

Unraveling Lignin Extraction: Molecular Dynamics Insights into Effective Biomass Valorization using p-Toluenesulfonic Acid/Solvents System

Jiayi Zheng,^a Liheng Chen,^{*,a,b} Zhichang Huang,^a and Xueqing Qiu,^{*,a}

¹ Guangdong Provincial Key Laboratory of Plant Resources Biorefinery, School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China.

² Jieyang Branch of Chemistry and Chemical Engineering Guangdong Laboratory, Jieyang 515200, China.

***Corresponding authors**

Email: lihengchen@gdut.edu.cn; cexqiu@scut.edu.cn.

Table of Contents

Table of Contents	2
Supplementary Figures	3
Figure S1	3
Figure S2	4
Figure S3	5
Figure S4	6
Figure S5	7
Figure S6	8
Supplementary Tables	9
Table S1. Concentration of compositions in the pretreatment liquor from the pine pretreated at different temperature.	9
Table S2. Quantitative information for subunits and inter-unit linkages of lignin extracted with different biomass.	10
Table S3. Quantitative information for subunits and inter-unit linkages of lignin extracted at different temperature.	11
Table S5. The color evaluation of extracted lignin.....	13
Table S6. SPF values of the pure creams blended with different amounts of lignin.....	15

Supplementary Figures

Figure S1

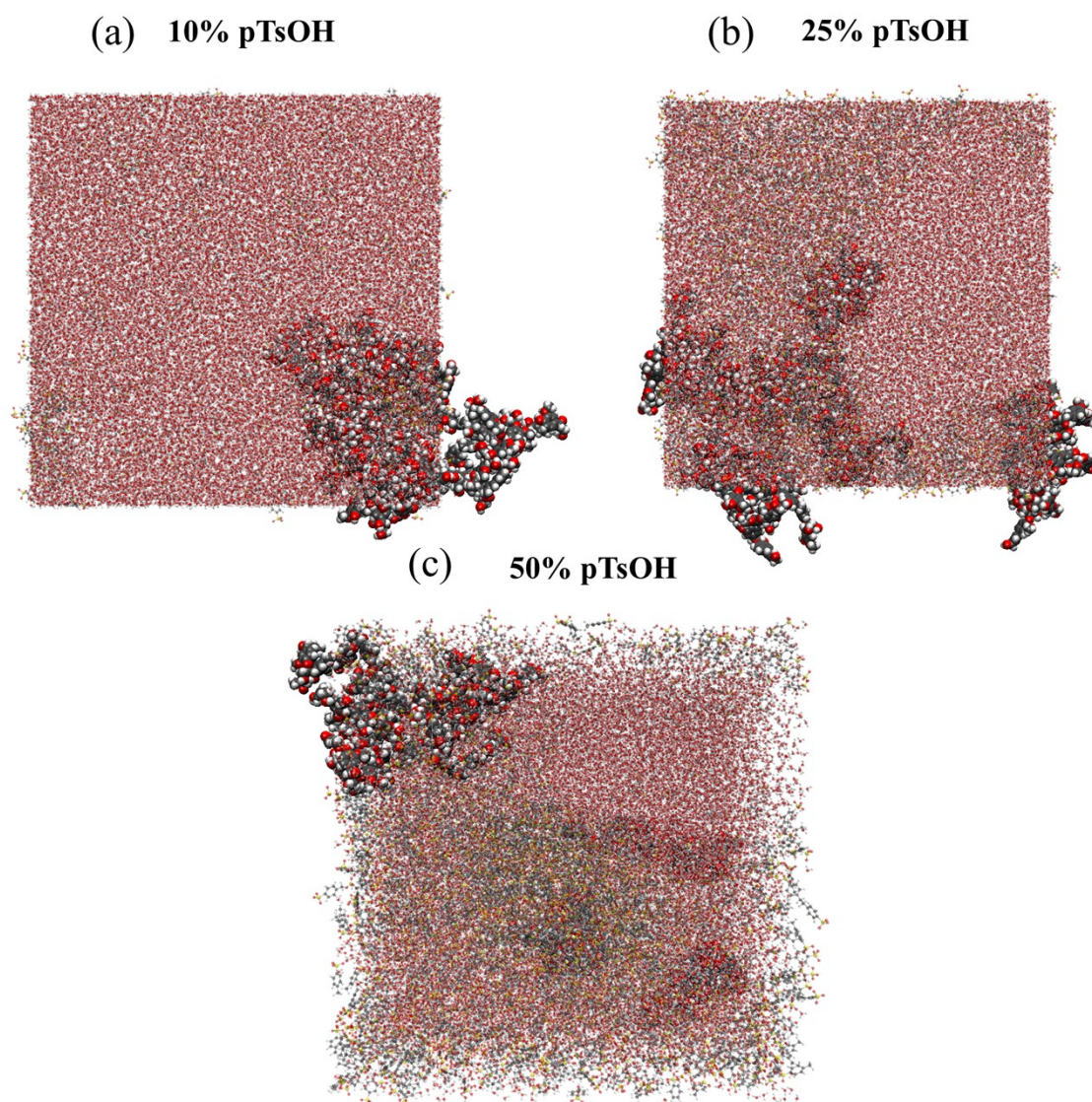


Figure S1. Snapshots after 100 ns molecular dynamics simulation of five lignin molecule clusters dissolving in the hydrotropic aqueous solution with different pTsOH content at 110 °C (lignin: VWD mode, pTsOH and water: CPK mode).

Figure S2

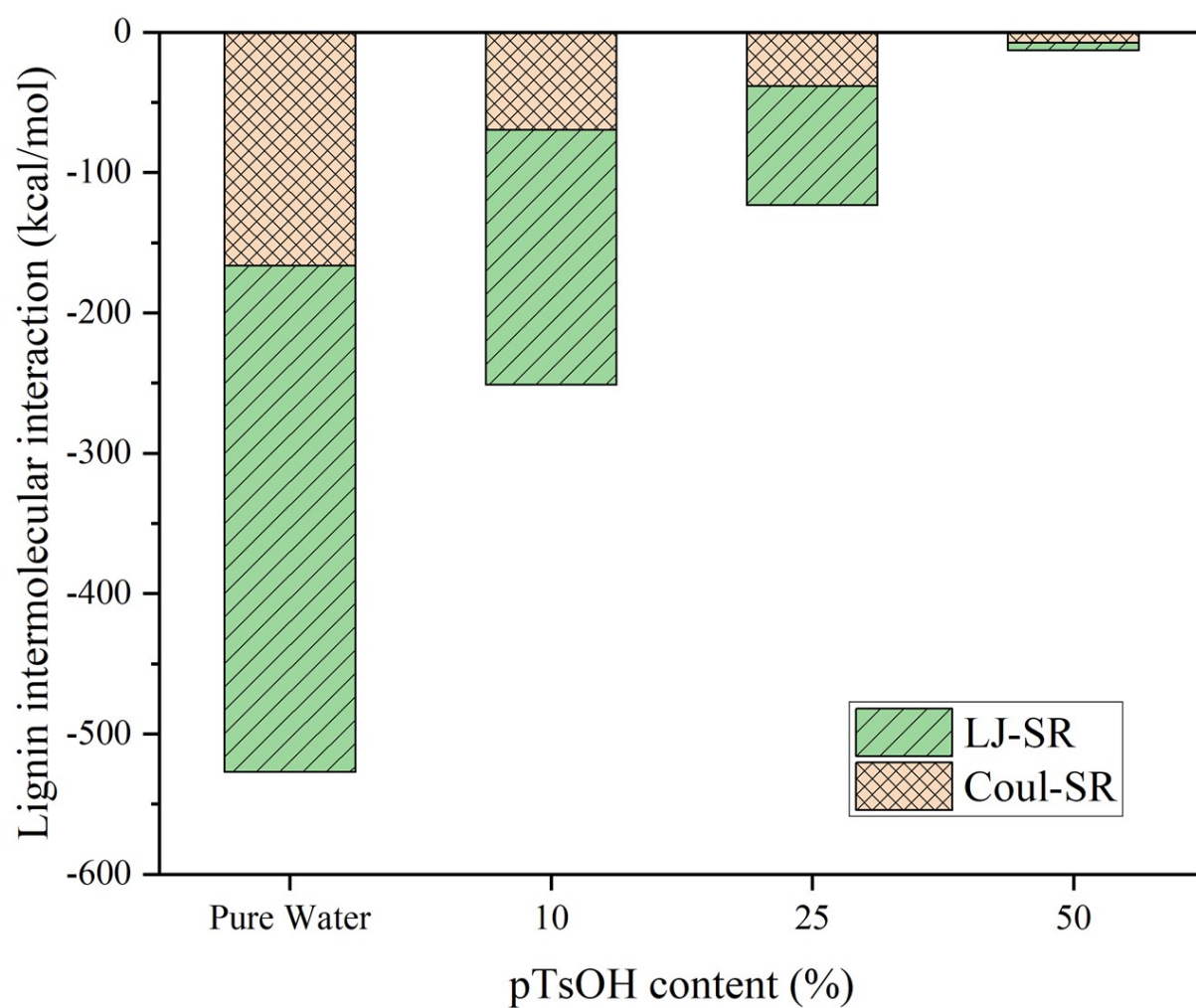


Figure S2. Intermolecular interaction of lignin dissolved in aqueous hydrotropic acid solution with different pTsOH contents.

Figure S3

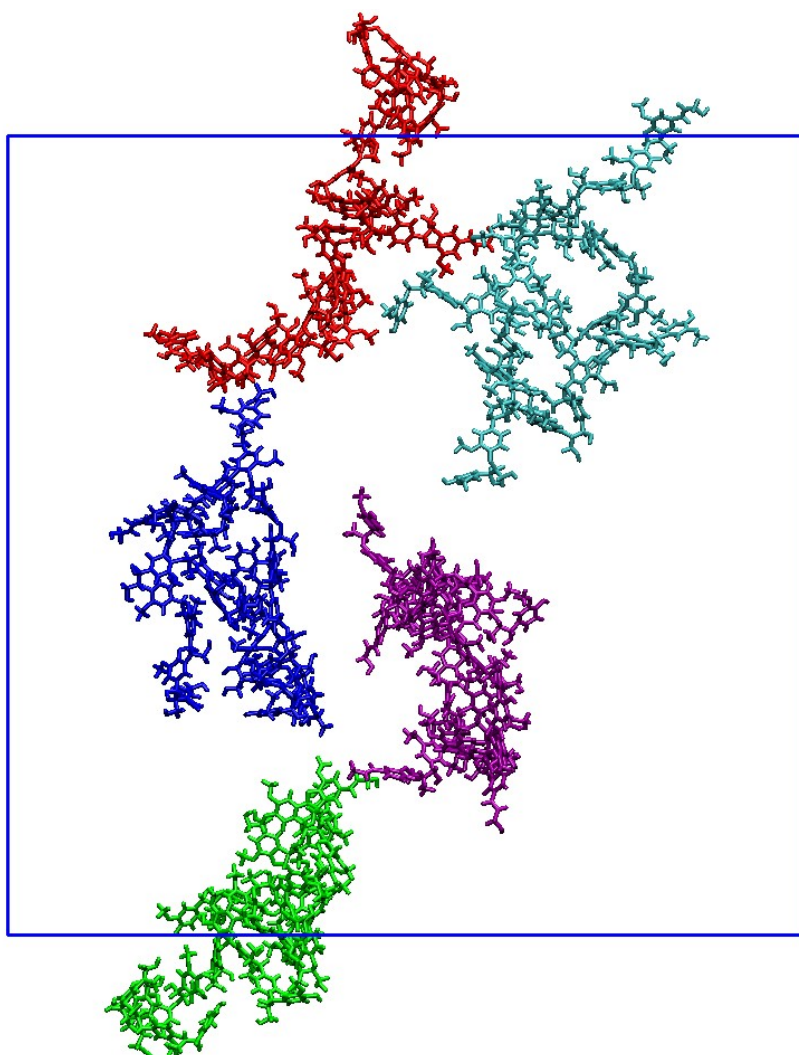


Figure S3. Snapshots after 100 ns molecular dynamics simulation of five lignin molecule clusters dissolving in 70% butanediol aqueous solution mixed with 10% p-toluenesulfonic acid at 110 °C.

Figure S4

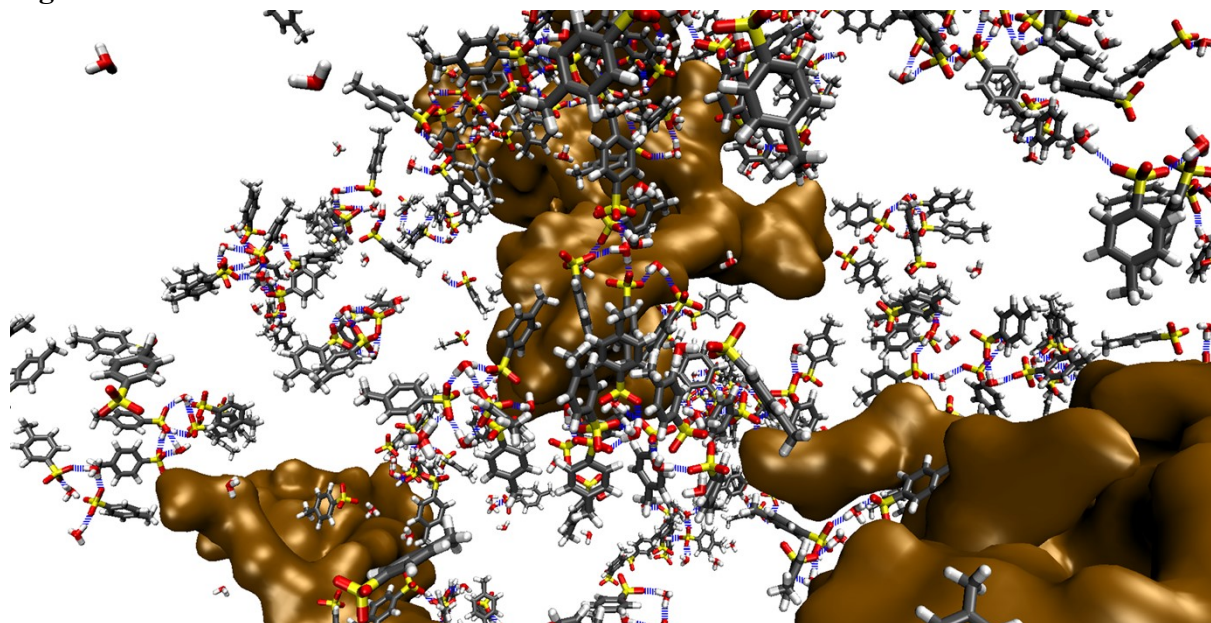


Figure S4. Snapshots of interaction between pTsOH and lignin after 100 ns molecular dynamics simulation of five lignin molecule clusters dissolving in 70% butanediol aqueous solution mixed with 10% p-toluenesulfonic acid at 110 °C (pTsOH, Licorice model, C-gray, H-white, O-red, S-yellow; lignin, QuickSurf model).

Figure S5

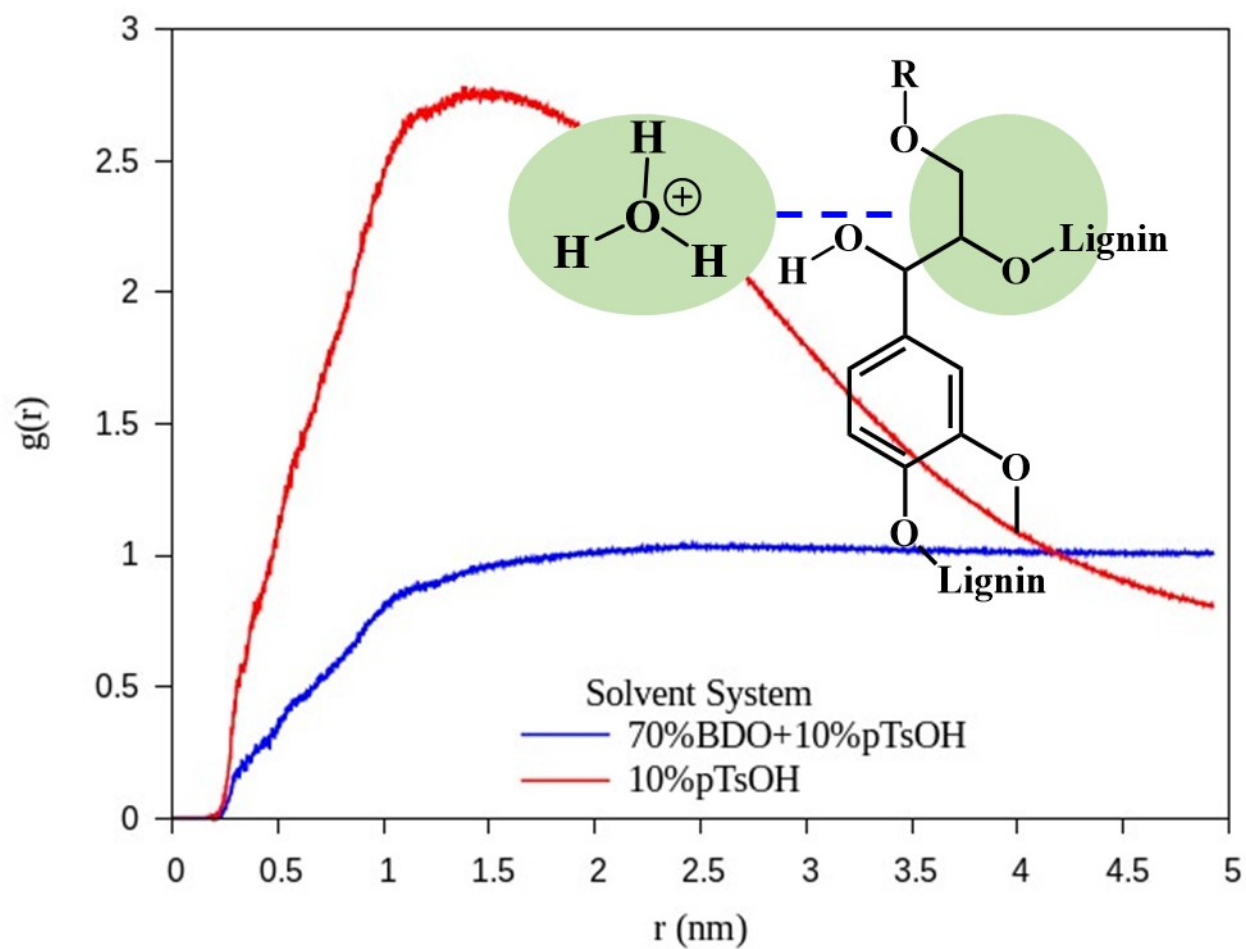


Figure S5. Radial distribution function (RDF) of hydronium with β -O-4 of lignin, respectively, in different solvent systems.

Figure S6

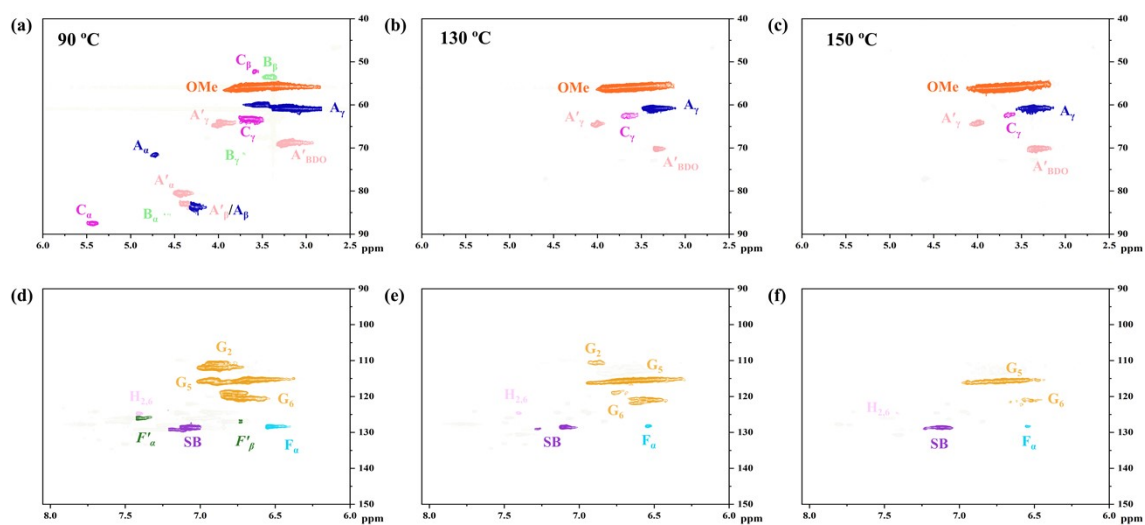


Figure S6. HSQC NMR spectra for the (a-c) side chain regions and (d-f) aromatic regions of lignin extracted from pine 70% BDO aqueous solution with 10% pTsOH for 4 h at different temperature.

Supplementary Tables

Table S1. Concentration of compositions in the pretreatment liquor from the pine pretreated at 70% BDO aqueous solution with 10% pTsOH for 4 h at different temperature.

Temperature (°C)	5-HMF (g/L)	Furfural (g/L)	Xylose and Mannose (g/L)	Glucose (g/L)	Arabinose (g/L)
110	0.0	0.2	4.3	0.5	2.9
130	1.7	3.3	2.7	3.1	0.8
150	1.8	2.2	0.0	0.0	2.3

Table S2. Quantitative information for subunits and inter-unit linkages of lignin treated in 70% BDO aqueous solution with 10% pTsoH at 110 °C for 4 h with different biomass.

Lignin units, linkages	L _{Wheat straw}	L _{Eucalyptus}	L _{Pine}
Lignin units (% C ₉ unit)			
G	61.2	30.6	96.1
H	6.2	ND ^a	3.9
S	30.0	66.1	ND
S'	2.6	3.3	ND
F	ND	ND	11.7
F'	ND	ND	1.7
SB	ND	ND	28.2
Linkages (% C ₉ unit)			
β-O-4	2.3	12.0	7.3
β-O-4'	25.0	30.9	30.8
β-5	2.0	3.9	10.1
β-β	2.4	7.3	3.5
HK	65.1	87.9	1.7

^aND, not detected

Table S3. Quantitative information for subunits and inter-unit linkages of lignin from the pine pretreated by 70% BDO aqueous solution with 10% pTsOH for 4 h at different temperature.









Lignin units, linkages	MWL-P	Samples			
		L ₉₀	L ₁₁₀	L ₁₃₀	L ₁₅₀
Lignin units (% C ₉ unit)					
G	97.9	96.4	96.1	97.6	97.8
H	2.1	3.6	3.9	2.4	2.2
F	ND ^a	19.2	11.7	3.7	3.4
F'	ND	6.6	1.7	ND	ND
SB	ND	65.7	28.2	41.7	55.0
Linkages (% C ₉ unit)					
β-O-4	40.1	4.6	7.3	ND	ND
β-O-4'	ND	32.8	30.8	ND	ND
β-5	13.7	9.7	10.1	ND	ND
β-β	3.3	2.4	3.5	ND	ND
HK	ND	0.0	1.7	ND	ND

^a ND, not detected

Table S4. Quantification of hydroxyl groups (mmol/g) of lignins from the pine pretreated by 70% BDO aqueous solution with 10% pTsOH for 4 h at different temperature.

	chemical shift (ppm)	Temperature (°C)			
		90	110	130	150
Aliphatic OH	150.0–145.5	3.47	3.51	1.52	0.92
Condensed-OH	144.5–143.2	0.07	0.11	0.23	0.22
	142.2-141.2	0.10	0.12	0.24	0.26
G-OH	141.0-138.4	0.76	0.78	1.20	1.18
H-OH	138.4-137.2	0.14	0.10	0.13	0.18
tricin	137.2-136.5	0.03	0.02	0.03	0.05
carboxylic OH	136.5-133.3	0.61	0.38	0.37	0.62
Total Phenolic OH	144.5-137.2	1.07	1.11	1.80	1.85
Total OH groups	-	5.18	5.02	3.72	3.45

Table S5. The color evaluation of lignin from the pine pretreated at different conditions.

Lignin samples	SCI				SCE					
	L*	a*	b*	ΔE	L*	a*	b*	ΔE		
White reference	99.5	-0.1	-0.1	0.0	97.3	-0.1	0.1	0.0	-	
Temperature (70% BDO, 10% pTsOH, 4 h)	L _{90°C}	50.5	12.5	26.5	57.2	50.6	12.5	26.6	55.1	
	L _{110°C}	74.1	5.3	14.6	29.9	74.1	5.4	14.7	27.9	
	L _{130°C}	46.7	8.1	26.5	59.7	46.4	8.2	26.5	57.9	
	L _{150°C}	34.1	6.0	17.9	68.1	34.1	6.0	18.4	66.1	
pTsOH content (70% BDO, 110 °C, 4 h)	L _{10%}	74.1	5.3	14.6	29.9	74.1	5.4	14.7	27.9	
	L _{20%}	56.4	6.9	14.5	46.0	56.5	7.0	14.5	43.9	
	L _{30%}	51.8	6.5	13.0	49.9	52.0	6.6	13.0	47.6	
	L _{40%}	47.7	6.1	10.9	53.4	47.6	6.2	10.9	51.2	

Time (70% BDO, 10% pTsOH, 110 °C)	L _{1h}	72.8	5.6	17.0	32.2	72.8	5.7	17.8	30.8	L _{1h}
	L _{2h}	71.0	6.0	16.1	33.4	71.2	6.1	16.2	31.3	L _{2h}
	L _{4h}	74.1	5.3	14.6	29.9	74.1	5.4	14.7	27.9	L _{4h}

Table S6. SPF values of lignin from the pine pretreated at 70% BDO aqueous solution with 10% pTsOH at 110 °C for 4 h blended with pure cream, physical sunscreen and chemical sunscreen.

Lignin	0%	2%	5%	10%	20%
SPF0	1.05±0.45	2.02±0.01	2.87±0.74	3.95±0.48	6.66±0.42
SPF15-P	12.95±0.48	8.78±0.88	7.38±0.64	6.33±0.27	-
SPF15-C	10.03±0.07	20.80±1.45	10.88±0.49	18.21±3.11	-