Electronic Supplementary Material (ESI) for Green Chemistry.

Synergizing Mitigated Spatial Confinement and Chemical Stabilization of Lignin Facilitates Full Utilization of Lignocellulose

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Experimental Section

Materials

The Scotch pine (Pinus sylvestris) obtained from Jiangsu China was ground and screened through a mesh size. It contained 28.6% lignin, 39.6% cellulose and 18.7% hemicellulose, respectively. 1,4-butanediol (1,4-BDO, AR, 98%) and acetic acid (AA, AR, ≥99.8%) were purchased from Aladdin Chemical Reagent Co., Ltd. Citric acid (CA, AR, ≥99.5%) and sulfuric acid (H_2SO_4, AR, 98.0%) were purchased from Guangzhou chemical reagent factory.

Preparation of milled wood lignin (MWL)

Firstly, pine powder was extracted with benzene/ethanol mixture for 15 h, and then extracted with ethanol for 24 h. After drying, the samples were ground in a ball mill for 96 h at 600 rpm. Then, 40 g milled pine powder was extracted with dioxane/water in nitrogen atmosphere for 24 h. After the reaction, the supernatant was collected, concentrated and dried to obtain crude MWL. The crude MWL was dissolved in acetic acid/water and dropped into ultrapure water to precipitate lignin followed by centrifuging and drying. The dried lignin was then dissolved in dichloroethane/ethanol, and re-precipitated by being dropped into diethyl ether. The precipitated lignin was dried to obtain the purified MWL.

Fractionation of pine components in 1,4-BDO/water

The pine powder, 1,4-BDO aqueous solution with a concentration ranging from 60% to 90% and acid catalyst were mixed and put in a reactor for composition fractionation at a set temperature (110, 130,150 and 180 °C). The solid-to-liquid ratio (g/mL) of pine wood powder and 1,4-BDO solution was 1:10. The mass proportion of acid catalyst was 5, 10, 15 or 20% of the volume of 1,4-BDO aqueous solution. In a specific experiment, a mixture of 3 g of pine wood powder, 3 g of citric acid, and 30 mL of a 70% (w/w) aqueous solution of 1,4-BDO was prepared and added to the reaction vessel. The reaction vessel was then heated to 110°C and

maintained at this temperature for 4 h. After the reaction, the pretreated mixture was filtered, and the filter cake was washed with hot butanediol and water. The washing solution and the filtrate were mixed, and water was added to precipitate the lignin. The precipitated lignin was then centrifuged and freeze-dried for analysis. The relevant calculations are as follows:

$$Pretreatment\ solid\ residue\ yield, Y_1 = \frac{M_R}{M_0} \times 100\%$$

$$Remained\ cellulose\ yield, Y_2 = Y_1 \cdot \frac{C_R}{C_0} \times 100\%$$

$$Removed\ hemicellulose\ yield, Y_3 = Y_1 \cdot (1 - \frac{H_R}{H_0}) \times 100\%$$

$$Extracted\ lignin\ yield, Y_4 = Y_1 \cdot (1 - \frac{L_R}{L_0}) \times 100\%$$

$$Precipitated\ lignin\ yield, Y_5 = \frac{M_L}{M_0 \cdot Y_4} \times 100\%$$

Where, M_0, M_R and M_L (in grams) are the mass of raw pine, pretreatment solid residue and lignin precipitated from the spent liquor, respectively. C_R, H_R, and L_R are the content percentages of cellulose, hemicellulose and lignin in the raw pine, respectively. C_0, H_0, and L_0 are the content percentages of cellulose, hemicellulose and lignin in the pretreatment solid residue, respectively.

Characterization of lignin

The two-dimensional ^{1}H-^{13}C heteronuclear single-quantum coherence (HSQC) NMR was used to investigate interunit linkage contents of lignin samples. Specifically, 25 mg of extracted lignin samples was dissolved in 0.5 mL dimethyl sulfoxide-d6 (DMSO-d6). The NMR spectra were recorded on a 600MHz NMR spectrometer (AVANCE III HD, Bruker, Germany).

The quantitative ^{31}P NMR spectra were used to determine the hydroxyl (-OH) and carboxyl (-COOH) groups of lignin. Typically, 20 mg of lignin was dissolved in pyridine and deuterated chloroform (1.6:1, v/v) mixed solution. The cyclohexanol as internal standard and chromium

acetylacetonate as relaxation reagent was added. Finally, phosphating reagent was added to the mixed solution, namely 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP). The obtained samples were also detected by a 600MHz NMR spectrometer.

The color of the lignin was measured using a Datacolor 200 colorimeter (Datacolor, America) with two different modes: specular component included (SCI) and specular component excluded (SCE).[1] SCI has been adopted to evaluate the actual color containing specular light and diffuse light, while SCE has been adopted to evaluate appearance color excluding any specular light. The color of lignin can be described using $L^*a^*b^*$ (CIELAB system), where L^* was considered as brightness, a^* and b^* are the redness and yellowness factor, respectively. The L^*, a^* and b^* were used to calculated the total color difference (ΔE) through the formula:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

Where the value of L^* varies between 0 (black) and 100 (white). $+a^*$ represents a red direction, $-a^*$ represents a green direction. $+b^*$ describe a yellow direction, and $-b^*$ describe the blue direction.

FT-IR analysis of lignin was employed by a Thermo Nicolet IS50. Briefly, 2 mg of the extracted lignin was ground and mixed with 100 mg potassium bromide. Then the mixture was pressed into pieces for the analysis of infrared spectroscopy at a range of 4000-500 cm^{-1} with 4 cm^{-1} resolution and 32 scans.

The molecular weight distribution of lignin was determined by GPC (Agilent, 1260, equipped with Ultraviolet and Refraction Index detectors). Firstly, 100 mg lignin was derivatized by acetylation in acetic anhydride and pyridine solution at dark for 72 h. Then, the acetylated lignin (2 mg) was fully dissolved in tetrahydrofuran (1 mL) and filtered through a 0.45 μm filter.

The morphology of lignin was characterized using Hitachi SU8220 scanning electron microscope. A small number of samples were stuck on the conductive adhesive, and SEM photos were taken at 15 kV.

The particle size and zeta potential of lignin were determined using a Malvern Nanoparticle Size and Zeta Potential Analyzer (Zetasizer NANO ZS). During the analysis, all the lignin samples were dispersed in ultrapure water and tested after ultrasonication.

Preparation and Characterization of lignin-based sunscreen

Lignin-based sunscreen were prepared by physically mixing lignin samples with hand cream without UV protection. Then, 3M medical tape was pasted on the clean quartz plate with an area of 12.5 cm^2. Immediately, the lignin sunscreen was evenly spread on the tape, and the sample distribution is about 2 mg/cm^2. After drying the sample in the dark for 30 min, the transmittance test was carried out at a wavelength of 290-400 nm. The sun protection factor (SPF) was calculated by:

$$SPF = \sum_{290}^{400}(E_\lambda \cdot S_\lambda)/\sum_{290}^{400}(E_\lambda \cdot S_\lambda \cdot T_\lambda)$$

Where E_λ = erythemal spectral effectiveness, S_λ = solar spectral effectiveness, T_λ = spectral transmittance of sample.

Enzymatic hydrolysis of pretreated pine

The solid residue obtained from pretreatment was applied to enzymatic hydrolysis. Simply, 0.5 g substrate, 25 mL citrate buffer (50 mM, pH 4.8) and Cellulase (25 FPU/g cellulose) were added to a conical flask (50 mL). Subsequently, enzymatic hydrolysis was carried out in an oscillating incubator at 50°C, 150 rpm. The hydrolysates were collected at different time, and the concentration of glucose in samples was determined for investigating the cellulose enzymatic digestibility of pretreated residues.

Computational Section

Molecular model construction

A dimer model of lignin, guaiacylglycerol-beta-guaiacyl ether (GGE), was employed for density functional theory (DFT) calculations. The molecular model for molecular dynamics (MD) simulations was constructed based on the HSQC NMR spectra of lignin (Figure S2). As extensively documented in the previous literature, etherification reactions of diols predominantly occurred at the C_α-OH of lignin.[2] Therefore, both DFT and molecular dynamics simulations in this work assumed that etherification occurred at the C_α-OH of lignin for simulating the etherification modification of lignin in the 1,4-BDO/water system. Similarly, the esterification reaction between lignin and carboxylic acid occurred at the C_γ-OH, which has also been reported in the previous literature.[3] Notably, in the treatment of lignin with 1,4-BDO and carboxylic acid, the etherification of the C_α-OH and the esterification of the C_γ-OH of lignin were further confirmed by the HSQC NMR spectra presented in our study.

Density functional theory (DFT) calculation

Conformational search. For each compound or intermedium, its conformation was first optimized to have a global energy minimum according to our previous method[4] through using molecular dynamics (MD), semi-empirical quantum mechanics (SQM) and density functional theory (DFT) in sequence performed in a Molclus software package.[5-8] Specifically, a large number of conformers of guaiacylglycerol-beta-guaiacyl ether (GGE) were generated using a molecular dynamics (MD) method implemented in xTB, an extended tightbinding semi-empirical program package. The generated GGE conformers were pre-optimized using the GFN0-xTB and GFN2-xTB methods. The resulting conformers within 5 kcal/mol of the global energy minimum were then re-optimized with the density functional theory (DFT) at the B3LYP-D3/6-311G* of the Gaussian 16 software packages under the SMD model of butanol/water, and frequency analysis was then conducted at the same level to confirm them without imaginary frequency. The single point energies of all of the optimized compounds and

intermedia were calculated at the PWPB95-D3/def2-QZVPP level[9] under the SMD model using ORCA 4.2 package. The conformer with the lowest energy were used for further analysis.

Calculation of solution-phase free energies of solutes (G_{soln}). The G_{soln} of optimized molecules in butanol/water was obtained by adding accurate values of the gas-phase free energies (G_{gas}) to the accurate values of the solvation free energies (ΔG_{solv}) as the followed equation (1)[10, 11].

$$G_{soln} = G_{corr\_gas} + G_{gas} + \Delta G_{solv} + 1.894 \quad (1)$$

Where G_{corr_gas} is the thermal correction to G_{gas}, calculated at the level of B3LYP-D3/6-311G*. ΔG_{solv} is the difference in free energy of the solute in the solution (SMD model) and gas phases, computed at M062x/6-31G*[11, 12] using Gaussian 16 code. G_{gas} was calculated at the level of PWPB95-D3/def2-QZVPP using ORCA 4.2 package. The last term of the equation, 1.894, represents the free energy change in kcal/mol associated with a molecule going from the gas-phase standard state (1 atm at 298.15 K) to the solution-phase standard state of 1 mol/L. The molecular thermochemistry properties of optimized intermedia at different temperature were calculated by a Shermo code.[13]

Calculation of non-covalent interaction. Thousands of clusters containing one GGE, one water and four butanol molecules were generated by MD, followed by optimization via Molclus program platform as the above processing of single molecule. The wavefunction file obtained from the single-point calculations of optimized cluster through ORCA at the level of PWPB95-D3(BJ)/def2-QZVPP was applied for the non-covalent interaction (NCI) analysis. The independent gradient model based on Hirshfeld partition (IGMH) method[14, 15] and Van der Waals electrostatic potential (ESP) were implemented for optimized compounds in Multiwfn 3.7 program[16] to investigate the NCI between lignin dimer and 1,4-BDO/water molecules. The NCI and ESP were visualized via VMD 1.9.3 program.[17]

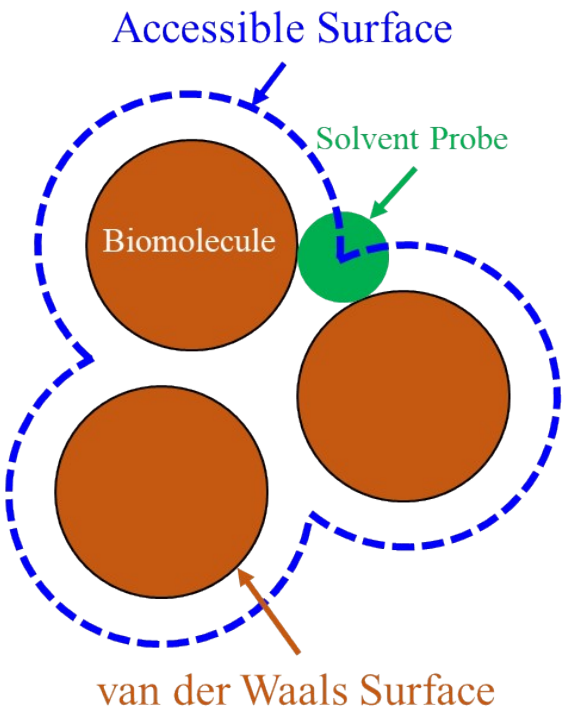
Molecular dynamics (MD) simulation

The 3D topological atomic models of lignin with and without modification for MD simulation was constructed via the LiginBuilder.[18] For investigating the dissolving mechanism of lignin in solvents, five lignin model molecules were initially fixed at specific positions and maintained in separated state in butanol, water or butanol/water mixture (mass fraction of butanol = 70%) in a cubic box with a size of 10 nm, respectively. The periodic boundary condition (PBC) was applied to all dimensions of the system. The lignin was described using lignin-optimized CHARMM force field[19] . In addition, the grafted groups of lignin, butanol molecule, along with a TIP3P[20] water model were described using the CHARMM general force field (cgenff). The simulation system was subjected to energy minimization using the steepest descent method to make maximum force lower than 100 kJ/mol/nm, followed by a 1 ns simulation run in NPT ensemble (T=298.15 K, P=1 bar). The production simulations were then run for 100 ns with a leap-frog integrator and step of 1 fs in NPT ensemble maintained at 1 bar through the use of Parrinello-Rahman barostat, and the trajectory data for the last 60 ns simulations were analyzed. The bonds involving hydrogen atoms were constrained by LINCS algorithm.[21] The cut-off for short-range van der Waals interaction was 1.0 nm, while a dispersion was corrected to the energy and pressure. Long-range electrostatic interaction was handled using particle mesh Ewald (PBE) method,[22] along with a real-space cutoff of 1.0 nm. All MD simulations and analysis in this work were performed with the GROMACS 2021.5 package.[23]

As for investigating the effect of acid catalyst on the conformation of lignin, modified lignin model was employed as shown in the Figure S7. Only one modified lignin molecule was dissolved in the 1,4-BDO/water (70% 1,4-BDO) binary solvent. Except for maintaining at an elevated temperature (110, 130, 150 and 180^{o}C) through the use of V-rescale thermostat,[24] the other simulation settings kept the same as the procedures above.

Molecular dynamics analysis.

The radius of gyration, a valuable parameter for characterizing polymer solutions, was calculated using the program gmx gyrate to provide an estimate of the compactness of lignin. Contact maps, an important tool in structural biology, were generated using the program gmx mdmat to analyze the contact patterns among lignin phenylpropane (C9) units. The radial distribution function g(r), which depicts the relative density as a function of distance (r) from a reference particle in a system of particles (e.g., atoms, molecules, colloids), was calculated using the program gmx rdf. The solvent-accessible surface area (SASA), a crucial factor in studying biomolecular folding and stability, was determined using the program gmx sasa. As depicted in Scheme S1, the accessible surface is delineated by dashed blue lines and is generated by tracing the center of the solvent probe sphere (shown in green) as it moves along the van der Waals surface. In this study, we have used a typical probe radius of 1.4 Å, which is approximately equivalent to the radius of a water molecule. However, it is important to note that the choice of probe radius can significantly affect the calculated surface area. Specifically, using a smaller probe radius can reveal more surface details and thus yield a larger surface area.



Scheme S1. Illustration of the solvent accessible surface.

Supplementary Figures

Figure S1

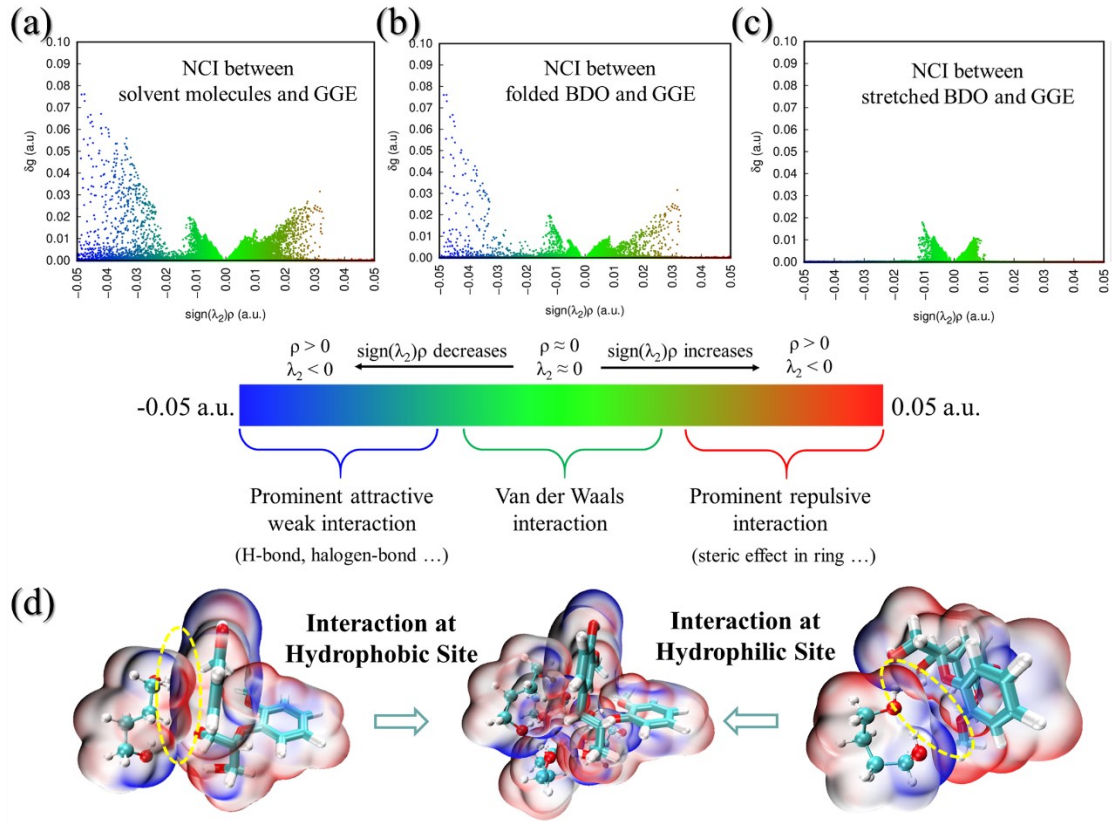


Figure S1. (a-c) Scatter graph of non-covalent interaction (NCI) between solvent molecules and lignin dimer guaiacylglycerol-beta-guaiacyl ether (GGE) described by independent gradient model based on Hirshfeld partition (IGMH). (d) Electrostatic potential (ESP) between solvent (CPK model, C-cyan, H-white, O-red) and guaiacylglycerol-beta-guaiacyl ether (GGE) molecules (Licorice model); the blue region represents negative charge accumulation, the red region represents positive charge accumulation, and the overlapping region represents intermolecular interactions.

Figure S2

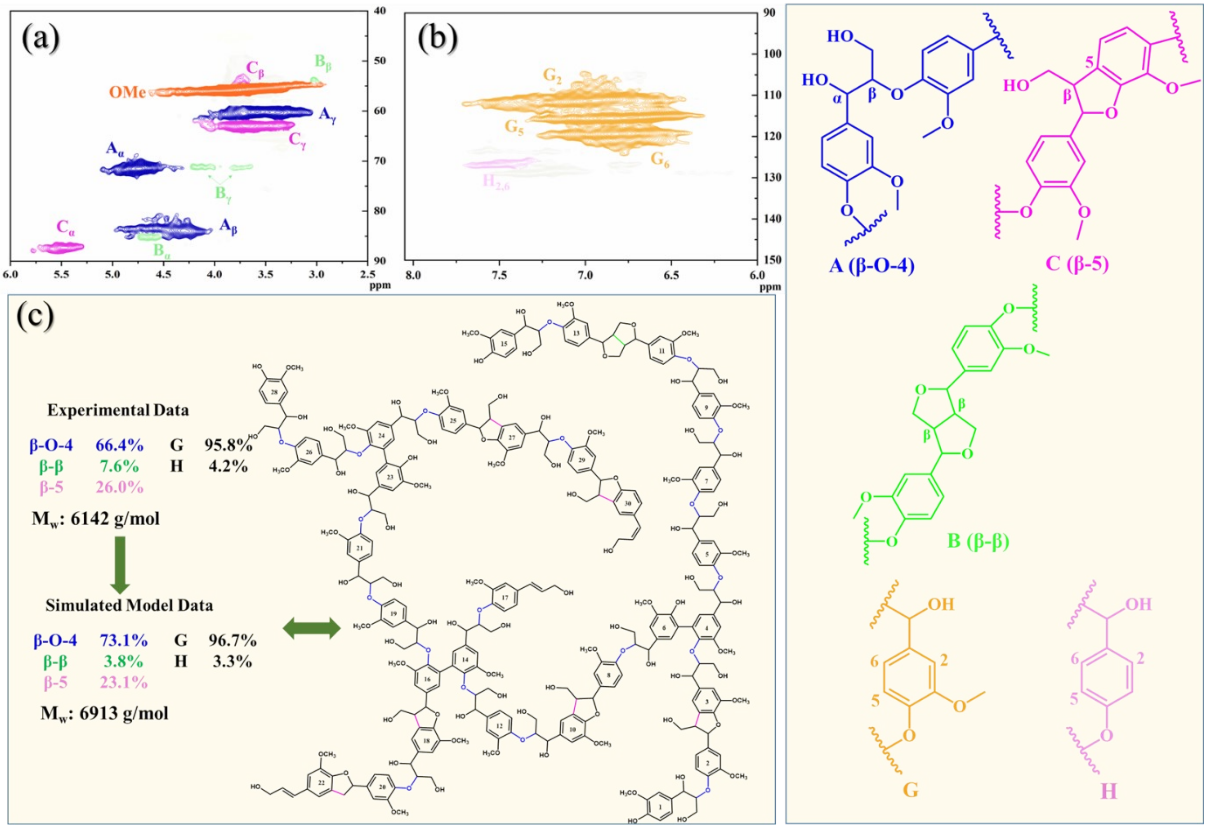


Figure S2. (a-b) 2D ^{1}H-^{13}C HSQC NMR spectra of MWL, and (c) lignin molecule model constructed based on the NMR spectra and molecular weight detected by GPC.

In side chain region (δ_C/δ_H 50.0-90.0/2.50-6.00), β-aryl ethers (β-O-4, A), resinols (β-β, B), phenylcoumarans (β-5, C) substructures were detected. In addition, the methoxy (OMe, δ_C/δ_H 55.9/3.73) was also detected in the MWL samples. MWL contain β-O-4 linkages that can be identified by signals at α, β and γ positions. Specifically, the C_α-H_α correlation (A_α) for β-O-4 linkages were observed at δ_C/δ_H 71.5/4.72, while C_γ-H_γ correlation (A_γ) were detected at δ_C/δ_H 60.7/3.39. The C_β-H_β correlations (A_β) of β-O-4 substructures were observed at δ_C/δ_H 83.3/4.34. In addition, the signals at the α, β and γ positions of the β-β resinol substructure (B_α, B_β, B_γ) can be observed at δ_C/δ_H 85.4/4.64, 53.7/3.45, and 71.2/4.03 and 71.5/3.76, respectively. The C_α-H_α correlation for phenylcoumarans (β-5) substructure (C_α) were observed at δ_C/δ_H 87.5/5.44, and C_γ-H_γ correlation (C_γ) were detected at δC/δH 63.3/3.69. Besides, a small number of C_β-H_β correlations of phenylcoumarans (β-5) substructure (C_β) was discovered at δ_C/δ_H 52.2/3.60.

Figure S3

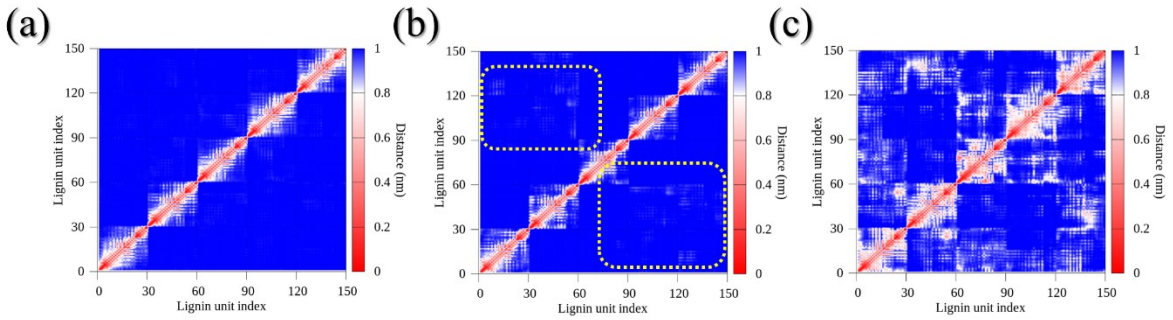


Figure S3. Lignin phenylpropane (C9) unit contact maps after 100 ns molecular dynamics simulation of five lignin molecule clusters dissolving in (a) 70% 1,4-BDO aqueous solution, (b) pure butanediol and (c) water, respectively.

Figure S4

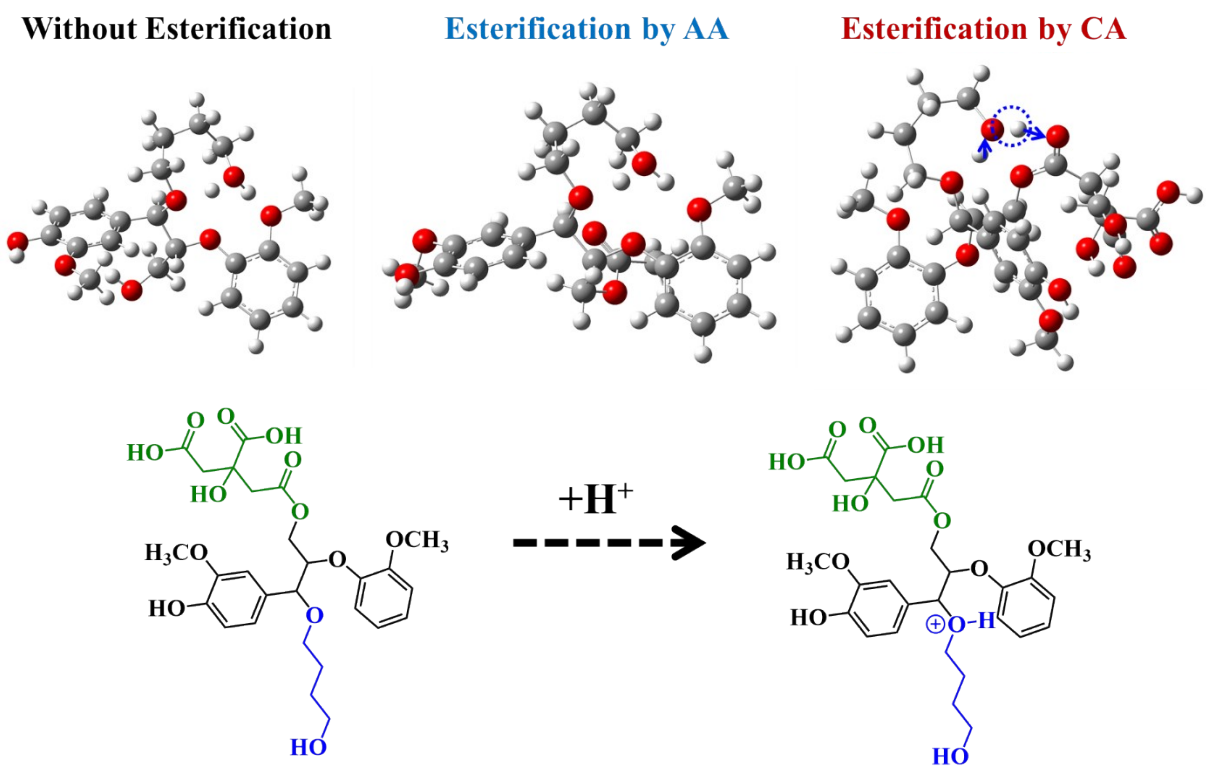


Figure S4. Optimized molecular conformations of oxonium ion of lignin modified by different acids, and reaction scheme.

Figure S5

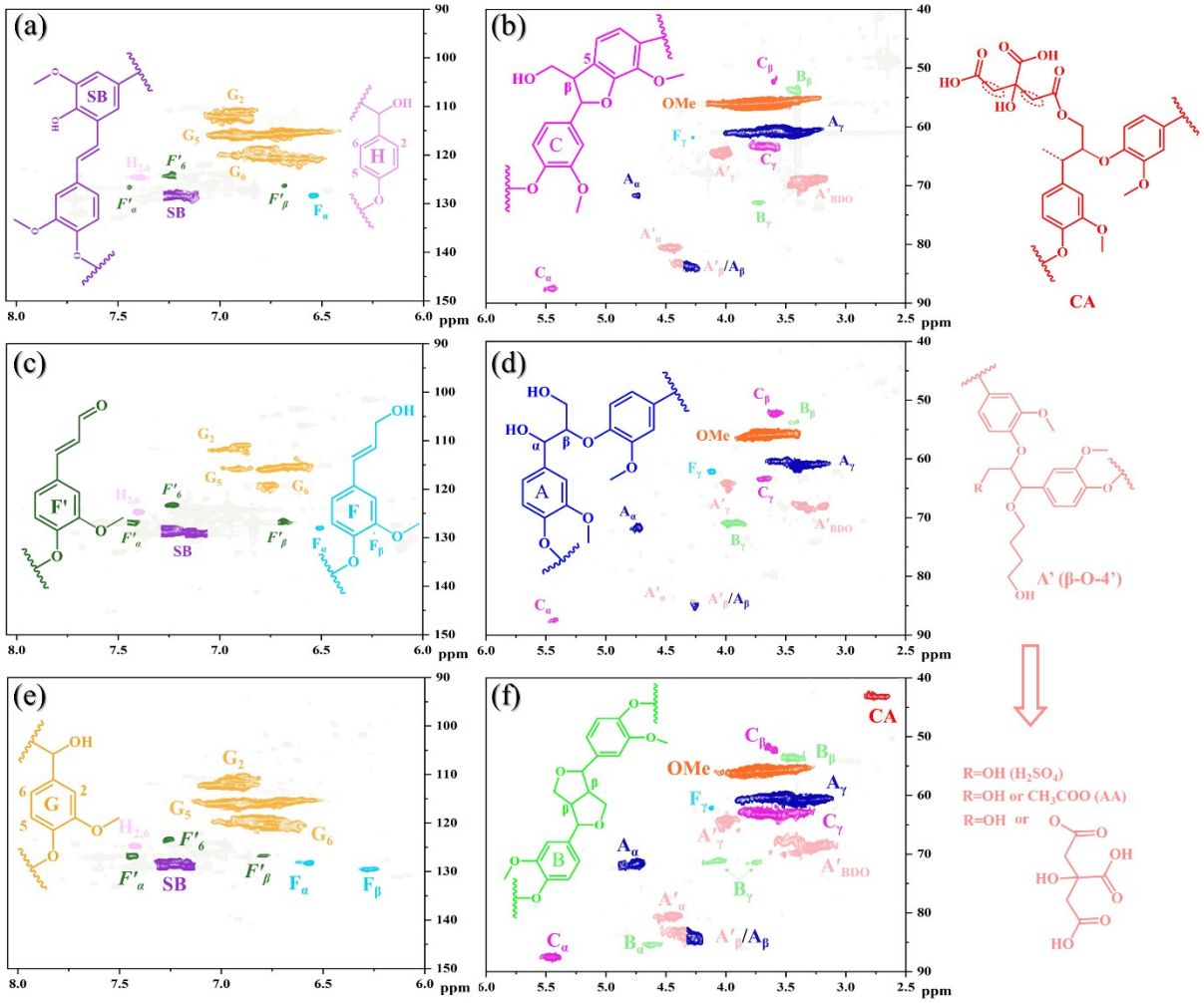


Figure S5. 2D ^{1}H-^{13}C HSQC NMR spectra of lignin extracted with 10% (a-b) sulfuric acid, (c-d) acetic acid, and (e-f) citric acid in 70% 1,4-BDO aqueous solution at 110°C for 4 h, respectively.

Figure S6

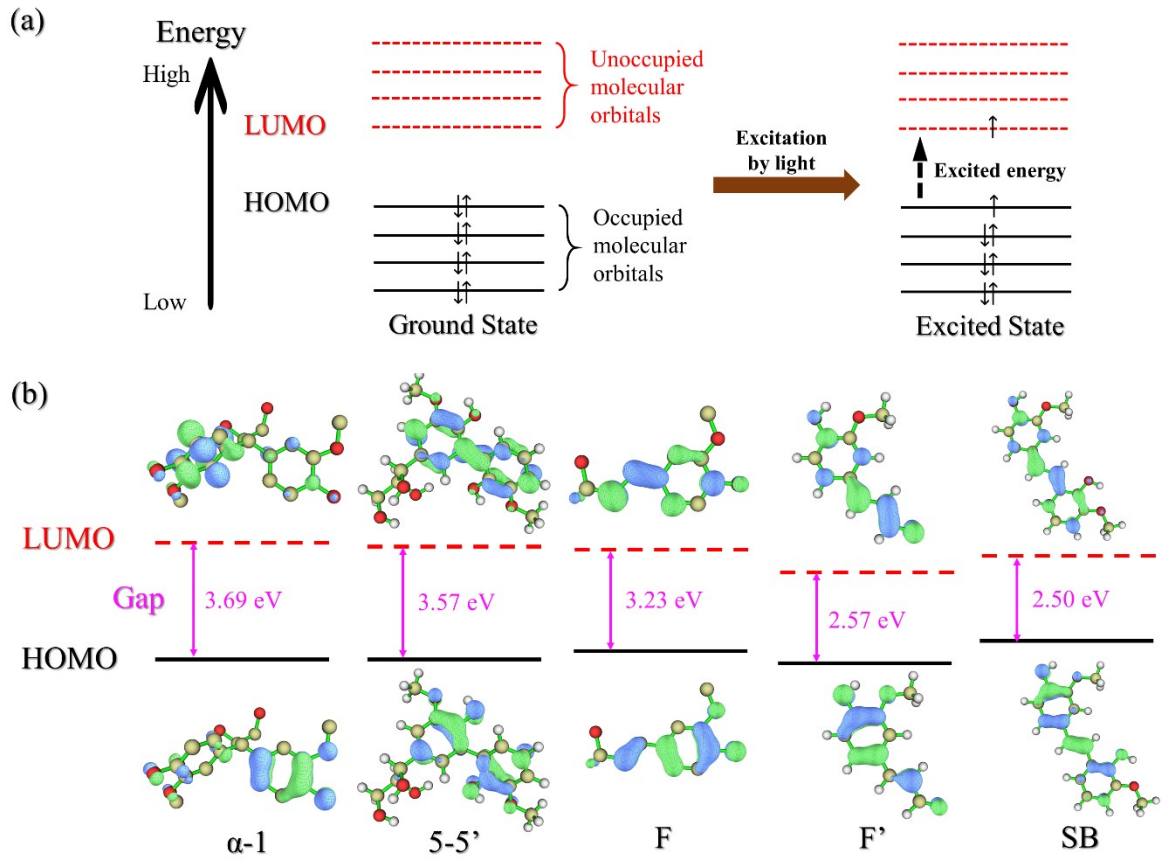


Figure S6. (a) Diagram of electron transition from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) of a molecule excited by light, and (b) energy gap between LUMO and HOMO of lignin represent condensed and conjugated enhanced units.

Figure S7

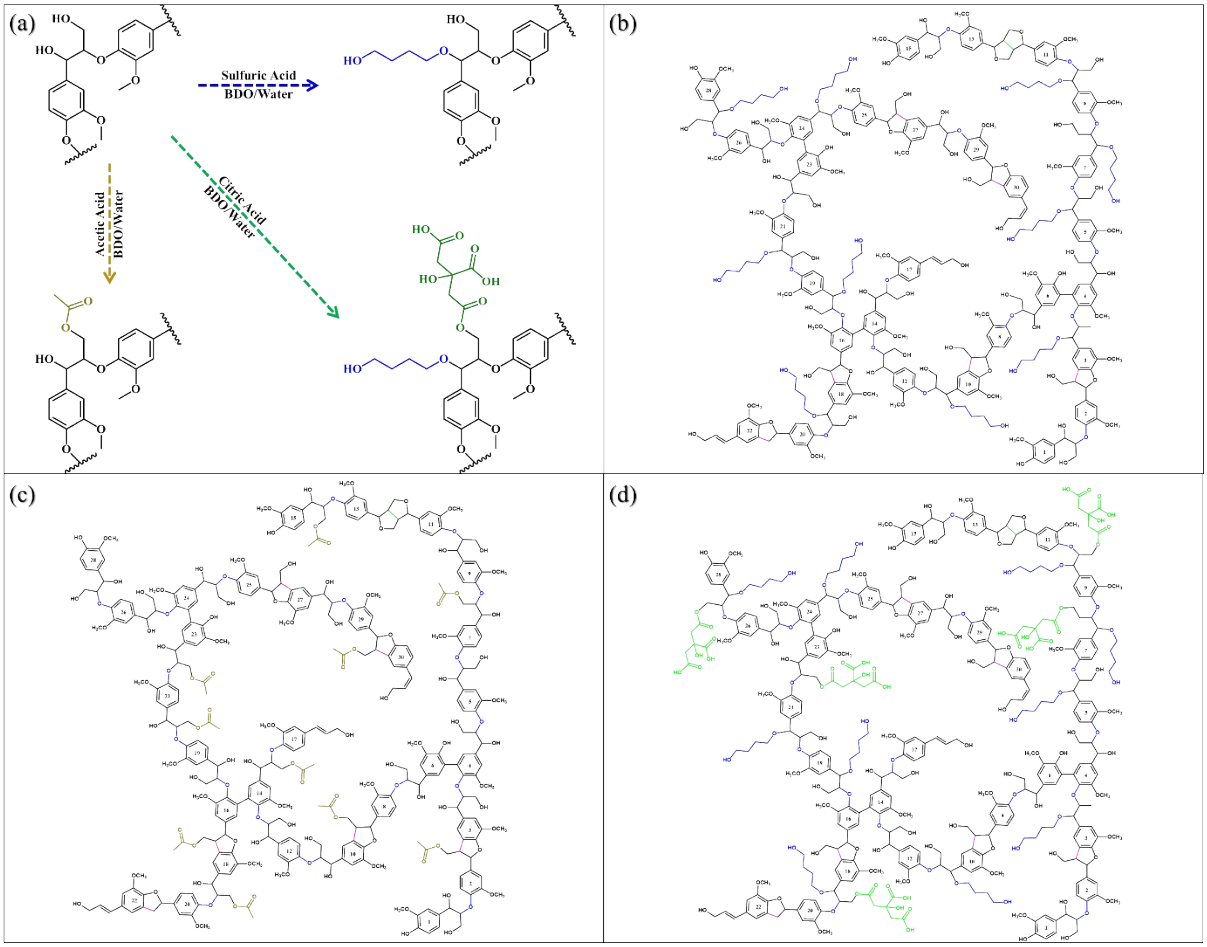


Figure S7. (a) Reaction scheme between lignin and different acids in 1,4-BDO/water, and (b-d) molecular models of lignin treated by sulfuric acid, acetic acid and citric acid in 1,4-BDO/water, respectively.

Figure S8

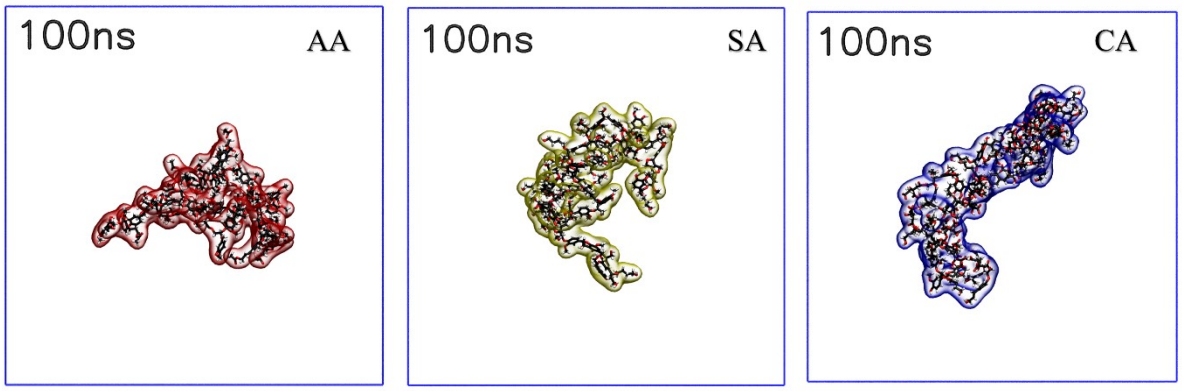


Figure S8. Molecular conformations after 100 ns molecular dynamics simulation (MDS) in 1,4-BDO/water of lignin treated by acetic acid (AA), sulfuric acid (SA) and citric acid (CA), respectively.

Figure S9

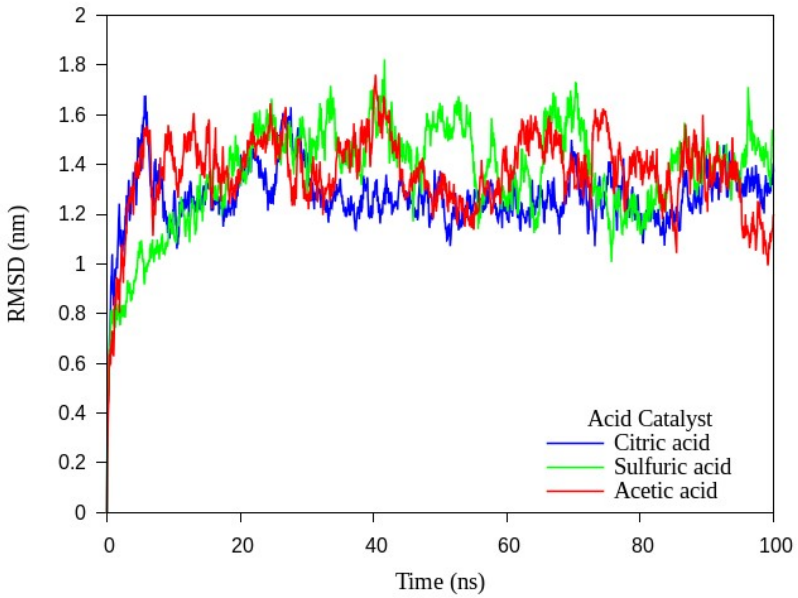


Figure S9. Simulation time-dependent root mean square deviation (RMSD) of lignin treated by sulfuric acid, acetic acid and citric acid in 1,4-BDO/water, respectively.

Figure S10

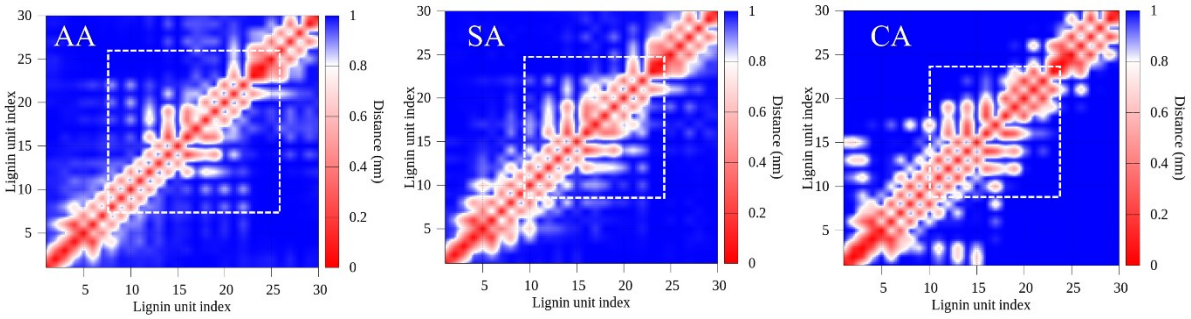


Figure S10. Lignin phenylpropane (C9) unit contact maps after 100 ns molecular dynamics simulation of lignin treated by sulfuric acid, acetic acid and citric acid in 1,4-BDO/water, respectively.

Figure S11

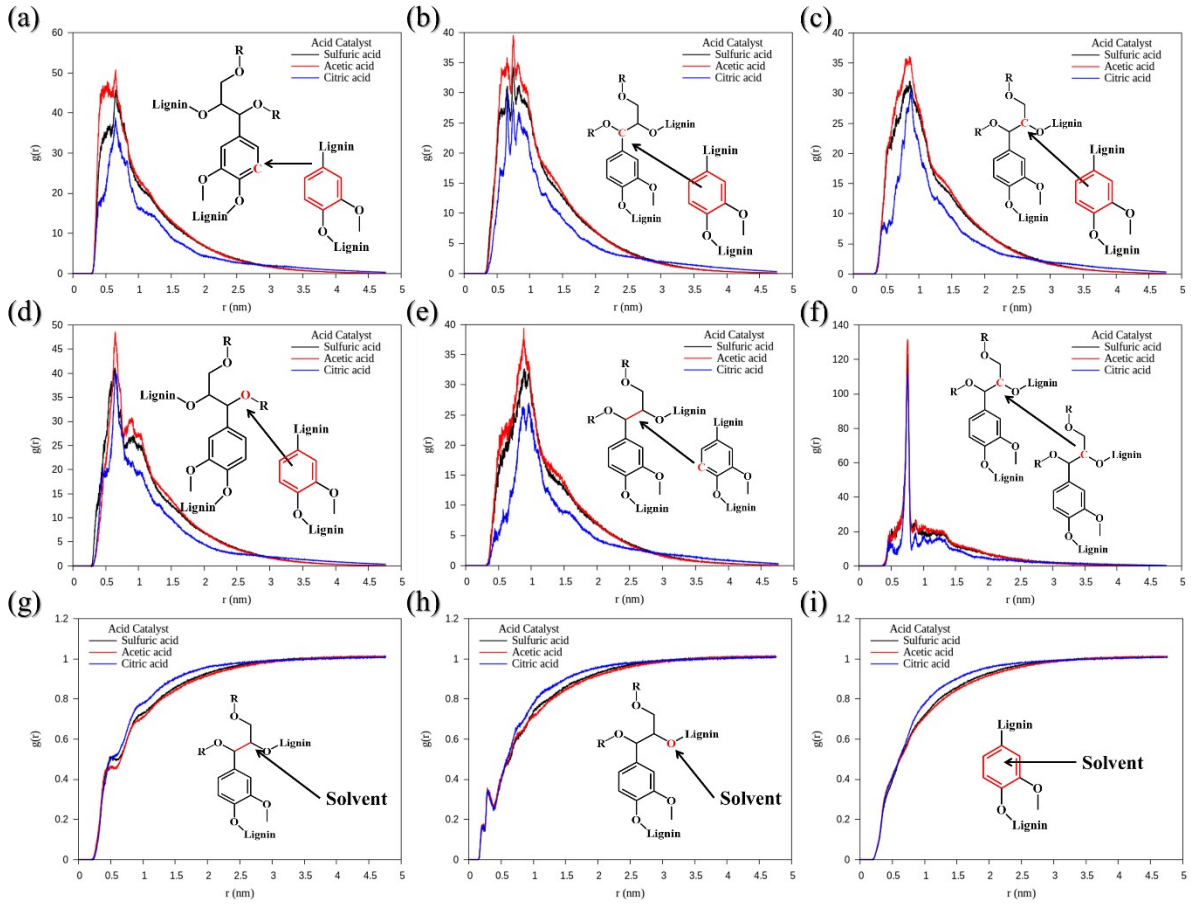


Figure S11. Radial distribution function (RDF) of selected groups and solvent molecules around reference groups of lignin obtained from different acid treatments**.**

Figure S12

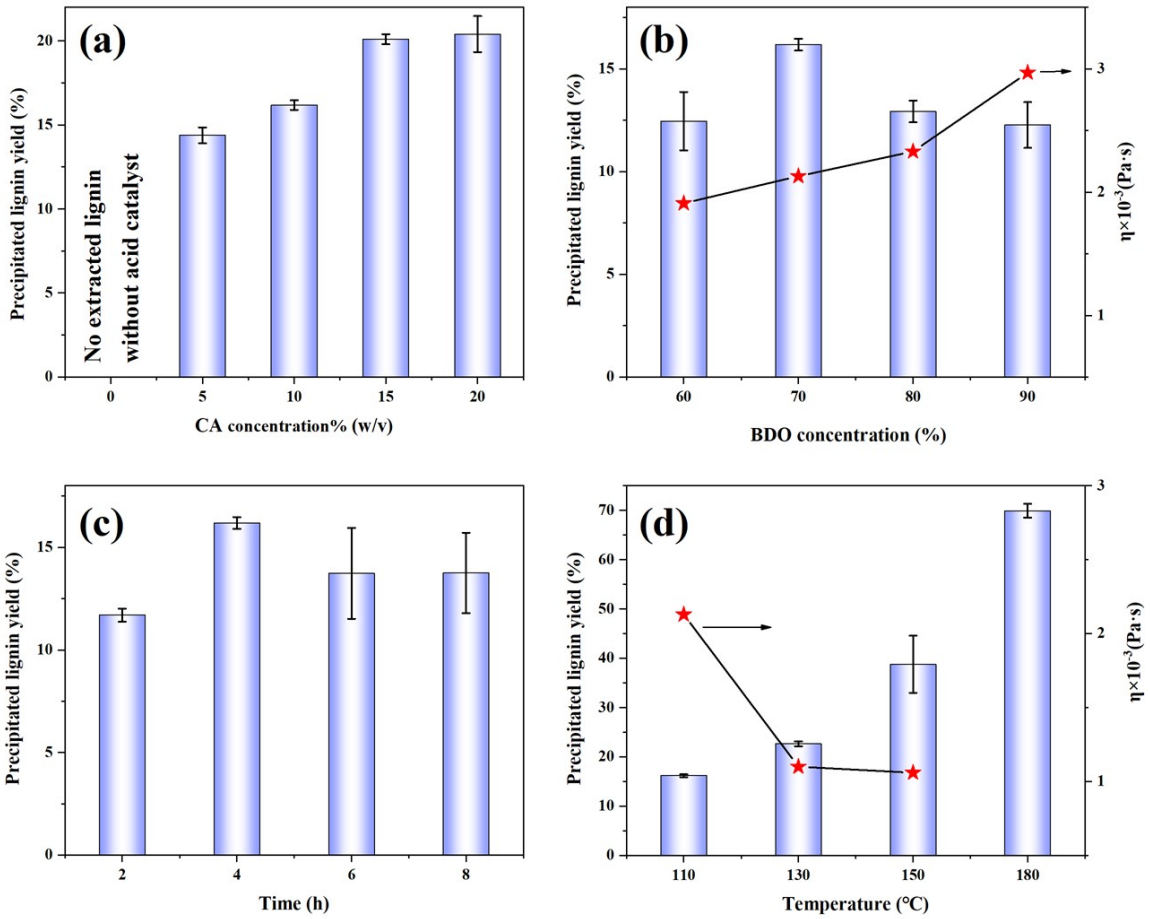


Figure S12. Effects of extraction conditions including (a) acid dosage, (b) 1,4-BDO concentration, (c) time, and (d) temperature, respectively, on the precipitated yield of lignin.

Figure S13

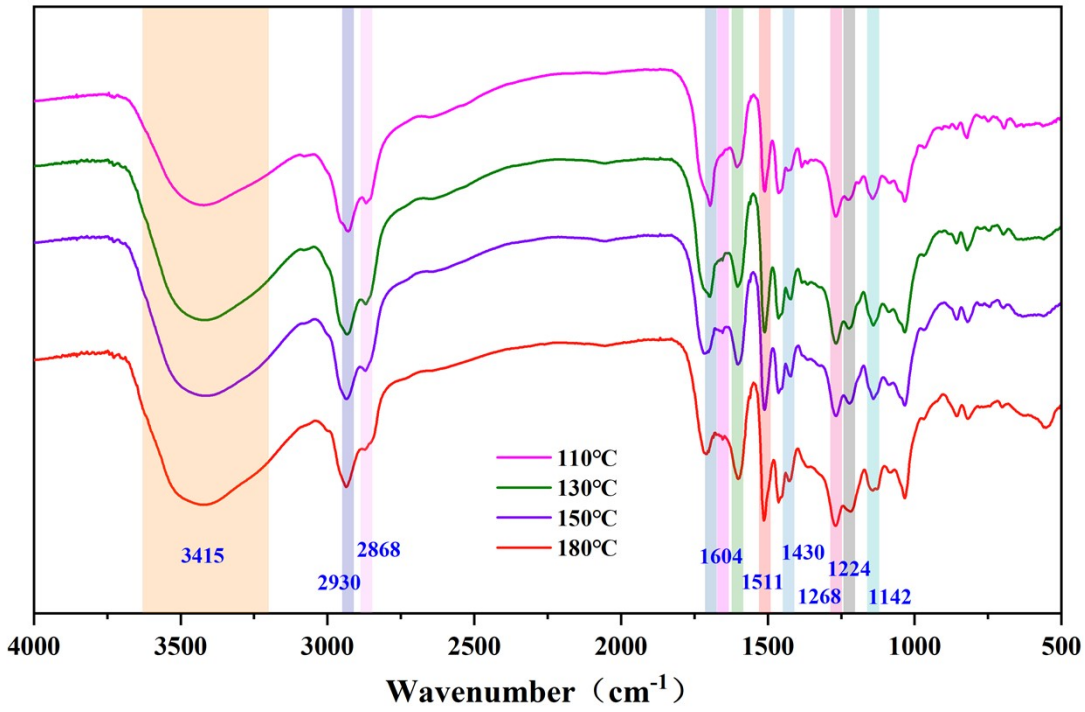


Figure S13. FT-IR spectra of lignin extracted with 10% citric acid in 70% 1,4-BDO aqueous solution for 4 h at different temperatures.

Figure S14

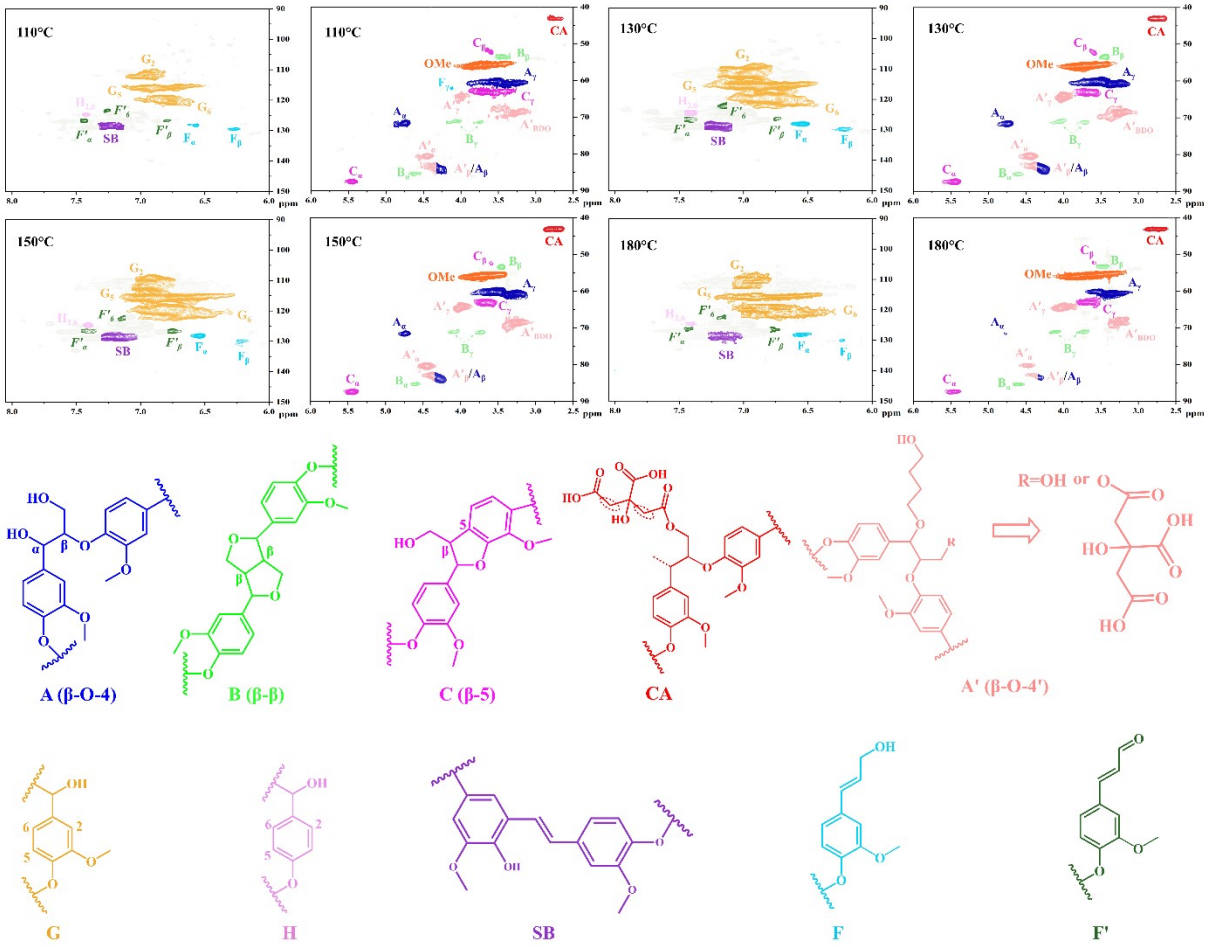


Figure S14. 2D ^{1}H-^{13}C HSQC NMR spectra of lignin extracted with 10% citric acid in 70% 1,4-BDO aqueous solution for 4 h at different temperature.

Figure S15

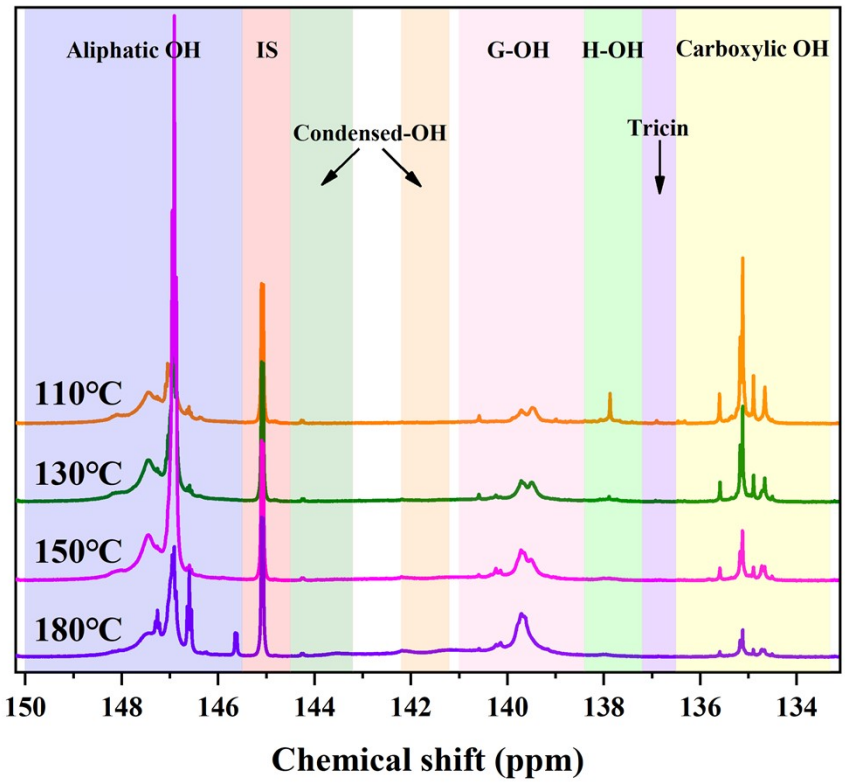


Figure S15. Quantitative ^{31}P NMR spectra of lignin extracted with 10% citric acid in 70% 1,4-BDO aqueous solution for 4 h at different temperatures.

Figure S16

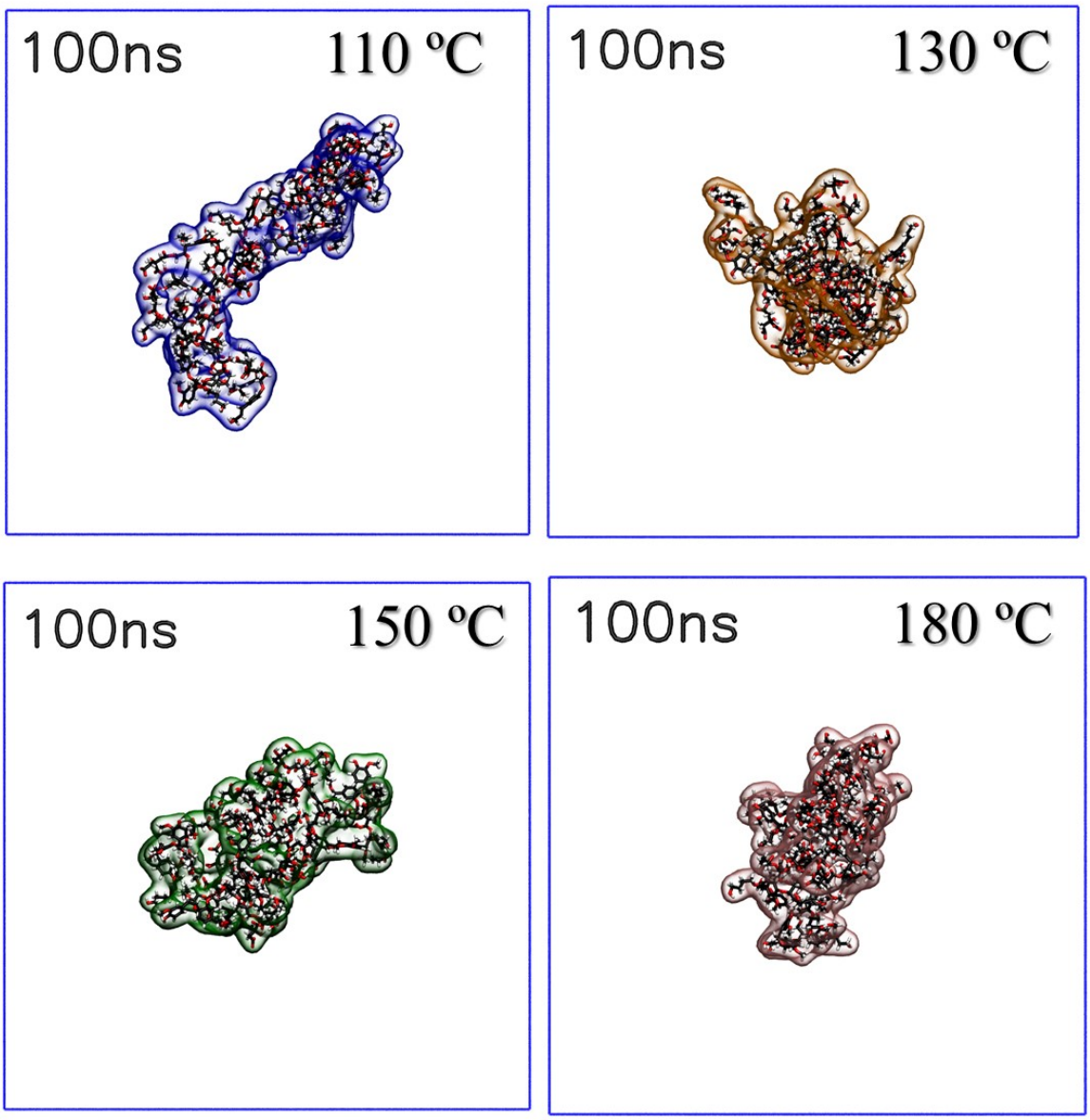


Figure S16. Molecular conformations after 100 ns molecular dynamics simulation (MDS) of lignin treated by citric acid in 1,4-BDO/water at different temperatures.

Figure S17

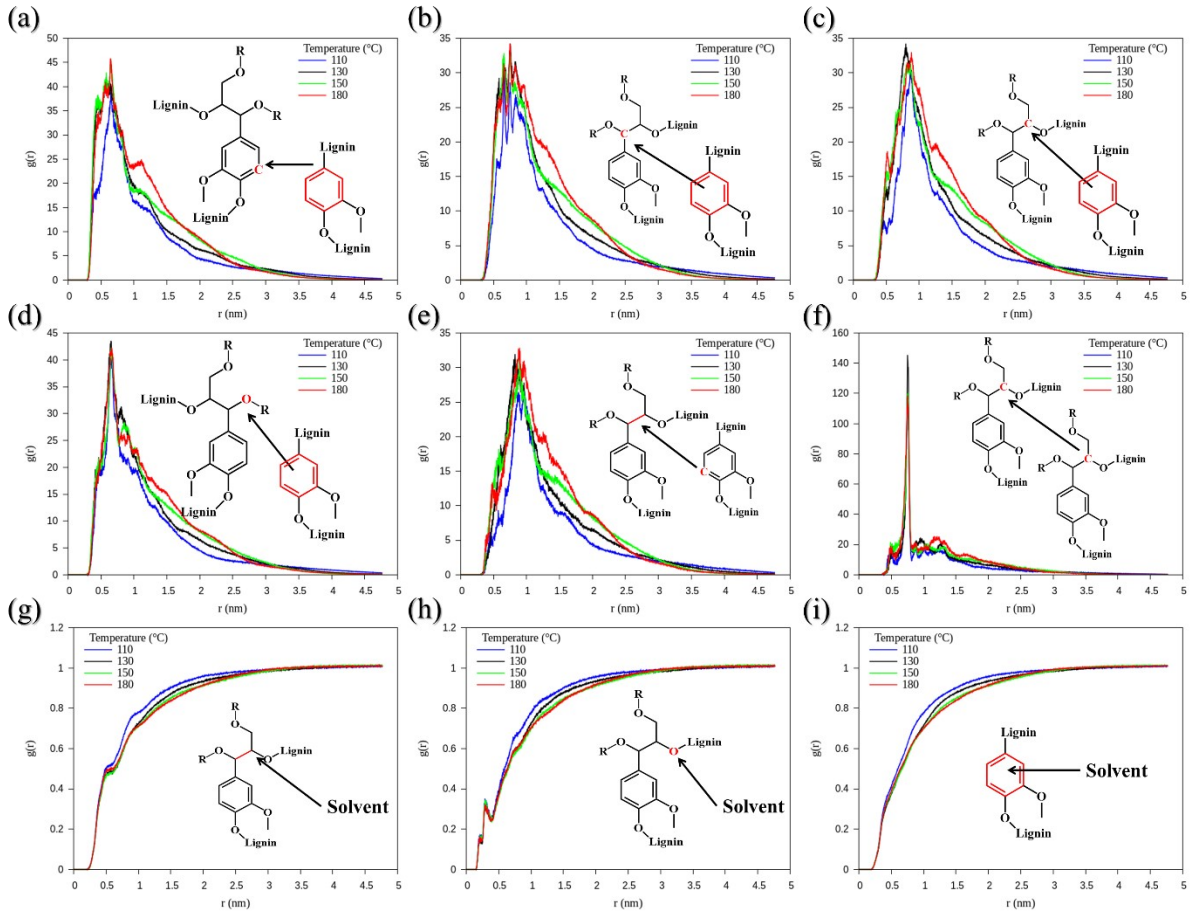


Figure S17. Radial distribution function (RDF) of selected groups and solvent molecules around reference groups of lignin at different temperature**.**

Figure S18

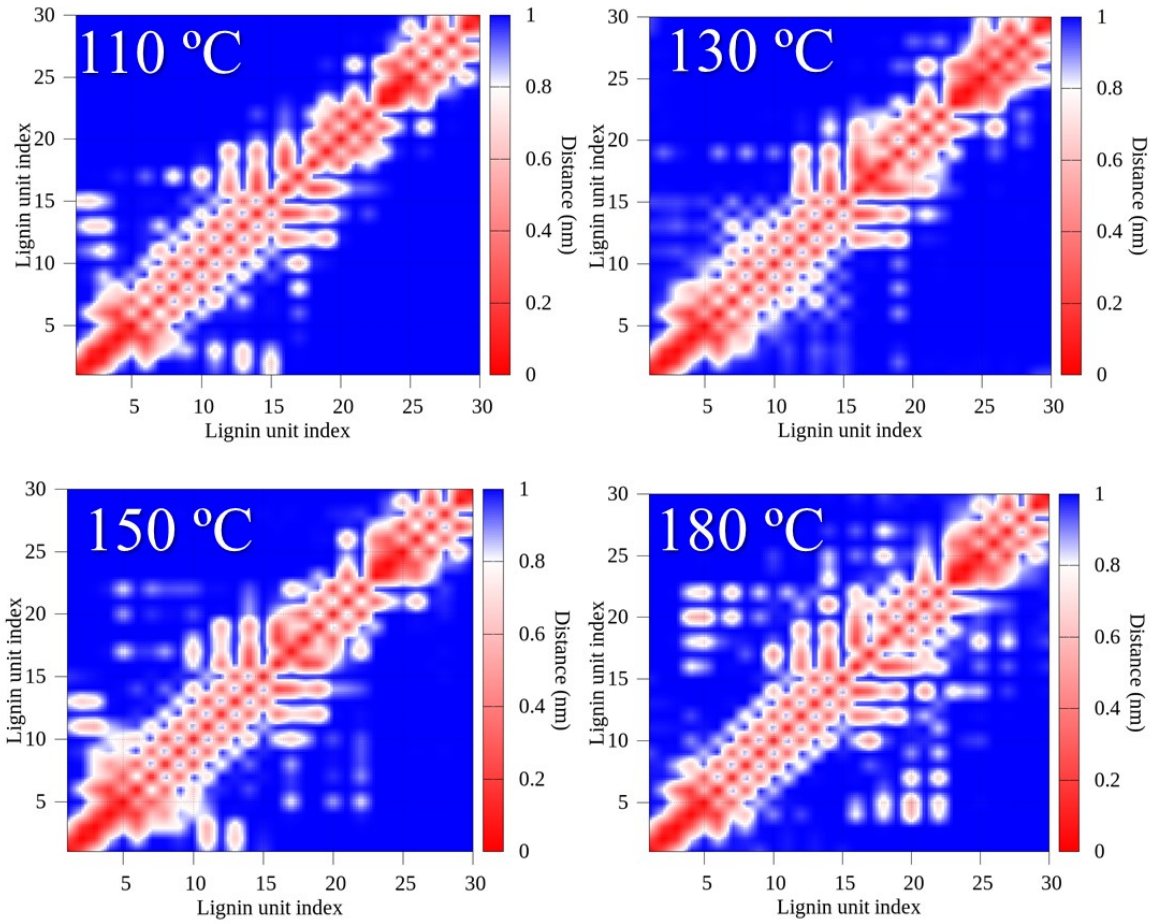


Figure S18. Lignin phenylpropane (C9) unit contact maps after 100 ns molecular dynamics simulation of lignin treated by citric acid in 1,4-BDO/water at different temperatures.

Figure S19

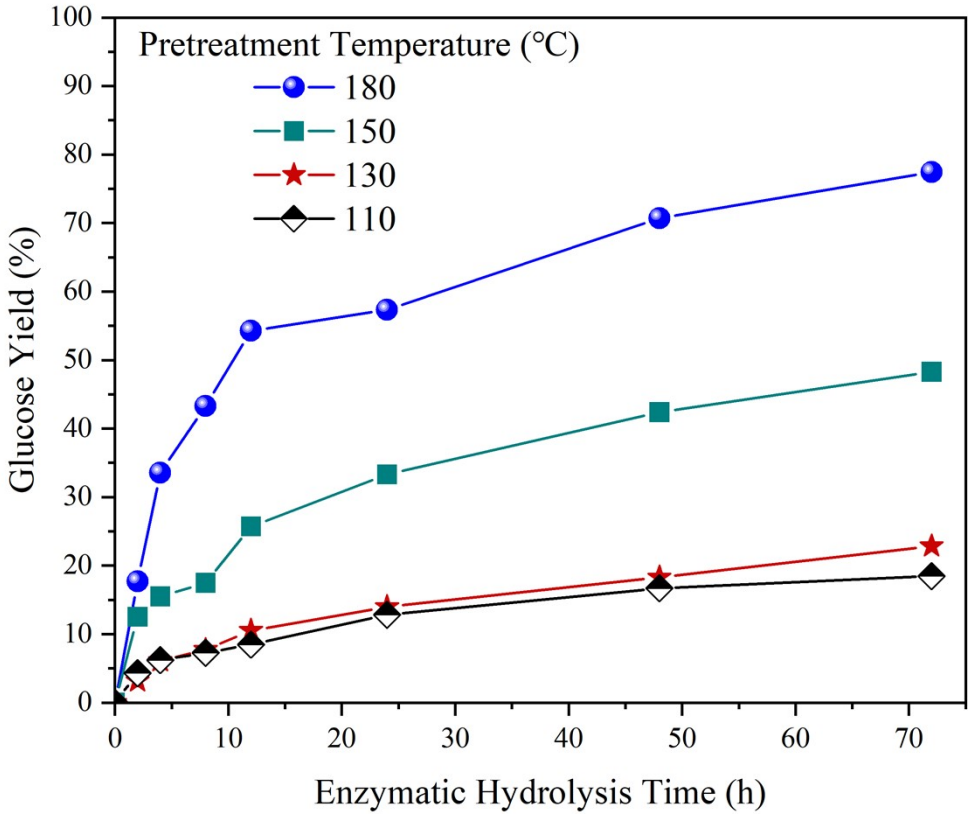


Figure S19. Cellulase enzymatic hydrolysis of pine treated by 10% citric acid in 70% 1,4-BDO aqueous solution for 4 h at different temperature.

Figure S20

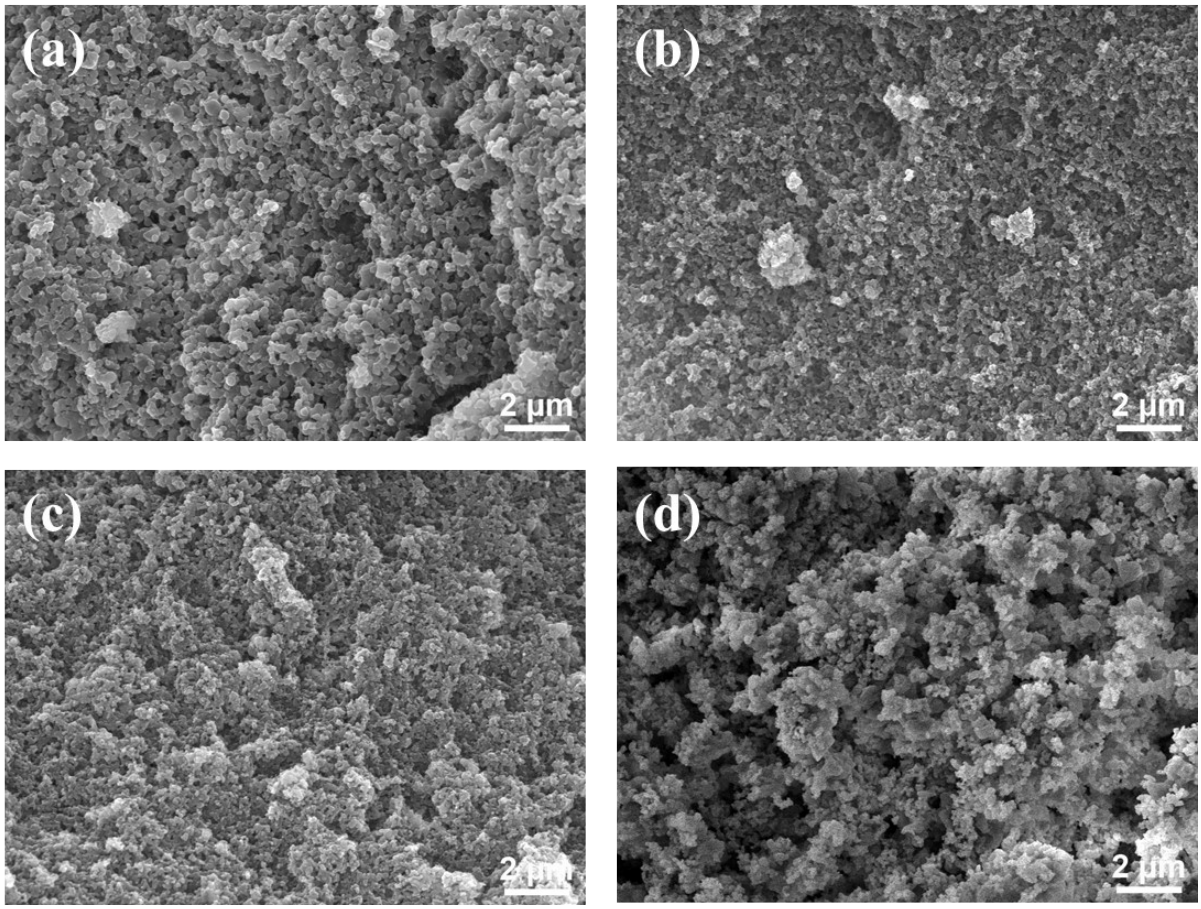


Figure S20. Morphology of nanolignin precipitated from lignin extracted with 10% citric acid in 70% 1,4-BDO aqueous solution for 4 h at (a) 110 °C, (b) 130 °C, (c) 150 °C, and 180 °C from pine, respectively.

Figure S21

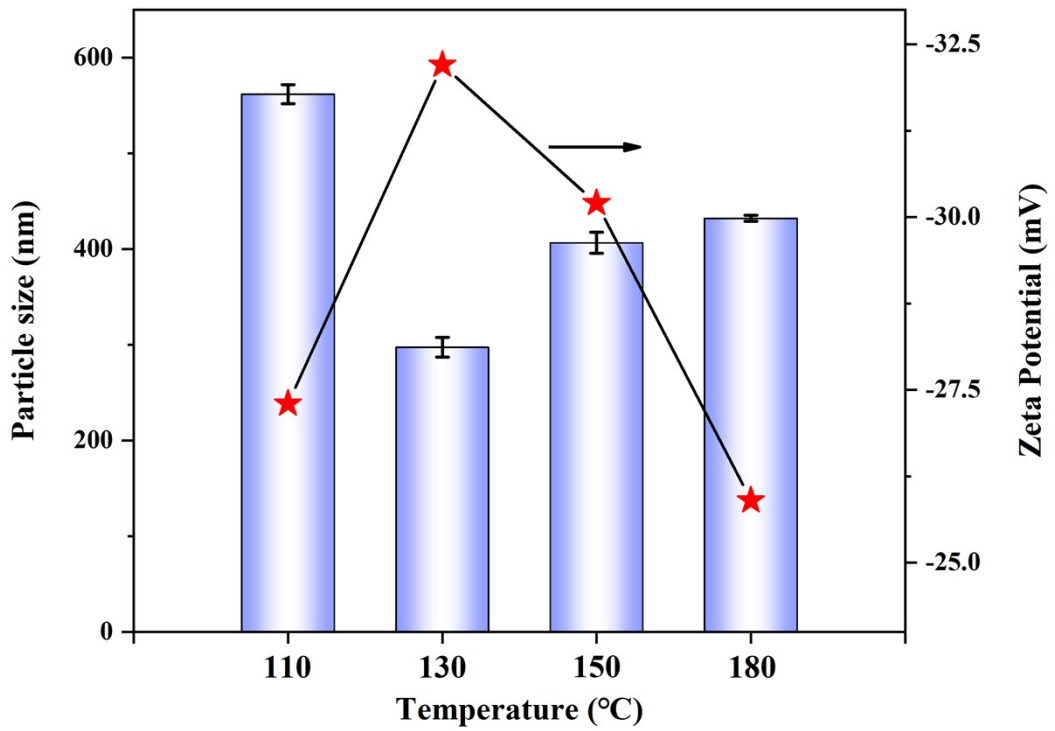


Figure S21 Effect of extracting temperature on the size and zeta potential of precipitated nanolignin.

Supplementary Tables

Table S1. Signal assignments of the ^{13}C-^{1}H correlation peaks in the 2D HSQC NMR spectra of the isolated pine lignin.[25-27]

Label	δC/δH	Assignment
OMe	(55.4-56.0)/(3.7-3.8)	C-H in methoxyls
A_α	(71.5-71.7)/(4.7-4.8)	C_α-H_α in β-O-4 substructures (A)
A_β/ A'_β	(82.9-84.0)/(4.2-4.5)	C_β-H_β in β-O-4 (A) and α-alkoxylated β-O-4 (A') substructures
A_γ	(60.1-61.1)/(3.3-3.6)	C_γ-H_γ in β-O-4 substructures (A)
A'_α	(80.3-80.6)/(4.4-4.5)	C_α-H_α in α-alkoxylated β-O-4 substructures (A')
A'_γ	(63.9-65.1)/(3.9-4.1)	C_γ-H_γ in α-alkoxylated β-O-4 substructures (A')
A'_{BDO}	(67.6-69.0)/(3.2-3.4)	C_{BDO}-H_{BDO} in 1,4-BDO molecule
B_α	(85.2-85.8)/(4.5-4.7)	C_α-H_α in resinol substructures (B)
B_β	(53.6-53.7)/(3.3-3.5)	C_β-H_β in resinol substructures (B)
B_γ	(70.9-71.4)/(4.0-4.2) (71.2-73.0)/(3.7-3.8)	C_γ-H_γ in resinol substructures (B)
C_α	(87.3-87.5)/(5.4-5.5)	C_α-H_α in phenylcoumaran (C)
C_β	(52.2-52.4)/(3.5-3.6)	C_β-H_β in phenylcoumaran (C)
C_γ	(63.3-63.5)/(3.6-3.7)	C_γ-H_γ in phenylcoumaran (C)
G_2	(110.8-112.2)/(6.9-7.0)	C_2-H_2 in guaiacyl units (G)
G_5	(115.5-116.3)/(6.9-7.0)	C_5-H_5 in guaiacyl units (G)
G_6	(119.0-120.6)/(6.7-7.0)	C_6-H_6 in guaiacyl units (G)
$H_{2,6}$	(124.4-124.8)/(7.3-7.5)	$C_{2,6}$-$H_{2,6}$ in H units (H)
F_α	128.1-128.4/6.5	C_α-H_α in cinnamyl alcohol end-groups (F)
F_β	129.0-130.2/6.2	C_β-H_β in cinnamyl alcohol end-groups (F)
F_γ	61.7-62.2/4.1-4.3	C_γ-H_γ in cinnamyl alcohol end-groups (F)
F'_α	126.3-126.8/7.4-7.5	C_α-H_α in cinnamaldehyde end-groups (F′)
F'_6	122.3-124.3/7.1-7.2	C_6-H_6 in cinnamaldehyde end-groups (F′)
F'_β	126.3-126.7/6.7-6.8	C_β-H_β in cinnamaldehyde end-groups (F′)
SB	128.4-129.1/7.1-7.4	Stilbene

Table S2. Quantitative information for subunits and inter-unit linkages of lignin extracted from softwood under different acid treatment.

Lignin units, linkages	MWL-P	Samples		
		L_{H2SO4}	L_{AA}	L_{CA}
Lignin units[a] (% C_9 unit)				
G	97.9	94.6	88.7	96.9
H	2.1	5.4	11.3	3.1
F	ND[b]	6.0	4.4	5.3
F'	ND	2.7	15.2	3.6
SB	ND	37.7	82.4	36.8
Linkages[a] (% C_9 unit)				
β-O-4	40.1	5.5	22.8	17.5
β-O-4'	ND	21.4	2.6	21.3
β-5	13.7	8.5	9.4	12.0
β-β	3.3	1.1	2.6	3.0

[a] Calculated using the quantitative data obtained via 2D HSQC NMR based on previous literature.[28, 29]

[b] ND, not detected.

Table S3. Color evaluation of different lignin ǂ.

Acid type	SCI				SCE			
	*L**	*a**	*b**	*ΔE*	*L**	*a**	*b**	*ΔE*
CA	74.0	5.8	21.7	34.1	74.1	5.8	21.8	32.4
AA	-	-	-	-	-	-	-	-
H_2SO_4	51.1	9.2	26.2	55.9	51.0	9.3	26.3	54.0
AL	38.3	9.7	19.6	65.0	38.6	9.7	19.6	62.7
EHL	45.5	8.8	22.0	59.1	45.6	8.8	22.1	56.9

ǂ Lignin extracted by acetic acid was too sticky to do the color evaluation.

Table S4. Color evaluation of lignin extracted with different conditions.

Condition		SCI				Color
		*L**	*a**	*b**	*ΔE*	
White reference	-	99.5	-0.1	-0.1	0.0	
1,4-BDO concentration (%)	60	77.3	4.8	18.4	29.3	60%
	70	74.0	5.8	21.7	34.1	70%
	80	70.1	6.7	21.3	37.0	80%
	90	66.3	7.4	21.1	40.1	90%
Time (h)	2	68.3	7.0	22.3	39.0	2 h
	4	74.0	5.8	21.7	34.1	4 h
	6	73.2	5.6	21.9	34.7	6 h
	8	70.4	6.1	19.5	35.6	8 h
Citric acid (%)	0	-	-	-	-	-
	5	-	-	-	-	-
	10	74.0	5.8	21.7	34.1	10%
	15	75.8	4.9	24.1	34.3	15%
	20	75.2	4.9	24.1	34.7	20%
Temperature (℃)	110	74.0	5.8	21.7	34.1	110℃
	130	66.2	6.4	17.2	38.1	130℃
	150	68.4	5.9	15.9	35.5	150℃
	180	60.4	7.9	25.6	47.4	180℃

Table S5. Quantitative information for lignin subunits and inter-unit linkages in pretreated lignin.

Lignin units, linkages	MWL-P	Extracting temperature (°C)			
		110	130	150	180
Lignin units[a] (% C_9 unit)					
G	97.9	96.9	96.4	98.0	98.1
H	2.1	3.1	3.6	2.0	1.9
F	ND[b]	5.3	2.0	1.7	1.1
F'	ND	3.6	2.3	1.5	1.2
SB	ND	36.8	23.7	22.0	19.2
Linkages[a] (% C_9 unit)					
β-O-4	40.1	17.5	11.3	7.3	2.9
β-O-4'	ND	21.3	21.2	21.3	8.9
β-5	13.7	12.0	11.9	11.6	10.1
β-β	3.3	3.0	2.3	1.7	1.7

[a] Calculated using the quantitative data obtained via 2D HSQC NMR based on previous literature.[28,29]

[b] ND, not detected

Table S6. Quantification of the functional groups in lignin by ^{31}P NMR spectroscopy.[30]

-OH Content (mmol/g)	chemical shift (ppm)	Extracting Temperature (℃)			
		110	130	150	180
Aliphatic OH	150.0–145.5	2.30	3.47	4.42	2.66
Condensed-OH	144.5–143.2	0.06	0.08	0.09	0.18
	142.2-141.2	0.08	0.12	0.16	0.31
G-OH	141.0-138.4	0.64	0.84	1.01	1.53
H-OH	138.4-137.2	0.20	0.12	0.09	0.06
tricin	137.2-136.5	0.04	0.03	0.02	0.03
carboxylic OH	136.5-133.3	1.02	0.70	0.48	0.33
Total Phenolic OH	144.5-137.2	0.99	1.17	1.35	2.09
Total OH groups	-	4.35	5.36	6.28	5.11

Table S7 SPF values of lignin blended with pure creams, physical sunscreen and chemical sunscreen.

Lignin	0%	2%	5%	10%	20%
SPF 0	1.05±0.45	1.89±0.40	3.11±0.32	5.63±0.24	13.78±0.17
SPF 15-P	12.95±0.48	18.01±0.45	13.85±0.65	8.89±0.26	-
SPF 15-C	10.03±0.07	10.13±1.14	27.63±2.02	30.45±1.43	-

Cartesian coordinates of optimized molecules for DFT calculation

GGE/BDO/H_2O complex in Figure 1b and 1c

C	2.56193500	-3.88458800	0.19447600
H	2.05220900	-4.85586700	0.19796300
H	3.27835900	-3.89183400	1.03229100
C	3.31332600	-3.67982100	-1.12308300
H	3.75317900	-2.67592700	-1.11423900
H	4.16085800	-4.37773200	-1.15619800
O	1.55213000	-2.90619600	0.40510600
H	2.01892600	-2.04751400	0.46666500
C	2.42655900	-3.86225600	-2.37226500
C	2.59244700	-2.76731700	-3.42973400
H	1.36972700	-3.87453500	-2.08290700
H	2.63196500	-4.83372300	-2.84154300
H	3.65213600	-2.63556500	-3.68944200
H	2.05874800	-3.05391800	-4.34309500
O	2.03925400	-1.51884400	-3.01586800
H	2.70666900	-1.02052300	-2.48666400
O	-0.79017900	-0.79355100	1.32833800
H	-1.67538300	-0.41129800	1.14221300
H	-0.83924500	-1.70378100	0.93449800
H	-1.10089200	6.12410100	1.06732300
O	-0.86274500	6.21891300	0.12810800
C	-0.63355500	4.96151300	-0.34283900
C	-0.23792000	4.75911500	-1.65948600
C	-0.79149700	3.85053500	0.51002700
H	-0.10830700	5.62332300	-2.30279400
C	0.00241600	3.46169200	-2.12392500
O	-1.17808700	4.17629900	1.78492500
C	-0.55814800	2.56552000	0.04101300
H	0.32708100	3.31558300	-3.15125300
C	-0.15473700	2.35981600	-1.28561000
C	-1.29933400	3.10894500	2.71888700
H	-0.69304800	1.71945300	0.69686600
C	0.07264200	0.94987300	-1.80426900
H	-0.34532800	2.58243600	2.84261700
H	-2.06672800	2.39716900	2.39221600
H	-1.59654000	3.56792800	3.66311200
C	-1.24893100	0.34095400	-2.31736800
O	0.70786300	0.10966700	-0.85331500
H	0.75429400	0.99577700	-2.66101800
C	-1.09237600	-0.96330700	-3.10646700
O	-2.06686600	0.14048700	-1.15507100
H	-1.71694000	1.08721700	-2.97116200
H	0.05190900	-0.17760700	-0.18157700
O	-0.49384900	-2.01621500	-2.37574500
H	-0.50293800	-0.75039400	-4.00884700
H	-2.08003000	-1.31643900	-3.41876700
H	0.47613800	-1.80845500	-2.31445100
C	-3.42012400	0.30784600	-1.22735000
C	-4.15788400	0.38885700	-2.40617700
C	-4.09103100	0.38451600	0.01308500
H	-3.65878200	0.32791700	-3.36530600
C	-5.54844400	0.53707800	-2.36344400
O	-3.29591300	0.34223200	1.13414900
C	-5.47444100	0.51902100	0.04831200
H	-6.10560400	0.59544700	-3.29327800
C	-6.20552700	0.59543000	-1.14208800
C	-3.93948700	0.15719700	2.39744500
H	-5.99075100	0.56684700	0.99909200
H	-7.28505900	0.69963600	-1.09950500
H	-4.52738100	1.04276400	2.66484900
H	-3.12901600	0.02472200	3.11585900
H	-4.55685100	-0.74315600	2.37126800
C	-1.24673300	-4.27814000	-0.00932900
H	-0.30197500	-4.45564600	-0.53038000
H	-2.03320200	-4.86968700	-0.50070800
C	-1.10216800	-4.68600700	1.45045700
H	-0.69669200	-5.70725700	1.45918800
H	-0.33467100	-4.04343300	1.89976500
O	-1.57256900	-2.88625900	-0.10905800
H	-1.23521600	-2.53584500	-0.97907200
C	-2.38253900	-4.66973300	2.30190300
C	-3.02342400	-3.29707500	2.54790600
H	-2.13620700	-5.10443200	3.28098100
H	-3.14415300	-5.32106200	1.85178100
H	-3.72839200	-3.38063200	3.38316800
H	-2.24310000	-2.57738900	2.84885800
O	-3.78297800	-2.80341600	1.45555700
H	-3.15567300	-2.68584900	0.71140400
C	2.92992500	3.47318800	0.29198700
H	3.70135200	4.25069400	0.34885200
H	1.97507800	3.97037900	0.08450100
C	3.24814200	2.49004800	-0.83457600
H	2.51451700	1.67942700	-0.80514800
H	3.10523200	3.00216000	-1.79673100
O	2.90987600	2.86426400	1.58212800
H	2.15151200	2.25598200	1.63393000
C	4.65999200	1.90588900	-0.76555100
C	4.90344300	0.78443100	-1.77427000
H	4.84607800	1.52649400	0.24676600
H	5.40584200	2.69423600	-0.93975000
H	4.74760800	1.15002300	-2.79673400
H	5.94583400	0.43802100	-1.70438200
O	4.02355400	-0.32696400	-1.59590700
H	3.72376000	-0.36738100	-0.65788300
C	1.58809700	-0.34634800	3.45000700
H	1.61179500	-1.37084900	3.05382300
H	0.80434100	-0.30822700	4.21742700
C	2.93368900	0.02692900	4.05884000
H	2.83287800	0.96808900	4.61187500
H	3.17330800	-0.75087800	4.79639700
O	1.25558000	0.55238300	2.37719100
H	0.45505700	0.15547600	1.95048500
C	4.09374900	0.17437000	3.05287000
C	4.14651600	-0.89464000	1.96447900
H	5.03951600	0.14732900	3.60828100
H	4.03875000	1.15532200	2.56893100
H	5.12148300	-0.88154300	1.46546700
H	4.00016300	-1.89998600	2.38342000
O	3.16034200	-0.67939900	0.93521600
H	2.47101800	-0.05397600	1.27149500

GGE

H	-4.42228500	-0.33494300	-0.54782300

O	-4.09830500	0.51693500	-0.89381800
C	-2.75013700	0.37466400	-1.13010700
C	-2.00418600	1.44992600	-1.59144800
C	-2.11822500	-0.86357100	-0.90566700
H	-2.50201700	2.39777100	-1.77164100
C	-0.62812500	1.30926500	-1.79680400
O	-2.95898500	-1.85305600	-0.45647800
C	-0.75339800	-1.00208600	-1.12693500
H	-0.05028300	2.16374200	-2.12636700
C	0.01489800	0.09779500	-1.54367400
C	-2.37409500	-3.10977000	-0.10753900
H	-0.28243900	-1.95824200	-0.94059400
C	1.53275300	-0.00976300	-1.69745200
H	-3.19395500	-3.72664000	0.26272600
H	-1.62064200	-2.98371800	0.67722500
H	-1.92072100	-3.58799400	-0.98289300
C	2.22103400	-0.83456900	-0.59033200
O	2.14314400	1.27797200	-1.77755600
H	1.76491000	-0.50574700	-2.64836300
C	3.67563400	-1.13691500	-0.91387600
O	2.26649000	-0.09394900	0.65573000
H	1.69851800	-1.78051400	-0.42393600
H	1.93302900	1.71998300	-0.92856900
O	4.28297100	-1.90787700	0.12118400
H	4.21849000	-0.19725600	-1.07876200
H	3.72660700	-1.73245800	-1.82948500
H	4.13258000	-1.40736000	0.94192300
C	1.08394100	-0.03586800	1.37463200
C	0.57665700	-1.15170600	2.02805100
C	0.41036900	1.19724200	1.43526300
H	1.12761300	-2.08542500	1.96861000
C	-0.63595100	-1.06620600	2.71852900
O	1.00986300	2.23634400	0.77380300
C	-0.80302600	1.28119900	2.12076900
H	-1.03644500	-1.94118300	3.22046700
C	-1.32271400	0.14624900	2.75300800
C	0.30536700	3.48081100	0.71620700
H	-1.34890800	2.21602800	2.15891800
H	-2.26962200	0.22295000	3.27865100
H	0.18620700	3.90440700	1.71896100
H	-0.67463300	3.35450300	0.24634800
H	0.92492900	4.14070800	0.10825300

IM1

H	-4.46940200	-0.37077800	-0.69793900
O	-4.14912700	0.47050700	-1.07433400
C	-2.79525800	0.35166800	-1.25029900
C	-2.06476700	1.40418900	-1.78498600
C	-2.13794100	-0.84269300	-0.89557700
H	-2.58186500	2.31485300	-2.06904200
C	-0.68261500	1.28664700	-1.94656100
O	-2.96530800	-1.81224900	-0.39456100
C	-0.76311800	-0.95868400	-1.05571400
H	-0.12955600	2.12550300	-2.35075800
C	-0.01739300	0.12060200	-1.55771900
C	-2.37455700	-3.05085300	0.01086200
H	-0.27932900	-1.88098500	-0.76865000
C	1.49266500	0.03224300	-1.66842300
H	-3.19750000	-3.66381600	0.37980500
H	-1.64428900	-2.88907600	0.81032400
H	-1.89352100	-3.54952600	-0.83782700
C	2.21530100	-0.85131600	-0.63437700
O	1.99019500	1.44203800	-1.51418400
H	1.81522400	-0.23521200	-2.67696300
C	3.64027800	-1.21347800	-1.03459400
O	2.32300000	-0.16847100	0.63192400
H	1.66012500	-1.78223800	-0.50396800
H	1.75030400	1.78691400	-0.56317900
O	4.22537200	-2.07747300	-0.07045100
H	4.24409900	-0.30455400	-1.17193300
H	3.61378600	-1.75517500	-1.98353800
H	4.18229800	-1.60548000	0.77910200
C	1.15754400	-0.08928700	1.38368800
C	0.64794600	-1.19456100	2.05196300
C	0.49905400	1.14719100	1.44810400
H	1.18314600	-2.13662400	1.98614700
C	-0.54745800	-1.08182000	2.76601900
O	1.10430200	2.19015200	0.76632800
C	-0.69808000	1.26221700	2.14998200
H	-0.95107800	-1.94588300	3.28341300
C	-1.21806900	0.14001500	2.80294400
C	0.38444800	3.43609100	0.65580000
H	-1.22770000	2.20598700	2.19000200
H	-2.15260500	0.23370300	3.34675500
H	0.27068900	3.88349500	1.64567000
H	-0.59050900	3.27226800	0.19052300
H	1.00495300	4.07157400	0.02493200
H	2.95979700	1.51965600	-1.64825900

IM2

H	-4.43847300	-0.00497200	-1.30021800
O	-3.99308500	0.69669800	-1.82365600
C	-2.68443300	0.52401400	-1.75415100
C	-1.83533500	1.42649900	-2.42932000
C	-2.15850700	-0.57548500	-0.99843000
H	-2.28184700	2.24154100	-2.98674800
C	-0.48234900	1.25016300	-2.34492100
O	-3.12625900	-1.33007600	-0.42840200
C	-0.80582400	-0.76239600	-0.92274900
H	0.19525500	1.93896700	-2.83728900
C	0.07885500	0.16176200	-1.58522700
C	-2.71554800	-2.45785300	0.36128000
H	-0.40021800	-1.59240400	-0.36260600
C	1.44611500	0.11227100	-1.45678700
H	-3.63760100	-2.91620900	0.71700600
H	-2.10511600	-2.12607400	1.20687300
H	-2.15451100	-3.16798000	-0.25440200
C	2.20966400	-0.82934100	-0.58718500
H	2.02966800	0.88370500	-1.95439500
C	3.61669100	-1.11467800	-1.08611900
O	2.37366800	-0.13582800	0.69432600
H	1.68749600	-1.77196100	-0.41364800
O	4.28652100	-2.00820200	-0.20895100
H	4.16160700	-0.16629300	-1.19415700
H	3.56238700	-1.59746100	-2.06564700
H	4.29115000	-1.58131700	0.66527800
C	1.26793000	-0.20987000	1.52767800
C	0.98958900	-1.37563400	2.23338500
C	0.42788600	0.91587100	1.62847300
H	1.66079600	-2.22197600	2.12262600
C	-0.13856700	-1.43911600	3.05264300
O	0.79702600	2.00328300	0.89606500
C	-0.70904700	0.84284500	2.44017200
H	-0.35572600	-2.34521700	3.60873500
C	-0.98359500	-0.33089300	3.14553200
C	-0.18343500	3.02847000	0.70249700
H	-1.37690000	1.69181800	2.52341200
H	-1.86822100	-0.37366100	3.77348000
H	-0.38688700	3.56067700	1.63786700
H	-1.11145100	2.60637800	0.30425800
H	0.25035300	3.71744800	-0.02317500

IM3

H	-4.28794700	0.47300300	-0.68365300
O	-3.75764800	1.16295100	-1.12386700
C	-2.49166700	0.65276300	-1.30029700
C	-1.49649700	1.44258100	-1.85941000
C	-2.20240400	-0.66956100	-0.90707400
H	-1.73690200	2.45752400	-2.15950500
C	-0.19973800	0.93740400	-1.99351800
O	-3.26951000	-1.34292700	-0.36411200
C	-0.91982300	-1.17799800	-1.06743300
H	0.58487600	1.57131400	-2.39332700
C	0.10279800	-0.36486900	-1.58982700
C	-3.01624000	-2.63243400	0.19927900
H	-0.68451700	-2.18346700	-0.74080200
C	1.49726400	-0.86665100	-1.64343900
H	-3.96611000	-2.96534000	0.61962600
H	-2.26073600	-2.56849800	0.98986300

H	-2.68720600	-3.33910700	-0.57058100
C	2.46908700	-0.46604000	-0.81630700
H	1.76098800	-1.61987400	-2.38301500
C	3.89915100	-0.90590100	-0.86789500
O	2.26435500	0.43684300	0.23468300
O	4.28916400	-1.57587600	0.33844000
H	4.54782100	-0.03530700	-1.04407200
H	4.04279000	-1.61280600	-1.68742700
H	4.14245900	-0.94281900	1.06235400
C	1.20952800	0.15628300	1.10225600
C	1.09034200	-1.08919600	1.70514400
C	0.28305600	1.17911600	1.36753400
H	1.83442100	-1.84708800	1.48322700
C	0.00953100	-1.35414200	2.54958100
O	0.51140800	2.37682800	0.75252700
C	-0.79919600	0.90713000	2.21017800
H	-0.08817900	-2.33132200	3.01180800
C	-0.93573200	-0.35776500	2.79034900
C	-0.49690600	3.38143700	0.88303900
H	-1.53869300	1.67288200	2.41018600
H	-1.78489800	-0.55347500	3.43792000
H	-0.59519800	3.70857000	1.92416200
H	-1.46306000	3.01842900	0.51707900
H	-0.16194400	4.21737800	0.26741900

GGE etherification by BDO

H	3.21116300	-3.64155900	-0.52807800
O	2.44632300	-3.70380500	0.07360500
C	1.61317800	-2.64861100	-0.22096100
C	0.45072100	-2.45139600	0.51002900
C	1.94075400	-1.76291400	-1.26748000
H	0.20858600	-3.14411700	1.30977800
C	-0.36974100	-1.35139700	0.23535100
O	3.11801500	-2.06068600	-1.90979600
C	1.10366800	-0.69491900	-1.56173700
H	-1.24604400	-1.17185300	0.84642100
C	-0.04832000	-0.46700800	-0.79044600
C	3.59011200	-1.12830500	-2.88480200
H	1.36024600	-0.00813600	-2.36025600
C	-0.86028300	0.79779100	-1.03131200
H	4.55078000	-1.51573100	-3.22663000
H	3.72661000	-0.13710500	-2.43922400
H	2.89833800	-1.06228000	-3.73185400
C	-0.03705100	2.06027200	-0.73232600
O	-2.04867600	0.83462900	-0.25198900
H	-1.12414400	0.86593500	-2.09811600
C	-0.84198000	3.34618800	-0.81716200
O	0.53034200	2.03744000	0.59960800
H	0.76782200	2.10990700	-1.46870800
O	0.01218400	4.48466800	-0.70062700
H	-1.61563600	3.35377500	-0.04039600
H	-1.33063500	3.40991200	-1.79329900
H	0.48680300	4.37120700	0.14121300
C	1.80022900	1.50527600	0.73147800
C	2.86517000	1.89629300	-0.07423900
C	2.00062900	0.55883700	1.75667600
H	2.70814400	2.66439900	-0.82436000
C	4.11839600	1.29329200	0.07139300
O	0.91823000	0.29904400	2.54980600
C	3.25227200	-0.04696600	1.89341400
H	4.93909600	1.59643100	-0.57112400
C	4.30306100	0.31210300	1.04267300
C	1.06158600	-0.71312900	3.54650300
H	3.41180700	-0.80075700	2.65481000
H	5.26766700	-0.17277700	1.15772900
H	1.82049100	-0.43438400	4.28645500
H	1.32278000	-1.67658300	3.09624100
H	0.08767200	-0.78903400	4.03232000
C	-3.12958700	0.10128200	-0.83658800
C	-4.28448600	0.08260600	0.14875600
H	-2.80712600	-0.92193200	-1.07051600
H	-3.42552900	0.58393800	-1.77987800
C	-5.49985500	-0.65771100	-0.41362100
H	-3.95086000	-0.39720800	1.07798400
H	-4.55578800	1.11616800	0.39954200
C	-6.65398100	-0.69122900	0.57495800
H	-5.83843500	-0.17471100	-1.33952000
H	-5.22400200	-1.68870100	-0.67124500
H	-6.33693900	-1.18429300	1.50589000
H	-6.95960300	0.33391300	0.83189000
O	-7.74339200	-1.40457900	-0.02390900
H	-8.46443600	-1.42022800	0.62602000

GGE esterification by acetic acid

H	3.83579600	-3.68023300	-0.85585100
O	3.10105900	-3.89924100	-0.25347700
C	2.12458800	-2.94855900	-0.44405600
C	0.96037800	-2.98336300	0.30995400
C	2.30648100	-1.93411000	-1.40593000
H	0.83246500	-3.77334000	1.04320900
C	-0.00995000	-1.98880900	0.14412700
O	3.50013600	-2.00525000	-2.08166900
C	1.32361400	-0.97153900	-1.59406700
H	-0.89118900	-1.98952000	0.77427100
C	0.16660400	-0.97911100	-0.79740200
C	3.82308900	-0.92792700	-2.96403600
H	1.46597300	-0.18485700	-2.32655400
C	-0.81806200	0.17367200	-0.91686700
H	4.82184200	-1.14469800	-3.34525100
H	3.82961200	0.02557700	-2.42524000
H	3.11432900	-0.87799400	-3.79808200
C	-0.17716300	1.50688400	-0.49254300
O	-1.98773100	-0.02413900	-0.13425500
H	-1.10406600	0.30522500	-1.97157600
C	-1.19792700	2.62331000	-0.44895400
O	0.41880500	1.43201900	0.81722700
H	0.58362000	1.75558400	-1.23461400
O	-0.45025500	3.85672300	-0.34427900
H	-1.85351100	2.50732100	0.41491400
H	-1.79298000	2.62630800	-1.36572400
C	1.75819600	1.09196200	0.87994300
C	2.73076100	1.70759100	0.09795500
C	2.12587800	0.10142300	1.81333800
H	2.44322900	2.50368600	-0.58074100
C	4.06411900	1.29292300	0.17514500
O	1.11535600	-0.39177200	2.59057100
C	3.45802600	-0.31298800	1.88345000
H	4.81242000	1.77127300	-0.44894100
C	4.42046700	0.27393000	1.05505800
C	1.43392900	-1.46377700	3.47822000
H	3.74921800	-1.09482800	2.57421000
H	5.45026800	-0.06451900	1.11603200
H	2.15670200	-1.14572700	4.23822000
H	1.83035300	-2.32520700	2.93054500
H	0.49400000	-1.73743100	3.95985500
C	-2.97173600	-0.83806500	-0.78139500
C	-4.10860400	-1.08000300	0.19515100
H	-2.52397700	-1.79000400	-1.09569000
H	-3.33115500	-0.32110800	-1.68338900
C	-5.22603700	-1.91802300	-0.42969200
H	-3.71171300	-1.58751500	1.08387300
H	-4.50472400	-0.11173600	0.52724300
C	-6.36141200	-2.17345700	0.54813100
H	-5.62750200	-1.40799400	-1.31509200
H	-4.82603800	-2.88272900	-0.76836300
H	-5.98132100	-2.69919000	1.43656200
H	-6.78816200	-1.21785900	0.88736900
O	-7.35914100	-2.96230900	-0.11268100
H	-8.06910800	-3.11971800	0.53039700
C	-1.08577700	5.04311800	-0.21746100
O	-0.39348000	6.04545700	-0.14042300
C	-2.58735300	5.05320500	-0.17710000
H	-3.00405000	4.59374400	-1.07929900
H	-2.95092800	4.48081200	0.68306500
H	-2.93006600	6.08506000	-0.09928300

GGE esterification by citric acid

H	-7.03031200	-1.03040100	-1.14147600

O	-6.85414300	-0.27514400	-0.55045800
C	-5.51266000	0.01428900	-0.65204800
C	-4.95932500	1.03399200	0.10895900
C	-4.69620200	-0.72625500	-1.53090900
H	-5.60149600	1.59896800	0.77714300
C	-3.58694900	1.29699700	0.03386800
O	-5.35935800	-1.70926900	-2.22392900
C	-3.34209900	-0.43610800	-1.63075900
H	-3.15161100	2.05806800	0.67010000
C	-2.77342000	0.56497300	-0.82604500
C	-4.57222000	-2.60162600	-3.01607900
H	-2.71035100	-1.01010700	-2.29918900
C	-1.26520500	0.75761200	-0.84655100
H	-5.27132300	-3.33228000	-3.42496300
H	-3.82270700	-3.10865900	-2.39893000
H	-4.07829600	-2.06742100	-3.83528000
C	-0.53044700	-0.48773900	-0.31865600
O	-0.84596900	1.87540400	-0.07566500
H	-0.92527700	0.88471700	-1.88562000
C	0.95546500	-0.23320300	-0.19151200
O	-1.00362300	-0.88833500	0.98125500
H	-0.68702700	-1.29377900	-1.03814000
O	1.57358900	-1.52182200	0.04846900
H	1.16363600	0.43286000	0.64685500
H	1.34002300	0.20122300	-1.11674500
C	-2.02971700	-1.81623900	1.01520000
C	-2.00058300	-3.00012100	0.28470600
C	-3.12034700	-1.53618500	1.86326000
H	-1.13372200	-3.22693600	-0.32695100
C	-3.08631100	-3.88055700	0.32548600
O	-3.02685000	-0.38655600	2.59589500
C	-4.20470600	-2.41638700	1.89735800
H	-3.05893400	-4.79489000	-0.25886200
C	-4.19045400	-3.57856800	1.11882600
C	-4.15268200	-0.02385500	3.39543300
H	-5.06349900	-2.19879300	2.52066200
H	-5.04424600	-4.24852900	1.15030800
H	-4.33553200	-0.76694400	4.18002500
H	-5.05196400	0.09231700	2.78159000
H	-3.89502700	0.93320000	3.85145300
C	-0.94547500	3.11896700	-0.77764200
C	-0.57337200	4.23661200	0.18004900
H	-1.96732800	3.25686800	-1.15479100
H	-0.26676400	3.10053600	-1.64307200
C	-0.62432400	5.60791500	-0.49678700
H	-1.26102100	4.21535300	1.03536100
H	0.43420800	4.04766300	0.57229800
C	-0.25495100	6.72880700	0.46120300
H	0.06329900	5.63032200	-1.35232000
H	-1.63237600	5.79461400	-0.88956100
H	-0.94224000	6.73073700	1.32021000
H	0.76122300	6.57037800	0.85181400
O	-0.33232500	7.97324100	-0.24570900
H	-0.09687900	8.67316200	0.38452400
C	2.91028900	-1.65093500	0.09626800
O	3.37253600	-2.75974000	0.31101100
C	3.75548800	-0.42392000	-0.15362500
H	3.63330400	-0.12995700	-1.20111600
H	3.40157800	0.41234700	0.45589000
C	5.23098100	-0.65675800	0.16924900
C	6.04646800	0.58343700	-0.30330500
H	5.85912700	0.76970200	-1.36124700
H	5.70517700	1.44080300	0.28446100
C	5.80669200	-1.88898400	-0.54611200
O	6.60431700	-2.64709400	-0.02674300
C	7.53328000	0.40510300	-0.11679000
O	8.34719000	0.32029500	-1.01777100
O	7.87533800	0.31825600	1.18915200
H	8.8335600	0.15142800	1.24283200
O	5.42675600	-1.96687700	-1.83094300
H	5.88315200	-2.73147300	-2.23731300
O	5.32001300	-0.83908600	1.56897400
H	6.26179000	-0.94884700	1.79346600

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