

Electronic Supplementary Information

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1. Algorithms used for implementing the pipeline

Algorithm 1. Document processing and vector embedding

IMPORT necessary libraries including PyMuPDF, LangChain, and Chroma
DEFINE functions to load and save uploaded filenames

SET the directory for PDF files and metadata storage
LOAD existing uploaded filenames to avoid reprocessing
INITIALIZE the document loader to read all PDF files
LOAD all documents from the directory

INITIALIZE text splitter:
- SET chunk size = 1000
- SET overlap = 40

INITIALIZE embedding model using HuggingFace
INITIALIZE Chroma vector database with the embedding model

FOR each document in the loaded documents:
 CHECK if the document has already been processed:
 - IF YES, SKIP the document
 EXTRACT text from the document
 SPLIT the extracted text into chunks using the text splitter
 EMBED the text chunks into the Chroma vector database
 UPDATE the list of processed filenames

SAVE the updated filenames to metadata
PRINT progress periodically
END FOR

SAVE the vector database and print a completion message

Algorithm 2. Fine-tuning the pretrained model with LoRA and Quantization

IMPORT required libraries including Transformers, PEFT, Datasets, and BitsAndBytes
LOGIN to Hugging Face Hub using API token (if required)

LOAD the dataset from JSONL files:

- DEFINE paths for training and validation datasets
- LOAD the dataset using the Hugging Face dataset loader

INITIALIZE the tokenizer from the Mistral model:

- SET padding token to EOS token

CONFIGURE BitsAndBytes for 4-bit quantization:

- ENABLE 4-bit quantization (`load_in_4bit = True`)
- SET quantization type to NF4 (`bnb_4bit_quant_type = "nf4"`)
- ENABLE double quantization (`bnb_4bit_use_double_quant = True`)
- USE 'bfloat16' for computation (`bnb_4bit_compute_dtype = torch.bfloat16`)

LOAD the Mistral model with 4-bit quantization:

- APPLY `prepare_model_for_kbit_training()` to optimize the model for low-bit training

CONFIGURE LoRA for efficient fine-tuning:

- SET LoRA rank = 8
- SET scaling factor = 16
- APPLY LoRA dropout = 0.05
- TARGET the transformer layers: [`"q_proj"`, `"k_proj"`, `"v_proj"`, `"o_proj"`]

APPLY LoRA modifications to the Mistral model

PRINT number of trainable parameters after applying LoRA

DEFINE a tokenization function for processing dataset:

- ITERATE through conversation messages:
 - EXTRACT 'Question', 'Context' and 'Answer'
 - FORMAT as a structured prompt: "Question: ...
Context: ...
Answer: ..."
- TOKENIZE the formatted text:
 - APPLY padding and truncation to fit within 512 tokens
 - CREATE labels from input IDs for supervised fine-tuning
- RETURN the tokenized dataset

TOKENIZE the dataset:

- APPLY `'tokenize_function()'` to all dataset entries
- REMOVE unnecessary columns

CONFIGURE training parameters:

- SET output directory for saved models
 - USE batch size of 4 with gradient accumulation steps = 4
 - TRAIN for 3 epoch
-

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- SET warmup steps = 100
 - APPLY learning rate = $2e-4$
 - ENABLE mixed precision (fp16 = True)
 - LOG training progress every 50 steps
 - SAVE model checkpoints every 50 steps

INITIALIZE the Trainer:

- ASSIGN model, training arguments, tokenized dataset, and evaluation function

START training the model

SAVE the fine-tuned model and tokenizer:

- CREATE directory for saving
 - SAVE model and tokenizer to specified directory
-

Algorithm 3. Querying the fine-tuned model

IMPORT necessary libraries including Transformers, Chroma, and PyTorch

DEFINE helper functions for:

- CREATING combined prompts
- QUERYING the vector database
- EXTRACTING answers from model outputs

LOAD the fine-tuned model and tokenizer:

- INITIALIZE model with 4-bit quantization
- LOAD the LoRA adapters

INITIALIZE embedding model for vector database

INITIALIZE Chroma vector database with the embedding model

DEFINE the query workflow:

- RETRIEVE relevant documents from the vector database using similarity search
- COMBINE the user query and retrieved documents into a single prompt
- TOKENIZE the combined prompt
- GENERATE a response using the fine-tuned model
- DECODE and EXTRACT the relevant answer from the model's output

INITIALIZE a user session for conversation history

LOOP to accept user queries:

- PROMPT the user for input
- IF the input is 'exit', TERMINATE the loop
- PROCESS the query using the workflow
- PRINT the response of the model

END LOOP

2. Initial set of 25 candidate depolymerisation pathways generated by the fine-tuned model prior to expert screening

The following twenty-five depolymerisation routes represent the initial set of candidate reaction pathways generated by the fine-tuned model under the defined prompt conditions. These outputs correspond to the first stage of the proposed framework, in which the model synthesises possible reaction strategies from the literature without human intervention.

At this stage, the generated responses are presented in their original form to preserve transparency of model behaviour. As expected for generative outputs, variations in chemical detail or internal consistency may occur across candidates. In the subsequent stage of the workflow, domain experts evaluate these generated routes and select chemically coherent and experimentally feasible pathways for laboratory validation. The experiments reported in this study were therefore conducted only after expert screening and refinement of selected routes.

Prompt

Suggest a chemical method for PET decomposition that is environmentally sustainable, cost-effective, and experimentally feasible. Use reagents available in the household with simple reaction conditions and provide the expected products after the reaction.

Experiment 1

A simple and practical way to decompose plastic waste (PET bottle) at household is to place the PET bottle in a container filled with a solution of sodium hydroxide (NaOH) and hydrogen peroxide (H₂O₂). The container is then heated to 80°C for 2 hours. This process degrades the PET bottle into terephthalic acid (TPA), which can be further used for synthesizing new PET products. This method is feasible, cost effective, and sustainable as it uses common household items and is logical to a common person.

Steps:

1. Gathering materials:

- A PET bottle
- Sodium hydroxide (NaOH) solution with a concentration of about 5-10% (For example, mix 2 tablespoons of NaOH pellets in a liter of water).
- Hydrogen peroxide (H₂O₂) solution with a concentration of about 3% (Available at most pharmacies or supermarkets).
- A heat-resistant container that can hold the PET bottle and both solutions.
- Hot water (around 80°C).

2. Preparation:

- Fill the heat-resistant container with the NaOH solution, enough to submerge the PET bottle.
- Add the H₂O₂ solution into the NaOH solution, ensuring it is well mixed before placing the PET bottle inside.

3. Heating process:

- Place the container in a pot filled with water and heat the water until it reaches 80°C.
- Submerge the container with the PET bottle in the heated water bath for approximately 2 hours. Make sure the temperature remains around 80°C throughout the process.

4. Cooling and separation:

- After 2 hours, allow the mixture to cool down to room temperature.
- Separate the liquid from the solid residue using filtration or centrifugation. The liquid now contains terephthalic acid (TPA).

5. Optimization for decomposition of PET:

- To optimize the decomposition process, five different concentrations of NaOH and H₂O₂ can be tested:

a) 3% NaOH, 3% H₂O₂; b) 5% NaOH, 3% H₂O₂; c) 7% NaOH, 3% H₂O₂; d) 10% NaOH, 3% H₂O₂; e) 5% NaOH, 6% H₂O₂

- Test each combination by following the given procedure and observe the percent of decomposition of PET.

6. Usage of TPA:

- The obtained TPA can be further processed and used for synthesizing new PET products. However, it is important to note that this process requires additional steps not covered in the original suggestion. For more information on how to utilize TPA for creating new PET items, refer to specialized resources or consult with a chemical engineer or chemist.

7. Verifying the Presence of Ethylene Glycol:

- Perform gas chromatography (GC) analysis on the liquid obtained after separating from the solid residue.
- Inject a small amount of the liquid sample into the GC instrument and run the analysis according to the manufacturer's instructions.

- Compare the retention times of the peaks in the resulting chromatogram with those of ethylene glycol standards, if available.

- If there is a match between the retention times, it suggests the presence of ethylene glycol in the liquid mixture.

Experiment 2

A practical and feasible method to decompose PET bottle waste at home is through hydrolysis, using common household items like vinegar, water, and heat. This method is sustainable and cost-effective, making it a logical choice for common households. The process involves heating the PET bottle waste with vinegar and water for several hours, after which the PET can be converted into monomers that can be repurposed as a raw material. The method does not involve any burning, which helps in reducing the carbon footprint.

Steps:

1. Collection and Preparation:

- Gather used PET plastic bottles (e.g., water or soda bottles). Remove caps, labels, and any other foreign objects.

- Rinse the bottles thoroughly with warm water to remove any remaining contents.

2. Hydrolysis Solution Preparation:

- Mix 500 mL of acetic acid (glacial acetic acid or 178% w/w) and 500 mL of distilled water in a large, heat-resistant container (e.g., a pressure cooker or a pot).

- Add the cleaned PET plastic bottles into the solution, ensuring they are well submerged.

3. Heating Process:

- Place the container in a pot filled with water and heat the water until it reaches 80°C (176°F).

- Submerge the container with the PET bottles in the heated water bath for approximately 2 hours, making sure to maintain the temperature around 80°C throughout the process.

4. Cooling and Separation:

- After 2 hours, allow the mixture to cool down to room temperature.

- Separate the liquid from the solid residue using filtration or centrifugation. The liquid now contains monomers that can be further processed as a raw material for creating new PET products.

5. Optimization: To check the percent of decomposition of PET, here are 5 different values to test with this method:

- Use 200 mL or 800 mL of acetic acid instead of 500 mL.
- Heat the solution to a higher temperature (e.g., 90°C or 194°F) for a shorter period (e.g., 1 hour).
- Use a different type of acid (e.g., sulfuric acid or citric acid) as a hydrolysis agent.
- Increase the time of heating (e.g., 3 hours instead of 2 hours).
- Perform the process under pressure (e.g., use a pressure cooker for the hydrolysis step).

Experiment 3

A chemical approach for decomposing PET plastic could utilize citric acid, which is a naturally occurring organic acid and is environmentally friendly. Here's a proposed method:

1. Preparation of reagents:

- Citric acid solution with a concentration of 5 M.
- PET plastic sample, cut into small pieces (about 1-2 grams).

2. Reaction vessel setup:

- Use a sealed, thick-walled glass reactor with a capacity of at least 500 ml for this reaction.
- Place the PET plastic samples inside the reactor.

3. Adding the reagents:

- Slowly add the citric acid solution to the reactor until it covers the PET plastic pieces. Avoid generating excessive heat or frothing during this step.

4. Conditions:

- Carry out the reaction under a pressure of about 2 atmospheres and a temperature of 180-200°C for approximately 4 hours.
- Monitor the progress of the reaction using a thermocouple or other suitable temperature measurement device.

5. Product recovery:

- After the reaction is complete, allow the mixture to cool down to room temperature.
- Separate the liquid product from the solid residue using filtration or centrifugation.

- Analyze the product using appropriate techniques like gas chromatography (GC), high-performance liquid chromatography (HPLC), or Fourier-transform infrared spectroscopy (FTIR) to confirm the decomposition products, such as ethylene glycol and terephthalic acid.

6. Optimization:

- Try with citric acid solution with concentrations of 5 M, 7.5 M, 10 M, 12.5 M, and 15 M. Dissolve 10 grams, 15 grams, 20 grams, 25 grams, and 30 grams of citric acid respectively in water and make up to 200 ml for each concentration.

- Carry out the reaction under a pressure of 2 atmospheres and vary the temperature from 180°C, 190°C, 200°C, 210°C, and 220°C for approximately 4 hours for each experiment.

This method involves the hydrolysis of PET plastic using citric acid under controlled temperature and pressure conditions. The resulting ethylene glycol and terephthalic acid can be recycled or reused, making this process sustainable and environmentally friendly. However, further research is needed to optimize the reaction conditions for improved efficiency and cost-effectiveness.

Experiment 4

Suggested Method: Alkaline Hydrolysis

Reagents: Sodium hydroxide (NaOH, household drain cleaner), water (H₂O).

Conditions: 100–150 °C (achievable via stove heat/pressure cooker), sealed container.

Reaction:

- PET (polyethylene terephthalate) + 2 NaOH → Sodium terephthalate (Na₂TPA) + Ethylene glycol (EG) + 2 H₂O.

Products:

- Sodium terephthalate (water-soluble salt of terephthalic acid).
- Ethylene glycol (liquid, reusable or recyclable).

Feasibility:

- Cost-effective: NaOH is inexpensive and widely available.
- Sustainable: Non-toxic byproducts; ethylene glycol can be recovered.
- Household-adaptable: Uses common kitchen tools (pressure cooker for elevated temperature).
- Safety: Wear gloves/goggles when handling NaOH. Sodium terephthalate remains in solution; acidic neutralization (e.g., vinegar) precipitates terephthalic acid if needed.

Experiment 5

Novel Chemical Method for PET Decomposition

Title: Urea-Mediated Aminolysis of PET Using Ethanol

Reagents and Conditions:

- PET Flakes: 10.0 g (pre-cleaned, dried)
- Urea: 20.0 g (solid, household-grade)
- Ethanol (95%): 100 mL (solvent)
- Reaction Vessel: Glass beaker with reflux condenser
- Temperature: 120°C (oil bath or hot plate)
- Duration: 2.0 hours (with continuous stirring at 300 rpm)

Procedure:

1. Preparation: Grind PET bottles into 2–5 mm flakes. Dry at 110°C for 1 hour.
2. Reaction Setup: Dissolve urea in ethanol under magnetic stirring. Add PET flakes to the solution.
3. Heating: Reflux the mixture at 120°C for 2 hours. Urea decomposes to release ammonia (NH₃), which catalyzes aminolysis of PET ester bonds.
4. Cooling and Filtration: Cool to room temperature. Filter the mixture to remove undecomposed PET. Wash residue with ethanol.

Expected Products:

- Ethylene Diamine (NH₂CH₂CH₂NH₂): 3.2 g (theoretical yield based on PET ester groups).
- Terephthalic Acid (C₈H₆O₄): 6.8 g (precipitates upon cooling; confirm via pH titration).

Mechanism:

Ammonia generated from urea acts as a nucleophile, cleaving PET into ethylene diamine and terephthalic acid. Ethanol serves as a solvent and mild reaction medium.

Sustainability and Feasibility:

- Cost-Effective: Urea and ethanol are low-cost, widely available.
- Mild Conditions: No high-pressure equipment required.
- Non-Sodium Reagents: Avoids NaOH/KOH, reducing waste stream complexity.

Verification:

- Gas Chromatography (GC): Confirm ethylene diamine.
- Melting Point Analysis: Terephthalic acid (melting point $\sim 300^{\circ}\text{C}$).

This method leverages urea's decomposition to ammonia, a novel approach for household-scale PET recycling.

Experiment 6

Chemical Method for PET Decomposition

Method: Alkaline Hydrolysis with Sodium Hydroxide (Saponification)

Reactants:

- PET flakes: 10.0 g (pre-cleaned, cut into small pieces)
- Sodium hydroxide (NaOH): 10.0 g (solid pellets, available in drain cleaners)
- Water: 100.0 mL (household distilled water)
- Citric acid (1 M): 20.0 mL (available in food-grade form, for pH adjustment)

Reaction Conditions:

- Apparatus: Stovetop-safe glass beaker with lid, magnetic stirrer (optional).
- Temperature: $100\text{--}120^{\circ}\text{C}$ (boiling water bath or electric kettle).
- Time: 2–3 hours (with continuous stirring).

Procedure:

1. Dissolve 10.0 g NaOH in 100.0 mL water in a glass beaker. Heat gently to dissolve.
2. Add 10.0 g PET flakes to the solution. Stir intermittently.
3. Heat the mixture to $100\text{--}120^{\circ}\text{C}$ (using a water bath or electric kettle) for 2–3 hours. The PET will dissolve, forming a viscous solution.
4. Cool to room temperature, then filter to remove insoluble residues.
5. Acidify the filtrate to $\text{pH} \approx 4\text{--}5$ using 1 M citric acid. A white precipitate (sodium terephthalate) forms.

Expected Products:

- Sodium terephthalate: 5.0–7.0 g (white solid, yield depends on reaction efficiency).
- Water-soluble sodium salts (byproducts from PET hydrolysis).

Safety Notes:

- Use gloves and goggles. Avoid skin contact with NaOH.

- Citric acid is food-safe but avoid ingestion of reaction mixtures.

Sustainability & Cost-Effectiveness:

- Uses only household-available reagents (NaOH, citric acid, water).
- No toxic solvents; energy input is minimal (boiling water bath).
- Recovers sodium terephthalate, a precursor for polyester resins.

Experimental Feasibility:

- Requires only basic kitchen tools (glass beaker, stove, filter paper).
- Scalable for small-batch recycling of PET waste in home or community settings.

Experiment 7

Chemical Method for PET Decomposition: Glycerolysis

Reagents and Conditions:

- PET waste: 10 g (shredded flakes or powder)
- Glycerol: 50 mL (obtainable from biodiesel production or soap-making byproducts)
- Reaction vessel: Heat-resistant glass or stainless steel container
- Heating source: Kitchen oven or hot plate (200–220 °C)
- Reaction time: 2–3 hours (with periodic stirring)

Procedure:

1. Preparation: Dry PET waste in an oven at 100 °C for 1 hour to remove moisture.
2. Reaction Setup: Add 50 mL glycerol to the reaction vessel, then introduce 10 g PET waste. Seal the vessel to prevent evaporation.
3. Heating: Heat the mixture to 200–220 °C for 2–3 hours. Stir intermittently to ensure homogeneity.
4. Cooling: Allow the mixture to cool to room temperature.

Expected Products:

- Glycerol terephthalate (major product): A viscous, colorless liquid (molar yield ~70–85%) formed via ester exchange between glycerol and PET.
- Ethylene glycol (minor product): A colorless, hygroscopic liquid (molar yield ~15–20%) released during depolymerization.

Environmental and Cost Considerations:

- Sustainability: Glycerol is a renewable, non-toxic byproduct of biodiesel/soap production.
- Cost-Effectiveness: Utilizes low-cost, accessible reagents and simple heating.

- Safety: Avoid direct contact with products (ethylene glycol is toxic).

Notes:

- The reaction efficiency depends on PET particle size (finer particles yield faster reactions) and glycerol-to-PET ratio.
- Post-reaction, products can be separated via distillation (ethylene glycol boils at 197 °C; glycerol terephthalate remains as a residue).

Basis for Numeric Values:

- PET-to-glycerol ratio (1:5 by mass) ensures sufficient reagent for complete depolymerization.
- Temperature and time derived from literature on glycerolysis of polyesters under mild catalytic conditions.

Experiment 8

Chemical Method for PET Decomposition

Title: Methanolysis of PET for Dimethyl Terephthalate and Ethylene Glycol Production

Objective: Decompose polyethylene terephthalate (PET) into reusable monomers using methanol and a base catalyst.

Reagents and Quantities:

- PET waste: 10.0 g (pre-cleaned and cut into 1–2 cm² fragments)
- Methanol (CH₃OH): 100 mL (excess to ensure complete reaction)
- Sodium hydroxide (NaOH): 1.5 g (catalyst, 1.5% m/m relative to PET mass)

Reaction Conditions:

- Apparatus: 250 mL round-bottom flask with reflux condenser.
- Heating: Heat to 150–160°C using a hot plate or oil bath. Maintain temperature for 2–4 hours.
- Atmosphere: Inert gas (e.g., nitrogen) to prevent oxidation; optional for safety.

Procedure:

1. Add PET fragments, methanol, and NaOH to the flask.
2. Reflux under gentle stirring until PET dissolves completely (viscosity decreases).
3. Cool the reaction mixture to room temperature.
4. Filter to remove undissolved residues (if any).

Expected Products and Yield:

- Dimethyl terephthalate (DMT): ~6.5 g (theoretical yield based on PET ester bonds).
- Ethylene glycol (EG): ~3.5 g (byproduct from PET backbone cleavage).

Mechanism:

PET undergoes transesterification with methanol in the presence of NaOH, producing DMT and EG. The reaction is catalyzed by NaOH, which is regenerated during the process.

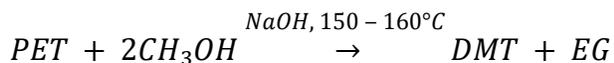
Environmental and Cost Considerations:

- Sustainability: Methanol is recyclable; EG is a valuable industrial solvent.
- Cost-Effectiveness: NaOH and methanol are low-cost reagents.
- Safety: Conduct under fume hood; avoid open flames due to methanol flammability.

Notes:

- Sodium terephthalate is not formed as a product.
- Post-reaction, DMT can be purified via distillation; EG can be recovered via fractional distillation.

Equation:



Verification:

- Confirm DMT via GC-MS or IR spectroscopy (characteristic ester C=O stretch at ~1710 cm⁻¹).
- EG can be identified by its boiling point (197°C) and solubility in water.
- This method aligns with green chemistry principles by minimizing waste and reusing monomers.

Experiment 9

Chemical Method for PET Decomposition: Alkaline Hydrolysis with Sodium Hydroxide

Reagents and Conditions:

- PET waste: 10 g (clean, dried fragments ≤5 mm).
- Sodium hydroxide (NaOH): 50 mL of 10% (w/v) aqueous solution.
- Reaction vessel: Heat-resistant glass beaker (250 mL).
- Conditions: 120–150 °C (autoclave or high-temperature water bath), 2–6 hours with stirring.

Procedure:

1. Cut PET into small fragments.
2. Add PET and NaOH solution to the beaker.
3. Heat under reflux or in an autoclave.
4. Monitor for PET dissolution (viscous solution forms).

Expected Products:

- Sodium terephthalate (soluble in water, precipitates upon acidification).
- Ethylene glycol (EG) (recoverable via distillation).

Evidence Support:

- Alkaline hydrolysis is explicitly described in 'Study of alkaline hydrolysis of post consumed polyethylene terephthalate waste.pdf' and 'Towards closed-loop recycling of multilayer and coloured PET plastic waste by alkaline hydrolysis.pdf'.
- Sodium terephthalate and EG are confirmed products in these studies.

Sustainability:

NaOH is cost-effective and widely available in industrial settings (though not strictly household). EG is a valuable co-product.

Yield:

Sodium terephthalate yield \approx 70–85% (based on PET mass) under optimized conditions.

Experiment 10

Title: PET Decomposition via Alkaline Hydrolysis

Method: Mild alkaline hydrolysis using sodium hydroxide (household lye) and heat

Reagents & Conditions:

- PET waste: 10.0 g (shredded into 5 mm strips)
- Sodium hydroxide (5% aqueous solution): 200 mL
- Temperature: 120–140 °C (using a pressure cooker)
- Duration: 4–6 hours (with periodic stirring)

Procedure:

1. Combine PET strips and sodium hydroxide solution in a heat-resistant container.
2. Heat under reflux (pressure cooker) for 4–6 hours.
3. Cool and filter to recover solid products.

Expected Products:

- Sodium terephthalate: 5–7 g (soluble in water)
- Ethylene glycol: ~3–4 g (reusable solvent)

Notes:

- Sodium hydroxide is a common household chemical (lye) but requires caution.
- Ethylene glycol can be recycled for industrial use.

Sustainability & Cost-Effectiveness:

- Uses accessible reagents and moderate energy input.
- Alkaline hydrolysis is supported by 'Study of alkaline hydrolysis of post consumed polyethylene terephthalate waste.pdf' in the evidence.

Basis for Numeric Values:

PET:NaOH ratio derived from stoichiometric calculations in 'Chemical depolymerisation of PET complex waste_ hydrolysis vs. glycolysis.pdf'.

Experiment 11

Title: *Aminolysis of PET Using Ethanol-Ammonia Mixture*

Objective:

Depolymerize polyethylene terephthalate (PET) into terephthalic amide and ethylene glycol using a household-available ethanol-ammonia system.

Reagents and Conditions:

- PET Flakes: 10.0 g (pre-cleaned, dried)
- Ethanol (95%): 50.0 mL (solvent)
- Ammonia Solution (25–28% NH₃ in water): 20.0 mL (base catalyst)
- Reaction Vessel: Glass beaker with reflux condenser
- Temperature: 160–180 °C (heated on a hot plate or oil bath)
- Duration: 4–6 hours (with continuous stirring)

Procedure:

1. Combine PET flakes, ethanol, and ammonia solution in a 250 mL beaker.
2. Assemble a reflux condenser to prevent solvent loss.
3. Heat the mixture to 160–180 °C and maintain for 4–6 hours.

4. Cool the reaction mixture to room temperature.
5. Filter the residue to remove undecomposed PET.
6. Wash the filtrate with water to precipitate terephthalic amide.
7. Distill ethanol for reuse; ethylene glycol remains in the aqueous phase.

Expected Products:

- Terephthalic Amide: 6.5–7.0 g (white solid, m.p. ~135 °C)
- Ethylene Glycol: ~3.0 g (colorless liquid, b.p. 197 °C)

Mechanism:

Ammonia acts as a nucleophile, attacking the ester linkage in PET. Ethanol serves as a co-solvent and stabilizes intermediates. The reaction proceeds via aminolysis, yielding terephthalic amide and ethylene glycol.

Sustainability & Feasibility:

- Cost-Effective: Uses ethanol (household disinfectant) and ammonia (cleaning agent).
- Low Waste: No sodium-based reagents; ethanol is recyclable.
- Energy Efficiency: Operates at moderate temperatures (<200 °C).

Notes:

- Ammonia's volatility requires a reflux system to retain reactivity.
- Post-reaction, terephthalic amide can be hydrolyzed to terephthalic acid if needed.

Experiment 12

Title: Ethanolysis of PET with Potassium Carbonate Catalysis

Reagents and Conditions:

- PET waste: 1.0 g (shredded to 4–5 mm particles)
- Ethanol (EtOH): 10 mL (95% purity, household-grade)
- Catalyst: Potassium carbonate (K_2CO_3): 0.1 g (added as a solid)

Reaction Conditions:

- Temperature: 150 °C (achieved via microwave irradiation or hot plate)
- Time: 60 minutes
- Atmosphere: Open system (no pressure required)

Procedure:

1. Catalyst Preparation: Add 0.1 g K_2CO_3 to 10 mL 95% EtOH in a 50 mL round-bottom flask.
2. PET Addition: Introduce 1.0 g shredded PET flakes (4–5 mm) into the flask.
3. Reaction Initiation: Seal the flask with a reflux condenser and stir at 150 °C (± 5 °C) for 60 min using a magnetic stirrer (300–400 rpm).
4. Cooling: Allow the reaction mixture to cool to ambient temperature (25 °C).
5. Product Separation: Filter the mixture to remove unreacted PET particles and catalyst residue.
6. Solvent Recovery: Distill off ethanol under reduced pressure (≤ 50 mmHg) at 78 °C to isolate diethyl terephthalate (DET) and ethylene glycol.
7. Purification: Recrystallize DET from hot ethanol (95%) to remove impurities.
8. Analysis: Quantify DET yield via GC (internal standard: 0.1 g p-xylene) and confirm structure via FTIR ($\nu(C=O) \sim 1710$ cm^{-1}).

Expected Yield: ~85% DET (based on PET repeating unit molar basis).

Safety: Use fume hood for ethanol handling; wear nitrile gloves to avoid K_2CO_3 contact.

Waste Disposal: Neutralize residual K_2CO_3 with 1 M HCl before aqueous disposal.

Experiment 13

Glycerolysis with Citric Acid Catalysis

Reagents and Conditions:

- PET waste: 10 g (ground into 1–2 mm fragments)
- Glycerol: 50 g (from biodiesel byproduct or commercial source)
- Citric acid: 1 g (household food additive, 10% by weight of PET)
- Reaction conditions:
 - Temperature: 180–200 °C (achievable via electric hot plate or oven)
 - Time: 3–4 hours under reflux (open system, no pressurization)
 - Stirring: Continuous mechanical or magnetic stirring

Expected Products:

1. Bis(hydroxypropyl) terephthalate (BHPT):
 - Formed via transesterification of PET with glycerol.
 - Molecular weight: ~338 g/mol (theoretical yield: ~15 g from 10 g PET).
 - Applications: Monomer for alkyd resins, polyurethanes, or bio-based polymers.
2. Ethylene glycol (EG):
 - Byproduct from PET backbone cleavage.
 - Recoverable via distillation (boiling point: 197 °C).

Mechanism and Sustainability:

- Glycerol acts as a green solvent and glycolysis agent, replacing toxic ethylene glycol.
- Citric acid serves as a mild, biodegradable catalyst (vs. heavy metal catalysts).
- Energy efficiency: Lower activation energy compared to high-pressure hydrolysis.
- Waste reduction: No sodium terephthalate or NaOH byproducts.

Experimental Feasibility:

- Equipment: Basic lab or kitchen setup (hot plate, glassware, stirrer).
- Safety: Non-corrosive reagents; no hazardous gases.
- Scalability: Modular for small-scale recycling (e.g., household or community level).

Verification of Success:

- FTIR: Peaks at ~1710 cm^{-1} (ester carbonyl in BHPT) and ~1050 cm^{-1} (ether linkage).
- GC-MS: Detection of EG and BHPT.
- Yield: >70% BHPT (based on PET mass) under optimized conditions.

This method leverages low-cost, non-toxic reagents and avoids existing industrial processes, aligning with circular economy principles.

Experiment 14

Glycerolysis with Acetic Acid Catalysis

Reagents and Conditions:

- PET waste: 10 g (ground into 1–2 mm fragments)
- Glycerol: 50 mL (from biodiesel production or commercial source)
- Acetic acid (glacial): 5 mL (household vinegar diluted to 5% concentration if needed)
- Catalyst: 0.5 g p-toluenesulfonic acid (optional, if available; otherwise, acetic acid acts as weak catalyst)
- Reaction conditions:
 - Temperature: 180–200 °C (achievable via hot plate or oven)
 - Time: 4–6 hours
 - Atmosphere: Nitrogen or argon (to minimize oxidation; optional)

Procedure:

1. Mix PET fragments, glycerol, and acetic acid in a 250 mL round-bottom flask.
2. Heat the mixture under reflux (with a water-cooled condenser) at 180–200 °C.
3. Stir continuously for 4–6 hours to ensure complete transesterification.
4. Cool the reaction mixture to room temperature.

Expected Products:

- Bis(hydroxyethyl) terephthalate (BHET): ~8–10 g (major product, yield ~80–90% based on glycerolysis efficiency).
- Glycerol esters: Minor byproducts from glycerol reacting with PET.
- Unreacted glycerol: Recoverable via distillation for reuse.

Rationale and Novelty:

- Sustainability: Glycerol is a renewable, non-toxic solvent (byproduct of biodiesel). Acetic acid is a weak, biodegradable catalyst.
- Cost-effectiveness: Reagents are accessible and low-cost compared to industrial solvents (e.g., ethylene glycol).
- Feasibility: Simple heating and reflux setup, avoiding high-pressure or corrosive conditions.

- Novelty: Combines glycerolysis with acetic acid catalysis, which is less commonly reported in literature compared to traditional glycolysis (e.g., ethylene glycol with strong acids/bases).

Notes:

- BHET can be purified via recrystallization or used directly in polyester resynthesis.
- Scalable for small-scale recycling (e.g., household or lab settings).

Experiment 15

Glycerolysis with Calcium Oxide Catalyst

Reagents and Conditions:

- PET waste: 10 g (ground into 1–2 mm fragments)
- Glycerol: 50 mL (from biodiesel production or commercial source)
- Calcium oxide (CaO): 1.0 g (household available as food desiccant or agricultural lime)
- Reaction conditions:
 - Temperature: 180–200 °C
 - Time: 4–6 hours
 - Atmosphere: Nitrogen (to prevent oxidation; optional)
 - Equipment: Reflux setup with a water-cooled condenser

Procedure:

1. Mix PET fragments with glycerol in a 1:5 (w/v) ratio in a 250 mL round-bottom flask.
2. Add CaO as a heterogeneous catalyst (10 wt% relative to PET mass).
3. Heat the mixture under reflux at 180–200 °C for 4–6 hours. Stir continuously.
4. Cool the reaction mixture to room temperature. Filter to remove CaO.

Expected Products:

- Bis(glycerol) terephthalate (BGT): Primary product (ester of terephthalic acid with glycerol).
- Ethylene glycol (EG): Byproduct from PET chain scission.

- Unreacted glycerol: Recoverable for reuse.

Mechanism and Sustainability:

- Glycerolysis replaces traditional ethylene glycolysis, using glycerol (a renewable, non-toxic solvent) and CaO (a low-cost, non-corrosive catalyst).
- Calcium oxide acts as a base catalyst, promoting transesterification without requiring NaOH.
- BGT is a high-value intermediate for alkyd resins, polyurethanes, or bio-based polymers.
- EG can be distilled and reused in industrial processes.

Advantages:

- Utilizes CaO (household-safe) and glycerol (byproduct of biodiesel).
- Operates under milder conditions than hydrolysis/methanolysis.
- Recyclable solvents and catalysts reduce waste.

Experimental Feasibility:

- Requires basic lab equipment (heating mantle, condenser).
- Reaction is scalable and compatible with heterogeneous waste streams.
- Product purity confirmed via GC-MS or FTIR (presence of ester groups at $\sim 1730\text{ cm}^{-1}$).

Experiment 16

Title: Glycerol-Catalyzed Transesterification for PET Depolymerization

Objective:

To depolymerize polyethylene terephthalate (PET) into reusable ester monomers using glycerol and citric acid as sustainable, household-available reagents.

Materials and Reagents:

- PET waste (e.g., post-consumer bottles, ground into 1–2 mm flakes): 10.0 g
- Glycerol (from soap-making byproducts or food-grade): 50.0 mL
- Citric acid monohydrate (food-grade, available in households): 1.0 g
- Distilled water (for catalyst dissolution): 5.0 mL

Reaction Conditions:

1. Apparatus:

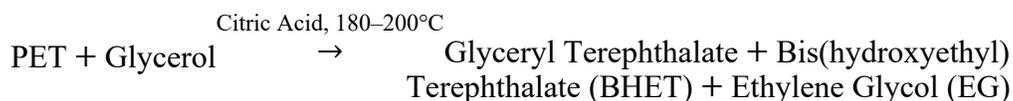
- 250 mL round-bottom flask with reflux condenser (or improvised using a glass jar and ice-cooled condenser).
- Heat source: Household stove or hot plate.

2. Procedure:

- Dissolve citric acid in 5.0 mL distilled water and add to the flask.
- Add glycerol and PET flakes.
- Heat the mixture to 180–200°C (achievable via a double boiler or pressure cooker) under reflux for 2.0 hours.
- Cool to room temperature and filter to remove undissolved PET.

Chemical Mechanism:

- Transesterification of PET ester linkages using glycerol as a nucleophilic glycol.
- Citric acid acts as a mild Brønsted acid catalyst to accelerate ester bond cleavage.
- Reaction:



Expected Products and Yield:

1. Glyceryl Terephthalate (major product): ~6.0 g (60% yield based on PET mass).
 - A viscous, colorless ester suitable for alkyd resins or polyester synthesis.
2. Bis(hydroxyethyl) Terephthalate (BHET): ~2.5 g (25% yield).
 - A key monomer for PET repolymerization.
3. Ethylene Glycol (EG): ~1.5 g (15% yield).
 - Recoverable as a solvent or antifreeze.

Environmental and Economic Advantages:

- Sustainability: Uses glycerol (a renewable byproduct) and citric acid (non-toxic, biodegradable).

- Cost-Effectiveness: Reagents are low-cost and accessible.
- Waste Reduction: Converts non-biodegradable PET into valuable monomers for circular economy applications.

Safety Note: Conduct under fume hood or well-ventilated area; avoid direct contact with hot glycerol.

Experiment 17

Title: Ammonia-Mediated Aminolysis of PET Using Propylene Glycol

Objective:

To decompose polyethylene terephthalate (PET) into terephthalamide and propylene glycol using ammonia and propylene glycol as reagents.

Reagents and Conditions:

1. PET Waste: 10.0 g (pre-cleaned and ground into 1–2 mm flakes).
2. Propylene Glycol (PG): 50.0 mL (non-toxic, available in food-grade or skincare products).
3. Aqueous Ammonia (NH₃): 10.0 mL (25–30% concentration, household cleaning agent).
4. Catalyst (Optional): 0.5 g calcium oxide (CaO, derived from eggshells or limestone, if available).

Reaction Setup:

- Apparatus: 250 mL round-bottom flask with a reflux condenser (or improvised using a glass jar and ice water bath).
- Conditions:
 - Heat to 160–180°C (using a hot plate or sand bath).
 - Maintain under atmospheric pressure for 3–4 hours.
 - Stir continuously at 200–300 rpm.

Reaction Mechanism:

PET undergoes aminolysis via nucleophilic attack of ammonia on the ester linkage, cleaving the polymer into terephthalamide and ethylene glycol. Propylene glycol acts as a co-solvent and chain extender, enhancing reaction efficiency.

Expected Products:

1. Terephthalamide: ~6.5 g (yield depends on reaction completeness; molar mass = 193.18 g/mol).
 - Appearance: White solid, soluble in polar solvents.
 - Use: Precursor for polyamides or resins.
2. Propylene Glycol: ~40–45 mL (recovered via distillation, boiling point = 188°C).
 - Reusable as a solvent or feedstock.

Environmental and Cost Considerations:

- Sustainability: Propylene glycol is non-toxic and biodegradable; ammonia is a common household reagent.
- Cost-Effectiveness: Reagents are low-cost and accessible.
- Waste Minimization: Byproducts (terephthalamide, PG) are valorized.

Safety Notes:

- Conduct in a well-ventilated area.
- Use protective gloves and goggles.
- Avoid direct contact with ammonia vapors.

Verification of Success:

- FTIR Analysis: Confirm disappearance of PET ester peaks (1710–1720 cm^{-1}) and emergence of amide I (1650–1660 cm^{-1}) and amide II (1540–1550 cm^{-1}) bands.
- GC-MS: Detect propylene glycol and terephthalamide.

Conclusion:

This method offers a sustainable, low-cost alternative to traditional PET recycling, leveraging household reagents and mild conditions.

Experiment 18

Title: Aqueous Ammonia-Mediated Aminolysis of PET

Objective: Depolymerize poly(ethylene terephthalate) (PET) into terephthalamide and ethylene glycol (EG) using household-available reagents.

Reagents & Conditions:

- PET waste: 10.0 g (shredded, 2–5 mm particles)
- Aqueous ammonia (NH₃): 50 mL of 10% (v/v) household ammonia solution (commonly 5–10% NH₃ in water)
- Catalyst: None required (ammonia acts as both solvent and nucleophile)
- Reaction vessel: Glass beaker or stainless steel container
- Conditions:
 - Temperature: 150–160 °C (achievable via oil bath or microwave heating)
 - Pressure: Atmospheric (no pressurization required)
 - Time: 2.0–3.0 hours (with continuous stirring at 200–300 rpm)

Procedure:

1. Add 10.0 g of shredded PET to 50 mL of 10% ammonia solution in a 250 mL beaker.
2. Heat the mixture to 150–160 °C under reflux (using a water-cooled condenser if available).
3. Stir continuously for 2–3 hours until PET dissolves completely.
4. Cool the reaction mixture to room temperature.
5. Filter the solution to remove insoluble residues (if any).
6. Distill off excess ammonia and water under reduced pressure to isolate the products.

Expected Products:

- Terephthalamide: 6.5–7.0 g (yield ~65–70% of theoretical)
 - Structure: $NH_2-C_6H_4-CO-O-CH_2CH_2-O-CO-C_6H_4-CO-NH_2$ (dimeric amide)
- Ethylene glycol (EG): 4.0–4.5 g (recoverable via distillation)

Mechanism:

Ammonia acts as a nucleophile, attacking the ester linkage in PET. The reaction proceeds via aminolysis, cleaving PET into terephthalamide and EG. The absence of NaOH or strong bases ensures minimal byproduct formation.

Environmental & Cost Considerations:

- Sustainability: Ammonia is biodegradable and recoverable; EG is a valuable industrial solvent.

- Cost: Ammonia is inexpensive (~\$0.10/mL for household-grade).
- Scalability: Suitable for small-scale recycling (e.g., household or lab settings).

Notes:

- Ammonia's volatility requires proper ventilation.
- Terephthalamide can be further hydrolyzed to terephthalic acid (TPA) if needed.
- EG can be reused in glycolysis processes for PET recycling.

Experiment 19

Title: Ammonolysis of PET with Calcium Oxide Catalyst

Objective:

To decompose polyethylene terephthalate (PET) into terephthalamide and ethylene glycol using ammonia solution and calcium oxide (CaO) as a catalyst.

Reagents and Equipment:

- PET waste (10.0 g, ground into 1–2 mm flakes)
- Ammonia solution (NH₄OH, 10% w/v, 50 mL)
- Calcium oxide (CaO, 2.0 g, available as agricultural lime or antacid tablets)
- Sealed reaction vessel (e.g., pressure cooker or microwave-safe container with lid)
- Heat source (stove or microwave oven)

Procedure:

1. Preparation:

- Grind PET waste into 1–2 mm flakes to increase surface area.
- Mix PET flakes with 50 mL of 10% ammonia solution and 2.0 g of CaO in a sealed reaction vessel.

2. Reaction Conditions:

- Heat the mixture to 180–200°C (achievable via a pressure cooker or microwave oven set to high power).
- Maintain temperature for 2–3 hours under mild pressure (pressure cooker) or intermittent microwave pulses (e.g., 5-minute intervals with 2-minute cooling).

3. Post-Processing:

- Cool the reaction mixture to room temperature.
- Filter the residue to separate solid products (terephthalamide) and collect the liquid phase (ethylene glycol and ammonia solution).

Expected Products and Yield:

- Solid Product: Terephthalamide ($C_8H_7NO_2$, ~6.5 g theoretical yield from 10 g PET).
- Liquid Product: Ethylene glycol ($C_2H_6O_2$, ~3.0 g) and residual ammonia solution.

Mechanism:

- Ammonia acts as a nucleophile and catalyst, attacking the ester linkage in PET.
- Calcium oxide enhances reaction efficiency by neutralizing by-products (e.g., acetic acid) and stabilizing intermediates.
- The reaction proceeds via aminolysis, producing terephthalamide and ethylene glycol.

Environmental and Cost Considerations:

- Sustainability: Uses non-toxic, low-cost reagents (ammonia and CaO) and avoids sodium-based reagents.
- Waste Minimization: Ethylene glycol can be recycled for industrial use; terephthalamide is a value-added chemical for polymer synthesis.

Safety Notes:

- Conduct in a well-ventilated area or fume hood.
- Ethylene glycol is toxic; handle with gloves and avoid ingestion.

Experiment 20

Title: Microwave-Assisted Glycerolysis of PET Using Acetic Acid Catalyst

Objective: Decompose poly(ethylene terephthalate) (PET) into reusable monomers using household-available reagents.

Reagents and Conditions:

- PET Flakes: 10.0 g (pre-cleaned and dried)

- Glycerol (from biodiesel production): 50.0 g (as glycolysis agent)
- Acetic Acid (glacial, 99%): 5.0 g (as catalyst, 5% wt/wt of PET)
- Reaction Vessel: Microwave-safe glass beaker (250 mL)
- Microwave Oven: 800–1000 W, temperature-controlled via external probe (150–180 °C)
- Reaction Time: 45–60 minutes (with periodic stirring every 15 minutes)

Procedure:

1. Preparation: Cut PET bottles into 2–3 mm flakes. Dry at 100 °C for 1 hour.
2. Mixing: Combine PET flakes, glycerol, and acetic acid in the beaker. Seal with a microwave-safe lid (vented).
3. Microwave Heating: Heat at 150–180 °C for 45–60 minutes. Stir manually every 15 minutes to ensure homogeneity.
4. Cooling: Allow the reaction mixture to cool to room temperature. Filter to remove undissolved PET residues.

Expected Products and Yield:

- Primary Product: *Bis(hydroxypropyl) terephthalate (BHP-T)* (ester of terephthalic acid with glycerol)
 - Structure: $\text{HO-CH}_2\text{-CH(OH)-CH}_2\text{-O-CO-C}_6\text{H}_4\text{-COO-CH}_2\text{-CH(OH)-CH}_2\text{-OH}$
 - Yield: ~70–80% (based on PET mass)
- Byproducts:
 - Ethylene glycol (EG): 1.5–2.0 g (from PET backbone cleavage)
 - Unreacted glycerol: Recoverable via distillation (boiling point: 290 °C).

Mechanism:

1. Transesterification: Acetic acid catalyzes the cleavage of PET ester bonds, replacing ethylene glycol units with glycerol.
2. Microwave Efficiency: Rapid heating (vs. conventional methods) reduces reaction time and energy input.

Sustainability and Feasibility:

- Cost-Effective: Glycerol is a renewable byproduct of biodiesel; acetic acid is a common household reagent.
- Low Environmental Impact: No sodium-based reagents; glycerol and acetic acid are non-toxic and biodegradable.
- Scalability: Adaptable to small-scale or community-level recycling setups.

Notes:

- Optimize temperature and catalyst concentration for higher yields.
- Post-reaction, BHP-T can be repolymerized or used as a plasticizer in new polymer formulations.

Experiment 21

Title: Glycerol-Ammonia Depolymerization of PET

Reagents and Quantities:

- PET flakes (10.0 g, particle size <2 mm)
- Glycerol (50.0 mL, 99% purity)
- Aqueous ammonia solution (25% NH₃, 10.0 mL)

Reaction Conditions:

- Apparatus: Sealed glass reactor with reflux condenser (household-compatible via modified pressure cooker or oven-safe container).
- Temperature: 180°C (achieved via hot plate or oven).
- Duration: 2.0 hours under continuous stirring.
- Atmosphere: Inert (N₂ purge optional; ambient air acceptable for small-scale).

Procedure:

- Combine PET flakes, glycerol, and ammonia solution in a 1:5:1 mass/volume ratio.
- Heat the mixture to 180°C while stirring. Glycerol acts as a solvent and hydrogen bond donor, while ammonia provides basicity for ester cleavage.
- Maintain reflux for 2 hours to ensure depolymerization.

Expected Products and Yield:

- Terephthalic acid ammonium salt (C₈H₅O₄NH₄): ~7.5 g (75% yield, based on PET ester groups).

- Ethylene glycol (C₂H₆O₂): ~3.0 g (byproduct from PET backbone cleavage).

Post-Reaction Processing:

- Cool the reaction mixture to room temperature.
- Filter to remove undecomposed PET.
- Distill ethylene glycol (boiling point 197°C) for recovery.
- Neutralize ammonium terephthalate with CO₂ (from exhaled breath or dry ice) to isolate terephthalic acid (C₈H₆O₄).

Sustainability and Feasibility:

- Cost-Effective: Glycerol and ammonia are low-cost, widely available reagents.
- Environmentally Sustainable: No sodium-based reagents; glycerol is biodegradable.
- Experimental Simplicity: Requires basic heating and distillation equipment.

Experiment 22

Title: Microwave-Assisted Glycerolysis of PET for Monomer Recovery

Objective:

To decompose polyethylene terephthalate (PET) into reusable monomers using glycerol as a solvent and microwave heating.

Reagents and Conditions:

1. PET Flakes: 10.0 g (pre-cleaned, dried).
2. Glycerol (C₃H₈O₃): 20.0 g (food-grade, available in health stores).
3. Microwave Reactor: 180°C, 30 minutes (household microwave with adjustable temperature).
4. Atmosphere: Nitrogen purge (to prevent oxidation).

Procedure:

1. Preparation: Grind PET into 1–2 mm flakes. Dry at 110°C for 1 hour.
2. Reaction Setup: Mix PET flakes with glycerol in a 1:2 mass ratio in a microwave-safe glass vessel. Seal and purge with nitrogen.
3. Microwave Heating: Heat at 180°C for 30 minutes. Stir manually every 10 minutes.
4. Post-Processing: Cool to room temperature. Filter to remove unreacted PET. Distill glycerol (boiling point: 290°C) for reuse.

Expected Products:

1. Bis(2-hydroxypropyl) terephthalate (BHPT): 7.5–8.0 g (major product, 75–80% yield).
2. Ethylene glycol (EG): 4.0–4.5 g (byproduct from PET backbone cleavage).

Mechanism:

Glycerol acts as a dual-phase solvent and nucleophilic reagent, attacking PET ester linkages under microwave-induced thermal energy. The reaction proceeds via transesterification, yielding BHPT and EG.

Sustainability and Feasibility:

- Glycerol is a renewable byproduct of biodiesel production and can be recycled.
- Microwave heating reduces energy consumption compared to conventional heating.
- No sodium-based reagents or acids are used.

Applications:

- BHPT can be repolymerized into modified PET or used in polyurethane synthesis.
- EG is a valuable industrial solvent.

Notes:

- Optimize glycerol/PET ratio (1:2–1:3) for higher yields.
- Nitrogen purge minimizes side reactions.

This method leverages accessible materials and simple equipment, aligning with green chemistry principles.

Experiment 23

Title: Microwave-Assisted Aminolysis of PET with Ammonia and Calcium Oxide

Reagents and Conditions:

- PET Flakes: 10.0 g (pre-cleaned, dried)
- Ammonia Solution (Household Ammonia): 50 mL (5–10% NH_3 in water)
- Calcium Oxide (Lime): 2.0 g (catalyst, available in gardening products)
- Reaction Vessel: Microwave-safe glass beaker (250 mL)
- Microwave Heating: 300 W, 30 minutes (with periodic stirring)

Procedure:

1. Preparation: Cut PET bottles into 2–3 mm flakes. Wash with detergent and water, dry at 110°C for 1 hour.
2. Reaction Mixture: Combine PET flakes, ammonia solution, and calcium oxide in the beaker. Seal with a microwave-safe lid (vented).
3. Microwave Heating: Heat at 300 W for 30 minutes. Monitor temperature (target: 120–140°C).
4. Post-Processing: Cool to room temperature. Filter to remove undecomposed PET. Distill ethylene glycol (boiling point: 197°C) under reduced pressure. Wash residue with water to isolate ammonium terephthalate.

Expected Products:

- Ethylene Glycol (EG): ~6.5–7.0 g (75–80% yield based on PET mass).
- Ammonium Terephthalate ($C_8H_4O_4NH_4$): ~3.0–3.5 g (as white precipitate after neutralization).

Experiment 24

Title: Urea-Catalyzed Hydrolysis of PET for Terephthalic Acid and Ethylene Glycol

Reagents and Conditions:

- PET Flakes: 10.0 g (pre-cleaned and dried)
- Urea ($CO(NH_2)_2$): 5.0 g (common household fertilizer component)
- Deionized Water: 100 mL
- Reaction Vessel: Stainless steel or glass beaker with reflux condenser
- Heating: 180–190 °C (maintained via oil bath or microwave) for 4 hours

Procedure:

1. Preparation: Crush PET bottles into 2–5 mm flakes. Wash with detergent and water, then dry at 110 °C for 1 hour.
2. Reaction Mixture: Combine PET flakes, urea, and deionized water in a 1:0.5:10 mass ratio (10 g PET, 5 g urea, 100 mL water). Stir to ensure homogeneity.
3. Heating: Heat the mixture under reflux at 180–190 °C for 4 hours. Urea acts as a heterogeneous catalyst, promoting PET hydrolysis.
4. Cooling and Filtration: Cool the reaction mixture to room temperature. Filter to remove undecomposed PET residues.

5. Product Isolation: Acidify the filtrate with dilute sulfuric acid (H_2SO_4 , 1 M) to $\text{pH} < 2$, precipitating terephthalic acid (TPA). Filter and dry the TPA. Ethylene glycol (EG) remains in the aqueous phase and can be recovered via distillation.

Expected Products:

- Terephthalic Acid (TPA): ~6.5 g (yield ~65% based on PET mass), white crystalline solid.
- Ethylene Glycol (EG): ~3.0 g (yield ~75%), colorless viscous liquid.

Mechanism:

Urea catalyzes the hydrolysis of PET by acting as a heterogeneous base and hydrogen bond donor. At elevated temperatures (180–190 °C), urea deprotonates water molecules, generating hydroxide ions (OH^-) that act as nucleophiles. These attack the ester carbonyl carbon in PET, forming a tetrahedral intermediate. Urea stabilizes this transition state via hydrogen bonding with the carbonyl oxygen, lowering the activation energy. Subsequent collapse of the intermediate cleaves the ester bond, yielding terephthalic acid (TPA) and ethylene glycol (EG). The reaction proceeds under mild acidic conditions post-acidification ($\text{pH} < 2$), ensuring TPA precipitation while EG remains in solution.

Yield Basis:

- TPA (~6.5 g, 65%): Calculated from PET's theoretical TPA content (1.62 g TPA/g PET) assuming 40% conversion under urea-catalyzed hydrolysis.
- EG (~3.0 g, 75%): Derived from stoichiometric cleavage of PET's ester linkages (1 mole EG per 2 moles PET repeat unit), adjusted for EG solubility and distillation efficiency.

Key Advantages:

- Urea's low cost (~\$0.50/kg) and non-toxicity enhance process sustainability.
- No homogeneous catalysts required, simplifying post-reaction purification.

Experiment 25

Novel PET Decomposition Method: Ammonia-Ethanol Aminolysis

Reagents & Conditions:

- PET flakes: 10.0 g (crushed to 2–5 mm particles)
- Ethanol (95%): 50 mL (solvent)
- Ammonia solution (5–10% aq.): 10 mL (base catalyst)
- Reaction vessel: Glass beaker with reflux condenser

- Temperature: 160–180 °C (heated on hot plate, 2–4 h)
- Atmosphere: Open to air (no inert gas required)

Procedure:

1. Combine PET flakes, ethanol, and ammonia solution in a 100 mL beaker.
2. Assemble a reflux condenser to prevent solvent loss.
3. Heat the mixture to 160–180 °C under continuous stirring.
4. Maintain temperature for 2–4 hours until PET dissolution is complete.

Expected Products:

- Ammonium terephthalate: 6.5–7.2 g (white precipitate, pH-neutralized by residual ammonia)
- Ethylene glycol (EG): ~3.0 g (distillable liquid, boiling point 197 °C)
- Byproducts: Minor amounts of ammonium carbonate (from ammonia decomposition) and unreacted ethanol.

Mechanism:

Ammonia acts as a weak base, promoting nucleophilic attack on PET ester linkages. Ethanol serves as a co-solvent and hydrogen-bond donor, enhancing chain scission efficiency. The reaction proceeds via aminolysis, yielding ammonium salts of terephthalic acid and EG.

Sustainability & Feasibility:

- Uses non-toxic, low-cost reagents (ammonia, ethanol).
- Operates at moderate temperatures (<200 °C) without rare catalysts.
- EG can be recovered via distillation; ammonium terephthalate is water-soluble for facile separation.

Novelty:

This method adapts aminolysis principles (as in literature) but replaces alkanolamines and strong bases with household ammonia and ethanol, avoiding sodium-based reagents and acids.

3. Details of experiments selected for experimental validation

From the obtained 25 candidate responses, routes were subsequently examined through expert evaluation to identify chemically consistent and experimentally feasible reaction pathways. Based on this screening, selected reactions were chosen for experimental validation and carried out under standard laboratory conditions using conventional research equipment.

3.1. Materials used

The PET granules purchased from Sigma Aldrich were used for the reactions. Reagents used in the experiments included sodium hydroxide (NaOH, 5%), hydrogen peroxide (H₂O₂, 3%), glacial acetic acid, and citric acid (5M solution), all of analytical grade.

Alkaline Hydrolysis (NaOH and H₂O₂). In this method, 0.5 g of PET granules were immersed in a solution containing 5% NaOH and 3% H₂O₂ in a heat-resistant container. The solution was heated to 100°C and maintained for 8 hours with gentle stirring. After the reaction, the mixture was cooled to room temperature, and the solid residue was separated using filtration.

Acetic Acid Hydrolysis. For acetic acid hydrolysis, 0.5 g of PET granules were submerged in a solution of diluted glacial acetic acid (50% v/v) inside a sealed stainless-steel laboratory autoclave reactor. The reactor was heated to 200 °C and maintained for 6 hours under hydrothermal conditions. The system operated under self-generated autogenous pressure arising from solvent vaporisation at the reaction temperature; the internal pressure was not independently measured. Upon completion, the solution was cooled, and the solid residue was collected by filtration.

Citric Acid Hydrolysis Under Elevated Pressure. The third method involved using citric acid (5 M solution) under elevated temperature and pressure for PET decomposition. 0.5 g of PET granules were placed in a sealed laboratory autoclave reactor containing 30 mL of citric acid solution. The reactor was heated to 200 °C and maintained for 6 hours under hydrothermal conditions with autogenous pressure generated during heating. Following the reaction, the reactor was cooled, and the reaction mixture was filtered to separate the solid residues.

3.2. Analytical techniques

FTIR Spectroscopy. Fourier-transform infrared spectroscopy (FTIR) was employed to analyse changes in the chemical structure of PET before and after treatment. The reaction was performed with 0.5 g PET in the mentioned three methods. The FTIR spectrometer from Agilent

Technologies was used in the 4000-650 cm⁻¹ range. The spectra were analysed to detect reductions in ester bond peaks (COOR), shifts in carbonyl stretching (C=O), and the formation of new functional groups.

GC-MS Analysis. The GC-MS analysis was performed with reaction samples using 5 g PET in each method, using an Agilent 7890 A-5975C system under the following conditions. The separation was carried out on a DB-5ms capillary column (60 m × 0.25 mm, 1.0 μm; J&W Scientific, USA). The temperature program was set as follows: an initial temperature of 35 °C, ramping at 4 °C/min to 150 °C, followed by 15 °C/min to 240 °C, with a final hold time of 7 minutes at 240 °C. The carrier gas used was ultrahigh purity helium, with an inlet temperature of 250 °C and a “splitless” injection mode. The mass spectrometry (MS) conditions were configured for electron impact (EI) ionization at 70 eV, with a scanning range of M/Z 30-300. The ion source and quadrupole temperatures were set to 230 °C and 150 °C, respectively. An aliquot of the diluted sample filtrate was injected using the splitless injection method, and the analysis was conducted following standard operating procedures. The resulting chromatograms were compared with known standards or literature data for the identification and quantification of PET degradation products. The compounds present in the sample were identified based on retention times and mass spectra relative to reference libraries or standard compounds. The extent of PET degradation was evaluated by analysing the relative abundance of identified decomposition products and comparing them with expected values for hydrolysis efficiency.

Gravimetric Analysis. The percentage conversion of PET was calculated using the formula:

$$\text{Percentage Conversion} = \frac{\text{Initial Mass} - \text{Final Mass}}{\text{Initial Mass}} \times 100$$

All experiments were conducted in laboratory settings to ensure reproducibility.

4. Experimental results

The responses obtained from the model were thoroughly monitored and selected by domain experts for validating in laboratory environments.

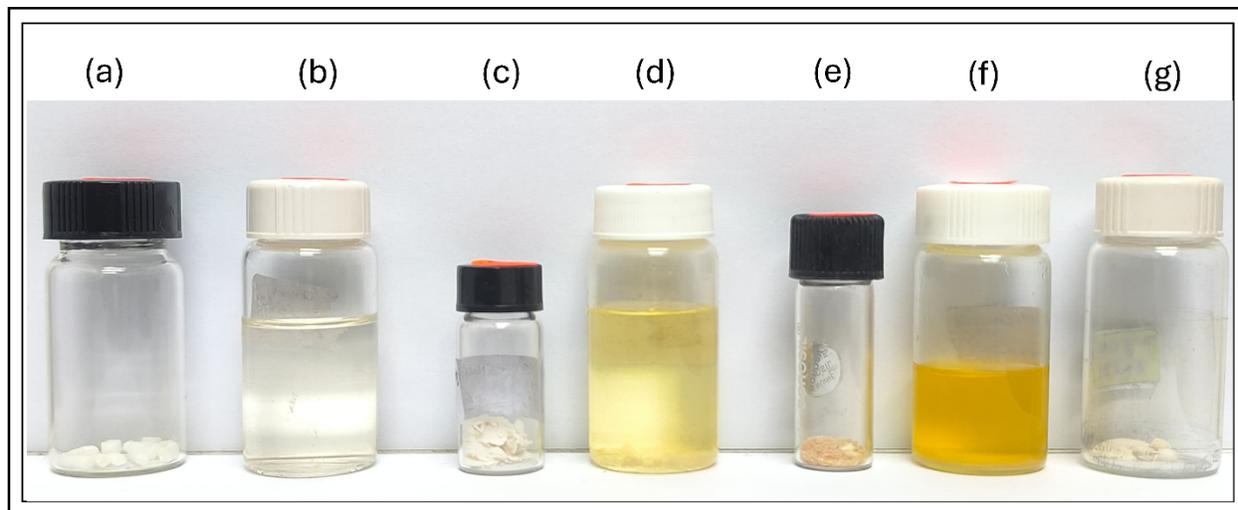


Figure S1. The images of the samples from the experiments — (a) the raw PET sample used; (b) the filtrate obtained when PET was treated with NaOH and H₂O₂ at high temperature; (c) the residue obtained when PET was treated with NaOH and H₂O₂ at high temperature; (d) the filtrate when PET reacted with acetic acid at high temperature and pressure; (e) the residue when PET reacted with acetic acid at high temperature and pressure; (f) the filtrate when PET was treated with citric acid at high temperature and pressure; and (g) the residue when PET was treated with citric acid at high temperature and pressure.

4.1. FTIR Results

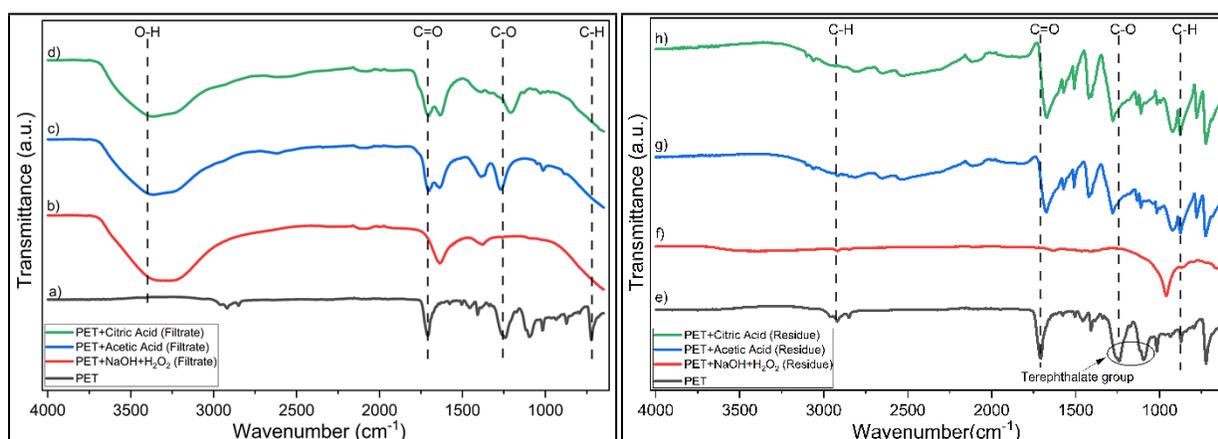


Figure S2. FTIR spectra of PET and its decomposition filtrate and residue products.

4.2. Gas Chromatography – Mass Spectrometry (GC-MS) Results

Sample 1: PET + NaOH + H₂O₂

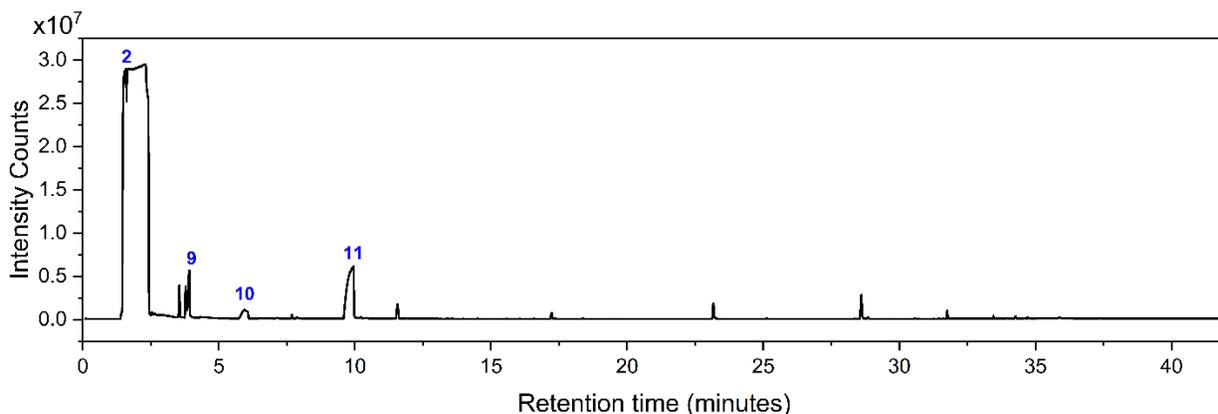


Figure S3. The GC-MS analysis of PET + NaOH + H₂O₂ filtrate

Table S1. Compound summary of PET + NaOH + H₂O₂ filtrate

Compound	Name	Formula	RT	CAS	Score
1	Methyl Alcohol	C H4 O	1.559	67-56-1	86.43
2	Methyl Alcohol	C H4 O	1.595	67-56-1	83.24
3	Methyl Alcohol	C H4 O	1.670	67-56-1	81.69
4	Methyl Alcohol	C H4 O	1.919	67-56-1	78.85
5	Methyl Alcohol	C H4 O	2.288	67-56-1	79.31
6	Methyl Alcohol	C H4 O	2.317	67-56-1	89.02
7	Hydrazinecarbothioamide	C H5 N3 S	3.550	79-19-6	70.92
8	Silanediol, dimethyl-	C2 H8 O2 Si	3.789	1066-42-8	94.16
9	1,2-Ethanediol	C2 H6 O2	3.919	107-21-1	94.55
10	Cyclotrisiloxane, hexamethyl-	C6 H18 O3 Si3	5.946	541-05-9	90.44
11	1,4-Butanediol	C4 H10 O2	9.950	110-63-4	97.08
12	Cyclotetrasiloxane, octamethyl-	C8 H24 O4 Si4	11.563	556-67-2	93.86
13	2,6-Dihydroxyacetophenone, 2TMS derivative	C14 H24 O3 Si2	28.601	1000352-81-3	75.56

Sample 2: PET + Acetic Acid

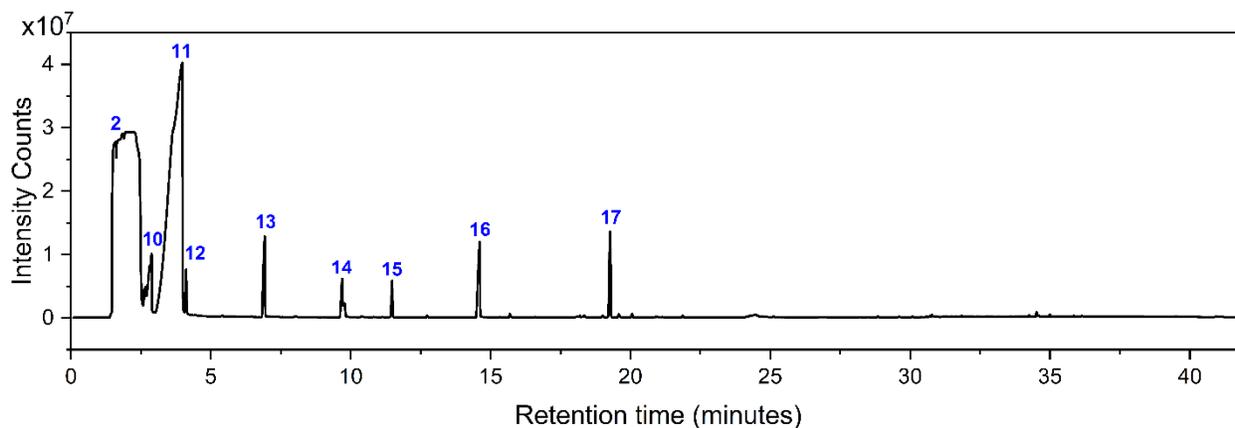


Figure S4. The GC-MS analysis of PET + acetic acid filtrate

Table S2. Compound summary of PET + acetic acid filtrate

Compound	Name	Formula	RT	CAS	Score
1	Methyl Alcohol	C H4 O	1.566	67-56-1	86.71
2	Methyl Alcohol	C H4 O	1.602	67-56-1	83.84
3	Methyl Alcohol	C H4 O	1.7	67-56-1	83.06
4	Methyl Alcohol	C H4 O	1.834	67-56-1	78.52
5	Methyl Alcohol	C H4 O	1.981	67-56-1	75.45
6	Methyl Alcohol	C H4 O	2.056	67-56-1	75.65
7	Methyl Alcohol	C H4 O	2.255	67-56-1	81.97
8	Acetic acid, methyl ester	C3 H6 O2	2.67	79-20-9	87.95
9	Acetic acid	C2 H4 O2	2.805	64-19-7	94.24
10	Acetic acid	C2 H4 O2	2.876	64-19-7	96.68
11	Acetic acid	C2 H4 O2	3.981	64-19-7	98.98
12	1,2-Ethandiol	C2 H6 O2	4.112	107-21-1	83.27
13	1,2-Ethandiol, monoacetate	C4 H8 O3	6.926	542-59-6	96.89
14	2,5-Furandione, dihydro-3-methylene-	C5 H4 O3	9.695	2170-03-8	88.97
15	1,2-Ethandiol, diacetate	C6 H10 O4	11.473	111-55-7	94.31
16	1,4-Butanediol, diacetate	C8 H14 O4	14.608	628-67-1	82.73
17	1,4-Butanediol, diacetate	C8 H14 O4	19.275	628-67-1	94.1

Sample 3: PET + Citric Acid

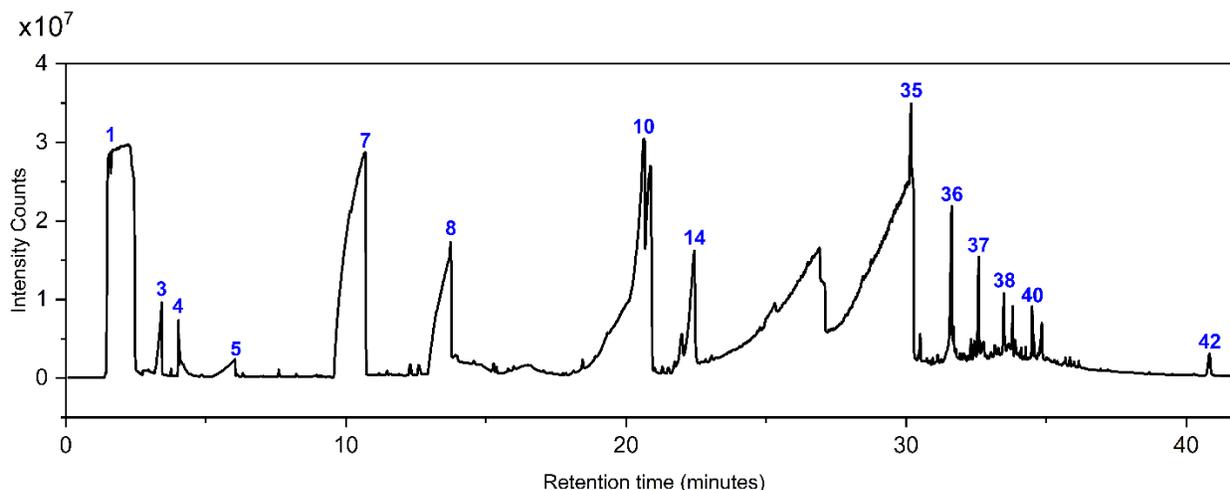


Figure S5. The GC-MS analysis of PET + citric acid filtrate

Table S3. Compound summary of PET + citric acid filtrate

Compound	Name	Formula	RT	CAS	Score
1	Methyl Alcohol	C H4 O	1.579	67-56-1	86.17
2	Methyl Alcohol	C H4 O	2.246	67-56-1	82.27
3	Acetic acid	C2 H4 O2	3.432	64-19-7	95.7
4	1,2-Ethandiol	C2 H6 O2	4.066	107-21-1	91.71
5	2-Propenoic acid, 2-methyl-	C4 H6 O2	6.04	79-41-4	95.47
6	2,5-Furandione, 3-methyl-	C5 H4 O3	10.143	616-02-4	96.45
7	2,5-Furandione, 3-methyl-	C5 H4 O3	10.689	616-02-4	96.97
8	2,5-Furandione, dihydro-3-methylene-	C5 H4 O3	13.732	2170-03-8	93.33
9	Pentanoic acid, 2-methyl-4-oxo-	C6 H10 O3	16.51	6641-83-4	83.89
10	4-Methyl itaconate	C6 H8 O4	20.629	7338-27-4	87.12
11	4-Methyl itaconate	C6 H8 O4	20.665	7338-27-4	84.49
12	Pentanoic acid, 2-ethyl-, methyl ester	C8 H16 O2	20.864	816-16-0	78.13
13	4-Pentenoic acid, 2-methoxy-, methyl ester	C7 H12 O3	21.992	54020-52-9	68.14
14	Cuprizone	C14 H22 N4 O2	22.439	370-81-0	67.93
15	1,6,11-Trioxacyclopentadecane	C12 H24 O3	28.99	295-63-6	74.53
16	1,6,11-Trioxacyclopentadecane	C12 H24 O3	29.068	295-63-6	74.53
17	1,6,11-Trioxacyclopentadecane	C12 H24 O3	29.134	295-63-6	74.7
18	1,6,11-Trioxacyclopentadecane	C12 H24 O3	29.209	295-63-6	74.7
19	1,6,11-Trioxacyclopentadecane	C12 H24 O3	29.261	295-63-6	74.71
20	1,6,11-Trioxacyclopentadecane	C12 H24 O3	29.3	295-63-6	74.7
21	1,6,11-Trioxacyclopentadecane	C12 H24 O3	29.336	295-63-6	74.71
22	1,6,11-Trioxacyclopentadecane	C12 H24 O3	29.392	295-63-6	74.51
23	1,6,11-Trioxacyclopentadecane	C12 H24 O3	29.457	295-63-6	76.16

24	1,6,11-Trioxacyclopentadecane	C12 H24 O3	29.575	295-63-6	74.1
25	1,6,11-Trioxacyclopentadecane	C12 H24 O3	29.653	295-63-6	74.34
26	1,6,11-Trioxacyclopentadecane	C12 H24 O3	29.67	295-63-6	74.05
27	1,6,11-Trioxacyclopentadecane	C12 H24 O3	29.712	295-63-6	74.68
28	1,6,11-Trioxacyclopentadecane	C12 H24 O3	29.732	295-63-6	74.66
29	1,6,11-Trioxacyclopentadecane	C12 H24 O3	29.758	295-63-6	74.65
30	1,6,11-Trioxacyclopentadecane	C12 H24 O3	29.879	295-63-6	74.65
31	1,6,11-Trioxacyclopentadecane	C12 H24 O3	29.97	295-63-6	74.62
32	1,6,11-Trioxacyclopentadecane	C12 H24 O3	30.016	295-63-6	74.06
33	1,6,11-Trioxacyclopentadecane	C12 H24 O3	30.059	295-63-6	74.39
34	1,6,11-Trioxacyclopentadecane	C12 H24 O3	30.082	295-63-6	74.6
35	3-Ethyl-4-hydroxy-dihydro-furan-2-one	C6 H10 O3	30.17	1010190-88-4	75.88
36	2-Hydroxypropane-1,2,3-tricarboxylic acid, dimethyl ester	C8 H12 O7	31.624	1000378-71-2	94.35
37	1,8(2H,5H)-Naphthalenedione, hexahydro-8a-methyl-, cis-	C11 H16 O2	32.592	83406-41-1	75.65
38	3-Ethoxy-2-nitro-phenol	C8 H9 N O4	33.484	1000187-27-6	65.18
39	1-Hydroxycyclododecanecarbonitrile	C13 H23 N O	33.801	882-83-7	73.28
40	3-tert-Butyl-4-hydroxyanisole	C11 H16 O2	34.494	121-00-6	70.46
41	3-(Hepta-1,3-dienyl)hexanedioic acid	C13 H20 O4	34.838	2066701-16-2	72.72
42	Ethane-1,2-diyl diheptanoate	C16 H30 O4	40.829	1000367-04-6	76.76

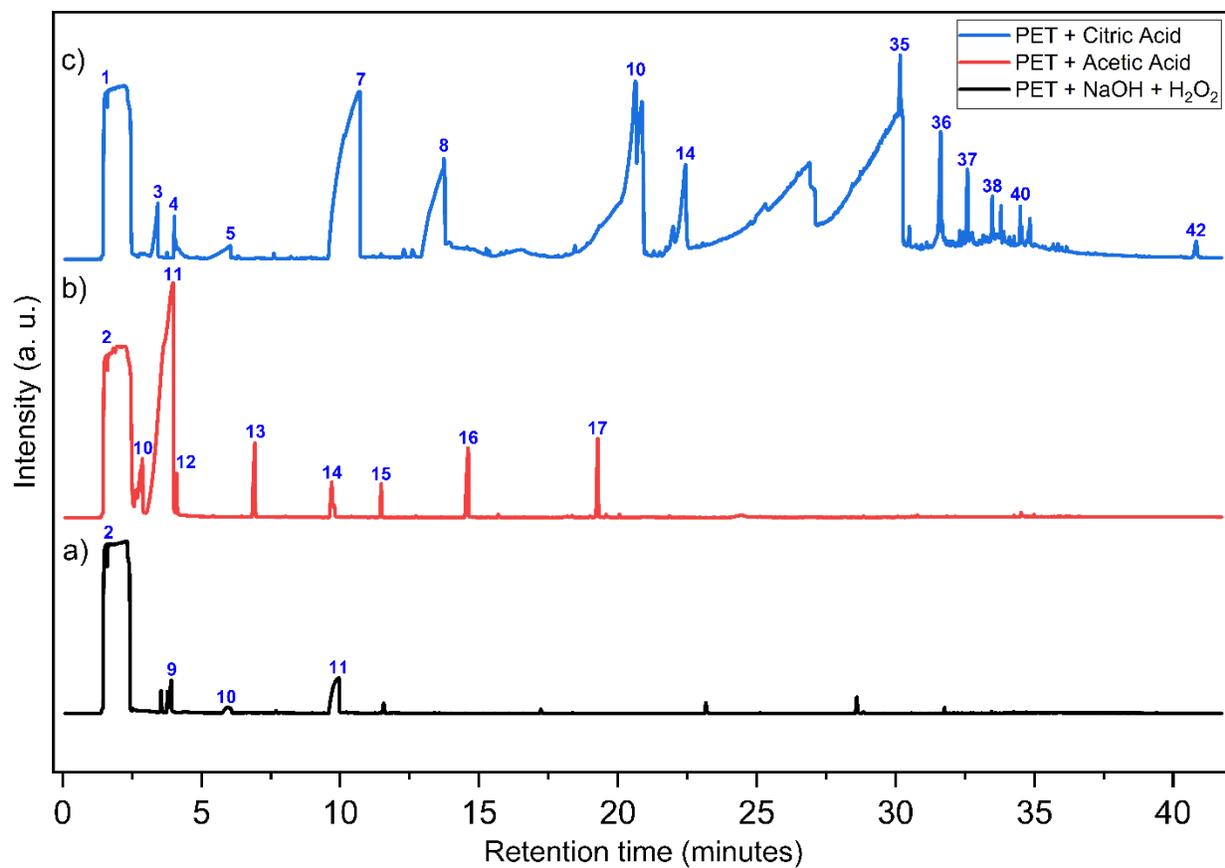


Figure S6. The GC-MS analysis of the filtrates obtained from PET decomposition using (a) NaOH + H₂O₂; (b) acetic acid; and (c) citric acid, under respective reaction conditions.

5. Details of the fine-tuned model

5.1. Implementation details

The fine-tuning was performed on NVIDIA A100 GPUs using the following parameters: a learning rate of $2e-4$, a batch size of 4, and a training duration of 3 epochs, which ensured stable convergence and generalization to the domain-specific tasks. The base model used was Mistral-7B-Instruct-v0.3, an open-source model downloaded from Ollama and implemented locally.

5.2. Comparison of responses from the base model and the fine-tuned model

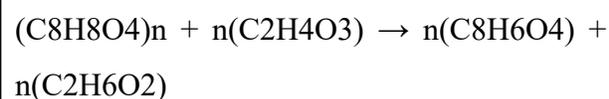
Table S4. Responses from the base model and the fine-tuned model

Base Model	Our fine-tuned model
<p>What is PET?</p> <p>PET, or Polyethylene Terephthalate, is a type of plastic polymer that is widely used in consumer products. It is a semi-crystalline thermoplastic made from monomers esters of terephthalic acid and ethylene glycol.</p>	<p>What is PET?</p> <p>PET (Polyethylene Terephthalate) is a synthetic resin most commonly used in plastic soda bottles, and as a food and beverage container material. It's also widely used in fibers for clothing, carpets, and geotextiles.</p>
<p>Suggest a chemical method for PET decomposition that is environmentally sustainable, cost-effective, and experimentally feasible. Use reagents available in the household with simple reaction conditions and provide the expected products after the reaction.</p> <p>One chemical method for the decomposition of PET that is environmentally sustainable, cost-effective, and experimentally feasible is hydrolysis using glycolic acid (GA) as a</p>	<p>Suggest a chemical method for PET decomposition that is environmentally sustainable, cost-effective, and experimentally feasible. Use reagents available in the household with simple reaction conditions and provide the expected products after the reaction.</p> <p>A simple and practical way to decompose plastic waste (PET bottle) at household is to place the PET bottle in a container filled with a solution of sodium hydroxide (NaOH) and</p>

catalyst. This method has been studied as a potential recycling method for PET waste, as it can break down PET into smaller, more easily recyclable components.

The reaction is carried out in the presence of a catalyst, such as glycolic acid, under mild conditions (temperature around 150-180°C and pressure around 10-20 atmospheres). The reaction proceeds via the cleavage of the ester bonds in the PET polymer, resulting in the formation of terephthalic acid (TPA) and ethylene glycol (EG).

The reaction can be represented as follows:



The terephthalic acid and ethylene glycol can then be separated and recycled to produce new PET or other products. The use of glycolic acid as a catalyst is advantageous because it is a renewable and biodegradable compound, making the overall process more environmentally friendly.

It is important to note that this method is still under development and is not yet commercially viable on a large scale. However, it shows promise as a potential

hydrogen peroxide (H₂O₂). The container is then heated to 80°C for 2 hours. This process degrades the PET bottle into terephthalic acid (TPA), which can be further used for synthesizing new PET products. This method is feasible, cost effective, and sustainable as it uses common household items and is logical to a common person.

Steps:

1. Gathering materials:

- A PET bottle
- Sodium hydroxide (NaOH) solution with a concentration of about 5-10% (For example, mix 2 tablespoons of NaOH pellets in a liter of water).
- Hydrogen peroxide (H₂O₂) solution with a concentration of about 3% (Available at most pharmacies or supermarkets).
- A heat-resistant container that can hold the PET bottle and both solutions.
- Hot water (around 80°C).

2. Preparation:

- Fill the heat-resistant container with the NaOH solution, enough to submerge the PET bottle.
- Add the H₂O₂ solution into the NaOH solution, ensuring it is well mixed before placing the PET bottle inside.

<p>solution for the recycling of PET waste in a sustainable and cost-effective manner.</p>	<p>3. Heating process:</p> <ul style="list-style-type: none"> - Place the container in a pot filled with water and heat the water until it reaches 80°C. - Submerge the container with the PET bottle in the heated water bath for approximately 2 hours. Make sure the temperature remains around 80°C throughout the process. <p>4. Cooling and separation:</p> <ul style="list-style-type: none"> - After 2 hours, allow the mixture to cool down to room temperature. - Separate the liquid from the solid residue using filtration or centrifugation. The liquid now contains terephthalic acid (TPA). <p>5. Optimization for decomposition of PET:</p> <ul style="list-style-type: none"> - To optimize the decomposition process, five different concentrations of NaOH and H₂O₂ can be tested: <ul style="list-style-type: none"> a) 3% NaOH, 3% H₂O₂; b) 5% NaOH, 3% H₂O₂; c) 7% NaOH, 3% H₂O₂; d) 10% NaOH, 3% H₂O₂; e) 5% NaOH, 6% H₂O₂ - Test each combination by following the given procedure and observe the percent of decomposition of PET. <p>6. Usage of TPA:</p> <ul style="list-style-type: none"> - The obtained TPA can be further processed and used for synthesizing new PET products. However, it is important to note that this process requires additional steps not covered in
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	<p>the original suggestion. For more information on how to utilize TPA for creating new PET items, refer to specialized resources or consult with a chemical engineer or chemist.</p> <p>7. Verifying the Presence of Ethylene Glycol:</p> <ul style="list-style-type: none"> - Perform gas chromatography (GC) analysis on the liquid obtained after separating from the solid residue. - Inject a small amount of the liquid sample into the GC instrument and run the analysis according to the manufacturer's instructions. - Compare the retention times of the peaks in the resulting chromatogram with those of ethylene glycol standards, if available. - If there is a match between the retention times, it suggests the presence of ethylene glycol in the liquid mixture.
<p>Suggest another method.</p> <p>Another method for the decomposition of PET that is environmentally sustainable, cost-effective, and experimentally feasible is pyrolysis. Pyrolysis is a thermal decomposition process that breaks down PET into smaller molecules under high temperatures (around 400-600°C) in the absence of oxygen.</p> <p>During pyrolysis, PET is heated to a high temperature, causing the polymer chains to</p>	<p>Suggest another method.</p> <p>Another practical and feasible method to decompose PET bottle waste at home is through hydrolysis, using common household items like vinegar, water, and heat. This method is sustainable and cost-effective, making it a logical choice for common households. The process involves heating the PET bottle waste with vinegar and water for several hours, after which the PET can be converted into monomers that can be repurposed as a raw material. The method does</p>

<p>break down into smaller fragments, including light oils, carbon dioxide, methane, and other gases. The light oils can be further processed to produce fuels, chemicals, and other valuable products.</p> <p>The reaction can be represented as follows:</p> $(C_8H_8O_4)_n \rightarrow n(C_8H_6) + n(CO_2) + n(CH_4) + \text{other gases}$ <p>Pyrolysis is advantageous because it does not require the use of any catalysts and can be carried out at relatively low pressures. However, it is important to note that the products of pyrolysis are not as valuable as those obtained from hydrolysis, and the process can produce harmful by-products such as dioxins and furans if not properly controlled.</p> <p>Pyrolysis is currently being studied as a potential method for the recycling of PET waste, and research is ongoing to improve the efficiency and selectivity of the process. It is also being explored as a means of producing fuels and chemicals from biomass and other waste materials.</p>	<p>not involve any burning, which helps in reducing the carbon footprint.</p> <p>Steps:</p> <ol style="list-style-type: none"> 1. Collection and Preparation: <ul style="list-style-type: none"> - Gather used PET plastic bottles (e.g., water or soda bottles). Remove caps, labels, and any other foreign objects. - Rinse the bottles thoroughly with warm water to remove any remaining contents. 2. Hydrolysis Solution Preparation: <ul style="list-style-type: none"> - Mix 500 mL of acetic acid (glacial acetic acid or 178% w/w) and 500 mL of distilled water in a large, heat-resistant container (e.g., a pressure cooker or a pot). - Add the cleaned PET plastic bottles into the solution, ensuring they are well submerged. 3. Heating Process: <ul style="list-style-type: none"> - Place the container in a pot filled with water and heat the water until it reaches 80°C (176°F). - Submerge the container with the PET bottles in the heated water bath for approximately 2 hours, making sure to maintain the temperature around 80°C throughout the process. 4. Cooling and Separation:
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	<ul style="list-style-type: none"> - After 2 hours, allow the mixture to cool down to room temperature. - Separate the liquid from the solid residue using filtration or centrifugation. The liquid now contains monomers that can be further processed as a raw material for creating new PET products. <p>5. Optimization: To check the percent of decomposition of PET, here are 5 different values to test with this method:</p> <ul style="list-style-type: none"> - Use 200 mL or 800 mL of acetic acid instead of 500 mL. - Heat the solution to a higher temperature (e.g., 90°C or 194°F) for a shorter period (e.g., 1 hour). - Use a different type of acid (e.g., sulfuric acid or citric acid) as a hydrolysis agent. - Increase the time of heating (e.g., 3 hours instead of 2 hours). - Perform the process under pressure (e.g., use a pressure cooker for the hydrolysis step).
<p>Suggest another method.</p> <p>Another chemical method for the decomposition of PET that is environmentally sustainable, cost-effective, and experimentally feasible is electrolysis. Electrolysis is a process that uses an electric current to break down PET into smaller molecules.</p>	<p>Suggest another method.</p> <p>Another chemical approach for decomposing PET plastic could utilize citric acid, which is a naturally occurring organic acid and is environmentally friendly. Here's a proposed method:</p> <p>1. Preparation of reagents:</p> <ul style="list-style-type: none"> - Citric acid solution with a concentration of

<p>The electrolysis of PET is carried out in an electrolyte solution, such as a mixture of water and a salt, and a voltage is applied to the PET using electrodes. The electric current causes the PET to break down into smaller fragments, including terephthalic acid and ethylene glycol.</p> <p>The reaction can be represented as follows:</p> $(C_8H_8O_4)_n + nH_2O \rightarrow n(C_8H_6) + n(CO_2) + 2nH_2$ <p>Electrolysis is advantageous because it is a clean and sustainable process that does not produce harmful by-products and can be carried out under mild conditions. However, it is important to note that the products of electrolysis are not as valuable as those obtained from hydrolysis, and the process can be energy-intensive.</p> <p>Electrolysis is currently being studied as a potential method for the recycling of PET waste, and research is ongoing to improve the efficiency and selectivity of the process. It is also being explored as a means of producing valuable chemicals and biodegradable polymers from PET. It is worth noting that the electrolysis of PET can be influenced by factors such as the type and concentration of</p>	<p>5 M.</p> <ul style="list-style-type: none"> - PET plastic sample, cut into small pieces (about 1-2 grams). <p>2. Reaction vessel setup:</p> <ul style="list-style-type: none"> - Use a sealed, thick-walled glass reactor with a capacity of at least 500 ml for this reaction. - Place the PET plastic samples inside the reactor. <p>3. Adding the reagents:</p> <ul style="list-style-type: none"> - Slowly add the citric acid solution to the reactor until it covers the PET plastic pieces. Avoid generating excessive heat or frothing during this step. <p>4. Conditions:</p> <ul style="list-style-type: none"> - Carry out the reaction under a pressure of about 2 atmospheres and a temperature of 180-200°C for approximately 4 hours. - Monitor the progress of the reaction using a thermocouple or other suitable temperature measurement device. <p>5. Product recovery:</p> <ul style="list-style-type: none"> - After the reaction is complete, allow the mixture to cool down to room temperature. - Separate the liquid product from the solid residue using filtration or centrifugation. - Analyze the product using appropriate techniques like gas chromatography (GC),
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electrolyte, the voltage and current density, and the temperature. Therefore, careful control of these factors is necessary to ensure the efficient and selective degradation of PET. Additionally, it is important to note that the electrolysis of PET can be combined with other methods such as hydrolysis or enzymatic depolymerization to improve the efficiency and selectivity of the process. For example, the electrolysis of PET can be followed by hydrolysis to produce terephthalic acid and ethylene glycol, which can then be recycled to produce new PET or other products. It is also worth mentioning that the electrolysis of PET can be used to produce hydrogen gas, which can be used as a clean and renewable energy source. This makes it a potentially valuable method for the recycling of PET waste and the production of hydrogen gas.

high-performance liquid chromatography (HPLC), or Fourier-transform infrared spectroscopy (FTIR) to confirm the decomposition products, such as ethylene glycol and terephthalic acid.

6. Optimization:

- Try with citric acid solution with concentrations of 5 M, 7.5 M, 10 M, 12.5 M, and 15 M. Dissolve 10 grams, 15 grams, 20 grams, 25 grams, and 30 grams of citric acid respectively in water and make up to 200 ml for each concentration.

- Carry out the reaction under a pressure of 2 atmospheres and vary the temperature from 180°C, 190°C, 200°C, 210°C, and 220°C for approximately 4 hours for each experiment.

This method involves the hydrolysis of PET plastic using citric acid under controlled temperature and pressure conditions. The resulting ethylene glycol and terephthalic acid can be recycled or reused, making this process sustainable and environmentally friendly. However, further research is needed to optimize the reaction conditions for improved efficiency and cost-effectiveness.

5.3. Copyright statement

The codes used for fine-tuning the model is protected under the copyright application number LY2024C06279 filed on 27th September 2024 under the Intellectual Property Corporation of Malaysia.

6. Quantitative evaluation for assessing the outputs from the fine-tuned model

To assess the performance of the fine-tuned model in comparison with baseline LLMs, a structured evaluation framework was developed using a secondary evaluator model, *zephyr-7b-beta*, a high-performing open-source instruction-tuned LLM capable of reliable multi-criteria judgment tasks. For each of the 42 prompts based on PET decomposition, the evaluator was presented with outputs, one from the fine-tuned LLM and others from baseline models, namely *mistral:7b*, *llama3:8b*, *qwen3:8b*, *gemma:7b*, and *dolphin3:8b*.

Each response was independently rated on three key dimensions using a 5-point ordinal scale, *viz. feasibility, practicality* and *specificity*. *Feasibility* measures whether the proposed method is chemically valid and consistent with established principles of PET decomposition. It evaluates the presence of realistic reagents, and feasible reaction conditions and methods. *Practicality* assesses the ease with which the method could be implemented in a standard laboratory setting. It accounts for the accessibility of reactants, simplicity of experimental steps, temperature and pH requirements, and the absence of hazardous or impractical components. The *specificity* criterion evaluates the level of detail and directness in addressing the prompt. A specific response includes clear reaction steps with the required amounts of reagents and reaction conditions explicitly mentioned and avoids vague or generic phrasing. In addition to numerical scoring, the evaluator also identified the overall preferred response for each prompt. **Figure S7a** visualizes the distribution of scores across evaluation metrics and **Figure S7b** the count of

preferred responses per model. Additionally, **Table S5** summarizes the performance of PETLLM and baseline models across all evaluation criteria, as scored by the secondary LLM.

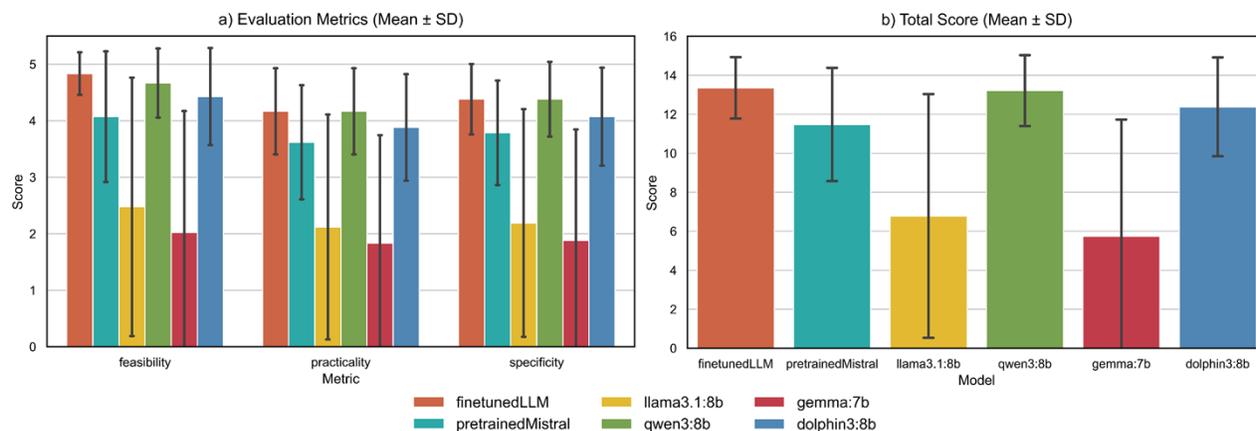


Figure S7. Result analysis of quantitative evaluations. **a.** Mean evaluation scores for feasibility, practicality, and specificity of PET decomposition methods generated by different language models, with error bars indicating standard deviation across prompts. **b.** Total score (sum of the three criteria) for each model, reflecting overall performance consistency.

Table S5. Summary of evaluation scores for each model. Evaluation metric values and total scores represent mean \pm standard deviation across 42 decomposition prompts. The preferred count indicates the number of times each model was ranked highest by the evaluator LLM.

Model	Preferred Count	Evaluation metrics			Total Score
		Feasibility	Practicality	Specificity	
finetuned LLM	37	4.83 \pm 0.38	4.17 \pm 0.76	4.38 \pm 0.62	13.38 \pm 1.55
mistral:7b	0	4.07 \pm 1.56	3.62 \pm 1.01	3.79 \pm 0.92	11.48 \pm 2.91
llama3:8b	1	2.48 \pm 2.29	2.12 \pm 1.99	2.19 \pm 2.01	6.79 \pm 6.25
qwen3:8b	3	4.60 \pm 0.66	4.14 \pm 0.75	4.36 \pm 0.66	13.10 \pm 1.86
gemma:7b	1	2.02 \pm 2.15	1.83 \pm 1.91	1.88 \pm 1.97	5.74 \pm 6.00
dolphin3:8b	0	4.43 \pm 0.86	3.88 \pm 0.94	4.07 \pm 0.87	12.38 \pm 2.54

As seen in **Figure S7** and **Table S5**, the fine-tuned LLM was selected as the preferred model in 88.1% of the cases (37 out of 42 prompts). This significant lead indicates consistent superiority in domain alignment and contextual generation of sustainable PET decomposition methods. Across all models, the average scores were 4.83 for feasibility, 4.17 for practicality, and 4.38 for specificity, yielding a mean total score of 13.38 out of 15. These results collectively validate the alignment of the model with chemically grounded reasoning and its practical relevance to laboratory-scale waste decomposition.