Electronic Supplementary Information for:

Revisiting alkaline aerobic lignin oxidation†

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A. Tables

Table S1 M_n, M_w and PD values of the reaction products and starting substrates as determined by GPC.[a]

substrate	M_n	M_w	PD
Figure 3b			
poplar - product from oxidation (5 bar O_2)	350	650	1,8
poplar - product from inert reaction (0 bar O_2)	640	1150	1,8
Figure 10			
poplar - oxidation product (with catalyst)	340	640	1,9
high-S poplar - oxidation product (with catalyst)	270	390	1,4
pine oxidation - oxidation product (with catalyst)	350	600	1,7
corn stover oxidation - oxidation product (with catalyst)	350	470	1,3
Figure 11a			
spruce Kraft lignin	1400	7700	5,4
corn stover DMR-EH lignin	2200	14000	6,5
corn stover DAP-EH lignin	1200	7400	6,1
corn stover AAP-AE lignin	380	500	1,3
Figure 11b			
spruce Kraft lignin - oxidation product (with catalyst)	390	670	1,7
corn stover DMR-EH lignin - oxidation product (with catalyst)	370	520	1,4
corn stover DAP-EH lignin - oxidation product (with catalyst)	370	530	1,5
corn stover AAP-AE lignin - oxidation product (with catalyst)	350	450	1,3

[a]The figures with the GPC profiles in the main manuscript are indicated. The experimental details of the reactions can be found in the captions of Figure 3 and Figure 9.

Table S2 Monomer yields (on lignin basis) from $LaMn_{0.8}Cu_{0.2}O_3$-catalyzed oxidation of various lignocellulose feedstocks and isolated lignins at varying reaction times.[a]

Substrate	Time (min)	Yield (wt%)										
		p-hydroxybenzaldehyde	vanillin	syringaldehyde	acetovanillone	acetosyringone	*p*-hydroxybenzoic acid	vanillic acid	syringic acid	*p*-coumaric acid	ferulic acid	**Total yield**
Native lignins												
poplar	0		7.4	13.4		2.0	5.9	0.9	1.2			**30.9**
	10		7.4	12.3		1.4	5.9	1.3	0.7			**28.9**
	30		6.5	9.4		0.3	5.6	1.4	0.3			**23.6**
	60		4.6	2.4		0.1	5.0	0.7	0.1			**12.9**
high-S poplar	0		2.8	20.1		3.7	1.9	0.5	2.0			**30.9**
	10		2.7	19.2		2.2	1.8	0.6	1.0			**27.6**
pine	0		14.3		1.3			2.1				**17.7**
	10		17.3		1.9			2.9				**22.1**
	30		16.7		1.8			3.9				**22.4**
corn stover	0	1.7	5.2	5.1	0.6	1.6	0.4	0.8	0.7	8.8	1.8	**26.7**
	10	2.6	5.4	4.8	0.6	0.9	0.5	1.0	0.2	6.8	0.6	**23.4**
Isolated lignins												
spruce kraft lignin	0		8.3		1.1			2.6				**12.0**
	10		6.0		0.6			0.7				**7.3**
corn stover DMR-EH lignin	0	2.4	4.2	5.5	0.5	0.9	0.4	1.1	0.5	9.8	1.1	**26.5**
	0[b]	1.3	2.2	2.9	0.3	0.5	0.2	0.6	0.3	5.2	0.6	**14.0**
	10	4.0	4.2	4.1	0.4	0.4	0.8	1.4	0.2	5.2	0.2	**20.8**
corn stover DAP-EH lignin	0	2.0	2.9	2.2	0.3	0.2	0.6	0.8	0.1	3.4	0.1	**12.7**
	0[b]	1.3	1.9	1.4	0.2	0.1	0.4	0.5	0.1	2.1	0.1	**8.0**
	10	2.7	2.5	1.2	0.2	0.1	0.9	0.5	0.0	1.2	0.0	**9.2**
corn stover AAP-AE lignin	0	3.6	6.9	5.5	0.8	0.9	1.0	1.2	0.2	10.1	1.0	**31.3**
	0[b]	1.1	2.1	1.6	0.2	0.3	0.3	0.4	0.1	3.0	0.3	**9.3**
	10	3.7	5.0	3.5	0.5	0.4	1.0	1.0	0.1	5.2	0.1	**20.7**

[a]Reaction conditions: 30 mL of 2 M NaOH aqueous solution, 10 mg $LaMn_{0.8}Cu_{0.2}O_3$, 175 °C, 5/15 bar O_2/He (at RT); poplar: 500 mg substrate /147 mg lignin; high-S poplar: 500 mg substrate / 115 mg lignin; pine: 500 mg substrate / 145 mg lignin; corn stover: 500 mg substrate / 93 mg lignin; spruce kraft lignin: 150 mg substrate / 140 mg lignin; corn stover DMR-EH lignin: 300 mg substrate / 160 mg lignin; corn stover DAP-EH lignin: 250 mg substrate /158 mg lignin; corn stover AAP-AE lignin: 15 mL of the AAP-AE liquor (0.1 N NaOH, containing 520 mg solids and 154 mg lignin) was combined with 15 mL of a 3.9 N NaOH aqueous solution to obtain 30 mL of a 2 M NaOH solution. [b]Monomer yield on total substrate basis. These yields are indicated in Table 2 in the main article.

B. Figures

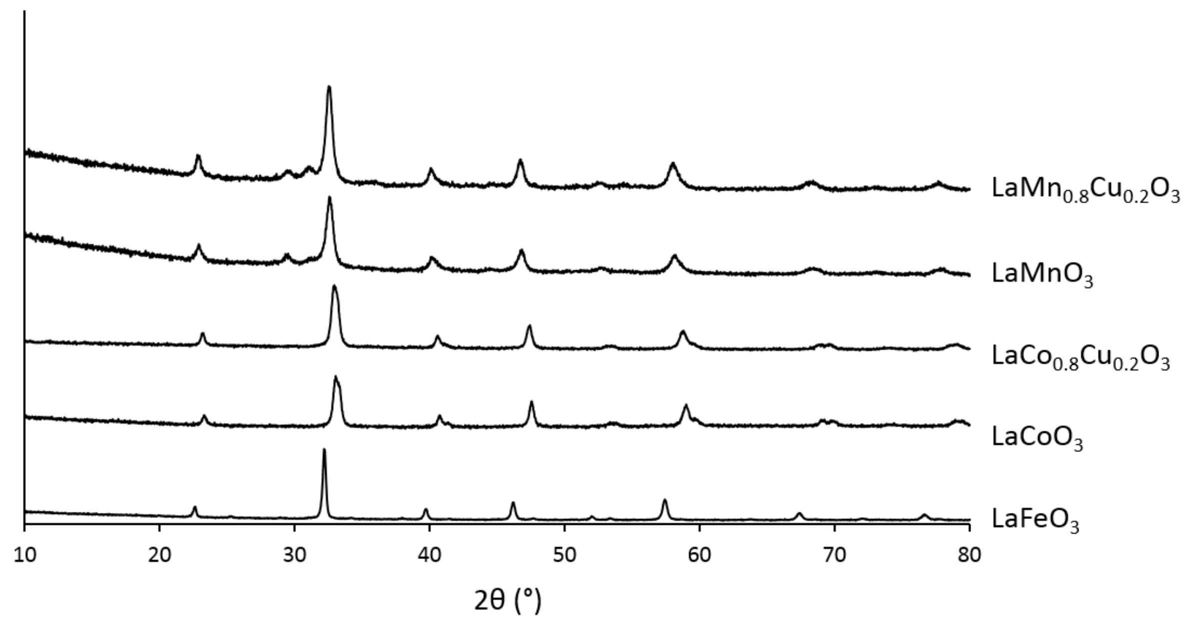

Figure S1 XRD patterns of the perovskite catalysts. The patterns all exhibit the characteristic reflections for perovskite oxides, indicating that the Cu^{2+} is incorporated in the perovskite structure. The reflection patterns were compared those published in literature: $LaFeO_3$[1-4]; $LaMnO_3$[1, 3, 5-7] and $LaMn_{0.8}Cu_{0.2}O_3$[5, 7, 8]; $LaCoO_3$[1, 9-11] and $LaCo_{0.8}Cu_{0.2}O_3$[11].

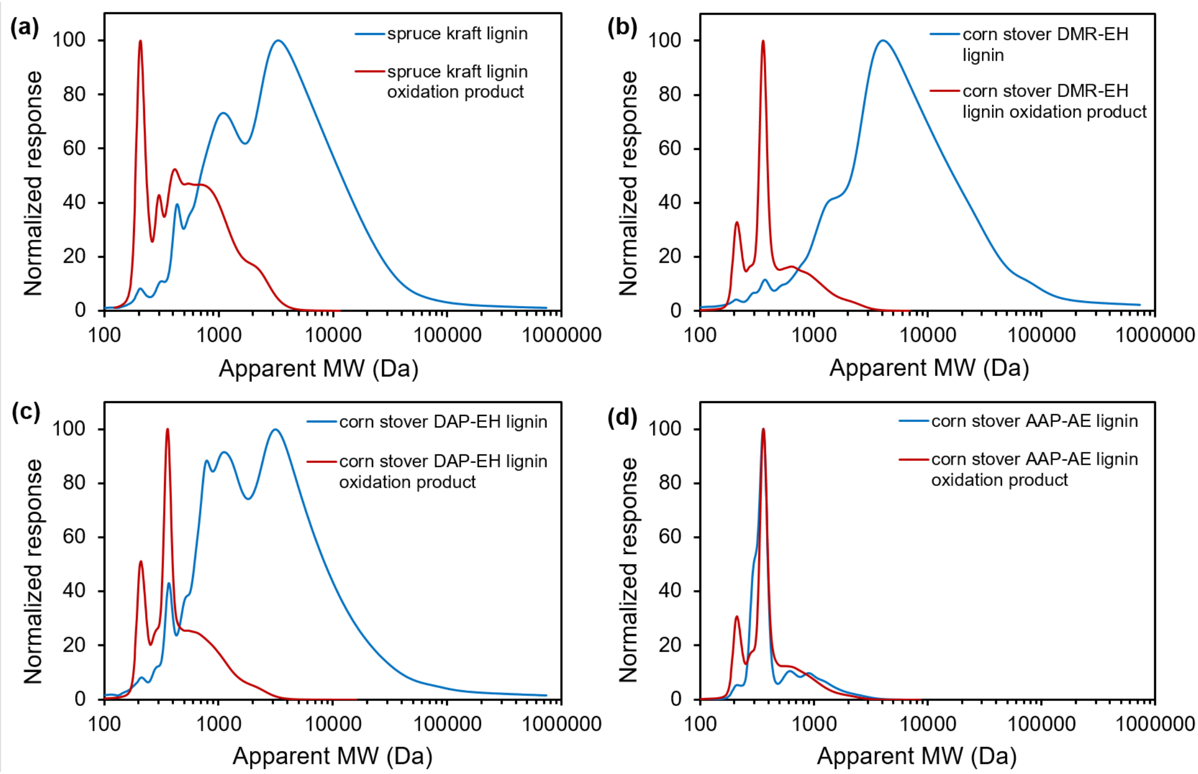

Figure S2 GPC profiles of the isolated lignins and their oxidation products.

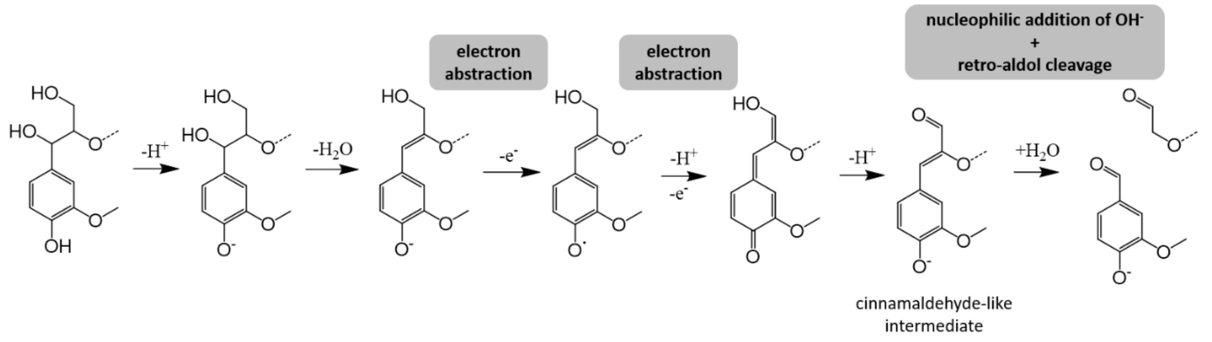

Figure S3 Mechanism of alkaline aerobic lignin oxidation according to Tarabanko *et al*.[12-15]

C. References

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