

Selective Degradation of Wood Lignin Over Noble Metal Catalysts in a Two-step Process

Ning Yan,^{a, b} Chen Zhao,^a Paul J. Dyson,^b Chen Wang,^a Ling-tao Liu,^a Yuan Kou^{a*}

Email: yuankou@pku.edu.cn

^a PKU Green Chemistry Center, Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

^b Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.

General procedure

5 wt% Pd/C, Pt/C, Rh/C, Ru/C, PdPt/C catalysts were purchased from BAOJI BOTONG Non-FERROUS METAL ENGINEERING CO.,LTD (China). All other chemicals were commercially available and used without further purification.

Gas chromatography was performed using an Agilent 6820 GC with an FID detector equipped with a 30 m (0.25 mm i.d) OV-101 column. Mass spectra were obtained on an Agilent GC 6890 with an Agilent 5973 *inert* mass selective detector.

Infrared spectra were recorded immediately after reaction on a Bruker Vector 22 Fourier transform infrared spectrophotometer with a resolution of 1 cm⁻¹.

¹H and ¹³C NMR spectra were recorded on either a Varian Gemini 300 MHz spectrometer or a Bruker ARX400 400 MHz spectrometer, using CDCl₃ as solvent.

Elemental analysis were tested on Elementar Vario MICRO CUBE(Germany). And ICP-AES analysis was done on LEEMAN, PROFILE.

Elemental analysis of sawdust and lignin

Klason lignin preparation:

2 g sawdust was extracted by ethanol/benzene 1:1 mixture in a soxlet for 12 h. After drying, the powder was first treated with 72 wt% H₂SO₄ at r.t. for 2 h then diluted to 20 wt% H₂SO₄. This solution was heated under reflux for 4 h and then cooled to r.t. The solution was filtered and the residue was washed with deionized water until the filtrate became neutral. The solid was collected and kept under vacuum at 120 °C for 12 h. Y: 0.38 g, 19%.

This Klason lignin was prepared for analysis of the lignin content in wood and for elemental analysis.

Organic Elemental Analysis

Sawdust: C, 45.83%, H, 6.23%

Klason Lignin: C, 50.18% H, 6.10%

Inorganic Elemental Analysis:

0.50 g saw dust sample was mixed with 10 ml boiling aqua regia and heated to reflux for 2 h. Then, the solvents were removed under reduced pressure and HClO₄/H₂O₂ (1:1, 10 ml) was added and the mixture was refluxed for another 2 h. The solvents were removed under reduced pressure and 1 % HNO₃ was used to dilute the residue to 50 ml. The sample was then analysed by ICP.

For lignin, the procedure is the same except 0.40 g starting material was used.

Table s1. ICP raw data for the elemental analysis of wood.

Element	Peak/nm	Concentration/mg L ⁻¹	Derivation	Analysis 1	Analysis 2	Analysis 3
Al	396.152	1.93	0.01	1.93	1.94	1.92
B	249.678	0.385	0.007	0.382	0.393	0.379
Sr	407.771	0.374	0.001	0.376	0.374	0.373
Ba	455.403	0.432	0.001	0.431	0.434	0.431
Na	589.592	3.36	0.036	3.40	3.33	3.34
Mg	285.213	6.29	0.031	6.30	6.31	6.25
Ca	317.933	39.6	0.181	39.4	39.8	39.7
Si	251.611	1.58	0.01	1.58	1.59	1.57
K	766.490	11.9	0.026	11.8	11.9	11.9
Ti	334.941	0.161	0.002	0.160	0.163	0.161
Fe	259.940	3.97	0.068	3.92	3.93	4.04
Cu	324.754	0.459	0.002	0.457	0.460	0.461
Zn	213.856	0.798	0.011	0.785	0.803	0.807

Table s2. ICP raw data for the inorganic elemental analysis of lignin.

Element	Peak/nm	Concentration/mgL ⁻¹	Derivation	Analysis 1	Analysis 2	Analysis 3
Al	396.152	0.74	0.014	0.724	0.744	0.751
B	249.678	0.114	0.003	0.112	0.117	0.112
Sr	407.771	0.024	0	0.024	0.024	0.024
Ba	455.403	0.122	0.001	0.121	0.123	0.121
Na	589.592	0.745	0.008	0.754	0.738	0.742
Mg	285.213	0.459	0.009	0.466	0.463	0.449
Ca	317.933	6.45	0.038	6.43	6.43	6.5
Si	251.611	0.588	0.003	0.591	0.587	0.587
K	766.490	0.254	0.004	0.255	0.249	0.257
Ti	334.941	0.125	0.001	0.125	0.123	0.125
Fe	259.940	0.684	0.002	0.685	0.686	0.682
Cu	324.754	0.241	0.001	0.24	0.242	0.242
Zn	213.856	0.246	0.004	0.246	0.241	0.25

Table s3. Inorganic element content in wood and lignin (in ppm).

	Al	B	Sr	Ba	Na	Mg	Ca	Si	K	Ti	Fe	Cu	Zn
Saw dust	193	38.5	37.4	43.2	336	629	3960	158	1190	16.1	397	45.9	79.8
Lignin	92.5	14.2	3.0	15.2	93.1	57.4	806	73.5	31.7	15.6	85.5	30.1	30.7

Empirical calculation of monomers and dimers existed in lignin

Lignin is a mixture of oxygenated polyaromatics with repeatedly, but randomly, cross-linked C₉ phenol units, which may also contain one or two ortho-methoxy groups. Most C₉ units are linked to two other C₉ units either by C-C or C-O bonds. Our strategy of producing monomers and dimers is through the cleavage of all the C-O linkages with retention of the C-C linkages. Thus, units which have both sides linked to other units by C-O bonds will be converted to monomers. Similarly, if two units are connected by C-C bond and linked to other parts by C-O bonds, they will be converted into dimers. If, for example, the total percentage of C-C linkage is x , then the percentage of C-O linkages will be $1-x$. Thus, the probability of a C₉ unit to be linked to other units by C-O bond on both sides is $(1-x)^2$, which means the ideal yield of monomer is $(1-x)^2$ based on all C₉ units. In a same way, the ideal yield of dimer is $x(1-x)^2$. Since the percentage of C-O linkages is between 2/3 and 3/4 for lignin, the yields of monomers and dimers can be estimated. The estimates are listed in Table 1 in the main text.

Lignin system:

Reaction of wood meal to lignin monomers (1) and derived lignin monomers to biofuels

(1) 4 g pre-extracted (extracted by ethanol/benzene 1:1 mixture in a soxlet for 12 h) birch wood sawdust, 0.3 g 5 wt% Rh/C (or Pd/C, Ru/C, Pt/C) catalyst, 70 ml de-oxygenated water or 70 ml mixture including dioxane/water (v/v=1:1), and 0.7 g 85 wt% H₃PO₄ (Beijing Chemical, AR grade) were mixed in an autoclave. After purging the reactor three times with H₂, the autoclave was pressurised with H₂ to 4 MPa at r.t. and then the temperature was increased to 473 K. After 4 h, the autoclave was cooled in an ice bath and the gas phase products were analysed by IR spectroscopy. Following filtration of the solution the residue was dried at 383 K for 2 h and weighed. The filtrate was immediately analysed by GC and GC-MS with *p*-propyl-phenol used as an internal standard. The catalyst was recycled according to the following procedure: after filtration, the residue was washed and dried in vacuum, then used directly in the next run.

(2) 3 x 150 ml cyclohexane was used to extract the monomers and dimers obtained from the first step. After evaporation of the solvent, the mixture containing lignin monomers and dimers, 0.1 g Pd/C catalyst and 30 ml 5 wt% H₃PO₄-H₂O were placed in an autoclave. After flushing with H₂ three times, the reaction was carried out at 523 K and 4 MPa H₂ for 2 h. After reaction, the products were extracted with diethyl ether (3 x 20 ml) and analysed by GC and GC-MS.

Lignin model compounds system:

Typical experiment of lignin monomers to alkanes

1.0 g lignin monomer (4-propylphenol and 2-methoxy-4-propylphenol)(Beijing Chemicals, AR grade), 0.1 g Pd/C (or Rh/C, Ru/C, Pt/C, PdPt/C) catalyst and 5 wt% H₃PO₄-H₂O solution (30 ml) were placed in an autoclave. The reactor was flushed three times with H₂, and then the reaction was carried out at 4 MPa H₂ and 523 K for 30 min. After reaction, the solution was filtered and the filtrate extracted with diethyl ether (3 x 20 ml). The diethyl ether layer was analysed by GC with a HP-innowax column and GC-MS.

Optimization of reaction conditions for monomer conversion to alkanes and methanol

Table s4. Conversion of lignin model monomers to C₉ and C₈-alkanes.

Entry	Substrate	Conv. (%)	Catalyst	Solv.	Selectivities (%)		CH ₃ OH (%) ^[a]
					C ₉ -alkane	C ₈ -alkane	
1	4-propylphenol	99.7	Pd/C	H ₂ O	75.1	-	-
2	2-methoxy-4-propylphenol	99.5	Pd/C	H ₂ O	10.3	3.7	-
3	2-methoxy-4-propylphenol	93.1	Pd/C	H ₂ O/ OH ⁻ [c]	0	0	-

4	2-methoxy-4-propylphenol	99.1	Pd/C	H ₂ O/ H ⁺	85.6	6.4	92.0
5	2-methoxy-4-propylphenol	97.7	Pd/C	H ₂ O/ H ⁺ [b]	72.6	4.0	90.2
6	2-methoxy-4-propylphenol	99.3	Ru/C	H ₂ O/ H ⁺	77.5	12.6	94.2
7	2-methoxy-4-propylphenol	97.7	PdPt/C	H ₂ O/ H ⁺	81.1	8.6	93.0
8	2-methoxy-4-propylphenol	100	Pt/C	H ₂ O/ H ⁺	85.0	5.3	95.0
9	2-methoxy-4-propylphenol	99.6	Rh/C	H ₂ O/ H ⁺	67.4	20.5	95.0

[a] The yield of methanol is the percentage (%) of the methanol obtained based on the total amount of methoxy groups in the corresponding monomers. [b] 1 % H₃PO₄ was added to the mixture. [c] 4 % NaOH was added to the mixture.

Reaction conditions: reactions were carried out in water using 5 wt% Pd/C, Pt/C, Ru/C, PtPd/C or Rh/C catalysts at 523 K, 4 MPa H₂. A reaction time of 30 min was used for each experiment.

Typical conversion of lignin dimers (two monomers connected together by C-O or C-C bond) to alkanes

1.0 g a-O-4 dimer (2-methoxy-1-(phenylmethoxy)-4-propylbenzene) or 0.5 g 5, 5' dimer (2,2'-Dihydroxy-3,3'-dimethoxy-5,5'-dipropylbiphenyl), 0.1 g Pd/C and 30 ml 5 wt% H₃PO₄-H₂O solution were placed in an autoclave. The conditions were the same as those described for "lignin monomers to alkanes" (see above).

Preparation of 2-methoxyl-4-propylphenol

2.0 g eugenol and 0.1 g 10% Pd/C was placed in 10 ml ethanol and transferred into a 100 ml autoclave. The mixture was treated with 40 bar hydrogen at ambient temperature for 24 h. Then, the solution was filtered over celite and the solvent was removed under vacuum to provide a colorless oil. Yield: 1.8 g, 90%. ¹H NMR (200 MHz, CD₂Cl₂), 1.00 (t, 3H, J = 7Hz), 1.68 (m, 2H), 2.59 (t, 2H, J = 7Hz), 3.93 (s, 3H), 5.60 (s, 1H), 6.75-6.87 (m, 3H). ¹³C NMR (50 MHz, CD₂Cl₂), 9.5, 20.9, 33.6, 51.8, 105.5, 108.7, 116.8, 130.7, 139.6, 142.4.

Preparation of 1-(benzyloxy)-2-methoxy-4-propylbenzene (a-O-4 dimer)

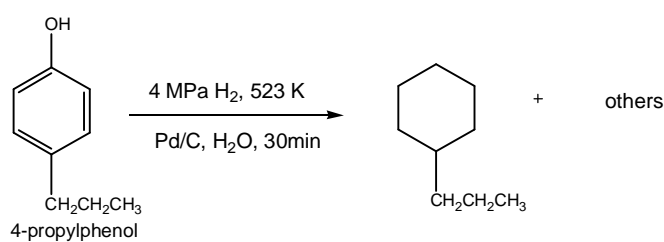
1.66 g 2-methoxyl-4-propylphenol (Beijing Chemicals, AR grade), 1.71 g benzyl bromide (Beijing Chemicals, AR grade), 0.645 g tert-butyl-amine bromide (Beijing Chemicals, AR grade), and 2 g K₂CO₃ were added to a 100 ml round bottle containing 30 ml toluene (Beijing Chemicals, AR grade) and 30 ml H₂O. The mixture was refluxed with stirring at 363 K for 3 h. Then 10 ml ether and 10 ml water was added into the mixture. The organic layer was washed with 10 ml water, dried over Na₂SO₄ and concentrated in vacuum. The raw product was purified by chromatography over silica gel (CH₂Cl₂, R_f = 0.7). The pure product was obtained as a colorless oil. Yield: 2.2 g, 85%. ¹H NMR (200 MHz, CD₂Cl₂), 1.01 (t, 3H, J = 7Hz), 1.66 (m, 2H), 2.60 (t, 2H, J = 7Hz), 3.91 (s, 3H), 5.11 (s, 2H), 6.75 (d, 1H, J = 8Hz), 6.82 (s, 1H), 6.90 (d, 1H, J = 8Hz), 7.31-7.47

(m, 5H). ^{13}C NMR (100 MHz, CD_2Cl_2), 13.6, 24.8, 37.6, 55.8, 71.1, 112.5, 114.0, 120.2, 127.7, 128.0, 128.5, 136.2, 137.6, 146.3, 149.6.

Preparation of 2-methoxy-4-propyl-6-(1-hydroxy-2-methoxy-4-propylbenzene)-phenol (5, 5 dimer)

The compound was synthesized according to literature (ref. 1) and purified by chromatography over silica gel (CH_2Cl_2 , $R_f = 0.25$). The purity of the compound will affect the following conversion reaction. ^1H NMR (200 MHz, CD_2Cl_2), 0.99 (t, 6H, $J = 7$ Hz), 1.67 (m, 4H), 2.59 (t, 4H, $J = 7$ Hz), 3.94 (s, 6H), 5.97 (s, 2H), 6.74 (s, 2H), 6.78 (s, 2H). ^{13}C NMR (50 MHz, CD_2Cl_2), 13.6, 24.9, 37.7, 56.1, 110.6, 122.8, 124.3, 134.6, 140.6, 147.1.

A



B

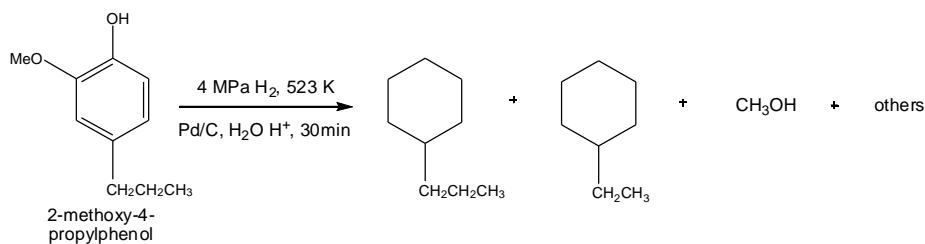
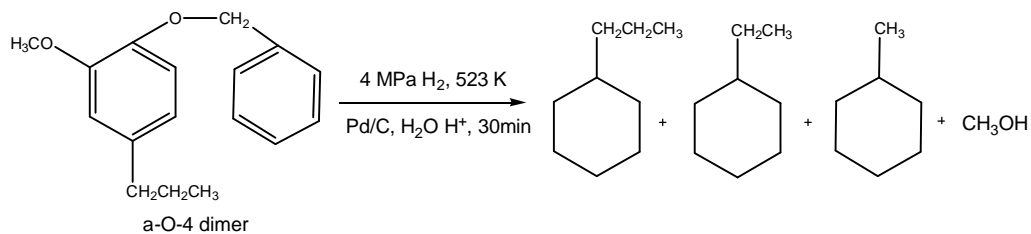


Fig. S1. Reactions for the conversion of lignin monomers into C_9 - and C_8 -alkanes.

A



B

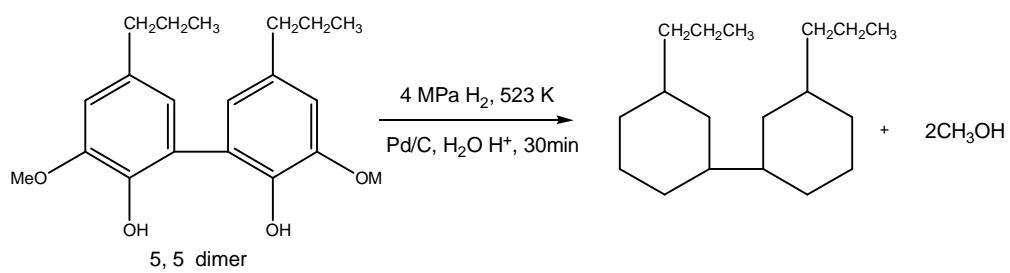


Fig. S2. Reactions for the conversion of lignin dimers into their corresponding alkanes.

Calculation of critical temperature and pressure of dioxane/water mixture:

The critical temperature and pressure of dioxane/water mixture (excluding the contribution from the substrates) are calculated according a literature method.²

With known critical temperatures of the components, the critical temperature of the mixture can be calculated approximately from a relationship based on the additivity rule:

$$T_{cr} = \sum T_{cr,i} y_i$$

where Y_i and T_{cr} are the mole fraction of the its component and its critical temperature.

From similar approaches, the critical pressure can be calculated from the formula:

$$P_{cr} = \sum y_i P_{cri}$$

where Y_i and P_{cri} are the mole fraction of the its component in the mixture and its critical pressure.

Table s5. The critical temperature and pressure of dioxane and water.^a

Component	T_{cr} °C	P_{cri} (atm)
Dioxane	314.8	51.4
H ₂ O	374.1	218.3

^a Data source: CRC handbook of chemistry and physics, 53rd edition.

Since the dioxane/water mixture used in this study is 50% by volume, the molar fraction of dioxane and water is 0.17 and 0.83, respectively. Thus, using the equations given above and the data in *Table s3*, the critical temperature and pressure of the dioxane/water mixture used in this study may be estimated as 364 °C and 190 atm.

References

1. F A Marques, F Simonelli, A R M Oliveira, G L Gohr, P C Leal *Tetrahedron Letters* **1998**, 39, 943.
2. N. P. Zhukov, V. I. Vychnok, I. A. Cherepennikov, S. N. Kuz'min *Chemistry and Technology of Fuels and Oils* **1993**, 29, 196.

