Supplementary Information (SI) for Green Chemistry.

Industrially viable and selective catalytic system: simple and sustainable pathway for efficient degradation of waste polyester textiles

1 PET samples, chemicals, and reagents

Polyester fibers made of PET (with a crystallinity of 40.28%, as determined by differential scanning calorimetry (DSC) in Fig. S1) were manually cut into approximately 1 cm pieces. Waste PET textiles, including curtains and scarves, were sourced from recycling stations, while cotton and nylon fabrics were purchased from Taobao. These fabrics were manually cut into approximately 1 cm × 0.5 cm pieces before use. Notably, EG was obtained from Tansoole. Sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), and potassium bromide (KBr) were provided by Jiangtian Chemical Reagent Co., Ltd. Sodium terephthalate (Na_2TPA) and TPA were acquired from Shanghai Aladdin Biochemical Technology Co., Ltd. Cellulase GC220 was obtained from Genencor International, Inc. All chemicals were used without further purification.

2 Characterizations

Scanning electron microscopy (SEM) images of the samples were obtained using a Hitachi S4800 field emission scanning electron microscope operated at 3.0 kV. Fourier transform infrared (FTIR) spectra were recorded on a Thermo Scientific Nicolet iS50 FTIR spectrometer in the range of 4000–400 cm^{-1}, with the sample tableted with KBr at a mass ratio of 1:100. Powder X-ray diffraction (XRD) was performed on a Bruker D8-Focus to examine the crystalline composition. DSC was conducted using a DSC Q2000 system with a heating rate of 10 °C min^{-1} in a nitrogen atmosphere. An ultraviolet (UV) absorption spectrophotometer (Agilent) was employed to determine the solubility of TPA or Na_2TPA. The ^1H NMR spectrum was acquired using 600 MHz JEOL JNM ECZ600R with dimethyl sulfoxide-D6 as the solvent. The degradation products of PET were analyzed by high-performance liquid chromatography (HPLC) using a C18 column from Agilent. The mobile phase comprised 100% acetonitrile and water with 0.1% w/v formic acid, with a flow rate of 0.8 mL min^{-1}. The retention times for the compounds were as follows: TPA at 10.8 min, MHET at 11.7 min, and BHET at 12.5 min. Aromatic compounds were detected using a UV/visible detector at 240 nm.

3 First-principles molecular dynamics simulation of HEG^- degrading PET

The meta-FPMD simulation was conducted using the CP2K 2024.1 software package[1] with the GFN-xTB method.[2] The HEG^--PET and NaOH-bis(2-hydroxyethyl) terephthalate (BHET) systems were initially constructed and equilibrated at 363.15 K for 500 fs with a 0.5 fs timestep. The canonical sampling through velocity rescaling thermostat was applied with a 100-fs time constant. The equilibrated structures then underwent 2000 fs of molecular dynamics at 363.15 K, using a 0.2 fs timestep and maintaining the same thermostat conditions as during the equilibrium stage. The first collective variable (CV) was defined as the distance between the oxygen (O) atom in HEG^- and the carbonyl C atom in the PET (or BHET) ester bond. The second CV was defined as the distance between the carbonyl carbon atom in the PET (or BHET) ester bond and the adjacent ether O atom. The scales of both CVs were set to 0.5, and the wall width was set to 1.5 kcal/mol. The free energy surface was estimated using the kernel density estimation method, which provided the energy barrier. All CP2K input files were generated using

Multiwfn software.[3, 4] The trajectory and conformations were illustrated using visual molecular dynamics.[5]

4 PET degradation

To establish the EG catalytic system, varying amounts of NaOH (molar ratio of EG: NaOH ranging from 12:1 to 4:1) were dissolved in 100 mL of EG by heating. PET polyester fibers were added and degraded at 30–130 °C for 5–60 min under magnetic stirring at 400 rpm. At the end of the reaction, the EG catalytic system was filtered to separate it from Na_2TPA. The EG catalytic system could be reused for PET degradation after adding the theoretical amount of NaOH consumed. Deionized water was added to dissolve Na_2TPA, and the solution was filtered to collect the unreacted PET, which was then washed and dried under vacuum at 80 °C. The potential of hydrogen (pH) of the Na_2TPA solution was adjusted to around 3.0 using H_2SO_4 to precipitate TPA. The TPA was similarly washed, dried under vacuum at 80 °C, weighed, and its yield was calculated.

The PET conversion was calculated using the following equation:

$$PET\ conversion = \frac{m_{PET}{}^{0} - m_{PET}{}^{1}}{m_{PET}{}^{0}} \times 100\%,$$

where $m_{PET}{}^{0}$ is the initial mass of PET and $m_{PET}{}^{1}$ represents the mass of residual PET.

The following equation was used to calculate the TPA yield:

$$TPA\ yield = \frac{\frac{m_{TPA}}{M_{TPA}}}{\frac{m_{PET}{}^{0}}{M_{PET}}} \times 100\%,$$

where the $m_{PET}{}^{0}$ denotes the initial mass of PET, m_{TPA} represents the mass of produced TPA, and M_{PET} and M_{TPA} represent the molecular weights of the PET repeating unit (192 g mol^{-1}) and TPA (166 g mol^{-1}), respectively.

To compare the degradation efficiency of the EG catalytic system with that of the alkaline hydrolysis system for PET polyester, the PET degradation test was conducted at 90 °C. The alkaline hydrolysis system contained the same mass of NaOH as the EG catalytic system. Subsequent PET conversion and TPA yield determinations were performed as described above.

5 Determination of solubility of TPA/Na_2TPA

Initially, 0.1 g of commercial TPA was dissolved in 6 mL of 1 M NaOH solution. The resulting Na_2TPA solution was then diluted to various concentrations to create a series of standard TPA solutions. A standard curve was generated based on the absorbance of these standard solutions measured at 240 nm (Fig. S3 c). A Na_2TPA solution was prepared using the same method as the standard solution to assess the purity of the produced TPA. For solubility testing, an appropriate amount of TPA or Na_2TPA was added to 2 mL of H_2O/EG, then stirred at room temperature (RT), 30 °C, 50 °C, 70 °C, or 90 °C for 1 h. The mixture was centrifuged at 10000 × g for 1 min. The supernatant was diluted, and the UV absorption at 240 nm was measured. The concentration of TPA or Na_2TPA in the supernatant was calculated using the standard curve and the dilution factor (Fig. S3 b).

After PET degradation, the EG catalytic system was separated from the PET degradation product Na_2TPA by filtration. The EG catalytic system was then analyzed by HPLC at room temperature and 90

°C to detect the Na_2TPA. Meanwhile, Na_2TPA was dissolved in water, and the retention time of the Na_2TPA solution was compared with that of commercial Na_2TPA using HPLC.

6 Scale-up test of the EG catalytic system

For the 1 L scale-up test, NaOH was dissolved in 1 L of EG (with a molar ratio of EG to NaOH of 6:1) by heating to establish the EG catalytic system. Then, 100 g of PET polyester fibers were gradually added for degradation at 90 °C for 1.5 h under mechanical stirring at 400 rpm. The subsequent purification and separation process of TPA and the calculation of PET conversion and TPA yield followed the previously described procedure.

For the 100 L scale-up test, NaOH was dissolved in 100 L EG (with a molar ratio of EG: NaOH of 6:1) by heating in a 200 L reactor to establish the EG catalytic system. Then, 7000 g of PET polyester fibers were added for degradation at 90 °C for 2 h. At the end of the reaction, a centrifuge (PSB450) was used to separate the EG catalytic system from the Na_2TPA and residual PET polyester fibers. The Na_2TPA was dissolved in water to filter out the unreacted PET, after which the residual PET polyester fibers were washed and dried under vacuum at 80 °C. Next, 12 kg of activated carbon was added to the Na_2TPA solution for decolorization at 70 °C for 2 h. Finally, to precipitate TPA, the pH of the Na_2TPA solution was adjusted to around 3 using H_2SO_4. Similarly, TPA was washed and dried under a vacuum at 80 °C to weigh and calculate the yield.

7 Fibre mixtures degradation

To investigate the selective degradation capability of the EG catalytic system for PET polyester fibers in blended textiles, we employed the EG catalytic system to degrade mixtures of cotton/polyester fibers and nylon/polyester fibers. NaOH was dissolved in 100 mL of EG (with a molar ratio of EG to NaOH of 6:1) by heating to establish the EG catalytic system. Then, 1.5 g of PET polyester fibers and 1.5 g of cotton were mixed and subjected to degradation at 90 °C for 1 h under magnetic stirring at 400 rpm. The process flow of the EG catalytic system for degrading mixed fibres was shown in Fig. S7. And the subsequent purification and separation process of TPA and the calculation of PET conversion and TPA yield followed the previously described procedure.

8 Enzymatic hydrolysis of cotton waste

A 0.2 g sample of waste cotton fabric was added to 20 mL of sodium sulfate wastewater generated by TPA acidification, with the pH adjusted to 4.8. The mixture was treated with cellulase at 18 filter paper units (FPU)/mL. The hydrolysis process was performed at 50 °C with continuous stirring at 150 rpm for 7 days. To monitor glucose production, 300 µL samples were collected daily simultaneously.

$$Glucose\ yield\ (\%) = \frac{m_{glucose}}{m_{cellouse} \times 1.111} \times 100.$$

The glucose concentration was measured with HPLC using an Aminex HPX-87 H column (Bio-Rad, USA) with 5 mM H_2SO_4 as the mobile phase. Commercial glucose was used as the standard, with the standard curve provided in the Supporting Information (SI).

Figures

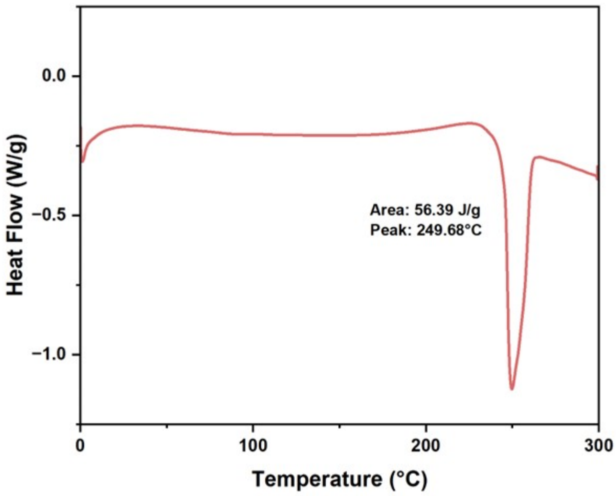

Fig. S1 DSC analysis of PET fiber (crystallinity: 40.28%).

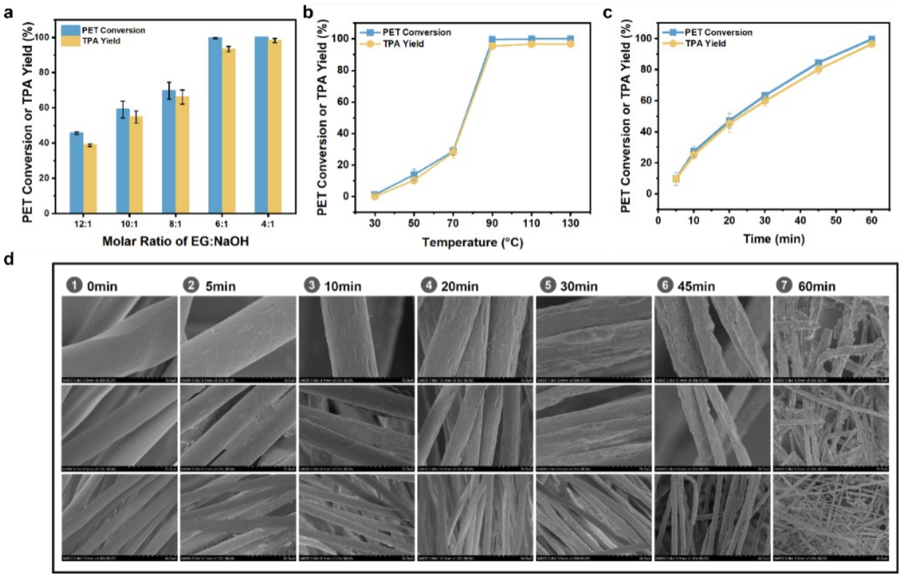

Fig. S2 The establishment of the EG catalytic system and its hydrolytic effect on PET.

(a) PET degradation effects of different molar ratios of EG to NaOH;

(b) Degradation effect of PET fiber in the EG catalytic system (with a molar ratio of EG to NaOH of 6:1) at different temperatures;

(c) Degradation effect of PET fiber in the EG catalytic system (with a molar ratio of EG to NaOH of 6:1) under 90 °C over time;

(d) SEM images of PET degradation in the EG catalytic system (with a molar ratio of EG to NaOH of 6:1) under 90 °C over time.

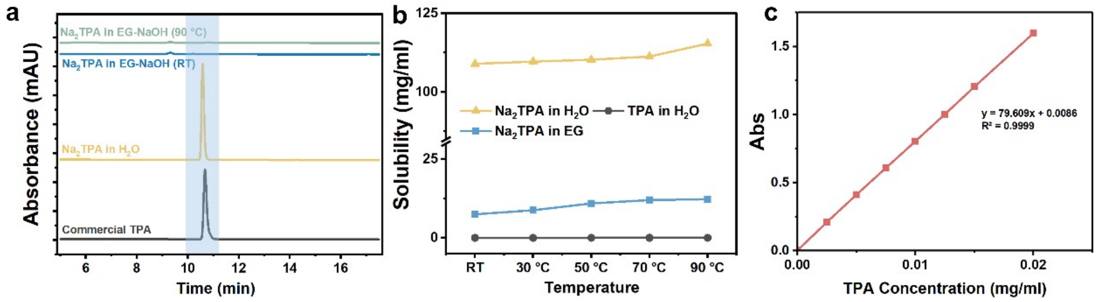

Fig. S3 Feasibility Analysis on direct separation of EG catalytic system and PET degradation products. (a)The HPLC analysis of Na_2TPA in the EG catalytic system; (b) Solubility of Na_2TPA in H_2O/EG and TPA in H_2O at different temperatures; (c) Standard curve based on the UV absorption values of TPA at various concentrations measured at 240 nm wavelength.

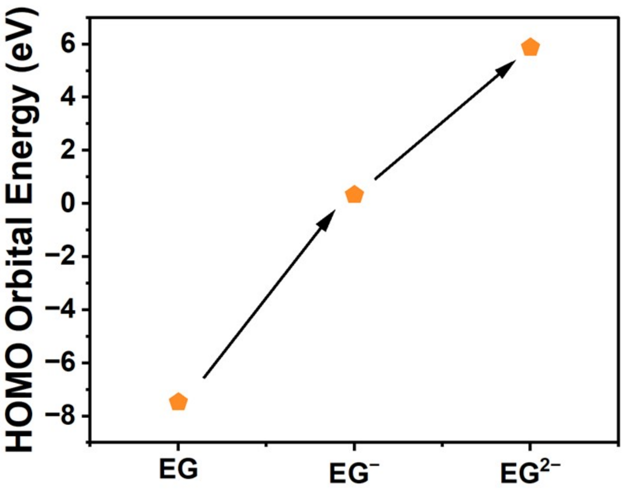

Fig. S4 HOMO energies of the neutral, monoanion and dianion states of EG.

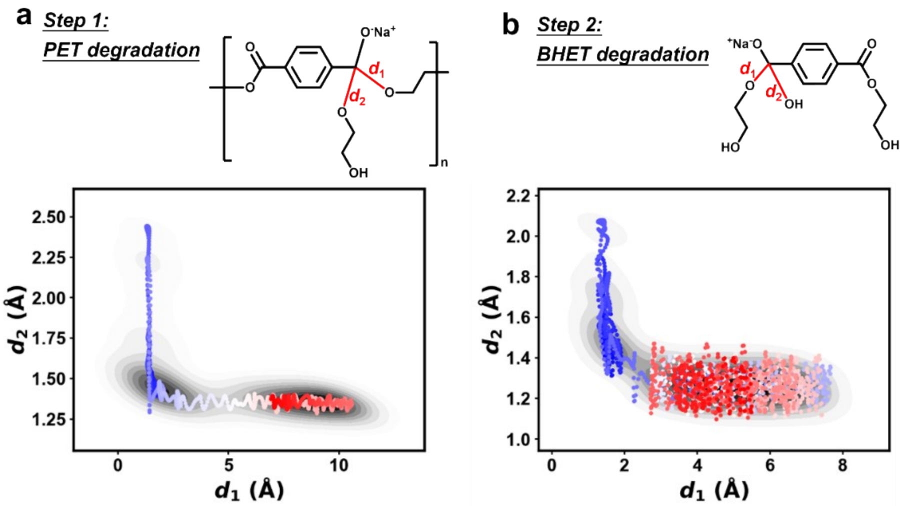

Fig. S5 The PET degradation mechanism in the alkaline hydrolysis system explored by FPMD.

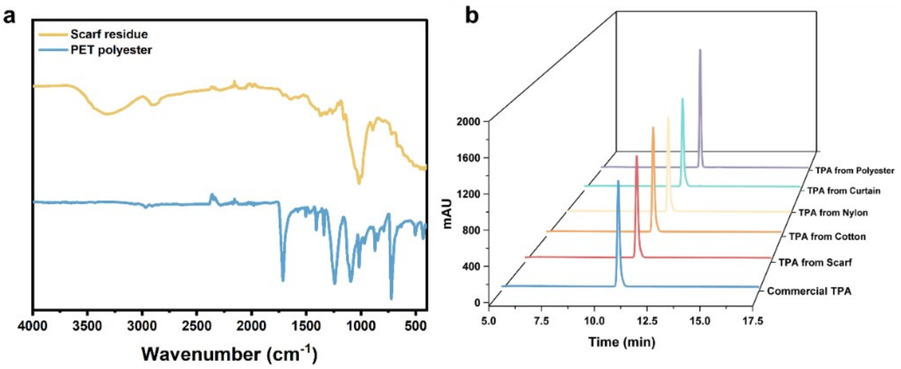

Fig. S6 Characterization of degradation residues and products of PET.

(a) FTIR analysis of PET polyester and scarf degradation residues and (b) HPLC analysis of commercial TPA and reproduced TPA.

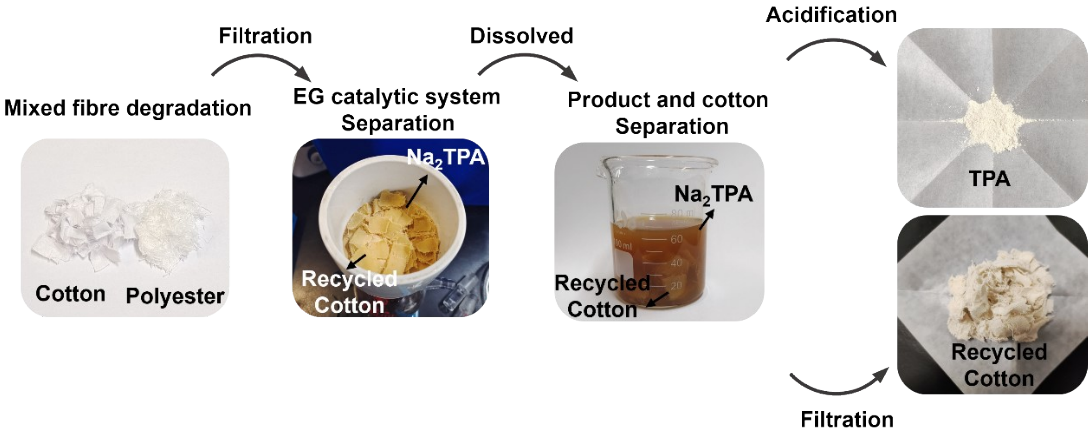

Fig. S7 The process flow of the EG catalytic system for degrading mixed fibres.

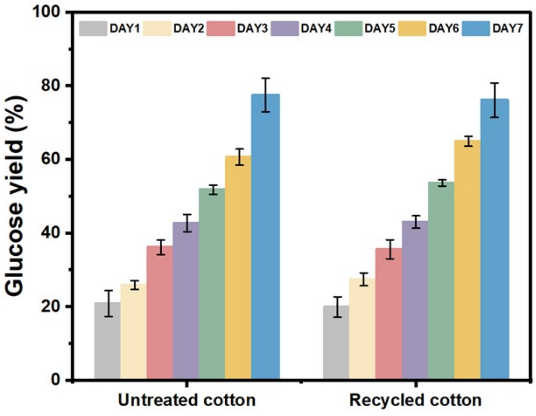

Fig. S8 Salt-containing wastewater was used as a cellulase buffer to degrade untreated cotton and residual cotton after PET degradation to produce glucose.

Table S1 Comparison of the performances of PET hydrolysis process

Reaction System	Substrate Types	Substrate Concentration	Alkaline Concentration	Reaction Conditions	PET Conversion	TPA Yield	
EG	PET polyester	30 g/L	10.7wt%	90 °C 1h	99.63%	95.46%	This work
		50 g/L			95.06%	90.67%	
		70 g/L		90 °C 1.5h	97.13%	94.28%	
		100 g/L			95.76%	90.26%	
H_2O	PET polyester	10 g/L	5wt%	90 °C 16h	100%	close to 100%	6
Tetrahydrofuran (60%) +EG	PET bottles and PET waste textiles	33 g/L	5%(w/v)	60 °C 1h	100%	97.50%	7
60 v% EtOH	PET pellets (Lighter™ C93)	20 g/L	10wt%	80 °C 20 min	95.23%	/	8
γ-valerolactone	PET bottles	7.5 g/L	15wt%	1. swell: 120 °C, 1 h; 2. dissolve: 170 °C, 2 min; 3. hydrolysis: 90 °C, 8 min	/	>99%	9
	PET bottles	7.5 g/L	15wt%	hydrolysis: 90 °C, 24 h	/	<40%	
DES (ChCl: *m*-cresol)	PET pellets	66.7 g/L	10wt%	1. stirring for 15 min at 60 °C 2. Microwave irradiation at 350 W for 92.5 s	85.37	82.48	10
H_2O with 0.5wt% Catal. ($[CTA]_3PW$)	PET pellets	10 g/L	4wt%	110 °C for 5 h in batch Teflon sealed reactor	>99%	>90%	11
H_2O with 10wt% Catal. (TBAI)	PET bottles	60 g/L	10wt%	Microwave irradiation at 200 W for 60 min	/	98%	12

Material accountancy process of PET degradation system (degrade 1kg PET)

EG catalytic system

EG utilization (EG^- can be directly recovered and recycled):

Under the 70 g/L PET addition amount, the degradation rate is 97.13%, then Volume of EG is

$$V_{EG} = \frac{1000\ g}{70\ g/L} \Big/ 97.13\% = 14.7\ L$$

Then Mass of EG is

$$M_{EG} = \rho_{EG} V_{EG} = 1.11\ g/cm^3 \times 14.7\ L = \ 1110\ g/L\ \times\ 14.7\ L\ =\ 16.317\ kg$$

According to the reaction details:

$$EG + NaOH \rightarrow EG^- + Na^+ + H_2O$$

$$[PET]_{n(s)} \xrightarrow{EG^-} n\ BHET$$

$$BHET + 2\ OH^- \rightarrow TPA^{2-}{}_{(s)} + EG_{(aq)}$$

NaOH Consumption is (Since EG^- acts as catalyst, the consumption of OH^- to produce EG^- is not considered):

$$n_{NaOH} = 2n_{[PET]_n} = \frac{2\ m_{[PET]_n}}{M_{[PET]_n}} = \frac{2 \times 1000\ g}{192\ g/mol} = 10.417\ mol$$

$$m_{NaOH} = n_{NaOH} M_{NaOH} = 10.417\ mol \times 39.997\ g/mol = 0.417\ kg$$

H_2SO_4 Consumption is (Assumption: NaOH is the only source of alkalinity of the textile waste and therefore identifies the amount of H_2SO_4 acid needed for neutralization):

$$H_2SO_{4\ (aq)} + 2\ NaOH_{(s)} \rightarrow Na_2SO_{4(s)} + 2\ H_2O_{(l)}$$

$$n_{H_2SO_4} = \frac{1}{2} n_{NaOH} = \frac{m_{NaOH}}{2\ M_{NaOH}} = \frac{417\ g}{2 \times 39.997\ g/mol} = 5.213\ mol$$

$$m_{H_2SO_4} = n_{H_2SO_4} M_{H_2SO_4} = 5.213\ mol \times 98.078\ g/mol = 0.511\ kg$$

Na_2TPA production:

$$n_{Na_2TPA} = \frac{1}{2} n_{NaOH} = \frac{m_{NaOH}}{2\ M_{NaOH}} = \frac{417\ g}{2 \times 39.997\ g/mol} = 5.213\ mol$$

$$m_{Na_2TPA} = n_{Na_2TPA} M_{Na_2TPA} = 5.213\ mol \times 210.094\ g/mol = 1.095\ kg$$

EG production:

$$n_{EG} = n_{Na_2TPA} = 5.213\ mol$$

$$m_{EG} = n_{EG}M_{EG} = 5.213\ mol \times 62.068\ g/mol = 0.3236\ kg$$

H_2O consumption:

$$m_{H2O} = m_{Na_2TPA}/S_{Na_2TPA} = \frac{1095\ g}{108.95\ g/L} = 10.050\ kg$$

where *S* means the solubility.

TPA production:

$$Na_2TPA_{(s)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + TPA_{(s)}$$

$$n_{TPA} = n_{H_2SO_4} = \frac{1}{2}n_{NaOH} = \frac{m_{NaOH}}{2\ M_{NaOH}} = \frac{417\ g}{2 \times 39.997\ g/mol} = 5.213\ mol$$

$$m_{TPA} = n_{TPA}M_{TPA} = 5.213\ mol \times 166.131\ g/mol = 0.866\ kg$$

Na_2SO_4 production:

$$n_{Na_2SO_4} = n_{H_2SO_4} = \frac{1}{2}n_{NaOH} = \frac{m_{NaOH}}{2\ M_{NaOH}} = \frac{417\ g}{2 \times 39.997\ g/mol} = 5.213\ mol$$

$$m_{Na_2SO_4} = n_{Na_2SO_4}M_{Na_2SO_4} = 5.213\ mol \times 142.042\ g/mol = 0.740\ kg$$

Aqueous alkaline hydrolysis: (5wt%NaOH)

H_2SO_4 Consumption:

Assumption: NaOH is the only source of alkalinity of the textile waste and therefore identifies the amount of H_2SO_4 acid needed for neutralization.

$$H_2SO_{4(aq)} + 2\ NaOH_{(s)} \rightarrow Na_2SO_{4(s)} + 2\ H_2O_{(l)}$$

$$n_{H_2SO_4} = \frac{1}{2}n_{NaOH} = \frac{m_{NaOH}}{2\ M_{NaOH}} = \frac{5000\ g}{2 \times 39.997\ g/mol} = 62.505\ mol$$

$$m_{H_2SO_4} = n_{H_2SO_4}M_{H_2SO_4} = 62.505\ mol \times 98.078\ g/mol = 6.130\ kg$$

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