

Supplementary Materials for

Hydrodeoxygenation of Condensed Lignins Followed by Acid-Mediated Methylation Enables Preparation of Lignin-Based Wood Adhesives

Guangxu Yang,^{‡^a} Zhenggang Gong,^{‡^a} Bei Zhou,^{‡^b} Xiaolin Luo,^a Jing Liu,^a Guanben Du,^{*^b} Chengke Zhao,^{*^a} and Li Shuai^{*^a}

^a. College of Materials Engineering, Fujian Agriculture and Forestry University, Fuzhou, 350002, China.

^b. Yunnan Provincial Key Laboratory of Wood Adhesives and Glued Products, College of Materials Science and Engineering, Southwest Forestry University, Kunming, 650224, China.

[‡] The authors contributed equally to this work.

* Corresponding author email: lishuai@fafu.edu.cn

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I. Tables

Table S1. Yields of monomers derived from hydrodeoxygenation of lignin samples that were extracted with different methods.

Samples ^a	Lignin monomer yields (mol%)					
	M1	M2	M3	M4	M5	Total
NL	7.2	2.3	15.3	2.0	24.3	51.1
EL	2.9	1.1	5.7	0.6	5.7	16.0
KL	2.7	0.4	0.9	0.0	0.0	4.0
DL	1.2	0.6	0.7	0.2	0.0	2.7

^a NL, EL, KL, and DL are abbreviations for native lignin, ethanol lignin, kraft lignin, and dioxane lignin, respectively.

Table S2. The contents (mol/mol) of different hydroxyl groups of lignin before/after acid-mediated methylation.

Samples ^a	Contents of hydroxyl groups (mmol/g) ^d						Total phenolic OH
	Aliphatic OH	Syringyl OH		Guaiacyl OH		Carboxylic group	
		C ^b	NC ^c	C ^b	NC ^c		
HKL	0.14	0.24	0.25	0.07	0.35	0.04	0.91
MHKL	0.29	0.3	0.27	0.1	0.24	0.07	0.91
HEL	0.34	0.46	0.27	0.04	0.21	0.01	0.98
MHEL	0.37	0.48	0.33	0.1	0.09	0.02	0.98
HDL	0.19	0.38	0.37	0.07	0.19	0.03	1.01
MHDL	0.35	0.4	0.4	0.12	0.09	0.07	1.01
Chemical shift (ppm) ¹	150.0–146.0	144.5–143.2	143.2–142.2	142.2–141.5	140.2–139.0	135.8–134.0	

^a HKL/HEL/HDL are abbreviations of hydrodeoxygenated KL/EL/DL. MHKL/MHEL/ MHDL are abbreviations of HKL/HEL/HDL after acid-mediated methylation. ^b C, condensed; ^c NC, non-condensed. ^d The contents of hydroxyl groups in lignin before/after acid-mediated methylation were calculated on the basis of molar quantities of total phenolic OH.

Table S3. The contents of the vacant reactive sites on the aromatic nuclei of lignin before/after acid-mediated methylation determined by 2D HSQC NMR.

Samp	O	S ₂	G ₂	G ₅
HKL	1	0.	0.	0.
MHK	1	0.	0.	0.
HEL	1	0.	0.	0.
MHE	1	0.	0.	0.
HDL	1	0.	0.	0.
MHD	1	0.	0.	0.

Table S4. The contents (mol/mol) of different hydroxyl groups of MHKL at different modification time.

Modification time (h)	Contents of hydroxyl groups (mmol/g) ^c						
	Aliphatic OH	Syringyl OH		Guaiacyl OH		Carboxylic group	Total phenolic OH
		C ^a	NC ^b	C ^a	NC ^b		
0	0.14	0.24	0.25	0.07	0.35	0.04	0.91
1	0.15	0.28	0.27	0.07	0.28	0.03	0.91
3	0.18	0.3	0.28	0.09	0.24	0.05	0.91
5	0.29	0.3	0.27	0.1	0.24	0.07	0.91
10	0.31	0.33	0.31	0.11	0.16	0.1	0.91

^a C, condensed; ^b NC, non-condensed. ^c The contents of hydroxyl groups in MHKL at different modification time were calculated on the basis of molar quantities of total phenolic OH.

Table S5. The contents (mmol/g) of different hydroxyl groups of lignins before/after hot-pressing.

Samples	Contents of hydroxyl groups (mmol/g) ^c					
	Aliphatic OH	Syringyl OH		Guaiacyl OH		Carboxylic group
		C ^a	NC ^b	C ^a	NC ^b	
MHKL	1.02	1.05	0.92	0.36	0.84	0.25
MHEL	1.24	1.41	1.25	0.34	0.25	0.07
MHDL	0.84	0.97	0.97	0.29	0.23	0.16
Hot-pressed MHKL (190 °C)	0.24	0.28	0.16	0.1	0.08	0.08
Hot-pressed MHEL (190 °C)	0.45	0.44	0.23	0.15	0.09	0.02
Hot-pressed MHDL (190 °C)	0.28	0.21	0.11	0.07	0.04	0.06

^a C, condensed; ^b NC, non-condensed. ^c The contents of hydroxyl groups in lignins before/after hot-pressing were calculated on the basis of mass of lignins.

Table S6. The contents of elements in the lignins before/after hot-pressing at the interface of wood veneers.

Samples	Elements contents (wt.%)		
	C1s Scan A	C1s Scan B	C1s Scan C
	C-C/C-H	C-O	O-C-O/C=O
MHKL	39.17	36.56	3.41
Hot-pressed MHKL (190 °C)	43.90	28.45	2.97
MHEL	33.97	39.52	2.78
Hot-pressed MHEL (190 °C)	57.02	21.05	1.51
MHDL	43.20	34.39	2.98
Hot-pressed MHDL (190 °C)	52.27	23.63	2.63

II. Figures

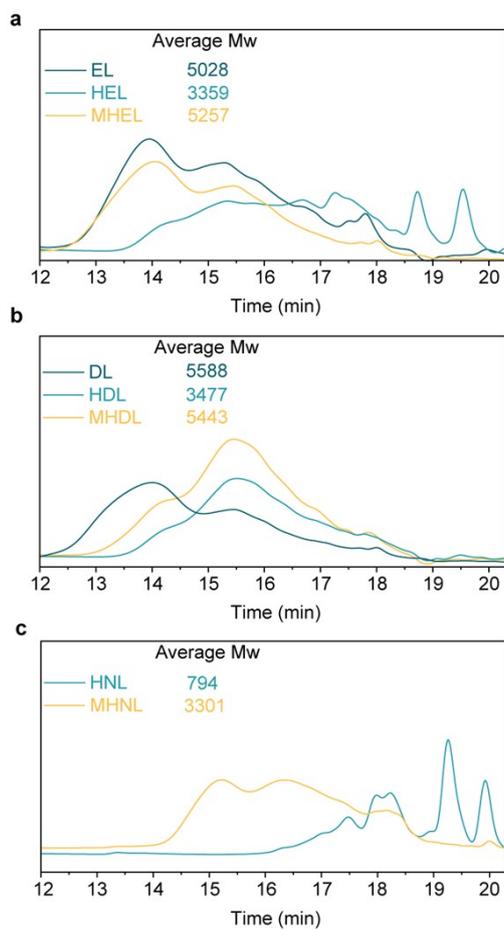


Figure S1. Molecular weights of lignins before/after hydrodeoxygenation and acid-mediated methylation. (a) Ethanol lignin. (b) Dioxane lignin. (c) Native lignin in eucalyptus wood particles.

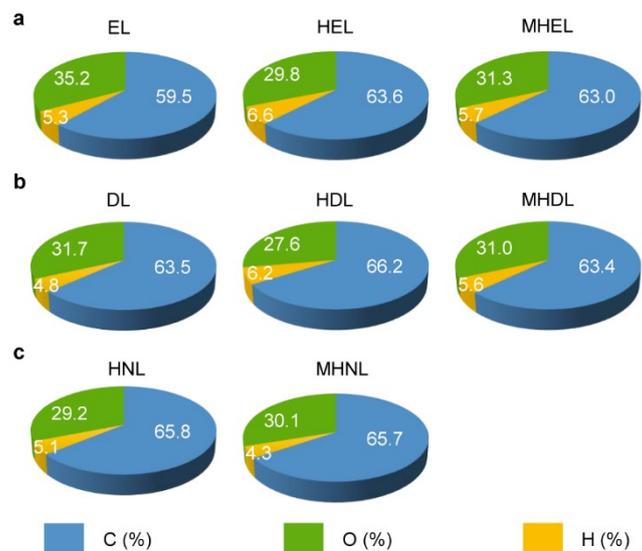


Figure S2. Elemental contents of lignins before/after hydrodeoxygenation and acid-mediated methylation. (a) Ethanol lignin. (b) Dioxane lignin. (c) Native lignin in eucalyptus wood particles.

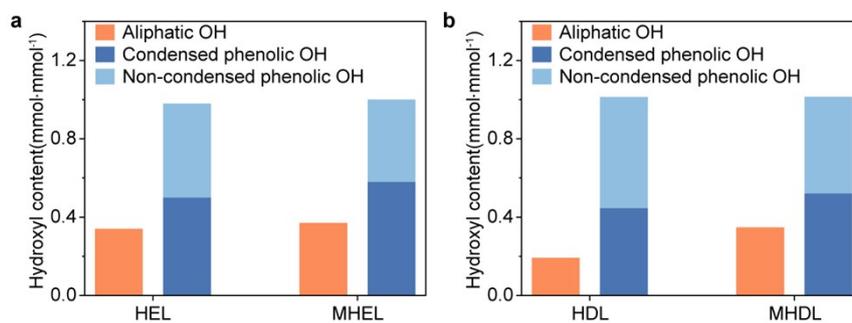


Figure S3. Hydroxyl contents of hydrodeoxygenated lignins before/after acid-mediated methylation. (a) Hydrodeoxygenated ethanol lignin. (b) Hydrodeoxygenated dioxane lignin.

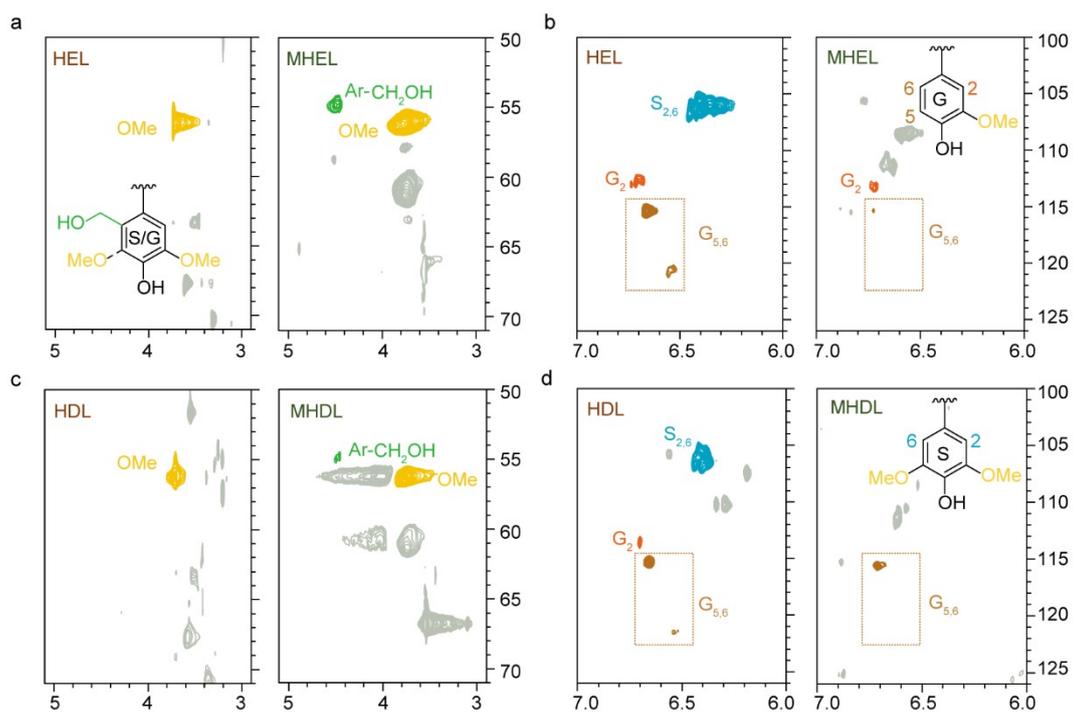


Figure S4. 2D HSQC NMR characterization of lignin before and after modification. (a) Partial side-chain regions and (b) aromatic regions in 2D HSQC NMR spectra of HEL and MHEL. (c) Partial side-chain regions and (d) aromatic regions in 2D HSQC NMR spectra of HDL and MHDL.

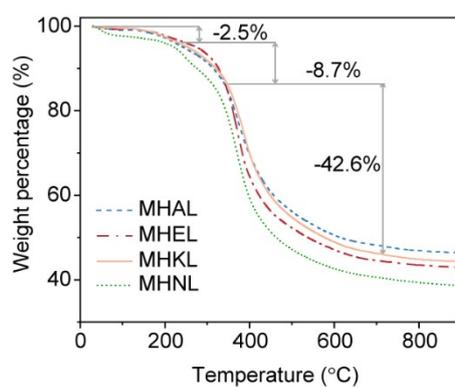
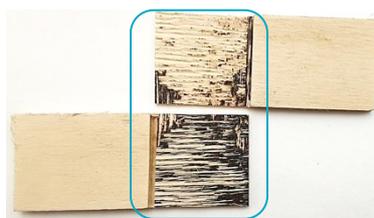


Figure S5. Thermogravimetric (TG) curves of various methylolated lignins.



Wood failure

Figure S6. Wood failure of the three-layer plywood prepared with the MHKL adhesive after a wet strength test.

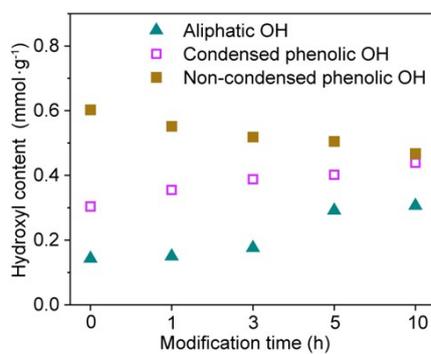


Figure S7. The effect of methylation time on hydroxyl contents of MHKLs.

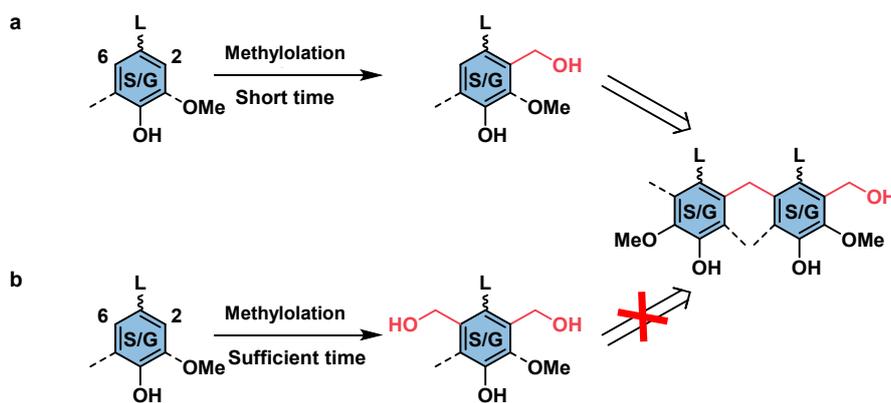


Figure S8. The effect of methylation on lignin crosslinking. (a) Short time methylation. (b) Sufficient time methylation.

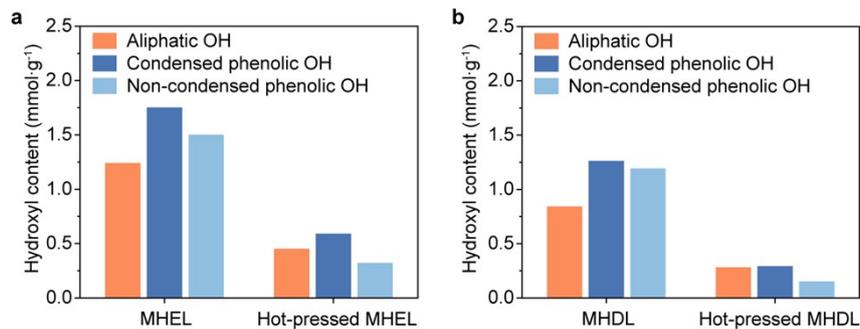


Figure S9. ³¹P NMR characterization of lignin before/after hot-pressing. (a) Hydroxyl contents of MHEL before/after hot-pressing. (b) Hydroxyl contents of MHDL before/after hot-pressing.

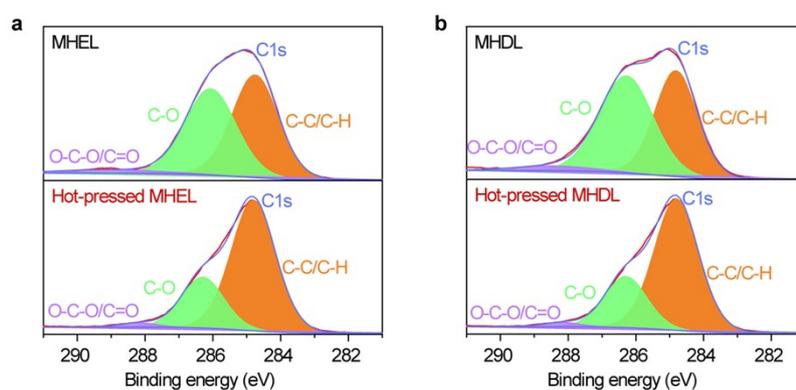
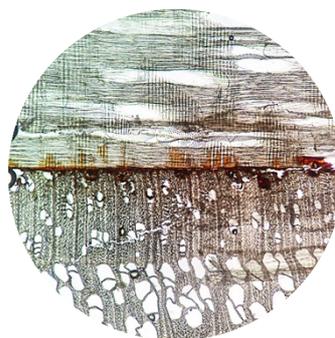


Figure S10. XPS characterization of lignin before/after hot-pressing. (a) C1s in XPS spectra of MHEL and hot-pressed MHEL. (b) C1s in XPS spectra of MHDL and hot-pressed MHDL.



Hot-pressed MHKL (190 °C)

Figure S11. Optical microscopy images of the glue lines in the plywood products.

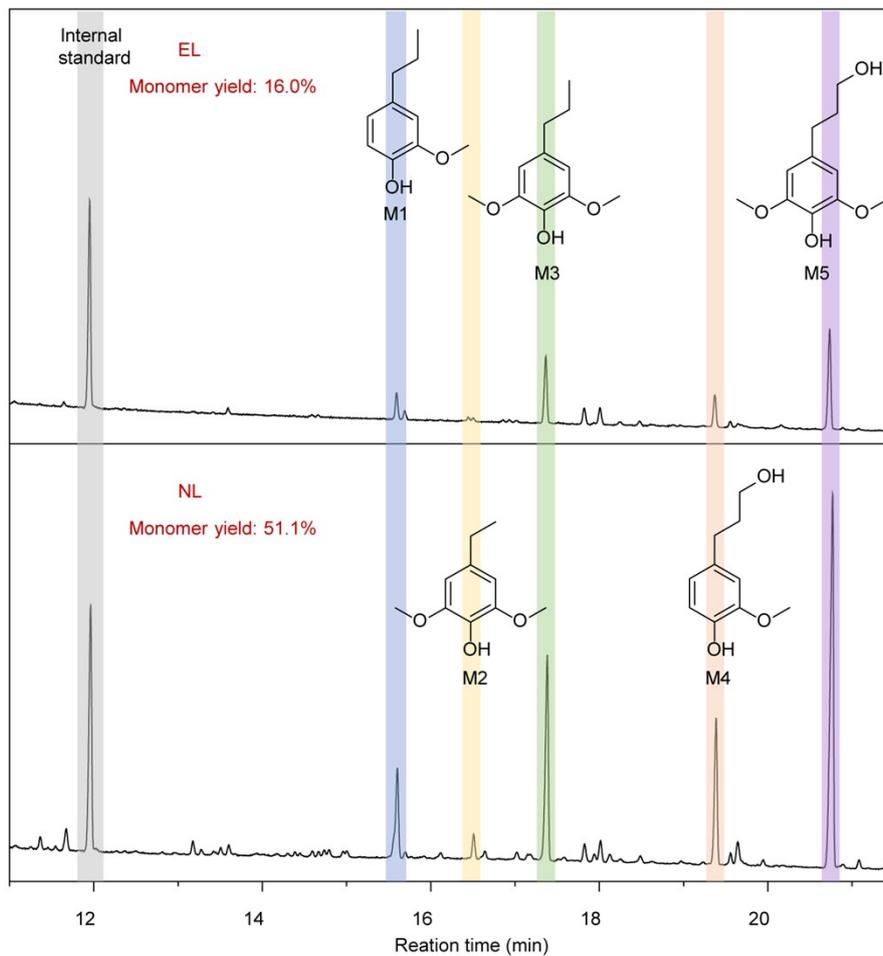


Figure S12. GC spectra of monomers from hydrogenolysis of lignin samples. (a) Ethanol lignin. (b) Native lignin in eucalyptus wood particles.

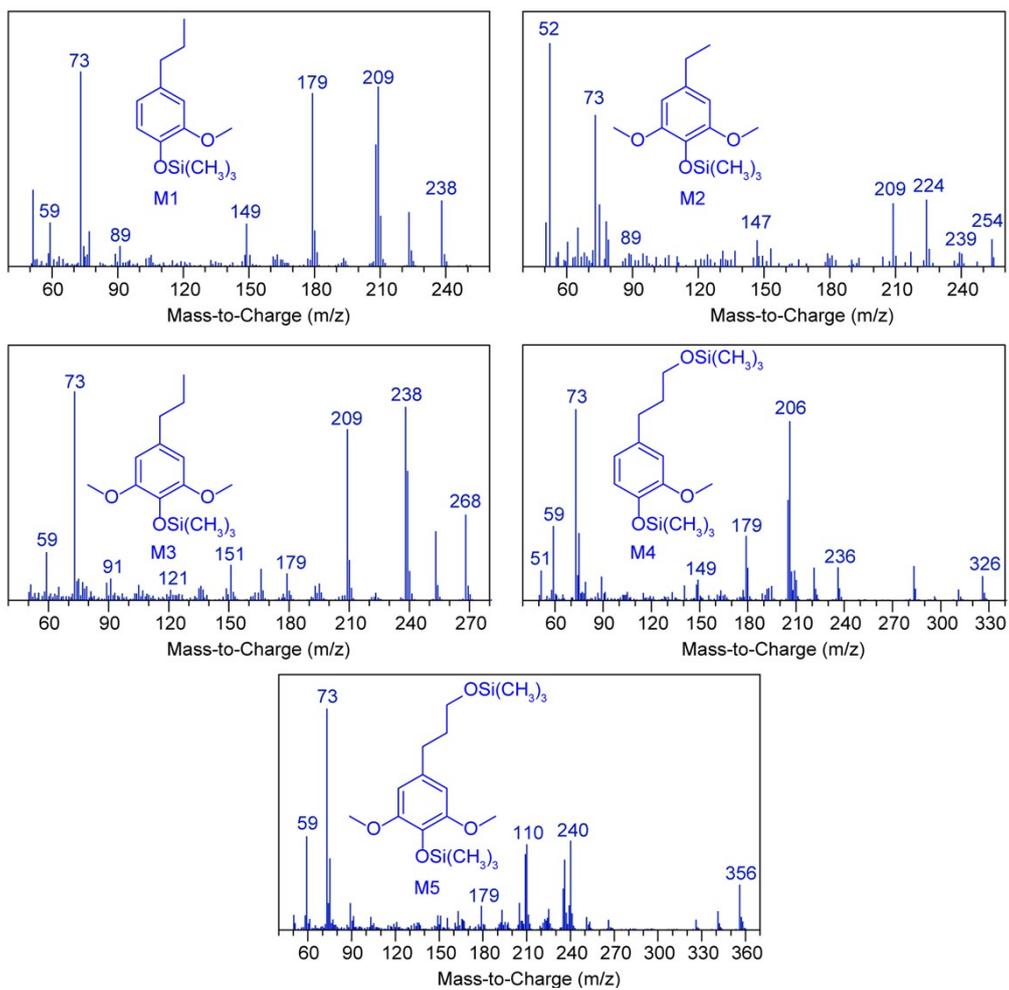


Figure S13. MS spectra of monomers from hydrodeoxygenation of lignin samples.

References

- 1 X. Meng, C. Crestini, H. Ben, N. Hao, Y. Pu, A. J. Ragauskas and D. S. Argyropoulos, *Nat. Protoc.*, 2019, **14**, 2627–2647.