Supplementary information

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

An integrated process for the valorization of corn stover promoted by NaCl in GVL/H_2O system

Yiping Luo[a*], Zhichen Zhao[a], Bin Jiang[a], Min Wei[a], Zheng Zhang[a], Lisha Zeng[a], James Clark[b] and Jiajun Fan[b*]

[a] *College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu, Sichuan 610059, PR China. Email：luoyiping@cdut.edu.cn*
[b] *Green Chemistry Centre of Excellence, Department of Chemistry, University of York, York, YO10 5DD, UK. Email:alice.fan@york.ac.uk.*

I. The conversion of corn stover in different conditions

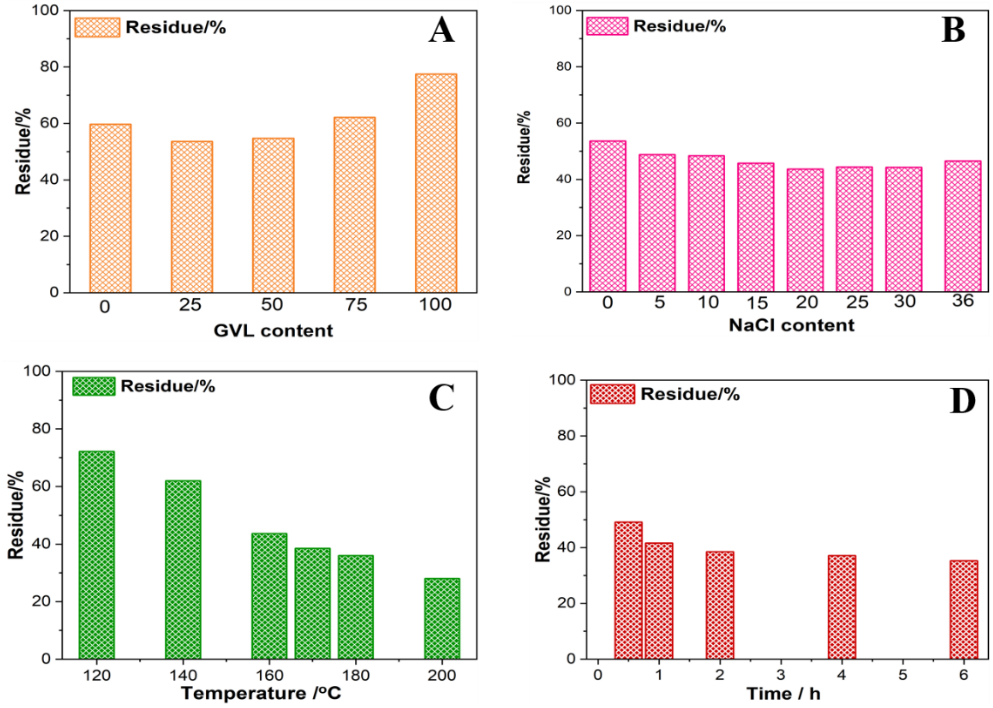


Figure S1 Effects of different reaction conditions on the conversion of corn stover:(A) Effects of GVL content in water at 160 ℃ for 2 h (Reaction conditions: 3 g corn stover, 60 mL GVL/H_2O with different contents of GVL); (B) Effects of NaCl content in 25%GVL/H_2O at 160 ℃ for 2 h (Reaction conditions: 3 g corn stover, 60 mL 25%GVL/H_2O with different contents of NaCl, the concentration of NaCl referred to that in the aqueous phase); (C) Effects of temperature in 25%GVL/H_2O-20% NaCl for 2 h (Reaction conditions: 3 g corn stover, 60 mL 25%GVL/H_2O with 20% NaCl); (D) Effects of time in 25%GVL/H_2O-20% NaCl at 170 ℃ (Reaction conditions: 3 g corn stover, 60 mL 25%GVL/H_2O with 20% NaCl).

II. XRD spectra of samples obtained at different temperatures

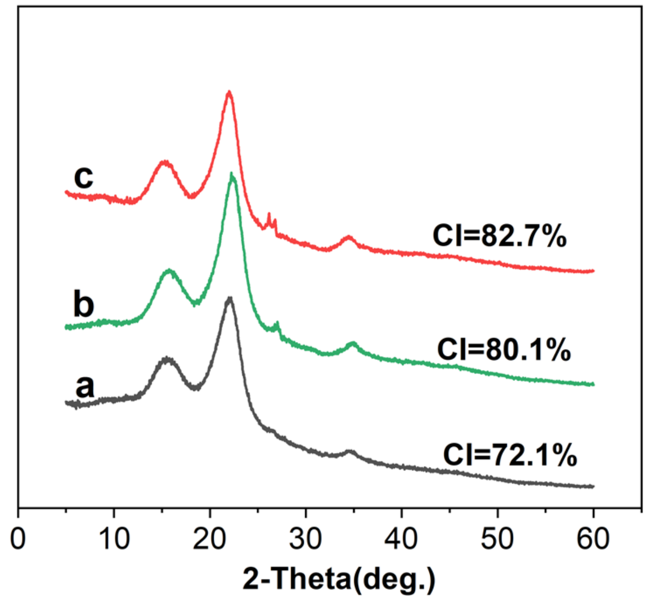


Figure S2 XRD spectra of samples obtained in 25% GVL/H_2O-20% NaCl at different temperatures for 2 h (a, 140 °C; b, 160 °C; c, 170 °C).

III. SEM microscopy of solid samples

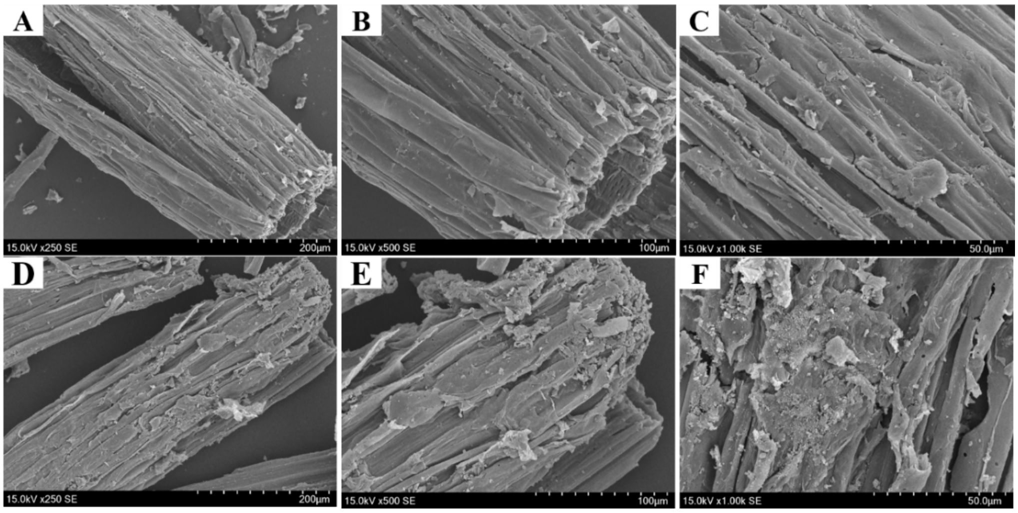


Figure S3 SEM microscopy of corn stover (A-C) and solid residues (D-F) obtained in 25% GVL/H_2O-20% NaCl system at 170 °C for 2 h at different magnifications.

IV. FT-IR spectra of solid samples after being treated by different temperatures

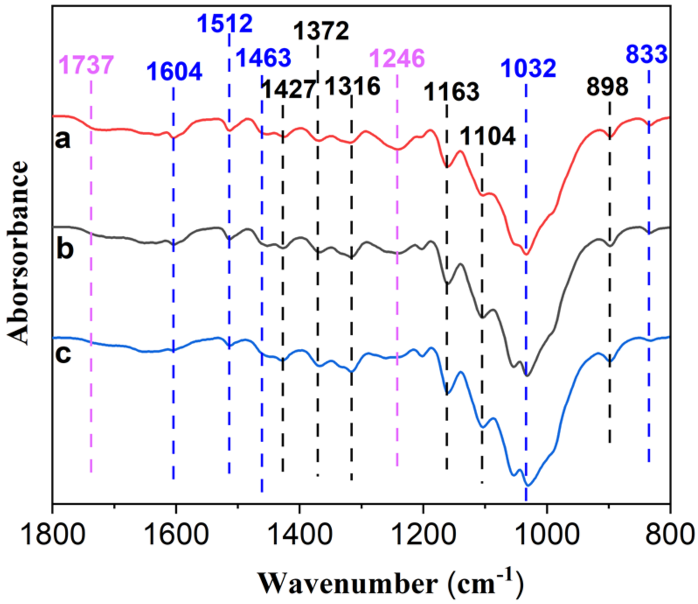


Figure S4 FT-IR spectra of samples after being treated by different temperatures for 2 h in 25%GVL/H_2O-20% NaCl system (a,140 °C; b, 160 °C; c,170 °C).

V. XRD, DTG and FT-IR results of samples obtained in different GVL/H_2O ratios

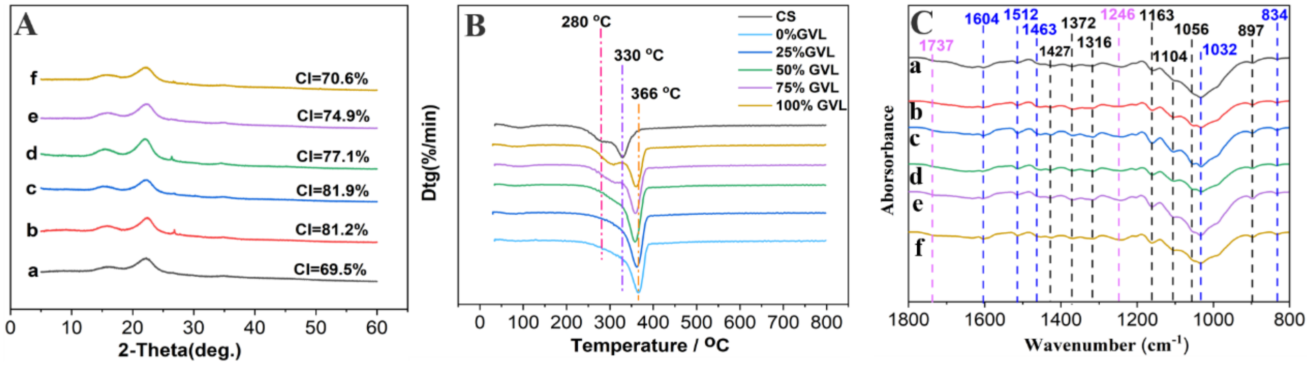


Figure S5 XRD, DTG and FT-IR results of different samples obtained in co-solvents with different GVL/H_2O ratios at 160 °C for 2 h (a, CS; b, 0% GVL; c, 25%GVL; d, 50%GVL; e, 75% GVL; f, 100% GVL).

VI. pH values with the change of NaCl amount

Table S1 The pH values of pure water and 25%GVL/H_2O system with increasing NaCl amount.

Solvent system	pH	Solvent system	pH
H_2O[a]	6.52	25%GVL/H_2O[b]	5.00
H_2O+10%NaCl[a]	4.62	25%GVL/H_2O-5%NaCl[b]	3.83
H_2O+15%NaCl[a]	4.51	25%GVL/H_2O-15%NaCl[b]	3.67
H_2O+20%NaCl[a]	4.27	25%GVL/H_2O-25%NaCl[b]	3.59
H_2O+30%NaCl[a]	3.99		

[a] 30 mL H_2O with 5-30% NaCl; [b] 30 mL 25% GVL/H_2O (7.5 mL GVL, 22.5 mL H_2O) with 5-30% NaCl, where the concentration of NaCl referred to that in the aqueous phase (calculated based on 22.5 mL H_2O).

VII. Effects of temperature and time on the yield of small molecular products from hemicellulose

Table S2 The yield of small molecular products from hemicellulose obtained from different NaCl contents in 25% GVL/H_2O system

Products		Yield /% (based on the weight of hemicellulose)					
		0% NaCl	5%NaCl	10%NaCl	15%NaCl	20%NaCl	30%NaCl
Monosaccharides	Glucose	2.30	4.34	4.65	1.54	1.11	1.04
	Xylose	2.93	6.83	9.42	9.75	12.09	10.82
	Arabinose	1.59	1.67	1.37	1.23	0.64	0.61
	Total sugars	6.82	12.84	15.44	12.52	13.84	12.47
Organic acids	Lactic acid	2.49	3.75	3.67	3.35	3.29	3.01
	Formic acid	37.51	39.34	38.93	34.80	35.43	30.10
	Acetic acid	8.47	9.10	9.52	9.22	8.99	11.06
	Levulinic acid	0.84	1.43	1.63	1.42	1.66	1.57
	Total organic acids	49.31	53.62	53.75	48.79	49.37	45.74
Furans	Furfural	2.72	5.14	5.85	8.95	7.33	16.11
Total yield/%		58.85	71.6	75.04	70.26	70.54	74.32

VIII. Effects of temperature and time on the yield of small molecular products from hemicellulose

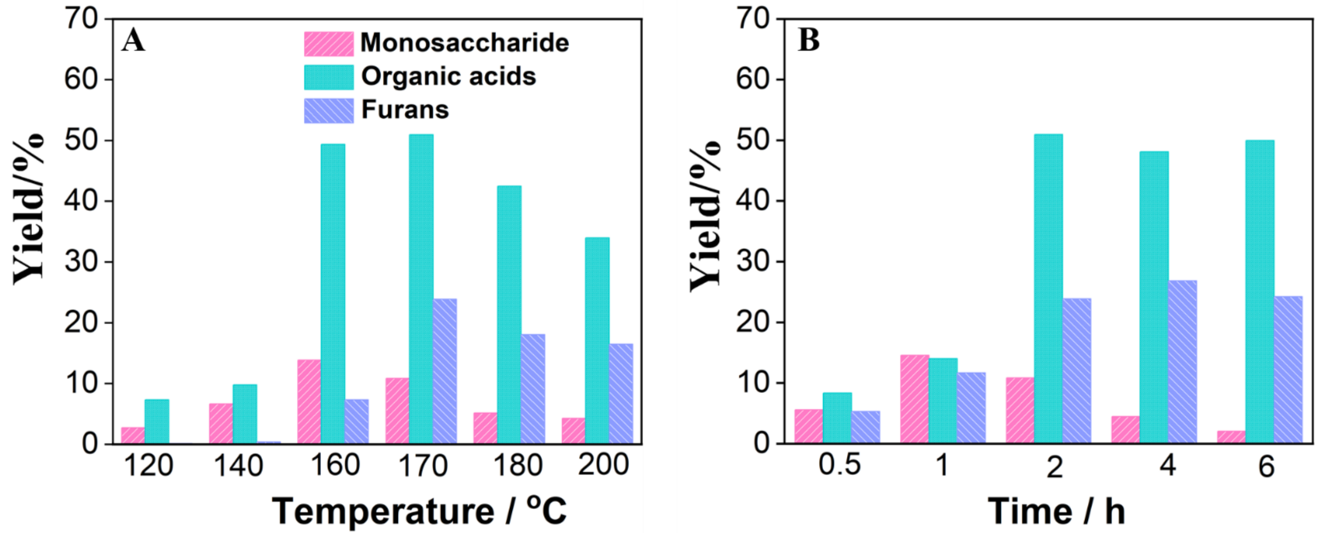


Figure S6 Effects of temperature for 2 h (A) and time at 170 ^oC (B) on the yield of small molecular products from hemicellulose (the yield was based on the weight of hemicellulose in corn stover)

Table S3 The yield of small molecular products from hemicellulose obtained from different temperatures for 2 h in 25% GVL/H_2O system

Products		The yield of products obtained from different temperatures (^oC) for 2 h based on the weight of hemicellulose					
		120	140	160	170	180	200
Monosaccharides	Glucose	2.04	1.89	1.11	1.88	2.40	2.94
	Xylose	0.63	1.65	12.09	8.80	2.58	1.30
	Arabinose	0.04	3.09	0.64	0.16	0.15	0.01
	Total sugars	2.70	6.63	13.84	10.84	5.13	4.25
Organic acids	Lactic acid	1.82	2.70	3.29	2.75	2.59	5.85
	Formic acid	2.54	2.53	35.43	32.24	25.61	2.42
	Acetic acid	1.49	3.06	8.99	13.96	14.19	23.37
	Levulinic acid	1.46	1.49	1.66	1.97	0.06	2.33
	Total organic acids	7.30	9.78	49.37	50.94	42.46	33.97
Furans	Furfural	0.11	0.38	7.33	23.87	18.05	16.46
Total yield/%		10.11	16.79	70.54	85.65	65.64	54.68

Table S4 The yield of small molecular products from hemicellulose obtained from different times at 170 ^{o}C in 25% GVL/H_2O system

Products		The yield of products obtained from different times (h) based on the weight of hemicellulose				
		0.5	1	2	4	6
Monosaccharides	Glucose	2.02	1.85	1.88	2.87	1.76
	Xylose	2.36	12.22	8.80	1.55	0.26
	Arabinose	1.19	0.49	0.16	0.04	0.02
	Total sugars	5.57	14.56	10.84	4.45	2.04
Organic acids	Lactic acid	3.92	3.78	2.75	4.53	4.38
	Formic acid	1.13	3.31	32.24	26.54	25.87
	Acetic acid	2.96	5.93	13.96	15.72	17.91
	Levulinic acid	0.36	0.97	1.97	1.32	1.80
	Total organic acids	8.36	13.99	50.94	48.11	49.96
Furans	Furfural	5.31	11.68	23.87	26.82	24.23
Total yield/%		19.24	40.23	85.65	79.38	76.23

Please do not adjust margins

IX. Effects of different inorganic salts on the yield of small molecular products

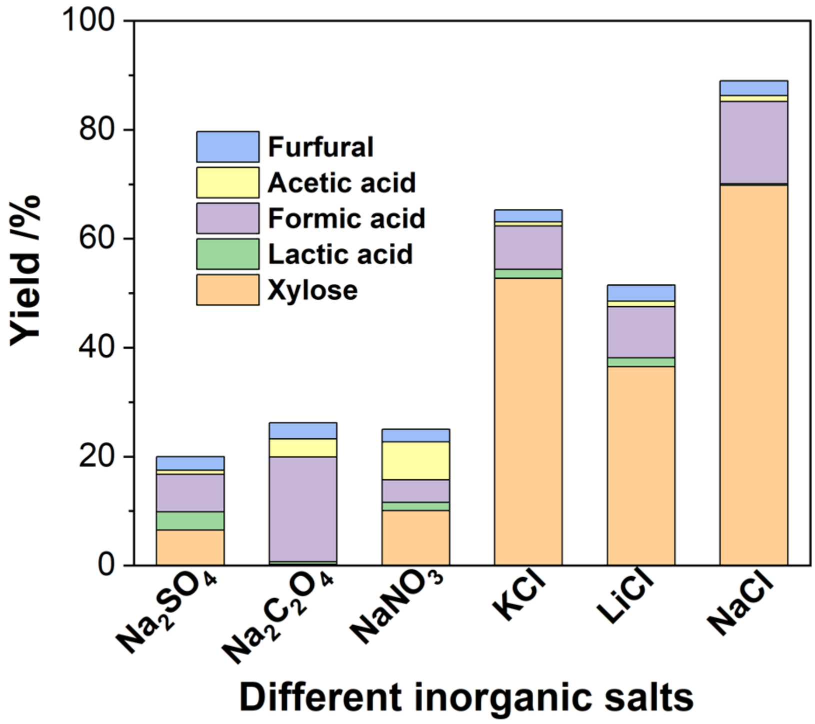


Figure S7 Effects of different inorganic salts on the yield of small molecular products from xylan in 25%GVL/H_2O system at 160 ^oC for 2 h (Reaction conditions: 0.5g xylan, 60 mL 25%GVL/H_2O, 20% NaCl(aq), the other sodium salts (Na_2SO_4, $Na_2C_2O_4$ and $NaNO_3$) and chlorine salts (KCl and LiCl) at the same molar concentration of Na^+ or Cl^- in NaCl, respectively)

X. The yield of monophenols from lignin

Table S5 The yield of monophenols from lignin obtained from different NaCl contents in 25% GVL/H_2O system at 160 ^oC for 2 h

Products	Yield/% (based on the weight of lignin)				
	0% NaCl	5% NaCl	15% NaCl	20% NaCl	30% NaCl
o-cresol	0.287	0.315	0.234	0.180	0.230
4-vinylphenol	1.361	3.029	2.120	6.957	4.884
4-propyl phenol	0.035	0.078	0.054	0.060	0.062
4-ethyl guaiacol	0.021	0.051	0.034	0.036	0.038
4-vinyl guaiacol	0.875	2.859	2.358	4.642	4.667
Syringol	0.000	0.088	0.098	0.170	0.155
Eugenol	0.000	0.000	0.000	0.000	0.000
4-propyl guaiacol	0.057	0.180	0.130	0.068	0.066
Isoeugenol	0.515	1.165	0.985	2.491	2.320
4-Hydroxy-3-methoxybenzoic acid	0.108	0.206	0.266	0.612	0.482
4-allyl genol	0.000	0.000	0.000	0.043	0.044
3-(4-Hydroxy-3-methoxyphenyl)-1-propanol	0.389	0.973	0.680	0.551	0.578
Syringaldehyde	0.106	0.273	0.303	0.395	0.378
Syringic acid	0.061	0.159	0.194	0.182	0.194
4-(3-Hydroxypropyl)-2,6-dimethoxyphenol	0.048	0.178	0.132	0.090	0.081
Total yield	3.863	9.554	7.588	16.477	14.179

XI. ESI-MS analysis

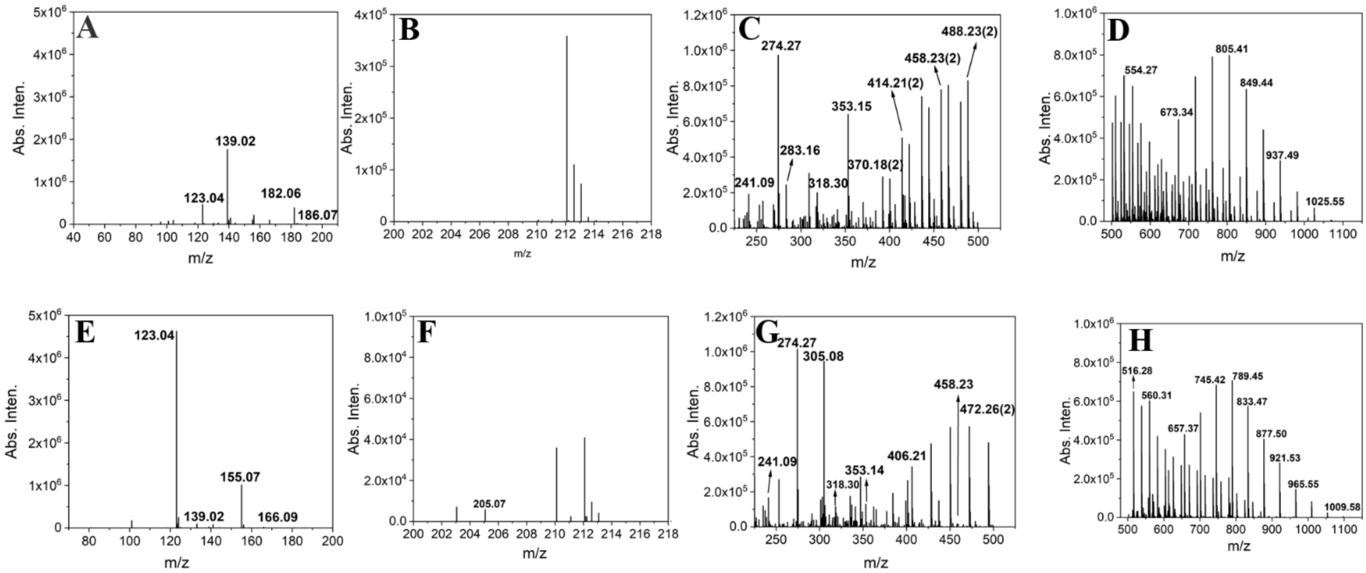


Figure S8 ESI-MS results of liquid products obtained from 25% GVL/H_2O system (A-D) and GVL-rich phase in 25%GVL/H_2O-20%NaCl system (E-F).

The lignin derived oligomers according to the molecular weights described in Figure S8 were listed below:

139.02=M(138.16)+H^+

155.07=(M(4-vinyl guaiacol)-H_2O+Na^+=M(150.17)-H_2O+Na^+

182.06=M(*p*-coumarate)+H_2O=M(164.19)+H_2O

186.07=M(168.19)+H_2O

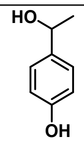
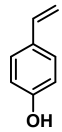
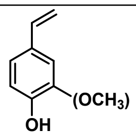
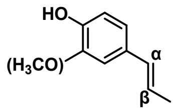
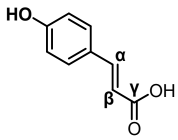
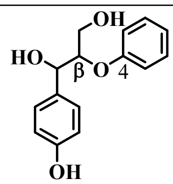
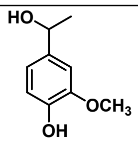
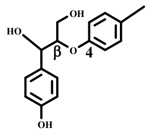
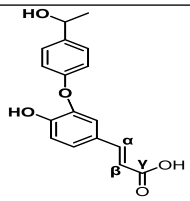
205.07=M(isoeugenol)+H_2O+Na^+=M(164.20)+H_2O+Na^+

241.09=M(4-vinyl phenol)×2+H^+=M(120.15) ×2+H^+

283.16=M(260.1)+Na^+

318.30=M(300.31)+H_2O

Table S6 Possible chemical structures of oligomers

Molecular weight	Chemical structure	Molecular weight	Chemical structure
138.16		120.15	
150.17		164.20	
164.19		260.10	
168.19		274.27	
300.31			

XII. 2D HSQC NMR assignment

Table S7 Assignment of main lignin ^{13}C-^{1}H correlation signals in 2D HSQC NMR spectra

Lables	δ_C/ δ_H	Assignment
A_γ	59.8/3.61	C_γ-H_γ in β-O-4' structure(A)
γ-Est	63.97/4.36	γ-ester
A_{5ax}	60.8/3.67	C_{5ax}-H_{5ax} in α-L-Araf
$H'_{2,6}$	130.8/7.56	$C_{2,6}$-$H_{2,6}$ in oxidized(C=O) p-hydroxyphenyl units(H')
$H_{2,6}$	128.2/7.19	$C_{2,6}$-$H_{2,6}$ in p-hydroxyphenyl units(H)
G_5	115.3/6.80	C_5-H_5 in guaiacyl units(G)
G_{5e}	118.3/6.79	C_5-H_5 in etherified guaiacyl units(G)
MeO	56.0/3.71	C-H in methoxyls
$PCA_{2,6}$	130.1/7.15	C_2-H_2 and C_6-H_6 in p-coumarate structure (PCA)
$PCA_{3,5}$	115.5/6.77	C_3-H_3 and C_5-H_5 in p-coumarate structure (PCA)
PCA_β/FA_β	113.5/6.27	C_β-H_β in p-coumarate structure (PCA) and ferulate (FA)
PCA_α/FA_α	144.4/7.51	C_α-H_α in p-coumarate structure (PCA) and ferulate (FA)
$R_{2''\beta}$	30.8/1.59	C_β-H_β in β-β' (resinol) substructures($R_{2''}$)
$R_{2'\alpha}$	40.5/2.63	C_α-H_α in β-β' (resinol) substructures($R_{2'}$)
$S_{2,6}$	104.4/6.72	$C_{2,6}$-$H_{2,6}$ in syringyl units(S)
$S''_{2,6}$	104.7/7.30	$C_{2,6}$-$H_{2,6}$ in (carboxylic group) syringyl units(S)

Please do not adjust margins

XIII. The distribution of products derived from hemicellulose in GVL-rich phase and water-rich phase

Table S8 The distribution of products derived from hemicellulose in the GVL-rich phase and water-rich phase

Solvent system			Ratio	
			Sugars	Organic acids
25% GVL/H_2O-20%NaCl	160 ^oC, 2 h	Water-rich phase	80.8%	76.5%
		GVL-rich phase	19.2%	23.5%
25% GVL/H_2O-30%NaCl	160 ^oC, 2 h	Water-rich phase	94.4%	70.0%
		GVL-rich phase	5.6%	30.0%
25% GVL/H_2O-30%NaCl	170 ^oC, 2 h	Water-rich phase	93.1%	76.9%
		GVL-rich phase	6.9%	23.1%

XIV. The classification of thermochemical processes

Table S9 The classification of thermochemical processes

Technological solutions	Final products	Notes	Ref.
Gasification	Syngas (H_2, CH_4, CO, and CO_2), process, heat, electric energy, transportation fuels, steam	Harsh reaction conditions, high temperature,high energy consumption, and a large amount of tar as by products, less economic, less eco-friendly	[1-3]
Direct combustion	Stem, process heat, electric energy	Low conversion efficiency (20~40%), high temperature	[2-4]
Pyrolysis	Bio-oils, charcoal, Fuel gas	high temperature, complex products limited the use and difficulty in downstream processing	[4-6]
“One-pot” transformation	Chemicals	Low temperature, complex products that limited the use and difficulty in downstream processing	[7-9]
Solvothermal selective transformation	Chemicals	Low temperature, high selectivity to products	[10-12]

References

[1] A.S. El-Shafay, A.A. Hegazi, S. H. El-Emam, F. M. Okasha, *International Journal of Scientific & Engineering Research*, 2019, **10**, 266.

[2] S. K. Sansaniwal, K. Pal, M.A. Rosen, S.K. Tyagi, *Renewable and Sustainable Energy Reviews*, 2017, **72**, 363.

[3] A. C. Caputo, M. Palumbo, P.M. Pelagagge, F. Scacchia, *Biomass and Bioenergy*, 2005, **28**, 35.

[4] T.Y.A. Fahmy, Y. Fahmy, F. Mobarak, M. El-Sakhawy, R.E. Abou-Zeid, Environment, Development and Sustainability, 2018, **22**, 17.

[5] J. Akhtar, N. Saidina Amin, *Renewable and Sustainable Energy Reviews*, 2012, **16**, 5101.

[6] T. Kan, V. Strezov, T.J. Evans, *Renewable and Sustainable Energy Reviews*, 2016, 57, 1126.

[7] J. S. Luterbacher, J. M. Rand, D. M. Alonso, J. Han, J. T. Youngquist, C. T. Maravelias, B. F. Pfleger, J. A. Dumesic, *Science*, **343**, 277.

[8] C. Li, M. Zheng, A. Wang, T. Zhang, *Energy&Environmental Science*, 2012, **5**, 6383.

[9] Y. Luo, Z. Li, X. Li, X. Liu, J. Fan, J.H. Clark, C. Hu, *Catalysis Today*, 2019, **319**, 14.

[10] S.K. Maity, Renewable and Sustainable Energy Reviews, 2015, **43**, 1446-1466.

[11] W. Fang, H. Sixta, *ChemSusChem*, 2015, **8**, 73.

[12] Q. Zhai, C.-y. Hse, F. Long, F. Wang, T.F. Shupe, J. Xu, Energy Technology, 2019, **1900949**, 1.