Electronic Supplementary Material (ESI) for

Degradation of polycarbonate waste to recover bisphenol A and dimethyl carbonate using urea as a green cheap catalyst

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Green metrics analysis

Environmental impact factor (abbreviated as E-factor, EF), introduced by R. A. Sheldon, has been extensively used as a metric to quantify the sustainability of a process.[1, 2] A traditional E-factor is calculated by the total amount of waste generated including 10% of solvent losses but excluding water divided by the mass of product (eqn 1). Besides, for comparison, two new metrics simple E-factor (sE-factor, sEF) and complete E-factor (cE-factor, cEF) are also proposed. Based on the definition of E-factor, the sEF does not consider solvents and water (eqn 2), while the cEF sums all solvents (eqn 3). The amount of waste generated in recycling a certain amount of PC was calculated by the eqn 4. A lower E-factor means less waste production and is more positive to the environment. Process Mass Intensity (PMI) introduced by the EPA and ACS GCI, assesses efficiency by considering all materials as well as water used in a process (eqn 5).[3] A lower PMI means greater efficiency and economy. Here we provide details of the green metrics analysis for the recycling of PC in two modes: 1) a single degradation; 2) 10 cycles of degradation (Table S5 and S6).

$$EF = \frac{\sum m(raw\ materials) + \sum m(catalysts) + \sum m(solvents) * 10\% - m(products)}{m(products)} \quad (1)$$

$$cEF = \frac{\sum m(raw\ materials) + \sum m(catalysts) + \sum m(solvents) - m(products)}{m(products)} \quad (2)$$

$$sEF = \frac{\sum m(raw\ materials) + \sum m(catalysts) - m(products)}{m(products)} \quad (3)$$

$$Waste\ amount = \frac{EF * m(products)}{m(PC)} \quad (4)$$

$$PMI = cEF + 1 = \frac{\sum m(input\ materials\ incl.process\ water)}{m(products)} \quad (5)$$

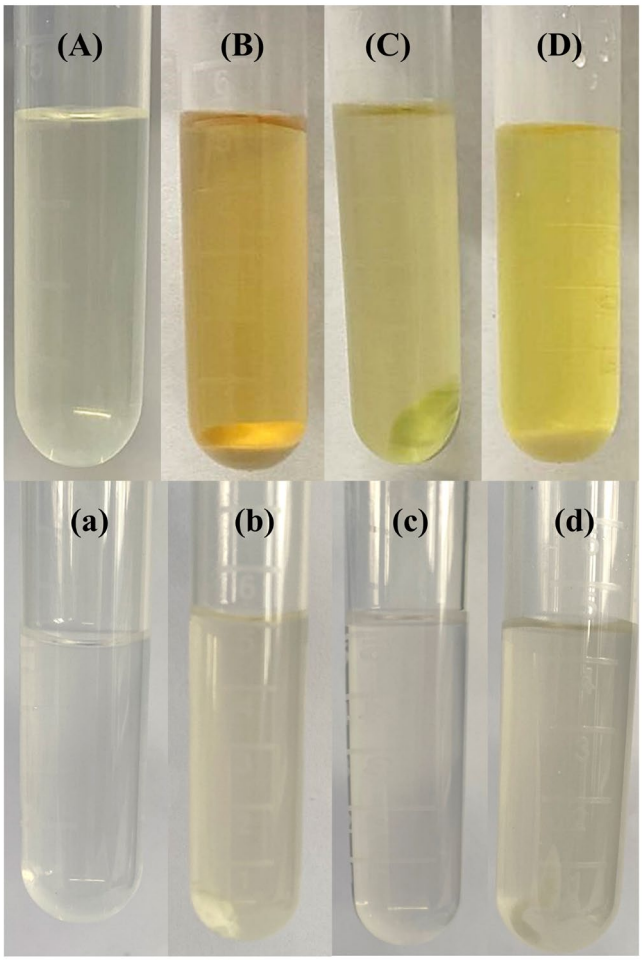


Fig. S1 PC degradation solutions catalyzed by NaOH (A−D) and urea (a−d). From A(a) to D(d), the depolymerizing reagents are H_2O, MeOH, EtOH, and MeOH-50 wt.% H_2O, respectively (0.2 g PC, 4 g depolymerizing reagent, 0.2 g catalyst, 140 °C, 3 h).

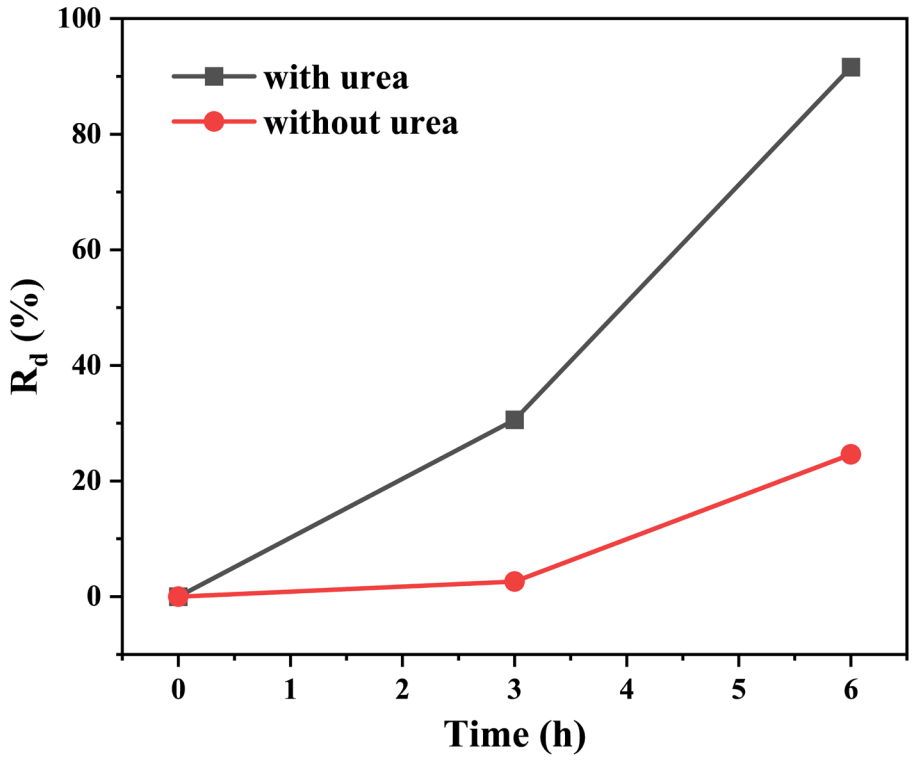


Fig. S2 PC methanolysis with or without urea.
Reaction condition: 0.2 g PC, 4 g methanol, with or without 0.02 g urea (42 mol% to PC), 140 °C.

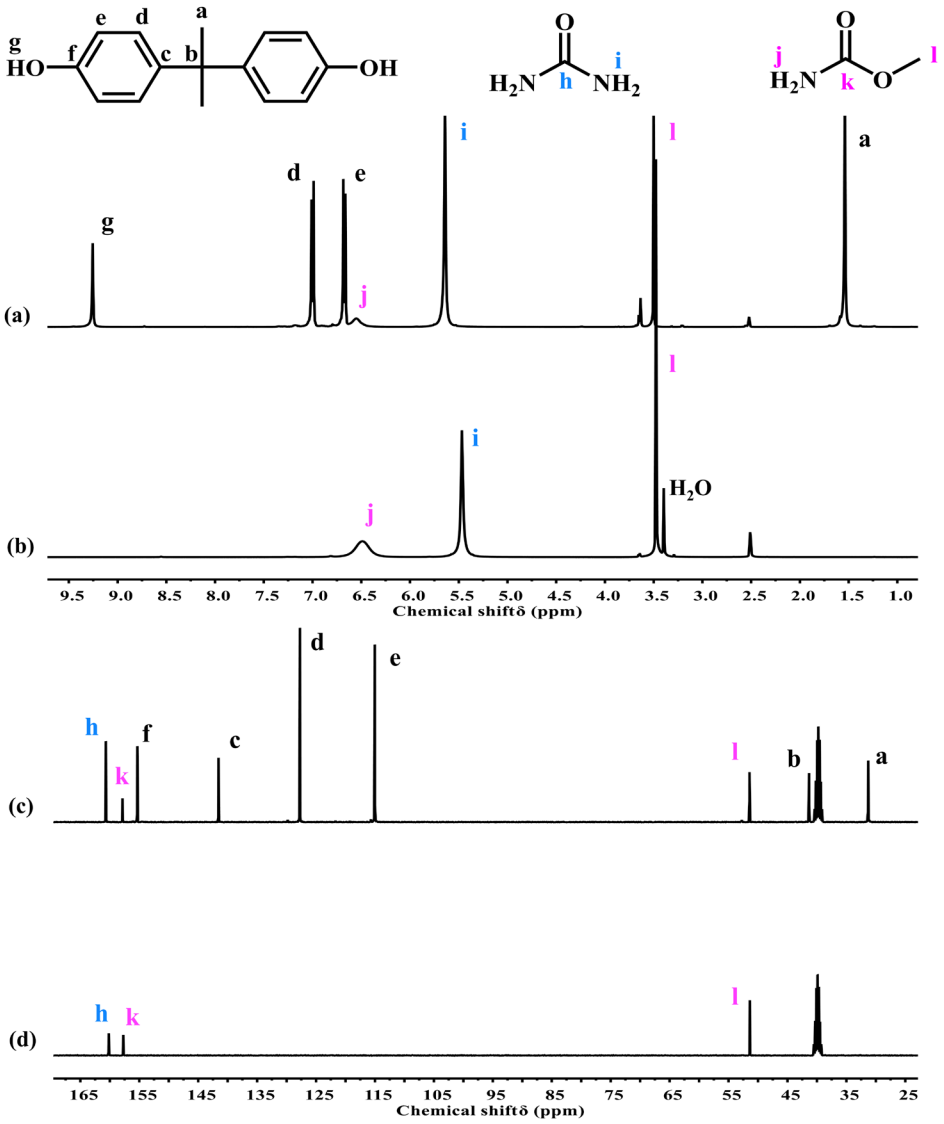


Fig. S3 ^{1}H NMR and ^{13}C NMR spectra of the distillation residue of PC degradation solution (a and c) and the reaction solution of methanol and urea (b and d).
Reaction conditions: (a and c) 0.2 g PC, 4 g methanol, 5 wt.% urea, 140 °C, 3 h. (b and d) 4 g methanol, 5 wt.% urea, 140 °C, 3 h.

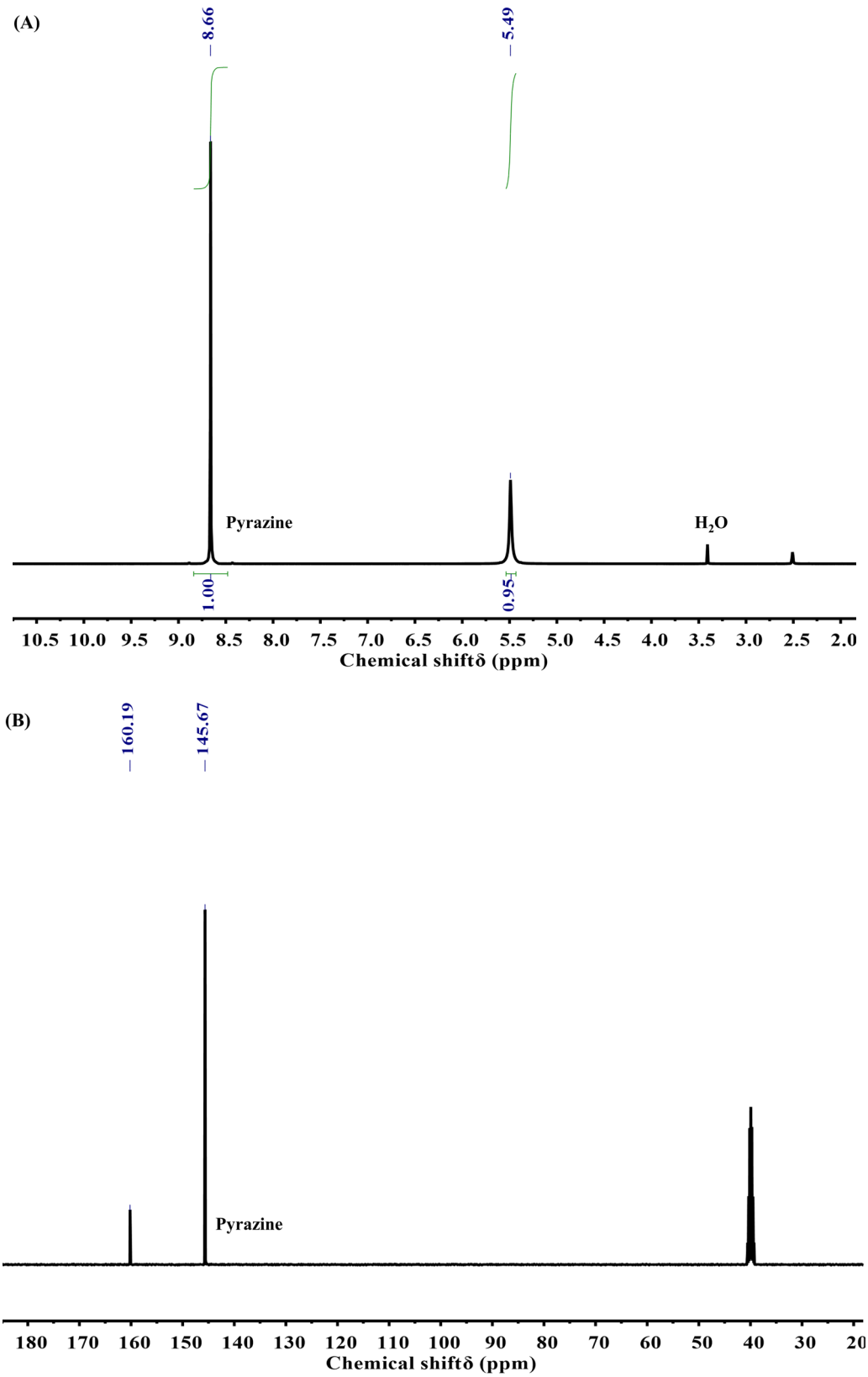


Fig. S4 ^{1}H NMR (A) and ^{13}C NMR (B) spectra of the isolated urea (Internal standard: pyrazine). Reaction condition: 0.2 g PC, 4 g methanol, 10 wt.% urea, 140 °C, 3 h.

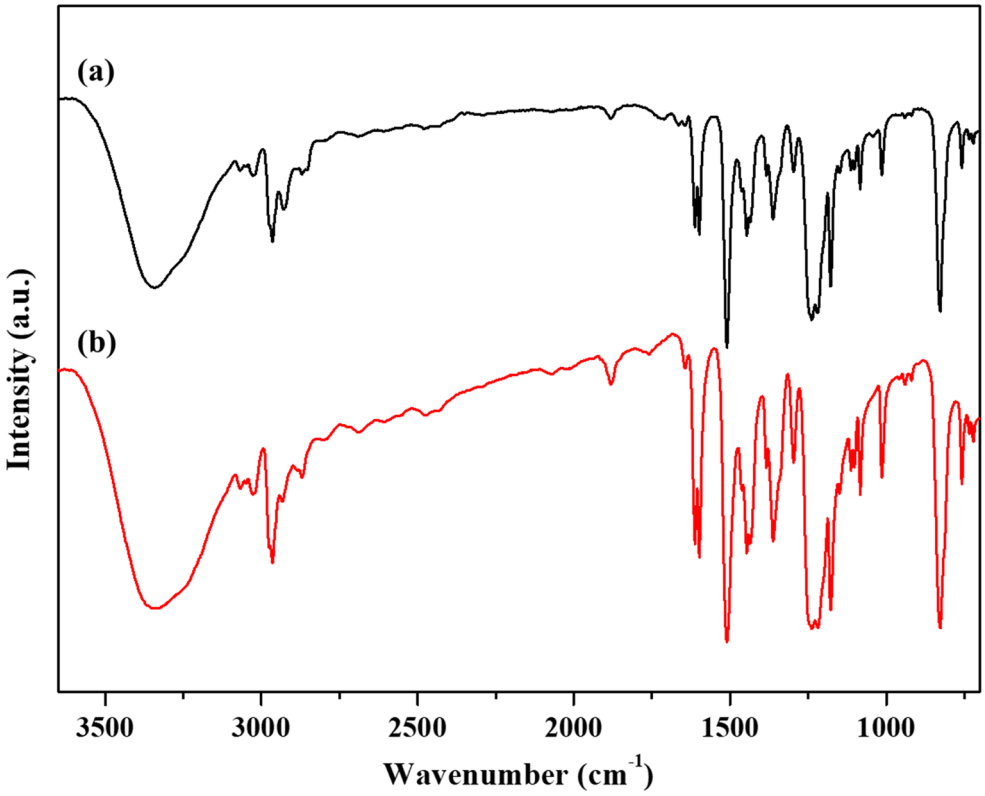


Fig. S5 IR spectra of (a) the degradation product BPA and (b) BPA standard. Reaction condition: 0.2 g PC, 4 g methanol, 10 wt.% urea, 140 °C, 3 h.

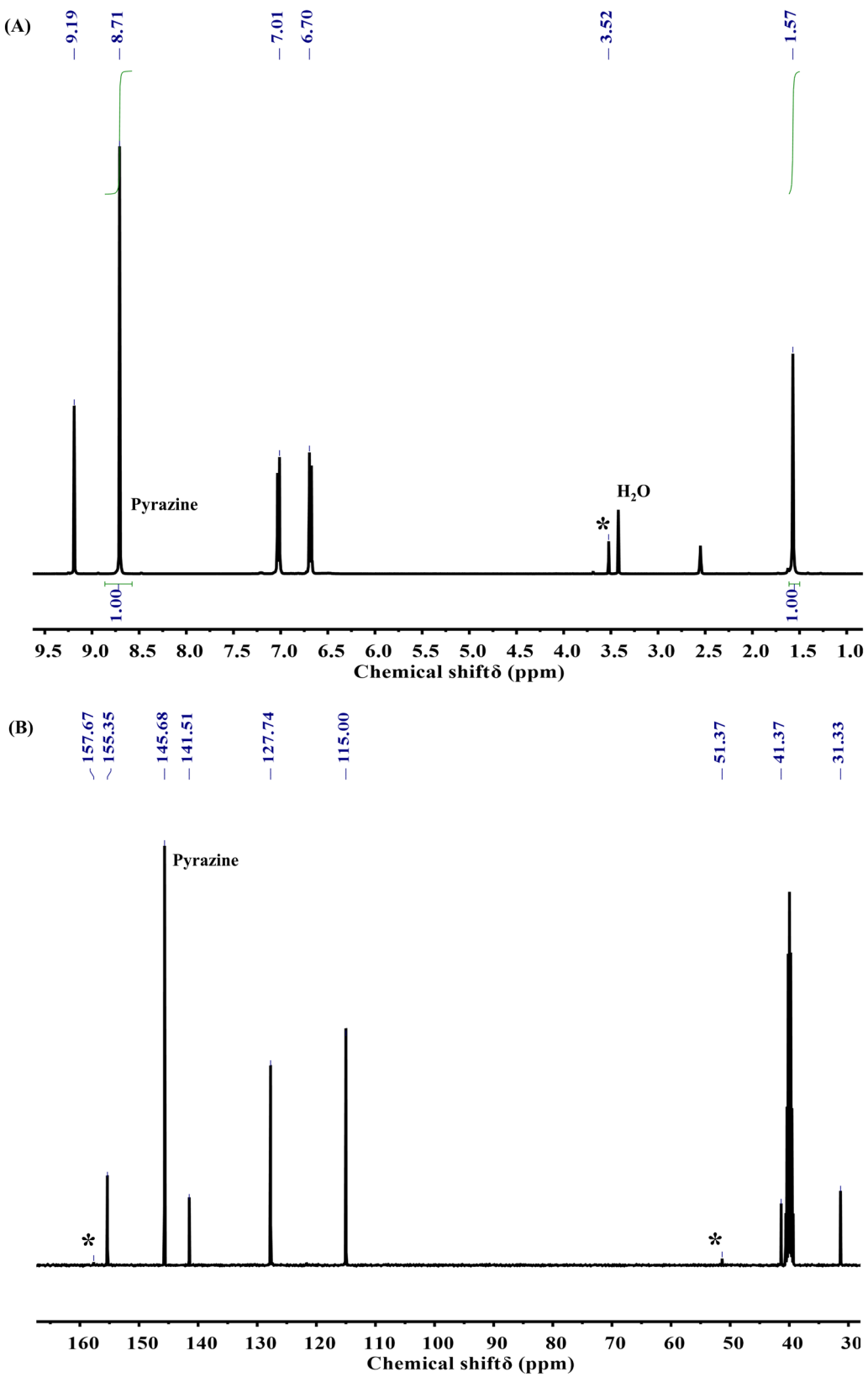


Fig. S6 ^{1}H NMR (A) and ^{13}C NMR (B) spectra of the degradation product BPA (Internal standard: pyrazine; ✶: methyl carbamate). Reaction condition: 0.2 g PC, 4 g methanol, 10 wt.% urea, 140 °C, 3 h.

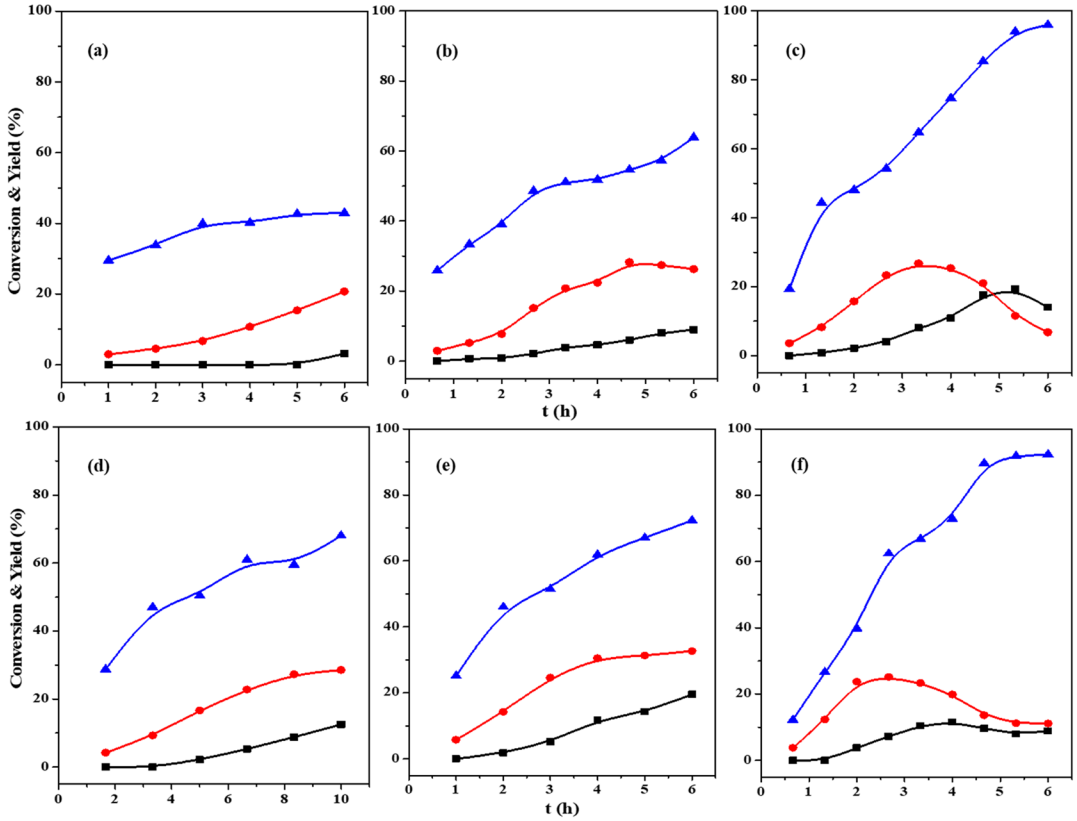


Fig. S7 DEC conversion (▲), EMC yield (●) and DMC yield (■) as a function of time at different temperatures at urea concentration of 10 wt.% (a, b and c at 140 °C, 160 °C, 180 °C, respectively) and 30 wt.% (d, e and f at 120 °C, 140 °C, 160 °C, respectively) (0.46 g DEC, 2.52 g MeOH (molar ratio is 1:20)).

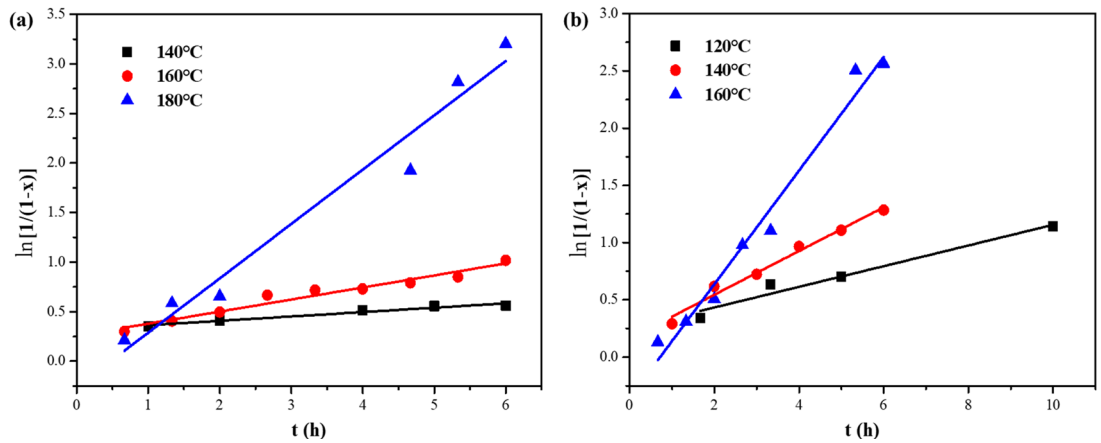


Fig. S8 ln[1/(1-x)] as a function of reaction time for the transesterification reaction between DEC and MeOH at different temperatures at urea concentration of (a) 10 wt.% and (b) 30 wt.% (x is the conversion of DEC).

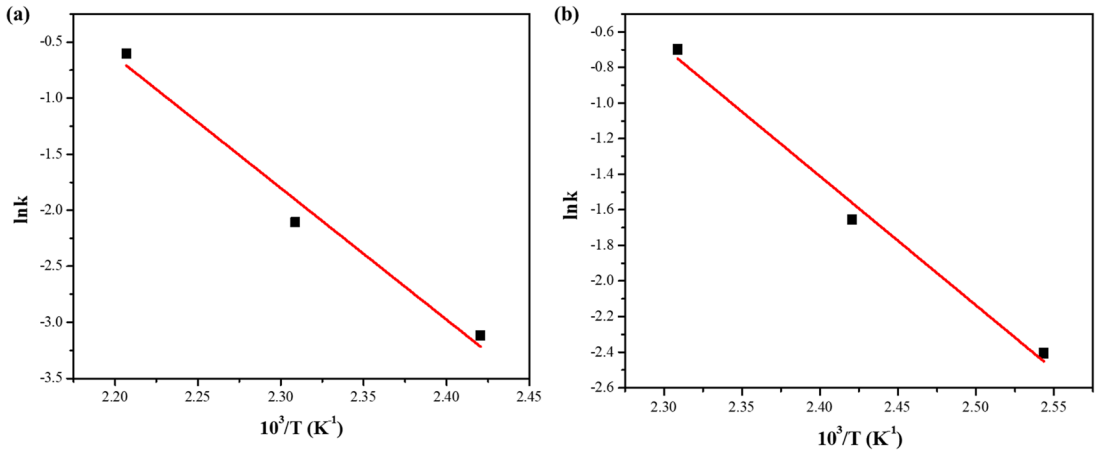
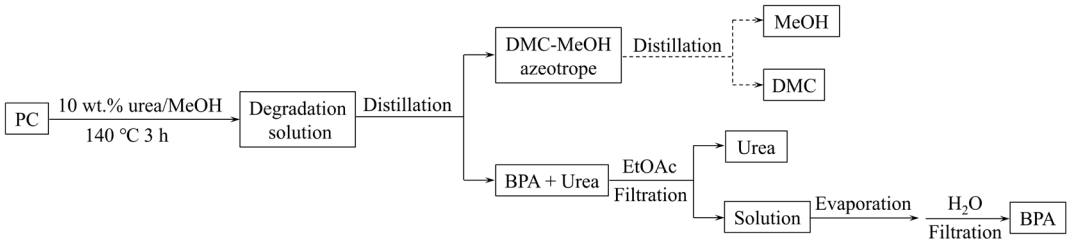


Fig. S9 Arrhenius plots for the transesterification reaction between DEC and MeOH at urea concentration of (a) 10 wt.% and (b) 30 wt.%.



Scheme S1 The flow chart of the recycling of PC.

Table S1 The pressures of the urea/methanol solutions at different concentrations and temperatures[a]

Temp./°C / Pressure/MPa / Urea concen./wt.%	130	140	150	160	180
0	0.69	0.93	1.25	1.60	2.54
5	0.66	0.90	1.19	1.55	2.45
10	0.64	0.88	1.15	1.48	2.36
30	0.59	0.80	1.03	1.32	2.12

[a] Reaction condition: Teflon-lined stainless autoclave.

Table S2 PC methanolysis catalyzed by urea or MC[a]

Entry	Catalyst	Time/h	Degraded or not
1	Urea	4	Yes
2	MC	18	No

[a] PC: 0.2 g, MeOH: 4 g, catalyst: 3.3×10^{-3} mol, reaction temperature: 140 °C; MC: methyl carbamate.

Table S3 Element analysis results of BPA samples

BPA sample	C (%)	H (%)	O (%)	N (%)
Isolated product	78.29	6.97	14.56	0.18
Standard	78.89	6.95	14.12	0.04

Table S4 The reusability of the PC degradation system[a]

Cycle	Degradation rate (%)	Cumulative yield (%)
0	100	—
1	100	—
2	100	—
3	100	—
4	100	—
5	100	—
6	100	—
7	100	—
8	100	—
9	100	—
10	100	BPA: 97.7, DMC: 33

[a] Reaction condition: 0.17 g PC, 3.38 g methanol, 0.34 g urea, 140 °C, 3 h. The degradation solution was reused directly by simply adding 0.17 g fresh PC at the end of each run.

Table S5 Material input-output table for the recycling of PC in two modes[a]

Mode	Input material	Input type	Output material	Input weight/g	Output weight/g	Yield/%
a single degradation	PC	Raw material		0.2075		
	MeOH	Solvent		4.0078		
	Urea	Catalyst		0.4021		
			DMC		0.0549	74.7
			BPA		0.1740	93.4
10 cycles of degradation[b]	PC	Raw material		1.8406[c]		
	MeOH	Solvent		3.3872		
	Urea	Catalyst		0.3432		
			DMC		0.2150	33[d]
			BPA		1.6144	97.7[d]

[a] m_{PC}: m_{MeOH}=1: 20, 10 wt.% urea, 140 °C 3 h. [b] The degradation solution was reused directly by simply adding 0.17 g fresh PC at the end of each run. [c] Total PC input. [d] Cumulative yield.

Table S6 Green metrics for the recycling of PC in two modes

Mode	sEF (kg/kg)	cEF (kg/kg)	EF (kg/kg)	Waste amount (kg/kg PC)	PMI (kg/kg)
a single degradation	1.66	19.17	3.41	3.76	20.17
10 cycles of degradation[a]	0.19	2.04	0.38	0.38	3.04

[a] The degradation solution was reused directly for the next reaction.

Table S7 Comparison of representative catalytic systems for the methanolysis of PC

Entry	Catalyst	Solvent	Y_{BPA}/%	Y_{DMC}/%	Reusability	Ref.	Notes
1	[EmimOH]Cl-2Urea	—	98	—	4	4	The catalyst or solvent has certain toxicity;
2	$[Ch]_3[PO_4]$	2-Me-THF	68	—	5	5	no recovering DMC
3	NaOH	THF	96.7	91.2	—	6	Use toxic solvents
4	NBu_4Cl/ZnO-NPs	THF	98	99	5	7	
5	Zn(2)Et[a]	2-Me-THF	96	86	—	8	
6	DBU	—	99	99	7	9	DBU is corrosive and irritating.
7	[Bmim][Cl]	—	95.8	96.5	8	10	The catalyst has certain toxicity; the preparation of ILs is cumbersome and costly.
8	Urea	—	93.4	74.7	10	This work	Urea is green, cheap, mass produced, and readily available; recover both BPA and DMC; no additional solvents

[a] A Zn^{II}-complex.

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