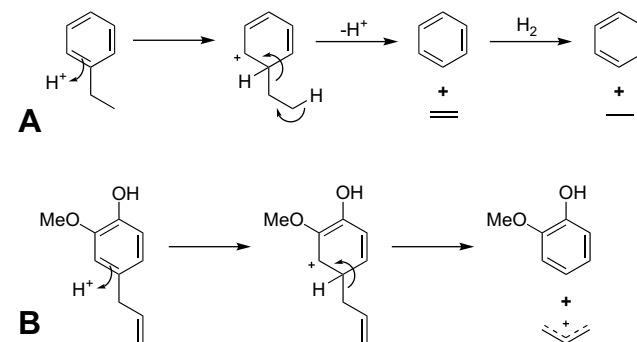


Fig. 5 – Acid-catalyzed mechanisms for dealkylation (A) Accepted mechanism for hydrogenolysis of ethylbenzene. (B) Proposed mechanism for deallylation of eugenol.

Table 3 – Conversion of eugenol in a range of ionic liquids.

Ionic liquid	Conversion (%)	Guaiacol yield (%)	4-Propylguaiacol yield (%)	Isoeugenol yield (%)
[EMIM]Cl	46.0	–	1.1	1.4
[EMIM]Br	49.1	–	0.3	11.8
[EMIM]OTf ^a	100.0	8.6	–	–
[EMIM]OMs	47.7	–	–	6.1
[EMIM]N(CN) ₂	15.3	–	–	2.4
[EMIM]OAc	56.6	–	–	4.7
[Et ₃ S]NTf ₂	99.4	7.1	4.2	–
[BMIM]BF ₄	41.8	0.3	–	–
[BMIM]PF ₆	84.1	1.3	–	–
[BMIM]TFA	100.0	–	0.7	2.7
[OMIM]Cl	35.8	–	–	0.7
[OMIM]BF ₄	38.8	–	–	0.7
[1-Butyl-1-methylpyrrolidinium]NTf ₂	99.3	7.4	3.5	–
[EMIM]AlCl ₄ –AlCl ₃	100.0	–	–	–

Conditions: 10 wt% substrate in ionic liquid, 10 mol% HOTs, 180 °C, 2 h, 6.9 MPa H₂. Conversions and yields assessed by GC.

^a 3.4 MPa psi H₂.

The effectiveness of the reaction depended strongly on the choice of ionic liquid solvent (Table 3). Ionic liquids with moderately basic anions such as chloride, bromide, acetate, and trifluoroacetate suppressed the dealkylation reaction, while very weakly basic counterions such as triflate, tetrafluoroborate, hexafluorophosphate, and triflimide favored the reaction. The dealkylation reaction required reaction temperatures at the upper end of ionic liquid stability (180–200 °C) [32,33], with reaction at 100 °C resulting in low conversion and little or no guaiacol product (data not shown). Higher acid loading also increased the guaiacol yield (Table 4). Catalyst loading of 10–20 mol% was most effective, while stoichiometric acid appeared to reduce the guaiacol yield. Notably, guaiacol selectivity was higher at higher conversion.

Low guaiacol yield at high conversion likely resulted from competing eugenol oligomerization reactions. GC analysis of reactor headspace revealed no hydrocarbon species, so degradation of eugenol into volatile products was unlikely. This analysis also did not detect any three-carbon species, the putative dealkylation coproducts. These results suggest that

eugenol and the three-carbon fragments resulting from guaiacol formation were incorporated into oligomeric side products which could not be detected by GC. This hypothesis is supported by the observation that dilution of crude reaction mixtures with water resulted in the precipitation of gummy solids. In addition, eugenol is known to dimerize under acidic conditions [45] and could also oligomerize through a cationic polymerization mechanism as shown in Fig. 6 [46,47].

3.3. Acid-catalyzed dealkylation of 4-ethylguaiacol and cleavage of 2-phenylethyl phenyl ether

While the guaiacol yield from eugenol dealkylation was modest, it was comparable to the reported yields of monomeric phenolic compounds from lignin [10,13,17] and suggested that similar reaction conditions could produce comparable yields of phenolics from lignin in ionic liquids. The generality of this reaction was investigated with other model compounds and organosolv lignin itself (Table 5). A saturated analog of eugenol, 4-ethylguaiacol, was much less reactive than eugenol under the acidic conditions and produced no observable guaiacol via dealkylation. This difference probably results from the lack of alkene functionality in 4-ethylguaiacol. While the allyl substituent of eugenol may be readily lost to produce a stabilized carbocation, 4-ethylguaiacol has no such reactive center and its dealkylation is not accomplished under these conditions. Similar

Table 4 – Effect of acid catalyst loading on conversion of eugenol to guaiacol in [EMIM]OTf.

HOTs loading (mol %)	Conversion (%)	Guaiacol yield (%)
0.1	27.1	–
1	27.9	–
3	74.4	0.4
4	92.2	0.9
8	99.1	2.9
10	100.0	4.0
15	100.0	6.0
20	100.0	7.3
100 ^a	100.0	1.4

Conditions: 10 wt% substrate in ionic liquid, HOTs catalyst, 180 °C, 2 h, 6.9 MPa H₂. Conversions and yields assessed by GC.

^a 200 °C.

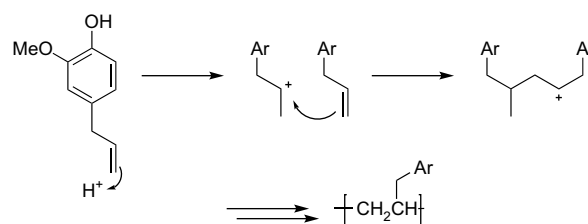


Fig. 6 – Proposed mechanism for acid-catalyzed oligomerization of eugenol. Protonation of the alkene bond may lead to cationic polymerization of eugenol.

Table 5 – Conversion of organosolv lignin and model compounds under conditions developed with eugenol.

Substrate	Catalyst	Conversion (%)	Guaiacol yield (%)	Phenol yield (%)
Eugenol	H ₂ SO ₄	100.0	7.8	–
Eugenol	HOTs	100.0	8.6	–
Eugenol	Nafion	100.0	11.6	–
4-Ethylguaiacol	H ₂ SO ₄	43.0 ^a	–	–
4-Ethylguaiacol	HOTs	16.0 ^a	–	–
4-Ethylguaiacol	Nafion	63.7 ^a	–	–
2-Phenylethyl phenyl ether	H ₂ SO ₄	46.6 ^a	–	4.3 ^a
2-Phenylethyl phenyl ether	HOTs	12.4 ^a	–	1.2 ^a
2-Phenylethyl phenyl ether	Nafion	62.9 ^a	–	6.7 ^a
Lignin, organosolv	H ₂ SO ₄	n/a	–	–
Lignin, organosolv	HOTs	n/a	–	–
Lignin, organosolv	Nafion	n/a	–	–

Conditions: 10 wt% substrate in [EMIM]OTf, 10 mol% catalyst, 180 °C, 2 h, 3.4 MPa psi H₂. Conversions and yields assessed by GC.
a Average of two trials. Typical yields were within ±5%.

behavior was observed with saturated 4-propylguaiacol formed *in situ* from eugenol. The Pt/zeolite catalysts with both acid and hydrogenation functions preferentially formed 4-propylguaiacol in good yield rather than guaiacol. Most likely, eugenol was quickly hydrogenated to 4-propylguaiacol which did not further react to form guaiacol despite the presence of acid catalysts competent for dealkylating eugenol. These results are consistent with previous reports. Bredenberg and coworker observed only moderate conversion of 4-propylguaiacol subjected to hydrogenolysis with cobalt-molybdenum catalysts at 245 °C, but increasing the reaction temperature to 345 °C enabled nearly complete reaction [48]. It is likely that higher temperatures would have facilitated increased conversion of 4-ethylguaiacol as well, but these conditions were problematic for the ionic liquid solvents.

The low reactivity of 4-ethylguaiacol suggests that saturated alkyl substituents of lignin can also defy

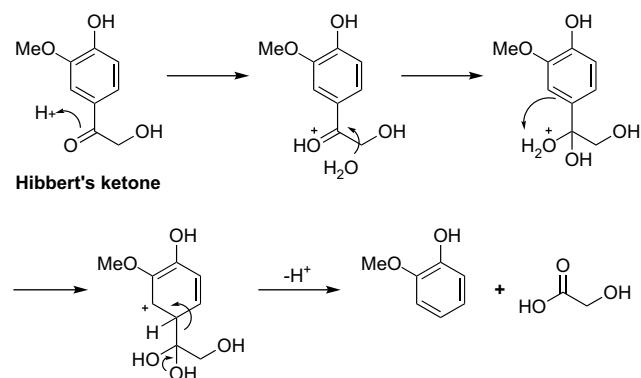


Fig. 7 – Proposed mechanism for acid-catalyzed deacylation of lignin-derived Hibbert's ketone. Under acidic conditions, this ketone may undergo a retro-Friedel-Crafts acylation to lose its aryl substituent.

dealkylation under the conditions investigated. Nevertheless, the lignin alkyl substituents are typically functionalized with hydroxyl groups, which may distinguish their reactivity from that of the naked ethyl group of 4-ethylguaiacol. For instance, under the influence of acid, lignin monomers connected by β-aryl ethers can depolymerize to form aryl-alkyl ketones known as Hibbert's ketones (Fig. 7) [6]. The aryl-alkyl ketone linkage has different chemistry than an aryl-alkyl bond, and can potentially undergo a retro-Friedel-Crafts acylation with trace water as shown in Fig. 7 to lose the keto substituent [49]. Future studies with Hibbert's ketone model compounds might investigate this potential reactivity.

In contrast to the other model compounds, 2-phenylethyl phenyl ether offers a minimal model of both the ether linkages and the substituted alkyl groups of lignin. Like 4-ethylguaiacol, 2-phenylethyl phenyl ether was only moderately reactive in the presence of acid catalysts (Table 5). Yet, it did form phenol (7) in modest yield. This result suggests that acids in ionic liquids can cleave lignin ethers. Unfortunately, benzene, the expected product of 2-phenylethyl phenyl ether cleavage followed by dealkylation, was not detected, and it is not clear what was formed from the phenylethyl fragment.

3.4. Reactivity of organosolv lignin in ionic liquid

Finally, organosolv lignin was reacted in [EMIM]OTf in the presence of acid catalysts (Table 5). While the red-brown lignin was soluble in the ionic liquid and turned very dark following the reaction, no monomeric products were observed by GC. The lignin used likely contains many alkyl linkages which, like the alkyl substituent of 4-ethylguaiacol, resisted cleavage under the relatively mild conditions. In addition, lignin is notoriously susceptible to self-condensation reactions which counteract depolymerization [6,14,17]. For instance, as shown in Fig. 8, α-ethers present in organosolv lignin may undergo acid-catalyzed elimination to form electrophilic methide intermediates. These can react with

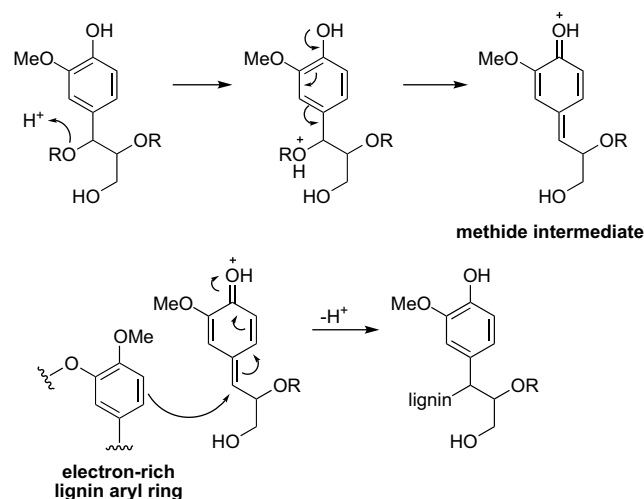


Fig. 8 – Proposed mechanism for self-condensation of lignin. Conversion of an α-ether or α-hydroxy lignin fragment into a reactive methide enables self-condensation reactions.

lignin nucleophiles to form condensed structures linked by carbon-carbon bonds [6]. Previous workers have countered this tendency by depolymerizing lignin in reactive solvents such as water, phenol, and cresols which can cap reactive sites on lignin to prevent cross-linking [14,15,17]. The ionic liquid solvent system lacks this ability. Both the low reactivity of the predominant alkyl linkages and self-condensation of the lignin likely contribute to the failure of lignin to form monomeric products.

4. Conclusions

Ionic liquids provided a suitable medium for the Brønsted acid-catalyzed dealkylation of eugenol, a lignin model compound. A wide range of strong acid catalysts enabled the formation of guaiacol from eugenol in as much as to 11.6% yield in ionic liquids with abasic anions. 2-Phenylethyl phenyl ether was broken down into phenol under similar conditions. On the other hand, 4-ethylguaiacol resisted conversion and lignin failed to depolymerize at the temperatures used in this study. These results suggest several conclusions for future studies of lignin depolymerization. Alkene-substituted aromatics and simple ethers are more reactive than lignin itself, making them deceptive model compounds. While eugenol and 2-phenylethyl phenyl ether likely show the same reactivity trends as lignin, they are probably transformed under much more mild conditions than necessary to convert lignin. The less reactive 4-ethylguaiacol may be a better guide for the reactivity of lignin alkyl linkages, and Hibbert's ketone compounds (Fig. 7) might be suitable models for aryl-alkyl ketone linkages formed during acid-catalyzed lignin conversion. In addition, lignin depolymerization chemistry must not only accomplish the cleavage of lignin linkages mimicked by model compounds but also address the unique challenge of preventing lignin self-condensation.

While this study demonstrates the challenges of lignin utilization, it may also present an opportunity for transformation of the carbohydrate components of biomass. While we have not observed reactions of lignin other than self-reaction in acidic ionic liquids at temperatures less than 200 °C, carbohydrates can readily be converted into useful products such as 2-furaldehyde and 5-(hydroxymethyl)-2-furaldehyde under these conditions [29]. This dichotomy suggests that acid-catalyzed transformation of biomass in ionic liquids may be able to selectively convert cellulose and hemicellulose without substantial interference from lignin [30].

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