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Journal Name

COMMUNICATION

Microwave-assisted fast conversion of lignin model compounds and organosolv lignin over methyltrioxorhenium in ionic liquids

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Catalytic conversion of a series of lignin β -O-4 model compounds 2-aryloxy-1-arylethanols and organosolv lignin to aromatic chemicals over methyltrioxorhenium (MTO) in ionic liquid without any oxidant and reducing agent under mild conditions were developed. Microwave irradiation accelerates the cleavage of aryl ether bonds and shortens the reaction time to 2 min.

With the gradual diminishing fossil fuel reserves and growing demand for energy, much more attention is focused on lignocellulosic biomass, which is a renewable resource that has the potential to serve as a feedstock for the production of chemicals and fuels.¹⁻² Lignin accounts for 10-35% by weight, up to 40% by energy in lignocellulosic biomass,³ and is the most abundant renewable source of aromatic units in nature. In comparison with the other two components (cellulose and hemicellulose) in lignocellulose, lignin has a more complicated structure that possesses a wide variety of linkages in it. An ideal chemical process would be able to depolymerize lignin into mono cyclic aromatic chemicals.⁴ Over the past few years there have been a number of studies that have been focused on lignin depolymerization.⁵ One approach is to thermally treat lignin with a hydrogen source using various supported metal such as Ru,⁶ Pd⁷, Pt,⁸ Rh,⁹ Ni,¹⁰⁻¹¹ Cu¹² and Mo¹³ as catalysts to produce mono cyclic aromatics. It is one of the most popular and efficient strategies applying in deconstruction of lignin into components such as low depolymerized lignin, phenols, and other valuable chemicals. However, high hydrogen pressures (> 4 MPa) as well as high temperatures (> 200 °C) are required in the reaction. Accordingly, oxidation reaction catalyzed by V,¹⁴ Co,¹⁵ Mn¹⁶ and Re¹⁷ can also produce aromatic chemicals from lignin including vanillin, syringaldehyde, and vanillic acid. This reaction usually occurs under the condition employing hydrogen peroxide or

molecular oxygen as additional oxidant agent with broad products distributions. The development of efficient and mild condition strategy for lignin depolymerization without additional source including hydrogen or oxidant agent remains an important challenge in catalysis due to the amorphous carbon-based inactive property and highly heterogeneous nature of lignin.¹⁸⁻¹⁹

Methyltrioxorhenium (MTO) has been used as a very efficient and versatile catalyst for several reactions particularly deoxydehydration reactions of biomass-derived polyols²⁰⁻²³ and lignin oxidation reaction.²⁴ Kühn and co-workers recently made an obvious progress for the application of MTO in lignin conversion. They reported for the first time that methyltrioxorhenium (MTO), which in situ generated by reduction of MTO, can effectively catalyze C-O bond cleavage of variety of lignin β -O-4 model compounds in *p*-xylene without oxidant.²⁵ Whereas in this system lignin feedstock conversion still faces challenge due to the poor dissolubility of lignin in *p*-xylene, and the relatively low reaction rate (typical 12 h was needed for model compounds conversion). One possible strategy to overcome the heterogeneous nature of lignin is to use ionic liquid (IL) solvents, since some of them readily dissolve lignin, which would make the catalyst more accessible to the substrates.²⁶⁻²⁷ More importantly, it is reported that ILs have excellent dielectric properties for transformation of microwave into heat,²⁸ the combination of microwave irradiation and ILs is expected to enhance the catalytic activity and improve the reaction rate. However, as compared with molecular organic solvent such as *p*-xylene, ionic liquid might lead to different reaction pathway due to the strong ion environment of ionic liquid.²⁹⁻³⁰ Based on above points, we present a strategy for selective cleavage of the C-O bonds of β -O-4 hydroxy aryl ether and organosolv lignin depolymerisation using MTO as catalyst without additional source in ionic liquids under mild conditions.

2-(2-Methoxyphenoxy)-1-phenyl ethanol (**1**), a common lignin β -O-4 dimeric model compounds, was first investigated for depolymerization reaction, with various catalyst concentrations and in different ILs (Table 1). The products were identified by GC-MS (see ESI E2). The catalyst activity and selectivity depends on the

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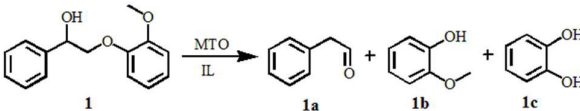
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Table 1. C-O bond cleavage of lignin model compound **1** in different reaction conditions.


Entry	Cat. Conc. [mol %]	Solvent	Conversion [%] ^a		Yield 1a [%] ^a		Yield 1b [%] ^a		Yield 1c [%] ^a	
			C ^b	M ^c	C ^b	M ^c	C ^b	M ^c	C ^b	M ^c
1	5	[Bmim]Cl	49	79	--	--	3	2	8	4
2	5	[Bmim]BF ₄	15	72	--	9	4	28	2	8
3	5	[Bmim]PF ₆	19	86	--	13	3	25	3	3
4	5	[Bdmim]Cl	55	75	--	--	4	2	5	15
5	5	[Bmim]NTf ₂	98	98	60	64	67	69	--	--
6	3	[Bmim]NTf ₂	38	79	25	46	31	46	--	--
7	1	[Bmim]NTf ₂	10	14	2	9	6	9	--	--

^a Conversion and yield were determined by HPLC with external standard technology.

^b Reaction conditions: 0.2mmol compound **1**, different amount of MTO in 1.0 g ionic liquid at 180 °C, t = 14 h; "C" is the abbreviation of conventional heating.

^c Reaction conditions: 0.2mmol compound **1**, different amount of MTO in 1.0 g ionic liquid under 240 W microwave irradiation, T = 180 °C, t = 2 min; "M" is the abbreviation of microwave heating.

ionic liquid solvent used (Table 1). A higher yields of the products were obtained in [Bmim]NTf₂ (Entry 5) as compared to other ILs such as [Bmim]Cl (Entry 1), [Bmim]BF₄ (BF₄ = Tetrafluoroborate) (Entry 2), [Bmim]PF₆ (PF₆ = hexafluorophosphate) (Entry 3) and [Bdmim]Cl ([Bdmim] = 1-butyl-2,3-dimethylimidazolium) (Entry 4) under both conventional (CON) or microwave (MW) heating. Kiefer³¹ and co-workers have shown that the hydrogen atom on C-2 position of the positively charged ring in 1,3-dialkylimidazolium-based IL is very active, which suggest that this functionality may be involved in the reactions for lignin depolymerization. To exclude the possibility of involvement of the hydrogen on C-2 position in this reaction, [Bmim]Cl and [Bdmim]Cl were used as solvents (Table 1 entries 1 and 4). Similar results were obtained with these two solvents, indicating that the C-2 proton of 1,3-disubstituted imidazolium cations has no clear effect on the conversion of compound **1**. Lower catalyst concentrations of 3 mol% and 1 mol% led to decreased conversions even though the reaction time is prolonged to 24 h under CON heating, and the selectivity of **1b** is lower under MW than under CON heating due that the olefin-intermediate is not completely converted to final product **1b** in such a short time with lower catalyst amount (Entry 6). A catalyst loading of 5 mol% was necessary to obtain complete conversion of lignin model compound **1** under both CON and MW heating. The catalyst activity is higher for MW heating compared to CON heating in all case in Table 1 except entry 5. The enhancement of catalytic activity might derive from the fact that ILs have excellent dielectric properties for transformation of microwave into heat.³² It has been reported that the higher the concentration of ions, the stronger the heat effect.³³ The pure ionic circumstance of ILs ensures that the

reaction mixture was heated up rapidly, volumetrically and simultaneously by the "specific microwave effects",³⁴⁻³⁵ and some known problems such as partly overheating under conventional conditions were avoided. A blank experiment without catalyst under the same conditions shows no conversion either under CON heating or MW irradiation. It is interesting to note that besides phenylacetaldehyde and guaiacol, catechol (**1c**) was detected when other ILs were employed, except for [Bmim]NTf₂, which

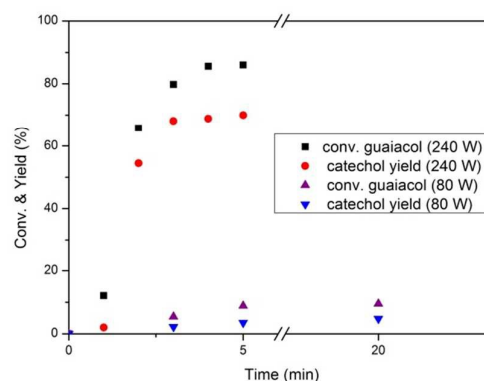


Figure 1. Time course of guaiacol conversion catalyzed by MTO in [Bmim]Cl under microwave irradiation of 80 W (50 °C) and 240 W (180 °C). Typical reaction procedure: after 2 mmol guaiacol and 5 mol% MTO were dissolved in 1.0 g [Bmim]Cl at 80 °C, the reaction mixtures was immediately subjected to microwave irradiation for a certain time.

did not produce any catechol (Table 1). Catechol might be generated from C-O bond cleavage of guaiacol. In order to verify this hypothesis, we monitored the time course of guaiacol conversion using [Bmim]Cl as reaction solvent under MW heating. The different microwave power of 80 W and 240 W stand for the different reaction temperature. The results indicate that within 20 min a 10% conversion of guaiacol and 5% yield of catechol were detected under microwave power 80 W (Figure 1). Further increasing the irradiation power to 240 W increased the catechol yield to 70% and guaiacol conversion to 86% within 5 min reaction time. This indicates that the depolymerization of lignin model compound guaiacol increases with increasing microwave irradiation power. The relative high acidity of [Bmim]Cl and the strong hydrogen bond may play important roles in the conversion of guaiacol to catechol.³⁶⁻³⁷ It has been reported that depolymerization of guaiacol is intractable due to the stable structures.³⁸⁻³⁹ For example, Savage's group reported that 75% conversion of guaiacol and 65% yield of catechol was obtained at 250 °C when using In (OTf)₃ as catalyst,⁴⁰ and Wahyudiono et al. hydrolysed guaiacol in water at 250 °C for 2 h and obtained 6% conversion.⁴¹ While in our systems 86% conversion of guaiacol and 70% yield of catechol was achieved in short time 5 min, which could be promising route for depolymerizing guaiacol.

LC-MS was performed to analyze the unknown species in [Bmim]Cl system (Table 1, Entry 1) and to try to explain why higher activity with [Bmim]NTf₂ was observed. The unknown products we detected were 2-aryloxy-1-arylethanols dimers (see ESI E3), such as 2-phenoxy-1-phenylethanol ([m-H]-/z of 213 at retention time 7.78 mins), and 2-(2-hydroxy-2-phenylethoxy)phenol ([m-H]-/z of 229 at retention time 10.35 mins). The former product was generated from elimination of methoxyl group of model compound **1**, while the latter product was produced from C-O bond cleavage of methoxyl group of the substrate. These results are in agreement with the results in Table 1 (Entry 1) and Figure 1 that show that [Bmim]Cl prefers to cleave C-O bond of methoxyl group. Additionally, isomeric olefins (E)- and (Z)-2(styryloxy) phenol with [m-H]-/z of 211 were detected at the retention time 13.87 and 14.24 min in the LC-MS spectra. These products were formed from dehydration of the substrate. Four additional peaks at retention time at 15.00, 15.67, 16.02 and 16.34 mins with the same [m-H]-/z of 277 were also detected. These peaks were probably chlorine substitution products of the substrate on different positions of aromatic ring. The above by-products are most likely responsible for the lower yields of the target products **1a** and **1b** when using [Bmim]Cl as the reaction solvent.

A series of 2-aryloxy-1-arylethanols with different substitution groups in R¹-R³ positions were employed as the substrates (Table 2) under the same conditions as Entry 5 in Table 1. The substrates in Table 2 have the same chemical groups as found in natural lignin.³ For example, 2-(2-methoxyphenoxy)-1-phenylethanol (Substrate **1** in Table 2), is a major β-O-4 moiety in hard wood such as birch.⁴² 2-Phenoxy-1-phenylethanol (Substrate **2**) without methoxy substitution on phenyl ring is one component in grass lignin.⁴³ After reaction, it was found that the aldehyde and phenol (compound **a** and **b** in Table 2) are dominant products in all cases, suggesting that in the [Bmim]NTf₂/MTO system the aryl C-O bonds of the substrates were selectively cleaved with the aryl rings intact in the products. It

Table 2. C-O bond cleavage of various 2-Aryloxy-1-arylethanols.

Subs	R ¹	R ²	R ³	Conv. [%] ^a		Yield a [%] ^a		Yield b [%] ^a	
				C ^b	M ^c	C ^b	M ^c	C ^b	M ^c
1	H	OCH ₃	H	98	98	60	64	67	69
2	H	H	H	96	97	46	65	52	66
3	H	OCH ₃	OCH ₃	92	98	48	61	47	57
4	OCH ₃	H	H	94	98	21	41	30	50
5	OCH ₃	OCH ₃	H	95	98	19	37	28	46
6	OCH ₃	OCH ₃	OCH ₃	94	97	25	29	28	41

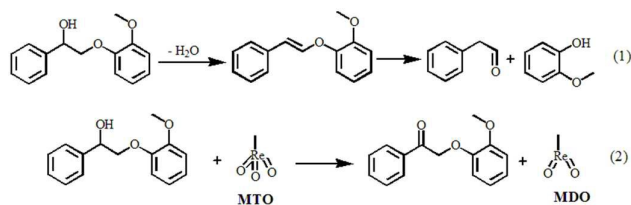
^a Conversion and yield were determined by HPLC with external standard technology.

^b Reaction conditions: 0.2mmol compound **1**, 5 mol% MTO in 1.0 g [Bmim]NTf₂ ionic liquid at 180 °C, t = 14 h; "C" is the abbreviation of conventional heating.

^c Reaction conditions: 0.2mmol compound **1**, 5 mol% MTO in 1.0 g ionic liquid under 240 W microwave irradiation, T = 180 °C, t = 2 min; "M" is the abbreviation of microwave heating.

is important to point out that the high selectivity in cleavage of aryl C-O bonds is in contrast to the hydrogenation of aryl ethers with heterogeneous catalysts. In the latter case, the products are typically a mixture of arenes, cycloalkanes and phenols.^{6,44} The conversions of all substrates are higher than 90% in our reaction system, while the aromatics yields varied (Table 2). The lignin model compounds with the methoxyl substitution in the R¹ position result in distinctly lower yields than those without methoxyl group (the substrates **1-3** vs **4-6**). The methoxyl groups in R² and R³ positions also have little influence on the yield of the depolymerization products. Under MW heating, the yields of both **a** and **b** were in the following order: **4** > **5** > **6**, implying that the methoxyl groups in R² and R³ positions have negative effect on the yields of the target products, which might arise from the stereochemical effect because of a relatively large metal compound of MTO catalyst. The substrates with two methoxyl groups in R² and R³ positions of the aryl group have been reported to be too cumbersome to cleave.⁴⁵⁻⁴⁶ It is interesting to note that the substrates **5** and **6** display moderate yields under MW heating. Similar conversion of all substrates was obtained with both microwave and conventional heating. However, the product yields were higher with MW heating. This further confirms that the combination of IL and MW heating exhibits great benefits for selective depolymerization of various lignin model compounds.

All investigated lignin model compounds **1-6** produced phenylacetaldehyde which is generated from 1,2-shift of the O atom and phenol, rather than 1-phenyl ethanol or methyl phenyl ketone. Model compound **1** was used as the probe substrate with CON heating at 180 °C to provide insight into the reaction pathway, which is monitored by GC-MS and ¹H-NMR technologies (see ESI E2 and E4). According to the ¹H-NMR results, during the conversion of the substrate **1** to **1a** and **1b**, an isomeric mixture of olefins – intermediates (see ESI E4, ¹H-NMR resonance shows signals at 5.48 ppm) formed via dehydration of compound **1** within 2 h. After 4 h



Scheme 1. Possible reaction pathway of C-O bond cleavage in lignin model compound β -O-4 (**1**); MDO formed from interaction between the substrate and MTO (**2**).

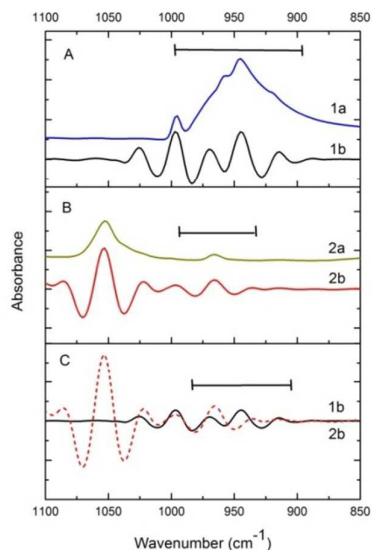


Figure 2. IR spectra of Re=O stretching range $850\text{--}1100\text{ cm}^{-1}$ of pure MTO (**1a**, **1b**), and MTO in the reaction (**2a**, **2b**). **1b** (solid line) and **2b** (dashed line) is the 4th derivative of the spectra.

product **1a** (see ESI E4, ¹H-NMR shows signals at 9.68 ppm) was observed. The substrate was first converted into olefins-intermediates, and then converted to the final products from the intermediates (Scheme 1). This result is in agreement with the work of Kühn et al,²⁵ suggesting that the substrate follows a same reaction pathway in ionic liquid compared to the reaction in organic solvent *p*-xylene. Trace amount of ketone was detected by GC-MS as well, which could be generated from the interaction between the substrate and MTO to form methyldioxorhenium (MDO).²⁰⁻²⁵

The experimentally observed vibrational fundamentals of pure CH_3ReO_3 and CH_3ReO_2 in the reaction are presented in Figure 2. The concentration ratio of the catalyst and substrate **1** is 1:1 in [Bmim]NTf₂ (100 mg) under 240 W within 30 second, which is examined by IR. The Re=O stretching mode of the MTO in the reaction is shifted to $\sim 997\text{ cm}^{-1}$, $\sim 966\text{ cm}^{-1}$, and $\sim 937\text{ cm}^{-1}$ in B spectra, which is in accord with what has been reported on MDO-Re(V) symmetry vibration modes.⁴⁷ The fourth derivatives (**1b** and **2b**) of the original spectra **1a** and **2a** are shown in Figure 2C. The clear wavenumber shift can be ascribed to a further distortion of the ReO local symmetry. These results are consistent with the work

of Kühn et al, in which MTO was reduced by the hydroxyl of the substrate to MDO that is responsible for the C-O bond activation.²⁰⁻²⁵ This finding matches well with the GC-MS results (see ESI E2) in which the trace amounts of ketone was produced via reduction of MTO by the hydroxyl.

The excellent results obtained from model compounds motivated us to investigate the conversion of organosolv lignin, a more realistic lignin feedstock. Organosolve lignin has been reported to have a structure close to natural lignin.⁴⁸ Organosolv lignin breaks down to a low molecular weight (LMW) oil with a yield of 34.2 wt % in [Bmim]NTf₂ within 2 min under MW heating. It is worthy to note that further increase the reaction time will lead to repolymerization of the products and other side reactions. 2min was found to be the optimum reaction time. The main components of the LMW oil are simple aromatic monomers shown in Table 3 (See ESI E5). Most aromatic products in the oil are generated from the cleavage reactions between lignin interunits, and are valuable chemicals and intermediates used in many industries. For example, syringaldehyde (**7**) is largely employed as a pharmaceutical precursor and dye agent,⁴⁹ and syringol (**1**) a composed of guaiacyl and syringyl units.⁵⁰ Compound **2** belongs to aguaiacyl origin, and compounds **1**, **7-10** could be associated with syringyl units. The structure **4** did not possess methoxyl group but tertiary butyl, probably due to radical reactions in the depolymerization process.

Table 3. Detected compounds by GC-MS in the degraded organosolv lignin products under MW irradiation within 2 min.

No.	Compound Structure formula	Relative area (%) ^a	No.	Compound Structure formula	Relative area (%) ^a
1		2.7	6		11.8
2		2.8	7		11.1
3		12.8	8		2.0
4		10.5	9		2.0
5		3.4	10		6.3

^a The relative percentages were calculated with peak area normalization method in GC-MS.

The carbonyl groups (ketone or aldehyde) in the α position of compounds **2**, **5-7**, and **9-10** might have been formed during ether-linkage cleavage between aliphatic carbon and the oxygen.⁵¹ The relatively high concentrations of syringyl and guaiacyl derivatives observed in this work are in agreement with our previous work of depolymerization of birch wood catalyzed by Ni-W₂C catalyst.⁵² All of above results suggest that breakage of the β -O-4 linkages are the main reaction route in this reaction. In contrast to other solvents, the high solubility of organosolv lignin in ionic liquid probably plays an important role in helping to depolymerize lignin.⁵³⁻⁵⁴ This mild system without additional reductant has several advantages over the heterogeneous catalytic systems that use a high hydrogen or oxygen pressure.⁵⁵

In summary, an efficient method was developed for conversion of lignin model compounds and organosolv lignin with a MTO catalyst in ionic liquid under mild conditions. A series of lignin β -O-4 model compounds were investigated that were able to be converted to their corresponding phenols as the primary products with high yields up to 69%. The IL is not only able to dissolve lignin, but also has excellent dielectric properties for transformation of microwave energy into heat. The combination of IL with microwave irradiation accelerated the degradation rate and increased the reaction activity. Depolymerization of a birch wood derived organosolv lignin under microwave irradiation produced 34.2 wt% yield of the main phenolic monomers- syringyl and guaiacyl derivatives within 2 min. MDO was generated by reduction of MTO via IR spectroscopic studies. NMR and GC-MS were used to track the formation of the intermediate products. This work demonstrates a strategy for the controllable production of value-added aromatic chemicals from lignin, which offers the advantages of fast reaction rate, high selectivity, mild conditions and no need of any oxidant and reducing agent.

Experimental Section

Typical procedure for C-O cleavage of lignin model compounds in oil bath: A 25 mL heavy wall glass tube with [Bmim]NTf₂ ionic liquid (1.0 g), the lignin model compound (0.2 mmol) and MTO (2.5 mg, 5 mol%) was heated for 14 h at 180 °C. After cooling to room temperature, the reaction mixture was diluted to 25 mL volumetric flask with CH₃CN/H₂O (6 : 4 by volume). The product samples were analyzed by HPLC using an external standard calibration curve method ($R^2 > 0.999$).

Typical procedure for depolymerization of lignin model compounds under microwave irradiation condition: Lignin model compounds (0.2 mmol) and MTO (2.5 mg, 5 mol%) were dissolved in ionic liquid (1.0 g) at 80 °C, the reaction mixture was then immediately subjected to microwave irradiation of 240 W at 180 °C for 2 min. The products in the reactor were rinsed to a 25 mL volumetric flask with CH₃CN/H₂O (6 : 4 by volume) for HPLC, using an external standard calibration curve method ($R^2 > 0.999$).

Catalytic produces for depolymerization of organosolv lignin: Organosolv lignin (100 mg) and MTO (10 mg) were dissolved in [Bmim]NTf₂ (1.0 g) at 80 °C. The reaction mixture was immediately subjected to microwave irradiation of 240 W at 180 °C for 2 min. The reaction mixture was cooled down to room temperature and

was then diluted by 15 mL acetonitrile. This mixture was then separated by centrifugation at 9000 rpm for 15 min. The organic phase was concentrated under vacuum and 34.2 mg of organic soluble fraction products after subtracting mass of IL and catalyst were obtained (after subtracting 1.0 g ionic liquid and 10 mg MTO). The ILs phase was extracted with diethyl ether (5 × 10 mL). After vacuum distilling diethyl ether, the sample was injected into a GC-MS for identification of depolymerization products.

Typical procedure for the extraction of organosolv lignin: Birch wood organosolv lignin was prepared as previously described.⁵⁶ The treatment for lignin extraction consisted of the digestion of birch wood powder in a mixture of ethanol-water (70 wt%) at 200 °C for 90 min in a stainless-steel autoclave (Parr, 100 mL) with constant stirring at 700 rpm. The solid (10 g)-to-liquid (60 g) ratio was 1 : 6 (w/w). After the high-temperature extraction, the mixture was cooled to room temperature and was filtered; two volumes of acidified water (pH = 2) were added to the liquid fraction in order to precipitate the lignin. The precipitated lignin was then separated by centrifugation (4000 rpm, 20 min) and dried at 80 °C overnight before use.

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Graphical Abstract:

