An overview of Mechanical and Chemical Recycling Methods for Polyethylene Terephthalate Plastics

By

Yaqub Adediji and Ayub Adediji

1. Introduction

Waste management has become one of the world's most pressing issues. Plastic is one of the most widely utilized materials in the modern world. Plastic manufacturing and usage have risen globally in recent decades due to its low weight and outstanding mechanical properties. Global plastic waste volume was 6.3 billion metric tonnes in 2015, with an anticipated value of roughly 12 billion metric tonnes in 2050[1].

Polyethylene terephthalate (PET), which is a polyester plastic, is one of the most widely used packaging materials for beverages. Due to its excellent transparency, lightweight, gas and water barrier properties, impact strength, UV resistance, and unbreakability (compared to a glass bottle), the production and use of PET bottles for beverage packaging has consistently increased worldwide.

According to the United States Environmental Protection Agency (EPA) in 2018, 35.7 million tons of plastic waste was generated in the United States, which was 12.2% of total municipal solid waste (MSW). In addition to PET bottle wastes, this plastic waste included polyolefin and polyester bags, wraps, bottles, and jars. Approximately 27 million tons of plastic (18.5% of US plastic waste) was discarded into landfills. Only 4.5% of plastic packaging was recycled [2].

Due to this high rate of consumption as well as accumulation of PET waste in the landfill, developing processes for the recycling of PET packaging waste have become increasingly important. Various polymer recycling technologies have been developed to handle PET wastes and these include mechanical recycling, chemical recycling, energy recovery or quaternary recycling.

This paper explores some of mechanical and chemical recycling methods available for recycling PET wastes into useful products from some published journal articles. It also evaluates the feasibility and techno-economic analysis of the methods as an efficient way of recycling PET wastes.

2. Mechanical Recycling of PET Wastes

Mechanical recycling is the most commonly used method for plastic recycling, and it consists of multiple phases such as collecting, screening, automatic or manual sorting, washing, shredding, extrusion, and granulation as shown in **Figure 1**. Melt extrusion is used to extract the PET polymer from the waste and reprocess it into granules. It entails trash sorting and separation, size reduction, melt filtering, and plastic material reforming [3]. The used Pet polymer products are transformed to various end products using this method.

Steps of mechanical recycling of plastics [4].

2.1 Re-Extrusion of PET Fibers

Altun et al. [5] explored the use of a re-extrusion process using a manufactured extruder to recycle post-industrial PET fiber wastes from textile. Firstly, the PET fiber wastes were first cut using a rotary-type cutting machine. This step is vital to prevent blockages in the extruder and complications with the screw winding. After cutting, the PET wastes were dried at 120°C for 60 minutes. This is crucial for removing moisture, which is important for the quality of the recycled product and the efficiency of the next stage. The core of the recycling process is the re-extrusion and granulation of dried PET wastes. Dried PET wastes were processed in a specially designed extruder (as shown in Figure 2). During this stage, the PET wastes were melted and formed into granules, which serve as the foundation for creating recycled PET products.

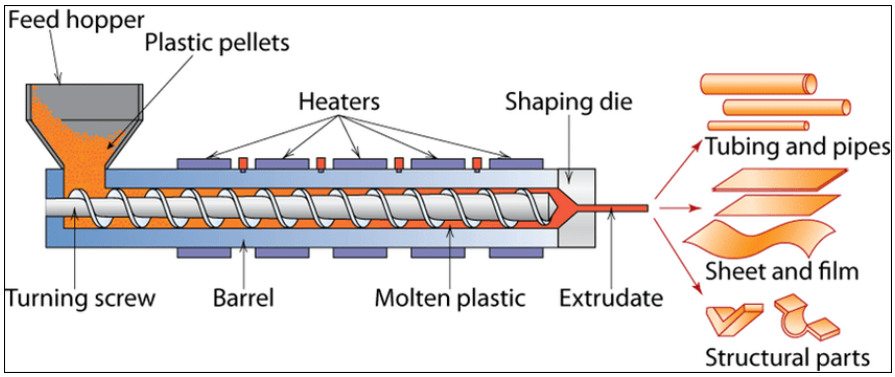


Fig. 2 Schematic of an extruder

To ensure the quality of the recycled material, the process includes rigorous quality control and analysis. Several experiments such as Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), and viscosity measurements were employed to assess the degradation levels and overall quality of the recycled PET fibers. These analyses are vital for monitoring the condition of the recycled material and ensuring it meets the required standards. The comparison results between the virgin and remelted PET wastes are shown in Table 1.

Table I. A Comparison Between Virgin and Re-melted PET Fiber Wastes

COOH end group (mmol/kg)		DEG amount (% weight)		Viscosity (dl/g)		Color *b* value		Melting point (°C)	
Virgin	Recycled	Virgin	Recycled	Virgin	Recycled	Virgin	Recycled	Virgin	Recycled
25.4	58	0.98	1.04	0.643	0.473	3.87	6.06	258.8	258.2
29	58	0.92	1.05	0.647	0.469	3.92	6.43	258.7	258.4
29.8	53	0.95	1.02	0.648	0.485	4.14	6.35	258.6	257.6
30.5	62	0.94	1.00	0.650	0.472	3.91	6.25	258.9	259.0
29.4	62	0.92	1.03	0.644	0.473	3.83	6.08	258.7	258.3
26.4	61	0.90	0.98	0.651	0.474	–	6.30	258.6	258.8
28.5	61	0.93	1.01	0.653	0.466	–	6.40	258.6	258.2
26.5	59	0.94	1.04	0.646	0.478	–	6.46	258.8	258.1
27.7	61	0.90	1.01	0.651	0.489	–	6.44	258.7	258.9
25.6	59	0.91	1.06	0.644	0.460	–	6.22	258.8	258.9
27.88	59.4	0.93	1.024	0.647	0.473	3.93	6.29	258.7	258.44
±1.82	±2.71	±0.024	±0.024	±0.003	±0.008	±0.120	±0.145	±0.103	±0.450

Fig. 3. A comparison between Virgin and Remelted PET Fiber Wastes

From Fig. 3, an increase in the ACOOH end groups between the virgin and remelted PET wastes mainly shows degradation due to thermal oxidation while a decrease in viscosity indicates that there are some polymer degradations in the extrusion step. The color value b of recycled PET is 60% higher than that of virgin wastes (3.93) which indicates a thermal degradation. Also, there was no significant difference between the melting point of the two samples. An increase in the amount of Diethylene Glycol (DEG) was also observed for the recycled wastes which is an indication of hydrolytic degradation of the polymer.

2.1.1 **Technical Feasibility (Process Efficiency, Technology Maturity, Scalability, and Environmental Impact)**

This recycling process includes steps like cutting, drying, re-extrusion, and granulation. These are standard procedures in recycling operations, indicating that the method is grounded in established recycling techniques with moderate environmental impact. The development of specialized equipment tailored to the specific needs of PET fiber waste recycling further supports

the technical feasibility of the method. However, the re-extrusion process causes the PET fibers to undergo considerable thermal, thermos-oxidative degradations, hydrolysis, and mechanical degradation which leads to significant changes in physical and properties, reduction in quality, visual and mechanical impact, and production challenges of the recycled PET wastes. Thus, this recycling method is not very efficient. Therefore, this recycling method is technically feasible with some considerations and challenges.

These degradation issues are significant enough to warrant careful control and optimization of the recycling process. Strategies like optimizing extruder parameters and parts (conical hopper, venting ports, filters), using stabilizers and additives, and controlling the drying and feeding processes such as transporting directly to the extruder from the drier without having contact with air are recommended to mitigate these degradation effects. This research was also conducted on a small scale, and it's not clear how scalable the process is for large-scale industrial applications. Nonetheless, this method’s scalability is feasible considering its mature technology and it’s suitability for small to medium-scale and industrial operations.

2.1.2 Economic Viability

As stated by Altun et al. [5], raw material costs account for a significant portion (75%) of the total costs in the production of PET fiber and thus the recycled PET fiber wastes can substantially reduce these raw material costs. This suggests that the recycling method can be economically advantageous by lowering the input costs for PET fiber production. However, the researchers failed to give detailed information about the specifications of the extruder as well as capital and operating costs. The recycling process involved several steps that add complexity and cost to the process, and It's not discussed whether simpler or more cost-effective methods could achieve similar

results. This research was also conducted on a small scale, and it's not clear how scalable the process is for large-scale industrial applications.

Therefore, some hypothetical calculations can be made to evaluate the economic viability with the assumptions as shown in Table 1.

Table 1: Assumptions and Calculations

Parameters	Assumptions	Calculations
Fixed Costs	Estimated initial investment of $2 million for setting up a medium-scale recycling facility (single screw extruder, drying, grinding machine and etc.).	Assume an annual processing capacity: **10,000 tons** of recycled PET/year.
Operating Costs	Assume $200 per ton of PET processed, covering labor, energy, maintenance, and other operational expenses	**Annual Operating Cost**: $200/ton * 10,000 tons = **$2,000,000/year**.
Revenue streams	The market price for recycled PET is estimated at $500 per ton.	Annual Revenue: $500/ton * 10,000 tons = **$5,000,000/year**
Break-Even Analysis	The break-even point would be reached when the revenue covers both the initial investment and ongoing operational costs.	**Annual Net Profit:** Revenue - Operating Cost = $5,000,000 - $2,000,000 = **$3,000,000**/year. **Break-Even Point:** $2 million / $3 million/year = approximately 0.67 years or approximately 8 months.
Return on Investment (ROI)	Calculated based on the net profit and initial investment.	**ROI:** (Annual Net Profit / Initial Investment) * 100 = (3,000,000 / 2,000,000) * 100 = **150%.**

Overall, based on these assumptions, the re-extrusion method appears to be economically viable. However, the significant degradation issues in this method needs to be tackled and the recycling process needs optimization.

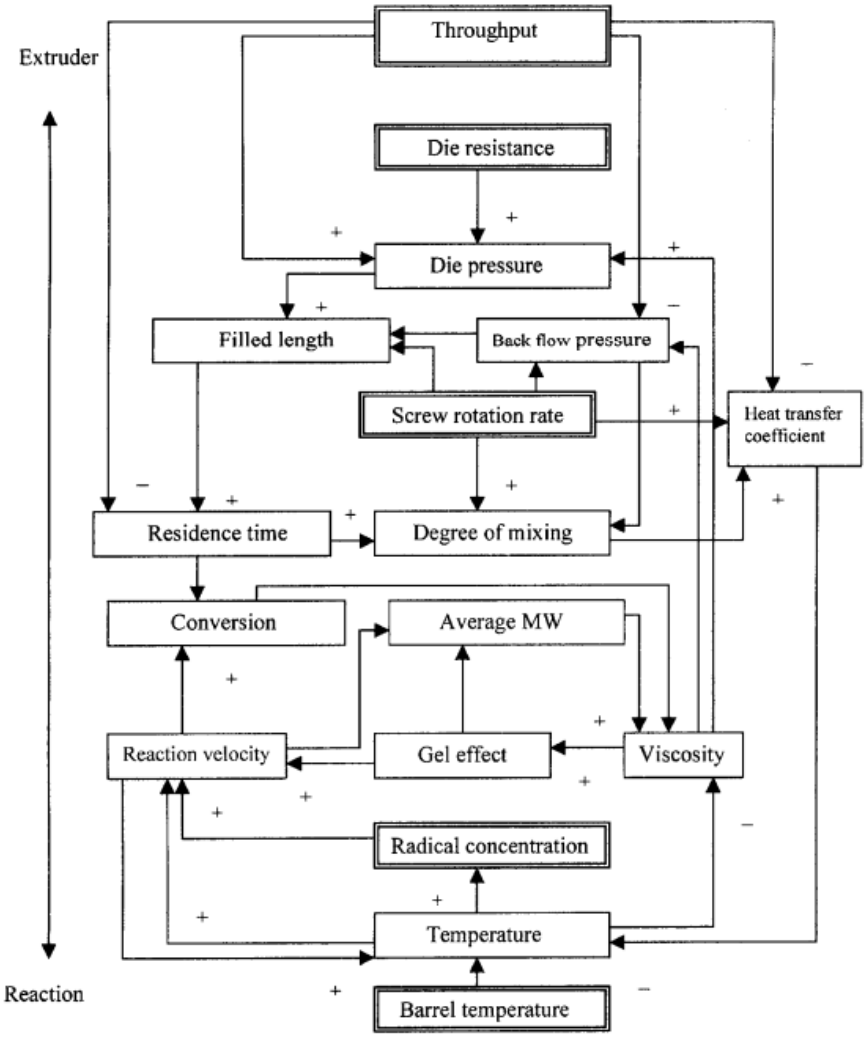
2.2 Recycling by Extrusion and Chain Extension of Post Consumer PET Bottles

Dimonie et al.[6] explored the use of extrusion process and chain extension to recycle post-consumer PET (POSTC-PET) bottles with polymer upgradation. The method involves the structural up-grading of POSTC-PET by macromolecular chain extension during mechanical recycling (reactive processing), a procedure considered efficient for the enhancement of its properties. This is to combat the strong degradation that occurs to the polymer during melt processing. Firstly, the first step involves collecting post-consumer PET bottles. These bottles are then sorted to separate PET materials from other types of plastics and contaminants. The sorted PET bottles are cleaned to remove labels, adhesives, and other residues. The bottles are ground into flakes, washed and dried properly to restrain hydrolysis during melt processing typically 3-7 hours at 140-180°C.The PET flakes are then fed into an extruder and stabilizers and chain extenders (reactive processing) are added during the extrusion process.

The reactive processing (RP) of POSTC-PET, takes place in extrusion process between the polymer melt and chain extenders. The chain extenders are mono, di, or polyfunctional organic compounds with low molecular weight and controlled polydispersity with functional groups typically like hydroxyl, carboxyl, anhydride, amine, epoxy, etc. Chain extenders are chemicals that react with the PET to rebuild the molecular chains, enhancing the material's strength and viscosity such as pyromellitic dianhydride (PMDA), tri-phenyl phosphit (TPP). Each extender, depending by its own chemical structure, yields typical extension reactions. This step is crucial for ensuring that the recycled PET retains or regains properties close to the original material. The melted PET wastes in the extruder were then formed into granules, which serve as the input for creating recycled PET products.

Dimonie et al.[6] stated that the effectiveness of chain extension reactions in the reactive processing of post-consumer PET (POSC-PET) depends on several factors including extender concentration, reaction temperature and time and parameters proper to the equipment in which the reactions take place as presented in Figure 3. Additionally, it was observed that for an extruder system to be considered stable, it must maintain consistent nozzle pressure, cylinder temperature, and flow rate.

The extruders utilized in the reactive processing should be outfitted with high-efficiency vacuum degassing areas to effectively remove volatile compounds and the vacuum system's pressure also requires precise control with minimal fluctuation.



Fig, 3. The factors influencing the stability of an extruder system used for chain extension

(+ positive influence; - negative influence).

Through this mechanical recycling by extrusion and chain extension (reactive processing) approach, an intrinsic viscosity exceeding 0.6 dlg^{-1} in recycled PET was said to be feasible to achieve . This level of viscosity was considered a fundamental quality benchmark for repurposing POSTC-PET in high-performance applications. Often, reactive processing enables the recycled material to attain melt and solid-state properties that are comparable to, or even surpass, those of virgin polymers. Therefore, the reactive processing of POSTC-PET was viewed as a significant

opportunity to enhance the value of post-consumer condensation polymers. This process not only adds technical value but also increases the economic worth of the resulting products.

2.2.1 **Technical Feasibility**

This chain extension recycling process includes steps like sorting, cleaning, cutting, drying, grinding and extrusion with chain extenders. These are also standard procedures in recycling operations, indicating that the method is grounded in established recycling techniques with moderate environmental impact. Reactive processing enables the recycled material to attain melt and solid-state properties that are comparable to, or even surpass, those of virgin polymers.

However, the extruders used in reactive processing must be equipped with high vacuum capabilities, twin screw extruders and this complexity adds challenges to the extrusion process. This requirement for specific equipment can be a limiting factor for its industrial applicability. Counter-pressure and pressure fluctuation are common instabilities described by researchers. Fluctuations can also occur in the high vacuum degassing system and the pressure in the vacuum system requires severe control and minimal variation. Finding the right balance of extender chemical structures and operating conditions is also a complex task. The chain extension reactions are controlled by the extender concentration, reaction temperature, and time, and parameters proper to the equipment in which the reactions take place and maintaining control over these parameters can be challenging.

This recycling method requires precise control over various parameters and is sensitive to fluctuations in reaction conditions, making it a complex and technically demanding approach. **Therefore, this approach is not yet technically feasible based on provided information.**

Nonetheless, with further research and innovative approaches, this method can be perfected for scalability for small to medium-scale and industrial operations.

2.2.2 **Economic Viability**

Dimonie et al.[6] failed to give detailed information about the specifications of the extruder as well as capital, operating costs, amount of chain extender needed per ton of PET waste extruded as well as costs of the chain extenders such as pyromellitic dianhydride (PMDA), tri-phenyl phosphit (TPP). The recycling process involved several steps that add complexity and cost to the process, and It's not discussed whether simpler or more cost-effective methods could achieve similar results. Nonetheless, some hypothetical calculations can be made to evaluate the economic viability with the assumptions as shown in Table 1.

Table 2: Assumptions and Calculations

Parameters	**Assumptions**	**Calculations**
Fixed Costs	Estimated initial investment of **$3 million** for setting up a medium-scale recycling facility (twin screw extruder, drying, grinding machine etc.).	Assume an annual processing capacity: **10,000 tons** of recycled PET/year.
Chain extenders	High purity PMDA chain extender from China fine chemicals [7] cost about $7 per kg ($7,000 per ton).	Assume for each ton of PET recycled, 0.05ton of PDMA is used. Cost = 0.05 *10,000 * 7000 = **$3,500,000**
Operating Costs	Assume $250 per ton of PET processed, covering labor, energy, maintenance, and other operational expenses	**Annual Operating Cost**: $250/ton * 10,000 tons = **$2,500,000/year**.
Revenue streams	The market price for higher grade recycled PET form Statista is estimated at $1,100 per ton[8].	Annual Revenue: $1100/ton * 10,000 tons = **$11,000,000/year**

Break-Even Analysis	The break-even point would be reached when the revenue covers both the initial investment and ongoing operational costs.	**Annual Net Profit:** Revenue - Operating Cost = $11,000,000 - $2,500,000 - $3,500,000= **$5,000,000**/year. **Break-Even Point:** $3 million / $5 million/year = approximately 0.6 years or approximately 8 months.
Return on Investment (ROI)	Calculated based on the net profit and initial investment.	**ROI:** (Annual Net Profit / Initial Investment) * 100 = (5,000,000 / 3,000,000) * 100 = **167%.**

Overall, based on these assumptions, the mechanical recycling by extrusion and chain extension (reactive processing) of post-consumer PET bottles method appears to be economically viable. However, the method requires precise control over various parameters and is sensitive to fluctuations in reaction conditions, making it a complex and technically demanding approach. not making it technically feasible based on the information provided.

3. Chemical Recycling of PET Wastes

Chemical recycling (also known as advanced recycling) is a process by which the PET polymer is either depolymerized into its original components and repolymerized to a new oligomer or solvated (solvolysis) to dissolve the polymer for subsequent purification [9].

PET can be chemically recycled in five different ways: methanolysis, glycolysis, hydrolysis, ammonolysis, and aminolysis to obtain various monomers such as terephthalic acid and ethylene glycol as shown in **Figure 4**. Only methanolysis and glycolysis, however, are primarily applied on a commercial scale [10].

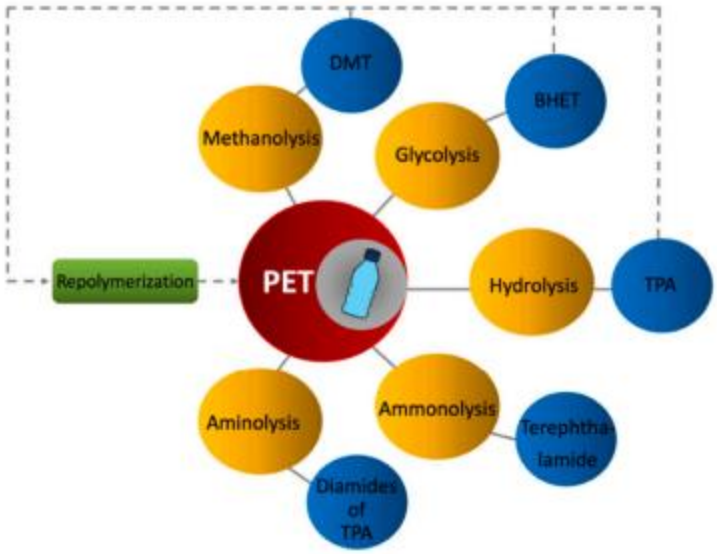


Fig. 4. Different chemical recycling routes of waste PET [11]

3.1 Alkaline Hydrolysis of PET Wastes

Hydrolysis is a chemical reaction in which a water molecule is used to break a bond. In the case of PET, hydrolysis can be used to break the ester bonds, which are the bonds connecting the monomer units. Vakili et al. [10] presented a two stage alkaline hydrolysis recycling process for post-consumer PET bottles.

In the first stage, reaction occurs between PET waste and sodium hydroxide, the ester linkages are cleaved, leading to the production of ethylene glycol and sodium terephthalate solution according to the reaction shown in equation 1 according to the reaction shown in equation 1.

$$PET + 2nNAOH = nNa_2C_8H_4O_4 + nC_2H_6O_2 \quad (1)$$

At the second stage, reaction occurs between produced sodium terephthalate from stage 1 and hydrochloric acid leading to the production of terephthalic acid according to the reaction shown in

equation 2. These steps were carried out in a 10 liter stainless steel mix reactor plant as shown in Figure 5.

$$Na_2C_8H_4O_4 + HCL = C_8H_6O_4 + 2NaCl \quad (2)$$

Fig. 5. 10 Liters Pilot plant for chemical recycling of PET

Firstly, the PET bottles were cut into 1mm × 1mm to 6mm × 6mm flakes. In the first stage, The PET and water were charged into reactor and the sodium hydroxide was then added. The reactor's temperature was then set at 110°C, maintained using circulating hot oil and the pH of the reactor solution was measured at 5-minute intervals. The reaction was deemed complete when the pH stabilized in the basic range. The produced ethylene glycol went to the condenser and collected in a steel vessel and sodium terephthalate was discharged from the reactor and was washed and dried. In the second stage, the sodium terephthalate, hydrochloric acid, and water were charged into the reactor and the temperature was set to 40°C. The pH of the solution was then measured at

5-minute intervals. Terephthalic acid, which is insoluble in water, settled at the bottom and was then extracted, washed, and dried.

Some important variables such as operational temperatures pressures and quantity of consumed sodium hydroxide and hydrochloric acid were studied and presented in figure 6. For the first stage, the optimal temperature for the reaction was determined to be 180°C achieving a conversion rate of 92%. 500 grams of sodium hydroxide was required per 1kg of PET and the products obtained from 1kg of PET were 200ml of ethylene glycol and 453 grams of sodium terephthalate salt. The reaction time for achieving this 1st stage conversion rate was approximately 180 minutes. For the second stage, the optimal temperature was found to be 90°C, achieving an 88% conversion rate. 166 grams of hydrochloric acid was used per 453 grams of sodium terephthalate, resulting in the production of 433 grams of terephthalic acid. The reaction time for the 2nd stage conversion rate was about 90 minutes.

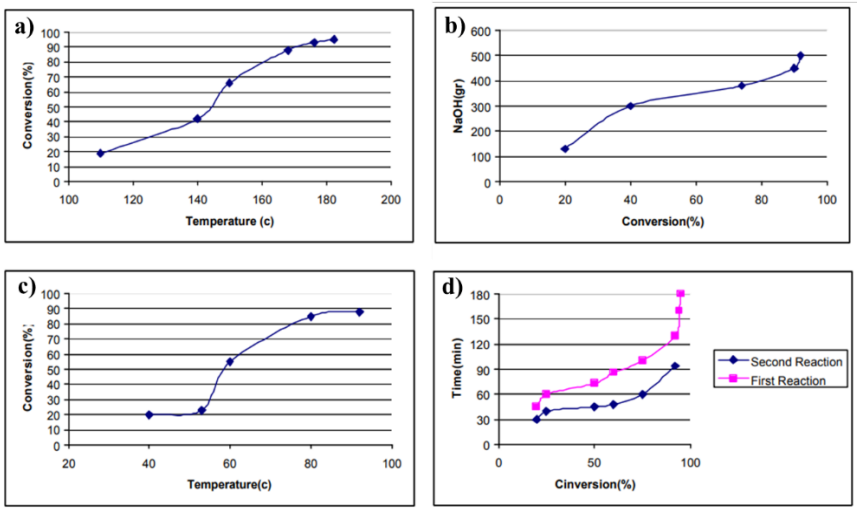


Fig. 6. a) Conversion variation of first reaction with temperature b) NaOH quantity variation with conversion in the first reaction c) Conversion variation of second reaction with temperature d)Variation of reaction time of two reactions with conversion

Using alkaline hydrolysis, PET waste bottles were effectively converted into ethylene glycol and terephthalic acid. The purity of the products obtained through this method was deemed acceptable. The IR spectrum analysis of the products, when compared with reference samples, showed a high degree of similarity which indicated that the products were of good quality.

3.1.1 Technical Feasibility (Process Efficiency, Technology Maturity, Scalability, and Environmental Impact)

The hydrolysis of PET with sodium hydroxide has been proven as an effective method for chemically recycling PET waste using the two-stage approach with moderate environmental impact. The efficiency of the recycling method was 92% and 82% in the first and second stage respectively and ethylene glycol and terephthalic acid obtained was deemed to be of high purity highlighting the high process efficiency.

However, the labelling/specifications of reactor such as type, size, or design was not highlighted. The reactor's design can significantly influence the reaction kinetics and efficiency. Accurate temperature control was also not ensured in this method and temperature fluctuations can significantly affect the reaction rate and product yield. Also, complementary methods, such as monitoring the concentration of reactants or products over time, would provide a more comprehensive view as opposed to measuring PH at 5-minutes interval to determine reaction completion. These points and omissions makes it challenging to replicate the recycling method accurately, affects the technical feasibility, as well as scaling of the process for small to medium-scale and large-scale industrial applications.

Therefore, this approach is not yet technically feasible. Nonetheless, with further research and detailed disclosures of reactor specifications, this method will be technically feasible and perfected for scalability for small to medium-scale and industrial operations.

3.1.2 Economic Viability

In this recycling process, **500 grams** of sodium hydroxide and 166g of HCl was required per 1kg of PET to produce **222g** of ethylene glycol and **433g** of terephthalic acid. The economic viability is evaluated by comparing the cost of the market available ethylene glycol and terephthalic acid and the cost it takes to produce ethylene glycol and terephthalic acid using this recycling process as shown in Table 3 and 4.

Table 3 Prices of Market Available Chemicals

Items	Cost/kg
Sodium hydroxide [12]	$11
Hydrochloric acid [13]	$250
Ethylene glycol [14]	$225
Terephthalic acid [15]	$80

Table 4: Calculations

Cost	Amount
Chemical Cost for Production	500g of NaOH ($5.5) + 166g of HCl ($41.5) = $47
Additional Operational Costs (Hypothetical based on 10 liter pilot plant)	Energy, Labor, Maintenance, etc.: $200.
Total Production Cost	$47 (Chemical) + $200 (Additional) = **$247**

Total revenue from produced ethylene glycol and terephthalic acid	222g of ethylene glycol ($50) + 433g of terephthalic acid ($35) = **$85**

Based on these calculations, it costs about $247 to produce **222g** of ethylene glycol and **433g** from 1kg of PET using alkaline hydrolysis which can be purchased from the market at about $85. Therefore, this method is not economically viable.

3.2 Glycolysis of PET Bottles

Pingale et al. [16] investigated the glycolytic depolymerization of post-consumer PET bottle wastes using ethylene glycol (EG) in the presence of various metal chloride catalysts of zinc, lithium, didymium, magnesium, and iron as catalysts to obtain virtual monomer bis (2-hydroxyethyl terephthalate) (BHET). Glycolysis involves transesterification reaction of PET with an excess amount of glycol in a temperature range of 180–240ºC in an inert atmosphere, which leads to the depolymerization of PET and the formation of polyhydric alcohols. Firstly, the PET bottles caps and labels were removed and then cut into approximately 1cm^2 chips and subsequently cleaned by boiling in weak detergent solution followed by washing and drying.

The PET waste is treated with ethylene glycol (EG) under reflux conditions (at 197°C) in the presence of various catalysts. These catalysts include zinc chloride, lithium chloride, didymium chloride, magnesium chloride, and ferric chloride, with concentrations ranging between 0.3% and 1% (w/w). The process is carried out for up to 9 hours. After the reaction, distilled water is added to the mixture with vigorous agitation. The glycolyzed product is obtained as a residue after filtration. The filtrate contains unreacted EG, BHET (bis(2-hydroxyethyl terephthalate)), and small quantities of water-soluble oligomers. White crystals of BHET are obtained by concentrating the

filtrate through boiling and then chilling it. The glycolyzed residue is further boiled with water to extract any remaining BHET. The crystalline powder of BHET is purified by repeated crystallization from water, dried, and weighed to estimate the yield.

The highest yield of BHET (73.24%) was achieved using 0.5% w/w zinc chloride as a catalyst, with a PET:EG ratio of 1:10 and a glycolysis time of 7 hours as shown in Figure 7c. Different catalysts was also found to require different PET:EG ratios and glycolysis times for optimal BHET yield. For example, zinc and didymium chloride catalysts required a 1:10 PET:EG ratio, while lithium, magnesium, and ferric chloride worked best with a 1:6 ratio as shown in Figure 7. To ensure the quality of the recycled material, the purified BHET undergoes various characterization techniques, including melting point determination, elemental analysis, NMR spectroscopy, FTIR spectroscopy, and differential scanning calorimetry (DSC). The structure of BHET was confirmed by FTIR and NMR spectroscopy indicating characteristic groups in the structure as shown in Figure 8b and 8c. DSC analysis further confirmed the melting point of 109–112°C for BHET as shown in Figure 8d.

a)

TABLE I
Effect of Concentration of Different Catalysts on the BHET Yield

Catalyst conc., % (w/w)	BHET yield (%) in presence of chlorides of				
	Zinc	Lithium	Didymium	Magnesium	Ferric
0.3	56.08	52.30	63.11	62.75	57.40
0.5	60.47	62.90	66.36	66.08	57.58
0.7	50.79	60.54	58.13	55.94	52.83
1.0	48.45	57.44	52.15	52.71	49.93

PET: EG: 1 : 6.
Time: 8 h.

b)

TABLE III
Effect of Glycolysis Time on the BHET Yield in Presence of Different Catalysts

Time (h)	BHET yield (%) in presence of chlorides of				
	Zinc	Lithium	Didymium	Magnesium	Ferric
4	71.77	–	68.82	34.94	–
6	71.93	59.50	70.65	60.21	58.35
7	73.27	60.52	70.58	65.56	62.75
8	73.12	63.08	71.56	65.55	61.12
9	72.66	60.87	72.46	60.53	56.67

PET: EG: 1 : 10 (for zinc and didymium chloride): 1 : 6 (for lithium, magnesium, and ferric chloride).
Catalyst conc.: 0.5% (w/w).

c)

TABLE II
Effect of PET: EG Ratio on the BHET Yield in Presence of Different Catalysts

PET: EG	BHET yield (%) in presence of chlorides of				
	Zinc	Lithium	Didymium	Magnesium	Ferric
1 : 4	54.41	59.15	52.91	60.18	44.97
1 : 6	61.63	62.43	65.29	65.93	61.05
1 : 8	64.31	60.25	67.76	66.78	61.27
1 : 10	73.23	59.46	71.01	55.67	56.28
1 : 12	73.86	–	71.75	–	–
1 : 14	74.73	–	67.05	–	–

Catalyst conc.: 0.5% (w/w).
Time: 8 h.

d)

TABLE IV
Characterization of BHET Obtained

Formula:	$C_{12}H_{14}O_6$
Molecular weight	254
Melting point:	109–112°C
Elemental analysis (%)	
C	55.9
H	5.4
O	38.7

Fig. 7. a) Effect of Concentration of Different Catalysts on the BHET Yield b) Effect of Glycolysis Time on the BHET Yield in Presence of Different Catalysts c) Effect of PET: EG Ratio on the BHET Yield in Presence of Different Catalysts d) Characterization of BHET Obtained

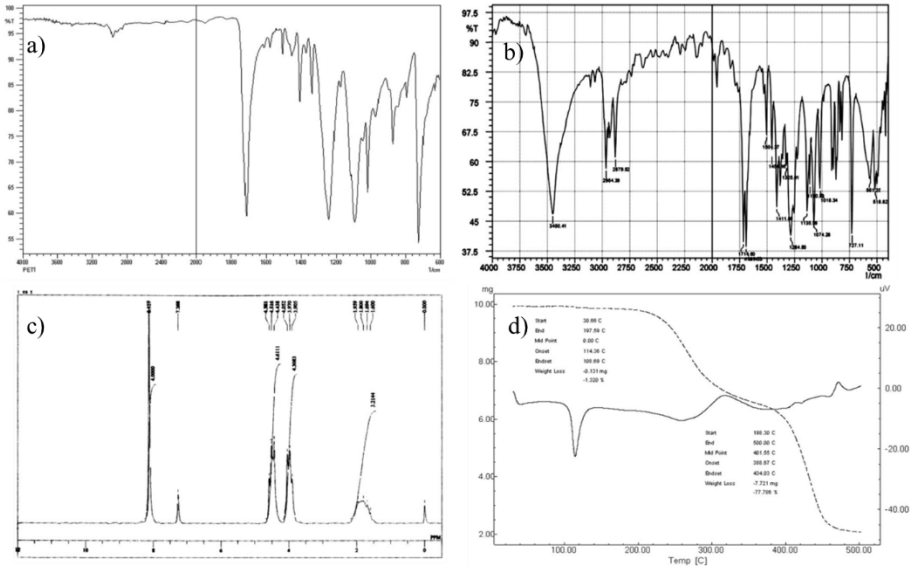


Fig. 8. a) FTIR spectra of PET b) FTIR spectra of BHET c) NMR spectra of BHET d) DTG of BHET

The study concluded that the PET bottle waste can be effectively glycolyzed into pure BHET monomer with good yield using metal chloride catalysts. The high yield and purity of BHET using this method indicates its potential for recycling into products useful in textile applications, such as dyes, softeners, dye retardants, and dye fixing agents.

3.2.1 Technical Feasibility (Process Efficiency, Technology Maturity, Scalability, and Environmental Impact)

The glycolysis of PET using zinc chloride as a catalyst achieved a high yield of bis(2-hydroxyethyl terephthalate) (BHET), with the highest yield being 73.24% under optimized conditions (0.5% w/w zinc chloride, PET: EG ratio of 1:10, and 7 hours of reflux). This indicates a high process efficiency, making it a promising method for PET waste recycling. While the method shows promise in a controlled laboratory setting, its scalability to small, medium, or large-scale industrial applications is not clearly addressed. Factors such as the cost of materials, energy requirements, and the adaptability of the process to larger reactors are crucial for practical application. The study also does not extensively discuss the environmental impact of using zinc chloride as a catalyst.

Overall, the glycolysis of PET using zinc chloride as a catalyst demonstrates high efficiency and potential for recycling PET waste. Therefore, it is technically feasible. However, several technical aspects require further research and clarification. Detailed information on reactor

design, improved temperature control mechanisms, and comprehensive reaction monitoring are necessary for accurate replication and scaling of the process.

3.2.2 Economic Viability

In this recycling process, glycolytic depolymerization of post-consumer PET bottle wastes using ethylene glycol (EG) in the presence of zinc chloride achieved the highest yield being 73.24% BHET under optimized conditions (0.5% w/w zinc chloride, PET: EG ratio of 1:10). Using this information, the amount of ethylene glycol and zinc chloride needed to glycolyze 1kg of PET as well as the amount of BHET produced can be estimated. Therefore, for 1kg of PET, 3.3kg of ethylene glycol and 22 grams of zinc chloride is needed to produce approximately 732.4g of BHET under the optimized conditions described. The economic viability is evaluated by comparing the cost of the market available BHET and the cost it takes to produce BHET using this recycling process as shown in Table 5 and 6.

Table 5: Prices of Market Available Chemicals

Items	Cost/kg
Ethylene glycol [14]	$225
Zinc Chloride [17]	$600
2-hydroxyethyl terephthalate (BHET) [18]	$500

Table 6: Calculations

Cost	Amount
Chemical Cost for Production	3.3kg of ethylene glycol ($743) + 22g of Zinc Chloride ($14) = $757

Additional Operational Costs	Energy, Labor, Maintenance, etc.: $200.
Total Production Cost	$2283 (Chemical) + $200 (Additional) = **$957**
Total revenue from produced BHET	732.4g of BHET = **$367**

Based on these calculations, it costs about $960 to produce 732.4g of BHET from 1kg of PET using glycolysis with zinc chloride as catalyst which can be purchased from the market at about $367. Therefore, this method is not economically viable.

3.3 Aminolysis of PET Wastes

Shukla et al. [19] studied the aminolysis of polyester staple fiber and post-consumer PET bottle wastes using excess of ethanolamine in the presence of different simple chemicals such as glacial acetic acid, sodium acetate and potassium sulphate as catalysts to produce pure and high yield bis(2-hydroxy ethylene)terephthalamide (BHETA).

Firstly, the PET bottles were cut into small pieces of approximate size 5x5 mm after separating from the non-PET components such as labels and caps. The polyester staple fiber waste was boiled with a solution containing Lentol FBOL (a non-ionic detergent) for 1 hour to remove any surface finish and dirt. The bottle pieces were washed with the same detergent solution, rinsed with hot water, and air-dried. Ethanolamine was used for the aminolysis in a molar ratio of 1:6 (PET:ethanolamine) under reflux with various catalysts for periods up to 8 hours. The catalysts used were glacial acetic acid, sodium acetate, and potassium sulphate in concentrations ranging from 0.3 to 1.5% by weight of polymer. After the reaction, distilled water was added to the mixture with vigorous agitation to precipitate out the product, bis(2-hydroxy ethylene)terephthalamide

(BHETA). The precipitate obtained was filtered, dissolved in distilled water by boiling, and recrystallized in water. It was then dried in an oven at 80°C and weighed for estimating the yield.

Furthermore, the yield of BHETA was significant with all catalysts. The highest yield was obtained using 1% (w/w) sodium acetate from the PET fibrous waste and an 8-hour reaction time as shown in Figure 9a. The yield was higher for PET fiber waste compared to bottle waste, with a maximum yield of 91.1% from fiber waste and 83.2% from bottle waste which was attributed to the molecular weight and its distribution in the samples as shown in figure 9b. In the absence of any catalyst, the yield was only 52%. To ensure the quality of the recycled material, the purified BHETA was characterized using various techniques like elemental analysis, melting point determination, IR spectroscopy, Nuclear Magnetic Resonance (NMR), and Differential Scanning Calorimetry (DSC). The results confirm that the product of the PET depolymerization was indeed BHETA as shown in Figure 10.

a) Effect of depolymerisation time on yield of BHETA

Time (h)	Yield % in the presence of					
	Acetic acid		Sodium acetate		Potassium sulphate	
	Fibre waste	Bottle waste	Fibre waste	Bottle waste	Fibre waste	Bottle waste
4	52.4	42.0	60.5	58.04	58.5	41.25
6	61.5	54.0	75.0	65.9	71.05	59.00
7	69.3	62.0	87.05	77.8	80.3	68.05
8	76.4	68.2	91.1	83.2	87.2	74.05
9	63.3	60.05	83.3	75.2	75.2	65.3

b) Effect of different catalysts on yield of BHETA

Catalyst concentration (w/w)	Yield % in the presence of					
	Acetic acid		Sodium acetate		Potassium sulphate	
	Fibre waste	Bottle waste	Fibre waste	Bottle waste	Fibre waste	Bottle waste
0.3	41	40.7	48.0	58.8	40.5	44.05
0.5	61.5	52.7	77.0	63.5	61.8	59.0
0.7	65.0	61.2	89.5	78.2	72.6	64.0
1.0	76.4	68.2	91.1	83.2	87.2	74.05
1.5	68.2	60.3	65.0	71.02	55.0	68.02

c) Elemental analysis of BHETA (formula, $C_{12}H_{16}N_2O_4$; molecular weight, 252; melting point, 227 °C)

Elemental analysis (%)	Calculated	Observed
C	57.14	57.10
H	6.34	6.25
N	11.11	11.05

d)

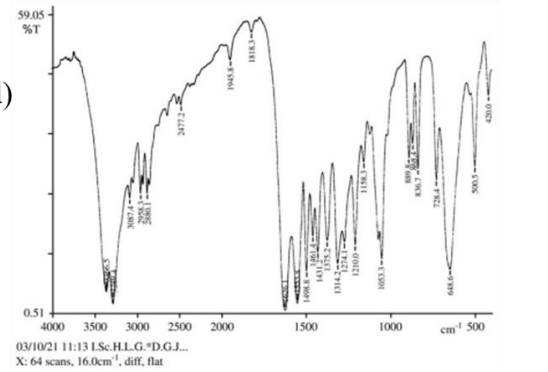


Fig. 9. a) Effect of depolymerization time on yield of BHETA b) Effect of different catalysts on yield of BHETA c) Elemental analysis of BHETA (formula, C12H16N2O4; molecular weight, 252; melting point, 227ºC) d) IR spectrum of bis(2-hydroxy ethylene)terephthalamide

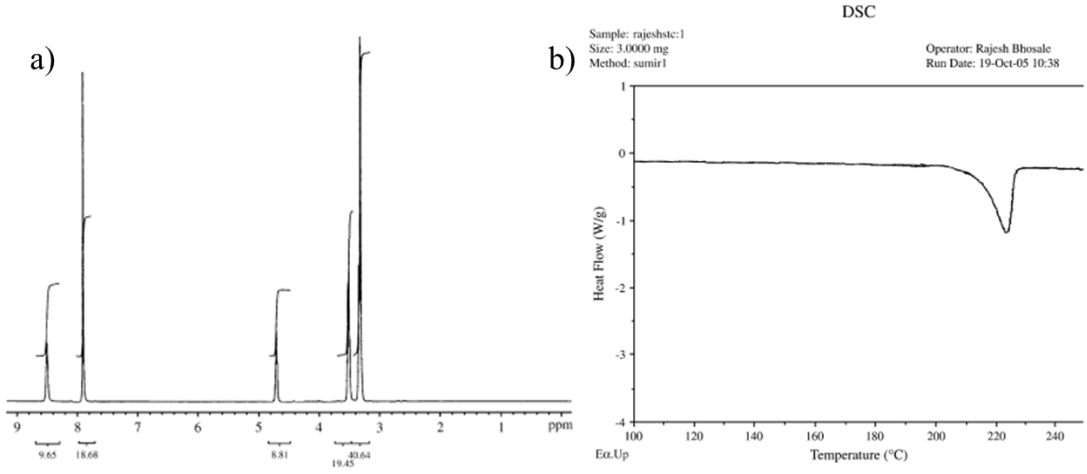


Fig. 10. a) NMR spectrum of bis(2-hydroxy ethylene)terephthalamide b) DSC spectrum of bis(2-hydroxy ethylene)terephthalamide

In summary, the study presented a successful method for the depolymerization of post-consumer PET bottle waste through aminolysis, yielding high amounts of BHETA. The process was shown to be effective with various catalysts and under different reaction conditions, providing a potential avenue for recycling PET waste into useful chemical products.

3.3.1 Technical Feasibility (Process Efficiency, Technology Maturity, Scalability, and Environmental Impact)

The aminolysis of PET using sodium acetate as a catalyst achieved the highest yield of BHETA. The process resulted in a high yield of BHETA, indicating an efficient depolymerization of PET. This also indicates a high process efficiency, making it a promising method for PET waste recycling. While the method shows promise in a controlled laboratory setting, its scalability to small, medium, or large-scale industrial applications is not clearly addressed. Factors such as the cost of materials, energy requirements, and the adaptability of the process to larger reactors are crucial for practical application. The study also does not extensively discuss the environmental impact of using zinc chloride as a catalyst. The safety and environmental implications of the chemicals used, and the byproducts produced during the process are crucial factors for industrial-scale application.

Ultimately, the aminolysis approach using sodium acetate as a catalyst is technically feasible and efficient for PET waste recycling in a controlled laboratory setting. However, further research and analysis are needed to evaluate its practicality for large-scale industrial applications.

3.3.2 Economic Viability

In this recycling process, ethanolamine was used for the aminolysis of PET waste materials in the molar ratio 1:6 (PET:ethanolamine) using 1% (w/w) sodium acetate as catalyst and this yield of 91.1% BHETA from fiber waste.

Using this information, the amount of ethanolamine and sodium acetate needed to glycolyze 1kg of PET as well as the amount of BHETA produced can be estimated. Therefore, for 1kg of PET, 1.91kg of ethanolamine and 29.1g of sodium acetate is needed to produce approximately 911g of BHETA under the optimized conditions described. The economic viability

is evaluated by comparing the cost of the market available BHETA and the cost it takes to produce BHETA using this recycling process as shown in Table 7 and 8.

Table 7 Prices of Market Available Chemicals

Items	Cost/kg
Ethanolamine [20]	$78
Sodium acetate [21]	$210
Bis (2-hydroxyethylene) terephthalamide (BHETA) [18]	$200

Table 8: Calculations

Cost	Amount
Chemical Cost for Production	1.91kg of ethanolamine ($150) + 29.1g of sodium acetate ($6) = $156
Additional Operational Costs	Energy, Labor, Maintenance, etc.: $200
Total Production Cost	$156 (Chemical) + $200 (Additional) = **$356**
Total revenue from produced BHETA if sold at market price.	732.4g of BHETA = **$183**

Based on these calculations, it costs about $356 to produce **911g** of BHETA from 1kg of PET using aminolysis with sodium acetate as catalyst which can be purchased from the market at about $183. Therefore, this method is not economically viable.

Conclusion

The recycling of PET packaging waste have become increasingly important due to its high rate of consumption as well as accumulation of PET waste in the landfill. In this paper,

various mechanical and chemical recycling methods have been discussed such as re-extrusion, extrusion, and chain extension (reactive processing), hydrolysis, glycolysis and aminolysis. Technoeconomic analysis was also performed to evaluate the methods as an efficient way of recycling PET wastes.

The future of PET waste recycling is marked by significant advancements, particularly in the field of chemical recycling technologies. These technologies aim to transform wastes especially Post-Consumer PET back into a virgin-like quality, a process that's rapidly moving from lab-scale to larger production facilities. The key to this smooth transition would be the support of effective recycling legislation and enhanced consumer participation in recycling efforts.

An important strategy for the future is the 'design for recycling' approach, which focuses on creating PET products that are easier to collect, sort, and recycle. This approach will improve the efficiency and yield of recycled PET. Technological innovations are also crucial as developing more efficient extruders for mechanical recycling and reactors, and incorporating advanced technologies like microwave and ultrasound energy, are steps towards improving the PET recycling process. Optimizing the chemical depolymerization of PET is another critical area, with a focus on reaction variables such as time, temperature, and catalyst use. Researchers are working on various strategies to achieve optimal monomer yield and make the recycling process more technoeconomically feasible and sustainable. In summary, the future of PET recycling hinges on technological advancements, legislative support, consumer participation, and innovative design and processing strategies, all aimed at enhancing the efficiency and sustainability of PET recycling.

References

[1] "Plastic waste volume globally 2050," Statista. Accessed: Nov. 12, 2023. [Online]. Available: https://www.statista.com/statistics/1019774/plastic-waste-volume-globally/

[2] O. US EPA, "Plastics: Material-Specific Data." Accessed: Nov. 12, 2023. [Online]. Available: https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/plastics-material-specific-data

[3] "Plastic bottle recycling rates worldwide 2018," Statista. Accessed: Nov. 13, 2023. [Online]. Available: https://www.statista.com/statistics/1166550/plastic-bottle-recycling-rates-in-select-countries/

[4] V. Beghetto, R. Sole, C. Buranello, M. Al-Abkal, and M. Facchin, "Recent Advancements in Plastic Packaging Recycling: A Mini-Review," *Materials*, vol. 14, no. 17, Art. no. 17, Jan. 2021, doi: 10.3390/ma14174782.

[5] S. Altun and Y. Ulcay, "Improvement of Waste Recycling in PET Fiber Production," *J Environ Polym Degr*, vol. 12, no. 4, pp. 231–237, Oct. 2004, doi: 10.1007/s10924-004-8150-4.

[6] D. Dimonie *et al.*, "Overview on Mechanical Recycling by Chain Extension of POSTC-PET Bottles," in *Material Recycling - Trends and Perspectives*, IntechOpen, 2012. doi: 10.5772/31841.

[7] "Pyromellitic dianhydride PMDA - ZIBO ANQUAN CHEMICAL CO., LTD. - page 1." Accessed: Nov. 16, 2023. [Online]. Available: https://chinafinechemicals.en.made-in-china.com/product-group/LbPAxuDjazUy/Pyromellitic-dianhydride-PMDA-1.html

[8] "Polyethylene terephthalate prices globally 2022," Statista. Accessed: Nov. 16, 2023. [Online]. Available: https://www.statista.com/statistics/1171088/price-polyethylene-terephthalate-forecast-globally/

[9] S. K. Das *et al.*, "Plastic Recycling of Polyethylene Terephthalate (PET) and Polyhydroxybutyrate (PHB)—a Comprehensive Review," *Mater Circ Econ*, vol. 3, no. 1, p. 9, Jun. 2021, doi: 10.1007/s42824-021-00025-3.

[10] D. Paszun and T. Spychaj, "Chemical Recycling of Poly(ethylene terephthalate)," *Ind. Eng. Chem. Res.*, vol. 36, no. 4, pp. 1373–1383, Apr. 1997, doi: 10.1021/ie960563c.

[11] P. Benyathiar, P. Kumar, G. Carpenter, J. Brace, and D. K. Mishra, "Polyethylene Terephthalate (PET) Bottle-to-Bottle Recycling for the Beverage Industry: A Review," *Polymers*, vol. 14, no. 12, Art. no. 12, Jan. 2022, doi: 10.3390/polym14122366.

[12] "Sodium Hydroxide, Laboratory Grade, 2 kg." Accessed: Nov. 17, 2023. [Online]. Available: https://www.flinnsci.com/sodium-hydroxide-laboratory-grade-2-kg/s0077/

[13] "Hydrochloric Acid, Certified ACS Plus, 36.5 to 38.0%, Fisher Chemical, Quantity: 500 mL | Fisher Scientific." Accessed: Nov. 17, 2023. [Online]. Available: https://www.fishersci.com/shop/products/hydrochloric-acid-certified-acs-plus-fisher-chemical-10/A144500#?keyword=

[14] "Ethylene Glycol, 98% min., MilliporeSigma, Quantity: 1 kg | Fisher Scientific." Accessed: Nov. 17, 2023. [Online]. Available: https://www.fishersci.com/shop/products/ethylene-glycol-98-min-emd-millipore/MEX05651

[15] "Terephthalic acid, 98+%, Thermo Scientific Chemicals, Quantity: 250 g | Fisher Scientific." Accessed: Nov. 17, 2023. [Online]. Available: https://www.fishersci.com/shop/products/terephthalic-acid-98-thermo-scientific/AAA1252736#?keyword=terephthalic%20acid

[16] N. D. Pingale, V. S. Palekar, and S. R. Shukla, “Glycolysis of postconsumer polyethylene terephthalate waste,” *Journal of Applied Polymer Science*, vol. 115, no. 1, pp. 249–254, 2010, doi: 10.1002/app.31092.
[17] “Zinc Chloride (Cryst./Certified ACS), Fisher Chemical, Quantity: 100 g | Fisher Scientific.” Accessed: Nov. 17, 2023. [Online]. Available: https://www.fishersci.com/shop/products/zinc-chloride-cryst-certified-acs-fisher-chemical-3/Z33500#?keyword=Zinc%20Chloride
[18] “Bis(2-hydroxyethyl) terephthalate 959-26-2.” Accessed: Nov. 17, 2023. [Online]. Available: http://www.sigmaaldrich.com/
[19] S. R. Shukla and A. M. Harad, “Aminolysis of polyethylene terephthalate waste,” *Polymer Degradation and Stability*, vol. 91, no. 8, pp. 1850–1854, Aug. 2006, doi: 10.1016/j.polymdegradstab.2005.11.005.
[20] “Ethanolamine, 99%, Thermo Scientific Chemicals, Quantity: 250 mL | Fisher Scientific.” Accessed: Nov. 18, 2023. [Online]. Available: https://www.fishersci.com/shop/products/ethanolamine-99-thermo-scientific/AC149580010#?keyword=Ethanolamine
[21] “Sodium Acetate Anhydrous (White Crystals or Granular Powder), Fisher BioReagents, Quantity: 500 g | Fisher Scientific.” Accessed: Nov. 18, 2023. [Online]. Available: https://www.fishersci.com/shop/products/sodium-acetate-anhydrous-white-crystals-granular-powder-fisher-bioreagents-2/BP3331#?keyword=Sodium%20acetate