SOLVOGENESIS – NON-DESTRUCTIVE POLYESTER UPCYCLING

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Abstract:

Plastics are versatile materials that are used in numerous applications; however, their energy-intensive production accounts for 4.5% of global CO2 emissions, and limited mechanical recycling methods have driven a global plastic waste crisis. Mostly, mechanical recycling is unable to remove several critical impurities and it is inherently degrading the material properties such as color and IV. Newer, emerging chemical or biological recycling technologies, such as methanolysis, glycolysis, or enzymolysis, rely on breakdown of the polymer into fuels or monomers. These processes are relatively complex, energy intensive, or need toxic chemicals. In addition, they sell PET's monomers back to existing petrochemical suppliers, which is a lower value product than finished high quality PET resin.

Macrocycle's "SolvoGenesis" process produces a virgin-quality recycled PET product suitable for FDA-approved food packaging without requiring breakdown of PET into monomers. The PET plastic waste is dissolved in a non-toxic solvent which has FDA approval in cosmetics. The reaction process drives cyclization through reactive distillation. Different reaction times, and other reaction conditions allow MacroCycle to tune the reaction and obtain customer-desired molecular weights and IV (intrinsic viscosity, e.g. 0.63 for polyester, 0.82 for bottles or 0.9 for tire cord). The solvent also allows for the removal of color by subsequent washing steps, to arrive at the required L, a, and b values while using colored bottle flake and dyed textiles. Maximizing concentration while retaining control over cycle content and molecular weight minimizes the total use of solvent. Non-PET impurities such as polyolefins do not participate in the underlying transesterification reactions and do not affect macrocyclic chemistry, which makes this process resilient to several traditional impurities. Techno-economic analysis of this process shows an energy demand of about 5.2 MJ/kg for the required processing steps. This is more than 90% less energy is needed for our process compared with traditional virgin PET production (71 MJ/kg), and 80-90% lower than competing advanced recycling technologies, such as methanolysis (50 MJ/kg), glycolysis (32 MJ/kg), enzymolysis (28 MJ/kg), per NREL's analysis of these processes.

Introduction and Motivation

The plastics supply chain consumes about 4.6 quads in the U.S., representing 14% of total industrial energy use (DOE, 2023)[1]. Plastic production from fossil fuels represents about 5% of global CO2 emissions (LBNL, 2024)[2,3]. PET for rigid food and consumer goods packaging as well as films is among the most energy-intense plastics to produce, consuming ~107 MJ/kg (NREL, 2023)[4]. Most plastics get landfilled or incinerated given that existing mechanical recycling is unable to fully remove contaminants from plastic waste and inherently degrades the output material. Plastic waste leaks into rivers and oceans (~8 million tons/year), choking marine life and entering our food supply[5]. Large international companies that depend on plastics, such as Coca Cola, Unilever, Nestle, etc., are regulatory pressure to increase recycled plastic, however struggle to find enough high-quality recycled resin at affordable prices.

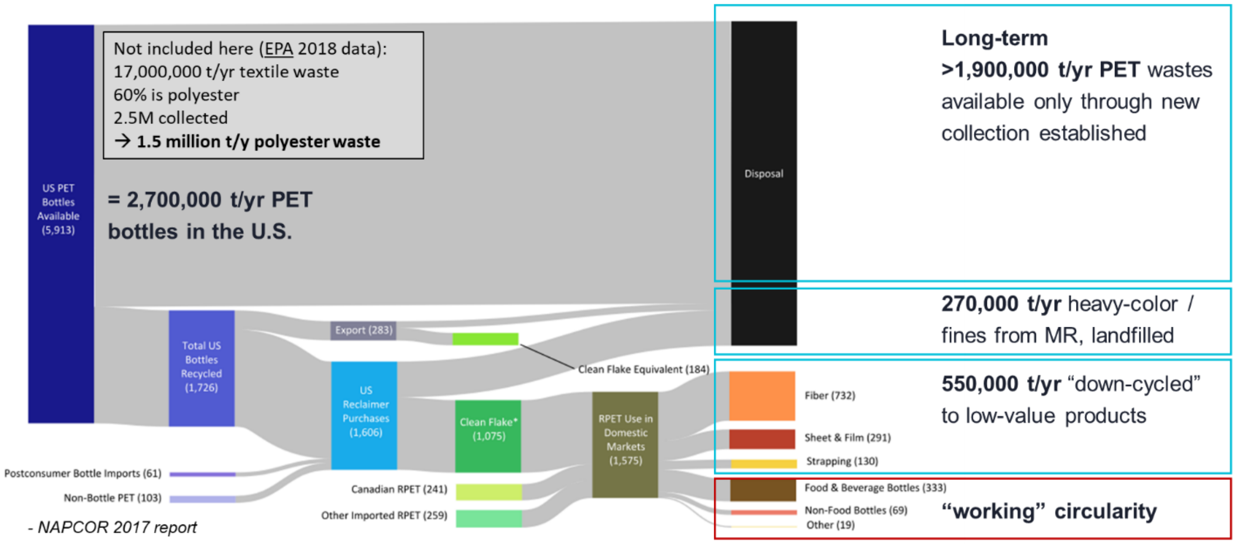

Figure 1: Sankey Diagram from NAPCOR report illustrates how most PET material value is currently lost or downcycled.

Current State of the Technology Industry Uses

Mechanical recycling struggles to remove color and other impurities that lead to lower quality PET in the recycling process. Insufficient removal of impurities, flake shredding, and remelting degrade the molecular weight and color of the material[6]. The molecular weights (MW) of the short "broken" polymer chains in recycled PET and polyester waste are too low to be reused for high value applications, such as bottles. MW and intrinsic viscosity (IV) are critical for plastic performance, affecting strength, durability, and gas diffusion barrier properties. Bottle-grade IV's are above 0.8 dL/g, while textile fibers only need about 0.4-0.65 dL/g. As a result, bottle waste with IV around 0.7 dL/g is readily "downcycled" into textile fibers, but never vice versa (**Figure 1**). The MW can be rebuilt through industrially established solid state polymerization (SSP), but this process also leads to discoloration and cannot remove colors or non-volatile impurities such as pigments, metals, or non-PET substances. Due to these drawbacks, only 20% of plastics are recycled globally, (even less in the U.S.), and the rest are incinerated or sent to landfills[7,8].

All advanced PET recycling technologies currently under development are almost exclusively focus on PET depolymerization into monomers: Methanolysis, Glycolysis, Hydrolysis, or Enzymolysis degrade the polymer back into its monomers, terephthalic acid (TA) variants and ethylene glycol (EG), which are then isolated and polymerized by established petrochemical processes to achieve high quality materials (Figure 2). Examples for companies in fossil production are large oil companies such as SABIC, Indorama, and Celanese. Enzymolysis companies are Carbios, Samsara Eco, Protein Evolution, Birch Biosciences and Epoch. Methanolysis is pursued by Eastman Chemical and Loop Industries. Glycolysis companies are ReJu, CuRe, SYRE, revalyu, Jeplan, Ioniqua. Hydrolysis is pursued by Circ and DePoly. However, these processes are more expensive than fossil fuel-based plastic production and typically offer only a 20-30% reduction in energy demand and CO2 emissions[4,9–12]. Carbios, one of the most advanced depolymerization companies, has announced EUR 2600/ton as their resin price, which is more than double the price of virgin PET (from fossil resources), which is a greater than 100% premium which most leading brand customers are unwilling to pay. The lack of competitiveness of depolymerization technologies and reliance on regulation have recently caused several plastic and textile recycling startups to file for bankruptcy[13,14].

Technology Approach

MacroCycle's SolvoGenesis Process achieves high quality without depolymerization

MacroCycle's unique "SolvoGenesis" technology produces high quality PET plastic resin from a variety of polyester and PET wastes, without the usual need to break the polymer down into monomers. Instead, MacroCycle's process selectively upgrades waste PET polymers via macrocyclic oligomers (macrocycles) to generate high-value macrocycle PET resin ("mPET") (**Figure 2A+C**). MacroCycle's chain upgrading technology is based on Ring-Opening Polymerization (ROP), a controlled polymerization technique that exploits ring-chain equilibria[15–18]. Instead of creating monomers through depolymerization and added end groups, MacroCycle inverts the process and removes end groups as well as impurities.

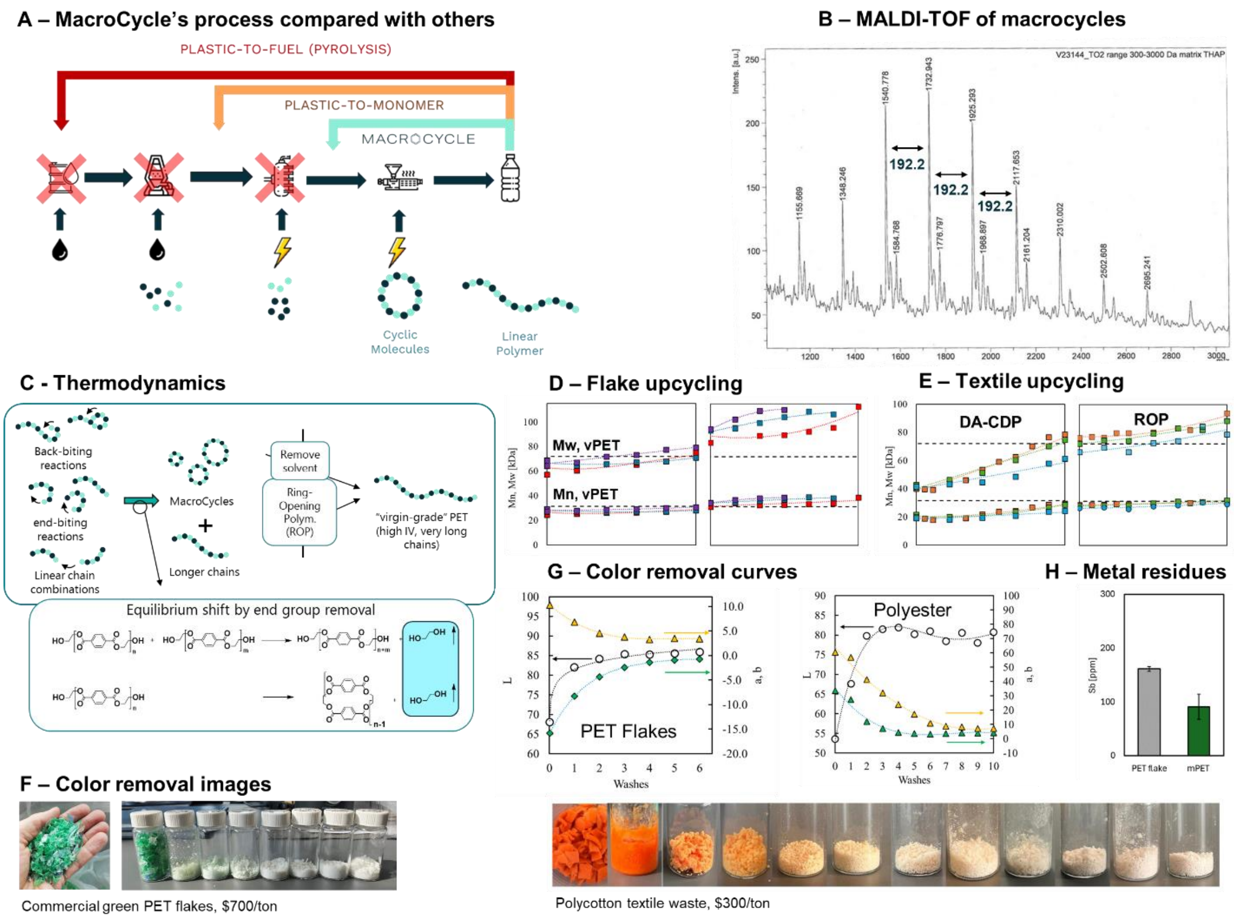

Figure 2. SolvoGenesis Technology. A) [add granules] MacroCycle's "SolvoGenesis" process takes contaminated PET packaging waste and upcycles it to "virgin-grade" PET without requiring breakdown into monomers. This is achieved by impurity separation, IV upgrading and color removal. In this grant, specifically PVC removal and extrusion will be derisked (red frames). **B**) MW is upgraded by distillation assisted cyclodepolymerization (DA-CDP) and ring-opening polymerization (ROP). **C**) MW's above bottle-grade can be reached for PET flakes, thermoforms, and polyester textile at 300 g/L, 0.2% catalyst.

PET waste, such as colored flakes, is dissolved in non-toxic solvents at concentrations up to 350 g/L (solvent-to-plastic ratio ~3), in presence of a transesterification catalyst such as standard PET catalyst Sb_2O_3, followed by distillation-assisted cyclodepolymerization (DA-CDP) based on thermodynamic ring-chain equilibrium to partially convert the waste polymers into cyclic oligomers and extend linear chain length through simultaneous polycondensation (**Figure 2C**). Dissolution of even coarse plastic pieces with crystallinities above 50% take 20-30 minutes at >200 °C and do not require highly fine shreds or cryomilling, as needed for techniques such as enzymolysis. No problems with viscosity, precipitation, or heterogeneity were observed with ordinary overhead lab stirrers at up to 350 g/L. Distillation in DA-CDP inherently removes endgroups and condensation products (mainly ethylene glycol as chains combine). An upgraded polymer/cycles mixture is then obtained by precipitation. Centrifugation, filtration and evaporation remove the solvent from the resulting cyclic/linear mixture. High MW polymer is obtained through ROP at temperatures near PET's melting point around 250°C within 30-60 minutes. Both PET flake and polyester textile waste can be upgraded in their molecular weight through this method (**Figure2D+E**). PET contaminated with polyolefin wastes such as HDPE or PP (e.g. from labels or caps) still yields increased molecular weights, as these polymers are inert to the transesterification chemistry. Metals also do not dissolve and can easily be separated by decantation. Waste materials are typically dried for 6h at 100C to remove moisture that can lead to ester cleavage, but moisture is also removed under vacuum during DA-CDP. Promising preliminary data shows that this solvent can remove green dyes from colored PET bottles and orange dyes from poly-cotton textile over several washing steps (**Figure 2F+G**). The selective precipitation process reduces metal content, such as antimony from Sb_2O_3 used as the standard catalyst in PET production (**Figure 2H**).

Discussion

Technoeconomic Analysis (TEA) and Benchmarking with Competing Technologies shows an energy demand of about 5.2 MJ/kg for MacroCycle's process. This is more than 90% less energy is needed for our process compared with traditional virgin PET production (71 MJ/kg), and 80-90% lower than competing advanced recycling technologies, such as methanolysis (50 MJ/kg), glycolysis (32 MJ/kg), enzymolysis (28 MJ/kg)[4,12,19]. Life cycle analysis (LCA) using the same process model results in a carbon footprint of about 0.4 t_{CO2}/t_{PET}, which is significantly lower compared with virgin PET production or other advanced recycling (3-4 t_{CO2}/t_{PET}). This is based on an average CO_2 emission factor for electricity generation in several suitable US states (NY, NH, WA, CA) of 0.048 kg_{CO2}/MJ. The model also accounts for scope 3 emissions from solvent and catalyst production and trucking transportation over 400 miles. Energy and CO_2 emission savings can be further bolstered by fully electrifying with renewable energy sources, thus achieving zero carbon emissions recycling. Similar to the energy performance, MacroCycle's process can offer significant emission reduction compared with other competing recycling technologies. Cost for heating and cooling solvents are major cost drivers of this process, which is why a minimization of solvent use, increase in concentration and reduction in temperatures and distillation efforts is desired.

Conclusions & Recommendations

MacroCycle's advanced recycling technology can greatly improve Plastic Circularity and establish the United States as a leader in recycling technologies. MacroCycle's process has the potential to convert and upcycle 90% of the 110 million tons / year unrecycled PET, polyester, polyamide, and polyurethane plastics into high molecular weight "virgin grade" polymers, and do so with lower energy demand and emissions compared with fossil based plastic and other recycling technologies. This process can also improve health of Americans by replacing the production plastic from polluting fossil resources. Disadvantaged communities living close to petrochemical factories will see healthier outcomes. Our improved recycling will mitigate leakage of plastics into waterways, which eventually ends up in fish and foods as microplastics. Profit margins from our process are expected to stimulate plastic collection. Collaboration with academic institutions and researchers, such as the REMADE community, can greatly support MacroCycle's technology development with experimental facilities and analytical expertise. MacroCycle is always looking for collaborators.

Acknowledgements

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Dr. Jan-Georg Rosenboom is co-founder and CTO of MacroCycle Technologies. He is a sustainable plastics expert with 10 years in polymer chemistry and process engineering. He obtained a PhD from ETH Zurich specializing in Ring-Opening Polymerization first for PEF and then for PET polymers, which formed the basis for MacroCycle's technology. He worked with SULZER ChemTech on process scaleup of the PEF synthesis technology after his PhD, until moving to MIT for postdoctoral work with Prof. Robert Langer before spinning out MacroCycle. He has published 18 papers with >2000 citations, 2 patents, and served as a plastics consultant for Apple, Henkel, and venture capital firms. He has won science outreach and public speaking awards, and gave 2 TEDx talks, including one on this technology: "Why plastic recycling is broken - and how to fix it".