

Electronic Supplementary Information

Simultaneous Delignification and Selective Catalytic Transformation of Agricultural Lignocellulose in Cooperative Ionic Liquid Pairs

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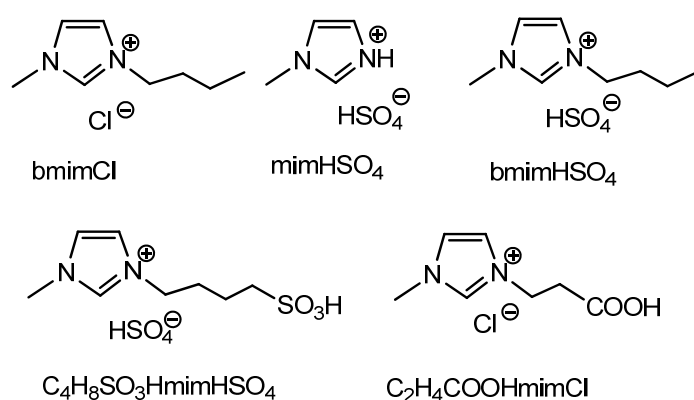
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Materials and methods

All reagents used in this study were analytic grade except special illumination. N-methylimidazole, 1,4-buthane sultone, ethyl chloropropionate, 1-chlorobutane, methanol (HPLC grade) and tetrahydrofuran (THF, HPLC grade) were purchased from Acros (Belgium) and used as received. Other reagents were supplied by Guanghua Chemical Factory Co., Ltd. (Shantou, China) and redistilled before use. The sugarcane bagasse were provide by Jinling sugar Co., Ltd. Others were obtained from the Panyu farm, the suburbs of Guangzhou, Guangdong province, China. All lignocelluloses used were acquired from the current season plant (the Autumn in 2011). They were milled and sieved to get powder with particles size among 40-60 meshes followed by dried under vacuum at 80 °C for 24 h prior to use. The ILs (Scheme S1) 1-butyl-3-methyl imidazolium chloride (bmimCl)¹, 1-(4-sulfobutyl)-3-methyl imidazolium hydrosulfate (C₄H₈SO₃HmimHSO₄)^{2,3}, N-methyl imidazolium hydrosulfate (mimHSO₄)⁴, 1-butyl-3-methyl imidazolium hydrosulfate (bmimHSO₄)^{5,6}, and 1-(2-carboxyethyl)-3-methyl imidazolium chloride (C₂H₄COOHmimCl)^{7,8} used in the experiments were synthesized according to reported procedures and characterized by ¹H-NMR, ¹³C-NMR, electrospray ionization-mass spectrometry (ESI-MS) and thermogravimetric analysis (TG). Ion chromatography and element analysis⁹ demonstrated that their purities were all greater than 99 %.



Scheme S1 ILs used in the experiment

Acidity determination of ILs

The acidic strength of acidic ILs in CH₃OH were evaluated using UV-vis spectra according to the reported method.¹⁰ Some details were as following: the 0.01 mol/L IL solvent was prepared using dry CH₃OH and IL that had been pre-dried under vacuum at 70 °C for 24 h. 2,4-Dinitroaniline was selected as an indicator. All spectra were obtained with a Shimadzu UV-2450 spectrophotometer.

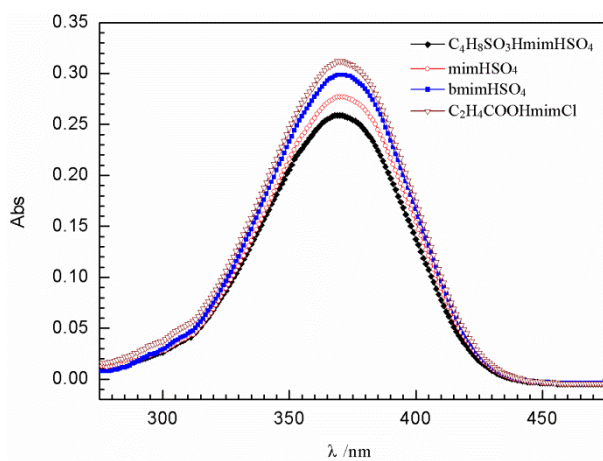


Figure S1 Acidic strengths of IL catalysts

Condition: 0.01 mol/L dried IL-methanol solution; 25 °C; 2,4-dinitroaniline used as indicator.

Primary ingredients and composited elements of original lignocelluloses

All raw materials were dried sufficiently under vacuum at 80°C until their weights weren't changed any more (24 h). TAPPI test method T249 cm-85 was used for determining the contents of cellulose and hemicellulose, and TAPPI test method T222 om-88 for lignin. The percentage of ashes was estimated by the conservation of mass on the assumption that lignocelluloses were only composed of cellulose, hemicellulose, lignin and ashes. The composited elements were determined by a vario EL III element analyzer, where the oxygen content was estimated by the conservation of mass based on the assumption that the samples only contain C, H, N, S and O. Main ingredients and composited elements of raw lignocelluloses were listed in Table S1.

Table S1 Primary ingredients and elements of natural lignocelluloses

Primary ingredients					
Lignocelluloses	Cellulose	Hemicellulose	Lignin	Ashes	
Bagasse	46.47	33.35	18.96	1.22	
Rice straw	45.51	29.69	9.66	15.14	
Rice husk	32.43	39.65	15.82	12.10	
Corn stalk	37.13	45.41	12.58	4.88	
Corncob	34.65	52.76	10.32	2.27	
Composited elements					
Raw material	C (%)	H (%)	O (%)	N (%)	S (%)
Bagasse	45.2	7.1	47.1	0.4	0.2
Rice straw	43.8	7.9	45.8	1.2	1.3
Rice husk	46.4	8.3	42.6	1.6	1.1
Corn stalk	44.9	7.9	45.4	1.3	0.5
Corncob	43.8	9.1	44.2	0.9	2.0

On a dry basis (the sample was dried under vacuum at 80 °C for 24 h)

Effect of catalyst on the molecular weight distribution of non-volatile fractions

The effect of acid IL catalysts on the molecular weight distribution of CH₃OH-soluble and THF-soluble fractions was determined by GPC analysis using extra standard method. Results were shown in Figure S2 and Table S2.

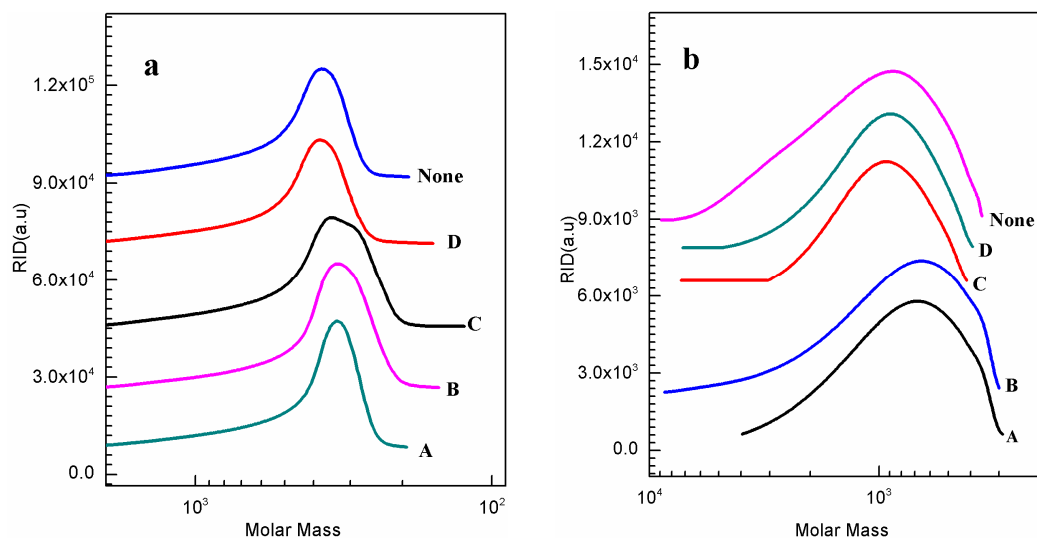


Figure S2 The molecular weight distribution of (a) CH₃OH soluble products; (b) THF soluble products. A: C₄H₈SO₃HmimHSO₄; B: mimHSO₄; C: bmimHSO₄; D: C₂H₄COOHmimCl

Table S2 Effect of catalyst on the average molar mass of CH₃OH-soluble and THF-soluble products from bagasse liquefaction

Entry	Catalyst	CH ₃ OH-soluble fraction			THF-soluble fraction		
		M _n	M _w	M _z	M _n	M _w	M _z
1	C ₄ H ₈ SO ₃ HmimHSO ₄	488	689	878	719	949	1283
2	mimHSO ₄	507	729	958	737	1076	1269
3	bmimHSO ₄	531	760	982	747	1107	1374
4	C ₂ H ₄ COOHmimCl	572	789	893	922	1150	1481
5	None	698	812	1053	990	1473	2251

Reaction conditions: 2.0 mmol catalyst, 10 g bmimCl (pre-dissolved in 5 mL CH₃OH), 3.0 g bagasse and 70 mL cyclohexane; 200 °C, 230 r/min, 15 min.

Ion chromatography analysis of Cl^- and HSO_4^-

The Cl^- and HSO_4^- content of fresh ionic liquids and the recycled one after 4 runs were measured by external standard method with a 792 Basic ion chromatography apparatus (Switzerland). Sodium chloride and potassium hydrogen sulfate were used as standard compound respectively.

^1H -NMR and ^{13}C -NMR analysis of fresh and recycled cooperative IL pairs

The ^1H NMR and ^{13}C -NMR spectrum of fresh and recycled cooperative IL pairs $\text{C}_4\text{H}_8\text{SO}_3\text{HmimHSO}_4/\text{bmimCl}$ under the optimized reaction conditions were measured by Bruker AVANCE III 400 apparatus with D_2O as solvent.

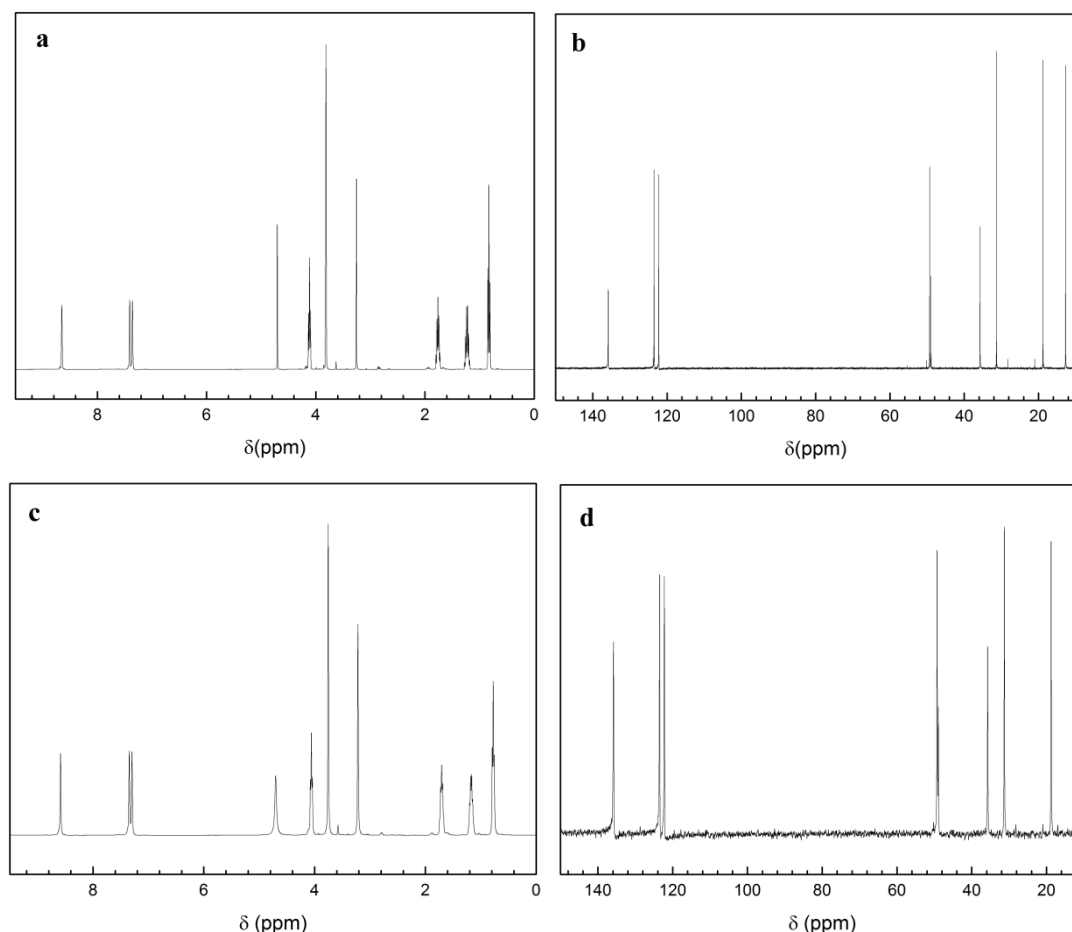


Figure S3 ^1H -NMR and ^{13}C -NMR spectra of fresh (a, b) and recycled (c, d) cooperative IL pairs $\text{C}_4\text{H}_8\text{SO}_3\text{HmimHSO}_4/\text{bmimCl}$

The cooperative IL pairs were composed of 10 g bmimCl and 2 mmol $\text{C}_4\text{H}_8\text{SO}_3\text{HmimHSO}_4$. Recycled IL pairs after 4 run were obtained under the optimized reaction conditions as shown in Table 1, Entry 12.

GC-MS analysis of the volatile biochemicals

The volatile products were analyzed on a Shimadzu QP 2010 plus GC-MS spectrometer and identified according to the NIST MS library (capillary column: Shimadzu RTX-5, 30 m×0.25 mm×0.25 μ m; programmed oven temperature: 60 °C, hold 3 min at 60 °C and then ramped up with 8 °C/min to 280 °C and hold for another 5 min; injector: kept at 280 °C in split mode with split ratio of 5: 1; helium as the carrier gas).

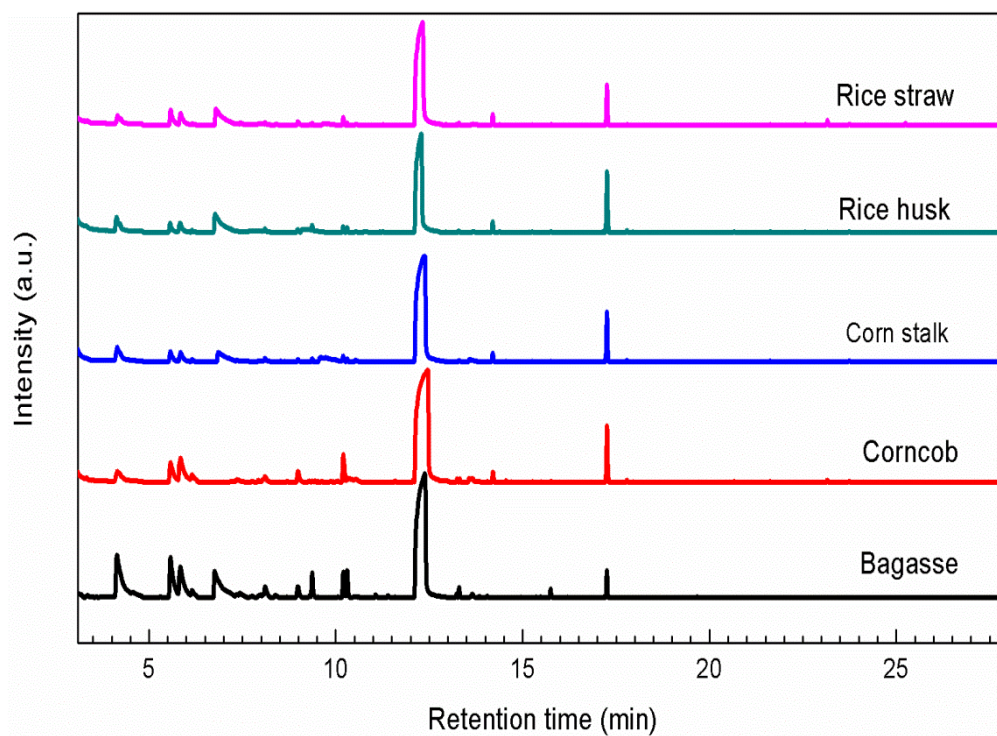


Figure S4 GC-MS spectrum of hexane-soluble fractions

Table S3 The chemicals in cyclohexane determined by GC-MS^[a]

RT (min)	Compounds	Percentage (%) ^[b]				
		bagasse	Rice straw	Rice husk	Corn stalk	Corn cob
3.12	N-methylpyrrole	0.64	0.81	0.92	0.68	0.75
3.32	2-methylpent-1-en-3-one	0.32	0.24	0.19	0.32	0.25
3.62	2-methoxypropan-1-ol	0.82	-	-	-	-
4.15	acetic acid, butyl ester	9.76	2.82	3.16	5.16	6.02
4.37	2-methoxymethyl-Furan	2.99	-	-	-	-
4.54	formic acid	2.14	-	0.03	-	-
4.93	butane-1,2-diol	1.02	-	-	-	-
5.58	2,2'-bi(1,3-dioxolane)	9.58	5.63	5.93	4.35	4.02
5.84	<i>n</i> -butyl ether	5.60	6.86	4.49	6.35	5.53
6.15	butyl propionate	1.25	2.13	0.53	0.80	0.99
6.85	cyclopent-2-enone	-	-	6.04	-	4.54
7.17	butyl isobutyrate	0.85	0.31	-	-	-
7.36	2-methyl-6,7-dihydrobenzo furan-4(5H)-one	0.28	0.70	0.19	0.14	0.51
7.49	methyl 4-oxopentanoate	0.88	0.57	0.83	-	-
8.05	methyl 3-methylene- cyclopentanecarboxylate	0.21	0.87	0.51	-	-
8.11	3-ethyl-2-hydroxy-2- cyclopenten-1-one	1.25	1.68	0.92	1.25	1.33
8.37	butyl 2-hydropropanoate	0.44	1.68	0.34	-	0.92
8.69	acetophenone	-	0.31	-	-	-
8.98	(<i>Z</i>)-prop-1-en-1-ylbenzene	-	-	1.19	0.92	-
9.17	phenyl acetate	-	-	-	1.07	-
9.28	2-methylbutanoic acid	1.07	3.20	0.20	-	-
9.36	(<i>E</i>)-butyl but-2-enoate	0.67	0.36	0.82	2.67	1.25
9.53	2-methoxypropan-1-ol	1.23	0.77	-	-	1.57
9.94	2-vinylfuran	-	-	0.51	-	0.86
10.20	butyl pentanoate	0.87	7.88	2.93	1.98	2.20
10.31	pentan-3-ol	0.65	1.38	0.75	1.71	1.25
10.37	phenol	-	1.02	-	-	-

Table S3 The chemicals in cyclohexane determined by GC-MS^[a] (**continued**)

RT (min)	Compounds	Percentage (%) ^[b]				
		bagasse	Rice straw	Rice husk	Corn stalk	Corn cob
10.53	3-methyldihydrofuran-2,5-dione	-	-	0.15	0.16	0.47
10.89	1-ethyl-4-methoxy benzene	0.72	0.92	-	0.13	0.12
11.15	dimethyl gultarate	1.31	0.12	-	0.12	0.30
11.58	1-methoxy-4vinyl benzene	0.88	0.39	-	-	-
12.07	<i>p</i> -(acetylamino)phenol	0.72	0.72	-	-	0.30
12.46	2-(diethoxymethyl)furan	35.13	36.92	39.23	40.81	45.03
13.24	butyl furan-2- carboxylate	0.76	1.09	0.16	0.58	0.14
13.32	<i>n</i> -butyl levulinate	1.42	1.04	0.32	-	0.69
13.57	(<i>E</i>)-2-methylhepta-1,5-diene	-	1.10	0.35	0.17	0.86
13.63	2-isopropyl-5-methylcyclohexyl acrylate	-	1.11	0.35	0.17	0.63
13.84	isobutyric anhydride	0.77	-	-	-	-
14.06	butyl 2-hydroxyacetate	1.89	0.23	-	-	-
14.21	dimethyl succinate	0.84	2.94	4.04	4.92	3.47
15.76	dimethyl-2-methyl succinate	1.55	0.46	-	0.19	0.17
17.26	pentadecane	6.53	12.01	15.39	12.30	9.92
17.79	3-methylpentyl nonadecyl succinate	-	0.59	0.20	0.78	0.56
23.15	2-methylpentanoic acid	-	0.60	1.89	0.32	0.28
25.25	allyl cyclobutane carboxylate	-	-	0.73	-	-

[a] Conditions: Shimadzu RTX capillary column: 30 m × 0.25 mm × 0.25 μm. The oven temperature was programmed as following: It hold at 60 °C for 3 min and then ramped up to 280 °C with 8 °C/min and hold for another 5 min; injector: kept at 280 °C in spit mode with spit ratio of 5: 1; helium as the carrier gas.

[b] Measured using peak area normalization method.

SEM images from different catalytic systems

The surface morphologies of residues from different liquefaction systems were obtained by Hitachi 3700 SEM apparatus.

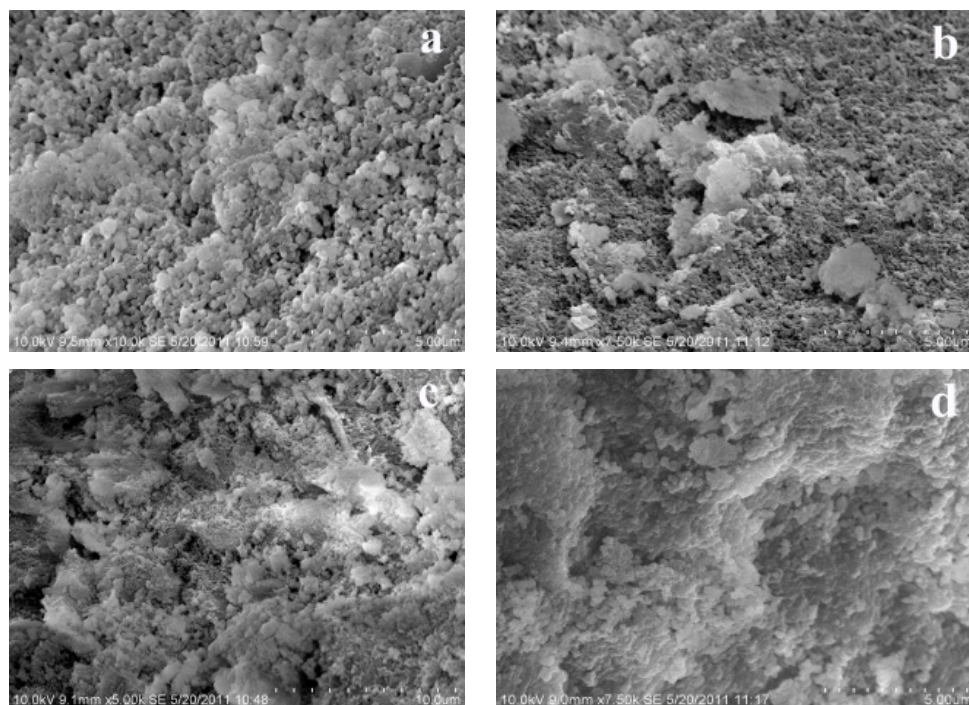


Figure S5 Surface morphologies of catalytic residues from bagasse liquefaction
(a) $C_4H_8SO_3HmimHSO_4$; (b) $mimHSO_4$; (c) $bmimHSO_4$; (d) $C_2H_4COOHmimCl$
Reaction conditions: 3.0 g bagasse, 10.0 g $bmimCl$ (pre-dissolved in 5 mL CH_3OH), 2.0 mmol acid IL and 70 mL cyclohexane; 200 °C, 30 min.

GPC analysis on the average molecular weight of extracted lignin

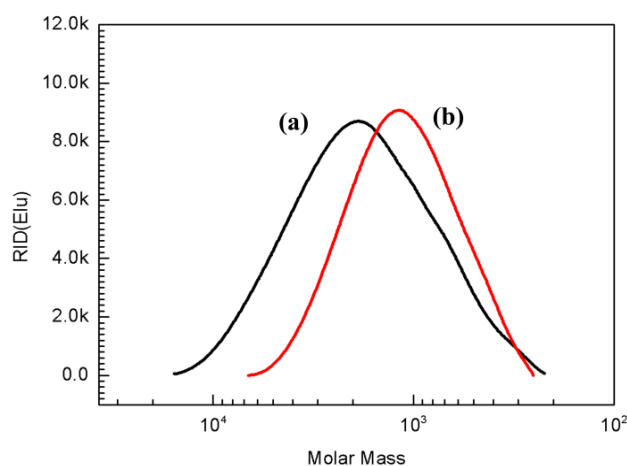


Figure S6 The molecular weight distribution of (a): lignin from original bagasse; (b): lignin from residue

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