Supporting information

Upcycling of poly(ethylene terephthalate) waste plastics to terephthalonitrile

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Keywords: poly(ethylene terephthalate) (PET), plastic upcycling, terephthalonitrile, palladium, life cycle analysis (LCA)

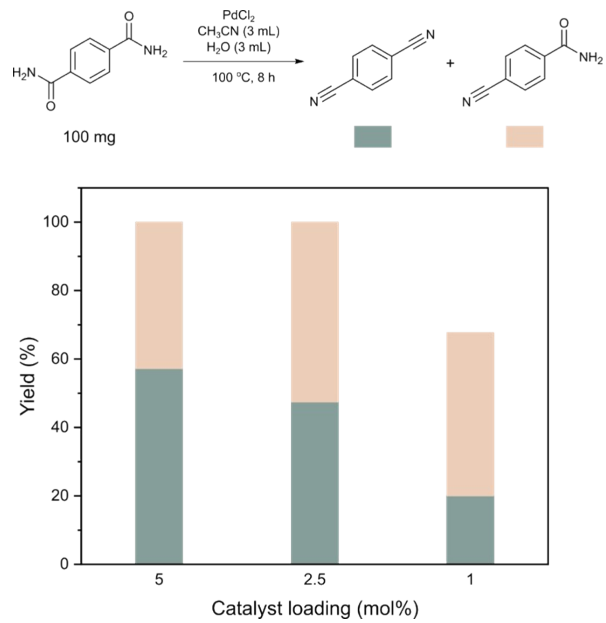


Fig. S1. Effect of $PdCl_2$ loading amount. Reaction conditions: terephthalamide (100 mg), $PdCl_2$ (1–5 mol%, corresponding to 1.2–6 mg), CH_3CN (3 mL), H_2O (3 mL), 100 °C, 8 h.

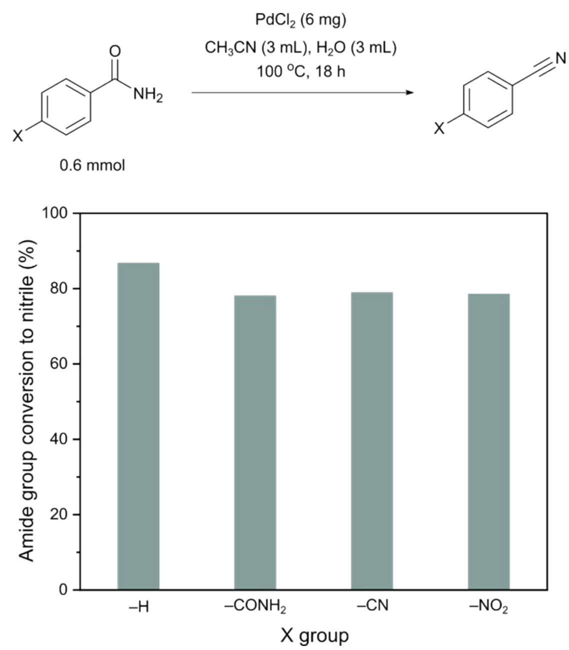


Fig. S2. The conversion of benzamides bearing different substituted groups to benzonitriles. Reaction conditions: (substituted) benzamide (0.6 mmol), $PdCl_2$ (6 mg), CH_3CN (3 mL), H_2O (3 mL), 100 °C, 18 h.

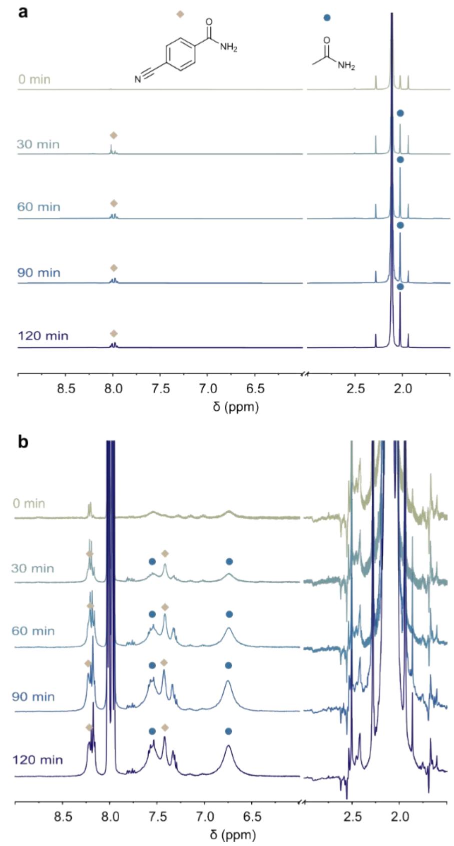


Fig. S3. NMR spectra of the reaction mixture in D_2O at different magnifications. Reaction conditions: terephthalamide (100 mg), $PdCl_2$ (6 mg), CH_3CN (3 mL), H_2O (3 mL), 100 °C. Terephthalamide and terephthalonitrile are not clearly visible in the spectra due to their low solubility in D_2O.

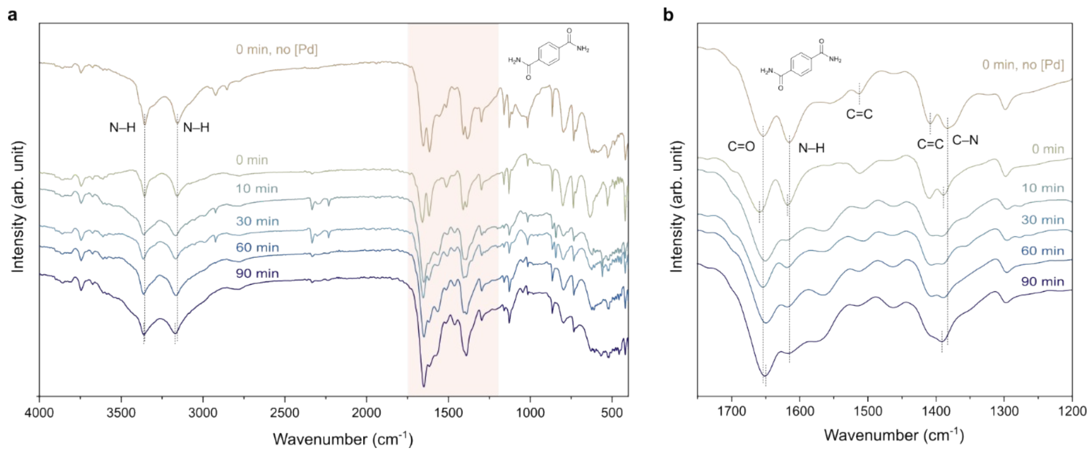


Fig. S4. FT-IR spectra of the dried reaction mixture: (a) full range (400 – 4000 cm^{-1}) and (b) zoom in at highlighted area (1200 – 1750 cm^{-1}). Reaction conditions: terephthalamide (10 mg), $PdCl_2$ (10 mg), CH_3CN (0.5 mL), H_2O (0.5 mL), 100 ^oC. Higher $PdCl_2$ content was used to amplify the interactions between the catalyst and the substrates and/or intermediates.

The FT-IR spectra of terephthalamide showed characteristic absorptions at 3351 cm^{-1} and 3154 cm^{-1} (N–H symmetric and asymmetric stretching), 1653 cm^{-1} (C=O stretching), 1616 cm^{-1} (N–H bending), 1513 cm^{-1} and 1408 cm^{-1} (C=C stretching), and 1383 cm^{-1} (C–N stretching).[1]

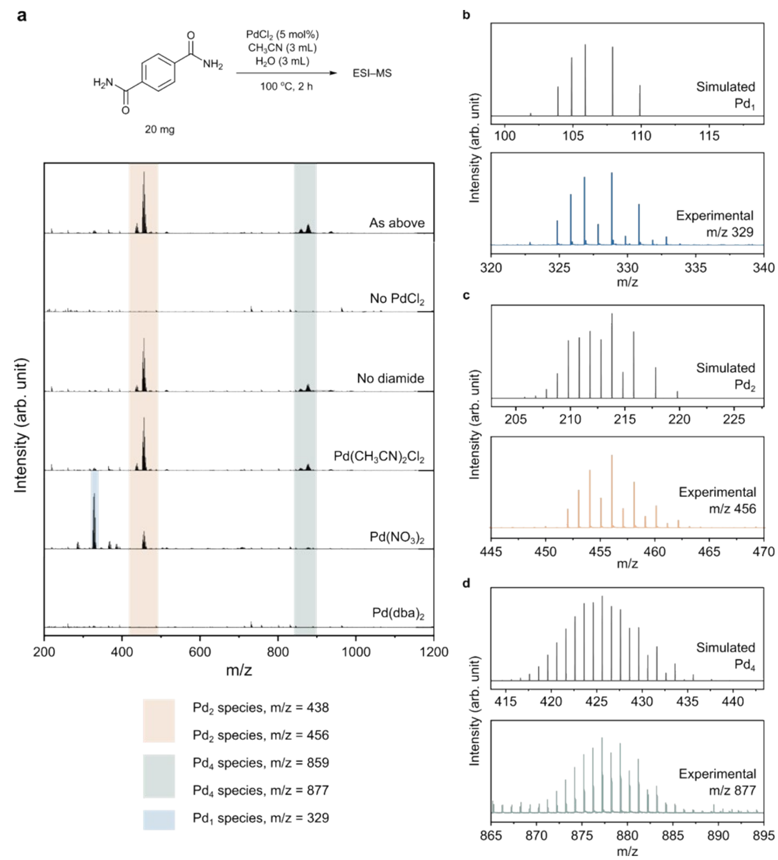


Fig. S5. (a) ESI-MS spectra of the reaction mixture under different conditions and identification of the major Pd species. Legands show the variation compared to the above condition. (b-d) Comparison of the simulated MS isotope distribution patterns of Pd_1, Pd_2, and Pd_4 species with the experimental monomeric, dimeric, and tetrameric Pd species, respectively.

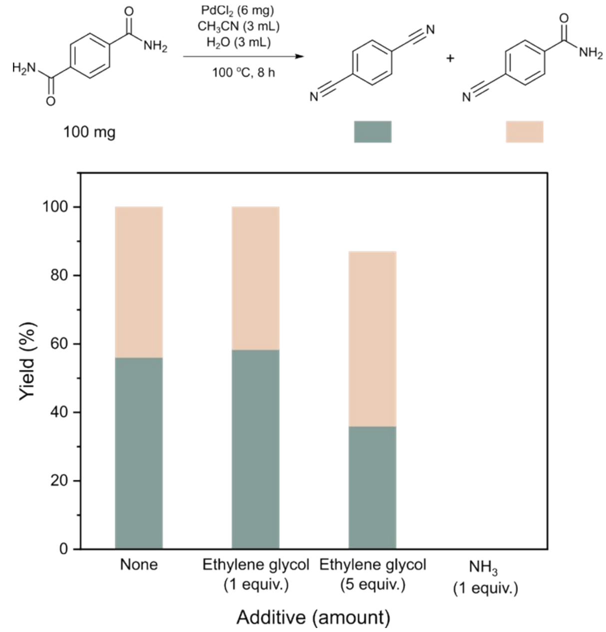


Fig. S6. Effect of possible residue from the ammonolysis step to the dehydration step. Reaction conditions: terephthalamide (100 mg), $PdCl_2$ (6 mg), additive, CH_3CN (3 mL), H_2O (3 mL), 100 ^oC, 18 h. NH_3 is from an 25% aqueous solution.

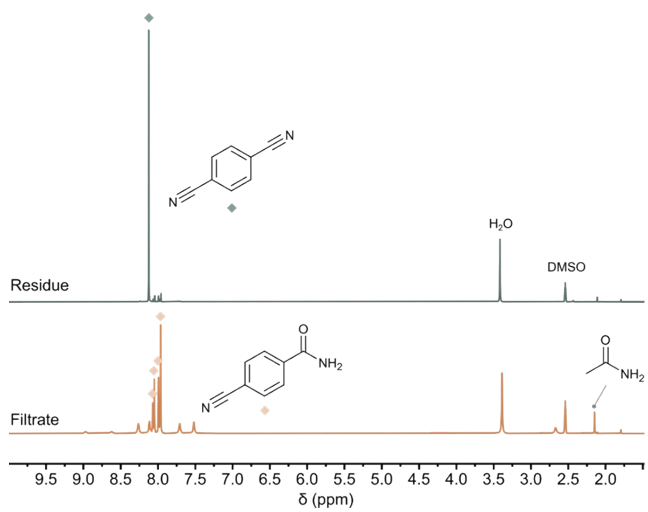


Fig. S7. NMR spectra of the residue and filtrate after washing the dried reaction mixture with water. Reaction conditions: terephthalamide (50 mg), $PdCl_2$ (6 mg), CH_3CN (3 mL), H_2O (3 mL), 100 ^oC, 6 h. A portion of acetamide may be lost during water evaporation of the filtrate when preparing the NMR sample.

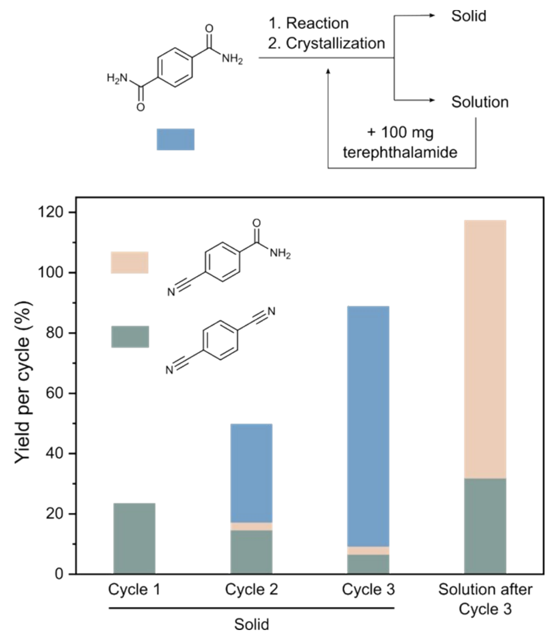


Fig. S8. Recycling test with terephthalonitrile isolation by crystallization. Reaction conditions: terephthalamide (100 mg), $PdCl_2$ (6 mg), CH_3CN (3 mL), H_2O (3 mL), 100 ^oC, 8 h. The reaction mixture was left overnight at room temperature for crystalization. The 4th column showed the GC yield of terephthalonitrile and 4-cyanobenzamide in the solution after filtrating the solid.

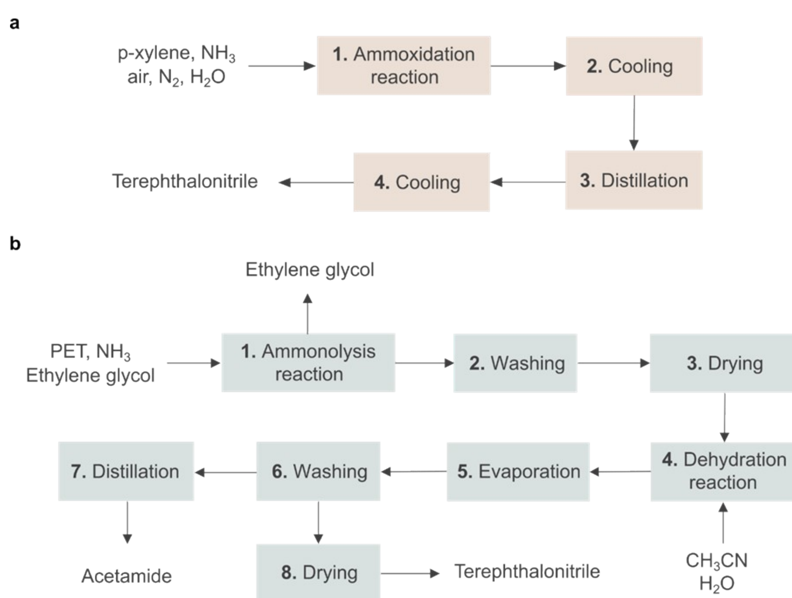


Fig. S9. System boundaries for the calculation of CO_2 emissions in terephthalonitrile production from **a** p-xylene and **b** PET (this work).

Scenario	Feed concentration (kg/m^3)	Terephthalonitrile yield (%)
1	33.3	50
2	16.7	60
3	8.3	70

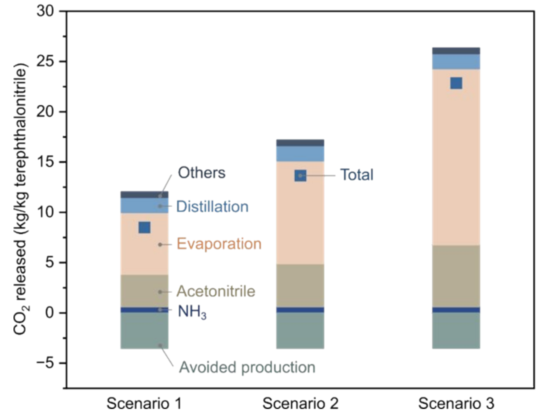


Fig. S10. CO_2 emissions comparison for scenarios with different feed concentrations for the dehydration step

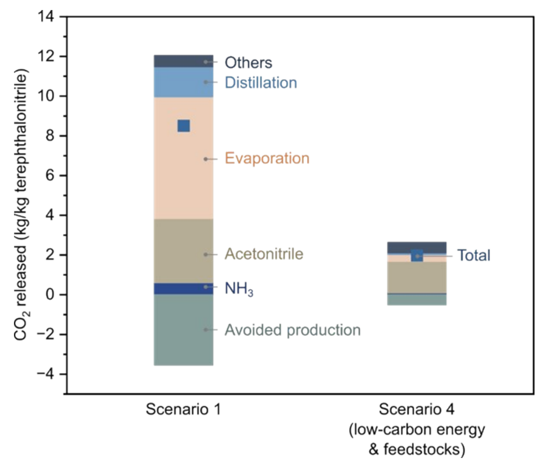
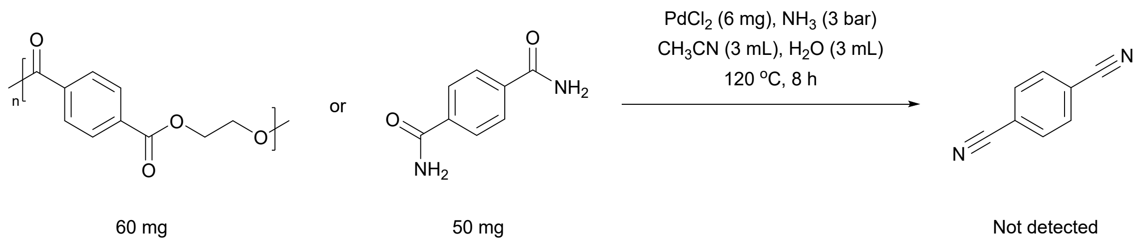
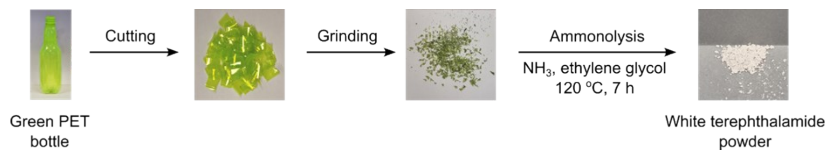


Fig. S11. CO_2 emissions reduction through low-carbon energy and feedstock integration (Table S8).

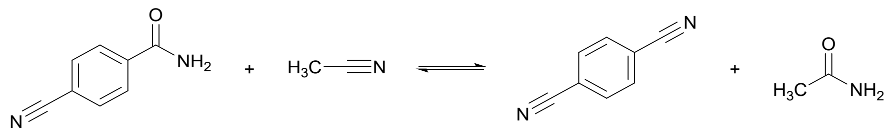


Scheme S1. Attempts to conduct one-pot transformation from PET to terephthalonitrile.



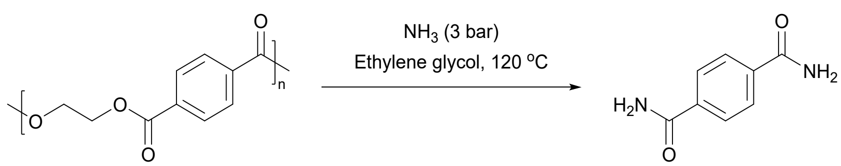
Scheme S2. Pretreatment and ammonolysis of green PET bottles.

Table S1. Calculation of equilibrium constant between 4-cyanobenzamide and terephthalonitrile. Acetonitrile amount is assumed to be a constant due to its excess amount.



Parameter	Forward reaction	Reversed reaction
Reaction conditions		
Substrate	Terephthalamide (100.5 mg, 0.612 mmol)	Terephthalonitrile (102.2 mg, 0.798 mmol) Acetamide (90.5 mg, 1.532 mmol)
Solvent	CH_3CN (3 mL), H_2O (3 mL)	
Temperature and time	100 ^oC, 18 h	
At equilibrium		
4-Cyanobenzamide (mmol)	0.2688	0.3916
Acetonitrile (mmol)	57.4800	57.4800
Terephthalonitrile (mmol)	0.3434	0.4060
Acetamide (mmol)	0.9075	1.0881
Equilibrium constant	0.0202	0.0196

Table S2. Condition screening for the ammonolysis step



No.	Main variation	Reaction temperature (^oC)	NH_3 feed temperature (^oC)	Reaction time (h)	PET amount (mg)	EG amount (mL)	NH_3/PET unit mol ratio	Yield (%)
1	As above	120	25	6	120	3	3.0	29.7
2	Add 5 mol% $Zn(OAc)_2$	120	25	6	120	3	3.0	26.5
3	Feed NH_3 at 0 ^oC	120	0	6	60	0.5	20.0	57.1
4	Feed NH_3 at -20 ^oC	120	-20	7	60	0.5	23.4	71.2

Table S3. Comparison of terephthalonitrile production from PET between this work and previous works. *Nitrile selectivity (%) = 100 − (% by-product, excluding intermediates), based on the reported products and pathways.

	Catalyst	Temperature (° C)	Yield (%)	Nitrile selectivity (%)*	By-product	Catalyst stability
This work	$PdCl_2$	100–120	51	100	No	Partial loss on recycling
Blackmon et al., 1990[2]	No	120–345	29	56	Carboxylic acid	N/A
Xu et al., 2019[3]	$Ca(OH)_2$/ γ-Al_2O_3	500	58	58	Char, gases, arenes	Slight deactivation after 4 cycles
Xu et al., 2019[4]	γ-Al_2O_3	500	58	58	Coke, gases, arenes	Slight deactivation after 5 cycles
Xie et al., 2024[5]	γ-Al_2O_3	550	33	33	Char, gases, arenes	Slight deactivation after 4 cycles

Table S4. Process parameters and key assumptions for the production of terephthalonitrile from p-xylene[6]

Step	Parameter	Value	Unit
1. Ammoxidation reaction	p-Xylene concentration	2.5	mol%
	NH_3 concentration	14.0	mol%
	O_2 concentration	8.3	mol%
	H_2O concentration	1.3	mol%
	Reaction temperature	450	°C
	Terephthalonitrile yield	29.0	%
	p-Tolunitrile yield	38.0	%
	p-Xylene conversion	70.2	%
	Recovery rate of p-Xylene and p-tolunitrile	0.98	
	Enthalpy change	-1330.4	kJ/mol
2. Cooling	Temperature after cooling	65	°C
3. Distillation	Distillation pressure	1	bar
4. Cooling	Temperature after cooling	25	°C

Table S5. Mass balance for the production of terephthalonitrile from p-xylene based on 1 kg of terephthalonitrile. GWP: global warming potential.

Materials	Amount needed (kg)	GWP (kg CO_2/kg material)	CO_2 released (kg CO_2)
p-Xylene	0.90	2.16	1.94
Ammonia	2.41	2.03	4.90
Air	11.62	0.11	1.24
Nitrogen	12.23	0.13	1.53
Water	0.24	0.00	0.00
		Total	9.62

Table S6. Energy balance for the production of terephthalonitrile from p-xylene based on 1 kg of terephthalonitrile

Step	Heat input (kJ)	Heat output (kJ)	CO_2 released (kg CO_2)
1. Ammoxidation reaction	16,205	9,782	1.26
2. Cooling		18,172	0.57
3. Distillation	4,677		0.27
4. Cooling	830		0.05
		Total	2.15

Table S7. Process parameters and key assumptions for the production of terephthalonitrile from PET

Step	Parameter	Value	Unit
1. Ammonolysis reaction[2]	Reaction temperature	120	^oC
	Terephthalamide yield	90.0	%
	Ethylene glycol to PET mass ratio	1.5	
	Recovery rate of ethylene glycol	0.98	
	Recovery rate of NH_3	0.95	
	Enthalpy change	-46.0	kJ/mol
2. Washing	Ethylene glycol residue	2	wt.%
	Water to ethylene glycol mass ratio	10	
	Initial temperature of washing water	25	^oC
3. Drying	Water content before drying	5.0	%
4. Dehydration reaction	Reaction temperature	100	^oC
	Terephthalamide concentration	[8.3, 33.3]	kg/m^3
	Terephthalonitrile yield	[70.0, 50.0]	%

	Unreacted amides recovery rate	0.98	
	Recovery rate of $CH_3CN–H_2O$ mixture	0.98	
	Enthalpy change	-13.7	kJ/mol
5. Evaporation	Evaporation pressure	1	bar
6. Washing	Water to terephthalonitrile mass ratio	10	
	Initial temperature of washing water	25	^oC
7. Distillation	Distilation pressure	1	bar
8. Drying	Water content before drying	5.0	%

Table S8. Mass balance and CO_2 from materials for the production of terephthalonitrile from PET (Case 1) based on 1 kg of terephthalonitrile. GWP: global warming potential. *Estimated based on GWP of acetic acid and ammonia using mass balance

Materials	Amount needed (kg)	GWP (kg CO_2/kg material)	CO_2 released (kg CO_2)
Material input			
PET	1.60	0.22	0.36
NH_3	0.30	2.03	0.61
Ethylene glycol	0.05	3.40	0.16
Acetonitrile	1.16	2.79	3.23
Water	0.72	0.00	0.00
Avoided production			
Ethylene glycol	-0.47	3.40	-1.58
Acetamide	-0.87	2.26*	-1.96
		Total	0.81

Table S9. Energy balance and CO_2 from energy usage for the production of terephthalonitrile from PET (Case 1) based on 1 kg of terephthalonitrile.

Step	Heat input (kJ)	Heat output (kJ)	CO_2 released (kg CO_2)
1. Ammonolysis reaction	272	345	0.03
2. Washing			0.00
3. Drying	149		0.01
4. Dehydration reaction	17	101	0.00
5. Evaporation	104645		6.13
6. Washing			0.00
7. Distillation	25796		1.51
8. Drying	113		0.01

Total	7.69

Table S10. CO_2 released per equivalant from energy and feedstock sources. *The conversion factor of 1.17 MJ primary fuel/MJ heat (GaBi database) was applied for all cases[7].

	From p-xylene & Scenario 1-3	Scenario 4
NH_3 (kg CO_2/kg)	2.03	0.31
Ethylene glycol (kg CO_2/kg)	3.40	0.49
Acetonitrile (kg CO_2/kg)	2.79	1.37[8]
Acetamide (kg CO_2/kg)	2.26	0.33
Heating* (g CO_2/MJ released from the fuel)	50.1 (from natural gas)	2.82[9] (from green hydrogen)
Cooling (g CO_2/MJ)	31.5 (natural gas-based electricity)	0.28 (nuclear electricity)

References

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