Enzymatic Recycling of Polyethylene Terephthalate

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Abstract

The goal of this project was to research and propose the implementation of a polyethylene terephthalate (PET) recycling plant. The recommended process is recycling PET flakes into its base polymers and monomers via a hydrolase enzyme biocatalyst. The current design with supporting utilities and operations has an estimated total capital investment of $54.68 million dollars. The team is recommending selling terephthalic acid (rTPA) at $2.21 per kilogram to reach a net present value of $0 after 10 years. This price is not competitive with the current market of virgin TPA, which historically has been between $1.00 and $1.50 per kilogram. This process also produces liquid ethylene glycol (EG) and sodium sulfate salt (SS) that can be sold as co-products. The return on investment (ROI) is 24.5% and the venture profit is $1.35 million.

The current state of the economic and PHA analyses leads the team to recommend proceeding with the process under the condition that there is opportunity for further optimization. This process is an important emerging green technology and proposes a circular approach to plastic production. Optimization of on-site wastewater treatment, and unit operation modification could bring the price of rTPA closer to that of virgin TPA.

Research into process and safety hazards of this process has been conducted using the What-If methodology and is discussed in the Process Hazard Analysis and Environmental Consideration section. There are a few notable process hazards and safety recommendations to remedy those identified.

Economic Analysis

Total Capital Investment: $54.68 MM

- Bare module cost of 56 pieces of equipment
- Cost of utilities, contingencies, contractors, land, royalties, and construction
- Working capital estimation

Operating Costs: $61.54 MM

- Raw materials, utilities, operations and overhead, depreciation, and general expenses
- Based upon 8,000 operating hours per year
- Based upon 5 shifts of 4 operators each

Profitability:

- rTPA price set to reach NPV of 0 dollars
- Selling price of rTPA: $2.21/kg
- Expected revenue: $83.9 MM
- Return on Investment: 24.5% with payback period of 2.2 years

Project Scope

Table 1: Feedstock and Product Hourly Rates

Feedstocks		Products	
Material	**Usage (kg./hr.)**	**Material**	**Production (kg./hr.)**
PET Flake	6,250	rTPA	3,946
Caustic	2,184	Wastewater Streams	19,811
Enzyme	28	SS	6,569
Sulfuric Acid	2,702	EG	827
		Solid Waste	1,025

The scope of this project involved the creation and isolation of the main product, recycled terephthalic acid. Throughout completion of the project a supplemental paper[13] was used as a reference for key process decision making. A process hazard analyses was created to determine the safest method of producing the final product. This project did have some major challenges. Most notably the unknown and experimental chemistry involving the use of the enzyme used to break down the recycled polymers.

The goal of this project is to present a method of producing rTPA from recycled plastics at a rate of 50,000,000 kilograms per year. This will be completed on a basis of 8,000 annual operating hours with a continuous process. The feed material usage for this process is displayed below in Table 1 at an hourly basis. The table also presents the hourly production rates, product, and waste streams.

Material and Energy Balance

Table 2: Overall Material Balance for Process

rTPA Production		
	Input (kg/h)	Output (kg/h)
PET Flake	6,250	0
Caustic	2,184	0
Enzyme	28	0
Sulfric Acid	2,702	0
Water	22,683	21,480
rTPA	0	3,946
SS	0	6,569
EG	0	827
Solid Waste	0	1,025
Total	33,847	32,178

Table 3: Overall Energy Balance for Process

rTPA Production		
	Input (MMBtu/h)	Output (MMBtu/h)
Feed Streams	-1.9	0
Product Streams	0	-73.2
Total Heating	79.0	0
Total Cooling	-3.9	0
Power Added	0	0
Power Generated	0	0
Total	73.2	-73.2

Process Flow Diagram

Depolymerization Section

- PET Flake Feedstock extruded, cooled, and microgranulated
- Process stream cooled
- Water, NaOH, and PET heated and introduced to reactors
- Reactor catalyst: Hydrolase enzyme
- Reactor product cooled

Clarification Section

- Filtration methods: solids filter, membrane unit, activated carbon column
- PET and biocatalyst leave process and are sent to landfills as nonhazardous solid waste
- Activated carbon column waste sent to be treated for proper disposal
- $rTPA^-$ and Na^+ ions combine with H_2SO_4 to precipitate TPA(s)

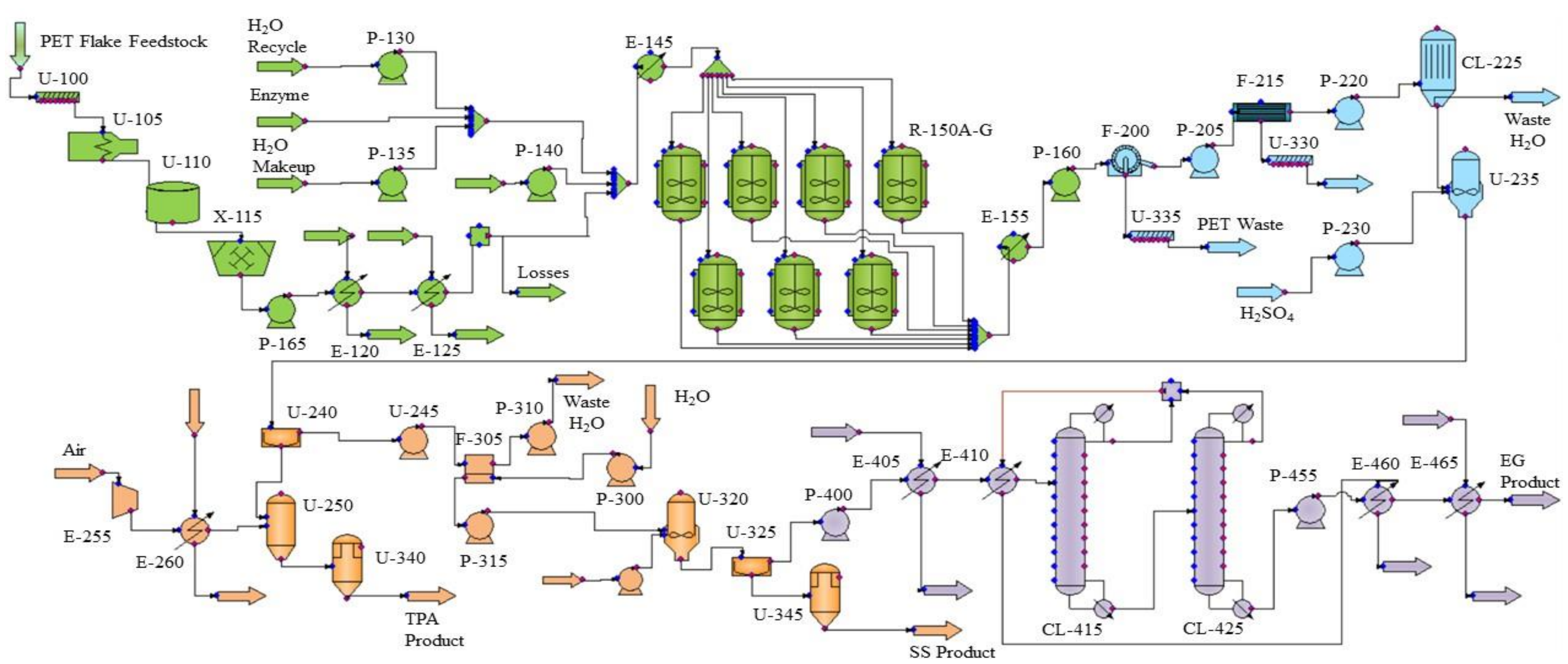


***Figure 1:** Overall Process Flow Diagram*

Co-Product Recovery Section: Sodium Sulfate and rTPA

- TPA flake is dried and purified and stored in supersac as final product
- Filtration methods: Centrifugal sedimentation, and RO membrane
- RO wastewater sent to be treated for proper disposal
- Na^+ and SO_4^- ions combine to precipitate sodium sulfate salt
- Supersacs store final sodium sulfate salt product

Co-Product Recovery: Ethylene Glycol Separation Section

- E-405 and E-410 pre-heat the Water/EG mixture
- CL-415 removes 8,200 kg/hr of water via the tops but leaves 2,700 kg/hr of water with the EG
- CL-425 removes the remaining water, leaving the EG stream 99.9% pure
- E-460 and E-465 cool the EG product while using the wastewater stream as the utility

Process Hazard Analysis and Environmental Considerations

Table 4: Chemical Hazards

Compound	Health Hazards	Fire Hazards	Reactivity
PET	N/A	Explosive in dust form	N/A
Ethylene Glycol	Targets cardiovascular and nervous system, eye irritation	NFPA Category 1	Reacts with strong acids and bases
Hydrolase Enzyme	Category 1 respiratory hazard	NFPA Category 1	N/A
TPA	N/A	N/A	N/A
NaOH	Severely corrosive to skin and eyes	N/A	N/A
H_2SO_4	Corrosive and toxic by inhalation	N/A	N/A
Na_2SO_4	Skin, eye, and respiratory tract irritation	N/A	N/A

Environmental Performance

- There are four waste streams identified
  - PET waste out of the filter press
  - Enzyme waste out of the ultra filtration membrane
  - Wastewater out of the activated carbon column
  - Wastewater out of the RO membrane
- PET and SS do not break down in the environment
- SA and EG are toxic to fish but do not bioaccumulate

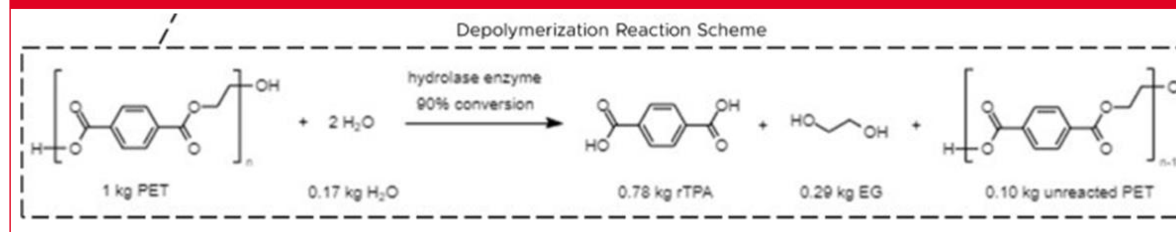
PHA Recommendations

1. Consider adding leak detection on all lines that contain EG, SA, and SS.
2. Consider inerting piping that contains dust or small particles.
3. Evaluate and design alarms, interlocks, and fail safes.
4. Look into adding catch systems for spills on the conveyor belts.
5. Consider installing weight sensors on the conveyer belts.
6. Consider keeping spare microgranulator blades in stores.
7. Look into designing manual override on valves and controls.
8. Think about adding in check valves to prevent back flow before necessary equipment.

Open Issues:

The main open issue found through the PHA was to have a team better trained and with more process knowledge perform a HAZOP analysis instead of the What-If analysis performed by this team.

Key Chemistry



rTPA Crystallization

$$rTPA^- + Na^+ + H_2SO_4 \xrightarrow[20°C]{} TPA_{(s)} + Na^+ + SO_4^-$$

Sodium Sulfate Crystallization

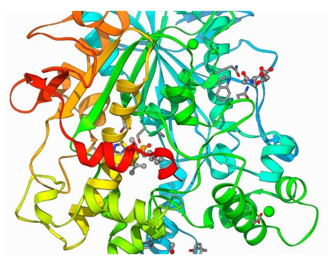
$$10H_2O + 2Na^+ + SO_4^- \xrightarrow[0°C]{} Na_2SO_4 * 10H_2O_{(s)}$$

Technology Risk: Catalyst Choice

Hydrolase: Biochemical Catalyst

Catalyst uses esterases (ex: Lipase) to cleave ester bonds

Current industries: Food, detergent, pharmaceuticals
Catalyzes esterification reactions in solid environments

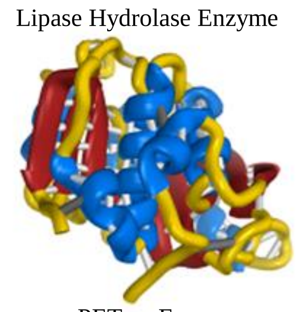


Lipase Hydrolase Enzyme

I. Sakaiensis: Plant-eating bacteria found in plastic-slicing worms
Secretes PETase when grown on PET films[6]

Drawbacks: slow and inefficient during depolymerization, cost

Enzyme strength and residence times need to be optimized in R&D stage



PETase Enzyme

Recommendations and Future Work

The final recommendation is to sell the rTPA at a market price of $2.21 per kilogram to reach a $0.00 net present value and return on investment of 24.5%. However, this price is not competitive when compared to the price of virgin TPA which is approximately $1.00 - $1.50 per kilogram. Further optimization of the process is recommended to directly compete with virgin TPA prices.

Cost Savings Recommendations

Currently, the wastewater streams have a large biological oxygen demand due to the presence of ethylene glycol and TPA despite having a low volumetric flow.

- Further wastewater treatment would greatly decrease the cost of the utility price of the wastewater streams
- The increased price of the wastewater utility operating cost led the unit price of rTPA to increase from $1.88 per kilogram to $2.21 per kilogram
- If the price can be lowered back down to $1.88 per kilogram, it is a semi-competitive price and much more attractive proposal

Further Considerations:

1. The increasing price of pure PET flakes from manufacturers and recyclers
2. Due to the increased demand for renewable feedstocks, companies may be willing to pay more for a recycled product so as to deem their products greener
3. Public sentiment shifting towards an expectation of green and sustainable products
4. Governmental incentives to develop green chemistry and recycled products

Future Work:

1. The efficiency and yield of the filtration steps in the clarification process needs to be evaluated with real time data. This information should be compared to theoretical data for ultrafiltration, crystallization, and centrifugal sedimentation units. A closer look at cyclones, and vacuum filtration are examples of alternatives to be considered.
2. From the process chemistry perspective, further lab development and research regarding which enzyme (PETase, lipase, or another hydrolase) to use in the process is needed. Since this is the beginning stage of the process, bench scale testing, then pilot plant testing, and large-scale production testing are needed.
3. Partner with the MRFs to obtain a reliable source of PET feedstock

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