

Supporting Information

Microwave-Assisted Organosolv Extraction for More Native-Like Lignin and Its Application as a Property-Enhancing Filler in a Light Processable Biobased Resin

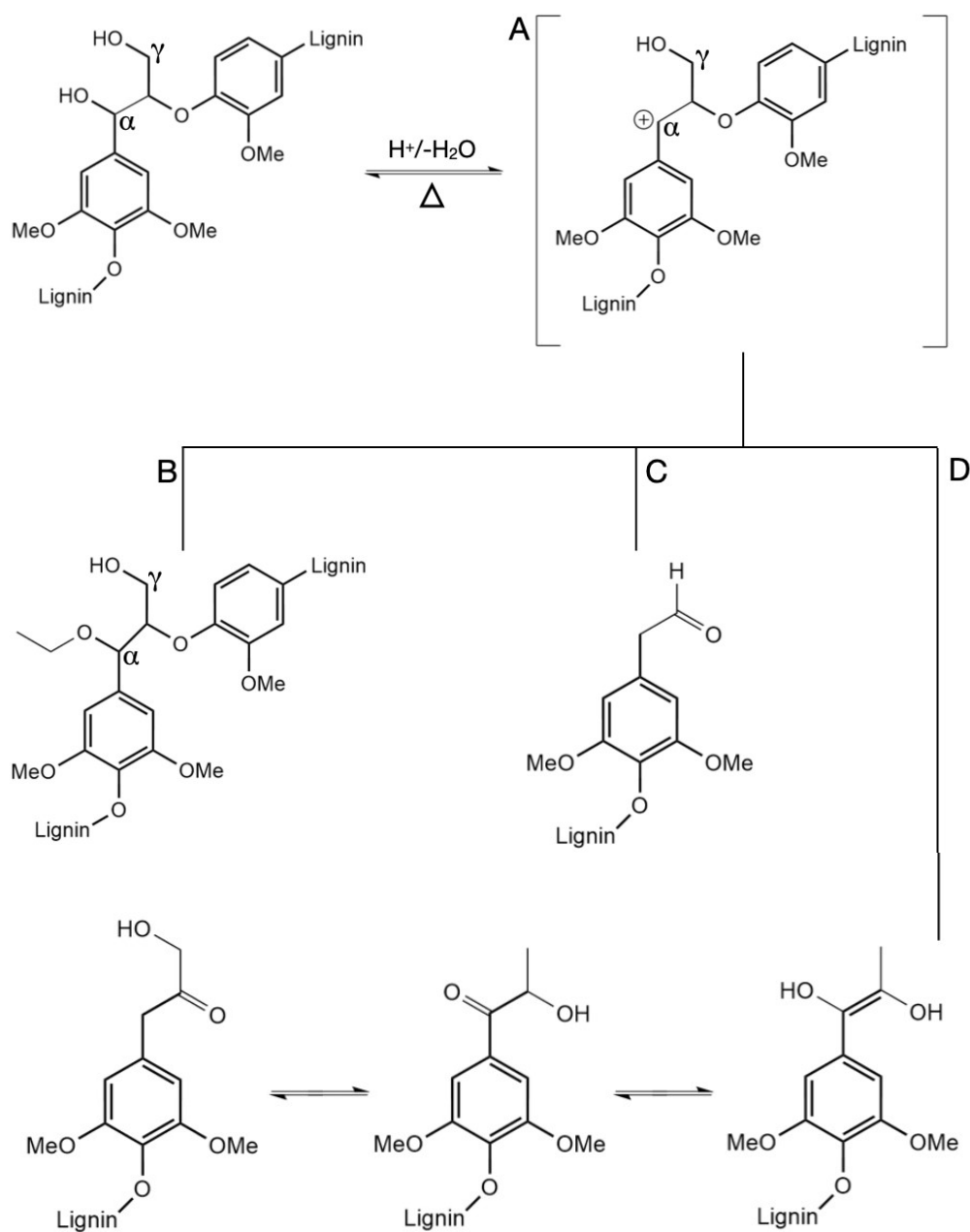
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This supporting information file contains 1 scheme, 5 tables, and 7 figures on 13 pages.

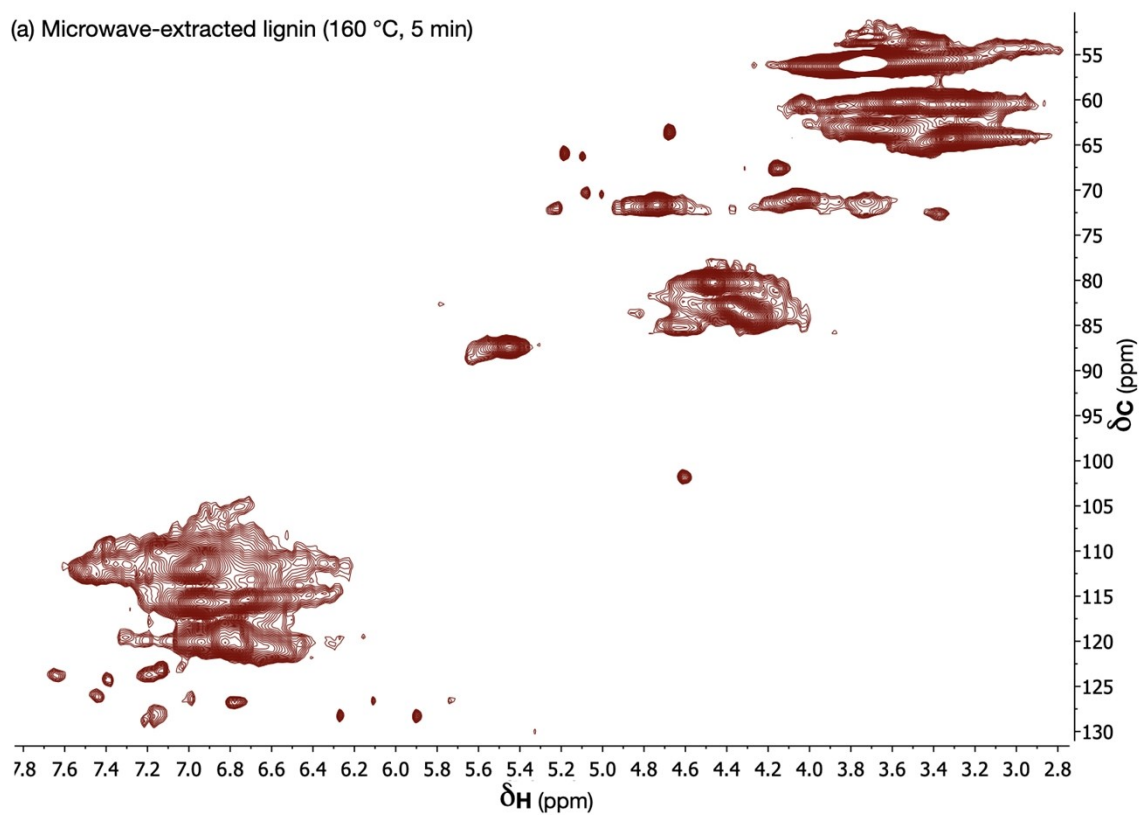


Scheme 1. Acid-catalyzed organosolv conditions can result to hydrolysis reactions that lead to (a) the formation of a reactive cationic intermediate that further undergo different reaction pathways, such as the formation of (b) benzylic ether (specifically α -ethoxylated β -O-4), (c) aldehydes that can further undergo condensation, and (d) Hibbert's ketones.¹⁻³

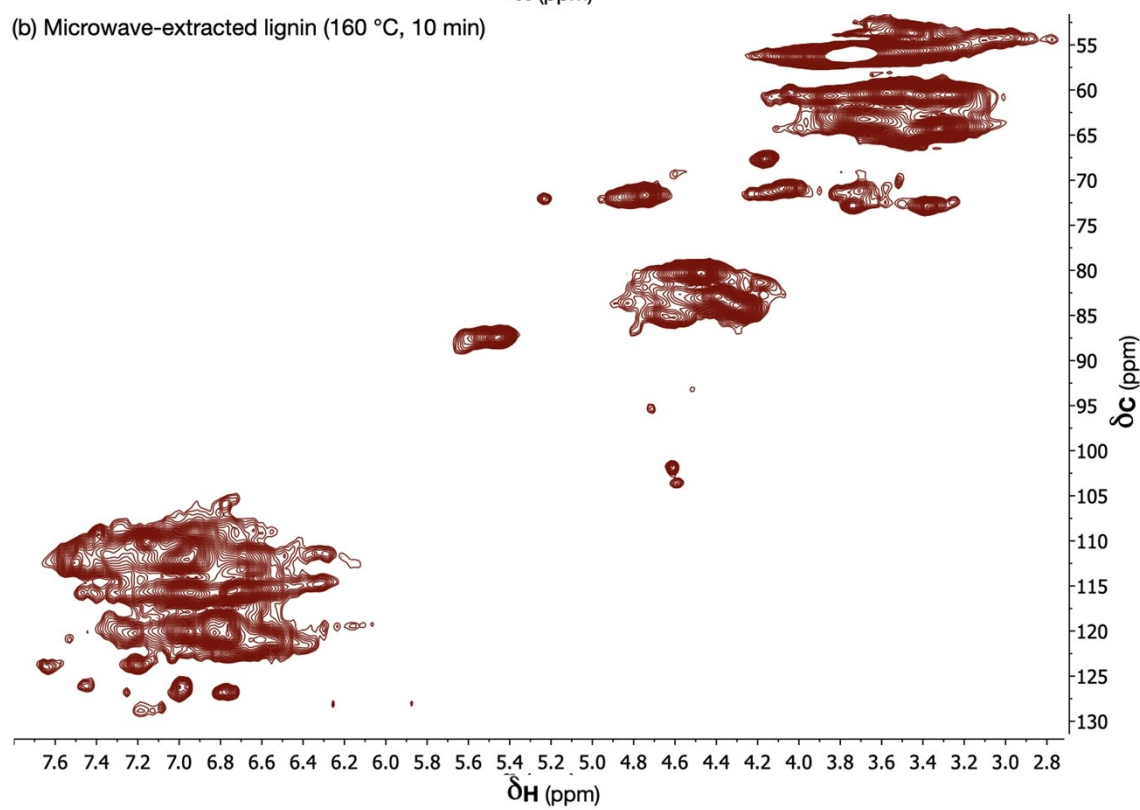
Table S1. Assignment of ^1H - ^{13}C correlation signals of substructures in extracted organosolv lignin from spruce (*Picea abies*) as detected by 2D HSQC NMR in DMSO- d_6 .^{4, 5}

	δ_{C} (ppm)	δ_{H} (ppm)	Description
$\beta\text{-O-}4_{\alpha}$	74.4-69.4	5.1-4.4	$\text{C}_{\alpha}/\text{H}_{\alpha}$ in α -hydroxylated $\beta\text{-O-}4$
$\beta'\text{-O-}4_{\alpha}$	81.4-77.2	4.73-4.0	$\text{C}_{\alpha}/\text{H}_{\alpha}$ in α -ethoxylated $\beta\text{-O-}4$
$\beta\text{-O-}4_{\beta}/\beta'\text{-O-}4_{\beta}$	85.9-81.2	4.6-3.9	$\text{C}_{\beta}/\text{H}_{\beta}$ in α -hydroxylated/ethoxylated $\beta\text{-O-}4$
$\beta\text{-O-}4_{\gamma}/\beta'\text{-O-}4_{\gamma}$	62.5-58.5	4.0-3.0	$\text{C}_{\gamma}/\text{H}_{\gamma}$ in α -hydroxylated/ethoxylated $\beta\text{-O-}4$
$\beta\text{-}5_{\alpha}$	91.0-83.2	5.8-5.0	$\text{C}_{\alpha}/\text{H}_{\alpha}$ in phenylcoumaran
$\beta\text{-}5_{\beta}$	54.6-51.1	3.9-3.1	$\text{C}_{\beta}/\text{H}_{\beta}$ in phenylcoumaran
$\beta\text{-}5_{\gamma}$	64.5-62.0	4.0-3.5	$\text{C}_{\gamma}/\text{H}_{\gamma}$ in phenylcoumaran
$\beta\text{-}\beta_{\alpha}$	88.6-83.9	4.7-4.4	$\text{C}_{\alpha}/\text{H}_{\alpha}$ in resinol structure
$\beta\text{-}\beta_{\beta}$	56.6-51.5	3.2-2.7	$\text{C}_{\beta}/\text{H}_{\beta}$ in resinol structure
$\beta\text{-}\beta_{\gamma}$	75.2-68.1	4.3-3.5	$\text{C}_{\gamma}/\text{H}_{\gamma}$ in resinol structure
HK_{γ}	69.3-65.8	4.3-4.0	$\text{C}_{\gamma}/\text{H}_{\gamma}$ in Hibbert's ketone
SB1_{α}	127.8-124.4	7.1-6.9	$\text{C}_{\alpha}/\text{H}_{\alpha}$ in $\beta\text{-}1$ -derived stilbene
SB5_{β}	122.7-117.8	7.5-7.1	$\text{C}_{\beta}/\text{H}_{\beta}$ in $\beta\text{-}5$ -derived stilbene
C_2	113.2-106.1	7.8-6.1	C_2/H_2 in guaiacyl units
C_5	117.8-113.7	7.2-6.5	C_5/H_5 in guaiacyl units
C_6	122.0-118.0	7.1-6.6	C_6/H_6 in guaiacyl units

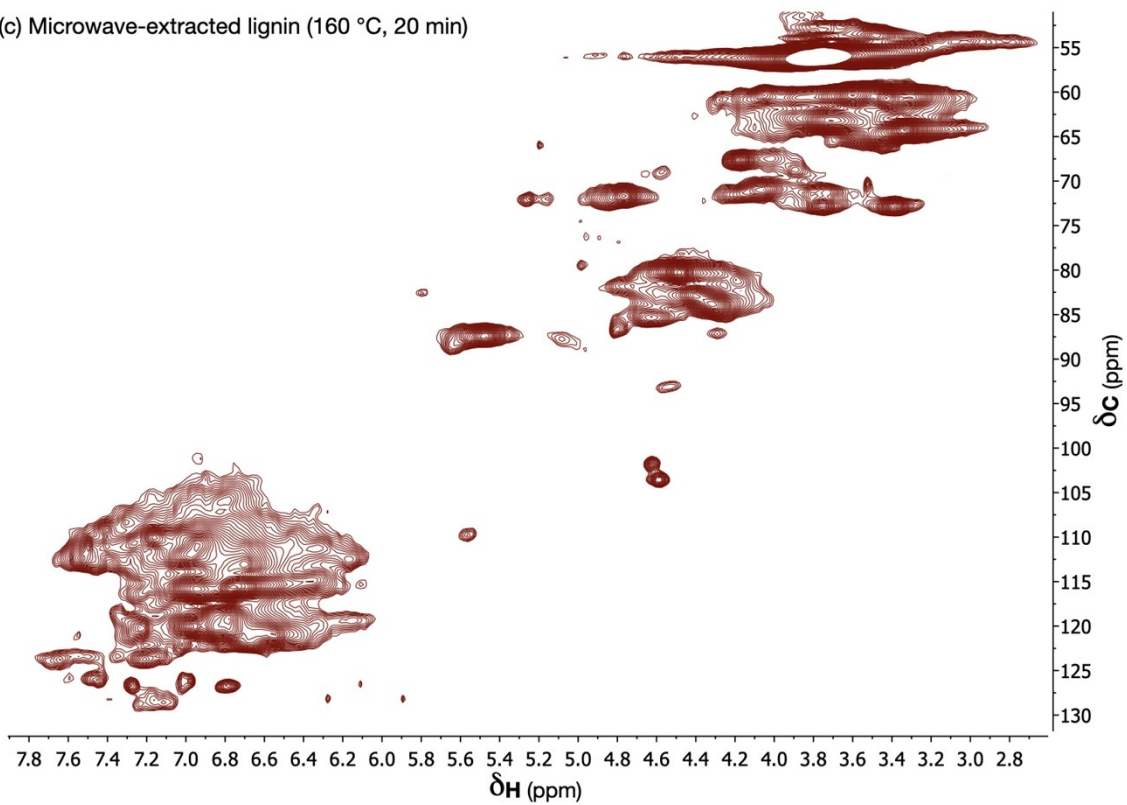
(a) Microwave-extracted lignin (160 °C, 5 min)



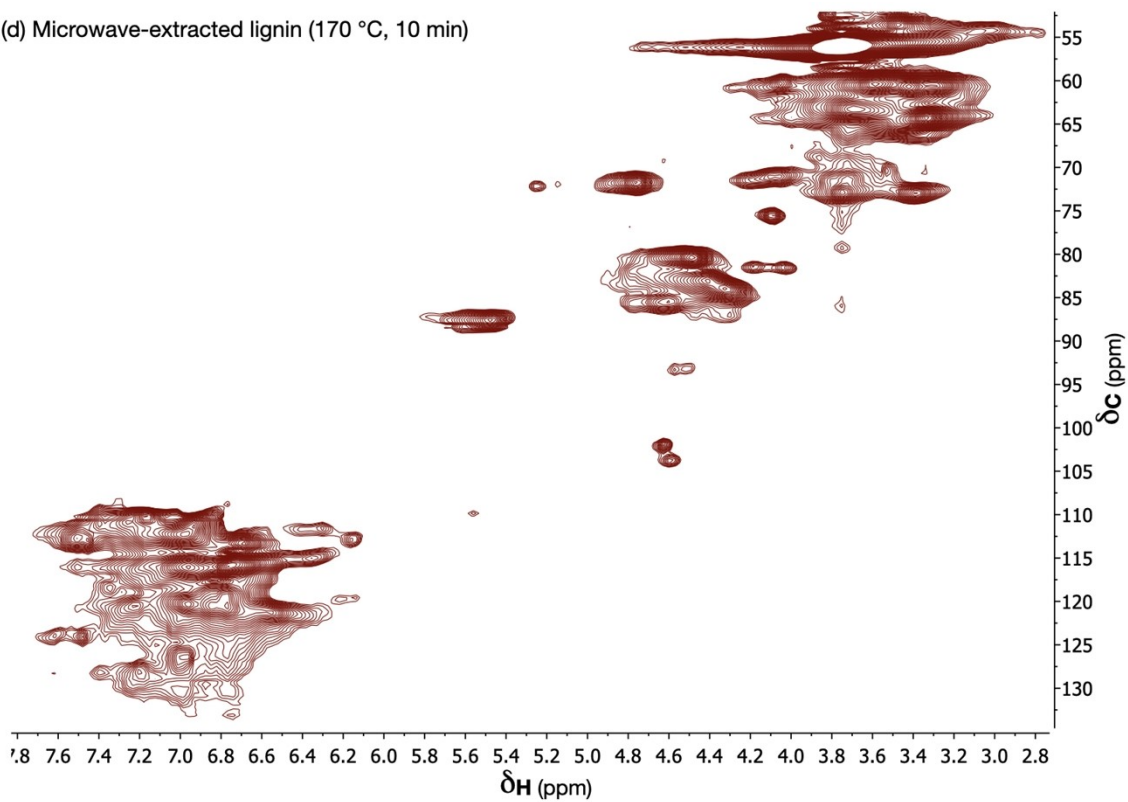
(b) Microwave-extracted lignin (160 °C, 10 min)



(c) Microwave-extracted lignin (160 °C, 20 min)



(d) Microwave-extracted lignin (170 °C, 10 min)



(e) Microwave-extracted lignin (190 °C, 10 min)

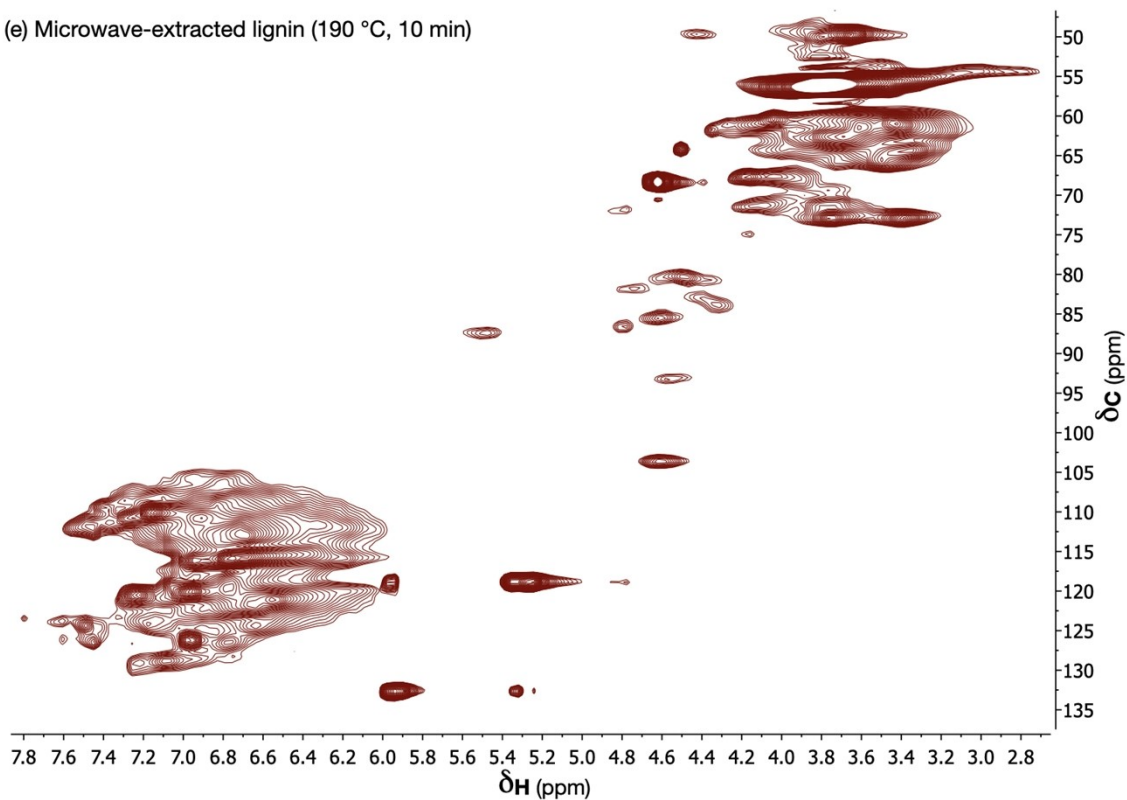


Figure S1. Full 2D HSQC spectra of microwave-extracted lignin at 160 °C from 5-20 min (a-c) and for 10 min at 170 °C (d) and 190 °C (e).

Table S2. Semi-quantification of major lignin interunit linkages (in % per 100 Ar) via 2D HSQC of microwave-extracted lignin at 170 and 190 °C for 10 min.

	170 °C	190 °C
β -O-4 $_{\alpha}$	12.3	4.7
β' -O-4 $_{\alpha}$	18.5	10.4
Sum of β-O-4$_{\alpha}$ units	30.8	15.1
β -5 $_{\alpha}$	15.4	6.3
β - β $_{\alpha}$	7.7	2.7
HK $_{\gamma}$	1.5	3.7
SB1 $_{\alpha}$	4.6	7.8
SB5 $_{\beta}$	10.8	10.3

Table S3. Monosaccharide composition (%) of the fibre byproduct from the microwave- (10 min) and cyclic-extraction methods. Carbohydrate analysis of the fibres from microwave-extraction was carried out using high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD). The sample was diluted to 1.5 mL by addition of 1375 μ L H₂O and heated to 100 °C for 3 h in a thermoblock. The samples were cooled to room temperature and diluted 10 times with H₂O. The diluted sample were filtered through 0.2 μ m Nylon filter and injected into an ICS3000 system (Dionex, Sunnyvale, CA) using a Dionex Carbopac PA20 column at 30 °C. Samples were compared to standards with concentrations 0.1, 0.05, 0.02, 0.01 and 0.005 mg/mL of arabinose, galactose, glucose, xylose and mannose. Data analyses were performed using Chameleon 7.0 software.

	Microwave-extraction	Cyclic-extraction*
Arabinose	0.2 \pm 0.1	0
Galactose	0.4 \pm 0.1	0
Glucose	86.5 \pm 0.1	71.4 \pm 1.1
Xylose	6.9 \pm 0.1	2.5 \pm 0.1
Mannose	6.0 \pm 0.3	3.0 \pm 0.2
Total carbohydrate content	86.9 \pm 7.9	76.9 \pm 0.8

*Data obtained from previously published results.⁵

Table S4. Integration regions for lignin in a ³¹P NMR spectrum.⁶

Functional group	δ_p (ppm)
Aliphatic OH	145.4-150.0
Phenolic OH	137.6-144.0
C5-substituted	140.0-144.5
4-O-5	142.3-142.39
B-5	143.5-143.59
Guaiacyl	139.0-140.2
<p>-Hydroxyphenyl</p>	137.8-137.89
Carboxylic acid OH	133.6-136.0

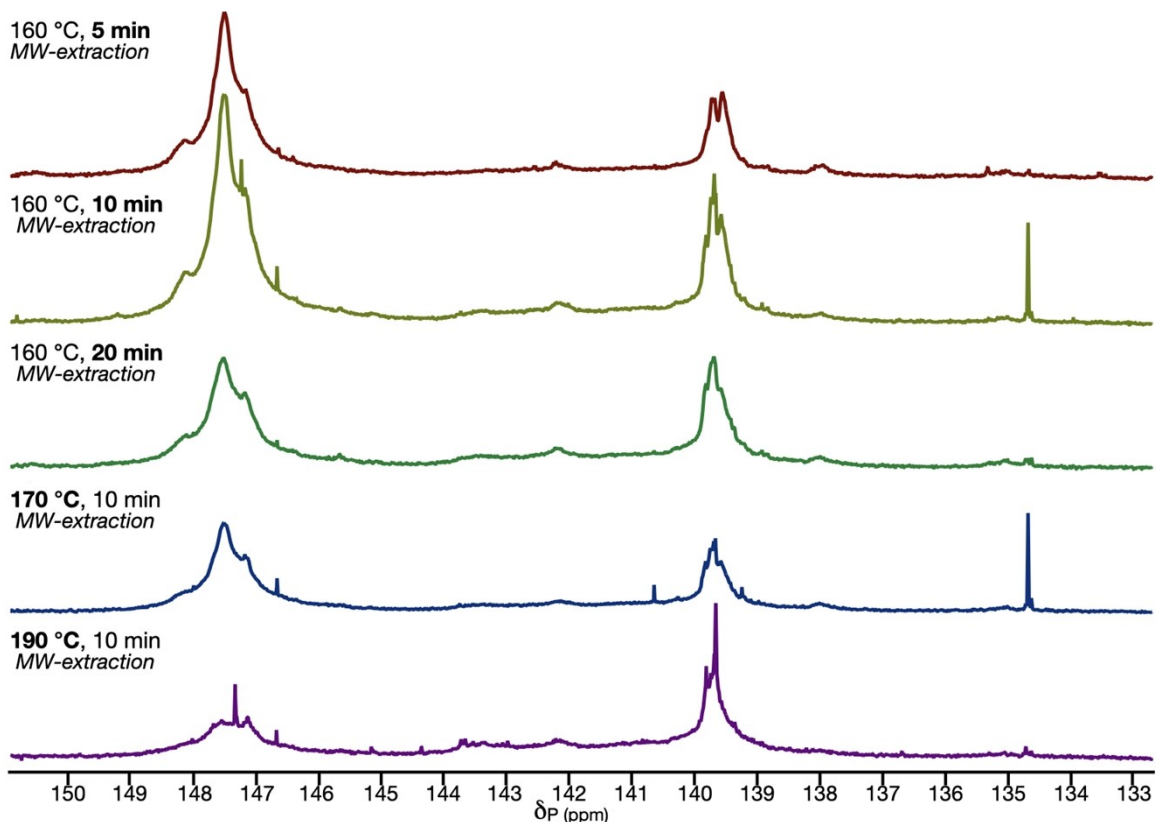


Figure S2. Quantitative ^{31}P NMR spectra of the microwave-extracted lignin at varying process conditions (160 °C from 5-20 min, and 170-190 °C at 10 min), derivatized with TMDP and using NHND as internal standard.

Table S5. Contents of different hydroxyl groups (mmol OH per g lignin) in microwave-extracted lignin at 170 and 190 °C for 10 min, determined by ^{31}P NMR.

Functional group	170 °C	190 °C
Aliphatic OH	2.8	1.3
Phenolic OH	2.3	2.7
C5-substituted	1.1	1.4
4-O-5	0.02	0.03
B-5	0.02	0.03
Guaiacyl	1.1	1.2
<p>-Hydroxyphenyl</p>	0.01	0.01
Carboxylic acid OH	0.09	0.5

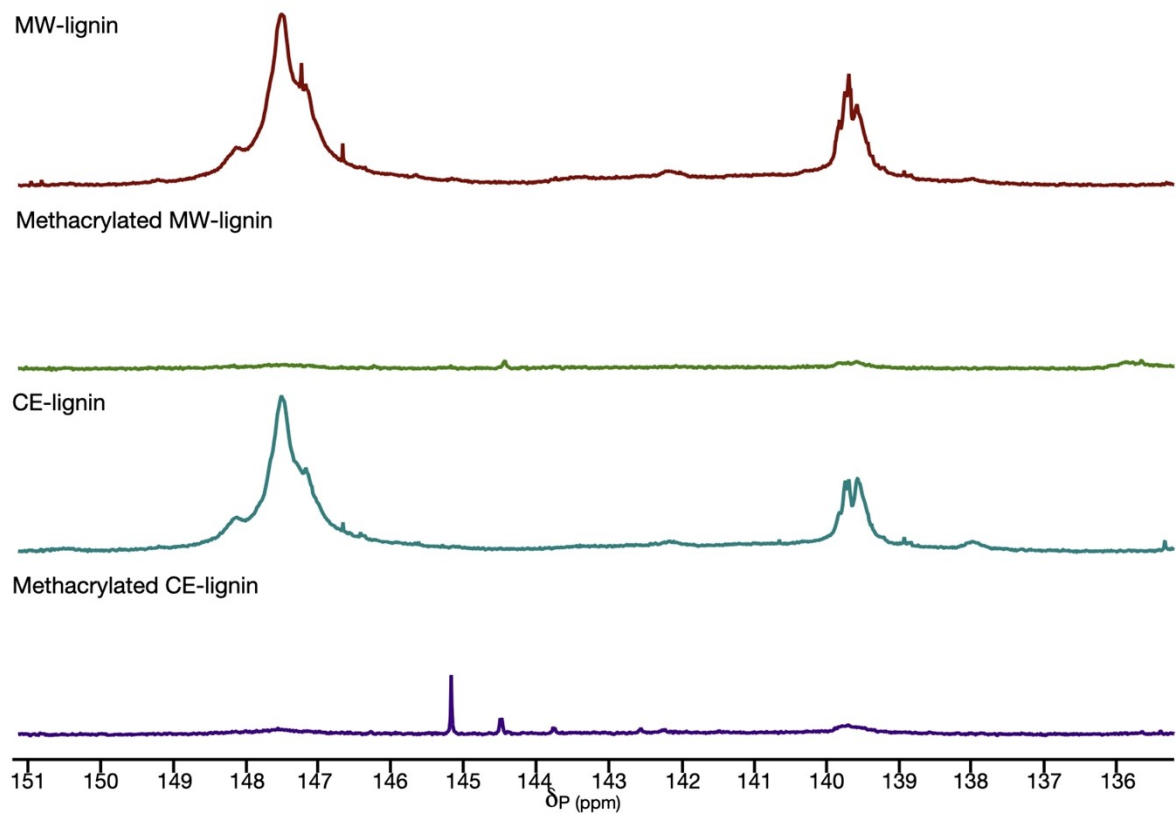


Figure S3. Quantitative ^{31}P NMR spectra of the methacrylated microwave (MW)- and cyclic-extracted (CE) lignin in comparison with the spectra of their non-methacrylated counterparts.

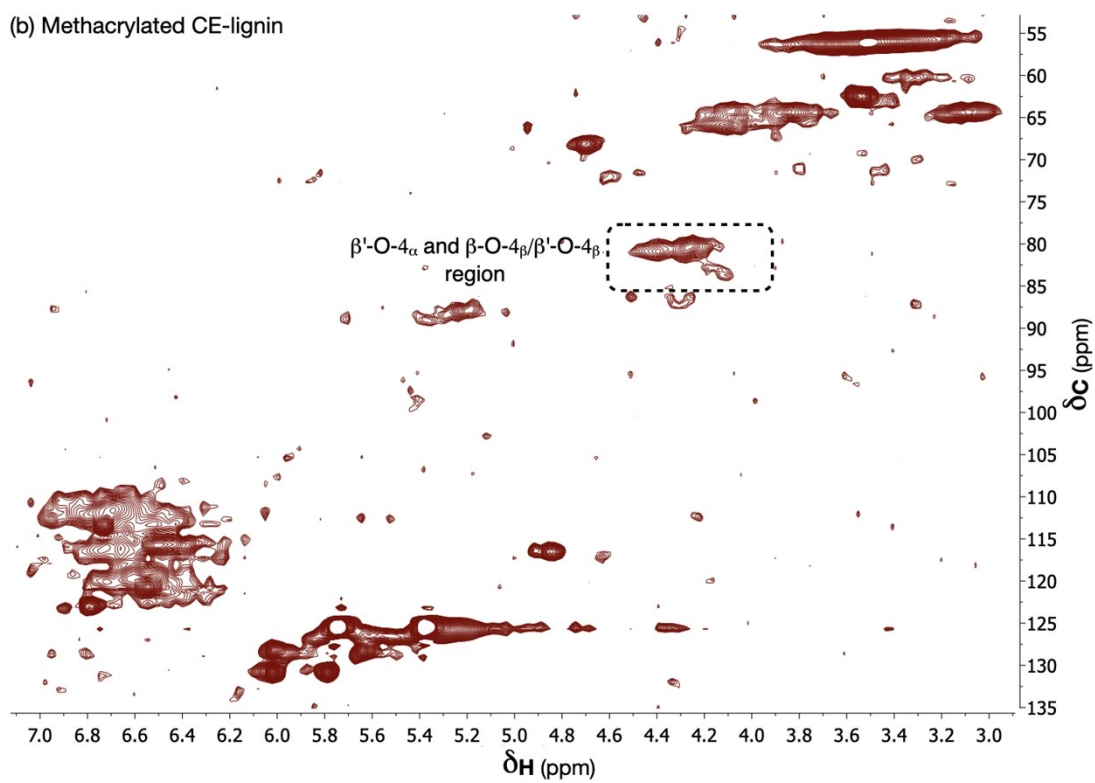
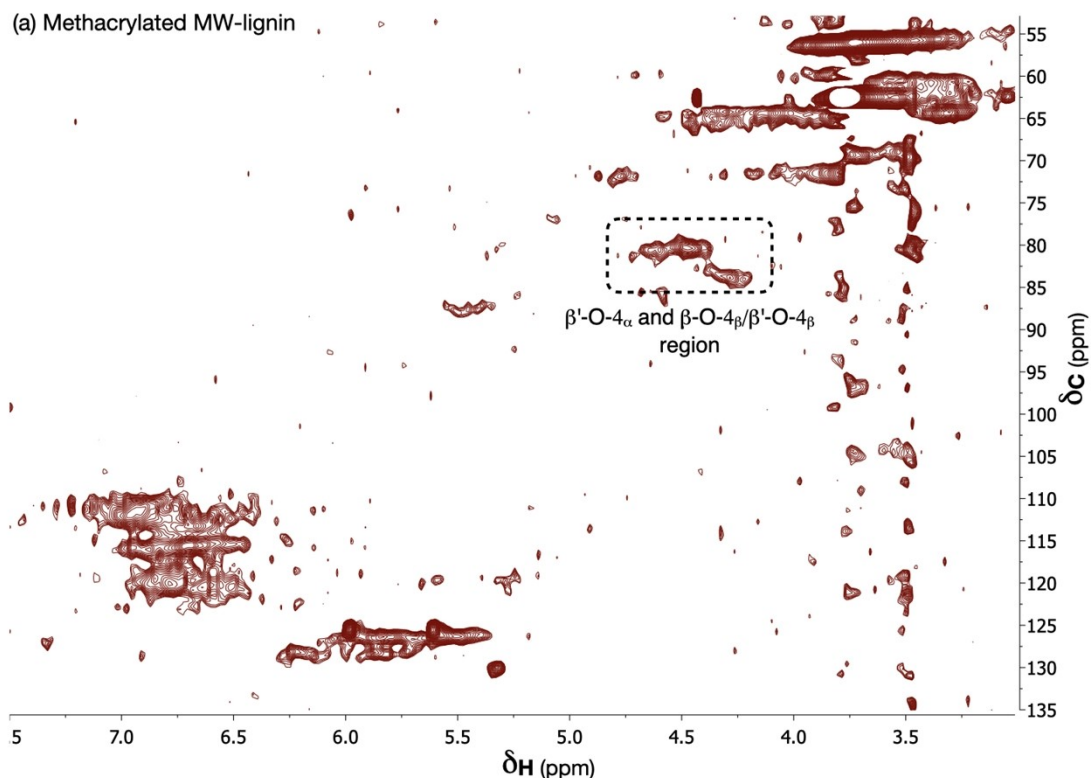


Figure S4. 2D HSQC NMR spectra of the methacrylated (a) microwave (MW)- and (b) cyclic-extracted (CE) lignin.

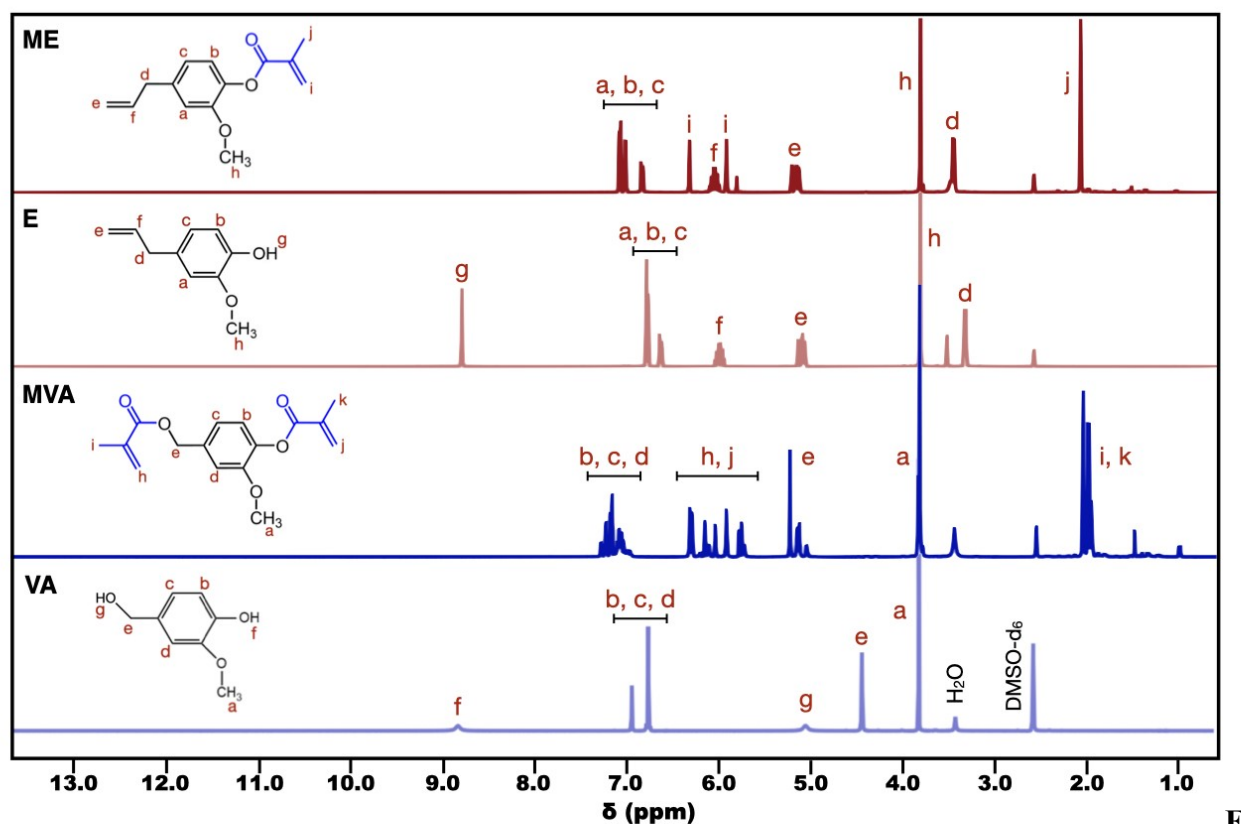


figure S5. ¹H NMR spectra of the biobased building blocks – eugenol (E) and vanillyl alcohol (VA), and their methacrylated derivatives – methacrylated eugenol (ME) and methacrylated vanillyl alcohol (MVA), in DMSO-d₆. Methacrylation is confirmed by the disappearance of peaks corresponding to hydroxyl groups (8.7 ppm for eugenol and 5.0 and 8.8 ppm for vanillyl alcohol), which indicates the consumption of said groups via acylation. The appearance of peaks indicating the presence of methyl (2.0 ppm for ME, and 1.9-2.0 ppm for MVA) and vinyl units (5.8 and 6.3 ppm for ME, and 5.7-6.3 ppm for MVA) demonstrate successful introduction of methacrylate moieties.

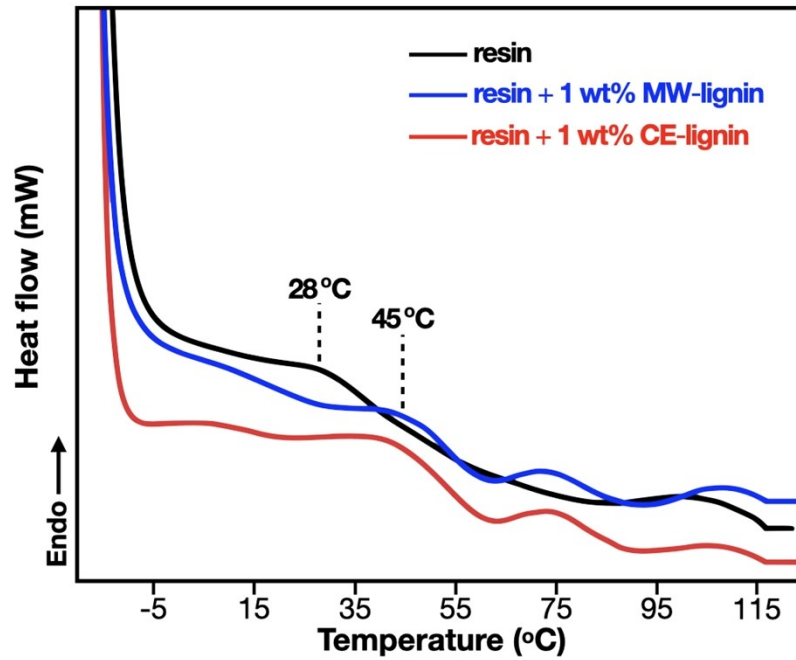


Figure S6. DSC DTG curves of the digital light processing (DLP) 3D printed thermosets composed of 80:20 (wt/wt) methacrylated eugenol:methacrylated vanillyl alcohol, and 1 wt% of microwave (MW)- or cyclic-extracted (CE) lignin.

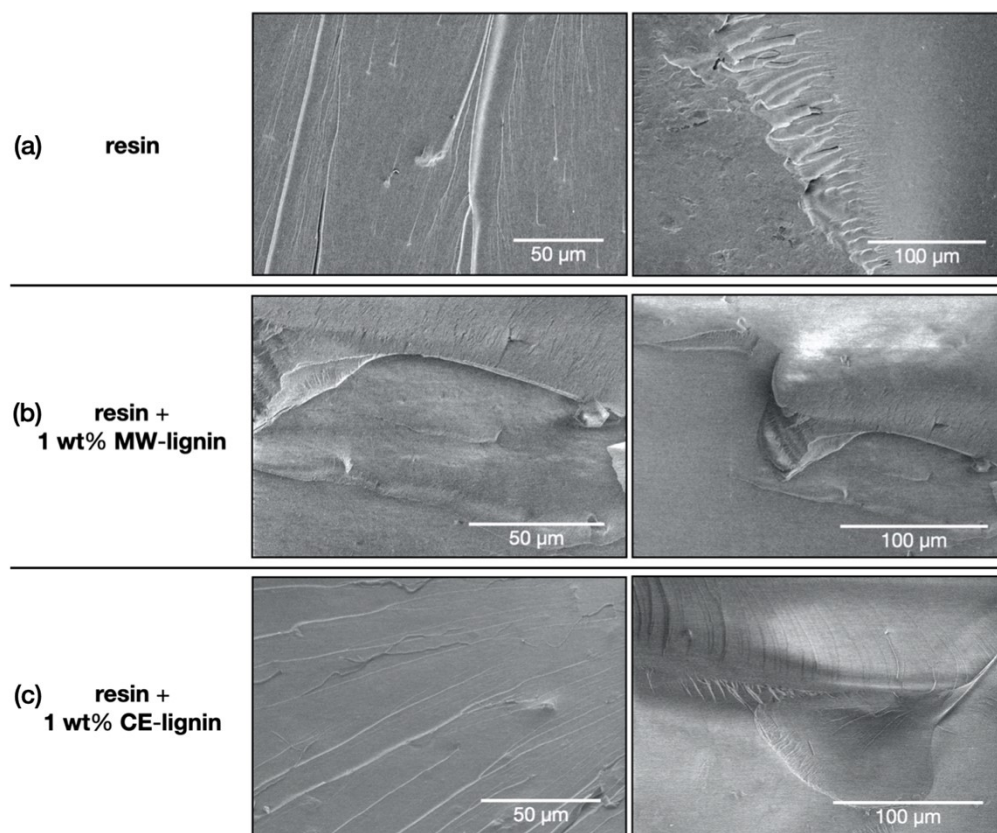


Figure S7. SEM micrographs of digital light processing (DLP) 3D printed (a) resin composed of 80:20 (wt/wt) methacrylated eugenol:methacrylated vanillyl alcohol, and the same resin with 1 wt% of (b) microwave (MW)-extracted lignin and (c) cyclic-extracted (CE) lignin.

References:

1. Lancefield, C. S.; Panovic, I.; Deuss, P. J.; Barta, K.; Westwood, N. J., Pre-treatment of lignocellulosic feedstocks using biorenewable alcohols: towards complete biomass valorisation. *Green Chem.* **2017**, *19* (1), 202-214.
2. Meyer, J. R.; Li, H. Y.; Zhang, J. L.; Foston, M. B., Kinetics of secondary reactions affecting the organosolv lignin structure. *ChemSusChem* **2020**, *13* (17), 4557-4566.
3. Lan, W.; Luterbacher, J. S., Preventing lignin condensation to facilitate aromatic monomer production. *Chimia* **2019**, *73* (7-8), 591-598.
4. Zijlstra, D. S.; Lahive, C.; Analbers, C. A.; Figueiredo, M. B.; Wang, Z. W.; Lancefield, C.; Deuss, P. J., Mild organosolv lignin extraction with alcohols: The importance of benzylic alkoxylation. *ACS Sustain. Chem. Eng.* **2020**, *8* (13), 5119-5131.
5. Karlsson, M.; Giummarella, N.; Linden, P. A.; Lawoko, M., Toward a consolidated lignin biorefinery: preserving the lignin structure through additive-free protection strategies. *ChemSusChem* **2020**, *13* (17), 4666-4677.
6. Meng, X. Z.; Crestini, C.; Ben, H. X.; Hao, N. J.; Pu, Y. Q.; Ragauskas, A. J.; Argyropoulos, D. S., Determination of hydroxyl groups in biorefinery resources via quantitative ^{31}P NMR spectroscopy. *Nat. Protoc.* **2019**, *14* (9), 2627-2647.