

H₂O₂-mediated Kraft lignin oxidation with readily available metal salts: what about the effect of ultrasound?

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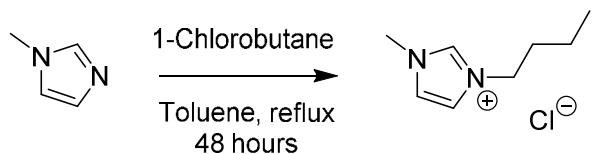
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Supporting information:

¹H NMR spectra were recorded on Bruker ALS-300 spectrometer. All NMR chemical shifts are reported as δ in parts per million (ppm) relative to chloroform for ¹H NMR ($\delta = 7.26$ ppm) in deuterated solvents. Data are reported as follows: chemical shift, multiplicity (s = singlet, t = triplet, m = multiplet), coupling constants (J) given in Hertz (Hz), integration and attribution. Infrared (IR) spectra were recorded on a SMART iTR-Nicolet iS10 spectrometer using Attenuated Total Reflectance (ATR) and the wavenumbers (ν max) are expressed in cm⁻¹.

Synthesis of 1-Butyl-3-methylimidazolium chloride, [BMIM]Cl



To a vigorously stirred solution of 1-methylimidazole (50.0 g, 0.61 mol, 1.0 equiv.) in 100 mL toluene at 25°C under inert conditions, 1-chlorobutane (62.0 g, 0.67 mol, 1.1 equiv.) is added. The solution was heated under reflux for 48 hours. The mixture is then concentrated *in vacuo*. The resulting oil is dissolved in a minimum of acetonitrile and added dropwise at 0°C into ethyl acetate in order to crystallize the salt. The solid is then filtered *in vacuo* and dried at 40°C for 24 hours. 1-Butyl-3-methylimidazolium chloride is obtained as white crystals (87.2 g, 0.54 mol, 89%).

¹H NMR (300 MHz, CDCl_3): δ 10.82 (s, 1H, Ar-H), 7.49 (s, 1H, Ar-H), 7.36 (s, 1H, Ar-H), 4.29 (t, 2H, $J = 7.4$ Hz, CH_2), 4.09 (s, 3H, CH_3), 1.92-1.82 (m, 2H, CH_2), 1.29-1.41 (m, 2H, CH_2), 0.93 (t, 3H, $J = 7.3$ Hz, CH_3).

Table S1. Lignin oxidative depolymerization catalyzed by various metal salts.

Entry	Catalyst	Yield, wt%, 25°C	Yield, wt%, 45°C	Monomers
1-1	None	0.24	0.19	A, B, C, D
1-2	Fe ₂ (SO ₄) ₃	0.12	0.15	
1-3	Fe(NO ₃) ₃ ,9H ₂ O	0.08	0.09	A, B, C
1-4	Mn(SO ₄) ₂ ,H ₂ O	0.13	0.14	
1-5	Bi ₂ (SO ₄) ₃	0.16	0.16	
1-6	Bi(NO ₃) ₃ ,5H ₂ O	0.19	0.25	
1-7	H ₂ WO ₄	0.15	0.25	A, B, C, D
1-8	Na ₂ WO ₄ ,2H ₂ O	0.21	0.51	
1-9 ^[a]	None	0.12	0.09	
1-10 ^[a]	Mn(SO ₄) ₂ ,H ₂ O	0.06	0.10	A, B, D
1-11 ^[a]	Na ₂ WO ₄ ,2H ₂ O	0.12	0.07	A, B, C, D

Reaction conditions: 400 mg of lignin, 2 equiv. 30% H₂O₂, 5 mol% catalyst in acetone/H₂O (1/1: V/V), 1 h.
[a]: reaction performed with 2 eq. NaHCO₃.

Table S2. Optimization of lignin oxidative depolymerization catalyzed by Na₂WO₄,2H₂O and hydrogen peroxide.

Entry	T, °C	Catalytic Charge	Oxidant charge	Yield, wt%	Monomers*
2-1	25°C	5 mol%	2 equiv.	0.21	
2-2	45°C	5 mol%	2 equiv.	0.51	
2-3	56°C	5 mol%	2 equiv.	0.28	
2-4	45°C	1 mol%	2 equiv.	0.23	A, B, C, D
2-5	45°C	2.5 mol%	2 equiv.	0.29	
2-6	45°C	10 mol%	2 equiv.	0.21	
2-7	45°C	15 mol%	2 equiv.	0.04	A
2-8	45°C	20 mol%	2 equiv.	0	—
2-9	45°C	5 mol%	1 equiv.	0.18	
2-10	45°C	5 mol%	3 equiv.	0.22	A, B, C, D
2-11	45°C	5 mol%	4 equiv.	0.06	A, B, C

Reaction conditions: 400 mg of lignin in acetone/H₂O (1/1: V/V), Na₂WO₄,2H₂O, 1 h, * GC MS determination.

Table S3. Solvent effect on the lignin oxidative depolymerization.

Entry	Solvent	T, °C	Yield, wt%	Monomers*
3-1	Acetone/H ₂ O (1/1: V/V)	45°C	0.51	
3-2	Acetone/H ₂ O (1/1: V/V) + 10 wt% [Bmim]Cl	45°C	0.21	A, B, C, D
3-3	AcOEt	45°C	0.37	
3-4	AcOEt + 10 wt% [BMIM]Cl	45°C	0.29	
3-5	[BEpip]NTf ₂	45°C	0.02	D
3-6	NaOH _{aq} 1M	45°C	0.21	A, B, C, D
3-7	NaOH _{aq} 1M	60°C	0.38	B, C, D
3-8	NaOH _{aq} 1M	80°C	0.41	
3-9	NaOH _{aq} 1M	100°C	0.35	A, B, C, D

Conditions: 400 mg of lignin, 2 equiv. 30% H₂O₂, 5 mol% Na₂WO₄.2H₂O, 1 h, *GC MS determination.

Table S4. Ultrasound effect on the lignin oxidative depolymerization.

Entry	Solvent	Activation	H ₂ O ₂ , eq.	T, °C	Yield, wt%	Monomers*
4-1	Acetone/H ₂ O (V/V: 1/1)	None	2	45°C	0.51	
4-2	Acetone/H ₂ O (V/V: 1/1)	U.S.	2	45°C	0.29	
4-3	Acetone/H ₂ O (V/V: 1/1)	U.T.	2	45°C	0.52	
4-4	AcOEt	None	2	45°C	0.37	A, B, C, D
4-5	AcOEt	U.S.	2	45°C	0.24	
4-6	NaOH _{aq} 1M	None	2	80°C	0.41	
4-7	NaOH _{aq} 1M	U.S.	2	80°C	0.25	
4-8	Acetone/H ₂ O (V/V: 1/1)	None	4	45°C	0.06	A, B, C
4-9	Acetone/H ₂ O (V/V: 1/1)	U.S.	4	45°C	0	—

Conditions: 400 mg of lignin, 5 mol% Na₂WO₄.2H₂O, 1 h, under silent (None), ultrasound (U.S.) or ultra-turrax (U.T.) conditions, *GC MS determination

Table S5. Choice of the catalyst and optimization - Experimental conditions and mass of the liquid products identified by GC-MS analysis.

Entry	Catalyst	Temp (°C)	Quant Oxidant	Catalytic Charge	Mass of the identified liquid products in µg				
					A	B	C	D	Total
1-a	Blank	25	2 eq.	-	281	340	141	208	970
2-a	Fe ₂ (SO ₄) ₃	25	2 eq.	5 mol%	196	178	96	Nd.	470
3-a	Fe(NO ₃) ₃ ,9H ₂ O	25	2 eq.	5 mol%	150	103	52	Nd.	305
4-a	Mn(SO ₄)	25	2 eq.	5 mol%	151	221	62	103	537
5-a	Bi ₂ (SO ₄) ₃	25	2 eq.	5 mol%	193	239	76	130	638
6-a	Bi(NO ₃) ₃ ,5H ₂ O	25	2 eq.	5 mol%	279	230	86	154	748
7-a	H ₂ WO ₄	25	2 eq.	5 mol%	188	231	65	116	600
8-a	Na ₂ WO ₄ ,2H ₂ O	25	2 eq.	5 mol%	446	238	71	81	836
9-a	Blank	45	2 eq.	-	258	265	95	154	772
10-a	Fe ₂ (SO ₄) ₃	45	2 eq.	5 mol%	248	203	133	Nd.	584
11-a	Fe(NO ₃) ₃ ,9H ₂ O	45	2 eq.	5 mol%	146	112	89	Nd.	347
12-a	Mn(SO ₄)	45	2 eq.	5 mol%	171	211	72	101	555
13-a	Bi ₂ (SO ₄) ₃	45	2 eq.	5 mol%	314	237	Nd.	106	657
14-a	Bi(NO ₃) ₃ ,5H ₂ O	45	2 eq.	5 mol%	400	291	201	97	989
15-a	H ₂ WO ₄	45	2 eq.	5 mol%	484	280	149	82	995
16-a	Na ₂ WO ₄ ,2H ₂ O	45	2 eq.	5 mol%	791	404	787	51	2033
17-a	Na ₂ WO ₄ ,2H ₂ O	56	2 eq.	5 mol%	587	273	195	55	1110
18-a	Na ₂ WO ₄ ,2H ₂ O	45	2 eq.	1 mol%	375	282	168	82	907
19-a	Na ₂ WO ₄ ,2H ₂ O	45	2 eq.	2.5 mol%	566	256	253	70	1145
20-a	Na ₂ WO ₄ ,2H ₂ O	45	2 eq.	10 mol%	403	213	137	81	834
21-a	Na ₂ WO ₄ ,2H ₂ O	45	2 eq.	15 mol%	149	Nd.	Nd.	Nd.	149
22-a	Na ₂ WO ₄ ,2H ₂ O	45	2 eq.	20 mol%	Nd.	Nd.	Nd.	Nd.	Nd.
23-a	Na ₂ WO ₄ ,2H ₂ O	45	1 eq.	5 mol%	281	220	151	51	703
24-a	Na ₂ WO ₄ ,2H ₂ O	45	3 eq.	5 mol%	404	275	133	82	894
25-a	Na ₂ WO ₄ ,2H ₂ O	45	4 eq.	5 mol%	129	73	46	Nd.	249

Nd.: Not detected

Reactions performed for 1 hour, in acetone/H₂O (1/1: V/V).

Table S6: Effect of the BAP system - Experimental conditions and product mass of the products identified by GC-MS analysis.

Entry	Catalyst	Temp (°C)	Quant Oxidant	Catalytic Charge	Mass of the identified liquid products in µg				
					A	B	C	D	Total
1-b	Blank	25	2 eq.	-	106	193	126	71	496
2-b	Mn(SO ₄)	25	2 eq.	5 mol%	150	256	Nd.	78	485
3-b	Na ₂ WO ₄ .2H ₂ O	25	2 eq.	5 mol%	93	142	Nd.	15	251
4-b	Blank	45	2 eq.	-	99	166	48	61	374
5-b	Mn(SO ₄)	45	2 eq.	5 mol%	89	91	53	36	269
6-b	Na ₂ WO ₄ .2H ₂ O	45	2 eq.	5 mol%	207	146	Nd.	31	384

Nd.: Not detected, reactions performed for 1 hour with 2 equiv. H₂O_{2(aq)}, 0.25 equiv. NaHCO₃ in action/H₂O (1/1: V/V).

Table S7: Effect of the solvent - Experimental conditions and product mass of the products identified by GC-MS analysis.

Entry	Temp (°C)	Solvent	Mass of the identified liquid products in µg				
			A	B	C	D	Total
1-c	45	Acetone/H ₂ O (1/1) +10 wt% [Bmim]Cl	472	183	151	45	851
2-c	45	Ethyl acetate	796	208	342	114	1459
3-c	45	Ethyl acetate +10 wt% [Bmim]Cl	789	279	Nd.	85	1153
4-c	45	[BEpip]NTf ₂	Nd.	Nd.	Nd.	79	79
5-c	45	1M NaOH _(aq)	86	214	505	45	850
6-c	60	1M NaOH _(aq)	Nd.	241	1175	96	1512
7-c	80	1M NaOH _(aq)	129	319	1121	81	1650
8-c	100	1M NaOH _(aq)	206	253	862	90	1411

Nd.: Not detected, reactions Performed for 1 hour, with 2 equiv. H₂O_{2(aq)}, 5 mol% of Na₂WO₄.2H₂O

Table S8: Effect of the Ultrasound - Experimental conditions and mass of the products identified by GC-MS analysis.

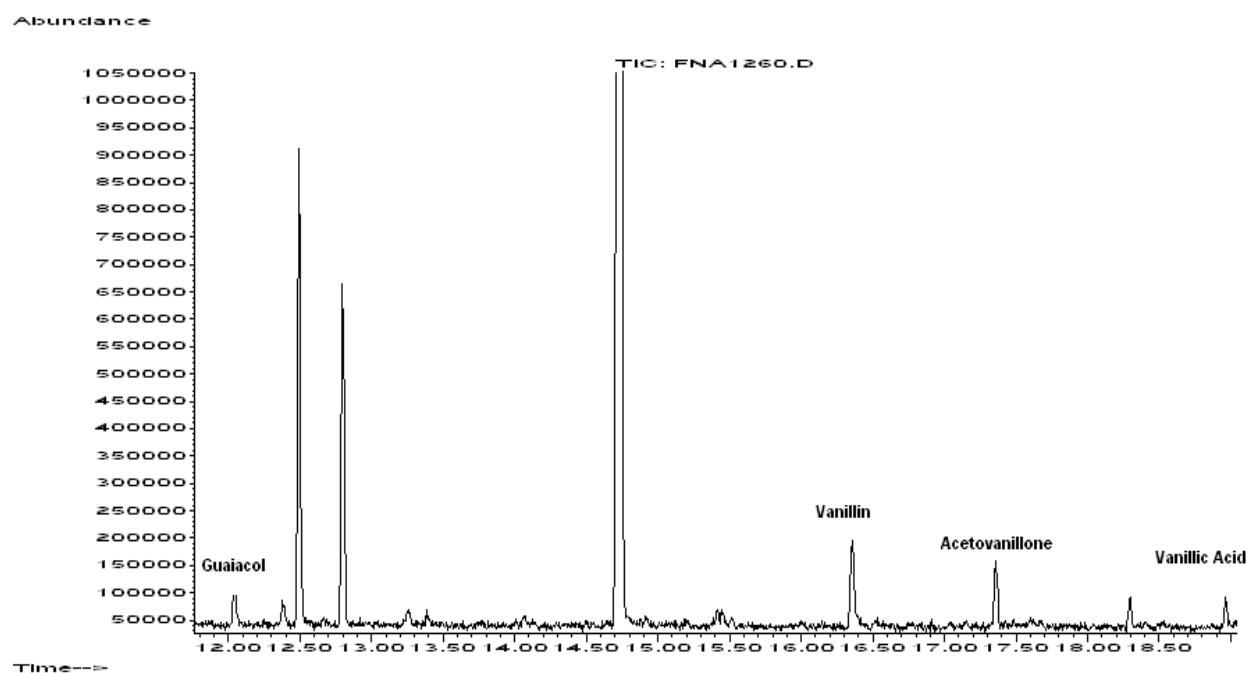
Entry	Sonication	Temp (°C)	Solvent	Quant oxidant	Mass of the identified liquid products in µg				
					A	B	C	D	Total
1-d	US (20kHz, 0.38 W.mL ⁻¹)	45	Acetone/H ₂ O (1/1)	2 eq.	583	305	138	126	1152
2-d	US (20kHz, 0.38 W.mL ⁻¹)	45	AcOEt	2 eq.	651	222	Nd.	80	953
3-d	US (20kHz, 0.38 W.mL ⁻¹)	80	1M NaOH(aq)	2 eq.	189	191	550	80	1010
4-d	US (20kHz, 0.38 W.mL ⁻¹)	45	Acetone/H ₂ O (1/1)	4 eq.	Nd.	Nd.	Nd.	Nd.	Nd.
5-d	Ultraturax	45	2 eq.	2 eq.	778	400	823	58	2059

Nd : Not detected

Reactions Performed for 1 hour, with 5 mol% of Na₂WO₄.2H₂O

Four monomers (Vanillin, acetovanillone, vanillic acid and guaiacol) were determined by GC-MS analysis after derivatization with BSTFA/TMSC (99/1).

Figure S1: GC chromatogram of lignin oxidative depolymerization.



Oxidative depolymerization conditions: 400 mg of lignin, 2 equiv. 30% H₂O₂, 5 mol% Na₂WO₄ in acetone/H₂O (1:1 V/V), 25°C, 1 h

Analysis conditions: 100 µL of BSTFA/TMS (99/1) were added to a solution of 100 µL of the organic layer in 1.0 mL acetone.

Figure S2: MS spectra of guaiacol.

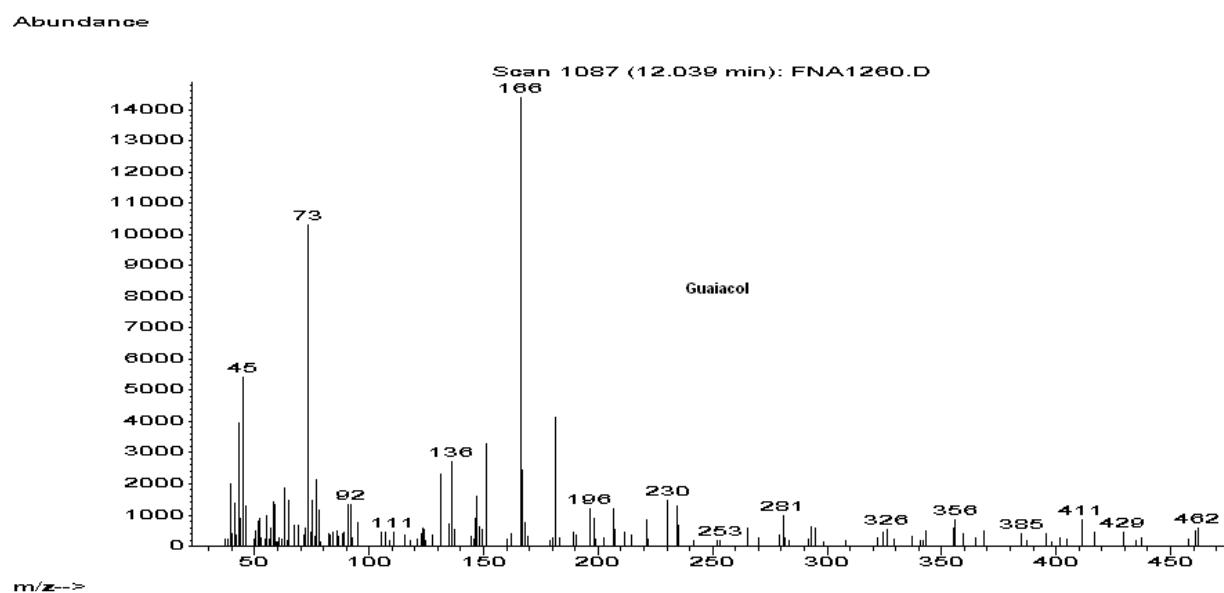


Figure S3: MS spectra of vanillin

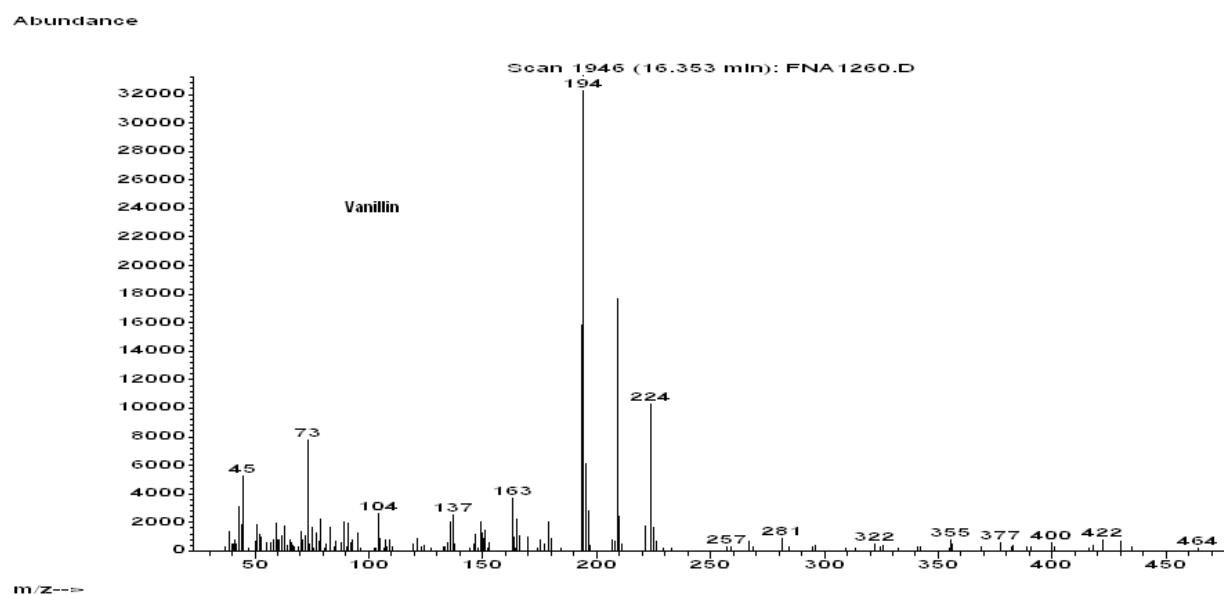


Figure S4: MS spectra of acetovanillone

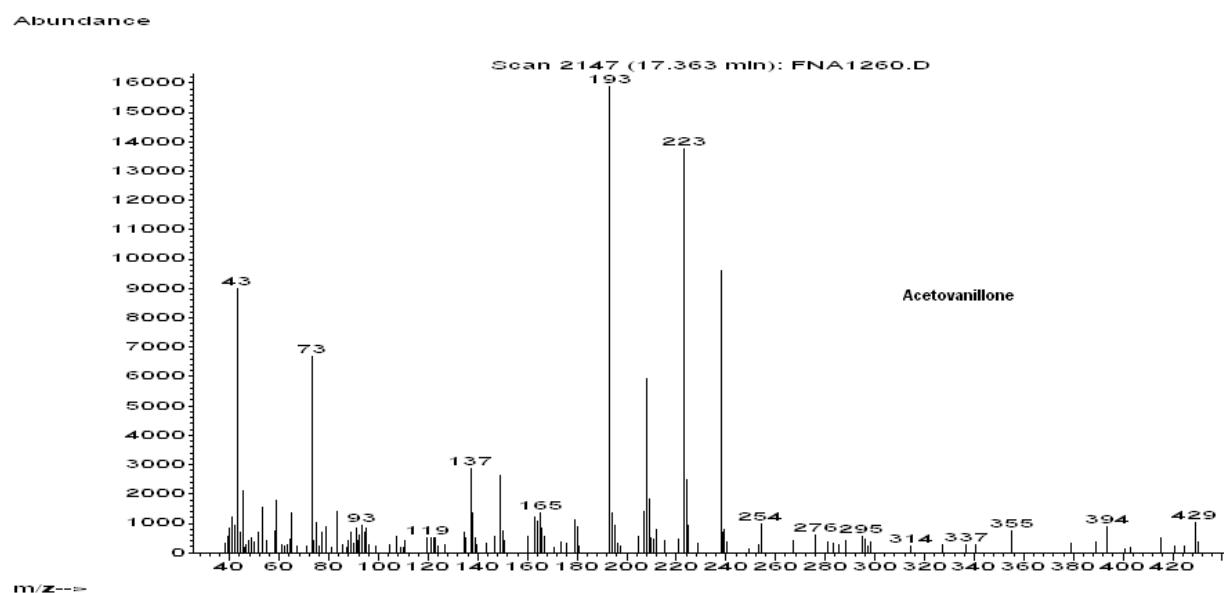


Figure S5: MS spectra of vanillic acid

