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Selective cleavage of C-O bond in lignin catalyzed by a simple rhenium oxide catalyst

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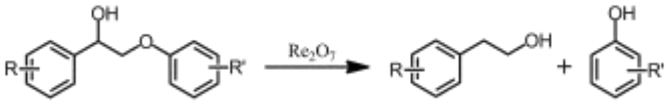
Dedication ((optional))

Abstract: The selective cleavage of C-O bond in typical β-O-4 lignin model compounds and deconstruction of realistic lignin feedstock catalyzed by simple Re_2O_7 has been described. High yields of C-O cleavage products (up to 97.8%) from model compounds and liquid oils (76.3%) from organosolv pinewood lignin were obtained respectively under mild condition. The pathway proof for this catalytic process has also been provided.

With the gradual diminishing of fossil fuel reserves and decreasing availability of energy resources, much attention is focused on utilizing lignocellulosic biomass, a renewable resource that has the potential to serve as a feedstock for the production of commodity chemicals and fuels.[1] As one of the major components in lignocellulosic biomass, lignin is a complicated three-dimensional amorphous polymer consisting of methoxylated phenylpropanoid units of various types, and is the most abundant renewable aromatic source in nature.[2] In recent years, the big potential for the conversion of lignin to a spectrum of aromatic compounds via catalytic approach is increasingly recognized as a promising strategy, which maybe an alternative to aromatic compounds that are traditionally obtained from fossil resources.[3] An important challenge in catalytic valorization concepts, however, is predominantly related to the recalcitrant polymer structure of lignin.[4] Thus much efforts has been made to develop homogeneous catalysts such as organometallic complexes[5] for the selective cleavage of the typical lignin ether linkages in model compounds. The research efforts in heterogeneous catalysis using supported noble metals,[6] carbides[7] and bimetallic catalysts[8] have also been developed for the depolymerization of lignin into small aromatic chemicals. Among all the transition elements, in the field of biomass conversion, rhenium has rapidly emerged as one of the most promising metal for both lignin depolymerization[9] and deoxydehydration of alcohols and polyols[10], presumably because of its unique Lewis acidity, large number of accessible oxidation states and its specific ability to transfer oxygen atom between rhenium-oxo complexes and substrates. The representative example is that $MeReO_3$, a Re (VII) complex, exhibited the ability to cleave of C-O bond of lignin β-hydroxy ethers without involving any external redox species through the reduction of Re^{VII} to Re^{V} by the substrate itself to generate the catalytically active species $MeReO_2$.[9] However, it is mainly devoted to model compounds study and meets huge challenge in depolymerization of the realistic lignin feedstocks.[11] In that regard, the realization of the biorefinery concept hinges on the development of highly active, and easily available catalysts, which could provide promising solutions for the large-scale application.

In recent years, rhenium oxide Re_2O_7 has been increasingly used as a sustainable, easy-to-handle, and low-cost catalyst in organic synthesis.[12] Although many excellent synthetic methodologies have been developed by using Re(VII)-oxo complexes as the catalysts, the reaction scopes are typically limited to direct C-O, C-N formation, and deoxydehydration.[13] As part of our ongoing interest in exploring rhenium oxides utilization in lignin depolymerisation, we report in this paper the easily available Re(VII) oxide (Re_2O_7) catalyst has the outstanding performance for the cleavage of C-O bond in both lignin model compounds (Scheme 1) and realistic lignin feedstocks. It should be noted that the application of Re_2O_7 in lignin remains unexplored.



Scheme 1. Cleavage of β-O-4 model comopounds catalyzed by Re_2O_7 catalyst.

Our initial investigation began with lignin model compounds due to the recalcitrant nature of lignin. Noting that β-O-4 linkage represents the predominant interconnecting bond (45.0% to 60.0%, depending on the wood type),[3c] 2-(2-methoxyphenoxy)-1-phenyl ethanol (compound **1**), a common β-O-4 dimeric model compound of lignin,[12] was initially studied to explore the activity of various catalysts for the cleavage of C-O bonds. As our interest is in the application of rhenium oxide towards cleavage of lignin ether linkages, we started our experiment using Re_2O_7 as the catalyst. As shown in Table 1, no reaction occurred at 200 °C in the absence of the catalyst (entry 1). In sharp comparison, 5 mol% Re_2O_7 afforded complete conversion with 2-phenylethanol (71.2%)

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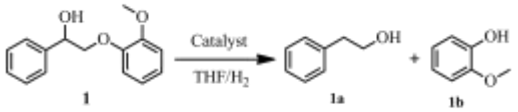
Table 1. Hydrogenolysis of 2-(2-Methoxyphenoxy)-1-phenyl ethanol catalyzed by different catalysts in THF.[a]



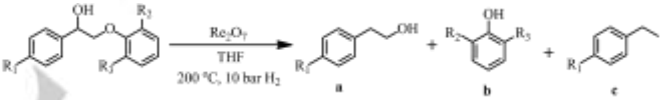
Entry	Cat.	Temp. [°C]	Time [h]	Conv. [%][b]	Yield [%][b] 1a	1b
1	--	200	3	0	0	0
2	Re_2O_7	200	3	99.9	71.2	97.8
3	Re_2O_7	200	1	10.6	4.8	8.0
4	Re_2O_7	200	8	99.9	69.9	99.3
5	Re_2O_7	120	3	8.4	2.4	5.4
6	Re_2O_7	150	3	42.1	16.7	25.8
7	Re_2O_7	180	3	51.3	27.8	39.1
8	ReO_2	200	3	0	0	0
9	ReO_3	200	3	0	0	0
10	CH_3ReO_3	200	3	19.2	0	11.5
11	WO_3	200	3	15.8	0	3.0
12	MoO_3	200	3	27.0	0	11.2
13	Fe_2O_3	200	3	9.1	0	2.9
14	CuO	200	3	0	0	0
15	ZnO	200	3	0	0	0
16	MgO	200	3	0	0	0
17	CeO_2	200	3	0	0	0

[a]The reaction condition is: 100 mg substrate, 5 mol% catalyst and 15 mL THF were added in a stainless-steel autoclave, this mixture was charged with 10 bar H_2.[b]The conversion of substrate and yields of the products were determined by GC-FID with mesitylene as an internal standard.

and guaiacol (97.8%) as the dominant products under 10 bar hydrogen for 3 h (entry 2). Shorter reaction time could not guarantee the completion of the reaction (entry 3), while prolonging the reaction time to 8 h provided similar results and on the other hand may induce side reactions (entry 2 vs 4). The catalytic activity highly depended on the reaction temperature. Low temperature (120 °C) led to very poor conversion (8.4%) with 2.4 % yield of 2-phenylethanol and 5.4 % yield of guaiacol (entry 5). With the increasing of the reaction temperature, not only the conversion of the substrate, but also the yields of the target products 2-phenylethanol and guaiacol were remarkably enhanced (entries 5-7), suggesting that Re_2O_7 catalyzed C-O bond cleavage is a thermodynamic controlling reaction,[14] and the reaction temperature is one of the key factors that controlling the overall rate. Taking economy and energy consumption into consideration, 200 °C was selected as the suitable reaction temperature. Interestingly, rhenium oxides with different rhenium valences such as ReO_2 and ReO_3 were inactive for the cleavage of β-O-4 bond (entries 8-9), implying that Re_2O_7 with the highest rhenium valence Re(VII) was essential for this reaction. This probably because that the chemical property of high valence of Re_2O_7 is more reactive than other Re species particularly rhenium oxide with low Re valence (ReO_2 and ReO_3).[15] Under the same condition rhenium complexes CH_3ReO_3 exhibited very low conversion (entry 10). For the sake of comparison, other acidic metal oxides, such as WO_3, MoO_3 and Fe_2O_3 showed much poorer conversion with less than 12.0 % yield of the target products (entries 11-13). We also tried alkaline oxides such as CuO, ZnO, MgO and CeO_2, even worse, no conversion was observed (entries 14-17). The above results suggested that Lewis acidity favors the reaction and high yields of the target products can be obtained only if using Re_2O_7 as the catalyst.

Encouraged by the good performance of Re_2O_7 in selectively cleavage of the aryl-ether linkages and the simple process, the substrate scope in the reaction was subsequently examined. A series of 2-aryloxy-1-arylethanols with different substituent groups in R_1-R_3 positions were employed as the substrates for the cleavage of β-O-4 bonds catalyzed by Re_2O_7 in THF solvent, and the results are summarized in Table 2. These substrates have similar chemical groups and are detected in different natural lignins.[16] For example, 2-(2,6-dimethoxyphenoxy)-1-phenylethanol with two methoxyl groups (substrate **3** in Table 2), typical syringyl unit, is a major moiety in birch lignin.[14b] 2-Phenoxy-1-phenylethanol (Entry 2) without methoxyl substitution on phenyl ring is one component in grass lignin.[17] All the investigated substrates provided 2-phenylethanol and phenol derivatives (compounds **a** and **b** in Table 3) as the major products, suggesting that the aryl C-O bonds of the substrates were selectively cleaved with the aryl rings intact. The conversions of all the substrates are higher than 94.0% whilst the yields of the aromatics varied. Lignin model compounds with the methoxyl substitution in R_1 position (substrates **4**-**6**) did not produce ethylbenzene (compounds **c**), while the compounds without methoxyl group in R_1 position (substrates **1**-**3**) afforded ethylbenzene with the yields of 1.3%-9.5%, suggesting that methoxyl group in R_1 position favoured the target products **a** and **b**. Electronic effect may play important role for the phenomenon because products **a** with additional electron-donating group ($-OCH_3$) is not easy to be further reduced. However, methoxyl groups in R_2 and R_3 positions showed some diversity in hydrogenolysis behaviour which did not have a straightforward orderliness. The methoxyl groups in R_2 and R_3 positions (entry 6) provided the relative lower yields of products **a** and **b** (2,6-dimethoxylphenol), probably owing to the effect of steric hindrance. It was found that the yield of **b** is slightly higher than the total yield of **a** and **c**, which might due to further transformation of **a** and other side reactions. To confirm this speculation, the stability of the products 2-phenylethanol (**1a**) and guaiacol (**1b**) was tested under the reaction condition in the presence of Re_2O_7. The results showed that the no reaction took place on guaiacol; in contrast, 21.6 % conversion of 2-phenylethanol and 5.8 % yield of ethylbenzene were obtained. This is possibly the major reason that the yield of 2-phenylethanol was lower than guaiacol. To further diversify the

Table 2. Re_2O_7 catalyzed C-O bond cleavage of various 2-Aryloxy-1-aryethanols in THF. [a]

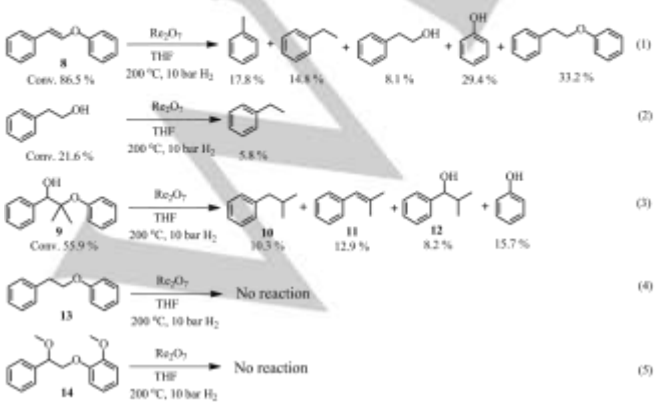


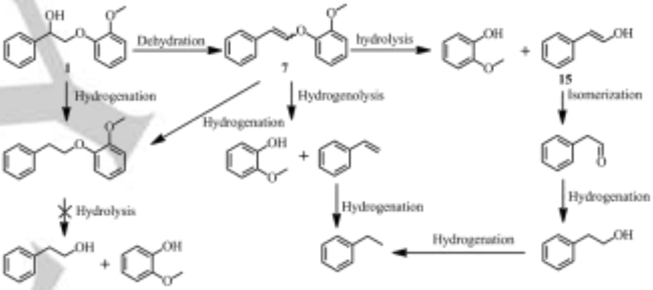
Sub.	R_1	R_2	R_3	Conv. [%][b]	Yield [%][b] a	b	c
1	H	OCH_3	H	99.9	71.2	97.8	1.3
2	H	H	H	98.2	80.9	95.9	9.5
3	H	OCH_3	OCH_3	94.2	73.0	87.4	6.7
4	OCH_3	H	H	99.9	71.1	87.6	0
5	OCH_3	OCH_3	H	99.9	74.4	97.3	0
6	OCH_3	OCH_3	OCH_3	99.9	63.2	78.7	0

[a] The reaction condition is: 100 mg substrate, 5 mol% Re_2O_7 and 15 mL THF were added in a stainless-steel autoclave, this mixture was charged for 3 h with 10 bar H_2 at 200 °C. [b] The conversion of substrates and yields of the products were determined by GC-FID with mesitylene as an internal standard.

scope of β-O-4 -derived chemicals accessible, 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol, a typical β-O-4 model compounds with γ-OH group which reflect the natural lignin structure was tested, guaiacol with the yield of 38 % and some aromatic compounds (yield: <1%) were obtained with 100% conversion (Figure S1). It's deserve to point out that in all above reactions, no cycloalkane product was detected, indicating that Re_2O_7 showed a good property in hydrocracking of lignin β-O-4 bonds without destroying the aromatic rings.

To explore the principal conversion route of β-O-4 cleavage, several mechanism verification experiments were conducted (equations 1-5). First, analysis of the liquid products suggested that besides the listed target products, (*E*)- and (*Z*)- 1-methoxy-2-(styryloxy)benzene (compound **7**) were observed in the conversion of compound **1** (Figures S3 and S4). Whereas these two isomers could not be detected at higher reaction temperatures, implying that they are active intermediates which readily undergo subsequent hydrolysis to 2-phenylethenol (compound **15**) and guaiacol. The former one with enol structure was easily liable to convert to phenylacetaldehyde via isomerization reaction. To confirm this point, we have synthesized compound (*E*)- (2-phenoxyvinyl) benzene (compound **8**), which was then catalyzed by Re_2O_7 under the same conditions in Table 2. Ethylbenzene and 2-phenylethanol with the yields of 14.8 % and 8.1 % were observed (equation 1), indicating that both hydrogenolysis and hydrolysis of compound **7** may occur. Furthermore, under this system 2-phenylethanol could convert to ethylbenzene (equation 2). We therefore conclude that 2-phenylethanol comes from hydrolysis reaction, whilst ethylbenzene may be from both hydrolysis and hydrogenolysis reactions. With the aim to confirm the hydrogenolysis reaction, substrate **9** with blocked C_β position (by two methyl groups) has been synthesized and was used in the reaction under the same condition (equation 3). Hydrogenolysis products such as 10.3% yield of **10**, 12.9% yield of **11**, 8.2% yield of **12** and 15.7% yield of phenol were obtained, suggesting that direct hydrogenolysis of compound **7** occurred. The above results confirmed that the reaction proceeded simultaneously through both hydrolysis and hydrogenolysis reaction. Since Table 2 showed that compounds **a** were the dominant products with trance ethylbenzene, it is therefore logical that the hydrolysis reaction is the major pathway. It is deserve to point out that aryl ethers **13** and **14** without Cα-OH groups failed to be cleaved under optimized conditions (equations 4-5), supporting that C_α-OH groups plays an important role in overall transformation, which probably reduced bond energy of β-O-4 linkage,[18] meanwhile, the presence of C_α-OH favours dehydration of compound **1** to generate intermediates **7**. To gain more insight into the apparent reaction pathway, two experiments under lower hydrogen pressure of 1 bar and 5 bar were conducted (Figure S5). These two reactions also provided very high conversion, whilst the products distributions were much different from that obtained under 10 bar hydrogen pressure (Figure S2). The reaction under 1 bar hydrogen pressure afforded new product phenylacetaldehyde with a high yield of 61.5%, whereas the yield of 2-phenylethanol was only 3.8%. Increasing hydrogen pressure to 5 bar also detected high yield of phenylacetaldehyde and 14.2% yield of 2-phenylethanol. The intermediate styrene were also examined in both systems. In comparison, 10 bar hydrogen pressure provided much higher yield of 2-phenylethanol (71.2%) without any phenylacetaldehyde. In all above three reactions, the yields of guaiacol were higher than 90%. We therefore concluded that the cleavage of β-O-4 first generate guaiacol and phenylacetaldehyde, the latter one was further hydrogenated to 2-phenylethanol. Based on the above discussion, the overall reaction pathway for the Re_2O_7-catalyzed conversion of β-O-4 model compound **1** is proposed in Scheme 2. The major pathway started by an initial dehydration of compound **1** to form intermediate **7** (including (*E*) and (*Z*) isomers) followed by hydrolysis of **7** to produce guaiacol and **15**, the latter intermediate with enol structure then fast isomerized to phenylacetaldehyde, which was further hydrogenated to 2-phenylethanol.





Scheme 2. Proposed reaction pathway for Re_2O_7 catalyzed 2-(2-methoxyphenoxy)-1-phenyl ethanol.

The excellent results obtained from model compounds motivated us to investigate the conversion of realistic lignin feedstock. Pinewood lignin, one typical softwood lignin, was isolated via the organosolv process because this isolation process provided lignin with structure more similar to the native lignin.[2] Fourier transform infrared spectroscopy (FTIR) characterization suggested that the isolated organosolv pinewood lignin (OPL) shared the basic skeleton of lignin and had a mixture of dominant guaiacol (G) and *p*-hydroxyphenyl (H) units (Figure S6 and Table S1), which is also strongly supported by 2D-Heteronuclear Single QuantumCoherence (HSQC) NMR analysis (Figure 1b). For the conversion of realistic lignin, small alcohol favors the dissolution of the feedstock and therefore is benefit for lignin depolymerization.[19] Methanol is thus chosen as a solvent to investigate the conversion of realistic lignin. Table S2 illustrates the phenolic oil yields and the monomer components of the oils. The results showed that pinewood lignin could be effectively converted to liquid oil with high yield up to 76.3 wt%. Regarding the monomer composition, pinewood lignin yielded a broad variety of phenolic compounds, being guaiacylpropene, guaiacylethanol, 4-oxhydryl-phenoland phenol as the main products (Table S2), which are derived from lignin guaiacyl (G) and *p*-hydroxyphenyl (H) units. Other G monomers include guaiacylethane, guaiacol, guaiacylpropane, methyl-4-

hydroxy-3-methoxybenzoate and trace 4-methoxyphenol and 4-ethylphenol. Noting that depolymerization occurred during lignin isolation process, as a comparison, raw pinewood powder (40 mesh) was also submitted to deconstruction catalyzed by Re_2O_7 at 200 °C under 3 MPa H_2 for 8 h. 18.8 wt% lignin oil was obtained, the distribution of monomer products being similar to that obtained from isolated lignin (Table S2). It should be noted that no cycloalkane was detected in the liquid oil, which further identified that Re_2O_7 is highly selective in activation of the linkages between the primary units in lignin without destroying aromatic ring.

In order to better understand the change of the lignin structure before and after reaction, 2D-HSQC NMR spectroscopy which has been regarded as an extremely powerful tool to provide detailed insight into the different ether linkages and aromatic units in the lignin structure was performed. In the side-chain region of 2D-HSQC NMR spectra (Figure 1a), OPL had a very high content of β-O-4 aryl ether linkages (up to 43.9 % for **A**: β-O-4 and **A'**: β-O-4') with phenylcoumaran (**B**: β-5, 42.1 %) and resinol (**C**: β-β, 14.0 %). After reaction, gratifyingly, most **A** and **C** as well as certain amount of **B** linkages disappeared in the side-chain region of the oil (Figure 1c), indicating that the three major linkages of **A**, **B**, and **C** were attacked by Re_2O_7. The molar ratios of **A**, **B** and **C** in liquid oil (39.4% : 50.5% : 10.1%) suggested that the lowest amount of **B** (β-5) was cleaved possibly because it possessed the highest bond dissociation enthalpy.[20] According to aromatic region of 2D-HSQC NMR characterization, bio-oil provided G:H molar ratio of 98.2 : 1.8 (Figure 1d), which is in good agreement with the composition of OPL (G:H molar ratio of 97.9 : 2.1 in Figure 1b). Furthermore, no **S** unit was detected in both samples (Figures 1b and 1d), suggesting that pinewood lignin belongs to G-type lignin which comprises a dominant amount of G units along with trace amount of H units.

Based on the conversion results and HSQC analysis, Re_2O_7-catalyst shows high activity not only in β-O-4 cleavage but also in the cleavage of more resistant β-5 and β-β linkages of pinewood lignin. MALDI-TOF mass spectrometry characterization offered another support on this point. It was found in Figure S7 that the obtained oil liquid from OPL is exclusively in the range of m/z 0-600 with most of the intensive peaks in the range of 100-400 m/z. Considering that typical **G** and **H** units for instance guaiacylethanol and 4-propylphenol have molecular weights of 210 and 136 g/mol, it could therefore be concluded that the obtained products from OPL are including monomers, dimers, trimers and tetramers with the former two as the main products. In contrast, the original OPL showed a M_w of 3294 g/mol, which was much higher than M_w of the oil fraction (452g/mol) according to GPC analysis (Table S3), indicating that Re_2O_7 has outstanding ability to catalyze the cleavage of the C-O linkages between the primary units in lignin.

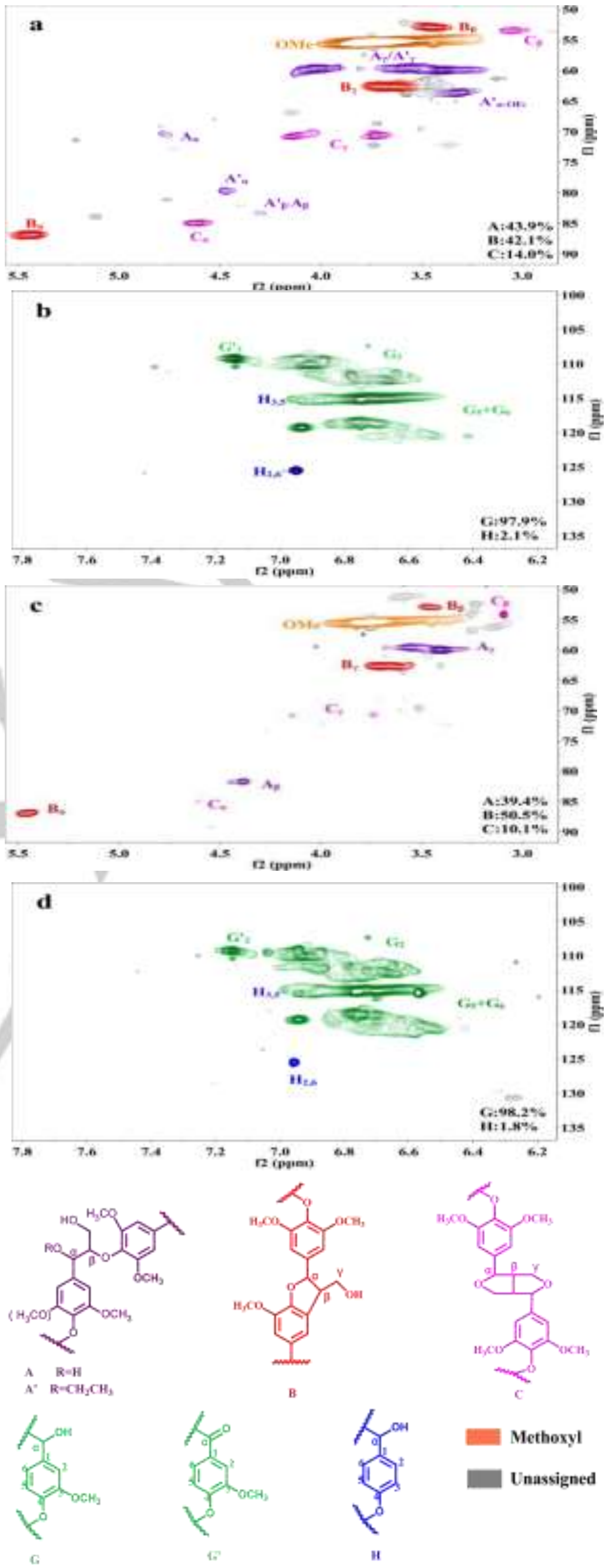


Figure 1. 2D-HSQC-NMR spectra of organosolv pinewood lignin (a, b) and pinewood oil (c, d) in DMSO-d^6/pyridine-d^5 (4:1 v/v).

Experimental Section

Isolation of pine wood lignin via organosolv process: The organosolv pine lignin (OPL) was prepared as described in our previous paper. [7] The treatment for lignin extraction consisted of the digestion of pine 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; and 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 ^{o}C for 24 h to obtain 0.4 g organosolv pine lignin.

Typical procedure for C-O cleavage of lignin model compounds: The catalytic conversion of lignin model compounds was carried out in a stainless-steel autoclave (Parr, 75 mL) with an initial H_2 pressure of 10 bar and 200 ^{o}C for 3 h. Typically, lignin model compound (100 mg), Re_2O_7 (10 mg), and THF (15 mL) were added in a stainless-steel autoclave (Parr, 75 mL), the autoclave was then charged with an initial H_2 pressure of 10 bar and stirred (800 rpm) at 200 ^{o}C for 3 h. After reaction, the reaction mixture was cooled to room temperature and was filtered. The liquid phase was analyzed by GC-FID and was quantified by internal standard method (standard: mesitylene, HP-5 column, 30 m × 0.32 mm × 0.25 µm).

Typical procedure for depolymerization of lignin feedstock： The catalytic conversion of lignin material was carried out in a stainless-steel autoclave (Parr, 100 mL) with an initial H_2 pressure of 10 bar and 200 ^{o}C for 6 h. Typically, lignin (100 mg), Re_2O_7 (10 mg), and methanol (30 mL) were charged in the autoclave and stirred at rate of 800 rpm. After reaction, the reaction mixture was cooled to room temperature and was filtered. The filtrate was concentrated under reduced pressure at 35 ^{o}C to obtain liquid oil, weighed. The liquid oil was then diluted to 2 mL with methanol, the monomer products in liquid oil were analyzed and quantified by internal standard method (standard: mesitylene) with HP 5973 GC–MS (HP-5 column, 30 m × 0.32 mm × 0.25 µm). The molecular weight distribution of the liquid oil was analyzed by MALDI-TOF with the mass range of m/z 50-1000.

Acknowledgements

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Conflicts of interest

There are no conflicts to declare.

Keywords: lignin depolymerization • rhenium oxide • C-O bond cleavage

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Re_2O_7-catalyzed selectively cleavage of lignin C-O bonds to produce aromatic chemicals is reported for the first time.

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Page No. – Page No.

Selective cleavage of C-O bond in lignin catalyzed by a simple rhenium oxide catalyst