Electronic Supplementary Material (ESI) for RSC Advances.

Fractionation and Characterization of Lignin from Sugarcane Bagasse Using a Sulfuric Acid Catalyzed Solvothermal Process

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Electronic Supplementary Information

Table S1 Product profile in liquid fraction during solvothermal fractionation process

Run No.	Response	Concentration of product in hydrolysate (g/L)							
	Hemicellulose removal (%)	Glucose	Xylose	Arabinose	Acetic acid	Formic acid	Lactic acid	HMF	Furfural
1	94.3	2.32	10.61	1.12	0.21	0.17	0.13	0.11	0.32
2	89.6	2.13	12.31	0.65	0.13	0.09	0.09	0.04	0.25
3	96.7	3.56	9.83	1.57	0.41	0.25	0.16	0.12	0.38
4	89.1	1.75	11.15	2.22	0.24	0.12	0.05	0.05	0.14
5	97.2	3.78	10.23	1.51	0.18	0.32	0.22	0.27	0.42
6	95.9	3.21	9.97	1.86	0.27	0.17	0.11	0.16	0.29
7	93.1	2.83	10.72	1.22	0.26	0.26	0.18	0.15	0.32
8	98.6	3.96	8.66	0.91	0.35	0.25	0.16	0.24	0.41
9	89.8	1.19	12.17	1.55	0.13	0.14	0.06	0.08	0.12
10	93.3	2.45	11.48	2.64	0.37	0.15	0.09	0.09	0.26
11	92.7	2.75	11.28	2.76	0.19	0.24	0.05	0.14	0.19
12	94.1	2.13	10.97	1.64	0.22	0.22	0.12	0.15	0.25
13	95.6	2.56	11.32	2.89	0.29	0.19	0.23	0.17	0.21
14	96.4	2.51	9.43	3.16	0.31	0.33	0.18	0.26	0.17
15	88.4	1.22	12.51	1.59	0.11	0.05	0.07	0.04	0.07

Table S2 Assignment of FT-IR spectra of native sugarcane bagasse and remaining pulp

Assignment	Wavenumber (cm^{-1})	
	Native sugarcane bagasse	**Remaining pulp**
O-H stretching vibrations of the -OH groups	3338	3332
C-H stretching vibrations	2916	2902
C=O ester group vibration of the acetyl and uronic ester groups	1734	N/A
O-H bending vibrations of absorbed water	1637	1637
Aromatic C=C in plane stretching of the aromatic ring	1514	N/A
C=C stretching vibration of the aromatic rings	1462	N/A
Acetyl groups present as branched groups	1232	N/A
C-O-H, stretching of alcohols	N/A	1053
C-O-C pyranose ring skeleton	1031	1029
Glycosidic C-H stretching vibration out of the plane of the aromatic ring	N/A	898

Table S3 Assignment of FT-IR spectra of commercial organosolv lignin and lignin recovery

Assignment	Wavenumber (cm^{-1})	
	Commercial organosolv lignin	**Lignin recovery**
O-H stretching	3410	3406
C-H stretching in CH_2 and CH_3 groups	2935, 2845	2935, 2845
C=O stretching, unconjugated	1699	1704
Aromatic skeletal vibrations (S > G)	1602	1605
Aromatic skeletal vibrations (G > S)	1514	1514
C-H deformations in $-CH_2-$ and $-CH_3$	1459	1463
Aromatic skeletal vibrations	1422	1427
Aliphatic C-H stretch in CH_3, not in OCH_3	1362	1367
S ring breathing	1330	1325
G ring breathing	1261	1265
C-C and C-O stretch, G condensed > G	1224	1219
C-O stretch in ester groups (HGS)	1173	1168
Aromatic C-H in plane deformation (S)	1127	1121
Aromatic C-H in plane deformation (G > S)	1030	1035
CH=CH- out-of-plane deformation (trans)	984	984
Aromatic C-H out-of-plane deformation (G)	N/A	N/A
Aromatic C-H out-of-plane deformation (S + H)	835	836
C-H bond in the aromatic ring from G	N/A	N/A

Table S4 Glass transition temperature of commercial organosolv lignin and lignin recovery

Sample	T_g onset (°C)	T_g (°C)
COL	145.7	154.1
BGL	102.5	111.6

Table S5 Summary of lignin properties from various biomass resource during solvothermal process.

Raw materials	Extraction process	Lignin yield (%)	M_w[a]	M_n[b]	PDI[c]	DTG_{max} (^oC)[d]	T_g (^oC)[e]	S:G:H[f]	Lignin substructures[g]	References
Sugarcane bagasse	One-step fractionation MIBK:methanol:water	87.1	1374	785	1.75	291 and 437	111.6	25.1:42.1:32.6	β-O-4′ linkages, resinol structures formed by β-β, syringyl unit, guaiacyl unit, *p*-hydroxyphenyl unit, *p*-coumarate, and ferrulate	This study
Sugarcane bagasse	Ethanol pretreatment	N/A	6441	4181	1.51	355	N/A	25.32:58.23:16.46	β-O-4, $C_γ$-acetylated β-O-4, phenylcoumaran, resinol, β-D-Xylopyranoside	[35]
Sugarcane bagasse	Glycerol pretreatment	60.4	4288	1958	2.2	N/A	N/A	51:43:5	β-aryl ether, phenylcoumaran, resinol, guaiacyl, p-hydroxyphenyl, syringyl, p-coumarate, ferulate, feruloyl glycerol	[41]
Sugarcane bagasse	Acid-catalysed crude glycerol pretreatment	85.2	N/A	N/A	N/A	N/A	N/A	46:45:9	Guaiacyl, p-hydroxyphenyl, syringyl, cinnamate, β-O-4, β-5, β-β, cinnamoyl glycerol	[42]
Sugarcane bagasse	Acetosolv extraction	55.6	2480	248	10	>500	46-60	N/A	Syringyl, oxidized syringyl, guaiacyl, p-hydroxyphenyl, p-coumarate, cinnamic aldehyde, aryl ether with A-α, β-O-4, ferulate, phenylcoumaran	[43]
Sugarcane bagasse	Acidified ethylene glycol	35.8	6518	3821	1.7	380	N/A		b-O-4 alkyl¡aryl ethers, b-O-4′ aryl ethers linkages with and p-hydroxybenzoated -OH at g-carbon, resinol, phenylcoumarane formed by b-5′ and a-O-4′, spirodienones formed by b-1′ and a-O-a′, p-hydroxyphenyl, syringyl, oxidised syringyl, guaiacyl, oxidised guaiacyl, p-hydroxybenzoate, p-coumaric acid	[37]
Aleppo	Ethanol/water	N/A	N/A	N/A	N/A	344 and	96.5	N/A	Syringyl, guaiacyl, methoxyl	[22]

pine	pretreatment					388			groups, etherified syringyl, etherified guaiacyl	
Chinese quince	Ethanol organosolv pretreatment	14.4	5636	2255	2.5	374	N/A	59.72:40.21:0.07	β-O-4′ linkage, C_α-ethoxylation-β-O-4′ linkage, resinol structures formed by β-β, phenylcoumaran formed by β-5′ linkage, spirodienone formed by β-1′ linkage, guaiacyl, p-hydroxyphenyl, cinnamyl alcohol end-groups, syringyl, oxidized syringyl units linked a carbonyl at C_α	[44]
Miscanthus	Organosolv pulping (Ethanol:water)	77.86	1261-1921	1066-1365	1-1.5	N/A	N/A	0.95-4.05: 8.61-22.23:36.72-39.60	N/A	[45]
Eucalyptus	One-step fractionation MIBK:methanol:water	N/A	10940	5163	2.1	351	N/A	62.5:30.3:0.9	β-O-4' alkyl-aryl ethers, β-β resinols, β-5' phenylcoumarans, syringyl, C_α-oxidized syringyl, guaiacyl	[46]

[a]Molecular weight according to GPC analysis

[b]Number-average molecular weight according to GPC analysis

[c]Polydispersity index (Mw/Mn) according to GPC analysis

[d]Derivative thermogravimetric curve according to TGA analysis

[e]Glass transition temperature according to DSC analysis

[f]Ratio of syringyl, guaiacyl, and p-hydroxyphenyl according to Py-GCMS analysis

[g]Llignin substructures according to NMR analysis