Transforming the Science and Technology of Plastics Recycling

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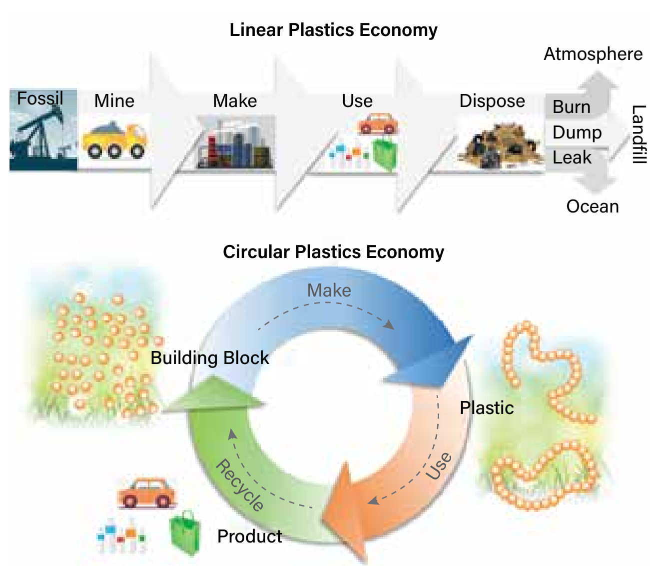
Finding solutions to the plastic waste problem will require public-private partnerships, innovation in deconstruction and upcycling technologies, and the invention of new recyclable-by-design materials.

Plastics have revolutionized modern life, but our reliance on these inherently nondegradable materials is causing a global pollution crisis *(1)*. Plastics manufacturing is predicted to account for 20% of global petroleum consumption in 2050, contributing substantially to greenhouse gas (GHG) emissions and carbon pollution *(2)*. Of the nearly 5 billion m.t. of plastics that have been discarded across the globe in the past decades, only 600 million m.t. have been recycled. Research and development (R&D) into new technologies is required to mitigate this problem and protect the environment from further harm.

To address these problems, and as part of the U.S. Dept. of Energy's (DOE's) Plastics Innovation Challenge, the National Renewable Energy Laboratory (NREL) is leading a new public-private partnership called the BOTTLE Consortium — short for Bio-Optimized Technologies to keep Thermoplastics out of Landfills and the Environment. The consortium was created to find solutions to the plastic waste problem and to enable the transition to a circular economy for polymers (Figure 1) *(3)*.



▲ **Figure 1.** Single-use plastic products must be phased out to transition from a linear economy to a circular economy.

Supported by the DOE's Bioenergy Technologies Office and Advanced Manufacturing Office, BOTTLE comprises industry and university members, government research laboratories, and other public and private agencies. The consortium's science leadership team consists of leading researchers from academia and national laboratories, including Eugene Chen (Colorado State Univ.), Yuriy Román-Leshkov (Massachusetts Institute of Technology), Jennifer DuBois (Montana State Univ.), Linda Broadbelt (Northwestern Univ.), John McGeehan (Univ. of Portsmouth), Meltem Urgun-Demirtas (Argonne National Laboratory), Taraka Dale (Los Alamos National Laboratory), Gregg Beckham (NREL), Adam Guss (Oak Ridge National Laboratory), and Chris Tassone (Stanford Linear Accelerator Laboratory).

BOTTLE's vision is to deliver selective, scalable technologies that enable cost-effective recycling and upcycling with high energy efficiencies. The mission is to develop robust processes to upcycle existing waste plastics and develop new, biobased plastics that are recyclable-by-design (RBD). To fulfill this vision and mission, the consortium is pursuing four long-term goals:

• develop selective, scalable processes to deconstruct and upcycle today's plastics

• redesign tomorrow's plastics to be RBD from biomass and waste plastic feedstocks

• work with industrial partners across the value chain to catalyze the plastics circular economy

• leverage investments from the DOE in analysis-guided R&D, integrated process development, chemical and biological catalysis, materials science, characterization, and modeling.

With the diverse team of experts and world-class facilities, BOTTLE is currently carrying out applied R&D to enable the design of processes for plastics deconstruction and upcycling that employ, compare, and combine multiple modes of catalytic transformations toward realistic process innovations. Concurrently, the team is developing new RBD plastics that source building blocks from biomass and waste plastic feedstocks. In all of the studies, it will be important to utilize consistent analyses — including technoeconomic analysis (TEA) and supply-chain lifecycle assessment (LCA) — when evaluating upcycling processes. Establishing such consistent analysis techniques represents another important area of research for the consortium. This article overviews important projects in each of these research areas and describes some of the critical gaps in upcycling and redesign that must be bridged.

Using DOE seed funds in the 2020 fiscal year, the BOTTLE leadership team assembled an integrated structure with three core research tasks: deconstruction, upcycling, and redesign (Figure 2), bolstered by three cross-cutting tasks: analysis, characterization, and modeling.

The current state-of-the-art in plastics upcycling and critical gaps

The small fraction of plastics that are currently recycled (16% in 2018) are primarily downcycled, given the degradation in properties that occurs during mechanical recycling *(4)*. Mechanical recycling requires rigorous sorting and washing of the waste feedstock to provide high-quality output. As such, color-free polyethylene terephthalate (PET) bottles are one of the only attrac-

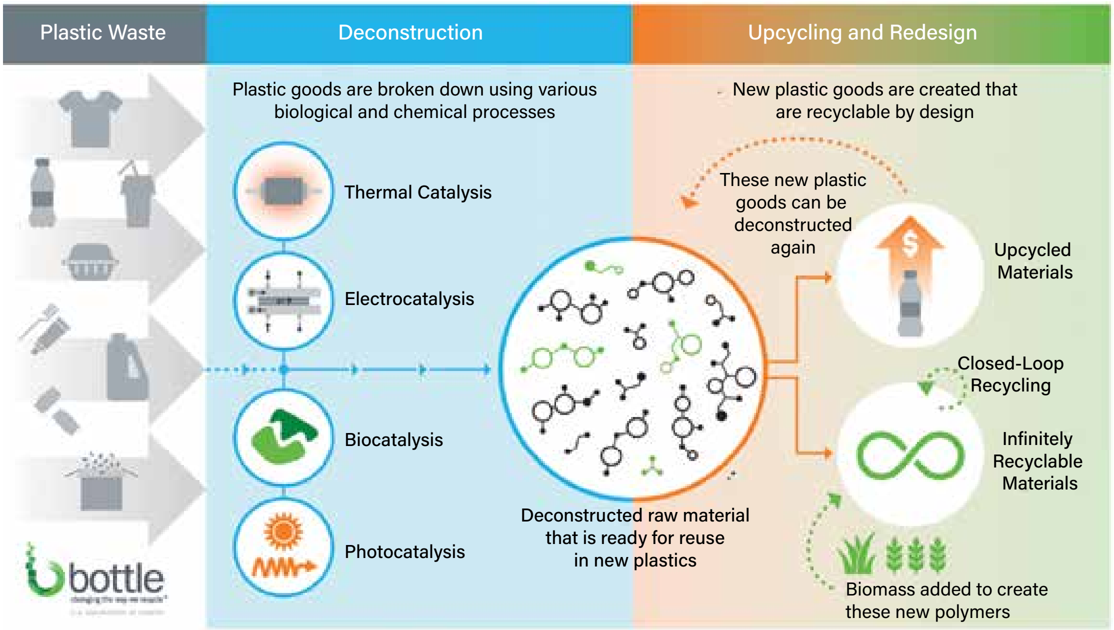


Figure 2. The BOTTLE research framework includes deconstruction of commodity plastics via chemical, catalytic, and biological transformations to intermediates that can be recycled or upcycled. New infinitely recyclable materials with biobased inputs are also being developed.

tive inputs. Alternative strategies to mechanical recycling include energy recovery, solvent processing *(5),* and advanced chemical recycling *(6).*

Energy recovery from plastics (*i.e.,* combustion to generate power) is a mature and widely used process. Industry is also scaling up solvent processing (PureCycle) *(7)*, pyrolysis (BASF, Sapporo) *(8)*, and gasification (JGC Corp.) *(9)*, which are all at high technology readiness levels (TRLs). Solvent processing uses a gas solvent and filtration to remove color, odor, and any other contaminants from a plastic waste to achieve virgin resin properties. Pyrolysis and gasification involve thermal deconstruction and typically produce fuels or plastics with the same recycling challenges. Some disadvantages of thermal-based deconstruction include contamination issues from heteroatoms, difficulties in feeding polymers to high-temperature, high-pressure unit operations, and uncertainty about the economics and sustainability impacts *(8).*

Chemical recycling of condensation polymers like PET is also being scaled based on the equilibrium nature of the polymerization and relative ease of C-O and C-N bond cleavage *(4).* However, today's chemical recycling methods for these polymers often yield detrimental waste streams, and many plastics (*e.g.,* polyolefins) cannot be chemically recycled. Selective chemical recycling has also been studied for PET and other materials, but most of this work is at a low TRL *(10).*

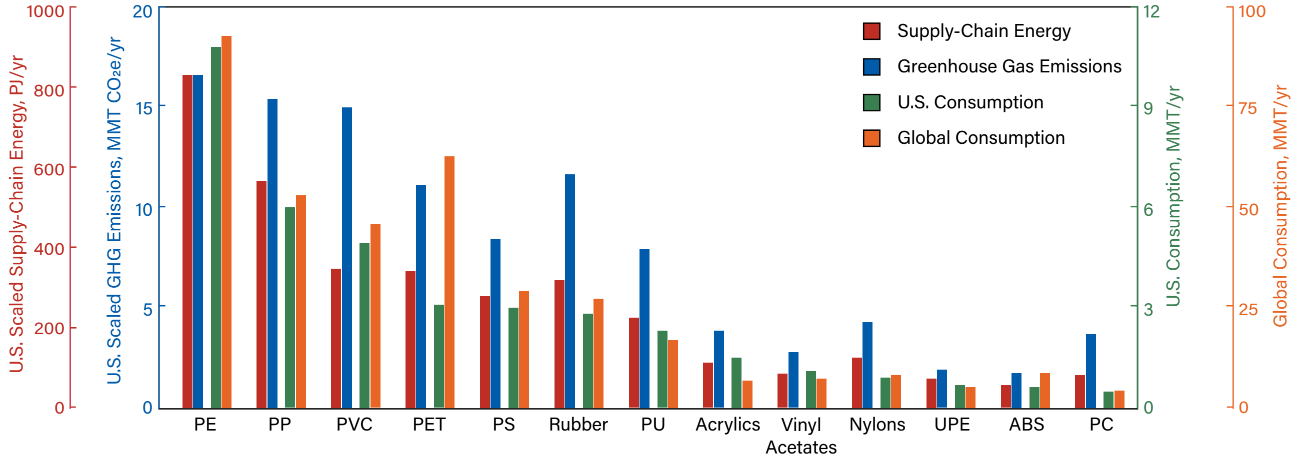
As part of the core research tasks, BOTTLE's R&D activities are targeted to address key gaps in deconstruction and upcycling to achieve:

- selective C-C bond cleavage catalysis for commodity polyolefin plastic wastes
- integrated processes for condensation/step-growth polymers, including polyesters, polyamides, and polyurethanes
- direct routes from polymer deconstruction to upcycled products.

Significant opportunity exists for the creation of new materials using biobased materials and monomers from the deconstruction of waste plastics. Such new polymers could be designed for high performance and recyclability. Many intrinsically recyclable polymers — including kinetically trapped thermoplastics and dynamically crosslinked thermosets (vitrimers or covalent adaptable networks) — were previously developed by harnessing reversible chemistries and functional group linkages *(11).* Although these reversible chemistries enable successful end-of-life processing, key issues remain, such as monomer synthesis costs and performance relative to today's plastics. In parallel, the number of potential bio- and waste-based polymers that can be synthesized has grown tremendously *(12).* For BOTTLE's redesign core research task, the team is addressing four key challenges in polymer design for real-world applications:

- achieve atom-efficient, energy-efficient, and selective polymer circularity
- combine chemical recyclability and lifetime performance
- achieve high-performance, crystalline circular polymers as polyolefin replacements
- overcome challenges with the economics and the vast scope of bio- and waste-based monomers.

Analysis-guided R&D. The BOTTLE team used the supply-chain modeling tool, Materials Flows through Industry (MFI), to estimate the supply-chain energies and GHG emissions of 13 plastics (Figure 3) *(13).* The analysis also included data for the U.S. and global consumption of each plastic. These data form the basis for BOTTLE's R&D portfolio from an energy and scale perspective. For research tasks related to deconstruction and upcycling, we compare energy,



▲ **Figure 3.** The supply-chain modeling tool, Materials Flows through Industry (MFI), was used to analyze the U.S. plastics consumption of the top 13 plastics: polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polystyrene (PS), rubber, polyurethane (PU), acrylics, vinyl acetates, nylons, unsaturated polyester (UPE), acrylonitrile-butadiene-styrene (ABS), and polycarbonate (PC).

economics, GHG emissions, and carbon recovery to virgin materials manufacturing *(14)*. For research related to redesign, we aim to replace the polymers in Figure 3 with RBD plastics and compare the energy and emissions of manufacturing and recycling of the RBD polymers to virgin plastics.

The following sections outline some of the ongoing projects within the BOTTLE consortium that fall within the research framework outlined in Figure 2.

Deconstruction of PET with enzyme catalysis

Enzymes are a type of biological catalyst that could be harnessed for low-energy recycling. Widescale deployment of enzyme-based recycling could allow us to reduce our growing requirements for fossil resources. In previous work *(15),* researchers from the Univ. of Portsmouth and NREL characterized the structure and function of PETase, secreted by the bacterium, *Ideonella sakaiensis,* originally discovered in a Japanese recycling center *(16)*. This enzyme has the remarkable ability to deconstruct one of the most commonly polluting thermoplastics, PET, found in single-use packaging and textiles. This naturally occurring enzyme is capable of breaking the ester bonds that connect the two monomers, ethylene glycol and terephthalic acid, which together form the polymer chains that provide PET with its durable and lightweight properties.

More recently, the team studied an enzyme called MHETase, secreted from the same bacterium. Crystal structures solved at the Diamond Light Source synchrotron facility were combined with bioinformatics, biochemistry, and molecular simulations to provide detailed insight into the function of this partner enzyme *(17)*.

Analyzing the activity of hundreds of reactions at varying concentrations and ratios, the team revealed that MHETase interacts synergistically with PETase to enhance the deconstruction of PET. These results inspired the design of a chimeric enzyme (Figure 4) that produced hydrolysis rates up to six-fold higher than PETase alone. Translating our growing understanding of naturally evolved breakdown processes into the laboratory offers great potential for the engineering of industrially relevant enzyme systems for the circular recycling of plastics.

Recyclable-by-design polymers

Our design of RBD circular polymers (CPs) aims for closed-loop lifecycles that progress from monomer to polymer and then back to monomer. A key challenge of this design includes innovation in monomer structure that enables not only efficient polymerization to polymers with properties rivaling today's polymers, but also selective depolymerization to recover the monomers with high yield and purity.

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However, these contrasting performance properties are difficult to combine in a single monomer structure and researchers find it extremely challenging to improve both properties concurrently. For example, high-ceiling-temperature (HCT) polymers exhibit high polymerizability and good performance properties, but poor chemical recyclability. Low-ceiling-temperature (LCT) polymers exhibit high chemical recyclability but lack robust performance properties.

The BOTTLE consortium is creating an HCT/LCT monomer design concept that hybridizes contrasting parent monomer structures in an offspring monomer that can unify conflicting polymerizability and performance properties. For example, structural hybridization of the HCT-7 lactone with the LCT-5 lactone yields a 5/7 bicyclic lactone hybrid. This hybrid is advantageous because the seven-membered ring renders high polymerizability, the five-membered ring ensures high recyclability (>95%), and the in-chain six-membered ring creates good performance properties — *e.g.*, both the glass-transition and melting-transition temperatures are roughly 200°C higher than the parent homopolymers or their copolymers (Figure 5) *(18)*.

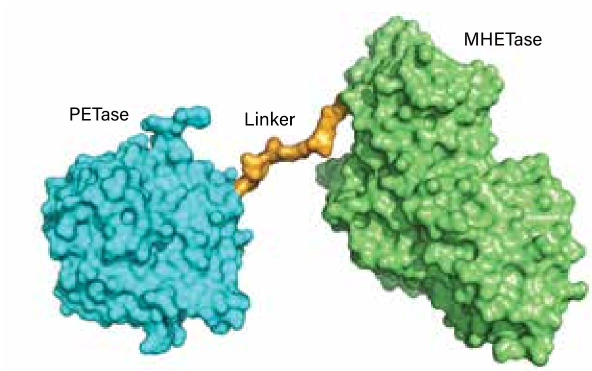

Figure 4. The PETase-MHETase chimera enzyme has an amino acid linker (orange) that connects PETase (blue) to MHETase (green).

Recycling of polyolefins by C-C bond hydrogenolysis

Polyolefin plastics used in plastic bags, bottles, and food packaging are among the most difficult to break down. The strong carbon-carbon bonds in polyolefins like polyethylene and polypropylene often require high temperatures to degrade (400–800°C) and harsh reaction conditions for processing. Like polyolefins, lignin — the organic polymer in the cell walls of biomass — also contains strong carbon-carbon bonds. Inspired by efforts in deconstructing lignin with noble metal catalysts, the BOTTLE team at the Massachusetts Institute of Technology (MIT) turned to these same systems to cleave the C-C bonds in polyolefins *(19)*.

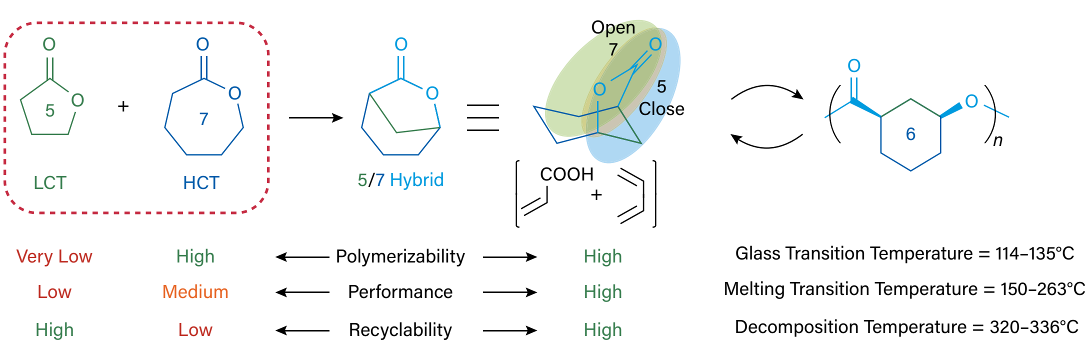

Figure 5. This schematic illustrates the design of a lactone hybrid monomer that can be derived from abundant, inexpensive building blocks. The monomer has high polymerizability via ring opening of the high-ceiling-temperature (HCT)-7 ring. The resulting polymer has full chemical recyclability and good performance properties.

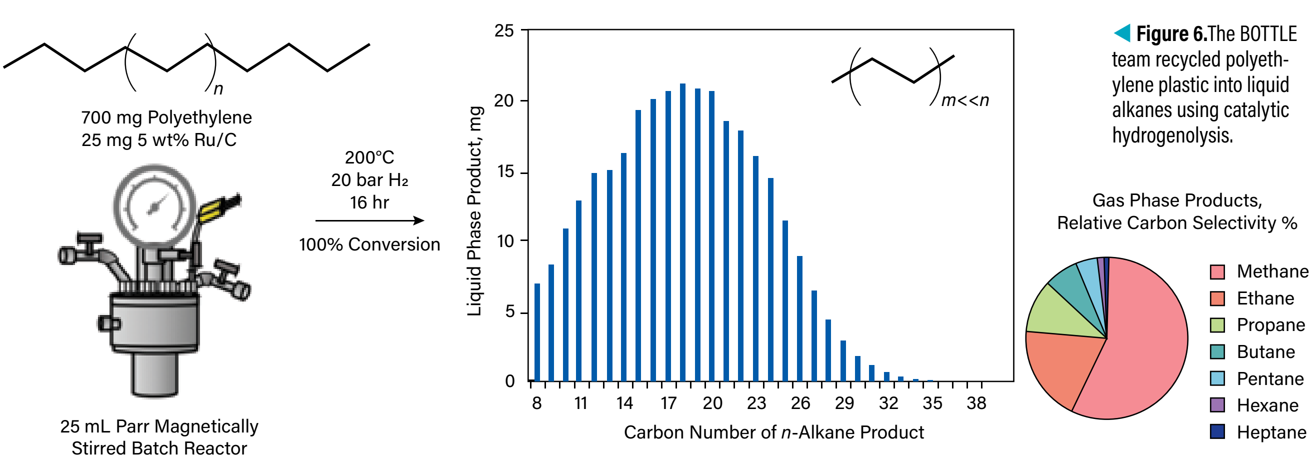

Figure 6. The BOTTLE team recycled polyethylene plastic into liquid alkanes using catalytic hydrogenolysis.

Ruthenium nanoparticles supported on carbon stood out as an active and selective catalytic material for the cleavage of C-C bonds in polyethylene. Using this catalyst in combination with hydrogen gas and heat, the researchers were able to convert polyolefin plastic into liquid alkanes under relatively mild conditions (200°C) in the absence of solvent (Figure 6).

These liquid alkanes could be used for a variety of applications or further processed to enable closed-loop polymer recycling. The researchers were able to produce alkanes from not only model polyethylene, but from real post-consumer plastic bottles as well. Further, the researchers found that the catalyst could be recovered and recycled without any additional regeneration procedure.

The implementation of a low-temperature and solvent-free process to valorize polyolefin waste is a promising step toward economical solutions to the plastic waste challenge. The team is currently working to expand the scope of plastic substrates that can be deconstructed using this method, as well as modifying the catalyst to further improve activity and selectivity.

Closing thoughts

Significant innovation is required to solve the plastic waste crisis. The BOTTLE Consortium brings together a world-class group of scientists and engineers to not only address today's waste problems but to also invent the sustainable polymers of tomorrow. As a result of these interdisciplinary research capabilities, the BOTTLE team can tackle the problems on a fundamental level using deep science, and then transition to solutions using applied science and engineering. Our strategy combines science and engineering with analysis-driven R&D. Overcoming the dual challenges of the efficient deconstruction of today's plastics and the creation of new, sustainable materials is the hallmark of the BOTTLE Consortium. CEP

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