SUPPLEMENTARY INFORMATION

Acid catalyst screening for hydrolysis of post-consumer PET waste and exploration of acidolysis

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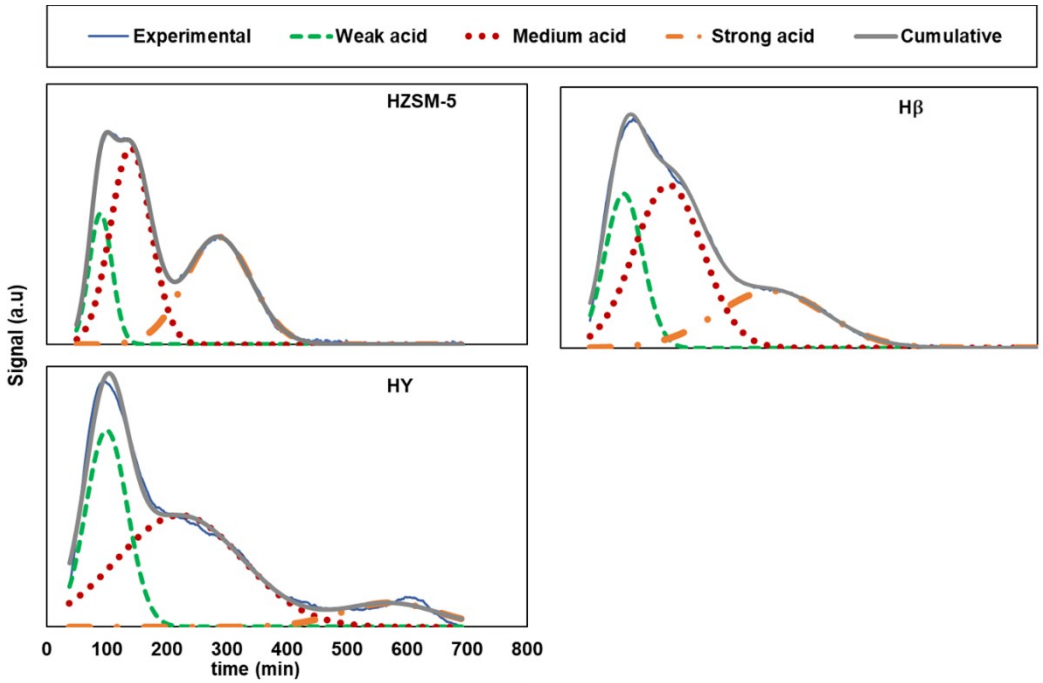

Figure S1. Peak deconvolution for weak, medium, and strong acid sites from NH_3-TDP of HZSM-5, Hβ, and HY.

Table S1. TPD peak temperatures and areas corresponding to weak, medium, and strong acid sites by deconvolution of NH_3-TPD experimental data for the zeolite catalysts.

	T (˚C)			Peak area (a.u.)		
	Weak acid	Medium acid	Strong acid	Weak acid	Medium acid	Strong acid
HZSM-5	90	139	285	2.43	5.59	4.66
Hβ	79	136	265	3.38	5.57	2.91
HY	99	222	572	3.08	4.64	0.67

Table S2. Catalyst and water loadings for PET hydrolysis experiments.

Results in Figure	Catalyst	*T* (˚C)	*pH* at room temperature	Catalyst loading	Water loading (mL)
1	None	200	(-)	0.0 mg	3.29
		270	(-)	0.0 mg	2.92
	HY, HZSM-5, Hβ	200	(-)	65.7 mg	3.29
		270	(-)	58.3 mg	2.92
2 S4 S7	Sulfuric Acid	200	0.63	0.0250 mL	2.07
		200	1.37	0.0039 mL	2.07
		200	1.50	0.0027 mL	2.07
		200	1.55	0.0023 mL	2.07
		200	1.60	0.0020 mL	2.07
		200	1.83	0.0010 mL	2.07
	IL	200	0.70	0.3400 mL	2.07
		200	1.40	0.0500 mL	2.07
		200	1.50	0.0400 mL	2.07
		200	1.60	0.0300 mL	2.07
		200	2.10	0.0100 mL	2.07
		200	2.70	0.0020 mL	2.07
		200	2.90	0.0013 mL	2.07
	IL-SO_3H	200	1.20	1580 mg	2.07
		200	1.38	840 mg	2.07
		200	1.86	160 mg	2.07
		200	2.42	20.0 mg	2.07
		200	2.91	4.0 mg	2.07
	Nitric Acid	200	0.71	0.2000 mL	2.07
		200	1.42	0.0620 mL	3.29
		200	2.01	0.0100 mL	2.07
3 S10 S13	Propanoic acid	200	2.59	0.0800 mL	2.07
		200	2.21	0.5000 mL	2.07
		200	1.94	1.5000 mL	2.07
	Glycolic acid	200	2.10	74.3 mg	2.07
		200	1.68	472.7 mg	2.07
		200	1.52	945.8 mg	2.07
	Acetic acid	200	2.75	0.0160 mL	2.07
		200	2.62	0.0280 mL	2.07
		200	2.50	0.0600 mL	2.07
		200	1.94	1.0000 mL	2.07
		200	1.89	1.3600 mL	2.07
		200	1.84	1.9600 mL	2.07
	Benzoic acid	200	(-)	65.8 mg	3.29
		200	(-)	501.1 mg	2.07

Table S2 (cont.). Catalyst and water loadings for PET hydrolysis experiments.

Results in Figure	Catalyst	*T* (˚C)	*pH* at room temperature	Catalyst loading	Water loading (mL)
		200	(-)	1004 mg	2.07
		200	(-)	1808 mg	2.07
	4-FBA	200	(-)	4.8 mg	2.07
		200	(-)	30.8 mg	2.07
		200	(-)	311.6 mg	2.07
		200	(-)	107.2 mg	2.07
	TPA	200	(-)	16.6 mg	2.07
		200	(-)	24.8 mg	2.07
		200	(-)	65.8 mg	3.29
		200	(-)	40.6 mg	2.07
		200	(-)	275.4 mg	3.29
	Stearic acid	200	(-)	7.7 mg	2.07
		200	(-)	160.7 mg	2.07
		200	(-)	512.5 mg	2.07
		200	(-)	1323 mg	2.07
4	ZnI_2	200	5.01	89.3 mg	2.07
		200	5.09	55.7 mg	2.07
		200	5.11	43.0 mg	2.07
		200	5.14	36.0 mg	2.07
		200	5.27	25.0 mg	2.07
	$ZnSO_4$	200	4.9	1050 mg	2.07
		200	5.47	60.0 mg	2.07
		200	5.52	40.0 mg	2.07
		200	5.53	60.0 mg	3.29
Table S5	4-FBA	200	(-)	0.0314 g	3.60
	TPA	200	(-)	0.0417 g	3.60
	Propanoic acid	200	(-)	0.08 mL	3.60
	Acetic acid	200	(-)	0.08 mL	3.60
	Benzoic acid	200	(-)	0.0736 g	3.60

Table S3. Zeolite properties as supplied by *Zeolyst International.*

	SiO_2/ Al_2O_3	Pore size, Å	Surface area, m^2/g
HZSM-5	50	5	425
Hβ	25	5-7	680
HY	5.1	12	925

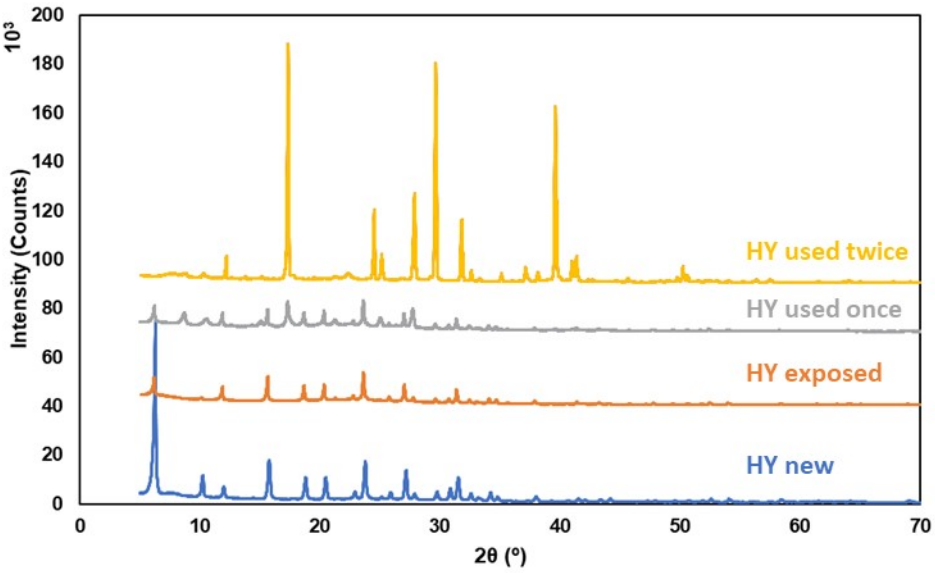

Figure S2. XRD patterns for HY zeolite, fresh after calcination (HY new), after hydrothermal exposure at 270 ˚C for 30 min (HY exposed), after one use for PET hydrolysis at 270 ˚C for 30 min (HY used once), and after two uses during PET hydrolysis at 270 ˚C for 30 min without recalcination (HY used twice).

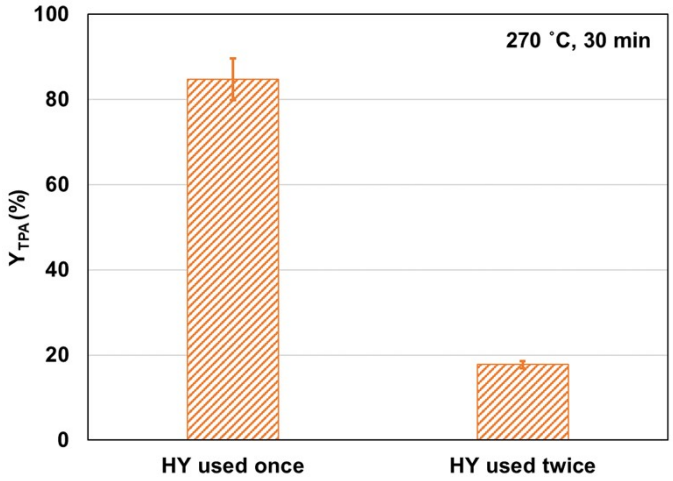

Figure S3. TPA yield after PET hydrolysis with HY in its first use (HY used once) and second use (HY used twice).

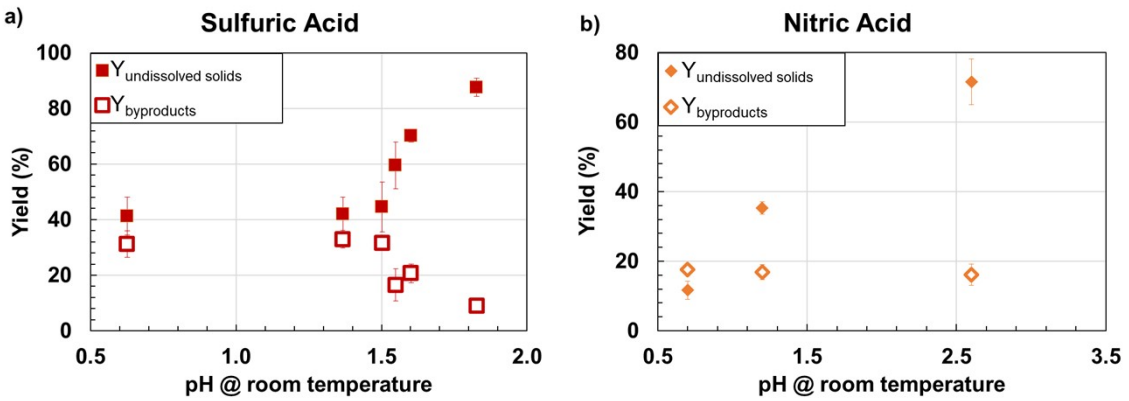

Figure S4. Effect of pH on yields of undissolved solids and byproducts for PET hydrolysis (200 ˚C, 2 h, 1/10 mass ratio PET/water) with a) sulfuric acid and b) nitric acid.

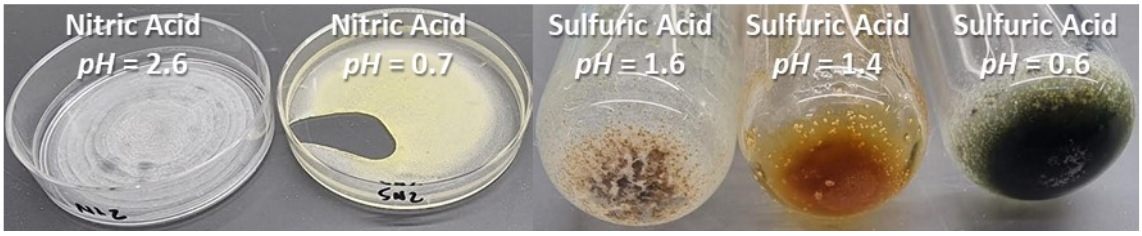

Figure S5. Dissolved solids from hydrolysis of PET. From left to right: Nitric acid at *pH* = 2.6 and 0.7, sulfuric acid at *pH* = 1.55, 1.4, and 0.6 (all *pH* values were measured at room temperature).

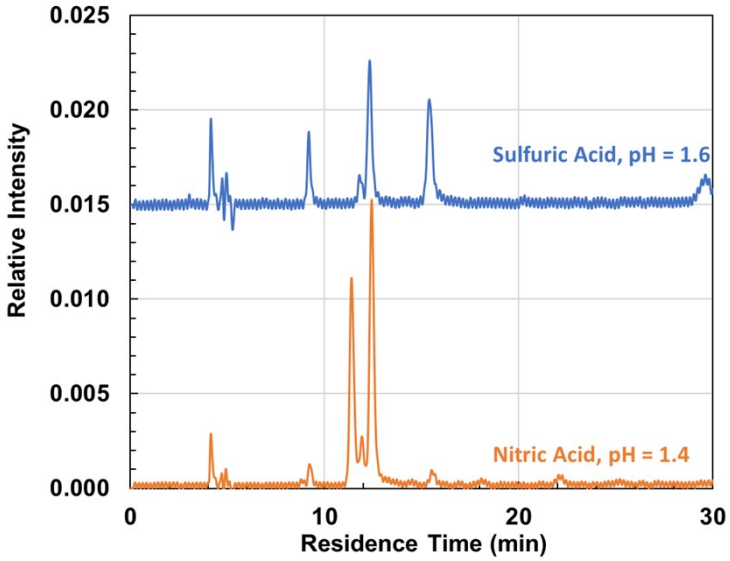

Figure S6. HPLC chromatograms of dissolved solids from hydrolysis of PET with sulfuric acid at *pH* = 1.6, and nitric acid at *pH* = 1.4 at 200 ˚C for 2 h.

Table S4. Number- and weight-average molecular weights (M_n, M_W) and degree of polymerization (*DP*) of undissolved solids from PET hydrolysis experiments at 200 ˚C for 2 h as determined by MALDI-T*o*F MS analysis. Bottle-grade PET has M_n of 24,000-36,000 g/mol.[1]

Catalyst	*pH*	M_n PET (g/mol)	M_w PET (g/mol)	*DP*
Acetic acid	2.5	1645	1756	8.6
	2.6	1373	1434	7.1
	2.8	(-)	(-)	(-)
Benzoic acid	(-)	1194	1227	6.2
IL	1.4	1568	1670	8.2
	1.5	1437	1500	7.5
	1.6	1562	1652	8.1
	2.1	1372	1454	7.1
	2.7	1529	1621	8
	2.9	1313	1331	6.8
IL-SO_3H	2.9	1655	1775	8.6
	2.4	(-)	(-)	(-)
	1.9	1596	1714	8.3
	1.4	1592	1592	8.3
Nitric acid	0.7	1359	1419	7.1
	1.4	1476	1506	7.7
	2.0	1514	1638	7.9
Sulfuric acid	0.7	1508	1599	7.9
	1.4	1624	1725	8.5
	1.5	1547	1668	8.1
	1.6	1686	1777	8.8
	1.6	1639	1757	8.5
	1.8	1295	1343	6.7

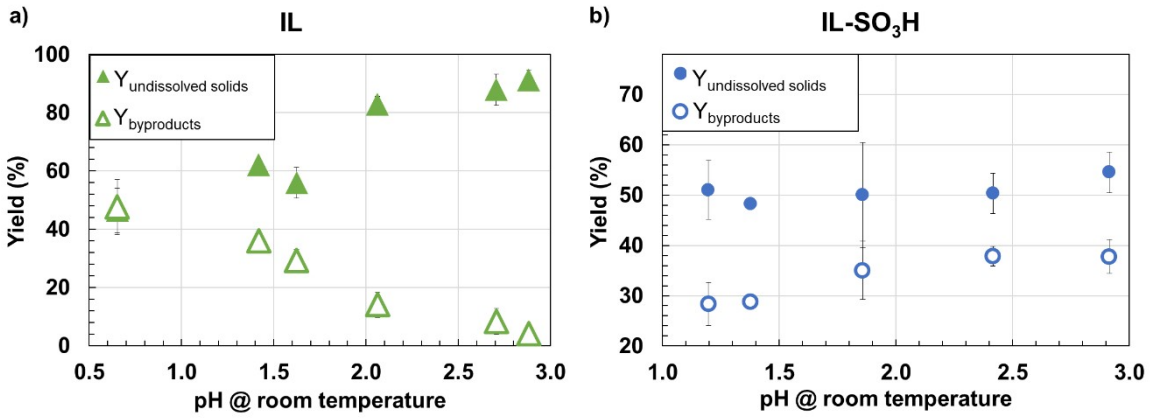

Figure S7. Effect of *pH* on yields of undissolved solids and byproducts for PET hydrolysis (200 ˚C, 2 h, 1/10 mass ratio PET/water) with a) IL and b) IL-SO_3H.

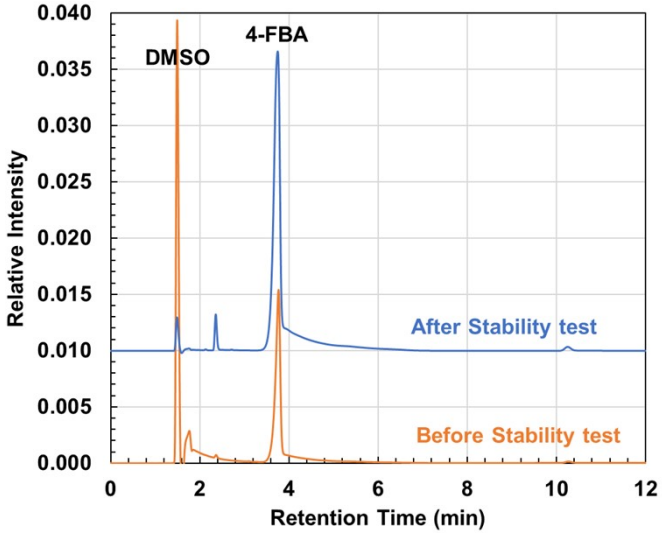

Figure S8. HPLC chromatograms of 4-formylbenzoic acid (4-FBA) before and after hydrothermal treatment at 200 ˚C for 2 h.

Table S5. TPA yield (Y_{TPA}) from PET hydrolysis experiments at 200 ˚C for 2 h and 1.6 MPa or ≈ 35 MPa.

Catalyst	Pressure 1.6 MPa		Pressure ≈ 35 MPa	
	mol_{cat}/g_{PET}	Y_{TPA} (%)	mol_{cat}/g_{PET}	Y_{TPA} (%)
4-FBA	0.0010	15 ± 8	0.0011	11 ± 2
TPA	0.0012	17 ± 2	0.0012	20 ± 9
Propanoic acid	0.0052	4 ± 3	0.0053	4 ± 2
Acetic acid	0.0051	16 ± 5	0.0067	26 ± 4
Benzoic acid	0.0016	32 ± 2	0.0012	35 ± 10

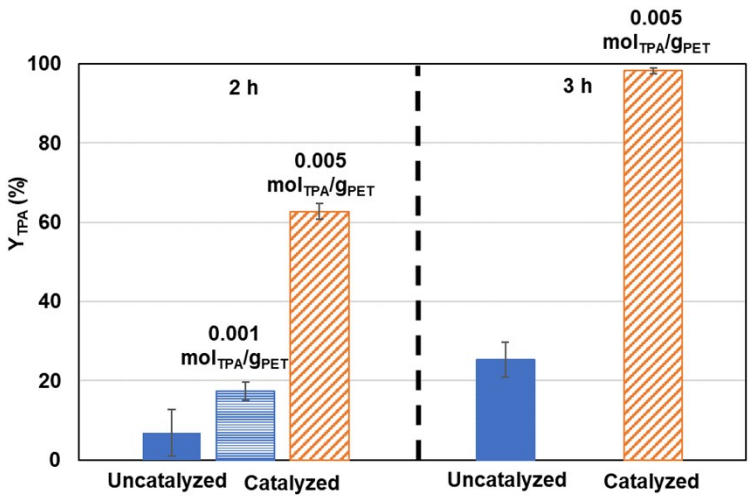

Figure S9. Effect of TPA loading on PET hydrolysis (200 ˚C, 1/10 mass ratio PET/Water).

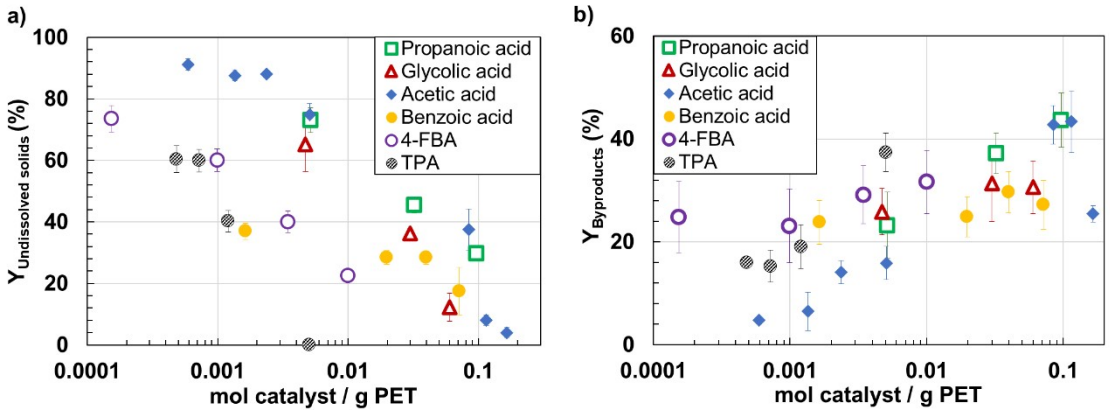

Figure S10. Effect of carboxylic acid loading on yields of a) undissolved solids and b) byproducts from PET hydrolysis (200 ˚C, 2 h, 1/10 mass ratio PET/water).

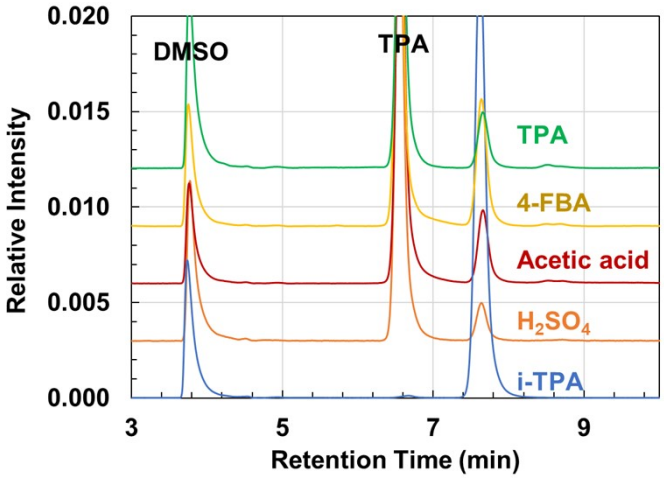

Figure S11. HPLC chromatograms of DMSO-soluble products from PET hydrolysis experiments (200 ˚C, 2 h, 1/10 mass ratio PET/water) with terephthalic acid, 4-formyl benzoic acid, acetic acid, or sulfuric acid and HPLC chromatogram of a standard solution of isophthalic acid. Apart from the solvent and TPA peak (observed at 6.6 min), all samples showed an additional peak at 7.6 min, and some exhibited a peak at 8.1 min. The peak around 7.6 min was most likely i-TPA. Commercial bottle-grade PET contains 1.5% isophthalic acid (i-TPA) as a comonomer. Although mono(2-hydroxyethyl) terephthalic acid (MHET) is also a potential byproduct,[2] it eluted at 7.7 min, and this peak was not observed in the samples.

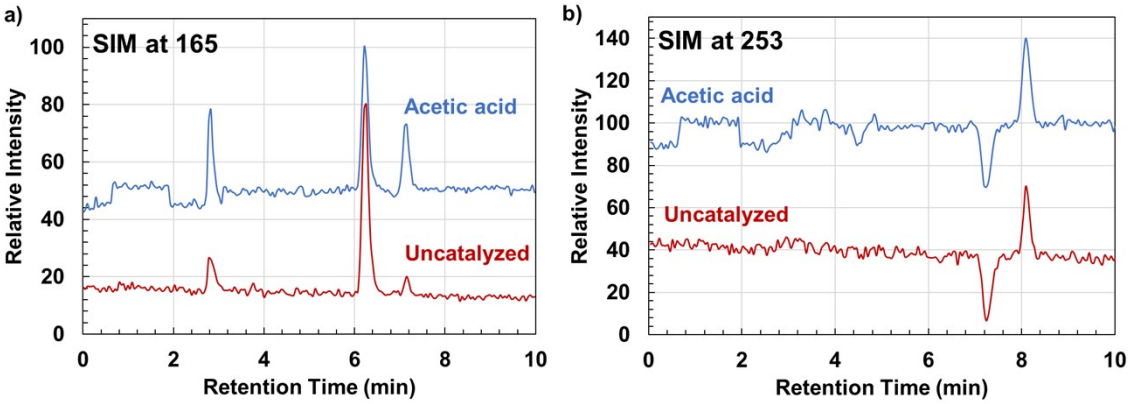

Figure S12. LC-MS selective ion chromatograms for the aqueous-phase products from PET hydrolysis without catalyst and with acetic acid (200 °C, 2 h, 1/10 mass ratio PET/water. a) SIM at 165 m/z confirms the identities of TPA and isophthalic acid (i-TPA) with retention times of 6.6 min and 7.6 min, respectively, and b) SIM at 253 m/z indicates the potential presence of bis(2-hydroxyethyl) terephthalate, a byproduct arising from the esterification of TPA with ethylene glycol.

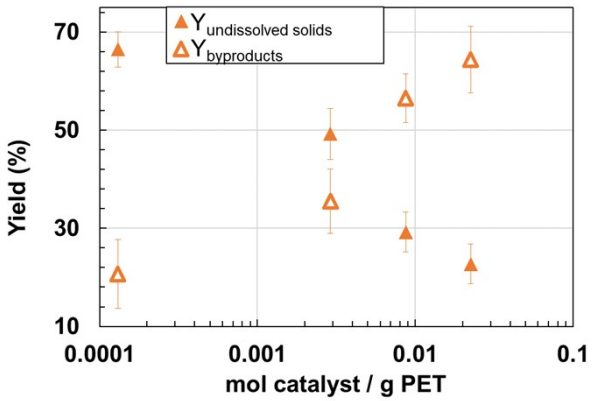

Figure S13. Effect of stearic acid loading on yields of undissolved solids and byproducts from PET hydrolysis (200 ˚C, 2 h, 1/10 mass ratio PET/water).

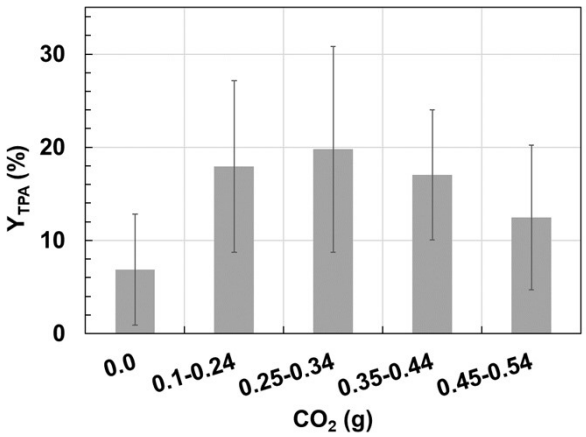

Figure S14. Effect of CO_2 loading on average TPA yield from PET hydrolysis (200 ˚C, 2 h, 1/10 mass ratio PET/water). Thermodynamic calculations[3–5] indicate the pH changed from about 3.7 to 3.3 for 0.1 to 0.54 g CO_2 added. Without CO_2 the pH is 5.4 at 200 ˚C.

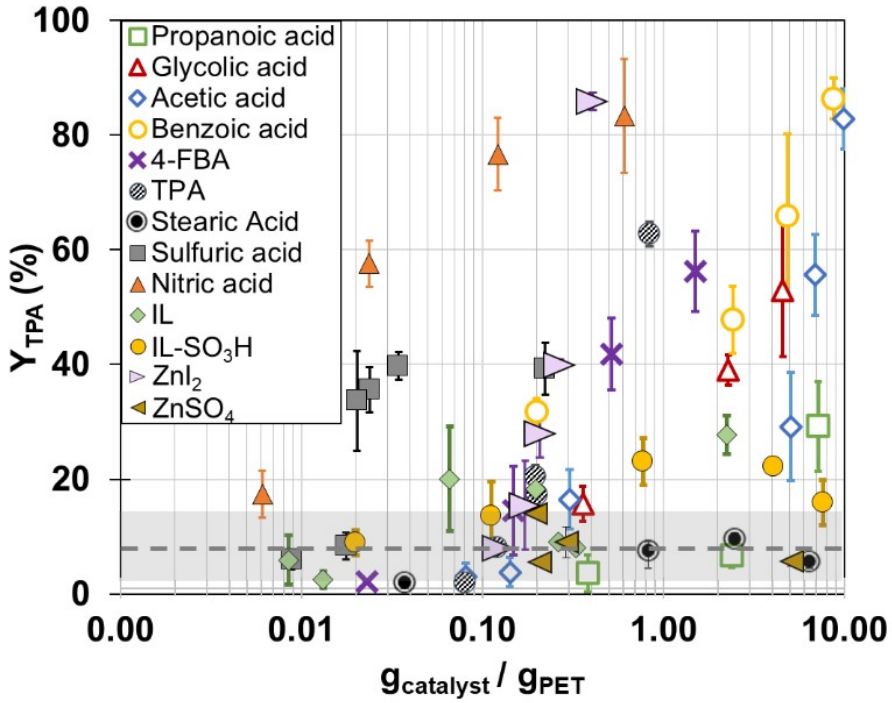

Figure S15. Influence of acid catalysts loading on the TPA yield from PET hydrolysis (200 ˚C, 2 h, 1/10 mass ratio PET/water). The dashed line represents the TPA yield average without catalyst, and the shaded area the standard deviation.

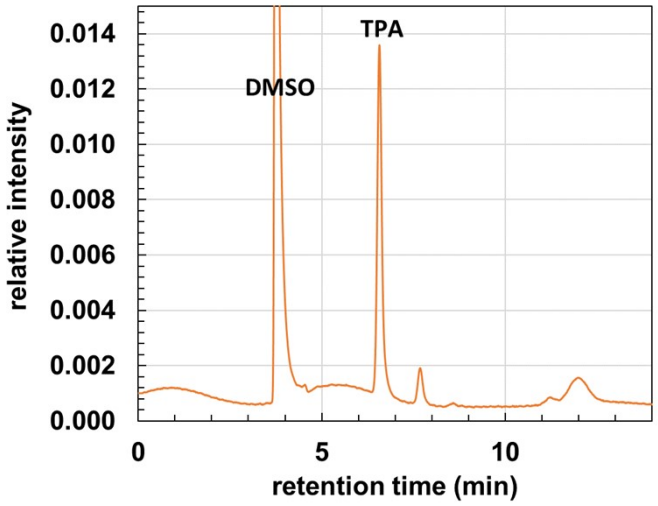

Figure S16. HPLC chromatogram of DMSO-solubles from PET acetolysis at 0.8 $g_{PET}/g_{acetic\ acid}$ (200 ˚C, 2 h) shows peaks in addition to TPA. These are byproducts.

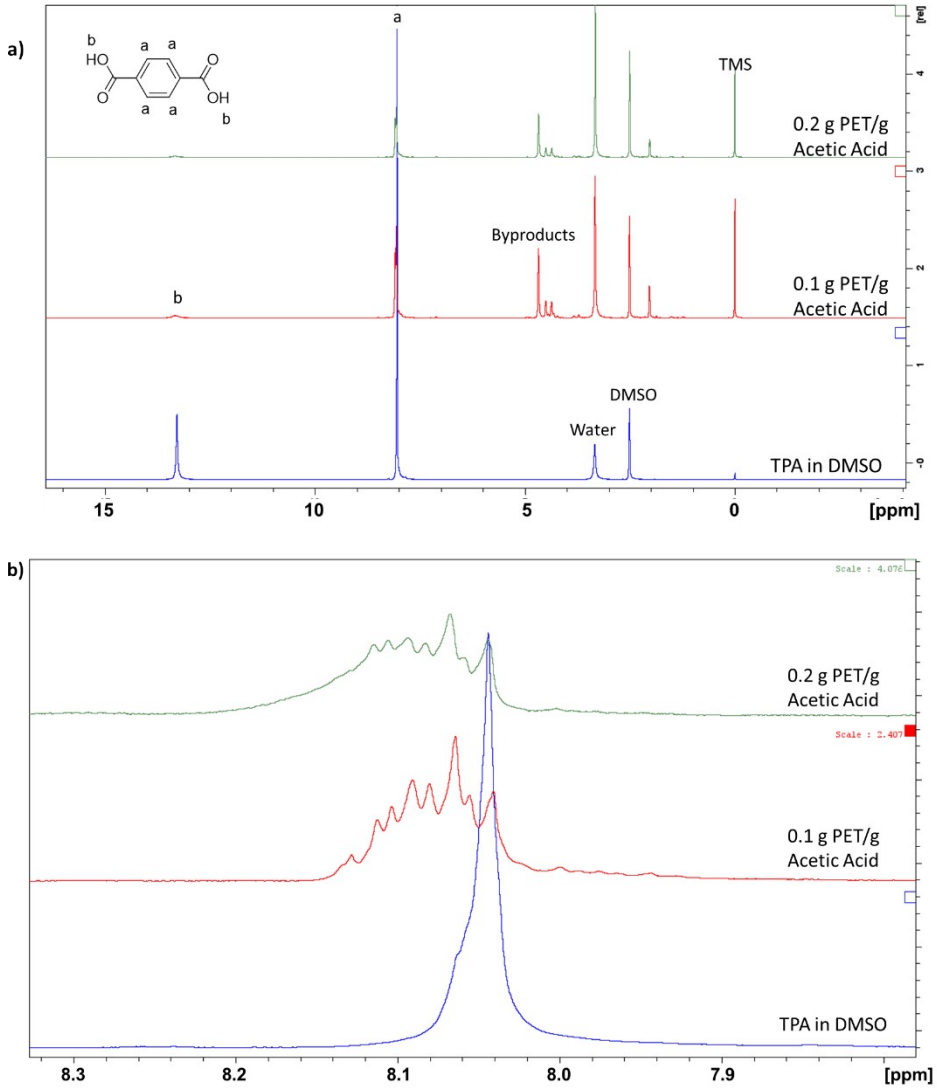

Figure S17. ^{1}H NMR analysis of DMSO-solubles from PET acetolysis (200 ˚C, 2 h, 0.2 g PET). a) full spectrum, and b) expanded view of aromatic proton region. Both panels show peaks arising from products other than TPA (*i.e.*, byproducts).

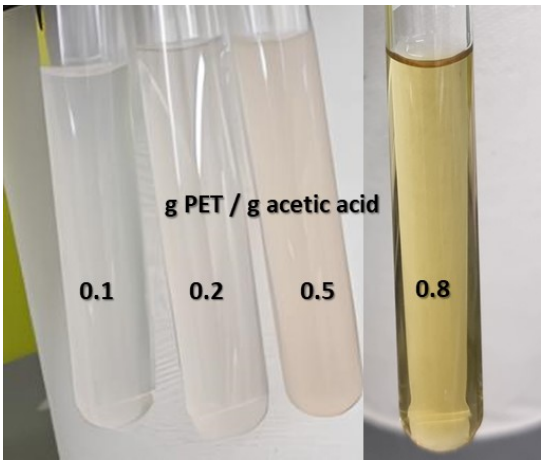

Figure S18. Dissolved solids in DMSO from PET acidolysis. From left to right: g PET / g acetic acid = 0.1, 0.2, 0.5, and 0.8.

References

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