BIOENERGY TECHNOLOGIES OFFICE (BETO)

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

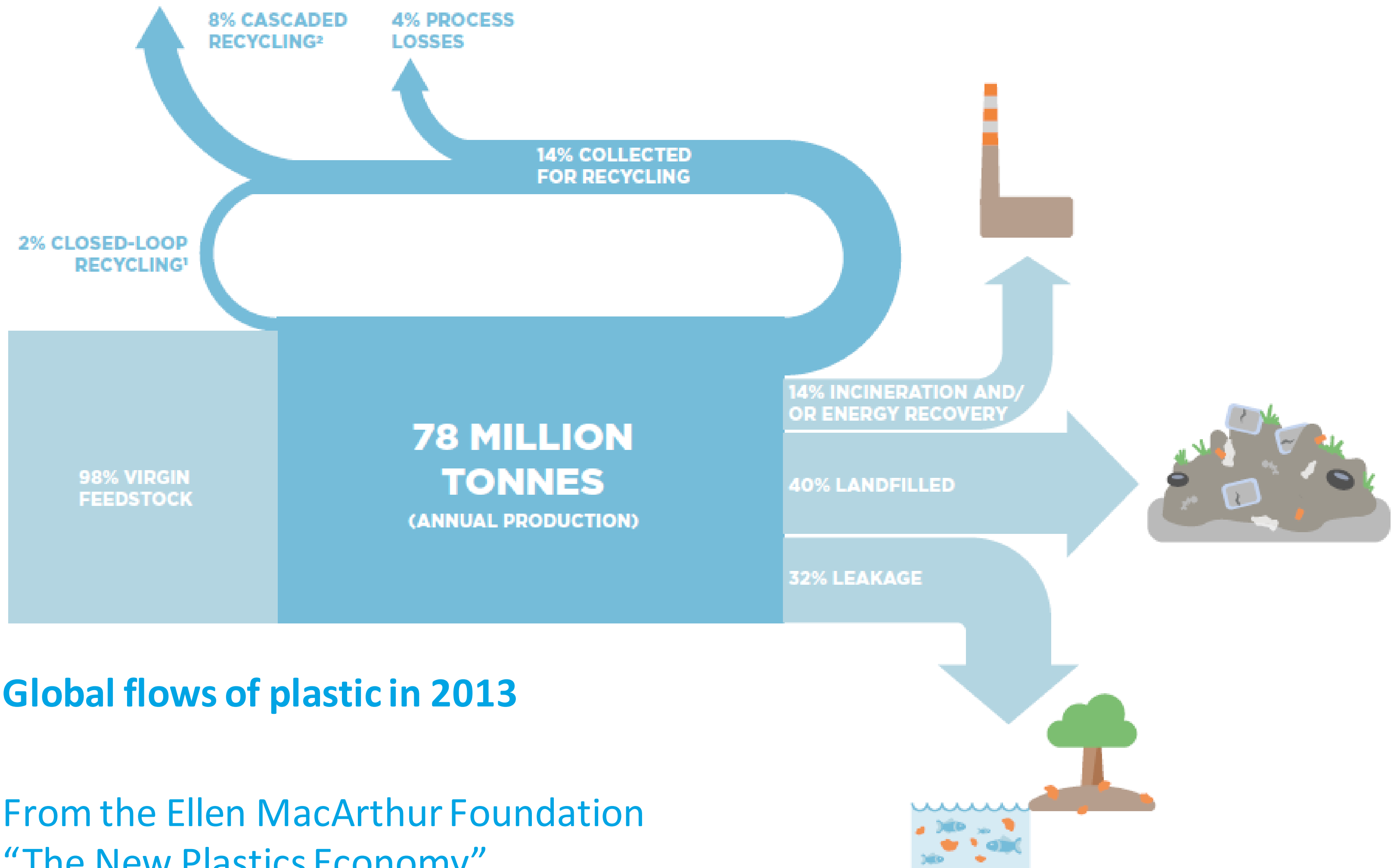
Recycling and Upcycling Plastics

March 6th 2019

Jay Fitzgerald

BETO Peer Review

The Challenge: A linear carbon economy for plastics



Global flows of plastic in 2013

From the Ellen MacArthur Foundation
"The New Plastics Economy"

1 Closed-loop recycling: Recycling of plastics into the same or similar-quality applications
2 Cascaded recycling: Recycling of plastics into other, lower-value applications

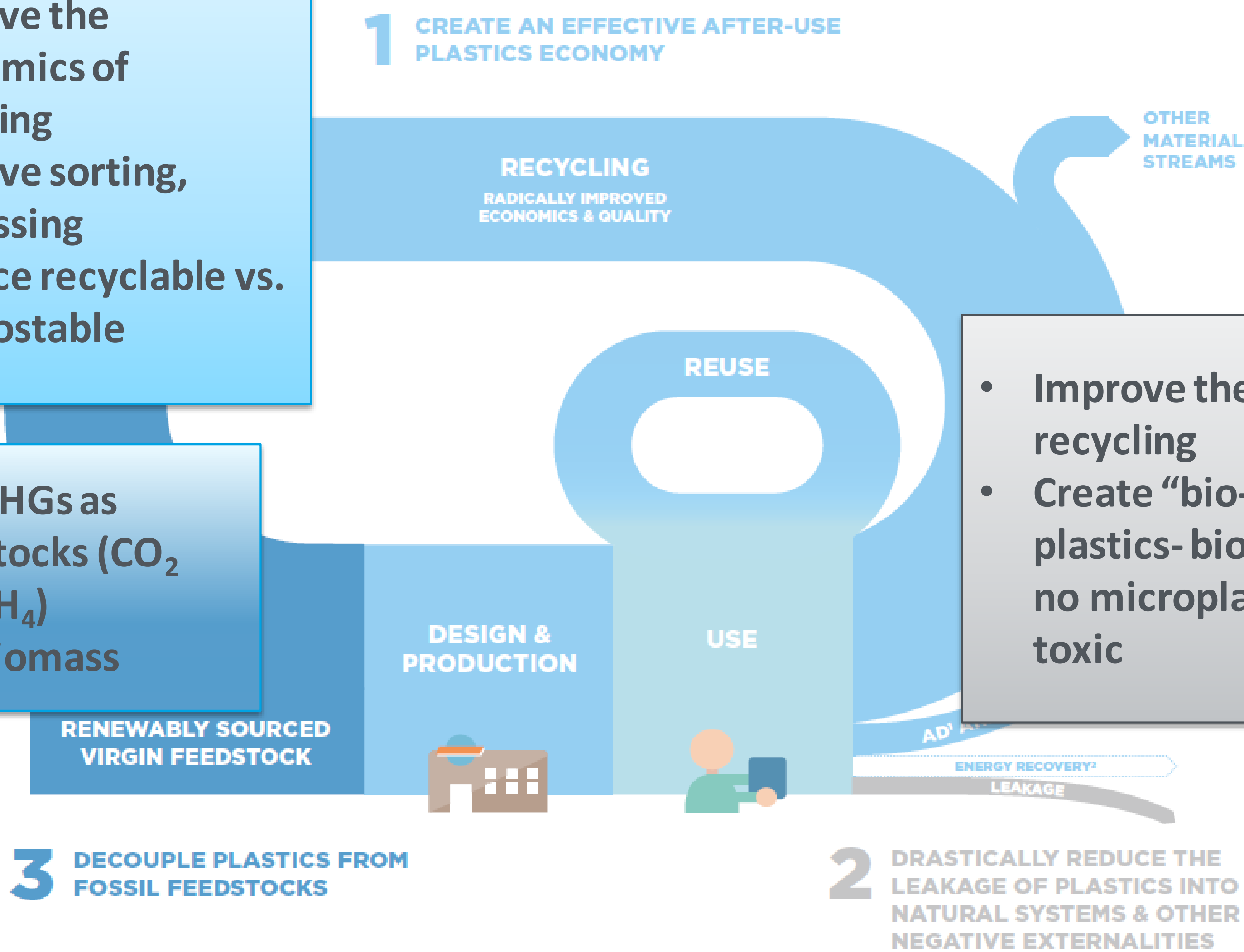
Source: Project Mainstream analysis - for details please refer to Appendix A in World Economic Forum, Ellen MacArthur Foundation and McKinsey & Company, *The New Plastics Economy — Rethinking the future of plastics*, (2016, http://www.ellenmacarthurfoundation.org/publications).

The Solution: A circular carbon economy for plastics

- Improve the economics of recycling
- Improve sorting, processing
- Balance recyclable vs. compostable

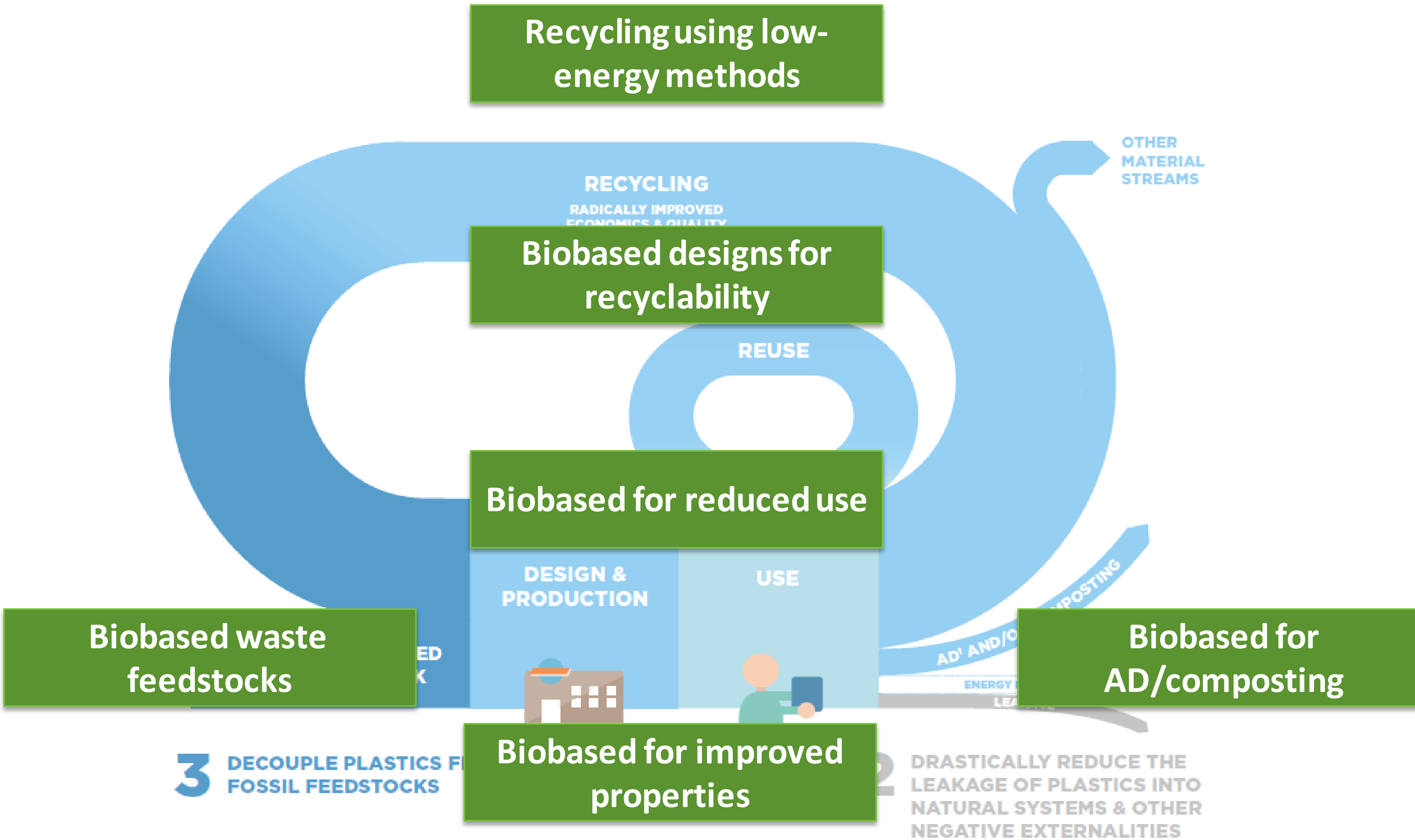
- Use GHGs as feedstocks (CO_2 and CH_4)
- Use biomass

- Improve the value of recycling
- Create "bio-benign" plastics- biodegradable, no microplastics, non-toxic



1 Anaerobic digestion
2 The role of, and boundary conditions for, energy recovery in the New Plastics Economy need to be further investigated

The BETO Opportunity: A circular carbon economy



1 Anaerobic digestion

2 The role of, and boundary conditions for, energy recovery in the New Plastics Economy need to be further investigated

Why are biobased approaches good for a circular carbon economy?

- Biobased feedstocks are renewable, and when collected properly, are sustainable
- Biobased encourages creative design and improved properties: capitalize on the highly functionalized nature of biomass to access products that would be too expensive to make from petroleum (e.g. PDO)
- Biobased can play a role in recyclability: designs for modern recyclables include highly functionalized monomers (e.g. vitrimers)
- Biobased can be amenable to anaerobic digestion or composting (e.g. PLA)
- Biobased approaches to plastics degradation can be used for breaking down intractable mixtures

Biobased waste feedstocks

Biobased for reduced use

Biobased for improved properties

Biobased for recyclability

Biobased for AD/composting

Recycling using low-energy methods

Plastics

Design

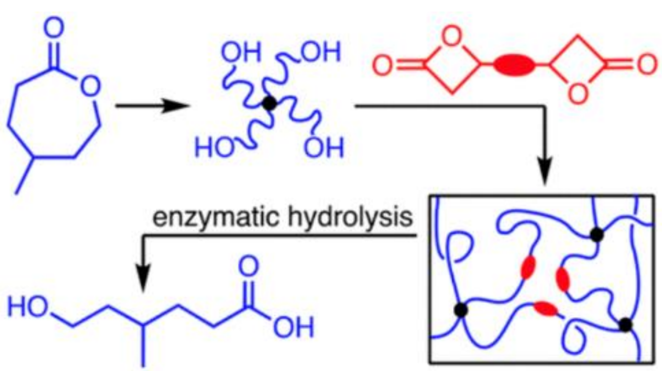
Deconstruction

Opportunities for BETO in Design and Deconstruction

Opportunity: Design

Goal: New biomass-derived plastics with:

- Superior properties
- Recyclability
- Less material



http://hillmyer.chem.umn.edu/publications

Opportunity: Deconstruction

Goal: New chemical and biological methods to break plastic down and upgrade it into new materials

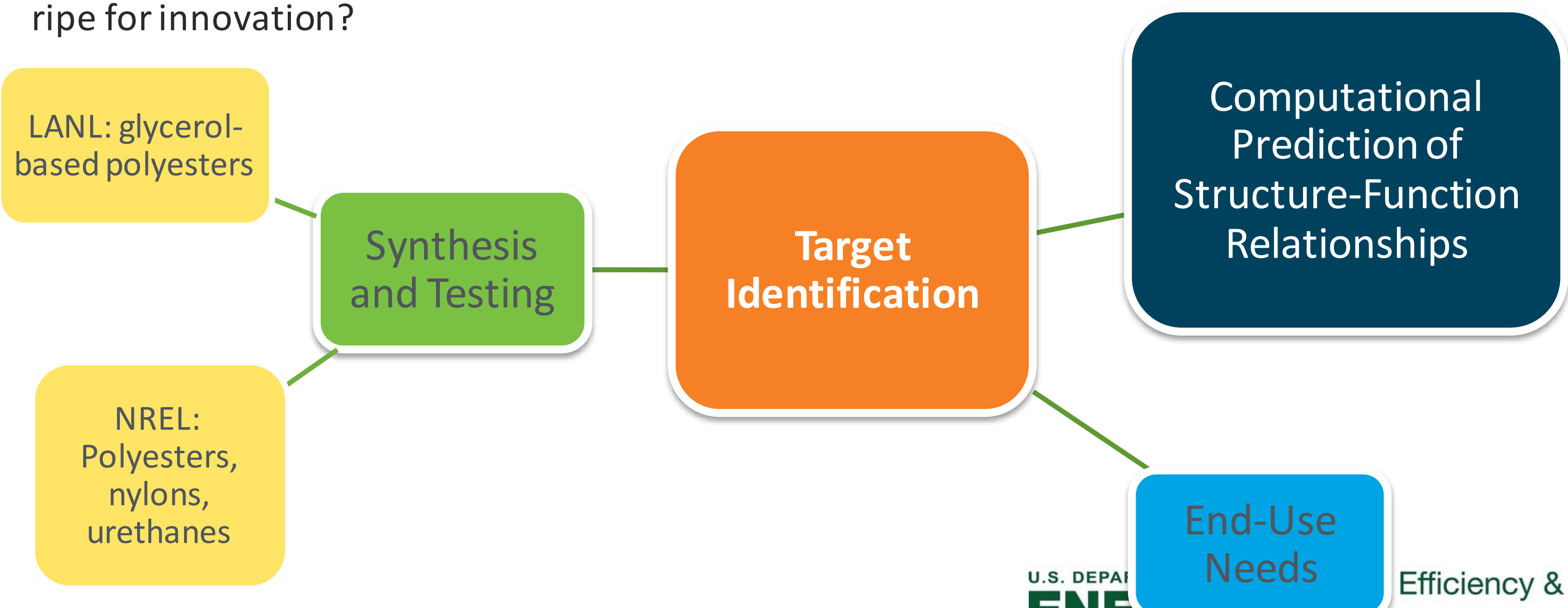
Microb. Biotechnol. 2015, DOI: 10.1111/1751-7915.12312)

Environ. Sci. Technol. 2014, DOI: 10.1021/es504038a

Design Opportunity: Performance Advantaged Bioproducts

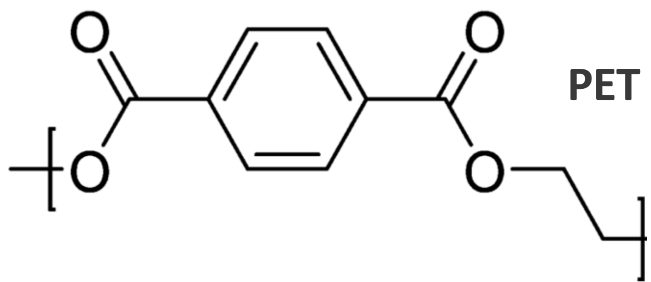
- FY18 began $1.9M mini consortium at NREL to identify novel, performance advantaged bioproducts; FY19 introduced LANL + NREL partnership
- Three focus areas that represent workshop stakeholder concerns:
  - Computational modeling to predict how biobased compounds will behave
  - High throughput screening of biobased compounds to understand what can be easily made and what
  - End Use Needs- can we look at existing products and assess what is ripe for innovation?

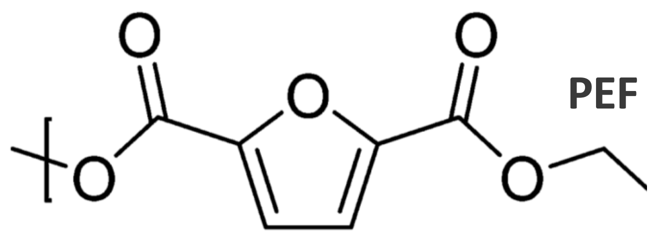
Workshop in June, 2017; report PUBLISHED (check BETO website)



Design Opportunity: Performance Advantaged Bioproducts

Soda bottles are thicker than water bottles in part because PET has a low O_2 barrier





Less plastic -> less waste

New properties -> new applications

https://www.avantium.com/yxy/products-applications/

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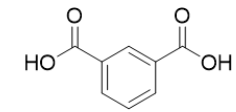
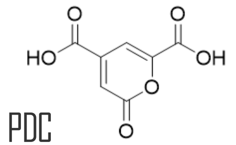
Replacing isophthalic acid in PET and polyaramids

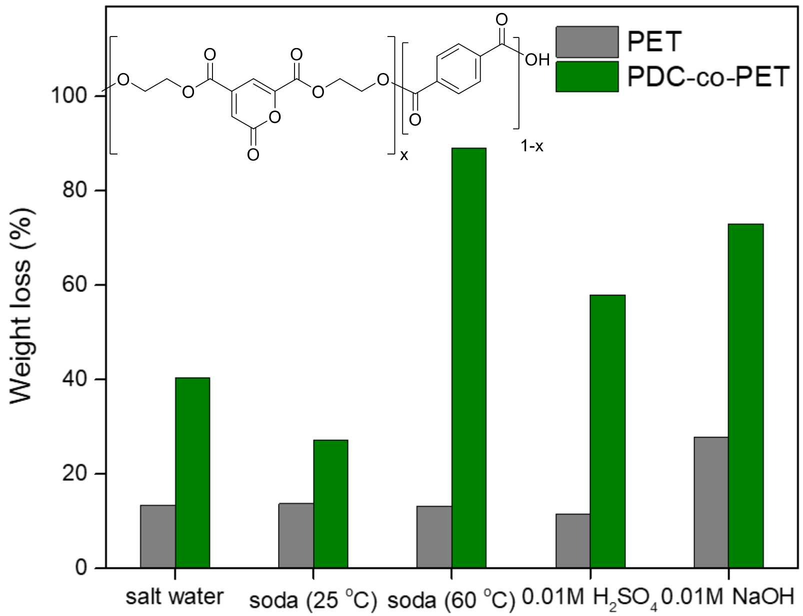
- Isophthalate used to tune PET crystallinity, for thermal barrier in Nomex
- **PABP need (PET): Enabling facile chemical recycling**
- **PABP need (polyaramid): Melt processing is challenging**
- **Hypothesis**: Lactone in PDC can offer route to facile chemical recycling
- **Bio-based monomer**: Pyrone-dicarboxylic acid (PDC) for isophthalate

Isophthalic acid

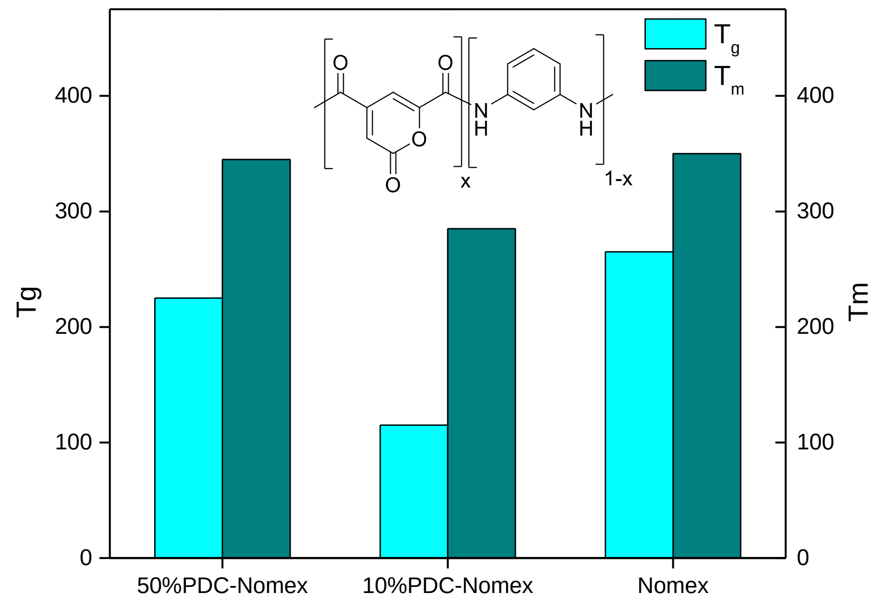




PDC



- **Lower resistance of PET-PDC enables facile recycling at same properties**

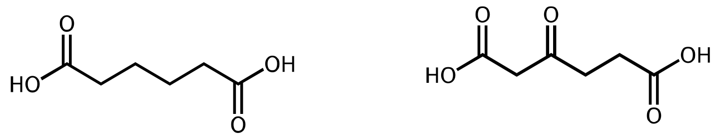


- Consistent thermal properties with Nomex, lower T_g leads to easier processing

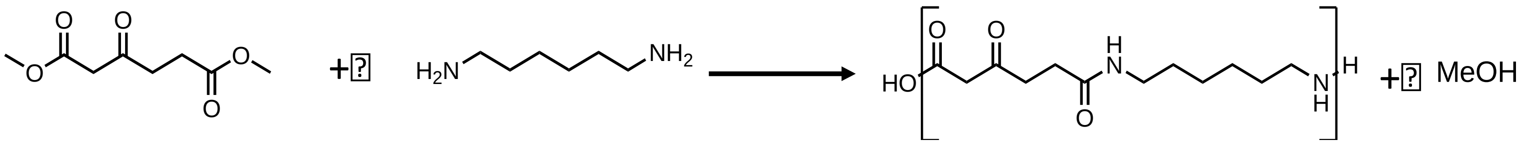
Courtesy of Gregg Beckham. Hoyt *et al.* in preparation

Design Opportunity: Performance Advantaged Bioproducts

ß-ketoadipic acid as a substitute for adipic acid



Adipic Acid β-ketoadipic Acid



Starting Diacid/Diester	*Glass Transition Temperature*	*Melting Temperature*	M_v *$*10^{-4}$ g/mol*	*Water Permeability* g*mm/m^2*day
Beta-keto Adipate	130	400*	5.2	8.0
Adipic Acid	60	260	3.3	10.1

Replacing adipic acid with ß-ketoadipic acid (derivable from sugars or aromatics) increases thermal properties, molecular weights, and lowers water permeability

Ketone likely induces rigidity in the backbone; currently employing computational approaches (molecular dynamics) to understand fundamental reason for property improvements

Beckham et al.

Johnson et. al Upcoming

Future Directions in Plastics Design at BETO

Questions moving forward:

- What can we make when we are no longer limited by the constraints of a petroleum starting material? What existing products are ripe for innovation?
- How do we design the plastics of the future to make recycling efficient and cost-effective?
- How do we design plastics that enable us to use less?
- How do we prioritize recyclability vs biodegradability vs less-use vs renewable?
- Can we design "bio-benign?" (recyclable, biodegradable, no microplastics, non-toxic sub-components)

Future Directions:

- PABP Consortium is looking at plastics design, but that is not the exclusive focus of the group
- Last week BETO released an SBIR topic on plastics design
- Plastics design will continue to be a priority for BETO

Opportunities for BETO in Design and Deconstruction

Opportunity: Design

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- Superior properties
- Recyclability
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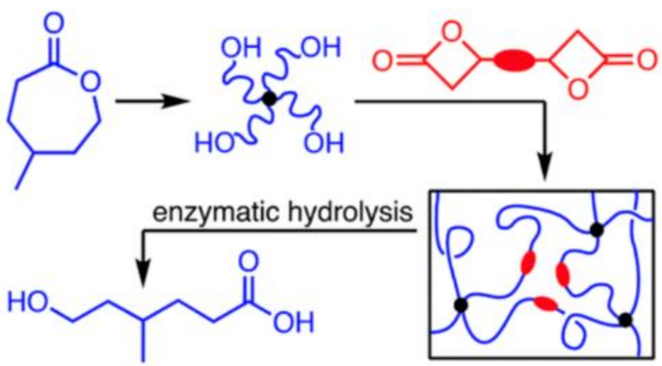

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Deconstruction Opportunity: mixed plastics

Materials: C-C Plastics

Materials: Polyesters

- PET
- Blends

Materials: Textiles & Foam

- Nylons, lactams, polyamides, polyurethanes

Challenges:

- Selective C-C chemistry
- Crystallinity
- Contamination
- Breakdown rate

Challenges:

- Selective C-O chemistry
- Contamination/ mixed streams
- Breakdown rate/ extent
- Crystallinity

Challenges:

- Selective C-O, C-N chemistry
- Contamination/ mixed streams
- Breakdown rate/ extent

Deconstruction Opportunity

Challenge: Selective C-O, C-N chemistry

- Need to break plastics down into tractable streams
- Maintain key monomer functionality

BETO competency: commercially-relevant chemistry

Microb. Biotechnol. 2015, DOI: 10.1111/1751-7915.12312)

Deconstruction Opportunity

Challenge: New, selective C-C chemistry

Environ. Sci. Technol. 2014, DOI: 10.1021/es504038a

- Selective C-C bond breaking chemistry is difficult
- Cannot directly reform monomers

BETO competency: novel organisms and catalysts

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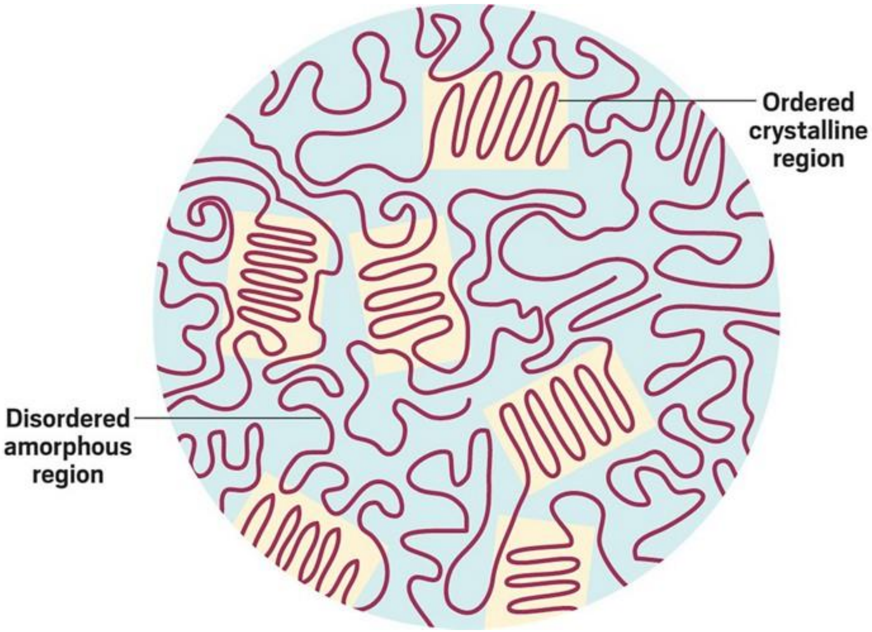
Deconstruction Opportunity

Challenge: Crystallinity



- Enzymes and catalysts can have difficulty accessing highly ordered crystalline polymers leading to slow and incomplete breakdown

BETO competency: lessons from cellulose

https://cen.acs.org/environment/sustainability/Plastics-recycling-microbes-worms-further/96/i25

Deconstruction Opportunity

Challenge: Mixed Streams

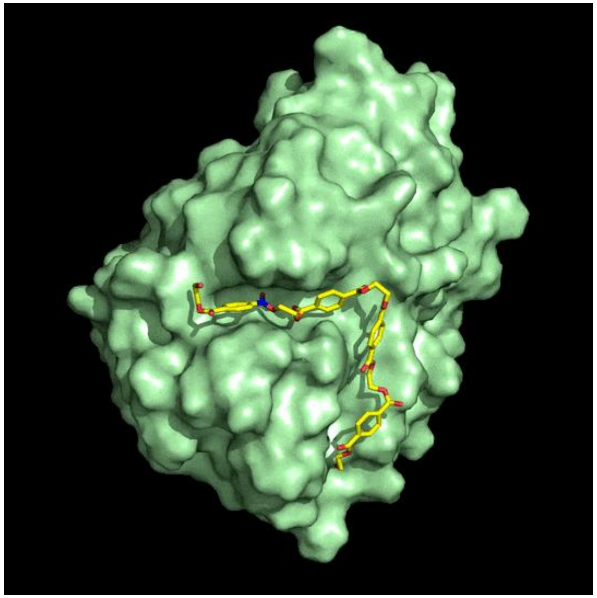
The Guardian. April 16 2018

Dirty Streams contain catalyst poisons and complex substrate mixtures

BETO competency: heterogeneous biomass valorization

Deconstruction Opportunity

Challenge: Breakdown rate/ completeness



- Current enzymes are too slow to be economically competitive
- Plastics are "new," evolutionarily speaking, so enzymes and organisms have not had incentive to evolve

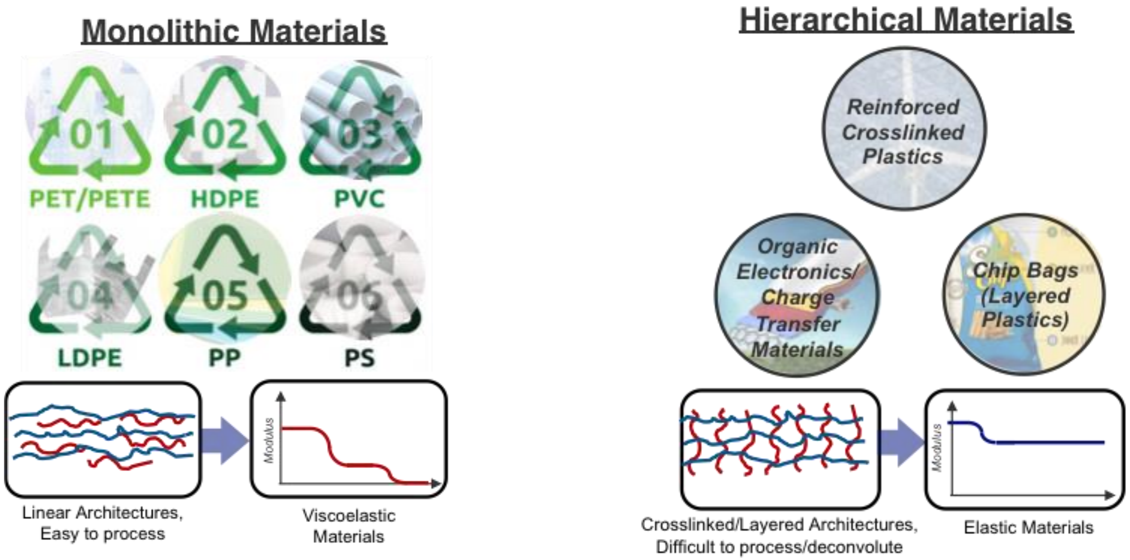
BETO competency: enzyme engineering

Credit: John McGeehan/University of Portsmouth

Watch a 360° rotation of the crystal structure of the PET-degrading enzyme (green space fill) with PET (yellow, blue, and red stick structure) docked in the active site.

Deconstruction Opportunity

Challenge: Thermosets



Can’t simply melt hierarchical materials to recover monomers

BETO competency: New polymer design

https://cen.acs.org/environment/sustainability/Plastics-recycling-microbes-worms-further/96/i25

AOP Portfolio Seed FY19

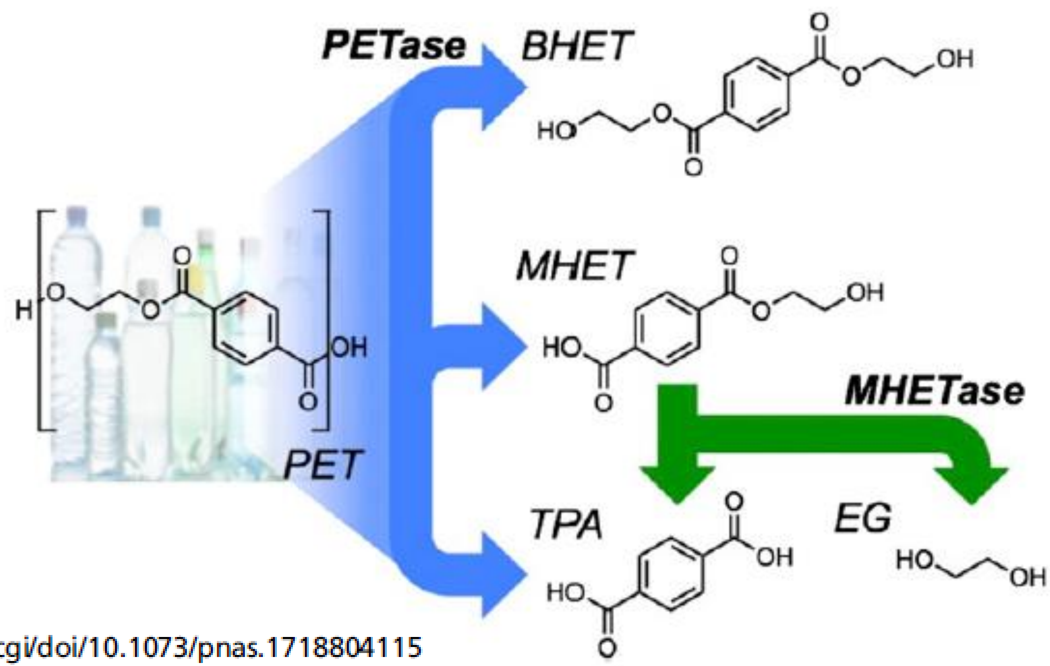
- Engineering better plastic degradation enzymes
- Builds off of highly-publicized work at the University of Portsmouth and NREL

Plastics

Scientists accidentally create mutant enzyme that eats plastic bottles

The breakthrough, spurred by the discovery of plastic-eating bugs at a Japanese dump, could help solve the global plastic pollution crisis

Damian Carrington
Environment editor



www.pnas.org/cgi/doi/10.1073/pnas.1718804115

Future Directions in Plastics Deconstruction at BETO

Questions Moving Forward:

- What is the best combination of chemical and biological treatment of plastics to maximize stream value?
- How tolerant to contaminants can these treatments be?
- How do we design a system to handle extremely heterogeneous streams?

Future Directions:

- Thinking of plastics as feedstocks
- Current SBIR topic on plastics deconstruction and upcycling

https://phys.org/news/2017-11-trash-islands-central-america-ocean.html