Electronic Supporting Information

Subcritical CO_2-H_2O Hydrolysis of Polyethylene Terephthalate as a Sustainable Chemical Recycling Platform

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Table S1. Effect of CO_2 addition (versus N_2) and CO_2 pressure on the hydrolysis of PET.

Reaction conditions					Product yield (%)		
T (°C)	**t (min)**	**Gas**	**Initial pressure (psi)**	**Final pressure (psi)**	**TPA**	**MHET**	**BHET**
180	100	CO_2	208	385±2	39.1±0.7	14.3±1.2	2.3±0.4
180	100	N_2	208	384±1	1.9±0.4	2.0±0.3	1.1±0.2
180	100	CO_2	108	258±1	12.6±1.4	7.3±0.8	2.3±1.6
180	100	CO_2	308	539±1	59.4±0.8	11.4±2.2	1.6±0.4
180	100	CO_2	408	694±2	73.6±0.6	7.1±0.6	0.9±0.1

Reaction conditions: PET to H_2O ratio 1:8 w/w (2.5 g PET: 20 g of H_2O); [a] Reactions were performed, at least, in duplicate.

Table S2. Performance of hot compressed H_2O (in absence of N_2 and CO_2) on the hydrolysis of PET at varying temperatures.

Reaction conditions		Product yield (%)[a]		
T (°C)	**t (min)**	**TPA**	**MHET**	**BHET**
180	100	0.5±0.0	0.5±0.5	0.2±0.2
190	100	0.1±0.2	0.2±0.2	0.1±0.0
200	100	2.4±3.4	2.7±3.4	1.4±1.9

Reaction conditions: PET to H_2O ratio 1:8 w/w (2.5 g PET: 20 g of H_2O); [a] Reactions were performed in duplicate. High product yield variability was obtained due to extremely low concentration of products dissolved in both H_2O and DMSO.

Table S3. Effect of H_2O and PET loading on the performance of subcritical CO_2-H_2O process on PET hydrolysis.

Reaction conditions					TPA yield (%)	PET conversion (%)
PET:H_2O loading (w/w)	**T (°C)**	**t (min)**	**Initial pressure (psi)**	**Final pressure (psi)**		
2.5g PET:20g H_2O	200	100	208	464	85.0	99.0
3.75g PET:20g H_2O	200	100	208	479	85.1	98.6
3.75g PET:30g H_2O	200	100	208	366	7.1	37.5

PET conversion is given as mass conversion into DMSO-soluble products.

Table S4. Effect of varying subcritical CO_2-H_2O conditions on the hydrolysis of PET.

Reaction conditions					Product yield (%)			PET conversion (%)
$CS_{p_{CO_2}}$	T (°C)	t (min)	Initial pressure (psi)	Final pressure (psi)	TPA	MHET	BHET	
-0.65	180	10	208	383±1	0.0±0.0	0.6±0.7	0.5±0.2	1.95±2.8
-0.05	180	40	208	383±1	5.8±4.3	5.0±4.3	2.1±2.4	28.8±2.0
0.35	180	100	208	385±2	39.1±0.7	14.3±1.2	2.3±0.4	88.2±0.5
-0.41	190	10	208	421±2	0.0±0.8	1.7±0.8	1.5±1.1	21.1±1.5
0.20	190	40	208	420±4	30.2±2.3	12.0±1.2	3.3±0.1	95.6±0.8
0.59	190	100	208	421±3	68.3±0.4	6.7±3.1	0.8±0.6	96.6±1.1
-0.16	200	10	208	461±4	0.8±0.4	4.5±1.0	2.8±0.1	41.0±2.3
0.44	200	40	208	465±1	59.8±2.7	12.1±0.8	2.3±1.3	97.2±1.8
0.84	200	100	208	466±0	85.0±1.3	3.1±1.0	0.2±0.0	99.0±1.4

Reaction conditions: PET to H_2O ratio 1:8 w/w (2.5 g PET: 20 g of H_2O); [a] Reactions were performed, at least, in duplicate. $CS_{p_{CO_2}}$values of -0.65, -0.41 and -0.16 were not included in Figure 3B in the manuscript because an insignificant production of TPA was observed under these reaction conditions. The effect of all calculated $CS_{p_{CO_2}}$values as a function of PET conversion (%) can be found in Figure S8. PET conversion is given as mass conversion into DMSO-soluble products.

Table S5. Robustness of subcritical CO_2-H_2O to hydrolysis PET: PE mixture and waste PET bottles.

Substrate	Reaction conditions				Product yield (%)		
	T (°C)	t (min)	Initial pressure (psi)	Final pressure (psi)	TPA	MHET	BHET
100 wt% powder PET	200	100	208	455±0	87.2±2.2	3.6±0.7	0.6±0.3
50:50 w/w powder PET:PE	200	100	208	461±4	83.5±0.3	4.2±0.0	0.1±0.0
100 wt% powder colored Canada Dry PET bottle	200	100	208	457±1	86.2±2.2	2.9±0.1	0.2±0.1
100 wt% powder colored Mountain Dew PET bottle	200	100	208	458±2	82.5±3.8	2.8±0.0	0.2±0.1
100 wt% powder colored Twist up PET bottle	200	100	208	452±1	79.8±2.0	3.1±0.4	0.2±0.0
100 wt% powder transparent Pure Life® PET bottle	200	100	208	465±1	87.0±1.0	4.4±0.0	0.4±0.0

Reaction conditions: PET to H_2O ratio 1:8 w/w (2.5 g PET: 20 g of H_2O); [a] Reactions were performed, at least, in duplicate.

Table S6. Crystallinity content, enthalpy of melting (ΔH_m), cold crystallization enthalpy (ΔH_{cc}) of Mountain Dew and Twist Up waste PET soda bottles used in this work.

Substrate	**Crystallinity (%)**	**ΔH_m (J/g)**	**ΔH_{cc} (J/g)**
Mountain Dew bottle	19.5 ± 0.2	27.4 ± 0.3	0
Twist Up bottle	19.7 ± 0.5	27.6 ± 0.7	0

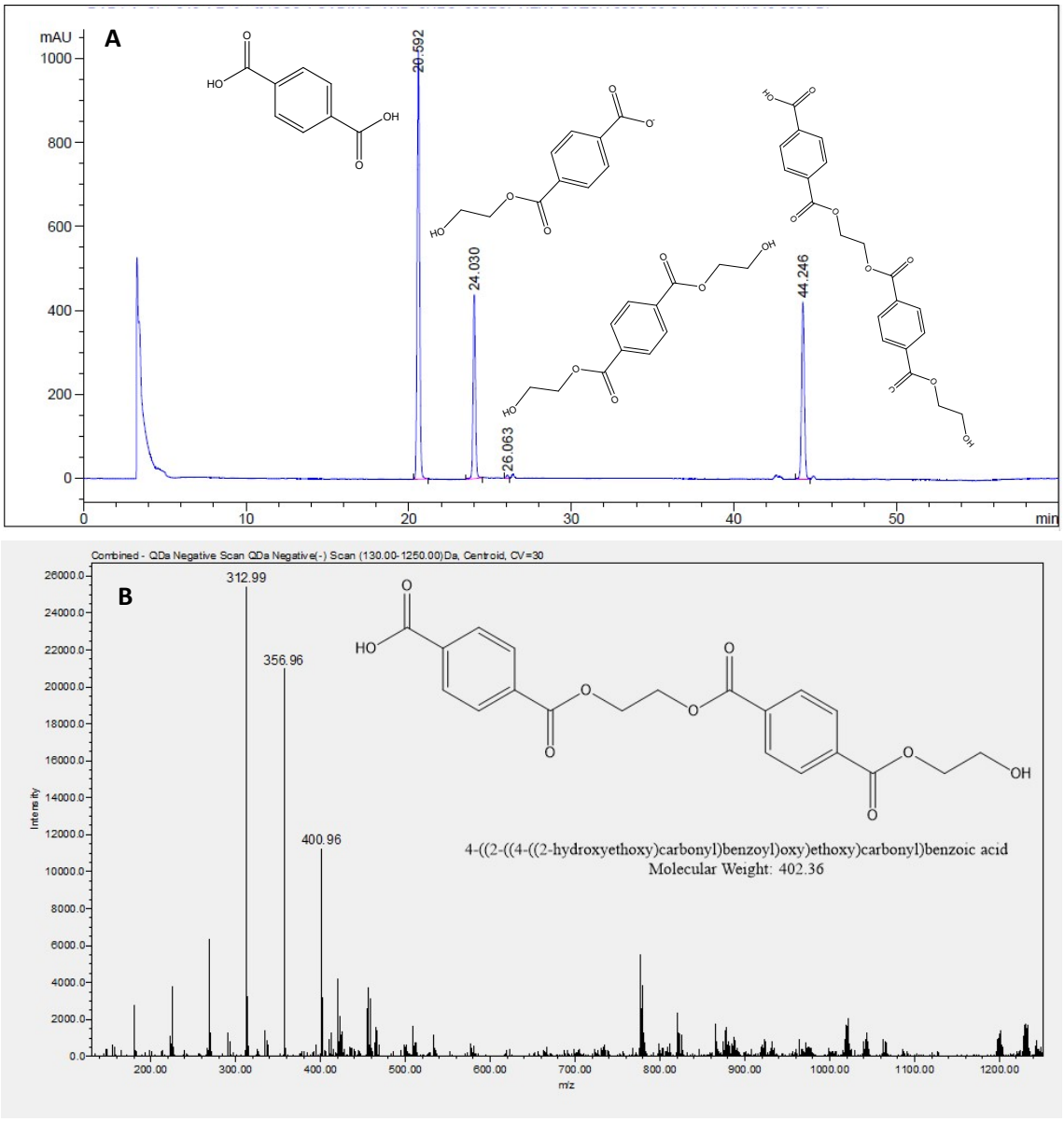

Figure S1 – A) Chromatogram of the liquid fraction obtained from subcritical CO_2-H_2O at 180 °C for 100 min. The compounds at 20.59, 24.03 and 26.06 minutes of retention time were identified using commercially available standards. The compound at 44.25 minutes of retention time was identified through Liquid Chromatography-Mass Spectrometry (LC-MS). B) Ion spectrum of the compound at 44.25 of retention time.

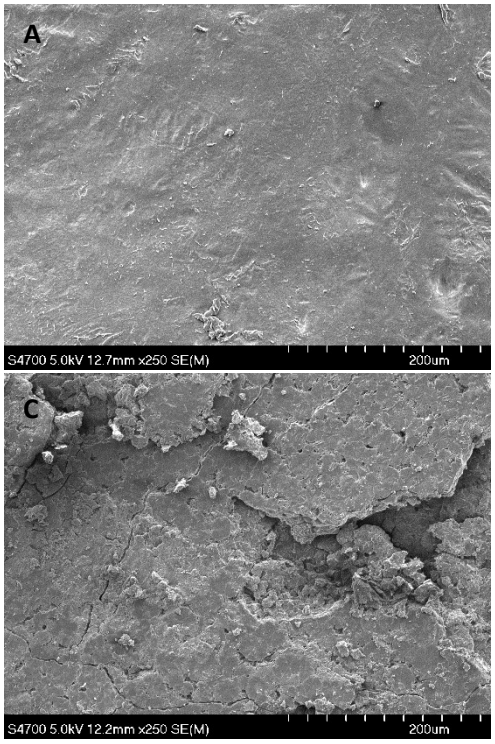

Figure S2 - Scanning electron microscopy of leftover PET samples from hot compressed H_2O (*i.e.* N_2-H_2O) reaction at 165 °C (non-isothermal conditions) (A), hot compressed H_2O (*i.e.* N_2-H_2O) at 180 °C for 10 min (B), subcritial CO_2-H_2O at 165 °C (non-isothermal conditions) with 208 psi of initial CO_2 pressure (C), and subcritical CO_2-H_2O at 180 °C for 10 min with 208 psi of initial CO_2 pressure (D).

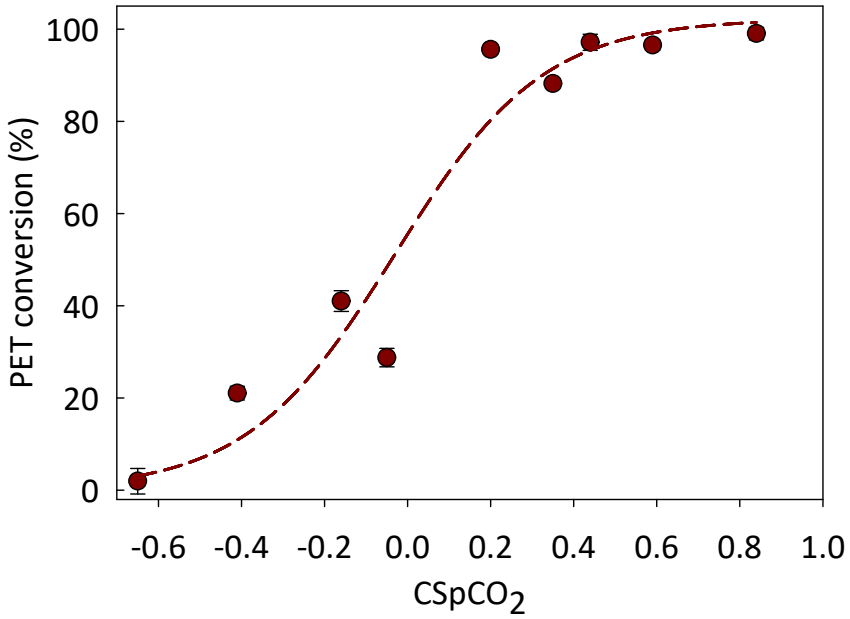

Figure S3 – PET conversion (mass conversion into DMSO-soluble products) as a function of combined severity factor (CS_{pCO_2}) follows a sigmoidal trend (R^2=0.935). PET to H_2O ratio 1:8 w/w (2.5 g PET: 20 g of H_2O) and 208 psi of initial CO_2 pressure at varying temperatures (180, 190 and 200 °C), and residence times (10, 40 and 100 min).

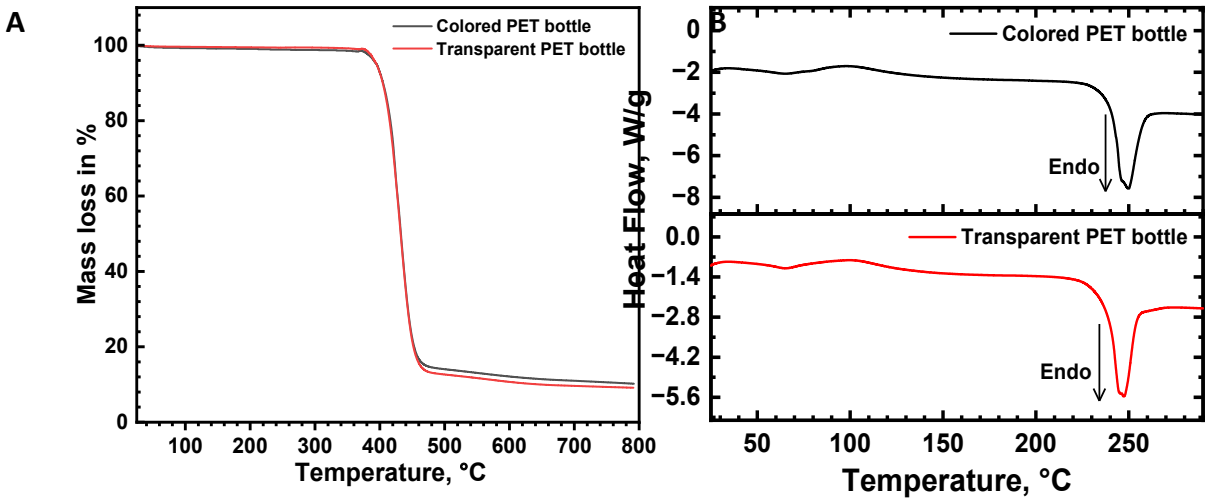

Figure S4 – Results from simultaneous thermogravimetric analysis (A) and differential scanning calorimetry (B) for both colored Canada Dry and transparent Pure Life® waste PET bottles.

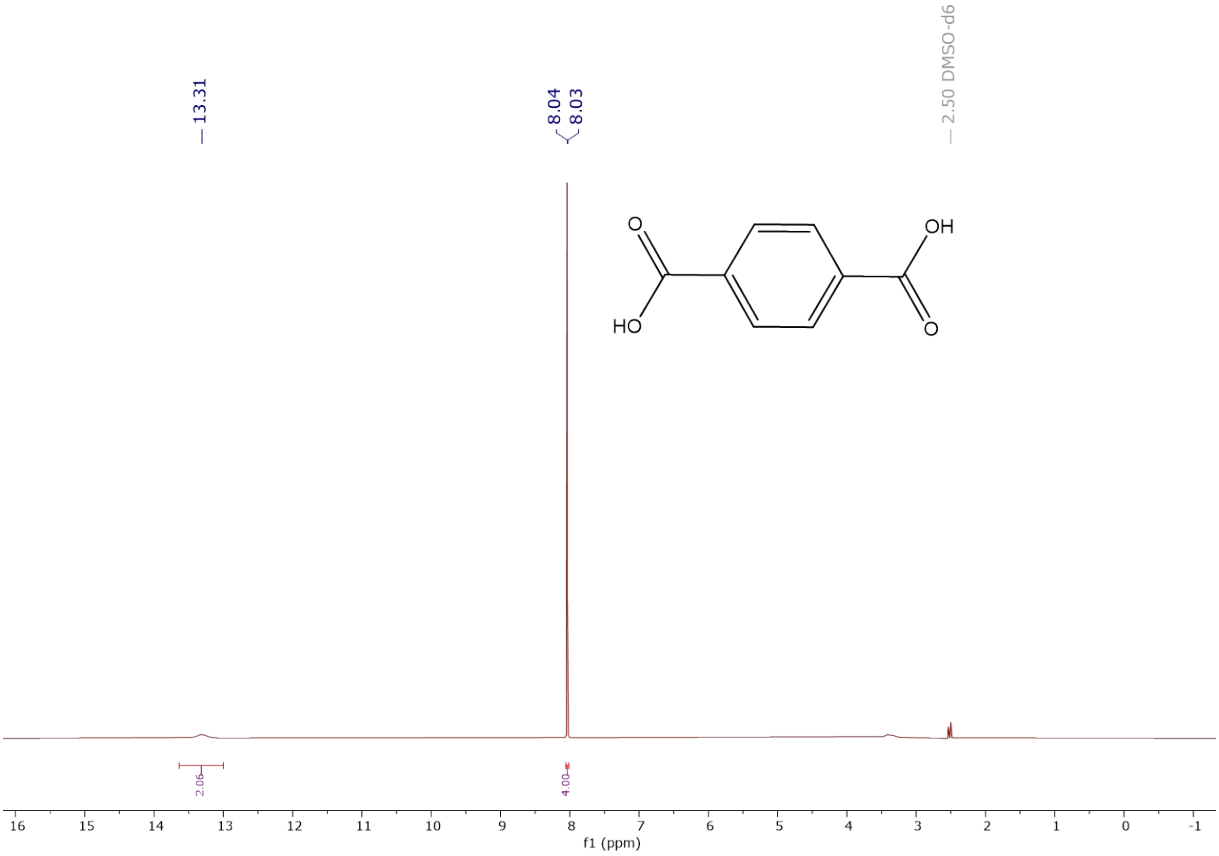

Figure S5 - ^{1}H NMR spectrum of TPA recovered from standard PET (free of pigments and other additives present in waste PET bottles) processed with subcritical CO_2-H_2O. ^{1}H NMR (400 MHz, DMSO) δ 13.31 (s, 2H), 8.04 (s, 4H).

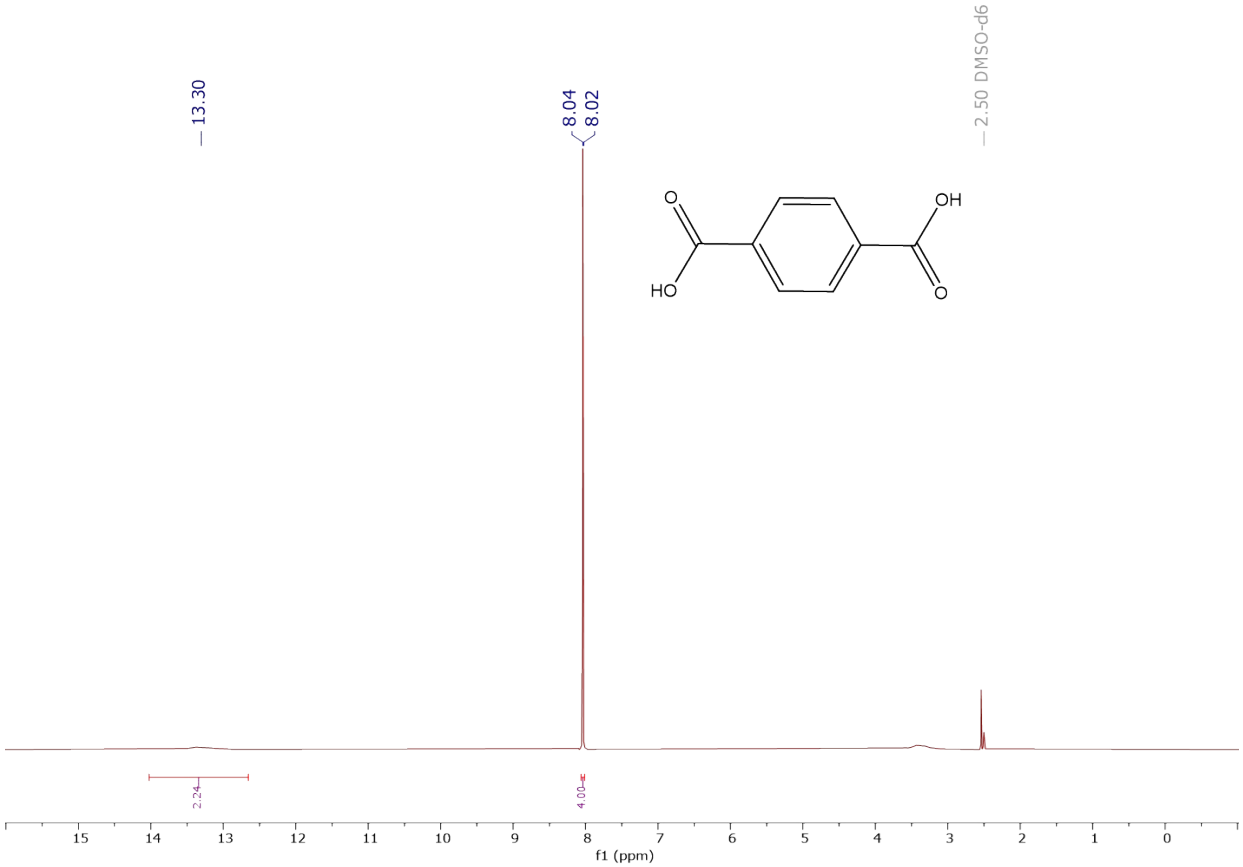

Figure S6 - ^{1}H NMR spectrum of TPA recovered from colored PET bottle processed with subcritical CO_2-H_2O. ^{1}H NMR (400 MHz, DMSO) δ 13.31 (s, 2H), 8.04 (s, 4H).

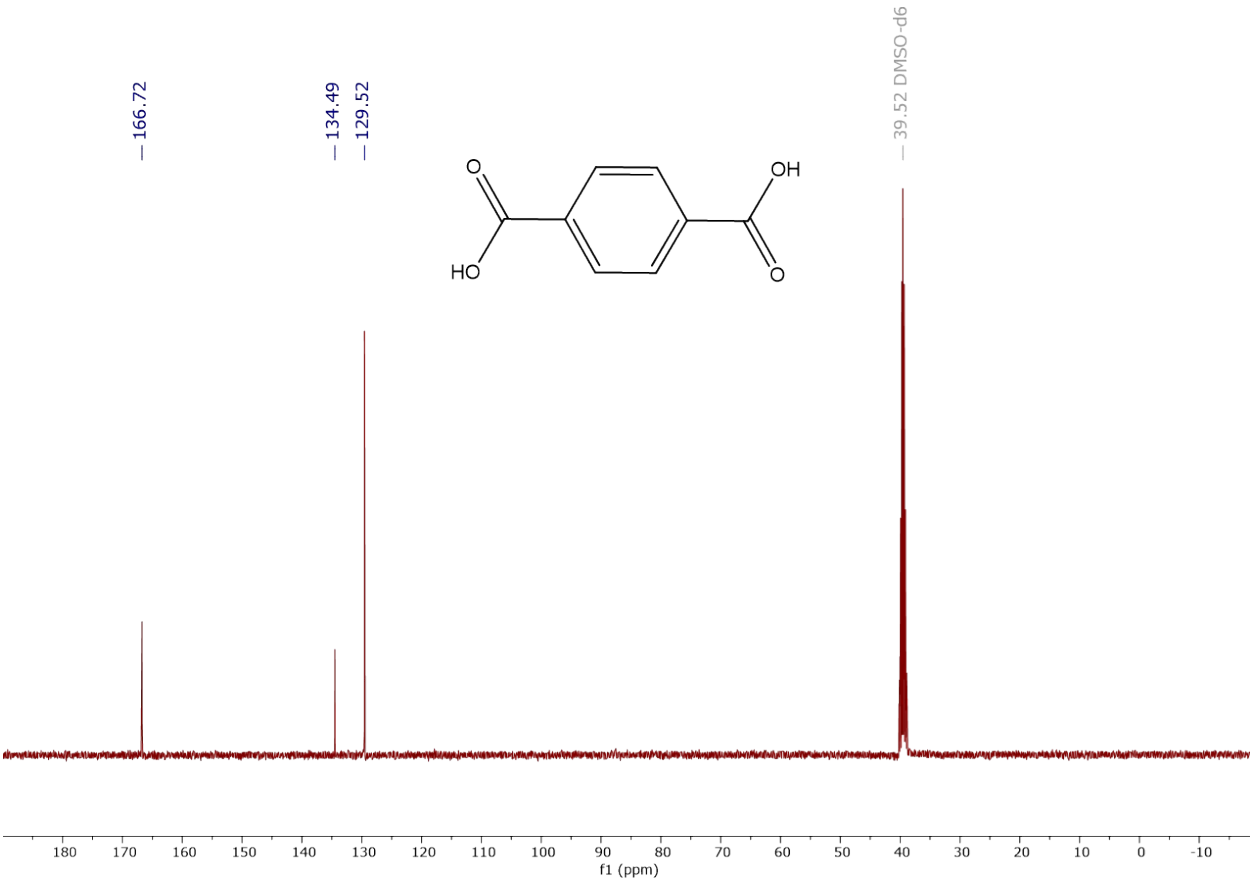

Figure S7. ^{13}C NMR spectrum TPA recovered from standard PET (free of pigments and other additives present in waste PET bottles) processed with subcritical CO_2-H_2O. ^{13}C NMR (101 MHz, DMSO) δ 166.72, 134.49, 129.52.

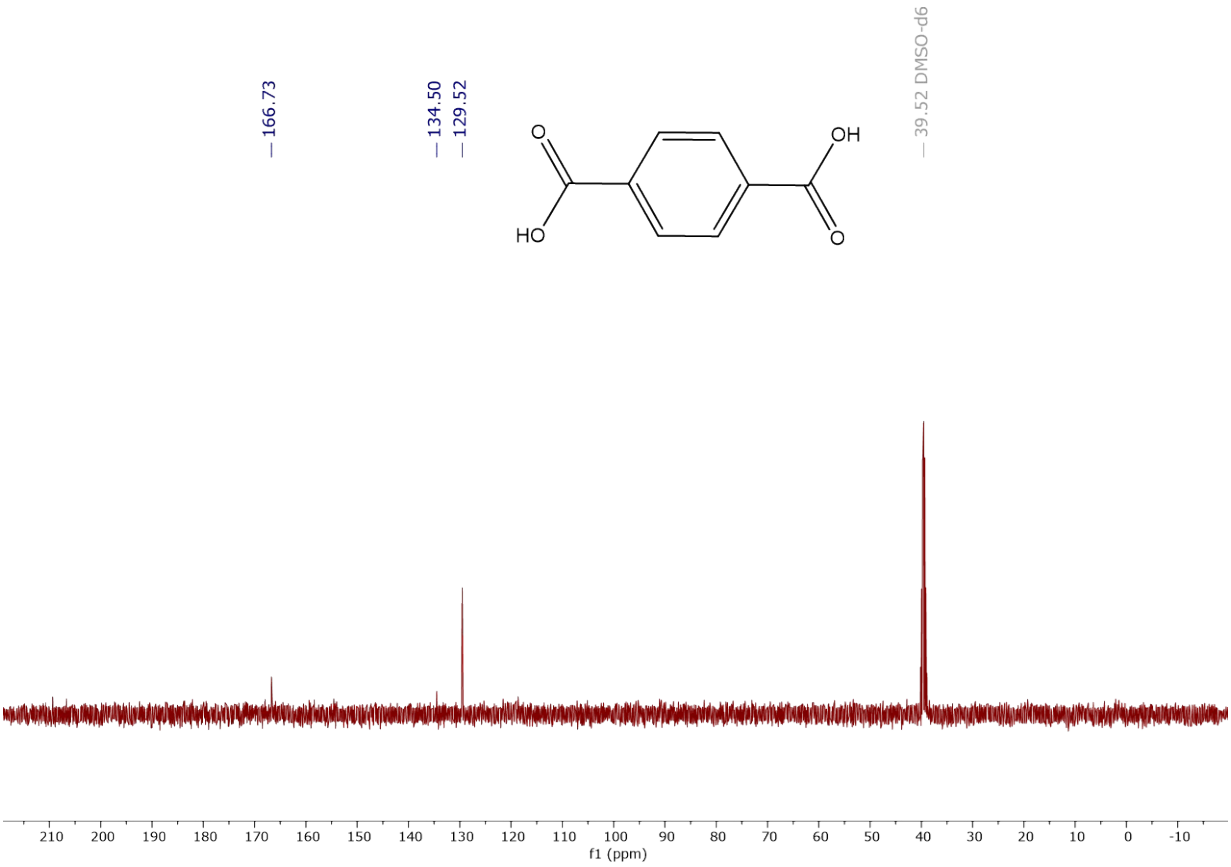

Figure S8. ^{13}C NMR spectrum of TPA recovered from colored PET bottle processed with subcritical CO_2-H_2O. ^{13}C NMR (101 MHz, DMSO) δ 166.73, 134.50, 129.52.

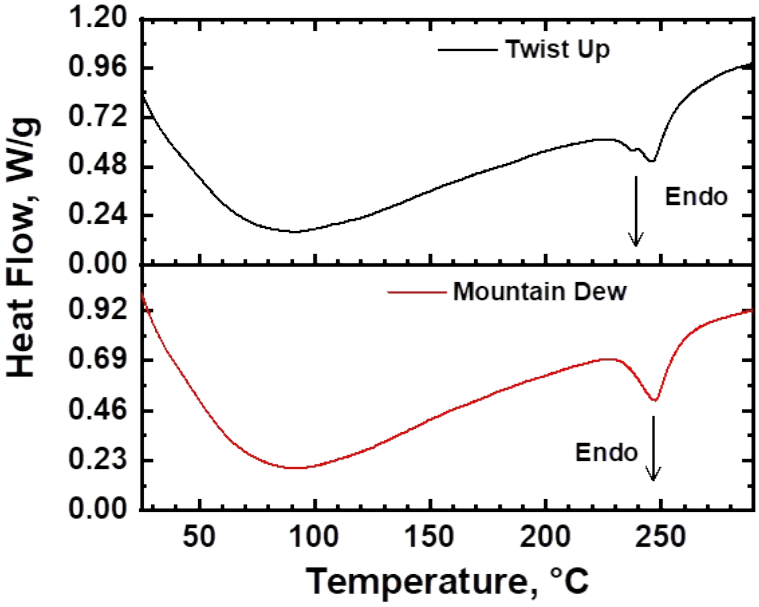

Figure S9 – Differential scanning calorimetry for both colored Twist Up and transparent Mountain Dew waste PET bottles.

Figure S10 – Reaction with subcritical CO_2-H_2O (2.5 g PET: 20 g of H_2O) at 200 °C for 100 min with 208 psi of initial CO_2 pressure with post-consumer waste bottles, Mountain Dew bottle (A), Mountain Dew post reaction solids (B), Mountain Dew post reaction filtrate (C), and Twist Up bottle (D), Twist up post reaction solids (E), Twist Up post reaction filtrate (F).