Electronic Supplementary Information

One Step Catalytic Conversion of Cellulose to Sustainable Chemicals Utilizing Cooperative Ionic Liquid Pairs

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Contents of the supplementary information:

Materials and methods

Microcrystalline cellulose (Alfa Aesar) was dried for 24 h at 333 K under vacuum prior to use, N-methylimidazole, 1,4-butane sultone, ethyl chloropropionate, bromoethane, 1-chlorobutane, THF (HPLC grade) and CH_3OH (HPLC grade) were purchased from Acros and used as received. Other reagents (analytical grade) were supplied by Guanghua Chemical Factory Co. Ltd. and redistilled prior to use. The ILs bmimBr, bmimCl,[1] bmimAc,[2] emimAc,[2] C_2H_4COOHmimCl,[3] bmimHSO_4,[4] mimHSO_4 and $C_4H_8SO_3H$mimHSO_4[5] were synthesized according to literature reports and characterized by ^{1}H-NMR, TG-DSC and Ion chromatogram.[6] Analytical results indicated that the purity of the ILs were all greater than 99%, and the structure of the ILs are shown in Scheme S1.

Scheme S1 Ionic liquids used in this study

Typical experiment for cellulose decomposition

Cellulose (5 g), bmimCl (20 g, pre-dissolved in 10 mL CH_3OH), $C_4H_8SO_3H$mimHSO_4 (3.5 mmol) and hexane (80 mL) were placed into a 150 mL stainless autoclave (Andorra MED1220, Premex Co. Ltd, Switzerland). The autoclave was then purged with N_2 3 times and heated to a designated temperature at 5 K/min and held at the designated temperature. After reaction, the reactor was quickly cooled with pressurized air to room temperature within 15 min.

Separation and analysis of the products

The separation process is shown in Figure S1. The gas was collected in a sacculus and analyzed by GC. It showed that the weight of gas was less than 50 mg once hexane and methanol were excluded. Therefore, the gasification of cellulose was negligible under the conditions and was not taken into consideration. The lighter fractions that dissolved in hexane, ethyl acetate and methanol phases were analyzed by GC-MS and GPC. The residues were analyzed by, GPC and elemental analysis. The lighter fractions were divided into two parts, part A contained vapor chemicals with an average molecular weight of around 100 and part B contained non-vaporized compounds with an average molecular weight of around 1000. The hexane, ethyl acetate and methanol phases were combined and evaporated at 353 K under vacuum for 12 hour to yield part B. The residues and part B were weighed and analyzed by elemental analysis. The yield of part A, part B and the degradation degree of cellulose were calculated according to the following equations:

$$Y_B=100\%\times(W_B\times C_B/C_C)/W_C \qquad (1)$$

$$Y_R=100\%\times(W_R\times C_R/C_C)/W_C \qquad (2)$$

$$Y_A=100\%-Y_B-Y_R \qquad (3)$$

$$Y_C=100\%-Y_R \qquad (4)$$

Y_A: percentage of cellulose converted to part A (%)

Y_B: percentage of cellulose converted to part B (%)

Y_C: Degradation degree of cellulose (%)

Y_R: Percentage of cellulose converted to residue (%)

W_B: Weight of part B(g)

W_C: Cellulose feed weight (5.0 g)

W_R: Weight of residue (g)

C_B: Carbon content of part B (%)

C_C: Carbon content of cellulose (%) (41%)

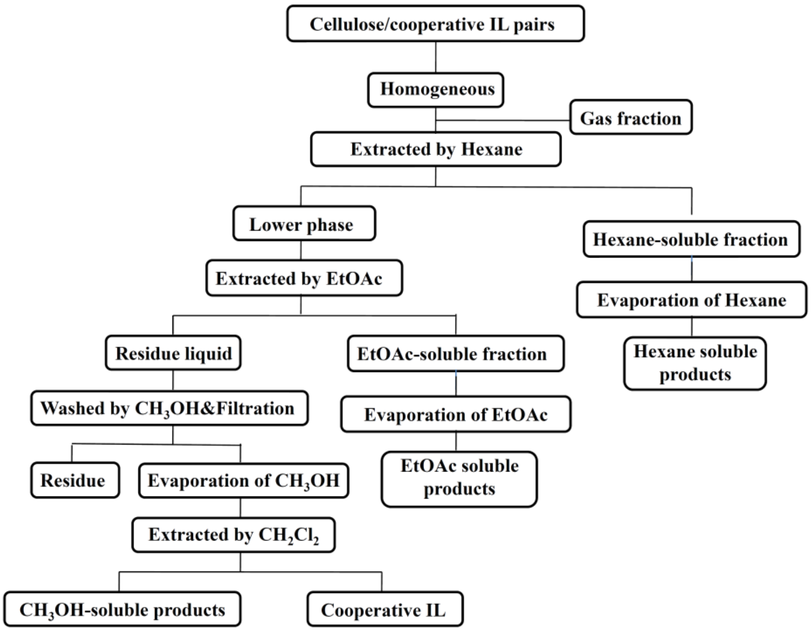

Figure S1 Separation process of degradation products

Cellulose regeneration

Microcrystalline cellulose (0.8 g) and ionic liquid bmimCl (10 g) were charged into a 100 mL round bottom flask equipped with a magnetic stirrer and a condenser. The mixture was heated to 373 K with an oil bath and vigorous stirring. After a homogeneous solution had been obtained and the mixture cooled to room temperature, 50 mL CH_3OH was added. A flaky precipitation was observed to form in significant quantities. Regenerated cellulose was obtained after filtration followed by drying under vacuum at 353 K for 24 hours.

SEM images of cellulose and residues

A SEI Qanta 200 HV SEM was used to observe the structure and surface morphology of raw cellulose, regeneration cellulose and residues obtained from a non-catalytic system (Table 1, entry 3) and $mimHSO_4$ catalytic system (Table 2, entry 2). The samples are coated with gold using a vacuum sputter coater before analysis by Scanning electron microscope (SEM).

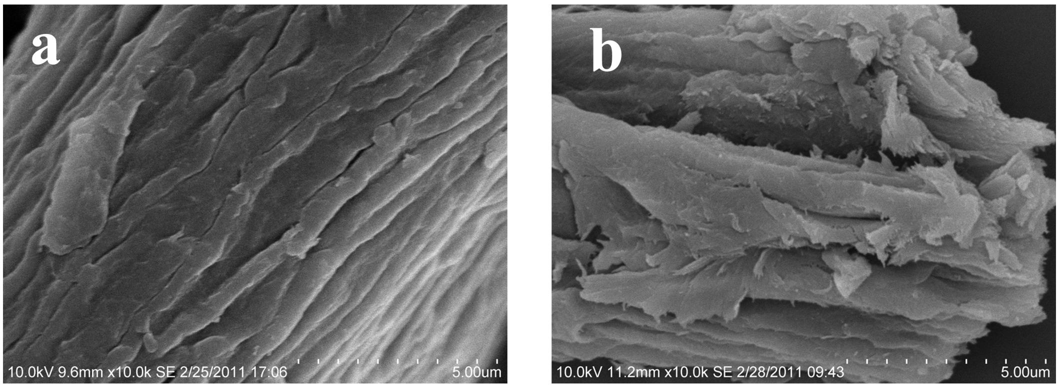

Figure S2 SEM images of raw cellulose and the residue from a non-catalytic system (a): Surface of raw microcrystalline cellulose under high amplification (Figure 2a); (b): residue from a non-catalytic system (Table 1, entry 3) at 473 K for 15 min (small image on the top right corner of Figure 2c)

Acidity determination of ionic liquids

The acidic strengths of ionic liquids/CH_3OH were evaluated using a standard pH method (pHS-25 digital meter) [3b]. The 0.01 mol/L ionic liquid solvent was prepared using dry CH_3OH and ionic liquids that had been pre-dried under vacuum at 343 K for 24 h. All UV-vis spectra of these IL solvent were measured by a Shimadzu UV-2450 spectrophotometer with 2,4-dinitroaniline was used as an indicator [7].

GPC analysis of the hexane soluble and ethyl acetate soluble substances

GPC analysis of hexane and ethyl acetate soluble fractions was carried out using an Agilent 1200

HPLC with a RID detector. THF was used as the eluent and the flow rate used was 1.0 mL/min. The system was calibrated with polystyrene standards. The results are shown in Table S1.

Table S1 Molecular weight of hexane and ethyl acetate-soluble products

Fraction	M_n	M_w	M_z
hexane-soluble	229	343	463
ethyl acetate-soluble	256	395	492

Condition: 5.0 g cellulose, 20 g bmimCl as 1st IL, 3.5 mmol $C_4H_8SO_3HmimHSO_4$ as 2nd IL, 10 mL CH_3OH, 80 mL hexane; heated from room temperature to 473 K at 5 K/min and held 15 minutes.

Determination of the average molecular weight of residues

Dried cellulose samples and residues were derivatized with phenylisocyanate in DMSO, resulting in cellulose tricarbanilates, which were readily soluble in THF. GPC analysis was carried out using an Agilent 1200 HPLC with a RID detector. THF was used as the eluent and the flow rate used was 1 mL/min. The system was calibrated with polystyrene standards.

Thermo-stability of cooperative IL pairs

The thermo-stability of cooperative IL pairs under the same conditions as those employed for the degradation of cellulose was studied intensively. 20 g IL solvent bmimCl (dissolved in 10 mL CH_3OH), 3.5 mmol acidic IL $C_4H_8SO_3HmimHSO_4$ and 80 mL hexane were charged into the autoclave sequentially. The same process as that used in the degradation reaction was then applied to the mixture. After the reaction was complete and cooled to room temperature, the mixture was extracted with hexane and ethyl acetate three times. GC-MS analysis showed that no degradation product was present in either phase.

GC-MS analysis

Lower boiling products were studied using a Varian 4000 GC/MS apparatus (capillary column, HP-VOC; 60 m×0.25 mm×0.25 μm) and identified by comparison with the NIST MS library. The oven was programmed as follows: 333 K (hold 3 min), increased (8 K /min) to 453 K (hold 10 min), then increased (8 K/min) to 523 K (hold 5 min). The injector was maintained at 533 K in split mode (split ratio: 5: 1) with helium as the carrier gas. The results are shown in Figure S3 and Table S2.

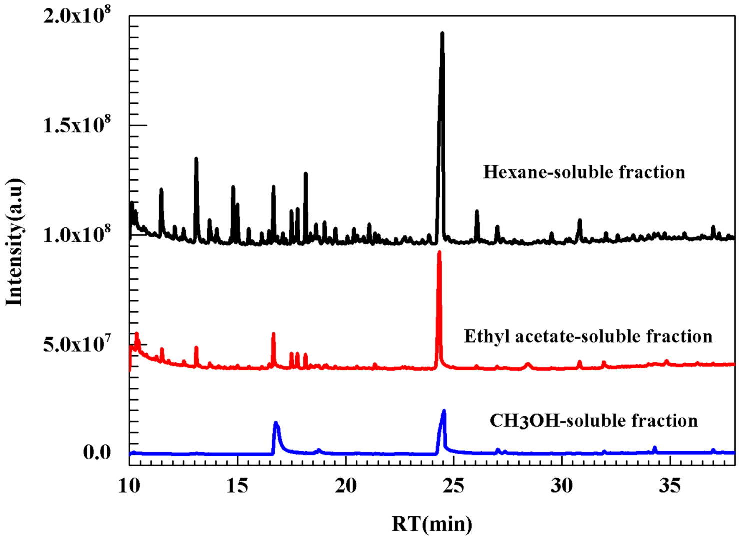

Figure S3 GC-MS analysis of products

Table S2 GC-MS analysis of products from degradation of cellulose in cooperative IL

RT (min)	Compound	Structure	Products (%)		
			Hexane	Ethyl acetate	Methanol
11.4	2-butylfuran		√		
11.5	methyl 3-methylenecyclopentane-carboxylate		√	√	
12.0	2-methylpent-1-en-3-one		√		
12.5	methyl 2-methoxypropanoate		√		
13.1	butyl acetate		√	√	
13.6	2-(methoxymethyl)furan		√		
14.1	furan-2-carbaldehyde		√	√	
14.2	2-methylfuran		√	√	
14.7	1-butoxybutane		√		
14.9	methyl 3,4-dimethylcyclopent-2-enecarboxylate		√		

Table S2 GC-MS analysis of products from degradation of cellulose in cooperative IL(**continued**)

RT (min)	Compound	Structure	Products (%)		
			Hexane	Ethyl acetate	Methanol
15.4	butyl propionate		√		
15.5	methyl 3-hydroxyhexanoate		√	√	
16.1	3-methylcyclopent-2-enone		√		
16.2	2,4-dimethylfuran		√		
16.4	3-methylfuran-2,4(3H,5H)-dione		√	√	√
17.4	5-methylfuran-2-carbaldehyde		√	√	
17.7	methyl 4-oxopentanoate		√	√	
18.1	butyl 2-hydroxypropanoate		√	√	
18.5	2-ethylfuran		√		√
19.1	2-hydroxy-3-methylcyclopent-2-enone		√	√	
19.5	dimethyl 2-methylsuccinate		√		
20.1	2-pentylfuran		√		
22.3	di(furan-2-yl)methane		√		
22.9	3-oxodecahydronaphthalene-4a-carboxylic acid		√		
23.5	2,6,6-trimethylcyclohex-2-enecarbaldehyde		√		
24.4	2-(diethoxymethyl)furan		√	√	√
26.0	butyl 4-oxopentanoate		√	√	
26.9	2-isopropyl-5-methylcyclohexyl acetate		√		

Table S2 GC-MS analysis of products from degradation of cellulose in cooperative IL(**continued**)

RT (min)	Compound	Structure	Products (%)		
			Hexane	Ethyl acetate	Methanol
27.0	2-isopropyl-5-methylcyclohexyl acrylate		√	√	
27.1	2-butyltetrahydrofuran		√		
27.2	isobutyric anhydride		√		
27.7	ethyl methyl succinate		√		
29.5	3,6-dimethyl-4,5,6,7-tetrahydrobenzofuran		√		
30.0	2-octylfuran		√		
30.8	3,5,5-trimethylcyclohex-3-enone		√		
31.9	2-butylcyclopentane-1,3-dione		√		√
32.0	dimethyl glutarate		√		
32.9	6-acetyl-4,8a-dimethyl-4a,5,6,7,8,8a-hexahydronaphthalen-2(1H)-one		√		
34.8	4,8a-dimethyl-6-(prop-1-en-2-yl)-4a,5,6,7,8,8a-hexahydronaphthalen-2(1		√	√	
36.9	bis(5-methylfuran-2-yl)methane		√	√	√

Conditions: HP-VOC 60 m × 0.25 mm × 0.25 μm; Temperature program: 333 K was held for 3 min , then increased to 453 K at 8 K/min, held at 453 K for 10 min before further increasing to 523 K at 8 K/min, and finally held at 523 K for another 5 min.

SEC analysis of methanol-soluble products

SEC analysis was carried out using an Agilent 1200 HPLC with a RID detector. CH_3OH was used as the eluent and the flow rate used was 1 mL/min. The sample concentration was 0.5 wt% in CH_3OH, and the injection volume was 20 μL. The average molecular weight of the samples was calculated using a calibration curve of polysaccharides. The effect of temperature on the average molecular weight is shown in Table S3.

Table S3 Effect of temperature on the average molecular weight of degraded cellulose

Entry	Temp.(K)	Time(min)	Peak I			Peak II		
			M_n	M_w	M_z	M_n	M_w	M_z
1	493	0	563	751	1166	100	107	115
2	473	15	788	1025	1500	97	99	103
3	453	15	785	1058	1572	99	105	113
4	433	15	841	1150	1575	102	109	117

Conditions: 3.5 mmol $C_4H_8SO_3HmimHSO_4$, 20 g bmimCl, 5.0 g cellulose, 10 mL CH_3OH, 80 mL hexane, 15 min.

The effects of reaction time on the molecular weight distribution of both CH_3OH soluble fraction and their residues at 433 K were also determined according the above method. GPC curves were shown in Figure S4 and S5 respectively.

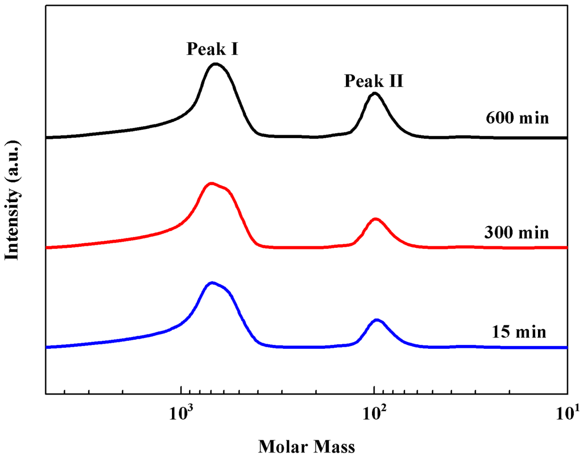

Figure S4 The effect of reaction time on the molecular weight distribution of CH_3OH soluble products

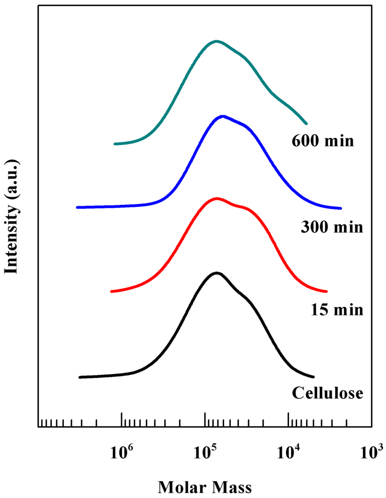

Figure S5 The effect of reaction time on the molecular weight distribution of residues

TG-DSC analysis of the IL pairs

The TG-DSC analysis of the cooperative IL was carried out using a NETZSCH STA449C apparatus, and the oven temperature was increased from 313 K to 873 K at a rate of 10 K /min.

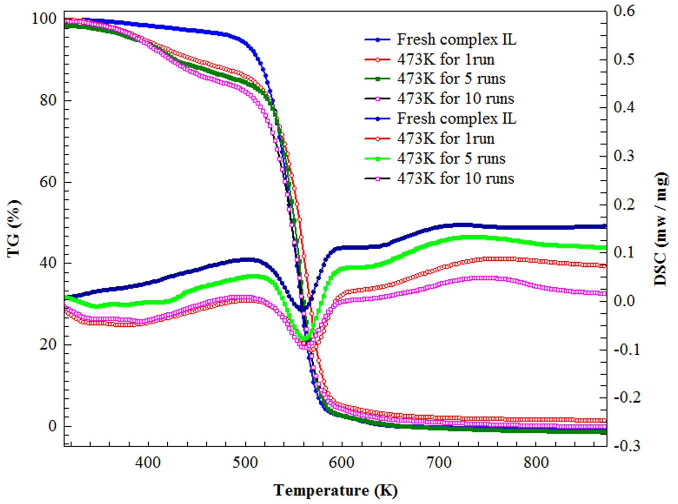

Figure S6 TG-DSC analysis on the thermal behavior of fresh and used cooperative IL

Fresh cooperative IL: 0.0035 mmol $C_4H_8SO_3HmimHSO_4$ and 20 mg bmimCl; used cooperative ILs: 21 mg

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