Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

A strategy for generating high-quality cellulose and lignin simultaneously from woody biomass

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Materials

Beech (Fagus sylvatica) sawdust was obtained from Dansk Træmeland. 1,4-Dioxane, methanol, ethanol, tetrahydrofuran, benzene, sulfuric acid, sodium hydroxide, glucose and nickel nitrate hexahydrate were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd.. Activated charcoal and tetrahydrofurfuryl alcohol (98%) were purchased from Aladdin Chemistry CO., Ltd.. D-xylose and eugenol (99%) were purchased from Alfa Aesar. 4-Methylsyringol (98%), syringol (98%), 4-ethylguaiacol (98%) and 4-methylguaiacol (99%) were purchased from J&K Chemical Ltd.. 3-(4-Hydroxy-3-methoxyphenyl)-1-propanol (98%) was purchased from TCI. 4-Propylguaiacol (99%) and [D6]DMSO were purchased from Sigma-Aldrich. Isoeugenol (99%) and 1,2,4,5-tetramethylbenzene (99%) were purchased from Acros Organics. All of chemicals were used as received without further purification.

Lignin model compounds

1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol: The β-O-4 model compound of guaiacylglycerol-β-guaiacyl ether (GGGE) was synthesized following the previously reported,[1, 2] the obtained NMR spectra data are consistent with those described in the literature.[3, 4]

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.14-6.84 (m, 7H, aromatic H), 5.60 (s, 1H, Ar-OH), 4.96 (d, 1H, $C_\alpha H$), 4.02 (m, 1H, $C_\beta H$), 3.91 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.63 (d, 1H, C_α-OH), 3.64 (m, 1H, $C_\gamma H$), 3.48 (m, 1H, $C_\gamma H$), 2.67 (m, 1H, C_γ-OH).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 151.5, 147.7, 146.8, 145.7, 131.6, 124.5, 121.9, 121.3, 120.4, 114.5, 112.3, 109.5, 89.8 (threo C_β), 87.6 (erythro C_β), 74.2 (threo C_α), 72.9 (erythro C_α), 61.2 (threo C_γ), 61.9 (erythro C_γ), 56.1 (Ar-OCH_3), 56.1 (Ar-OCH_3).

THFA substitution of GGGE model compound: GGGE (0.10 g) was dissolved in 1,4-dioxane (10 mL). After the addition of THFA (0.15 mL) and 37 wt% HCl solution (0.15 mL), the mixture was heated to 45 °C and refluxed for 10 h. The mixture was quenched by addition of $NaHCO_3$ and stirred for 1 h. Then dried $MgSO_4$ was added to remove H_2O. After filtration, the mixture was concentrated by rotary evaporation and dried under vacuum. The model compound of GGGE modified by THFA at C_α position was obtained as pale yellow oil.

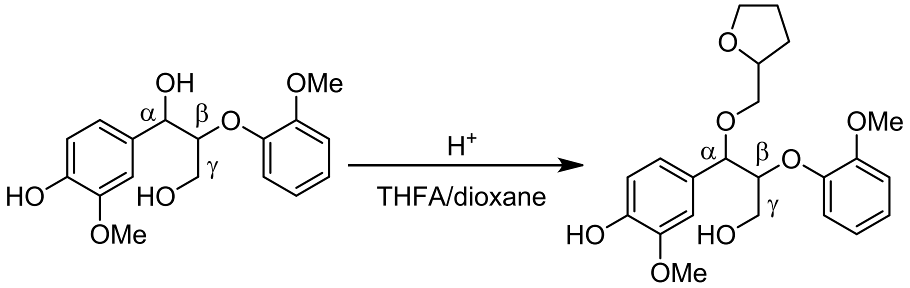


Table S1. The treatment in different mixed solvents[a]

Solvent	Isolated fraction yield (wt%)[b]			Pulp composition (wt%)[d]			Delignification (%)	Purity of cellulose (%)[e]
	Pulp	Precipitate	Liquid[c]	Cellulose	Lignin	Hemicellulose		
1,4-Dioxane/H_2O	67.3	6.4	26.3	45.3	10.1	11.8	52.4	67.4
Methanol/H_2O	64.3	6.6	29.1	45.5	5.9	9.9	72.2	70.7
Ethanol/H_2O	59.1	12.4	28.5	43.6	5.0	10.2	76.2	73.9
Tetrahydrofuran/H_2O	54.6	15.7	29.7	43.6	4.4	5.9	79.0	79.8
THFA/H_2O	54.4	14.5	31.1	44.8	2.8	6.4	86.8	82.4

[a] The solvent thermal treatment conditions: 2 g beech sawdust, 24 mL mixed solvent (v/v, 6/4), 175 °C, 200 min, 1 atm N_2, 1000 rpm. [b] The yield of pulp, precipitate and liquid were the mass percentage relative to the mass of raw beech sawdust, the total yield of pulp, precipitate, liquid were 100%. [c] The yield of liquid fraction was calculated according to the yield of pulp and precipitate fractions, and liquid fraction mainly contains hemicellulose, along with soluble lignin, cellulose, pectin, protein, etc. [d] Pulp composition was the mass percentage of cellulose, lignin and hemicellulose relative to the mass of raw beech sawdust. [e] Purity of cellulose was measured in cellulose pulp.

Table S2. Recovered lignin and retained cellulose from solvent thermal treatment

Solvent	Recovered lignin (%)	Retained cellulose (%)
1,4-Dioxane/H_2O	30.2	96.4
Methanol/H_2O	31.1	96.8
Ethanol/H_2O	58.5	92.8
Tetrahydrofuran/H_2O	74.1	92.8
Tetrahydrofurfuryl alcohol/H_2O	68.4	95.3

After THFA/H_2O treatment at 175 °C, the recovered lignin and retained cellulose in cellulose pulp were calculated as follows:

$$Recovered\ lignin(\%) = \frac{14.5}{21.2} \times 100\% = 68.4\%$$

$$Retained\ cellulose(\%) = \frac{44.8}{47.0} \times 100\% = 95.3\%$$

Table S3. The content of hemicellulose in cellulose pulp and liquid fractions[a]

Solvent	Pulp fraction (%)	Liquid fraction (%)
1,4-Dioxane/H_2O	56.5	43.5
Methanol/H_2O	47.4	52.6
Ethanol/H_2O	48.8	51.2
Tetrahydrofuran/H_2O	28.2	71.8
THFA/H_2O	30.6	69.4

[a] The total percentage of hemicellulose in cellulose pulp and liquid fractions were 100%, the hemicellulose in liquid fraction was calculated according to the percentage of hemicellulose in cellulose pulp.

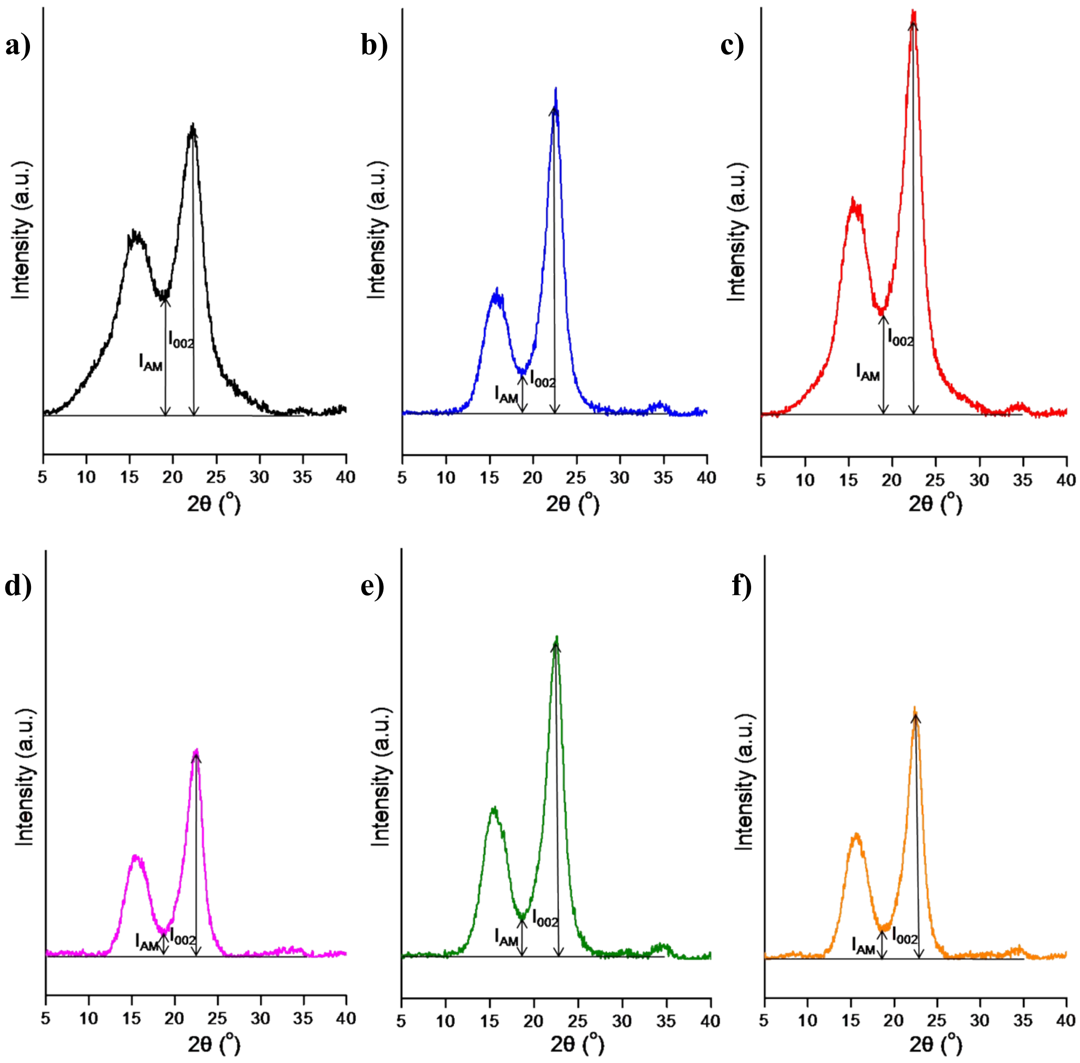


Fig. S1. XRD patterns of samples. a) Raw beech sawdust, and cellulose pulp from the treatment in b) 1,4-dioxane/H_2O, c) methanol/H_2O, d) ethanol/H_2O, e) tetrahydrofuran/H_2O, f) THFA/H_2O.

Table S4. Recovered lignin and retained cellulose from the THFA/H_2O treatment

Treatment temperature (°C)	Recovered lignin (%)	Retained cellulose (%)
170	49.1	91.7
175	68.4	95.3
180	75.5	97.0
185	75.9	97.9
190	77.4	92.8
195	80.7	93.0
200	80.7	91.7
175[a]	70.9	72.8

[a] The treatment was performed in THFA/H_2O with 0.01 M H_2SO_4 at 175 °C.

After THFA/H_2O treatment at 190 °C, the recovered lignin and retained cellulose in cellulose pulp were calculated as follows:

$$Recovered\ lignin(\%) = \frac{16.4}{21.2} \times 100\% = 77.4\%$$

$$Retained\ cellulose(\%) = \frac{43.6}{47.0} \times 100\% = 92.8\%$$

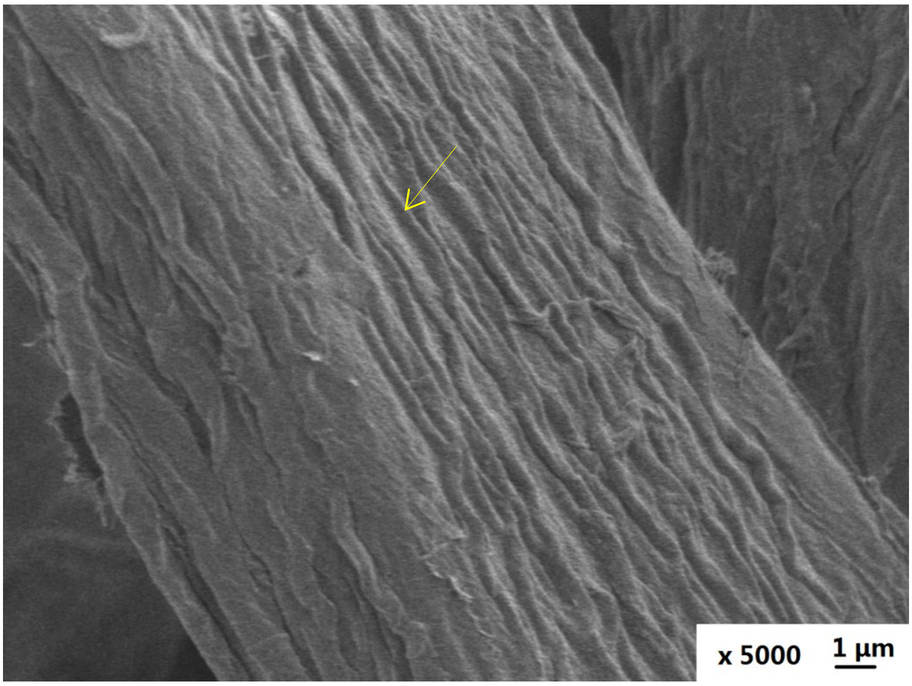


Fig. S2. SEM image of cellulose pulp. The cellulose pulp was from the treatment in THFA/H_2O at 190 °C. The arrow in figure indicates macrofibrils presented in the surface of cellulose fibers. Reaction condition: 2 g beech sawdust, 14.4 mL THFA and 9.6 mL H_2O mixed solvent, 190 °C, 200 min, 1 atm N_2, 1000 rpm.

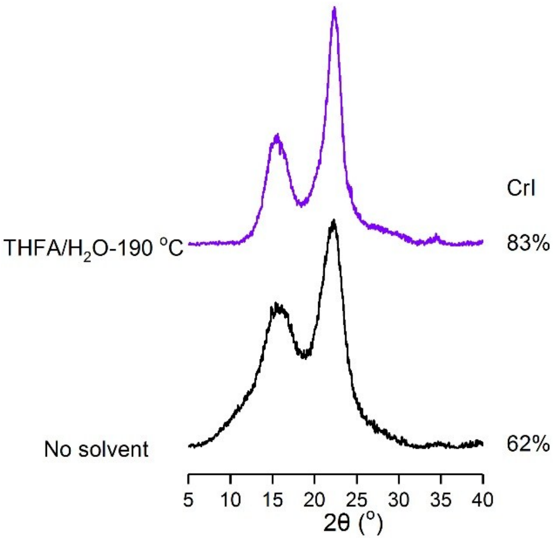


Fig. S3. XRD patterns of raw beech sawdust and cellulose pulp. The cellulose pulp was from the treatment in THFA/H_2O at 190 °C.

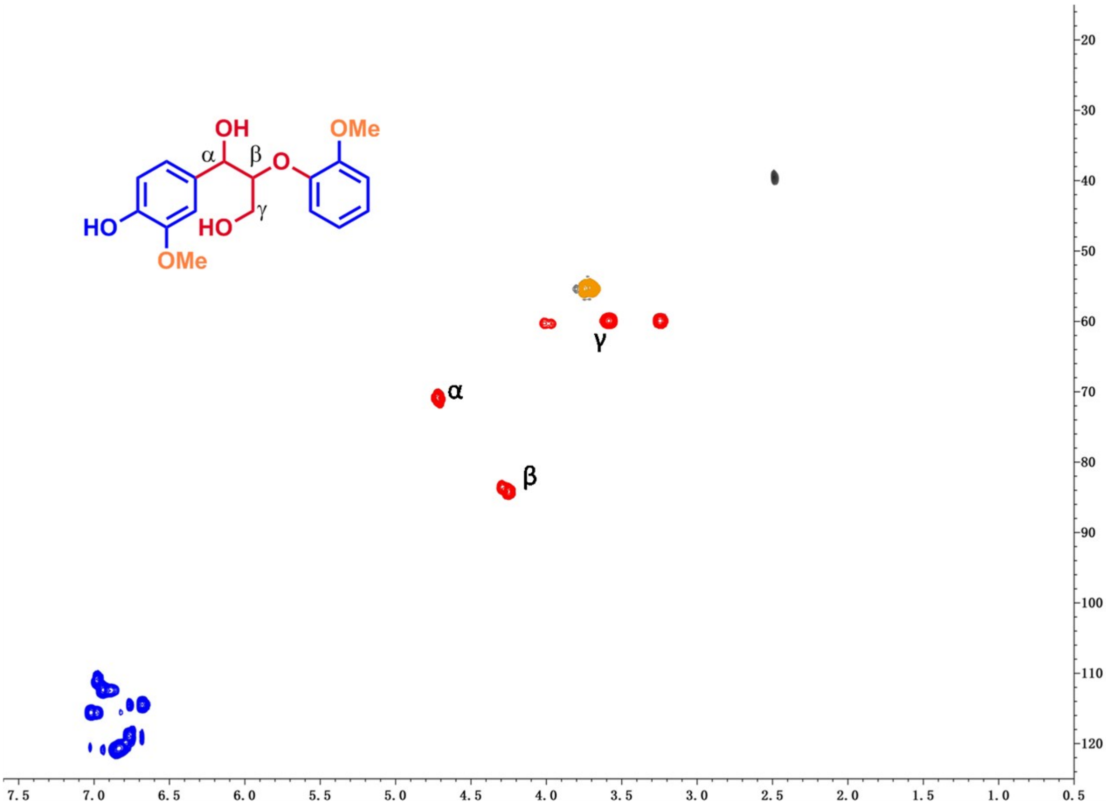


Fig. S4. 2D NMR spectra of lignin model compound GGGE.

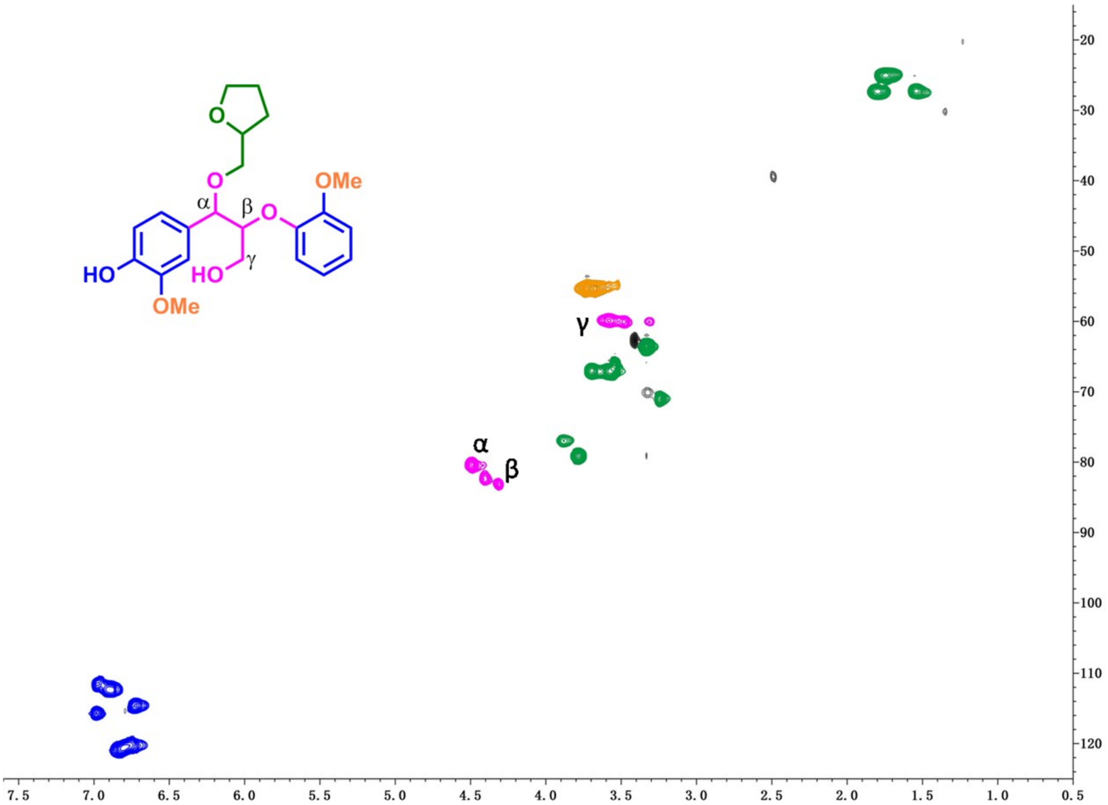


Fig. S5. 2D NMR spectra of lignin model compound GGGE modified by THFA.

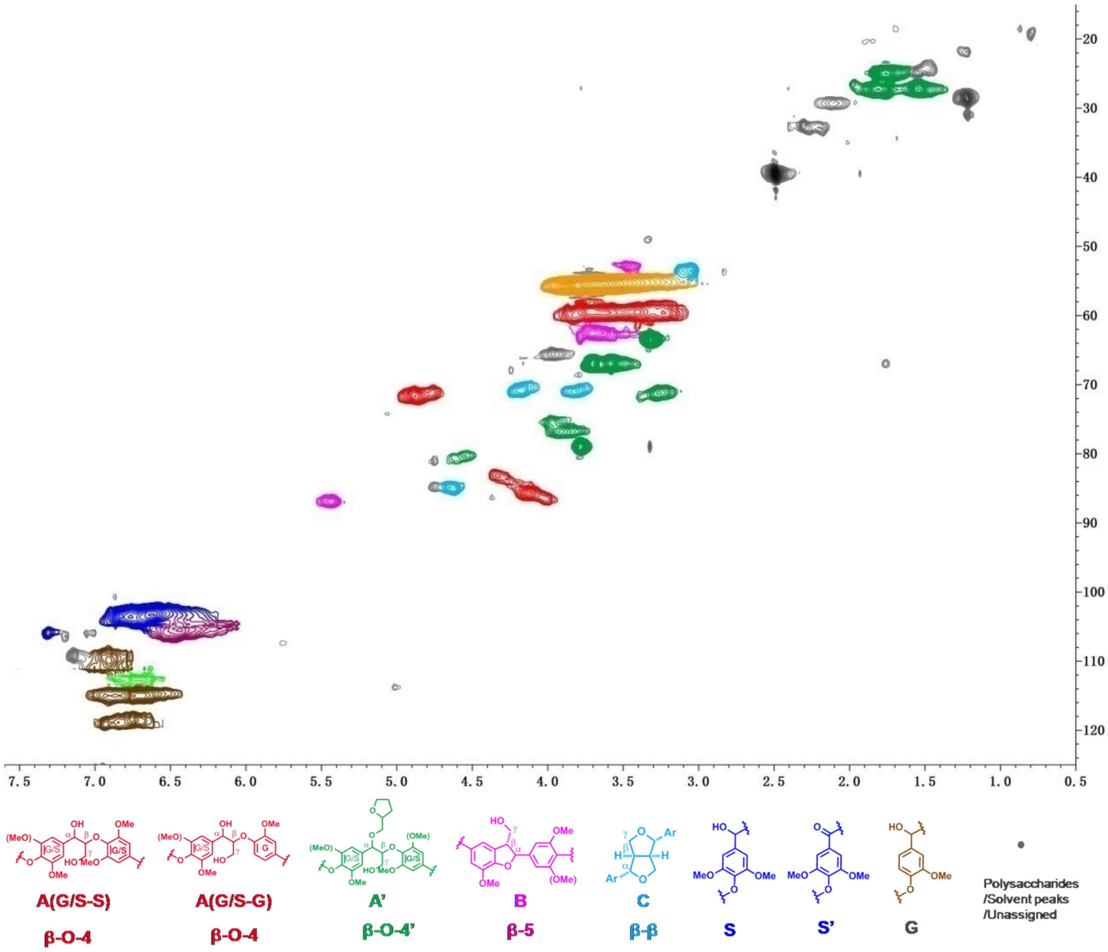


Fig. S6. The full 2D NMR spectra of THFA lignin. It was from the treatment in THFA/H_2O at 200 ^{o}C.

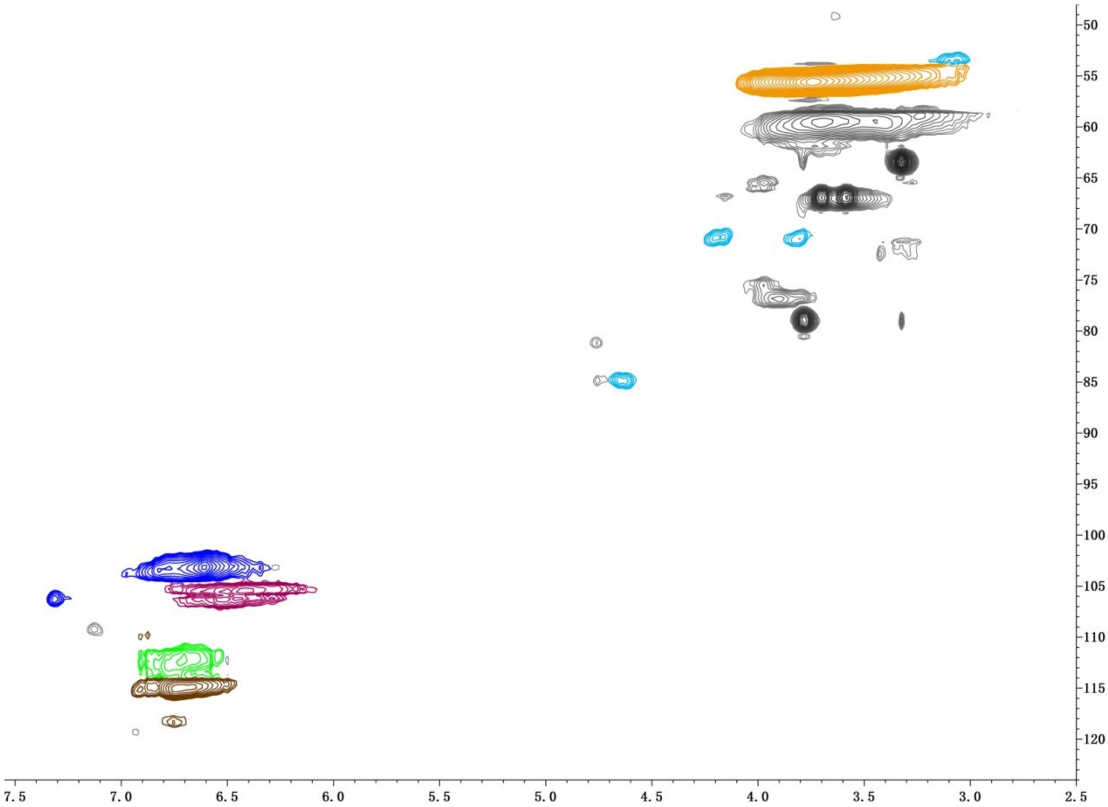


Fig. S7. 2D NMR spectra of powder lignin. It was from the treatment in THFA/H_2O with 0.01 M H_2SO_4 at 175 ^oC.

Table S5. Amount of inter-unit linkages (% of C9 units) and S/G ratio in THFA lignin

Treatment temperature (°C)	Total β-O-4 (%)	β-5 (%)	β-β (%)	Condensed (%)	S/G ratio
170	48.1	4.6	8.1	3.8	2.5
175	40.1	5.0	8.2	6.4	2.7
180	36.1	5.0	8.1	8.8	2.4
185	31.8	5.0	7.8	11.1	2.6
190	24.3	4.9	7.2	15.8	2.4
195	22.8	5.1	6.9	17.5	3.1
200	20.1	5.1	7.1	19.6	3.5
175[a]	0	0	4.7	57.3	1.7

[a] The treatment was performed in THFA/H_2O with 0.01 M H_2SO_4 at 175 °C.

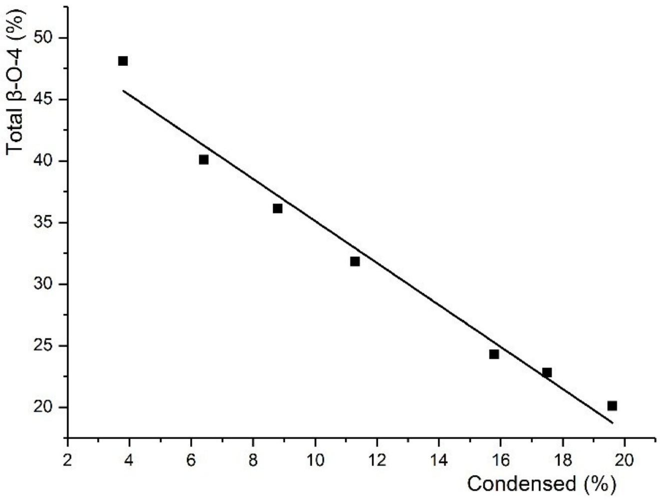
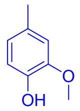
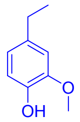
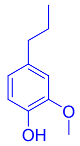
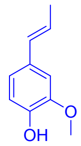
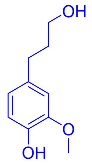
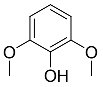
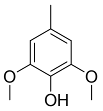
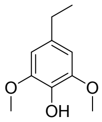
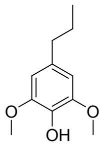
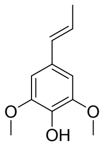
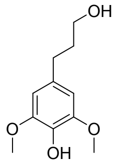


Fig. S8. The linear negative correlation between the percentage of total β-O-4 linkages and condensed linkages.

Table S6. Identified phenolic monomers in the catalytic depolymerization of THFA lignin

Retention time (min)	Molecule and name	Standard used for GC-FID quantification	Category
11.002	 4-Methylguaiacol	4-Propylguaiacol	G-type monomers
12.235	 4-Ethylguaiacol	4-Propylguaiacol	G-type monomers
13.426	 4-Propylguaiacol	4-Propylguaiacol	G-type monomers
14.486	 4-Propenylguaiacol	4-Propylguaiacol	G-type monomers
16.935	 Guaiacylpropanol	Guaiacylpropanol	G-type monomers
13.169	 Syringol	4-Propylsyringol	S-type monomers
14.400	 4-Methylsyringol	4-Propylsyringol	S-type monomers

15.375	 4-Ethylsyringol	4-Propylsyringol	S-type monomers
16.372	 4-Propylsyringol	4-Propylsyringol	S-type monomers
17.661	 4-Propenylsyringol	4-Propylsyringol	S-type monomers
20.482	 Syringylpropanol	4-Propylsyringol[a]	S-type monomers

[a] The monomers were quantified by using the 4-propylsyringol standard curve and further correcting with the calibration factor between guaiacylpropanol and 4-propylguaiacol.

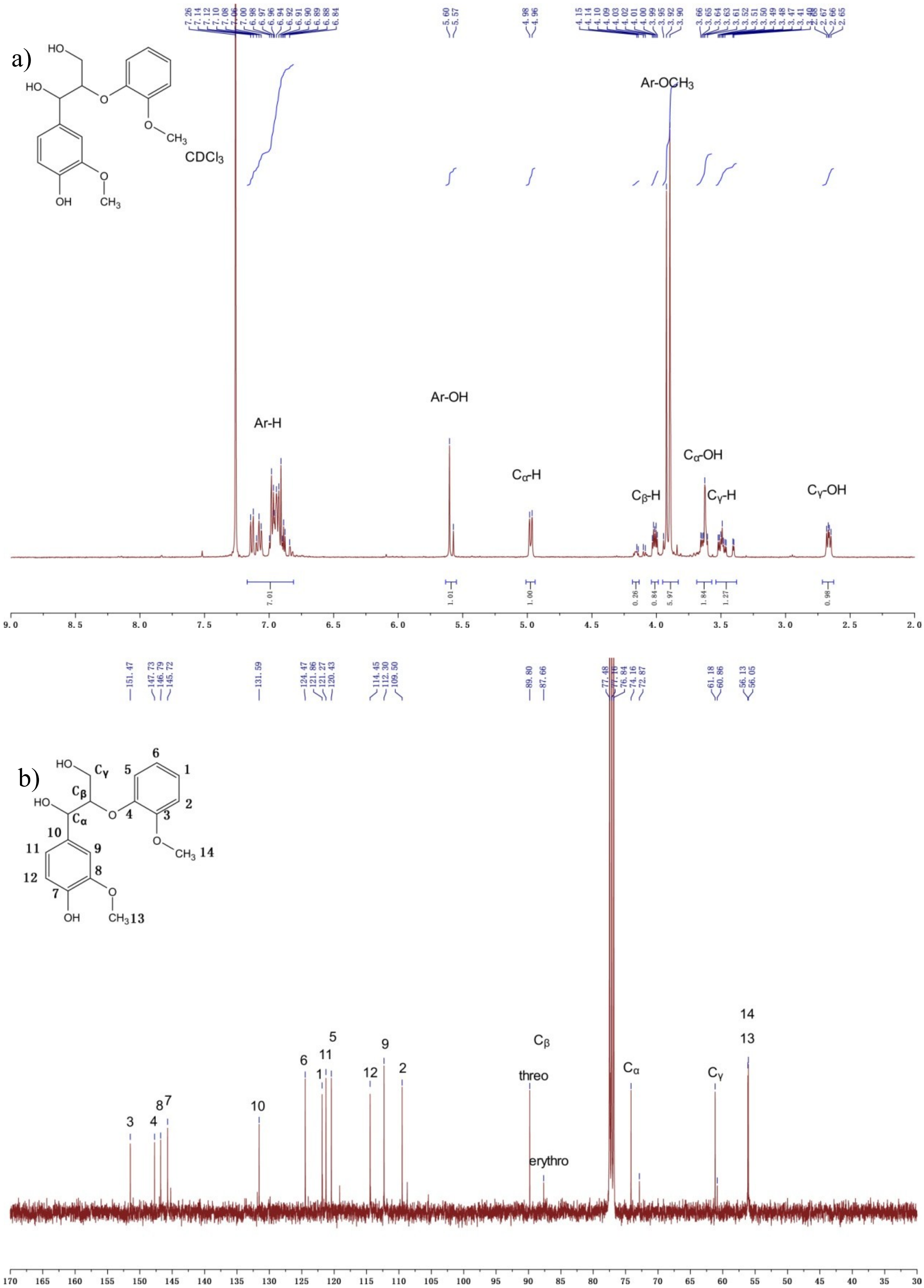


Fig. S9. a) ^{1}H and b) ^{13}C NMR spectra of lignin model compound GGGE.

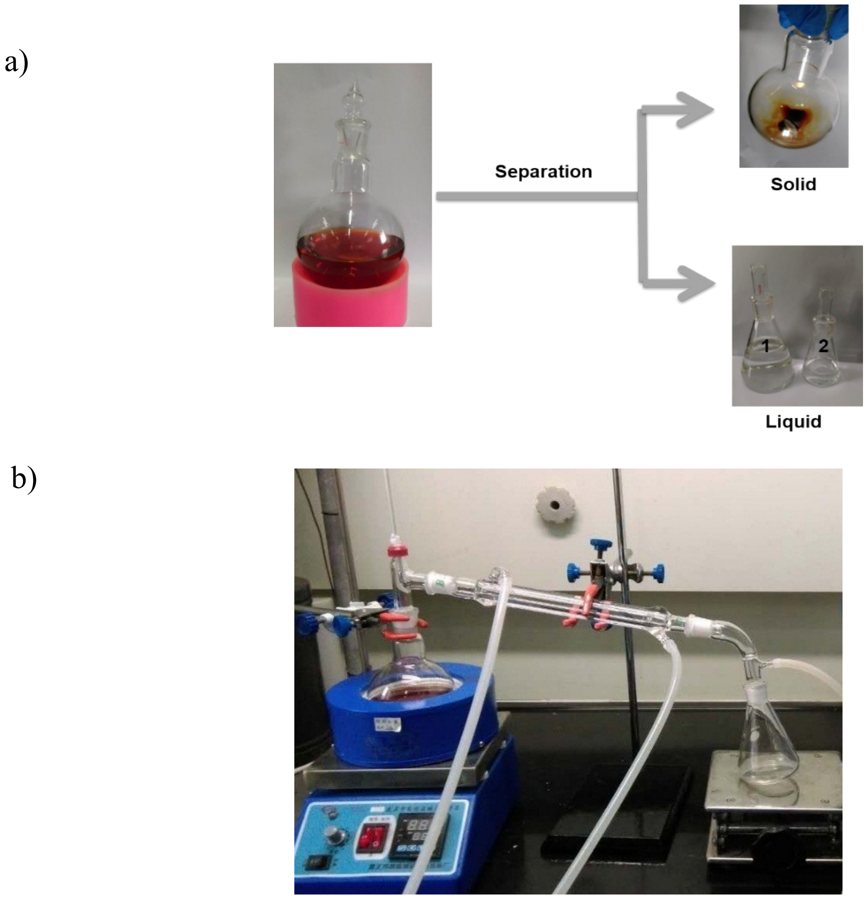


Fig. S10. a) The fractionation of liquid fraction from solvent thermal treatment in THFA/H_2O at 175 ^oC. After separation, solid contains most hemicellulose and soluble lignin. THFA and H_2O were separated and recycled by distillation, liquid 1 was H_2O with the recovery efficiency reaching 99.3%, and it was separated by atmospheric distillation at 115 ^oC. Liquid 2 was THFA with the recovery efficiency reaching 72.3%, and it was separated by vacuum distillation at 110 ^oC. The GC chromatogram of liquid 1 and 2 were listed in Fig. S11. H_2O and THFA were recycled and could be reused. b) The distilling apparatus used in the fractionation of liquid fraction.

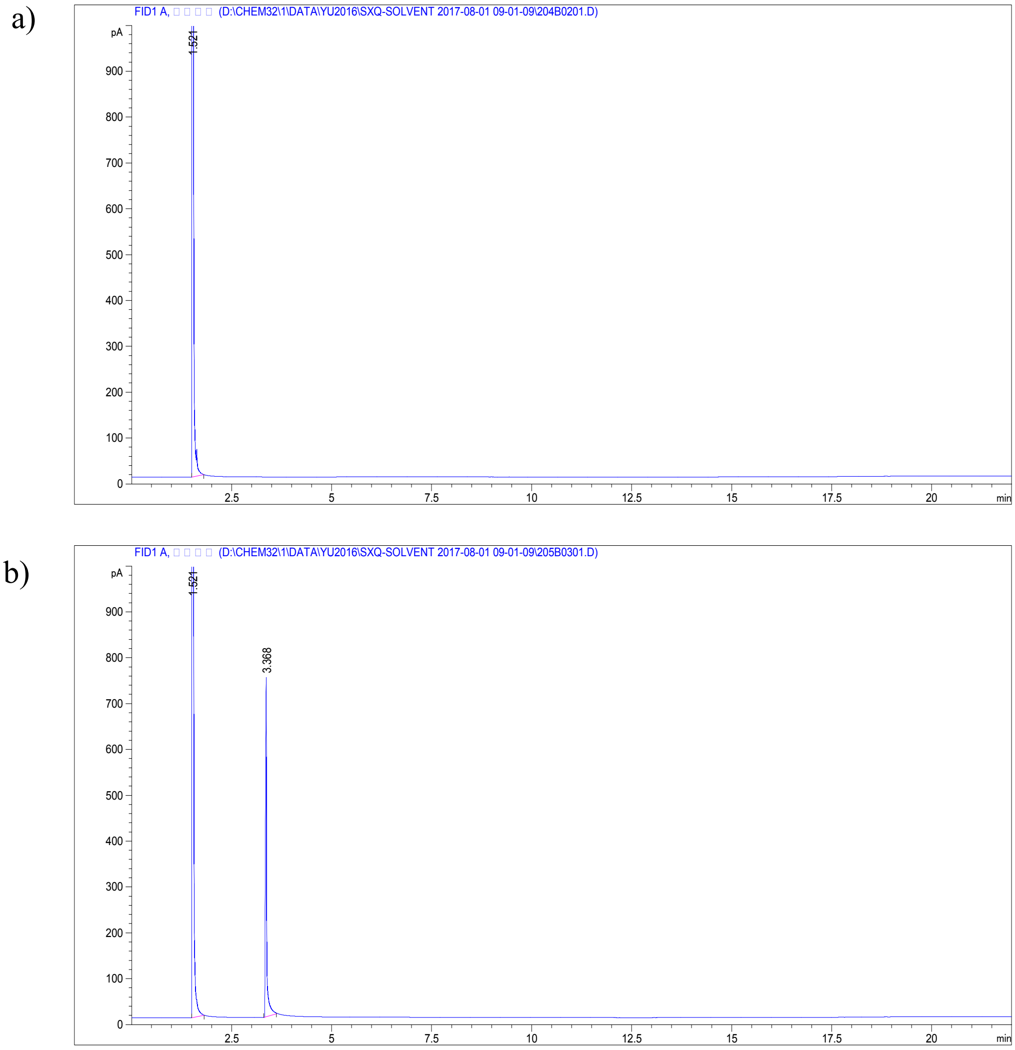


Fig. S11. The GC chromatogram of a) liquid 1 and b) liquid 2. The peak at 1.521 min was methanol solvent, the peak at 3.368 min was THFA. Liquid 1 and 2 were separated H_2O and THFA, respectively. Hence, H_2O and THFA were recycled, which could be reused in the solvent thermal treatment.

References

1. C. Crestini and M. D'Auria, *Tetrahedron*, 1997, **53**, 7877-7888.
2. Q. Song, F. Wang and J. Xu, *Chem. Commun.*, 2012, **48**, 7019-7021.
3. R. DiCosimo and H.-C. Szabo, *J. Org. Chem.*, 1988, **53**, 1673-1679.
4. J. Buendia, J. Mottweiler and C. Bolm, *Chem. Eur. J.*, 2011, **17**, 13877-13882.