Challenges and Opportunities in Plastics Upcycling: The Role of Biological and Chemical Recycling

Gregg T. Beckham
National Renewable Energy Laboratory

SPC Advance
October 8th, 2019

National Renewable Energy Laboratory Scope of Mission

Sustainable Transportation

- Vehicle Technologies
- Hydrogen
- Biofuels

Energy Productivity

- Residential Buildings
- Commercial Buildings

Renewable Electricity

- Solar
- Wind
- Water: Marine Hydrokinetics
- Geothermal

Systems Integration

- Grid Integration of Clean Energy
- Distributed Energy Systems
- Batteries and Thermal Storage
- Energy Analysis

Partners

- Private Industry
- Federal Agencies
- State/Local Government
- International

National Renewable Energy Laboratory Scope of Mission

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Our group develops green processes and products from biology and chemistry

Enzymes for biofuels production

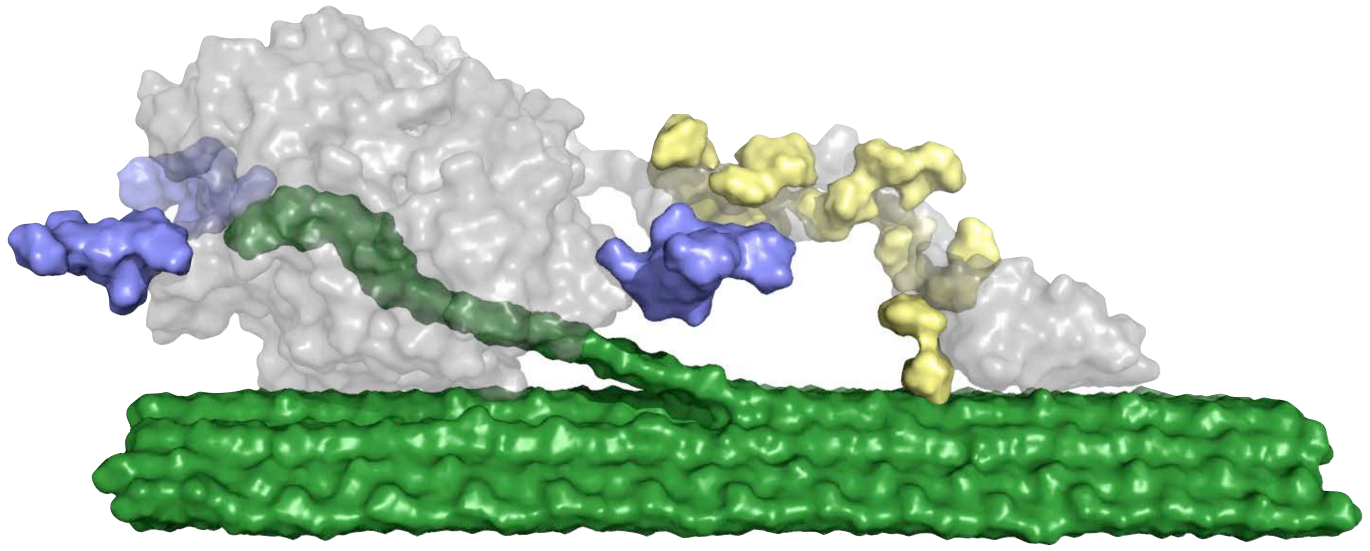


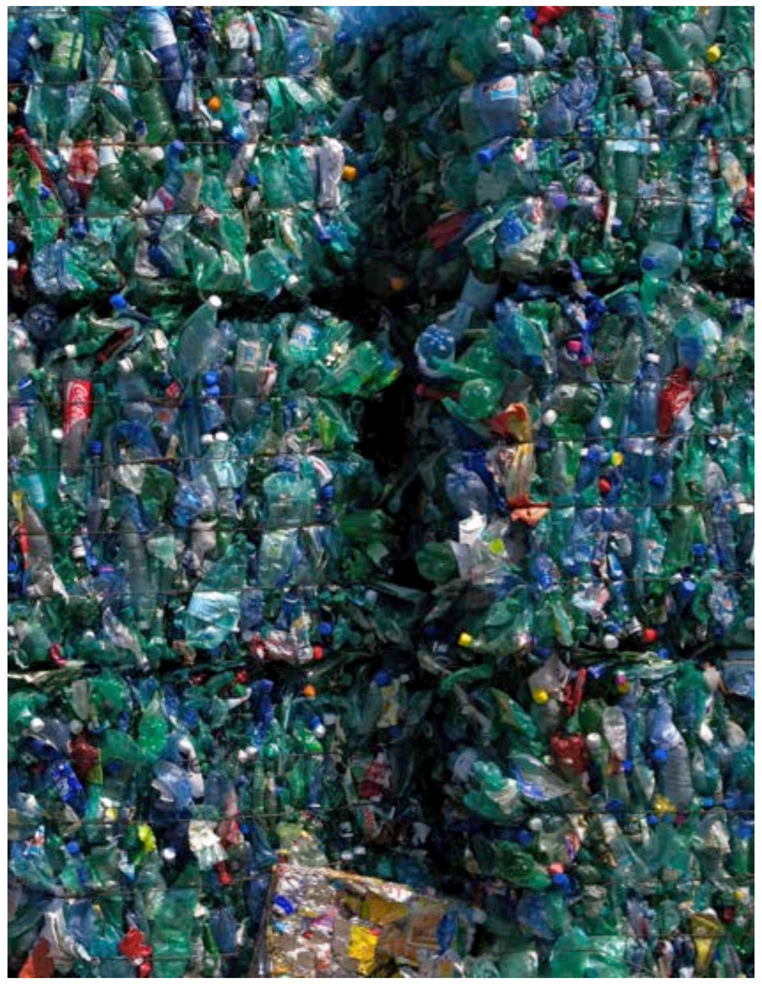
Image: M. Sandgren

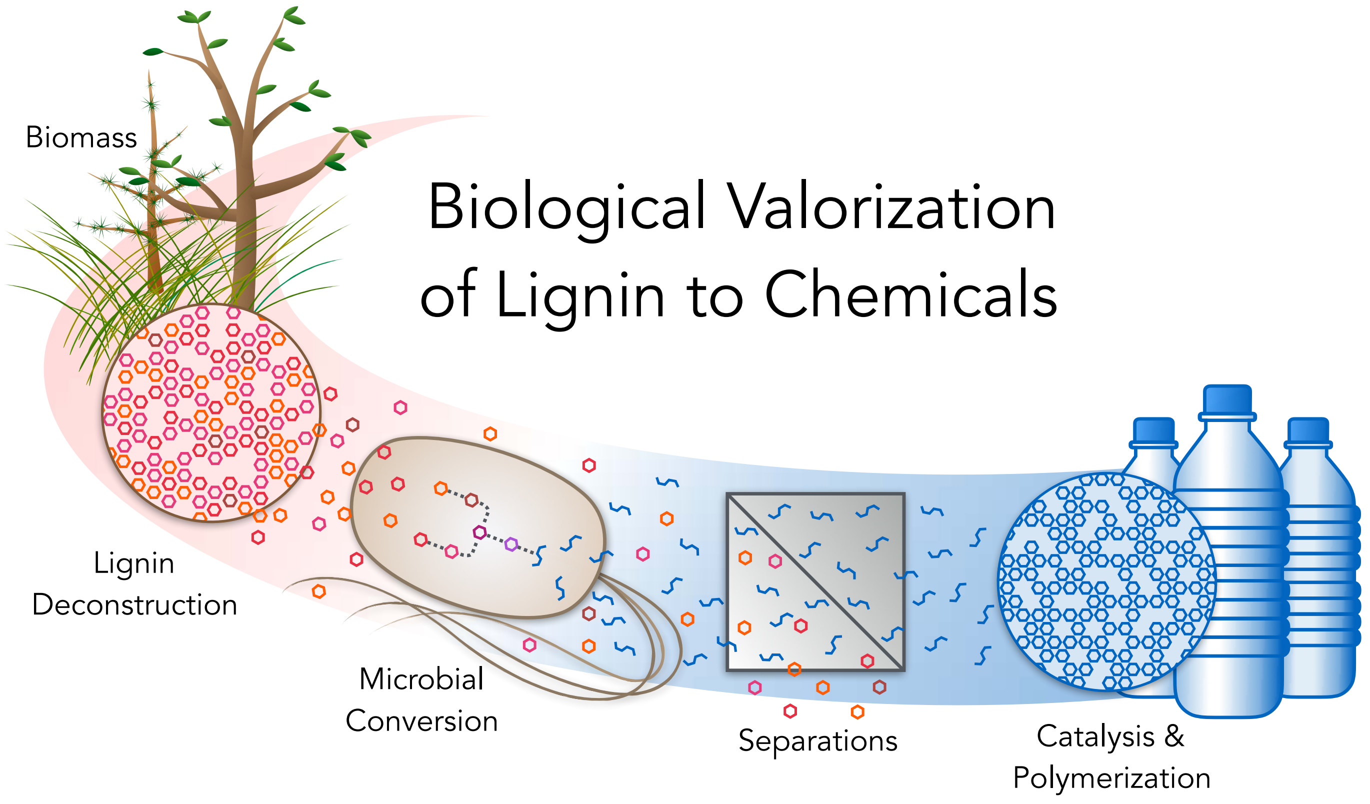
Image: S. Cragg

Upcycling plastics to enable the Circular Economy

Image: D. Kunkel

Image: CNN





New biology and chemistry to convert lignin to chemicals

G.T. Beckham *et al.*, *Curr. Opin. Biotech.* 2016

Green processes for bio-based carbon fiber

Karp *et al.*, *Science* 2017

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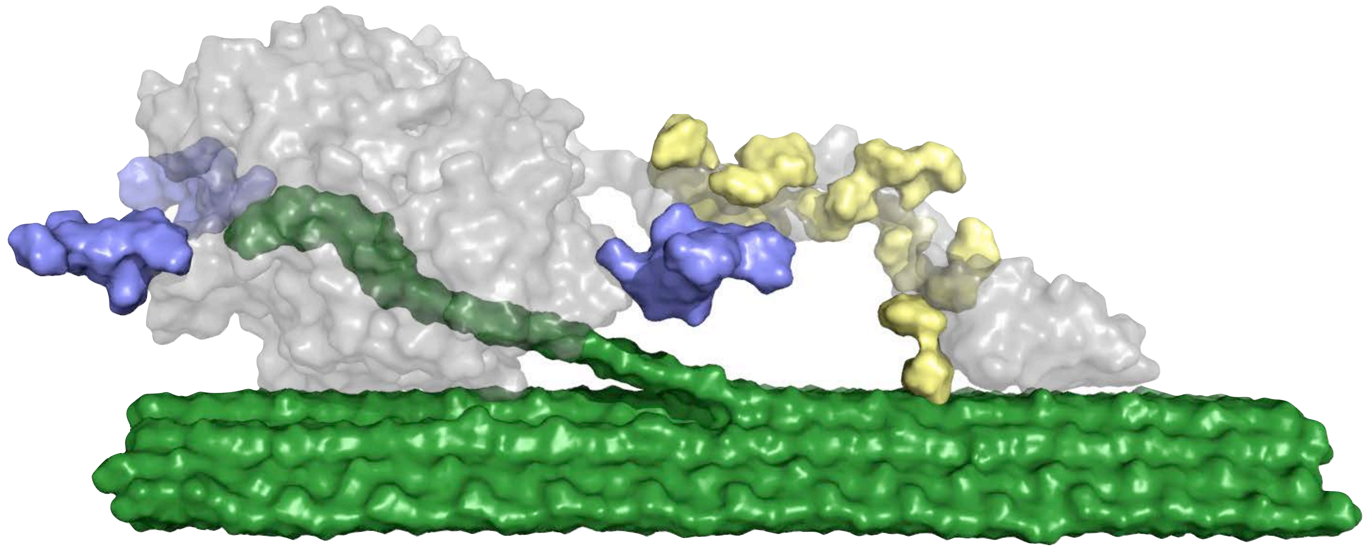

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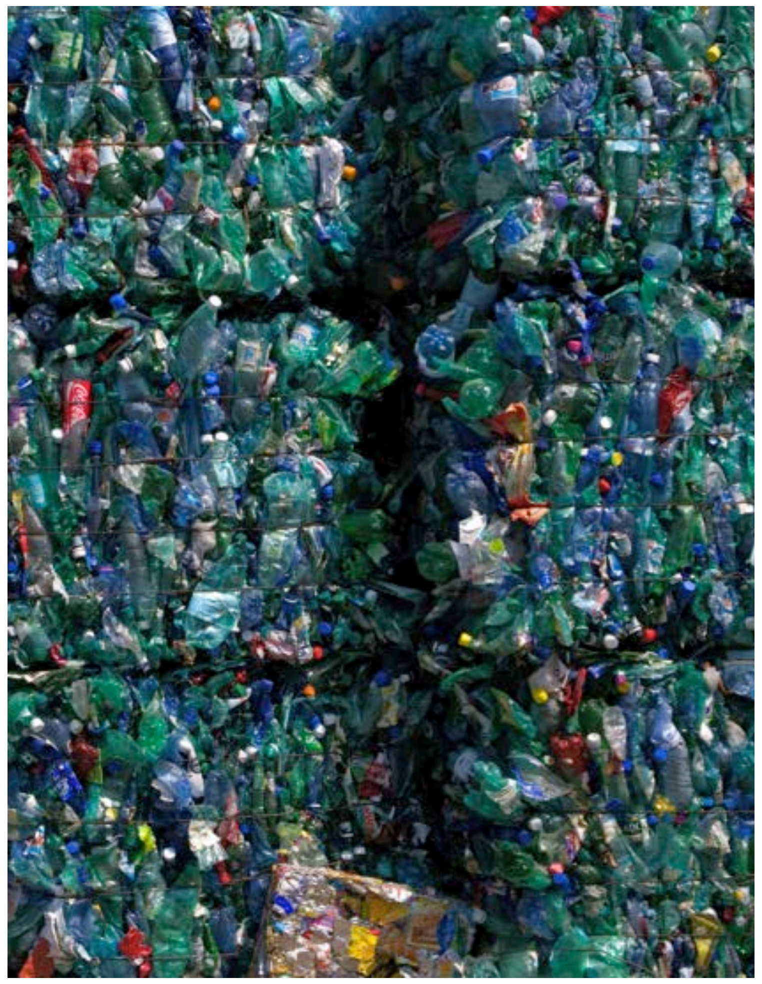

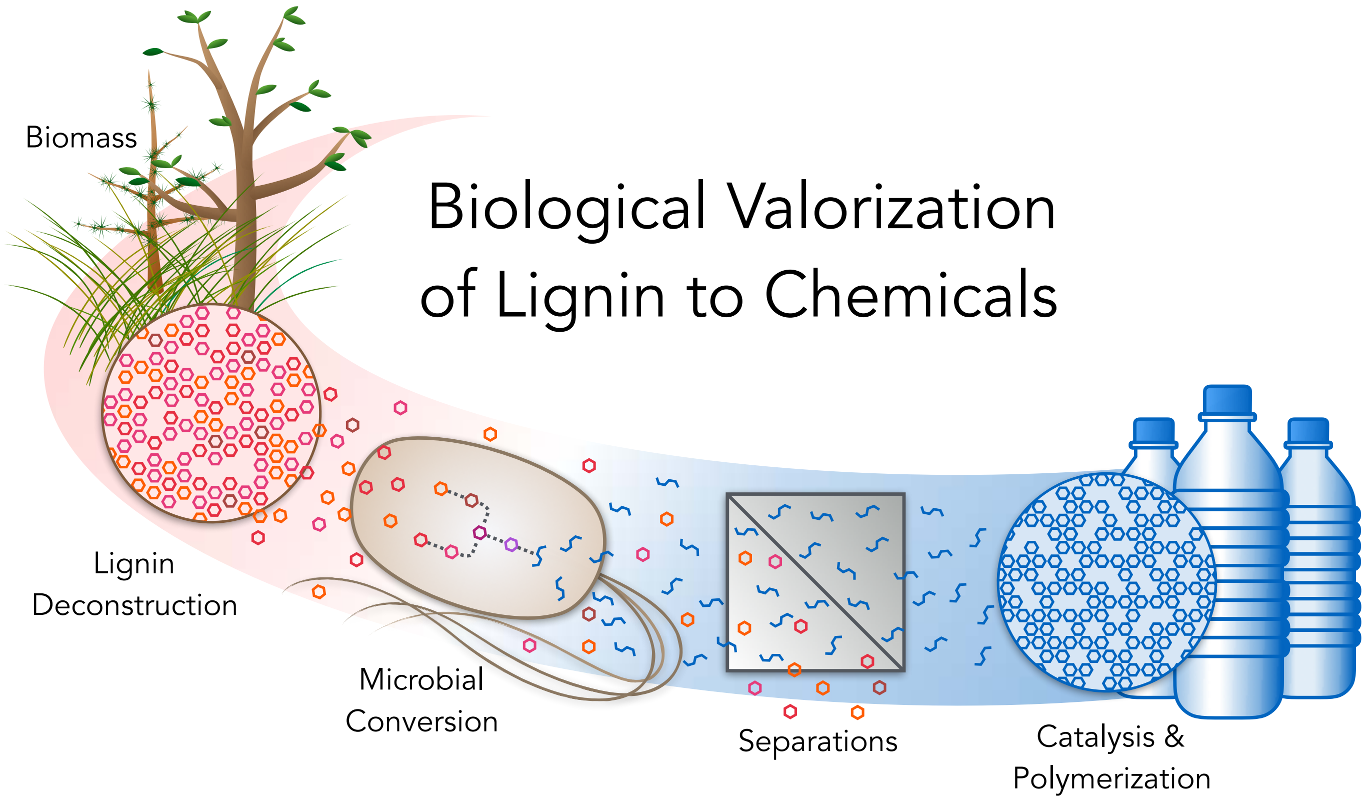

New biology and chemistry to convert lignin to chemicals

G.T. Beckham *et al.*, *Curr. Opin. Biotech.* 2016

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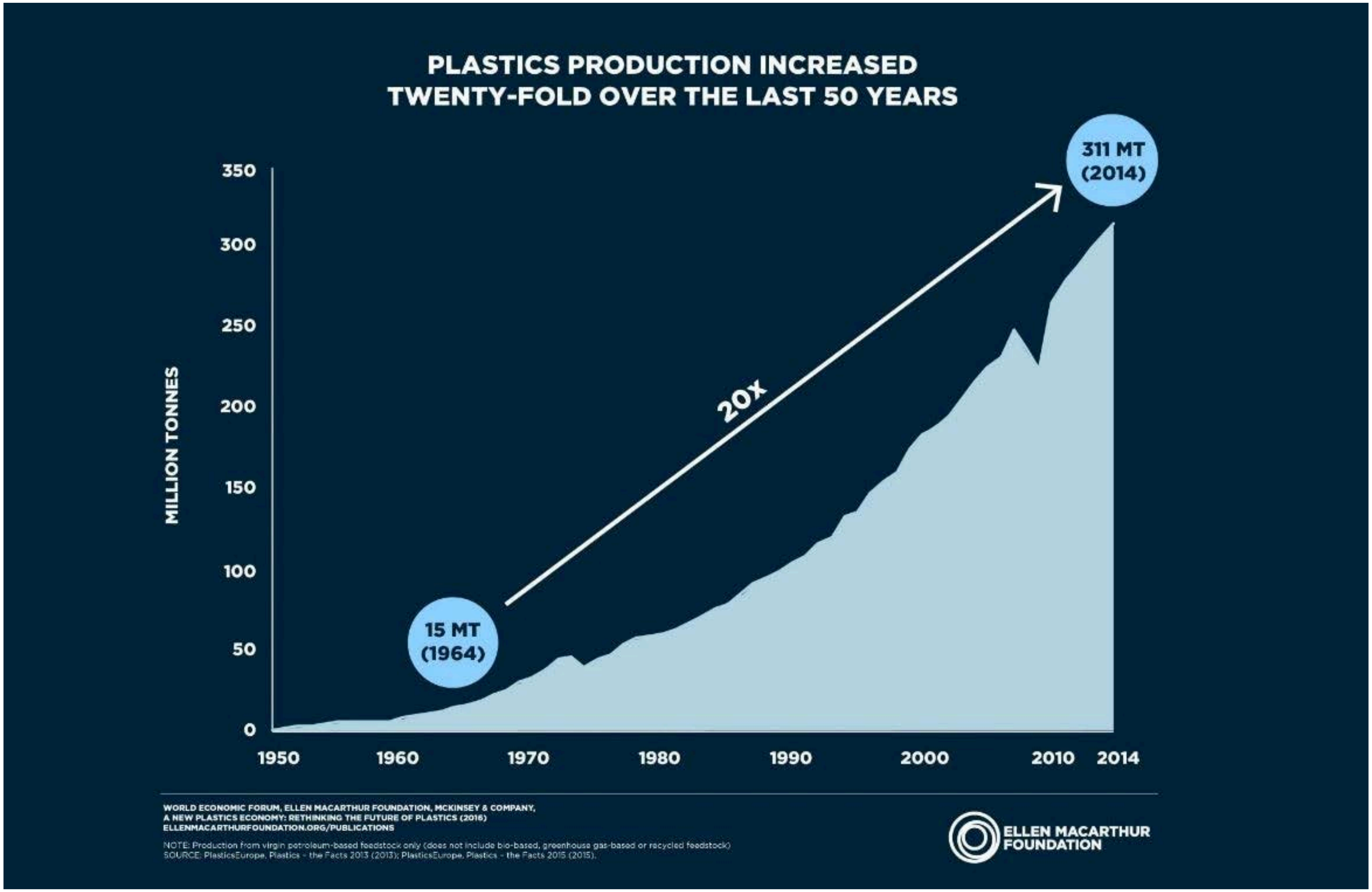
Plastics are ubiquitous in modern society

~300 MM tonnes per year produced worldwide


PLASTICS PRODUCTION INCREASED TWENTY-FOLD OVER THE LAST 50 YEARS

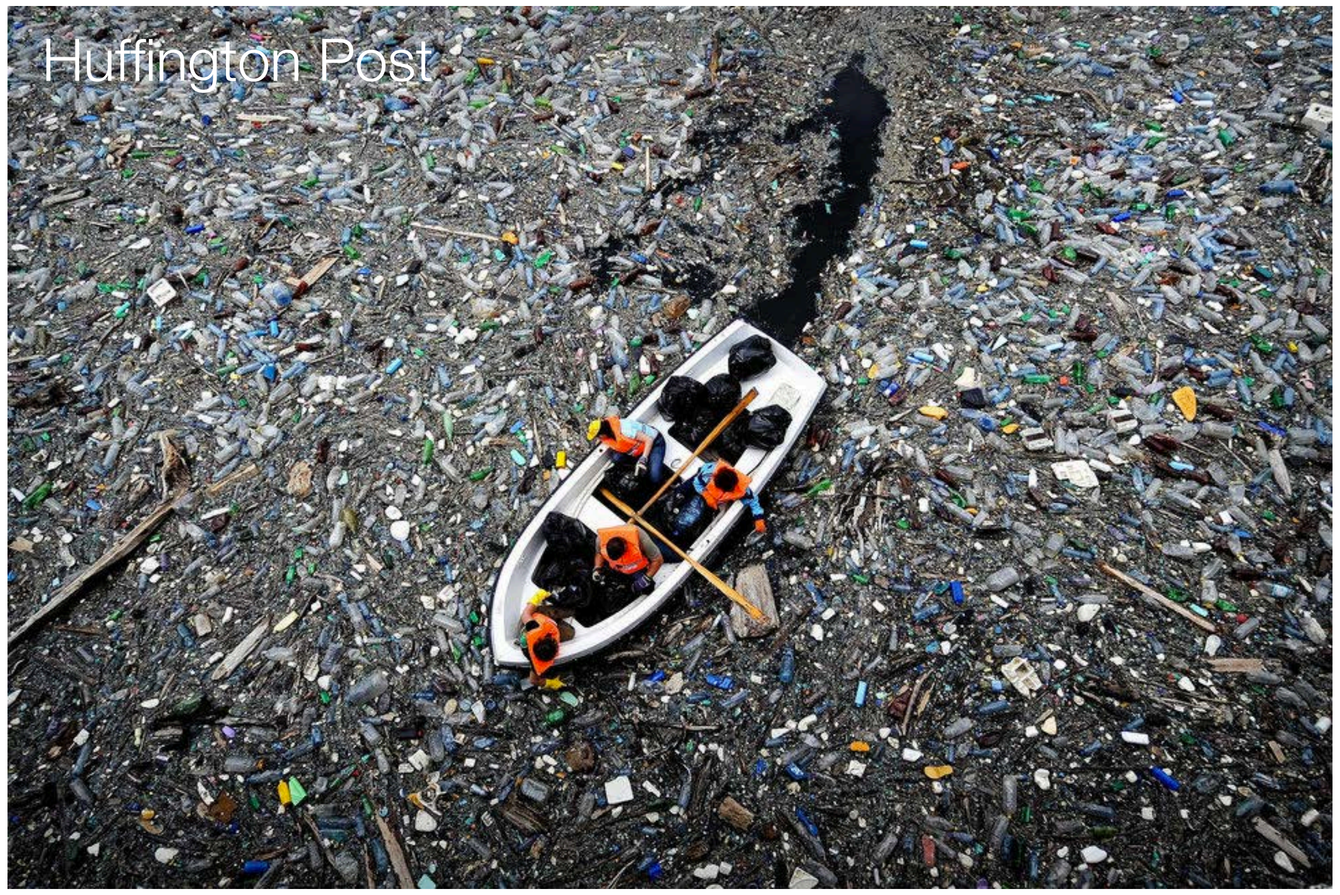
WORLD ECONOMIC FORUM, ELLEN MACARTHUR FOUNDATION, MCKINSEY & COMPANY,
A NEW PLASTICS ECONOMY: RETHINKING THE FUTURE OF PLASTICS (2016)
ELLENMACARTHURFOUNDATION.ORG/PUBLICATIONS

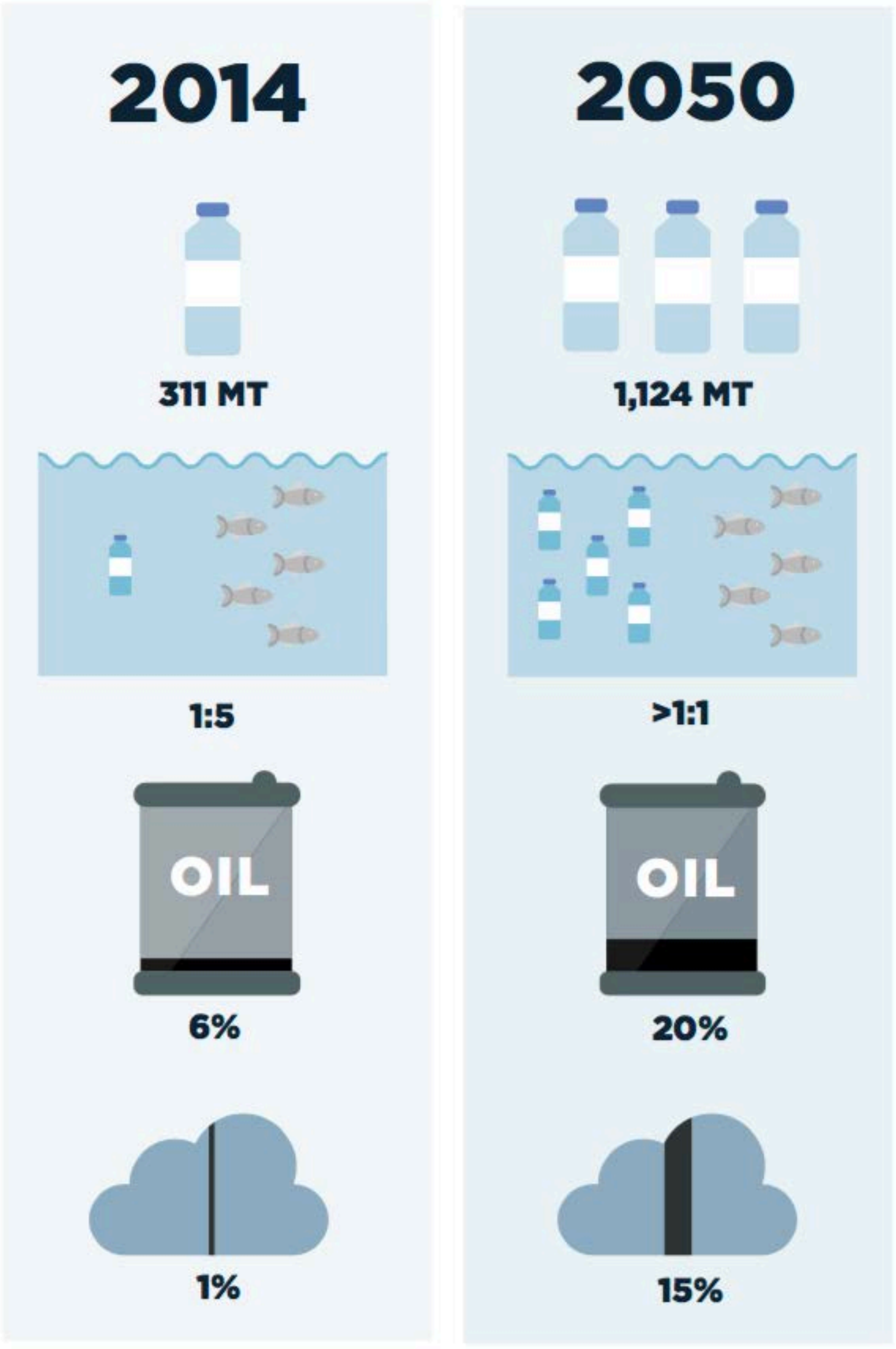
NOTE: Production from virgin petroleum-based feedstock only (does not include bio-based, greenhouse gas-based or recycled feedstock)
SOURCE: PlasticsEurope, Plastics - the Facts 2013 (2013); PlasticsEurope, Plastics - the Facts 2015 (2015).

Ellen MacArthur Foundation, 2016

Plastics are creating an environmental catastrophe

~8 MM tonnes per year of plastics enter the ocean

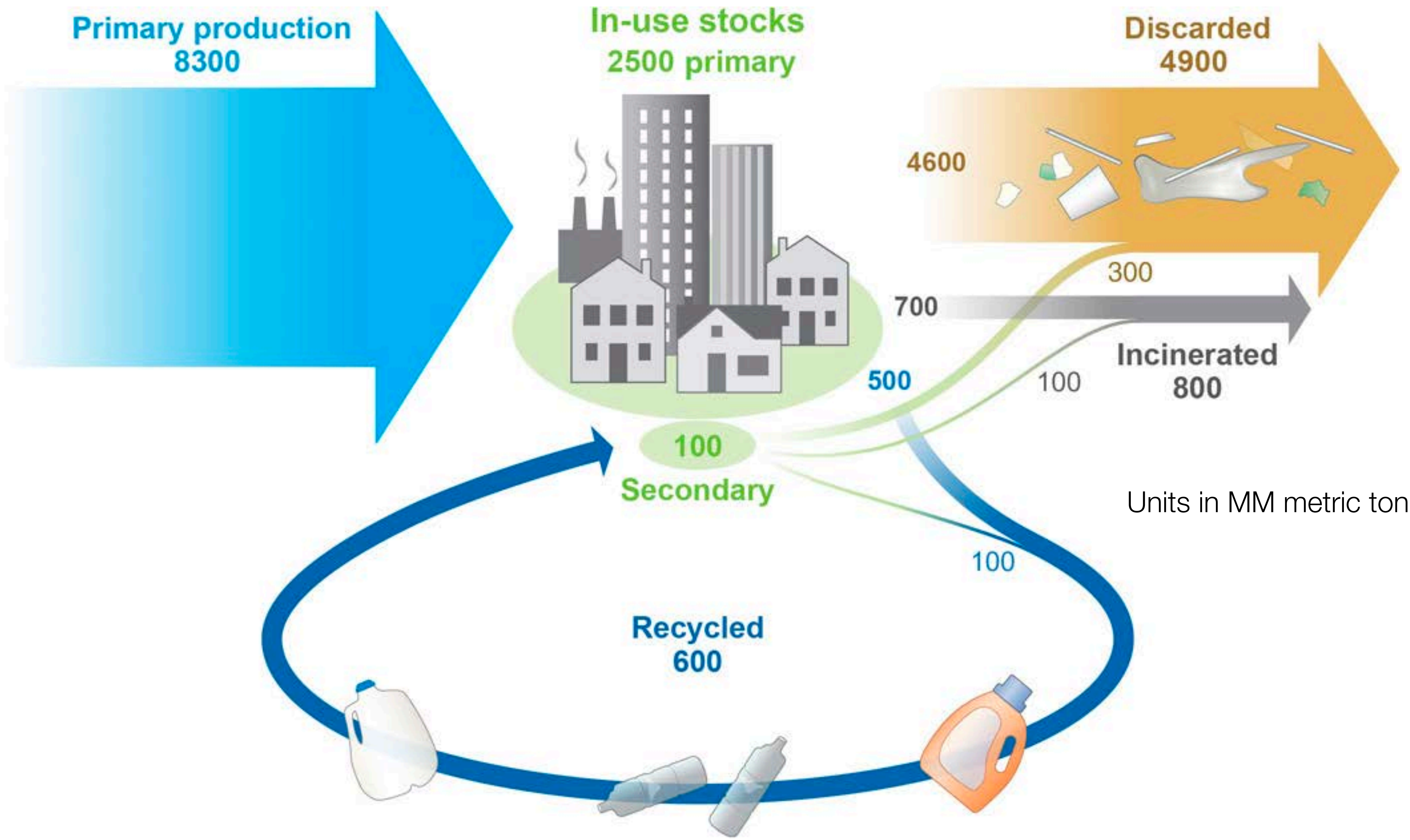




	2014	2050
PLASTICS PRODUCTION	311 MT	1,124 MT
RATIO OF PLASTICS TO FISH IN THE OCEAN[1] (BY WEIGHT)	1:5	>1:1
PLASTICS' SHARE OF GLOBAL OIL CONSUMPTION[2]	6%	20%
PLASTICS' SHARE OF CARBON BUDGET[3]	1%	15%

Ellen MacArthur Foundation, 2016
Jambeck *et al.*, *Science* 2015

Recycling rates remain low and most recycling is "down-cycling"



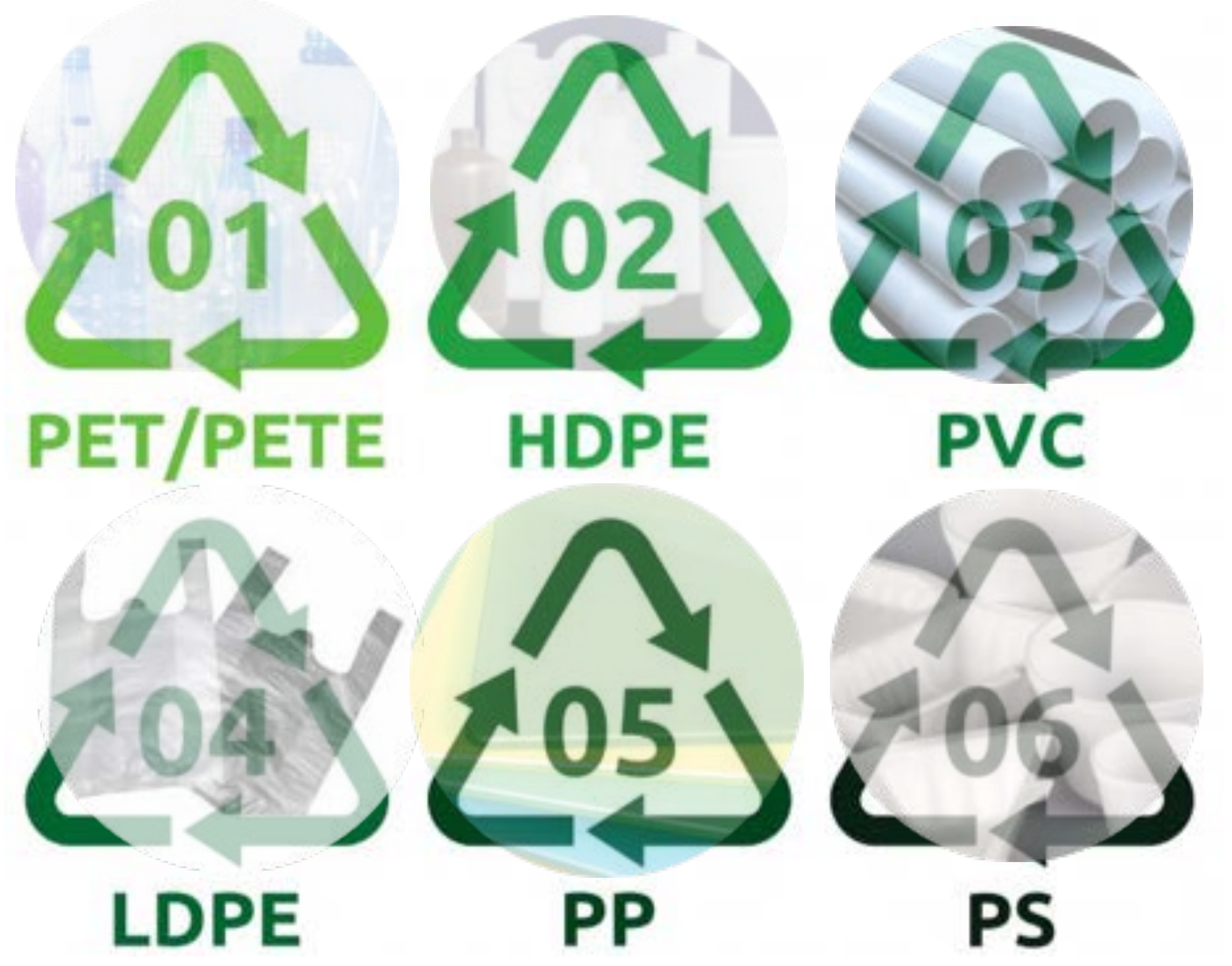
Units in MM metric tons

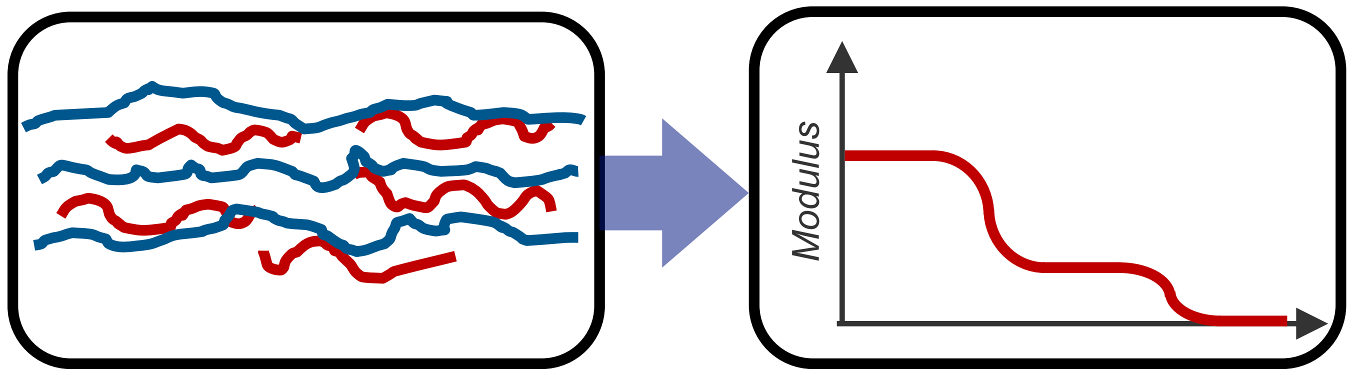
Recycling can save between 40-90% of embedded energy in plastics

Geyer, Jambeck, Law, *Science Adv.* 2017
Rahimi and Garcia, *Nature Rev. Chem.* 2017

Challenge 1: What do we do with the plastics we make now?

Monolithic Materials

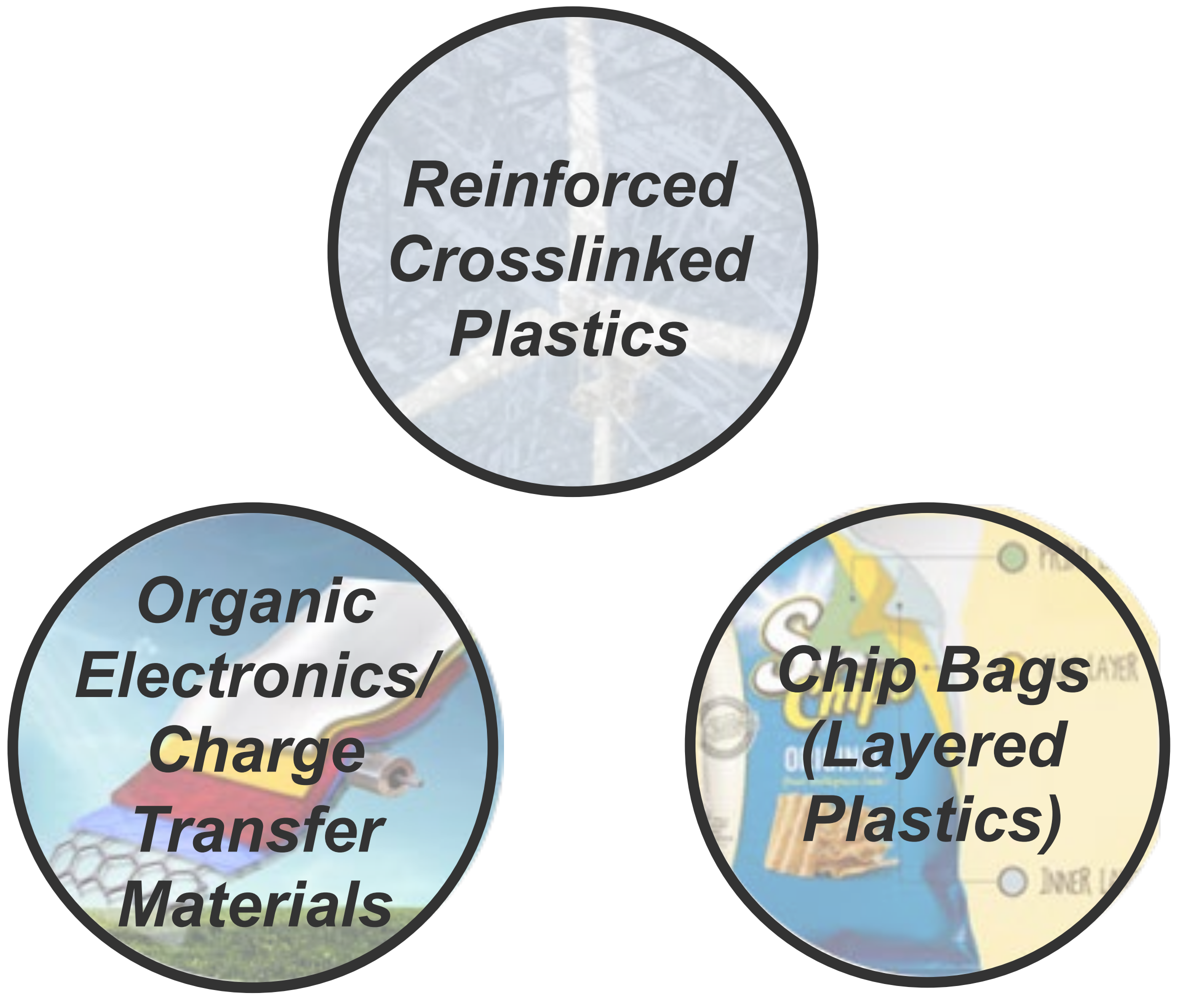




Linear Architectures,
Easy to process

Viscoelastic
Materials

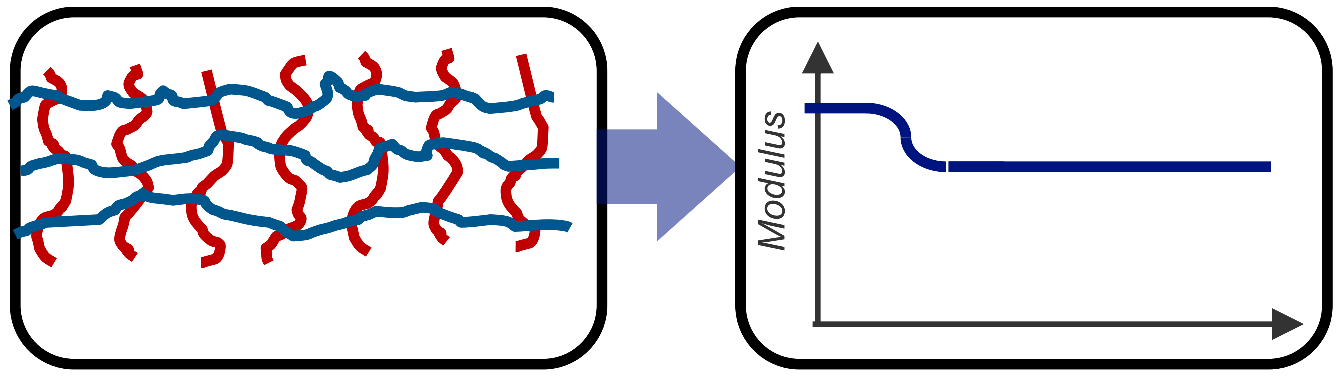
Hierarchical Materials



Reinforced Crosslinked Plastics

Organic Electronics/ Charge Transfer Materials

Chip Bags (Layered Plastics)

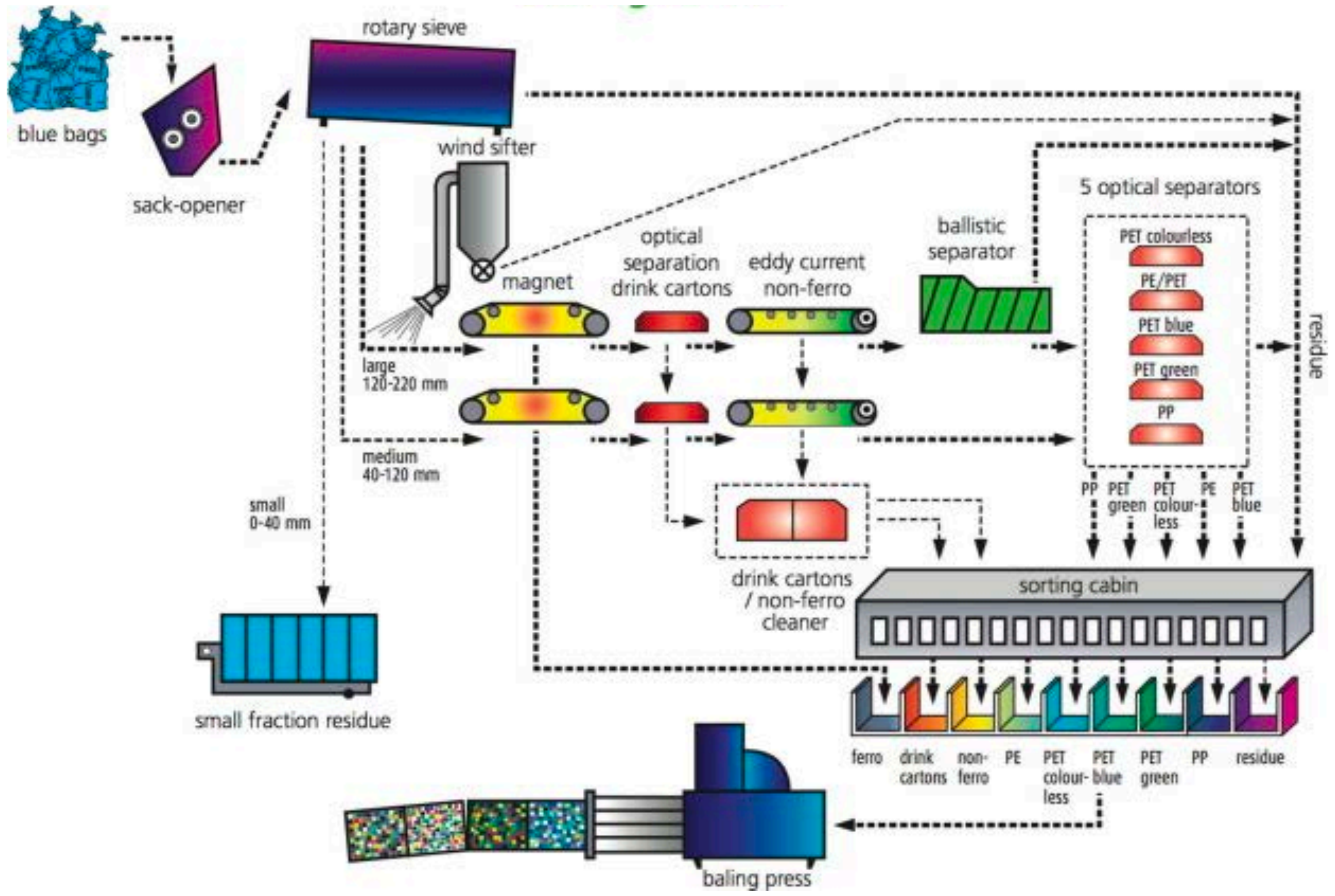


Crosslinked/Layered Architectures,
Difficult to process/deconvolute

Elastic Materials

Options for recycling and upcycling of plastics

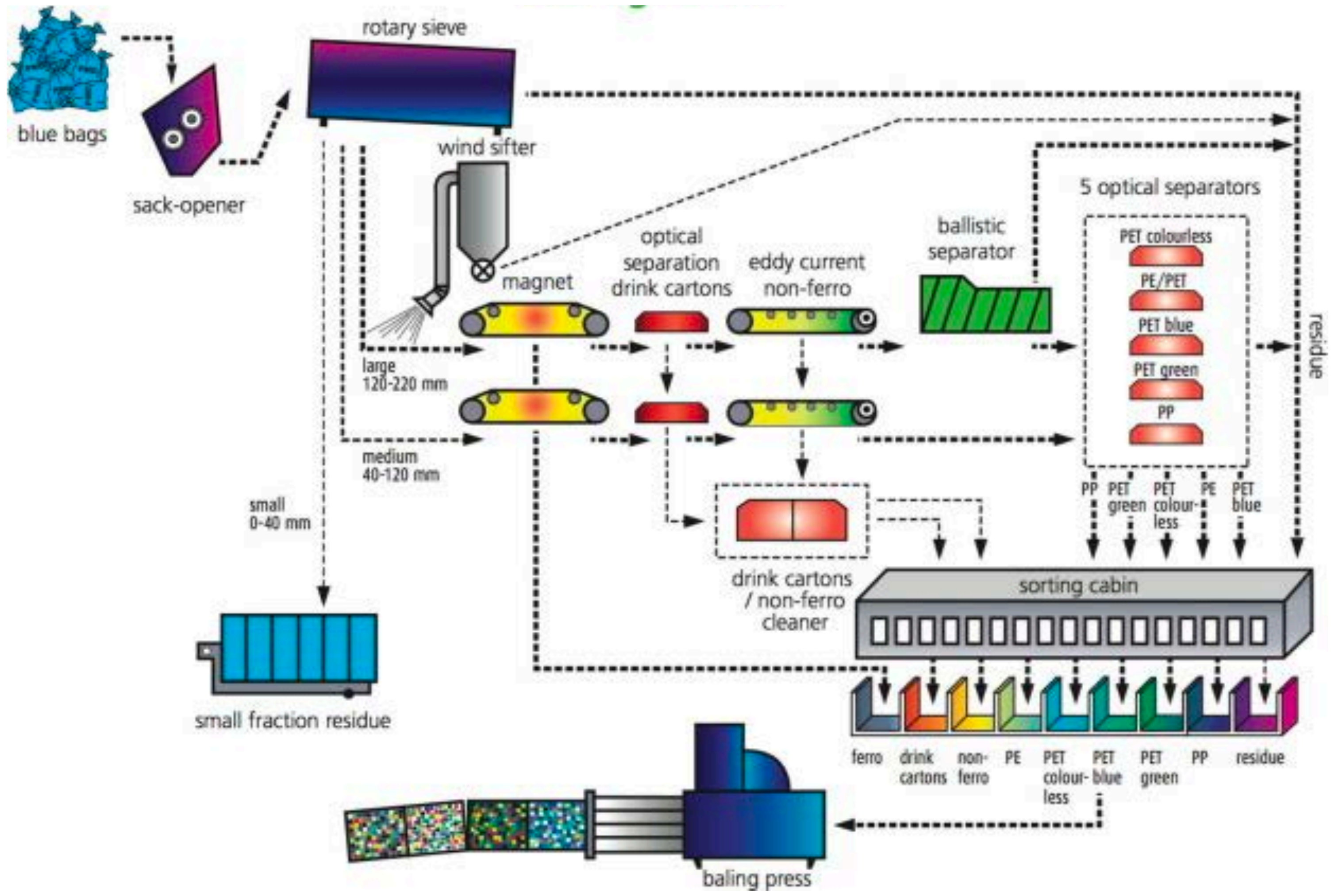
Mechanical recycling



Van Geem *et al.* 2017

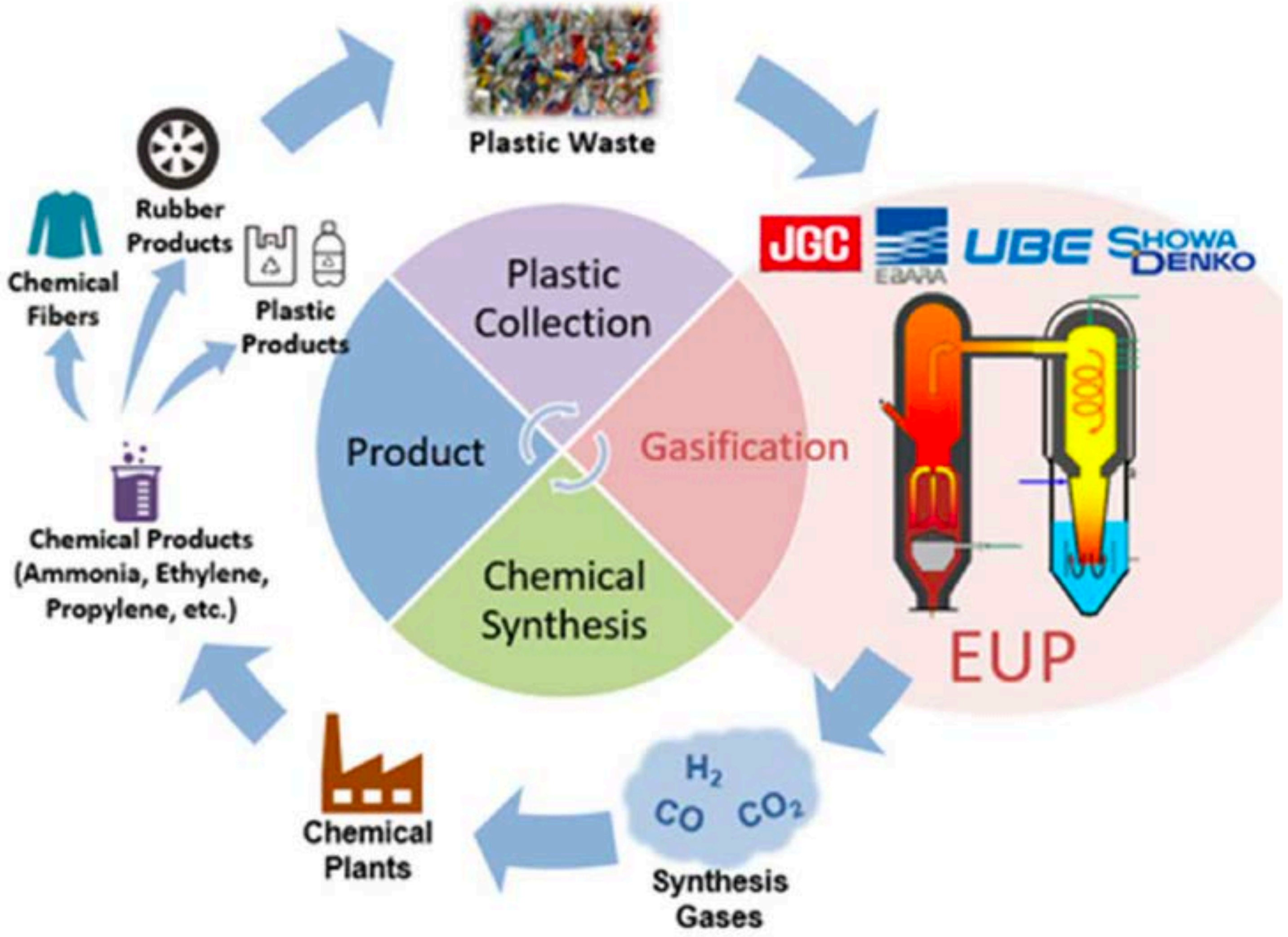
Options for recycling and upcycling of plastics

Mechanical recycling



Van Geem *et al.* 2017

Gasification



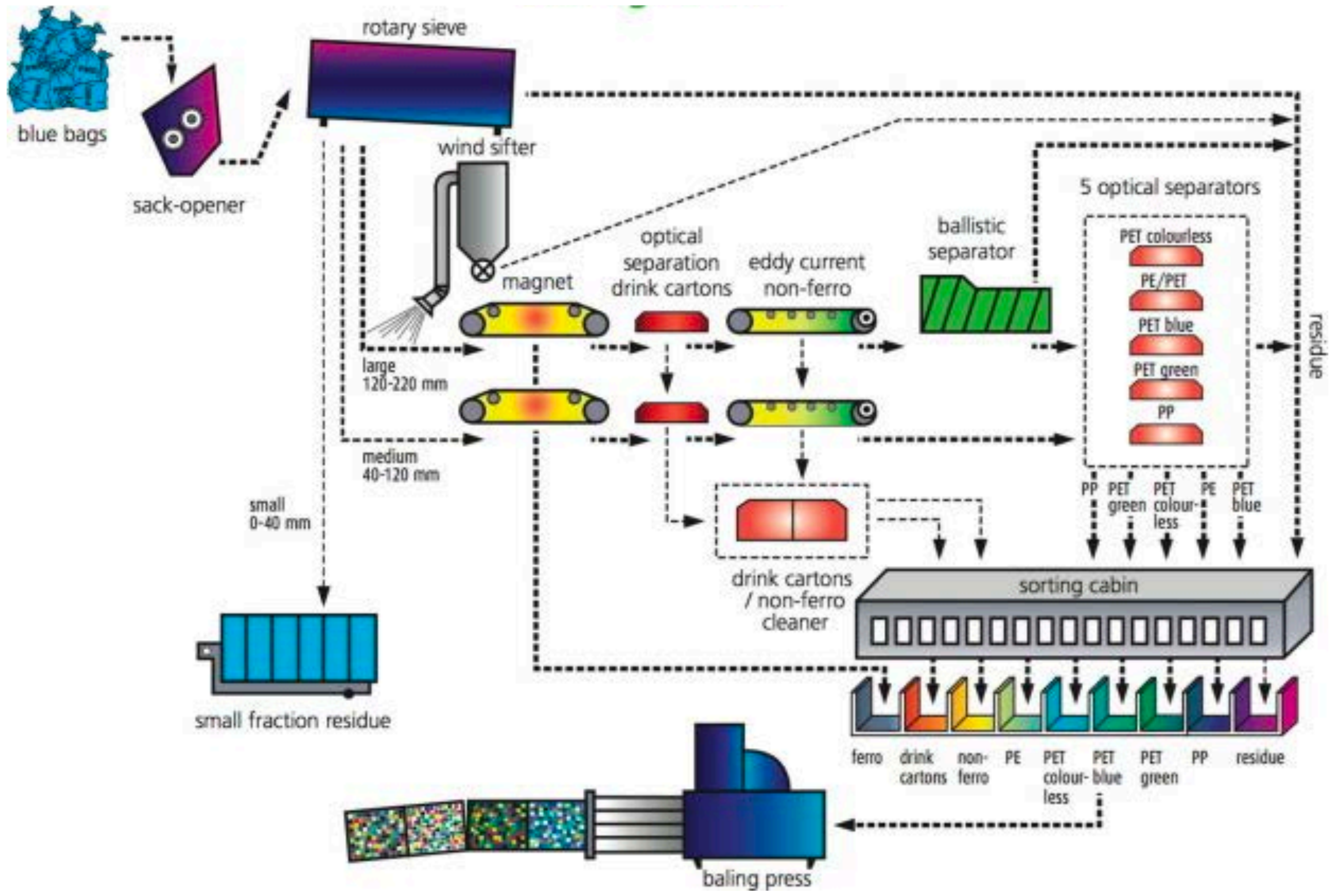
Plastics News Europe

Pyrolysis (and refinery integration)

Mitsubishi

Options for recycling and upcycling of plastics

Mechanical recycling



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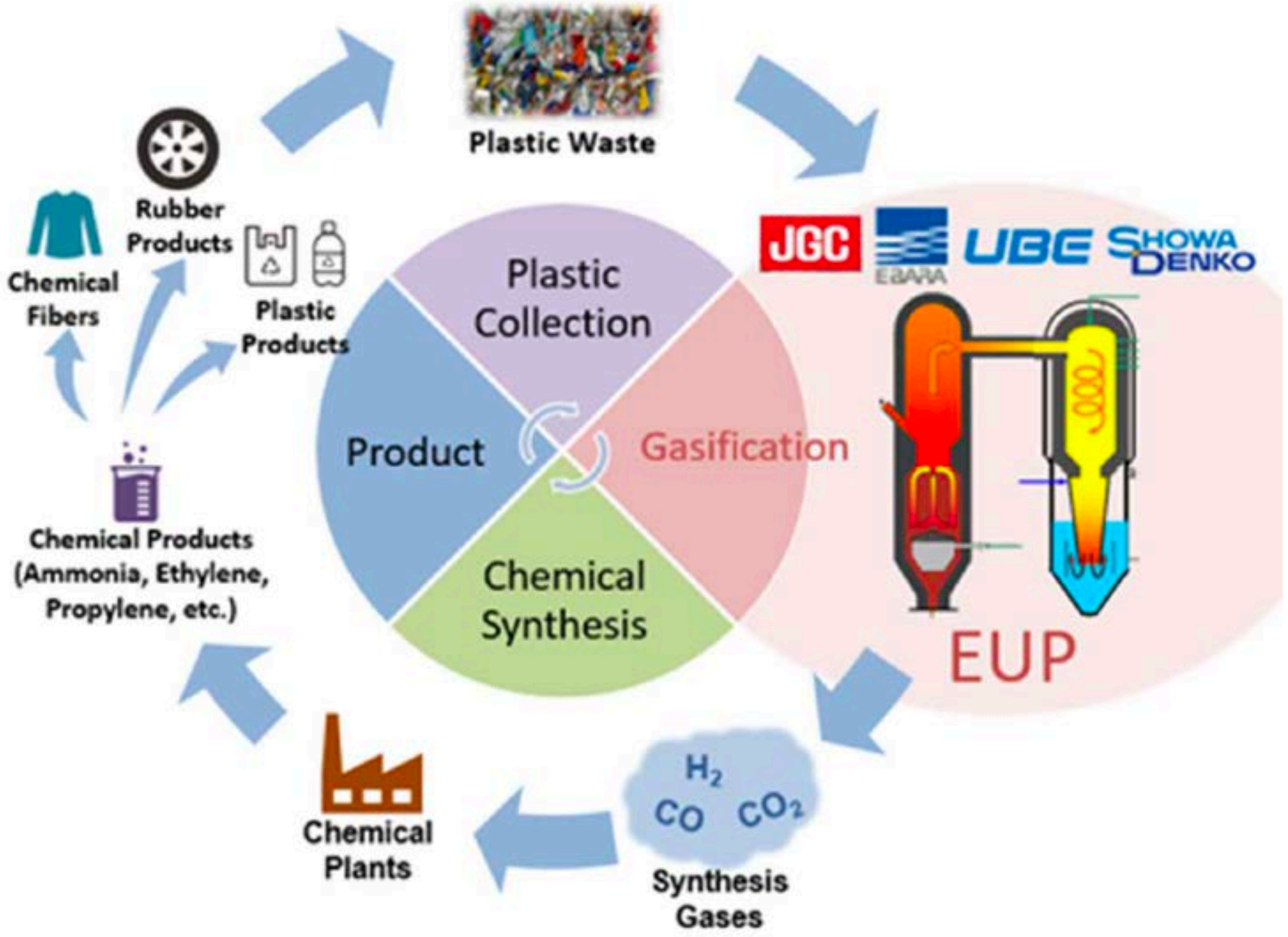


Plastics News Europe

Pyrolysis (and refinery integration)

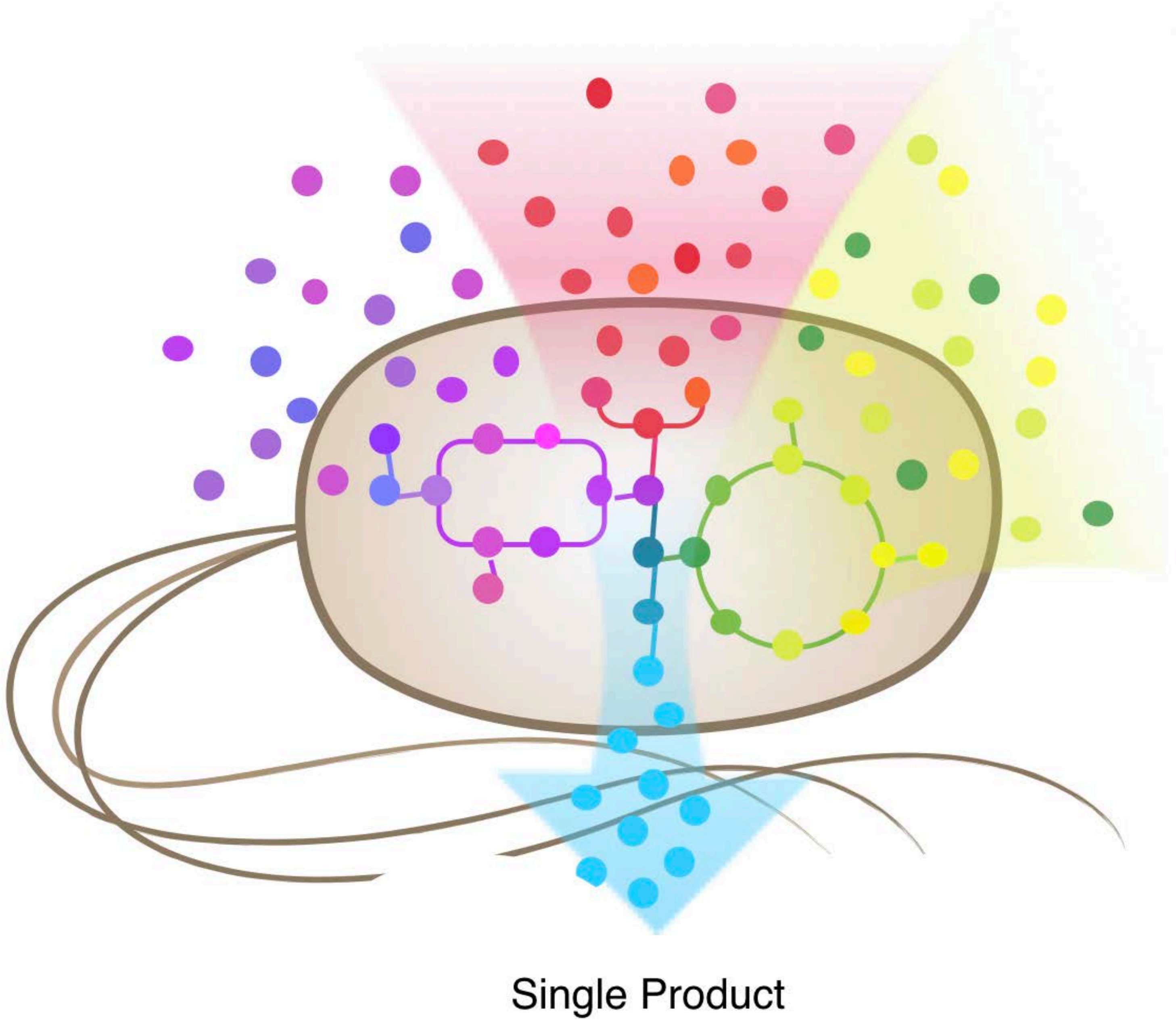
Mitsubishi

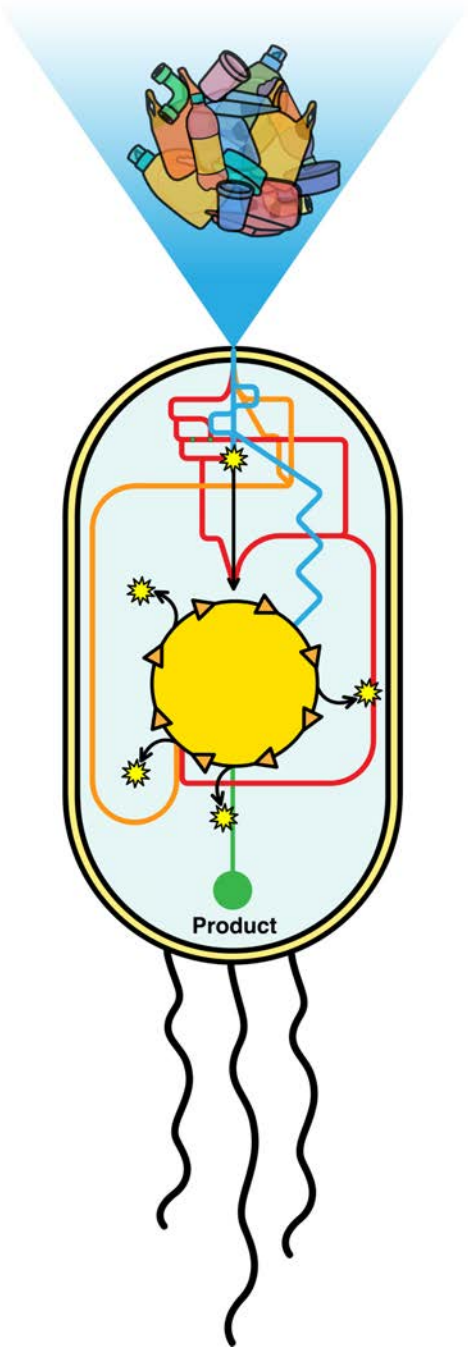
Disadvantages for pyrolysis & gasification:

- Low selectivity to products
- Tar, char production
- Contaminants
- Feeding of solid plastics at high pressure
- Little economic and energy incentive relative to mechanical recycling or virgin polymer production

Biological (or selective) recycling is another option

Microbes can selectively "funnel"
multiple substrates to a single product





Concept demonstrated for lignin,
wastewater, and mixed nylon/PET waste

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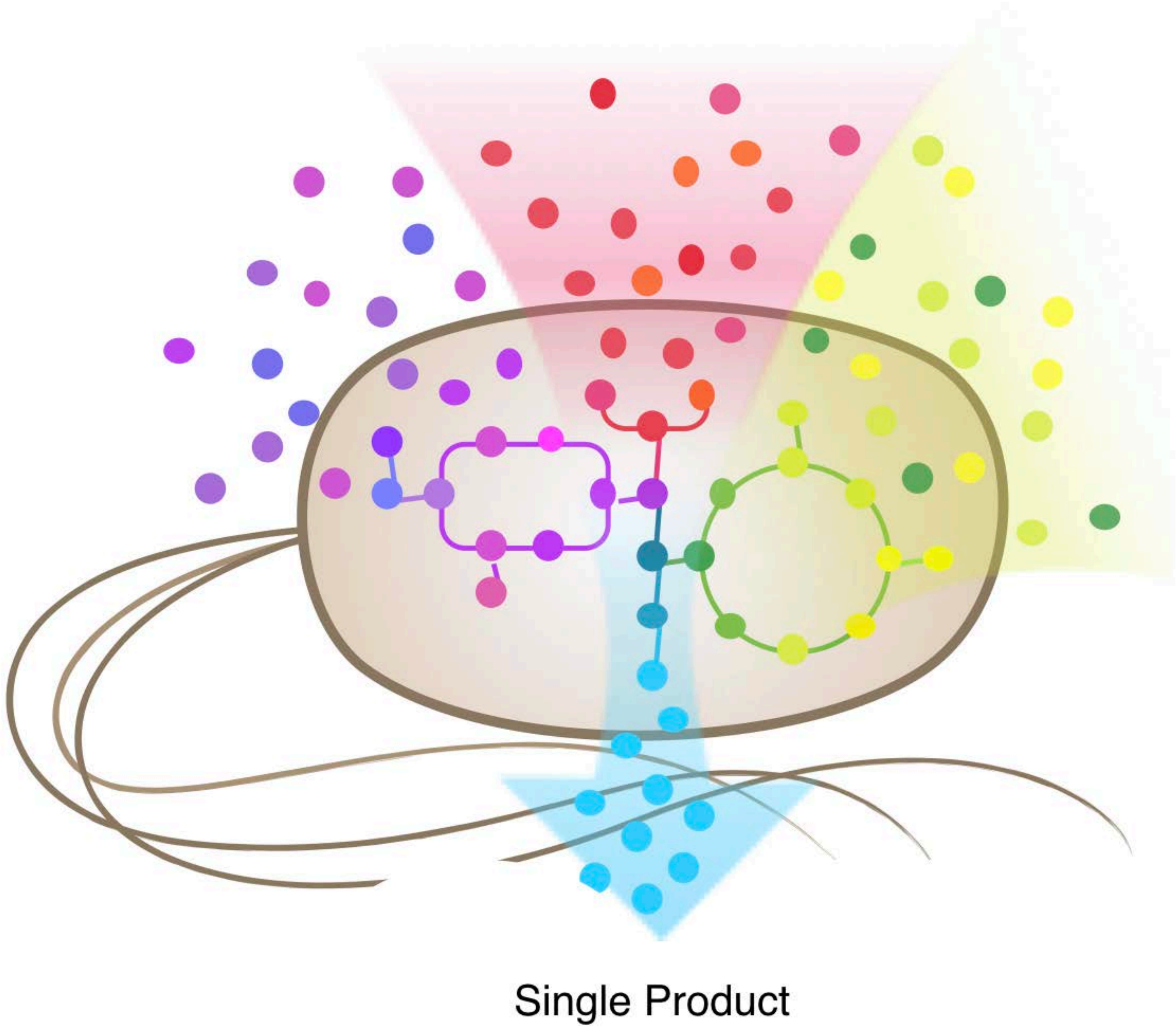
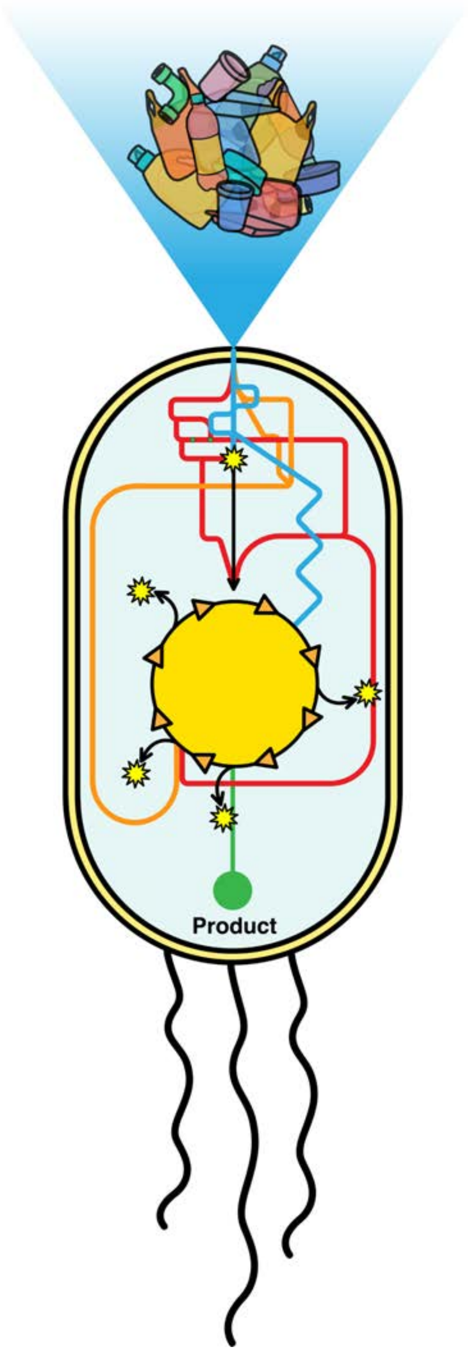




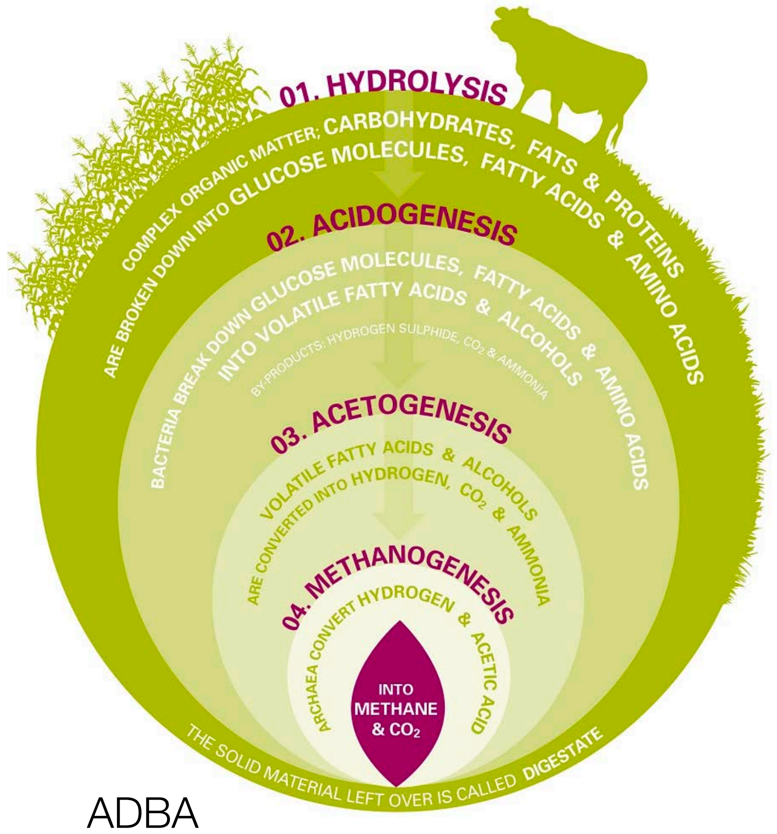
Advantages for biological recycling:

- Selective for heterogeneous inputs including contaminants from food
- Low T, P, and energy
- Sorting is not a problem
- Upstream (catalytic, mechanical, thermal) processes do not need to be selective
- Can harness existing/similar infrastructure to anaerobic digestion

Concept demonstrated for lignin,
wastewater, and mixed nylon/PET waste

What can we make from biological recycling and upcycling?

Today: methane from anaerobic digestion of compostable plastics



ADBA

NPR

What can we make from biological recycling and upcycling?

SY Lee *et al*, *Nature Catalysis* 2018

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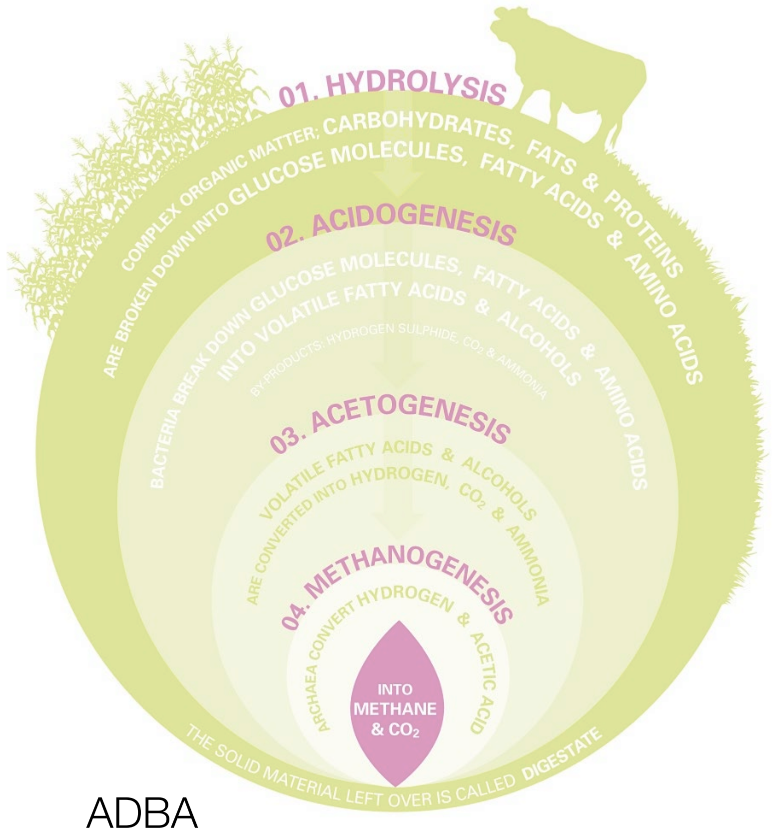
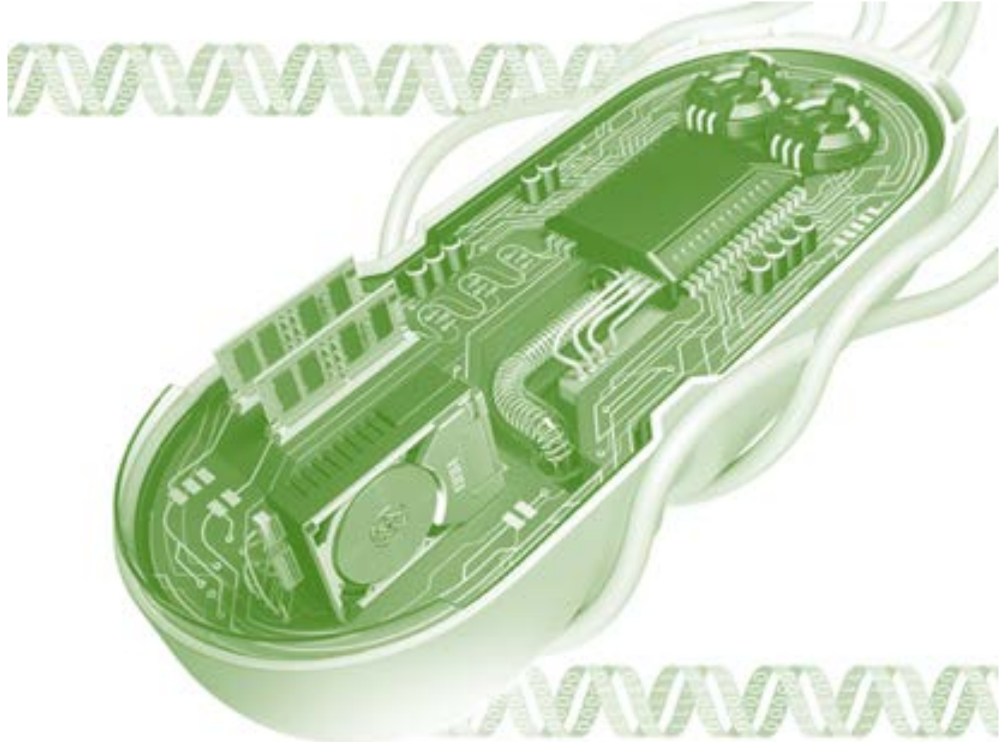
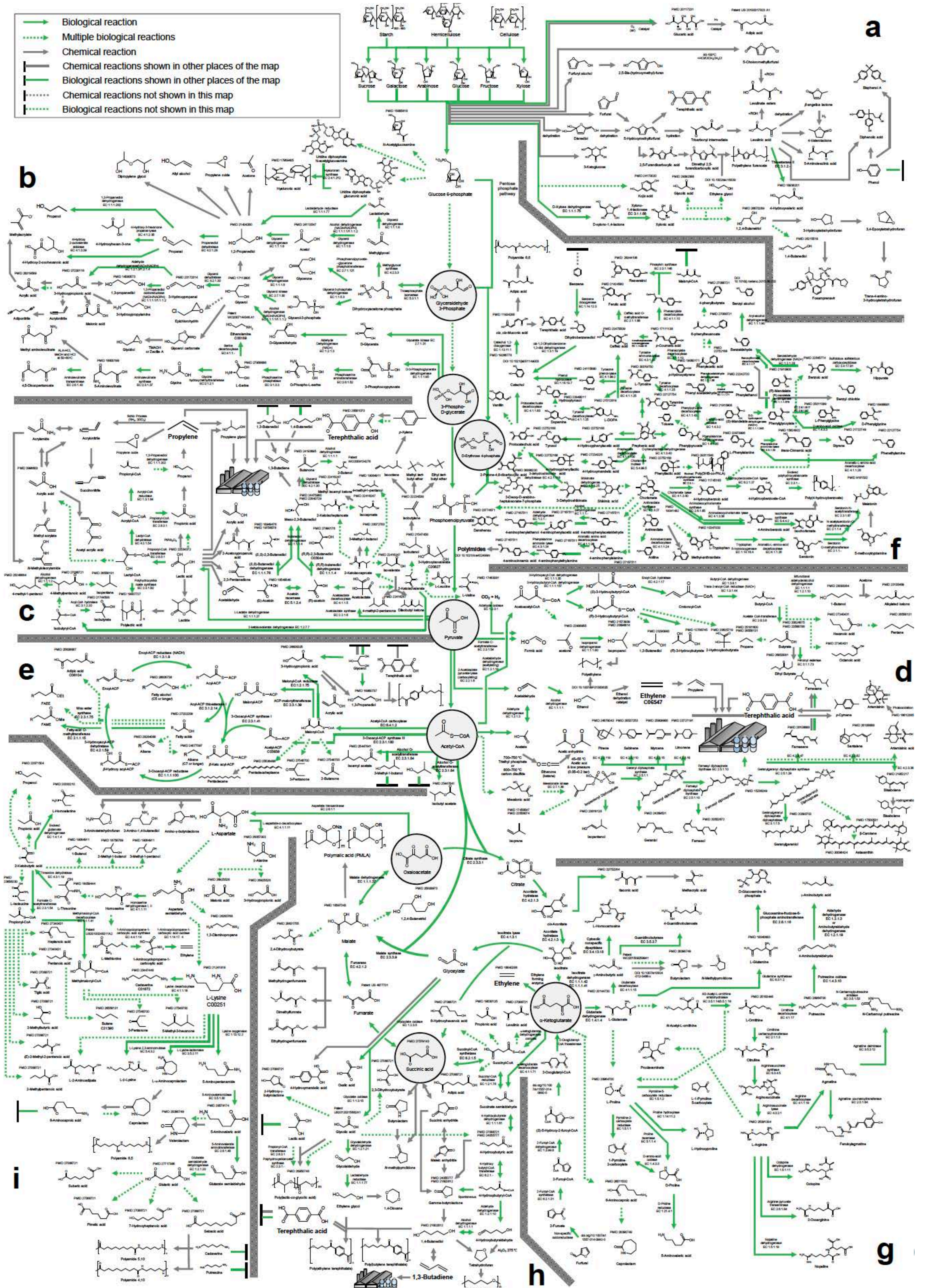


ADBA

NPR

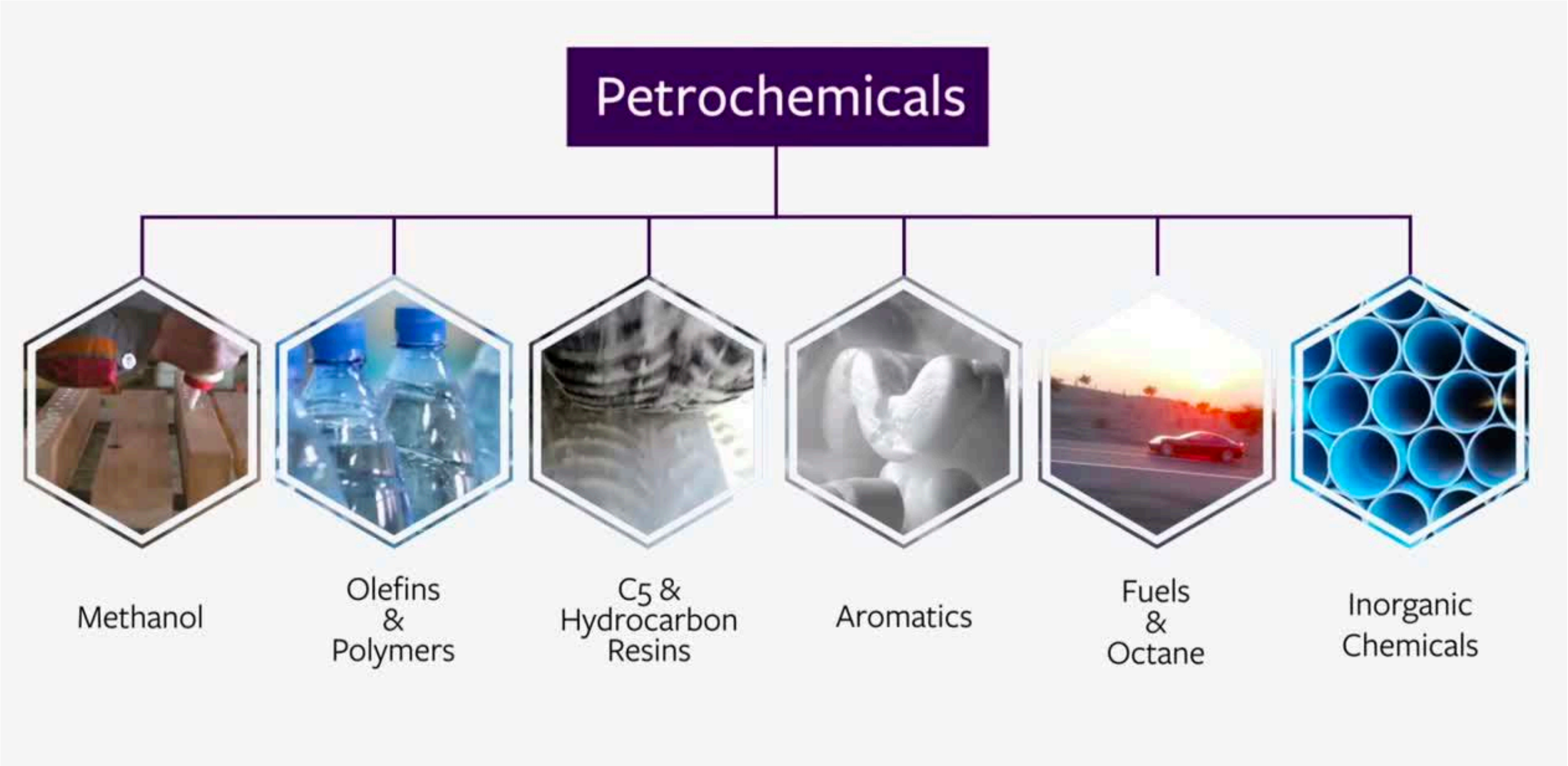
Tomorrow: anything you can make from synthetic biology!



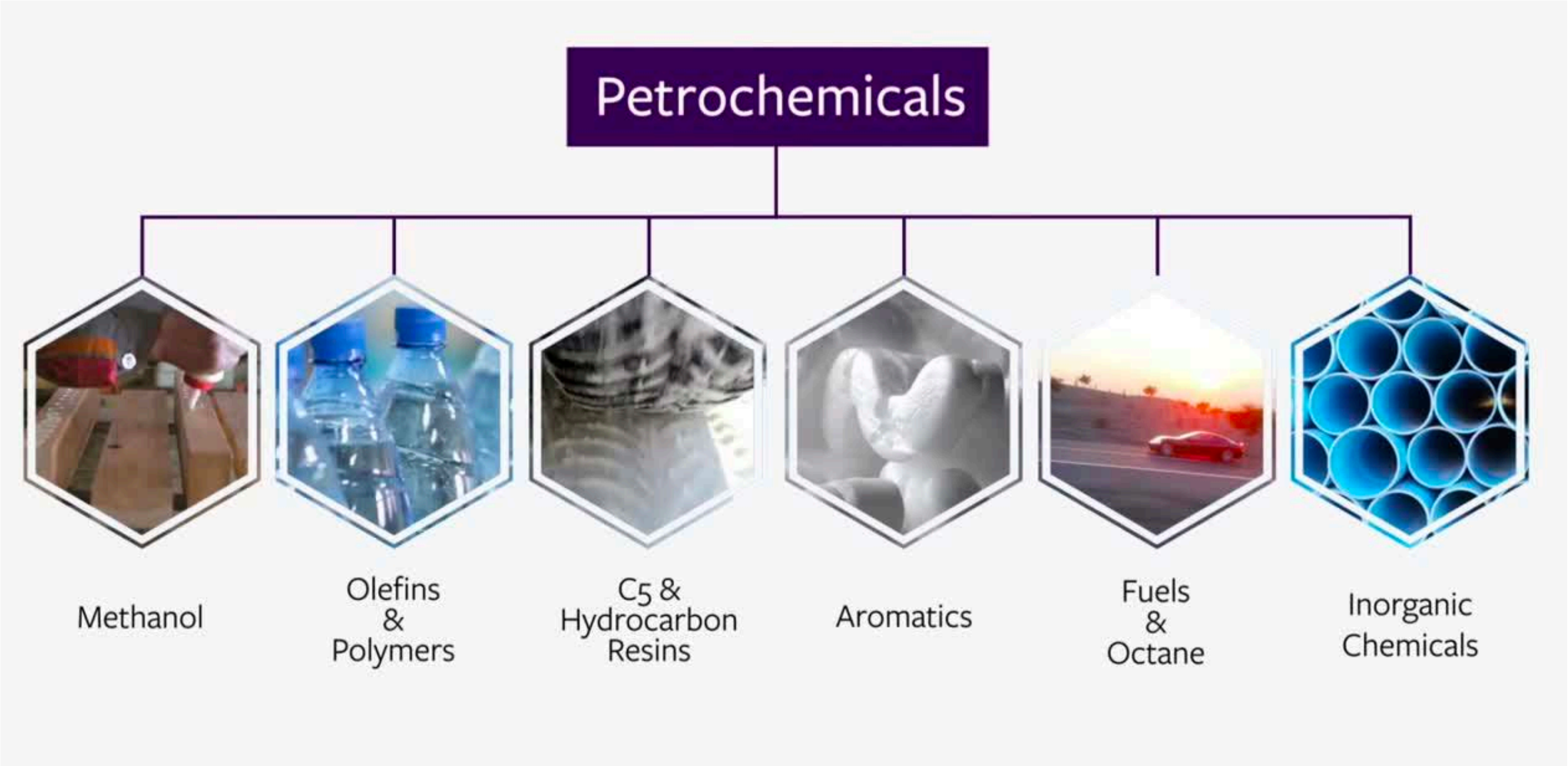


Product options from biological recycling and upcycling

Direct replacements are compounds that are chemically identical to today's petroleum-based chemicals

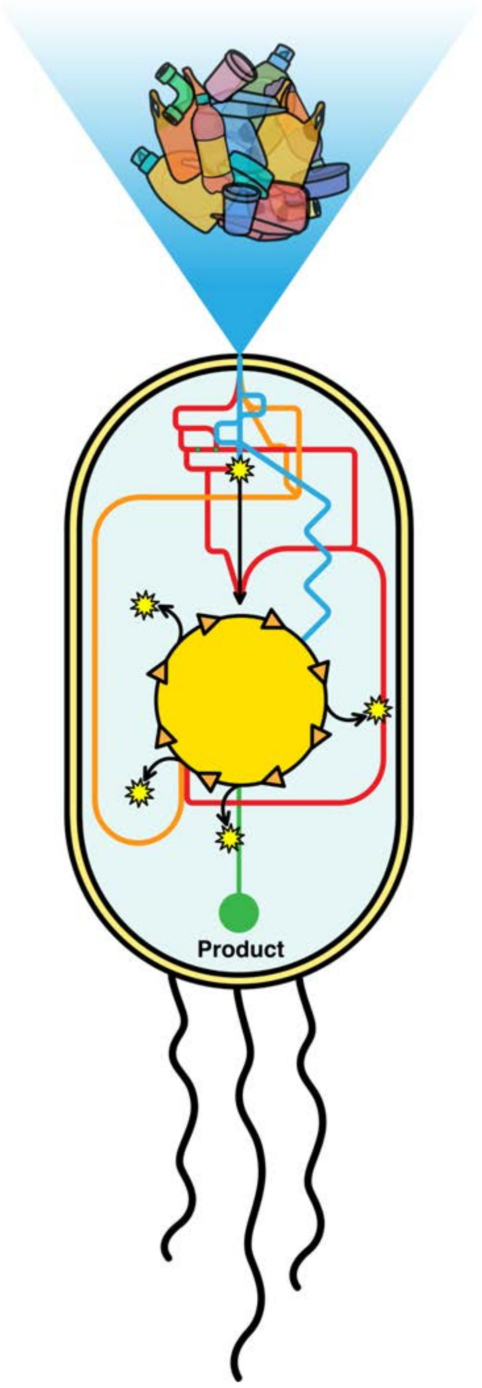


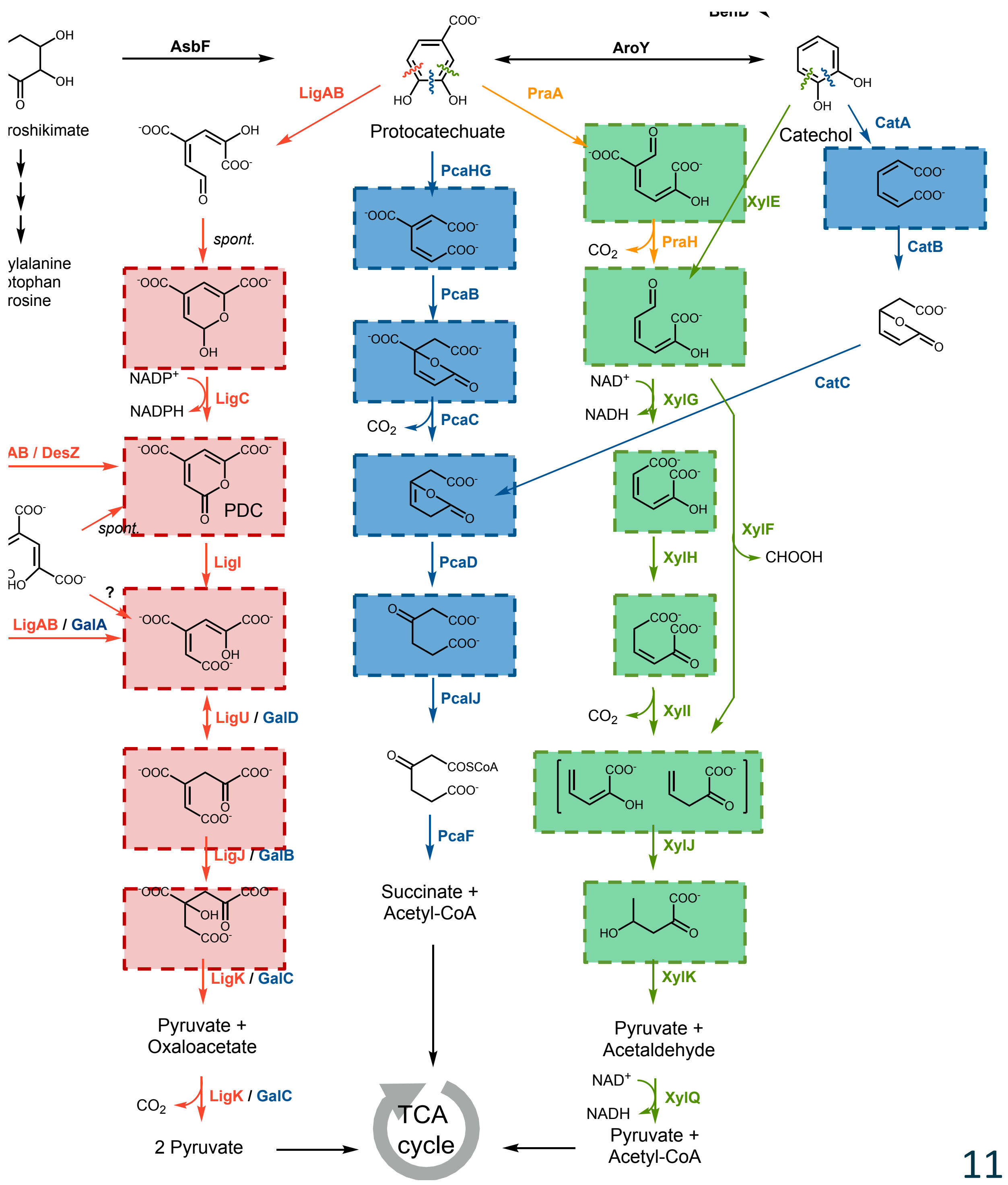
Product options from biological recycling and upcycling



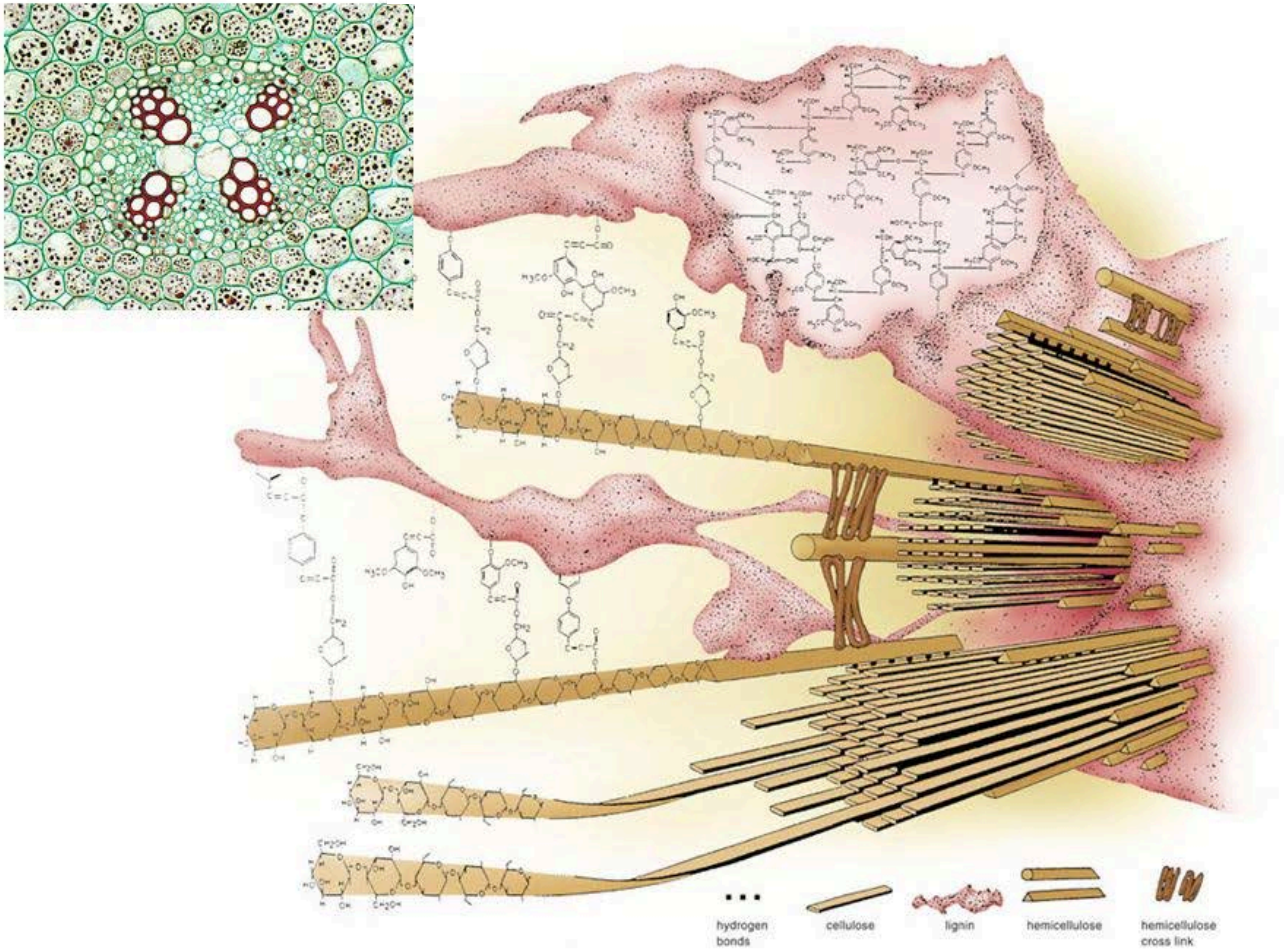
Direct replacements are compounds that are chemically identical to today's petroleum-based chemicals

Performance-advantaged bioproducts are bio-based molecules that do not resemble petroleum-derived molecules, but offer a performance advantage over today's products





A brief aside to plants…



Biomass “recalcitrance” is all about unlocking polymers in a heterogeneous material

Bidlack, Oklahoma Academy of Science, 1993

Cellulose is a VERY recalcitrant material

$t_{1/2}$ ~ 5 million years

Cellulose (wood) degradation in the environment

S. Cragg

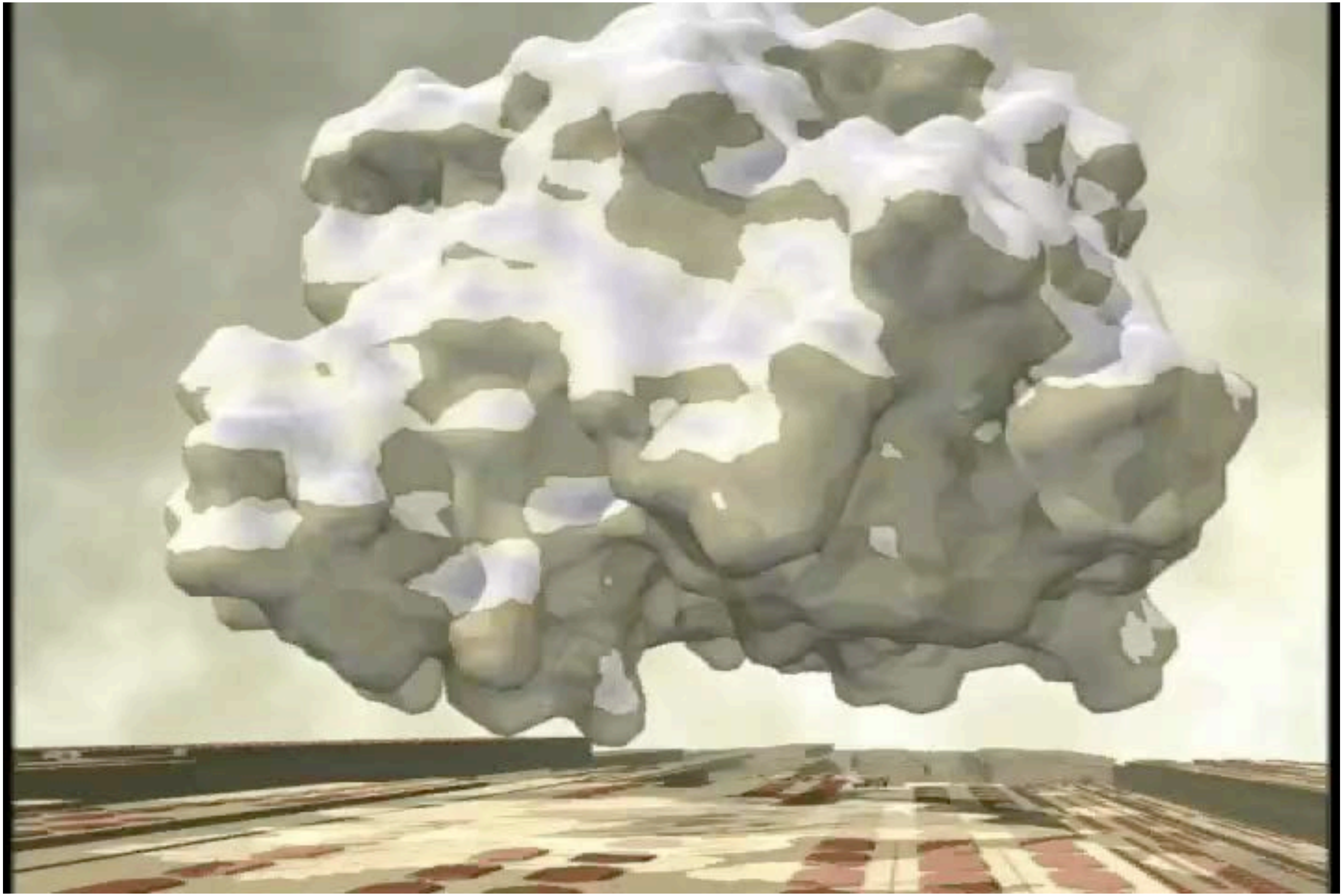
The Gribble

S. Cragg

The Gribble

S. Cragg

How do Gribbles break down cellulose polymers?



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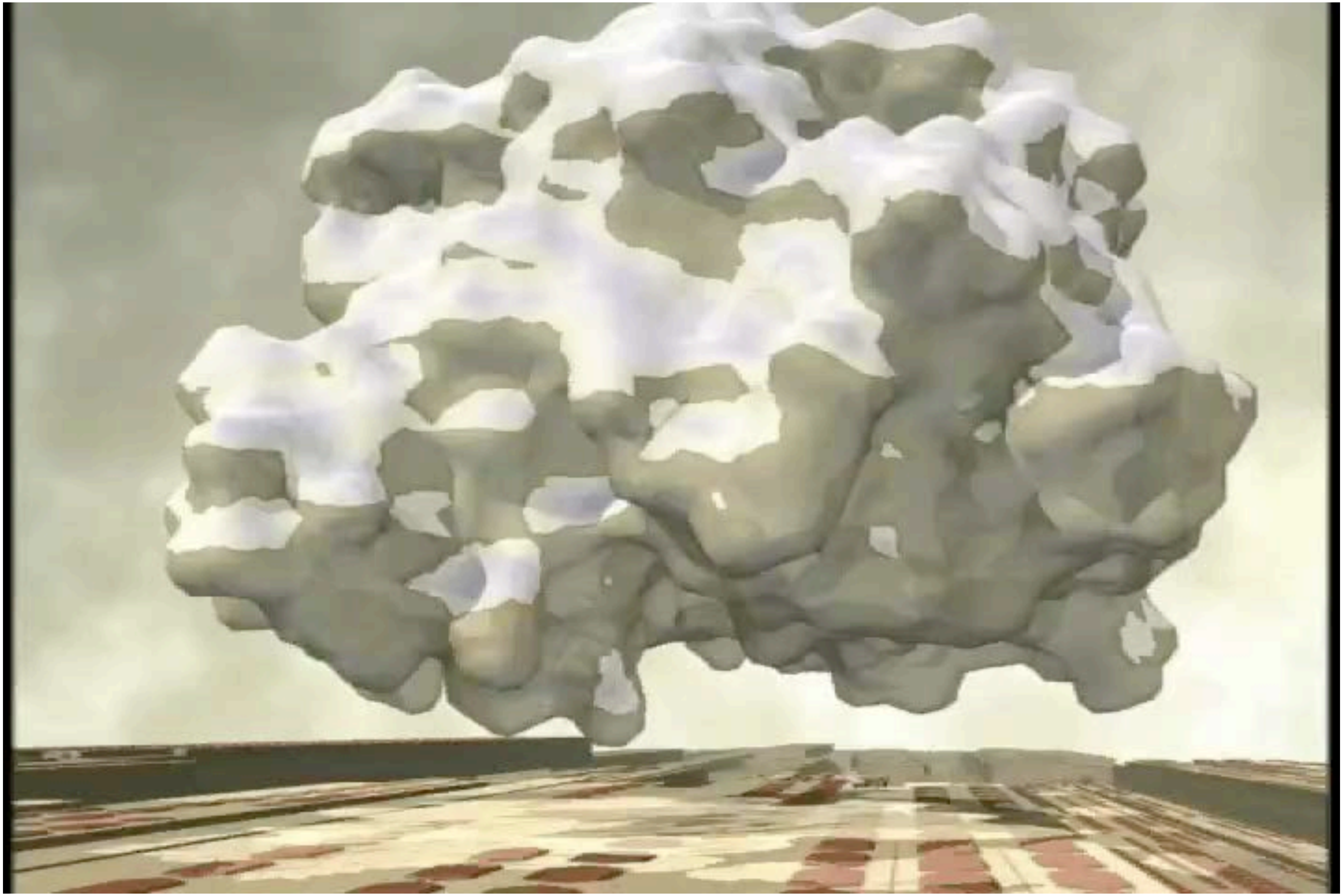

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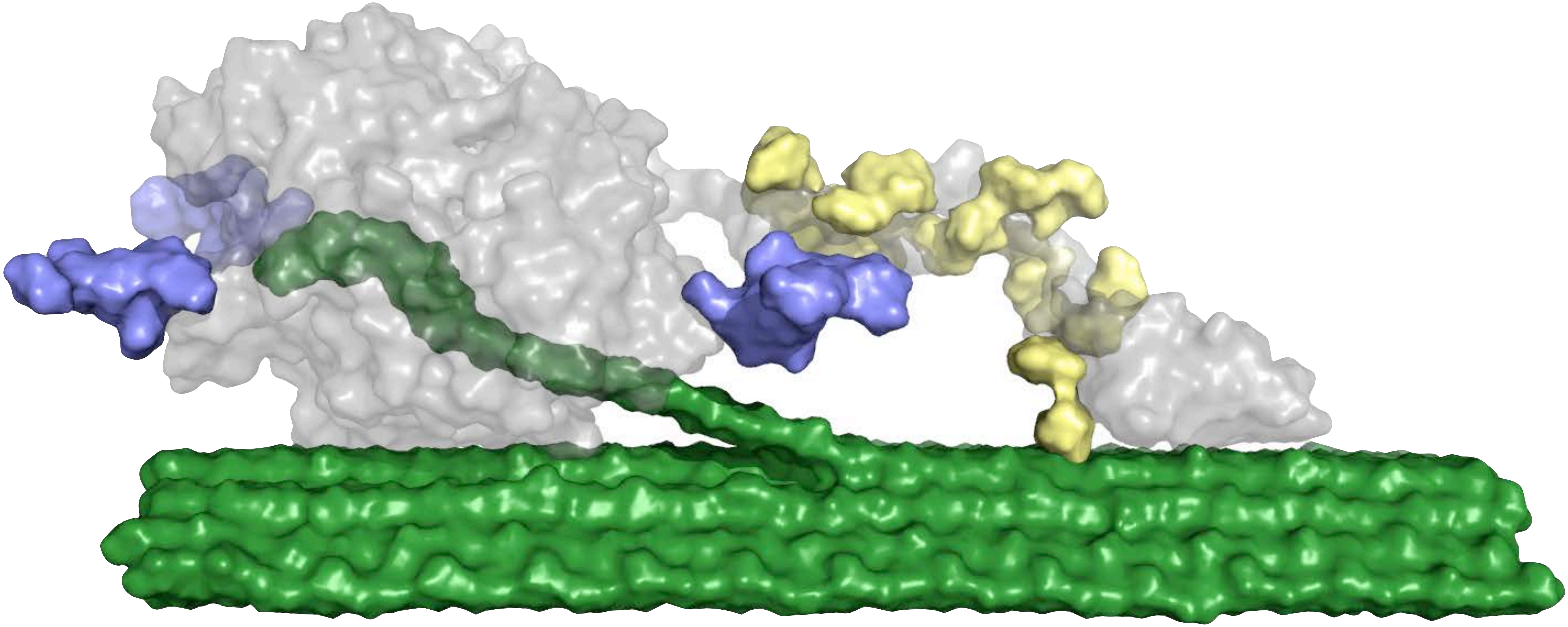
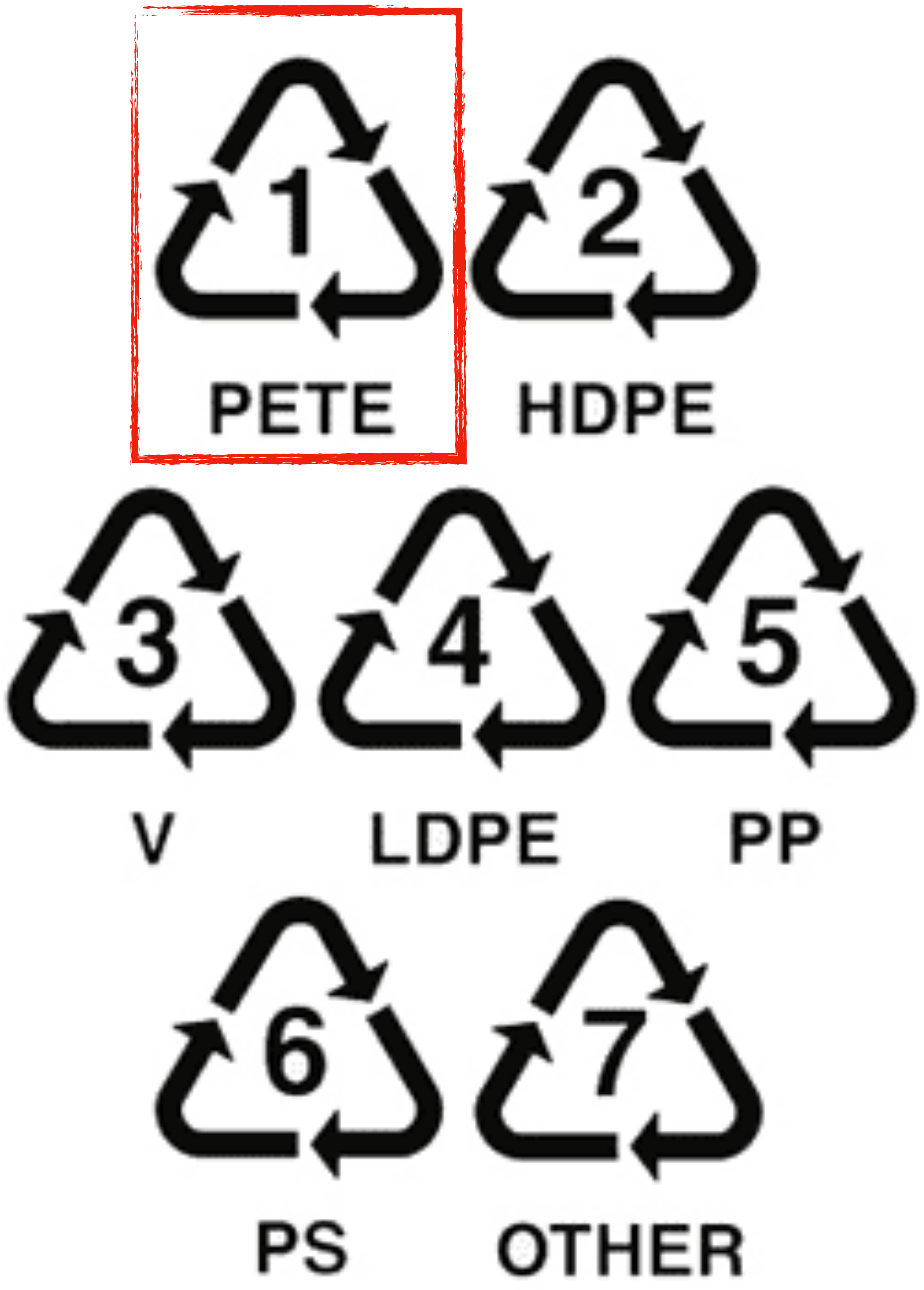


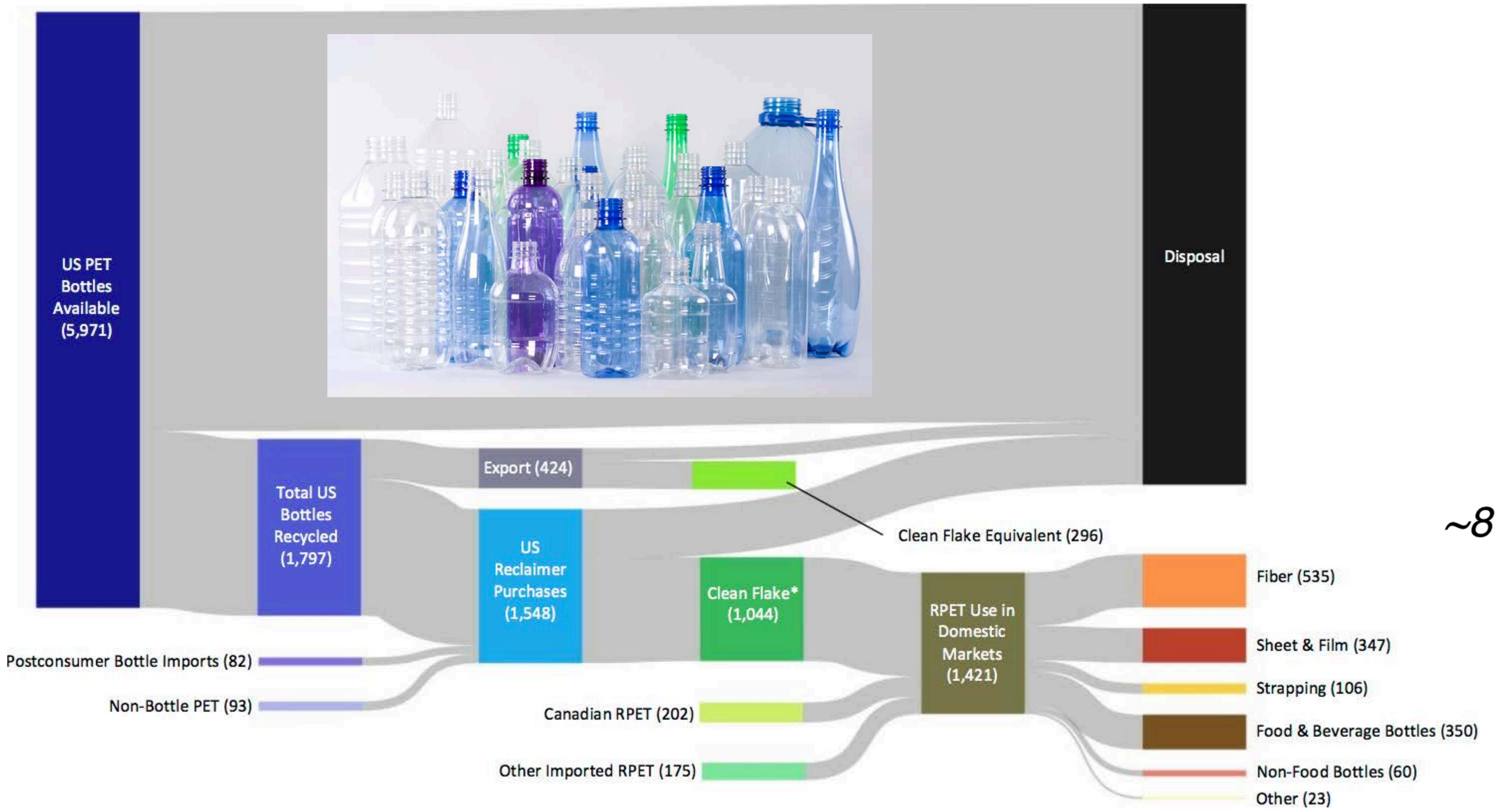
Microbes have had millions of years to evolve to breakdown cellulose polymers – can we accelerate this process for synthetic plastics with biology and chemistry?

M. Kern, J. McGeehan *et al*. *PNAS* 2013

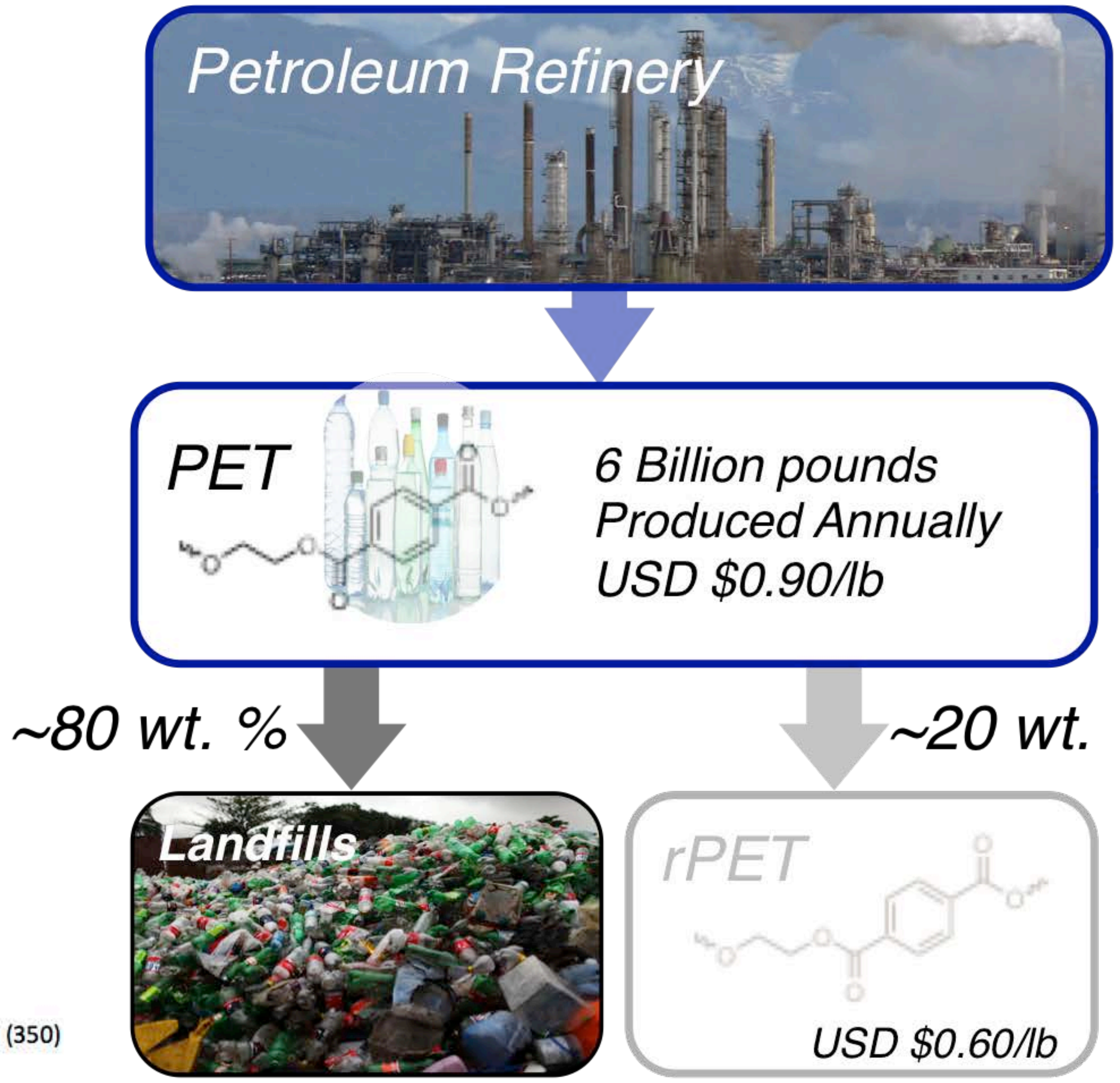
Where we started in terms of plastics?



Status quo for recycling of PET

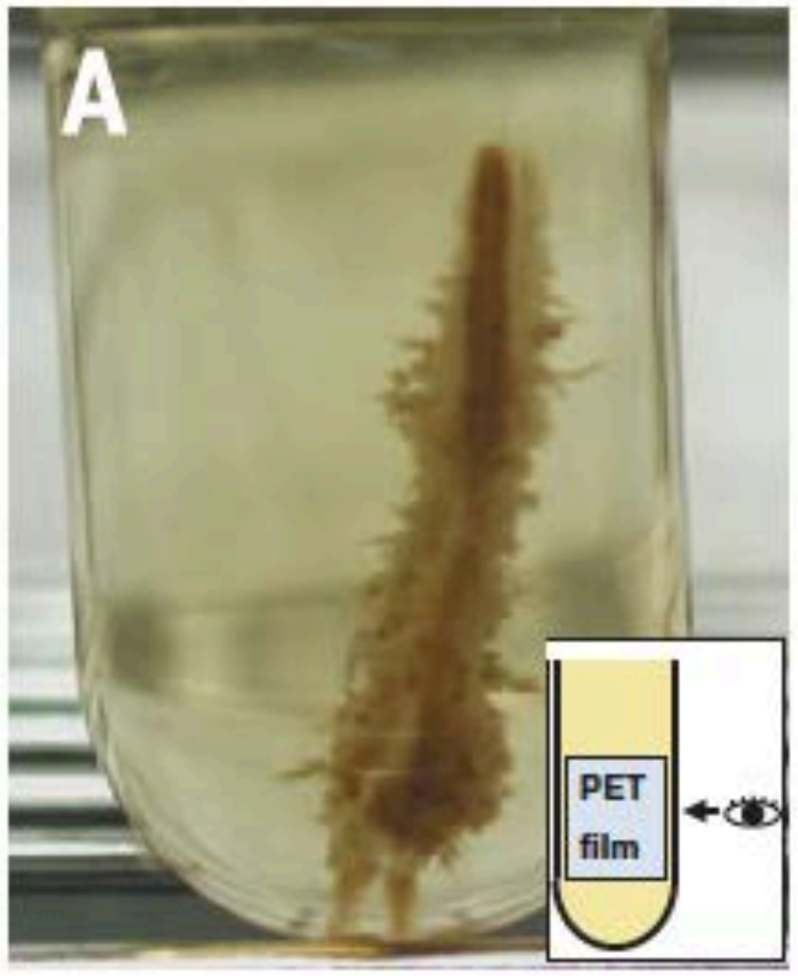


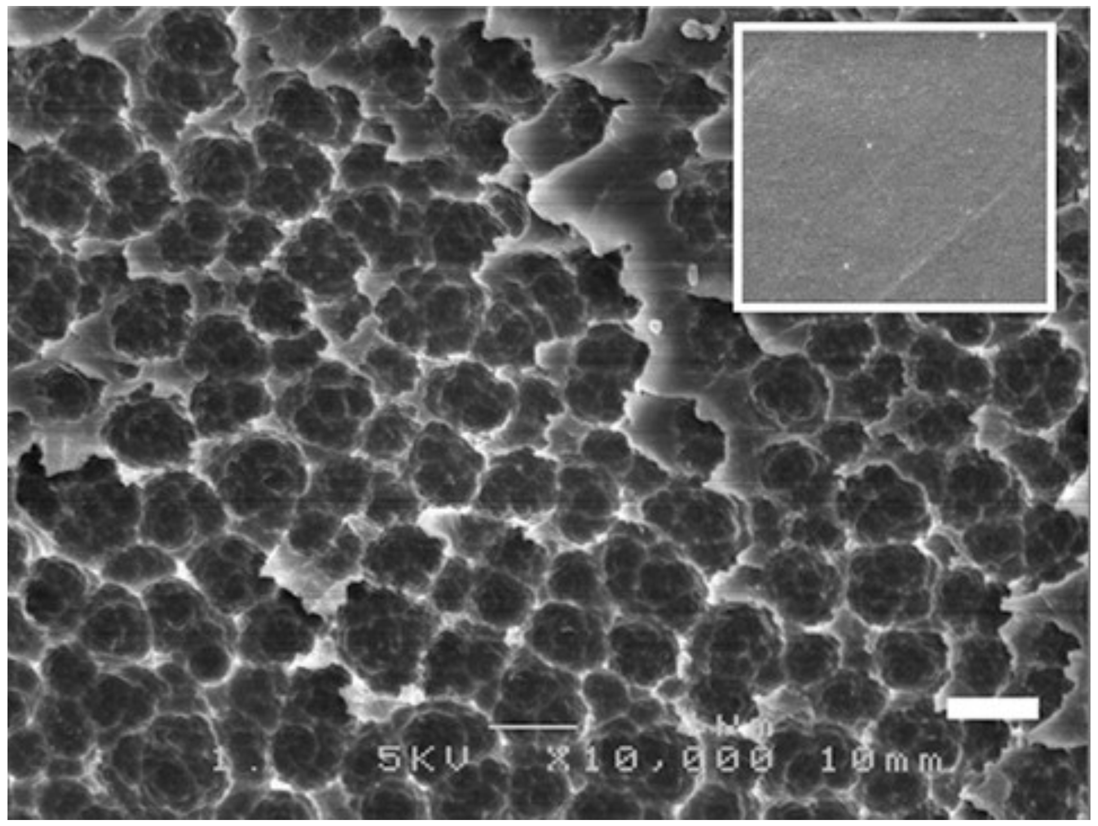
* This total represents all clean flake sold into end markets by US reclaimers. See figure 7 for detail on total flake produced by US reclaimers from bottles.

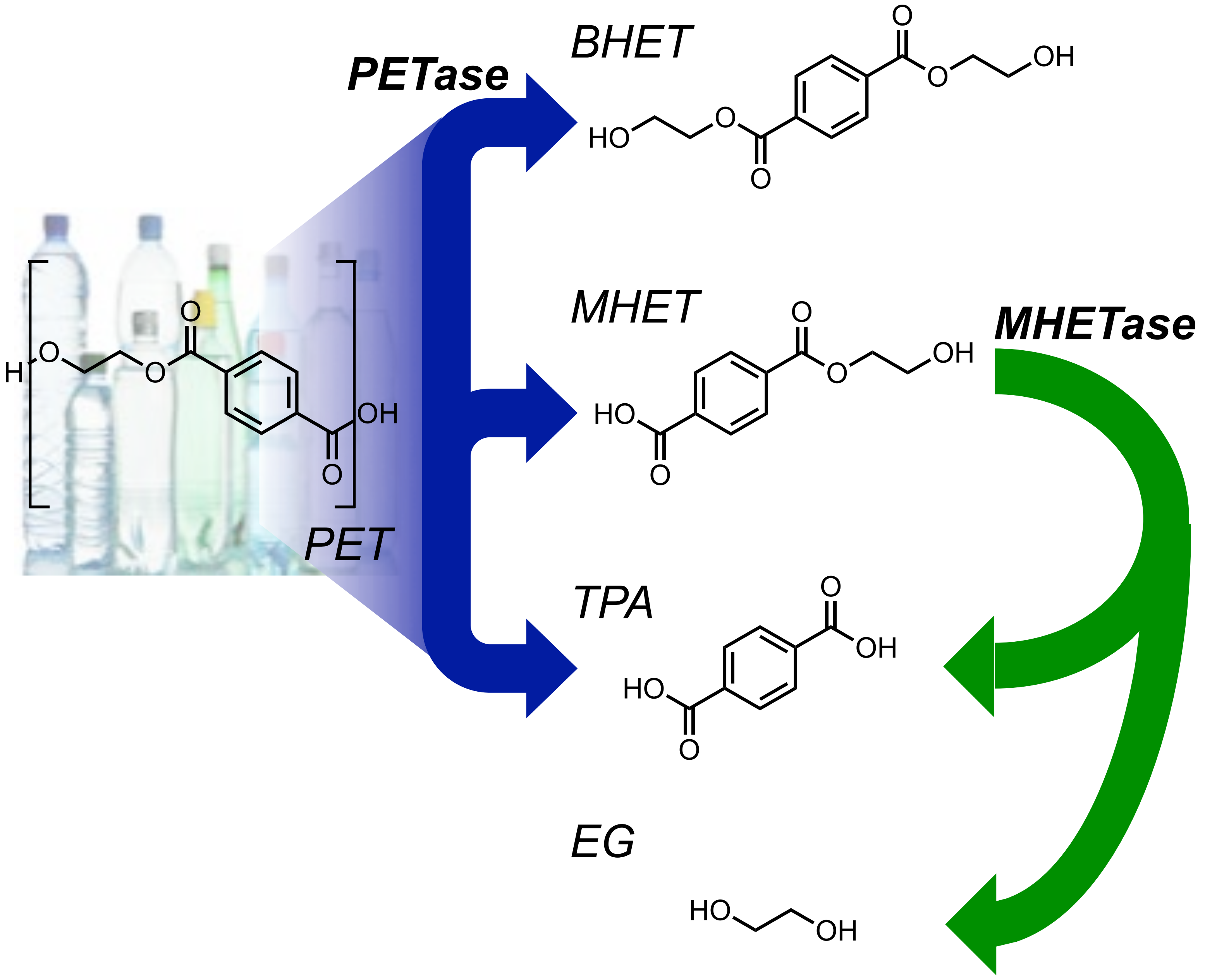


Plastics recycling is mostly mechanical today, which is down-cycling…

Designing **enzymes** for plastics upcycling







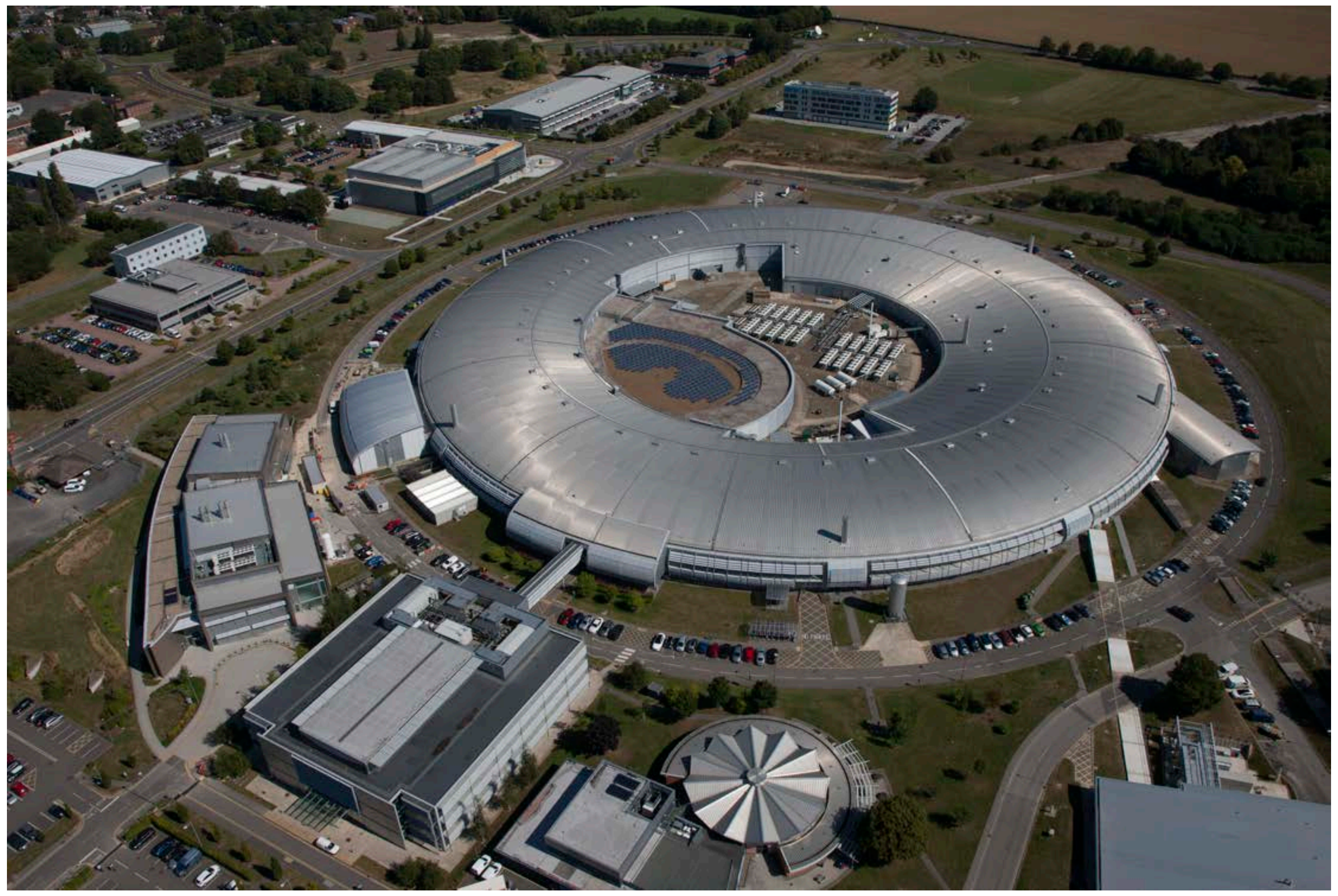
BIODEGRADATION

A bacterium that degrades and assimilates poly(ethylene terephthalate)

Shosuke Yoshida,[1,2]* Kazumi Hiraga,[1] Toshihiko Takehana,[3] Ikuo Taniguchi,[4] Hironao Yamaji,[1] Yasuhito Maeda,[5] Kiyotsuna Toyohara,[5] Kenji Miyamoto,[2]† Yoshiharu Kimura,[4] Kohei Oda[1]†

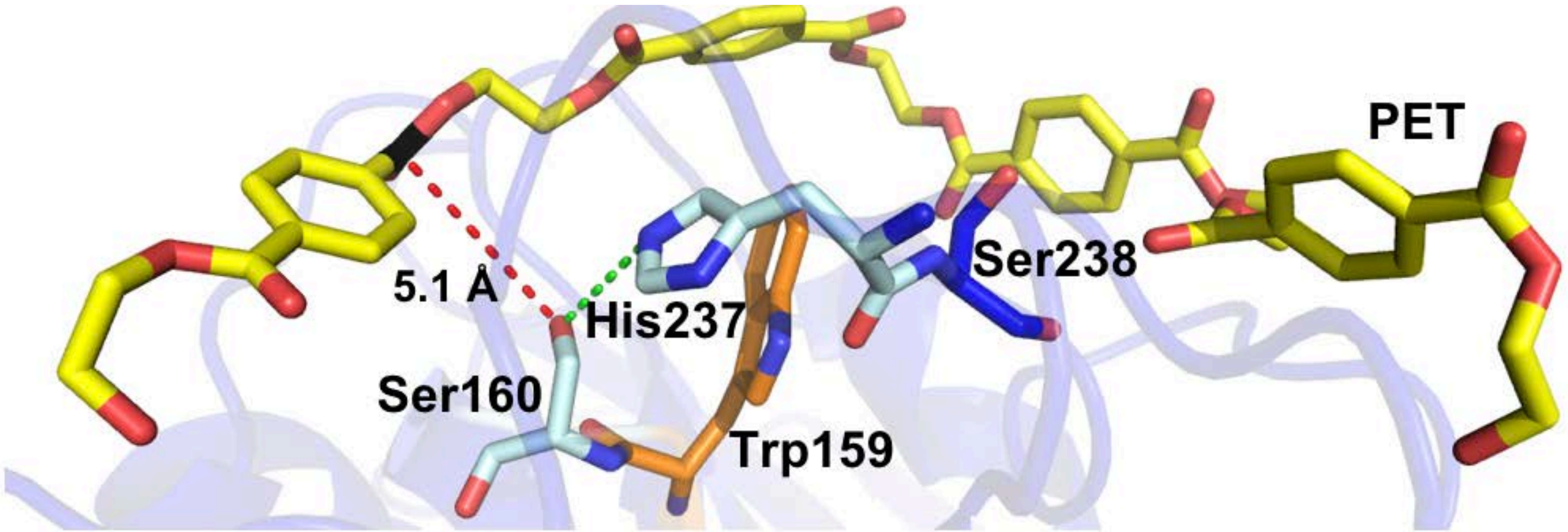
Yoshida *et al.*, *Science* 2016
Austin *et al.*, *PNAS* 2018

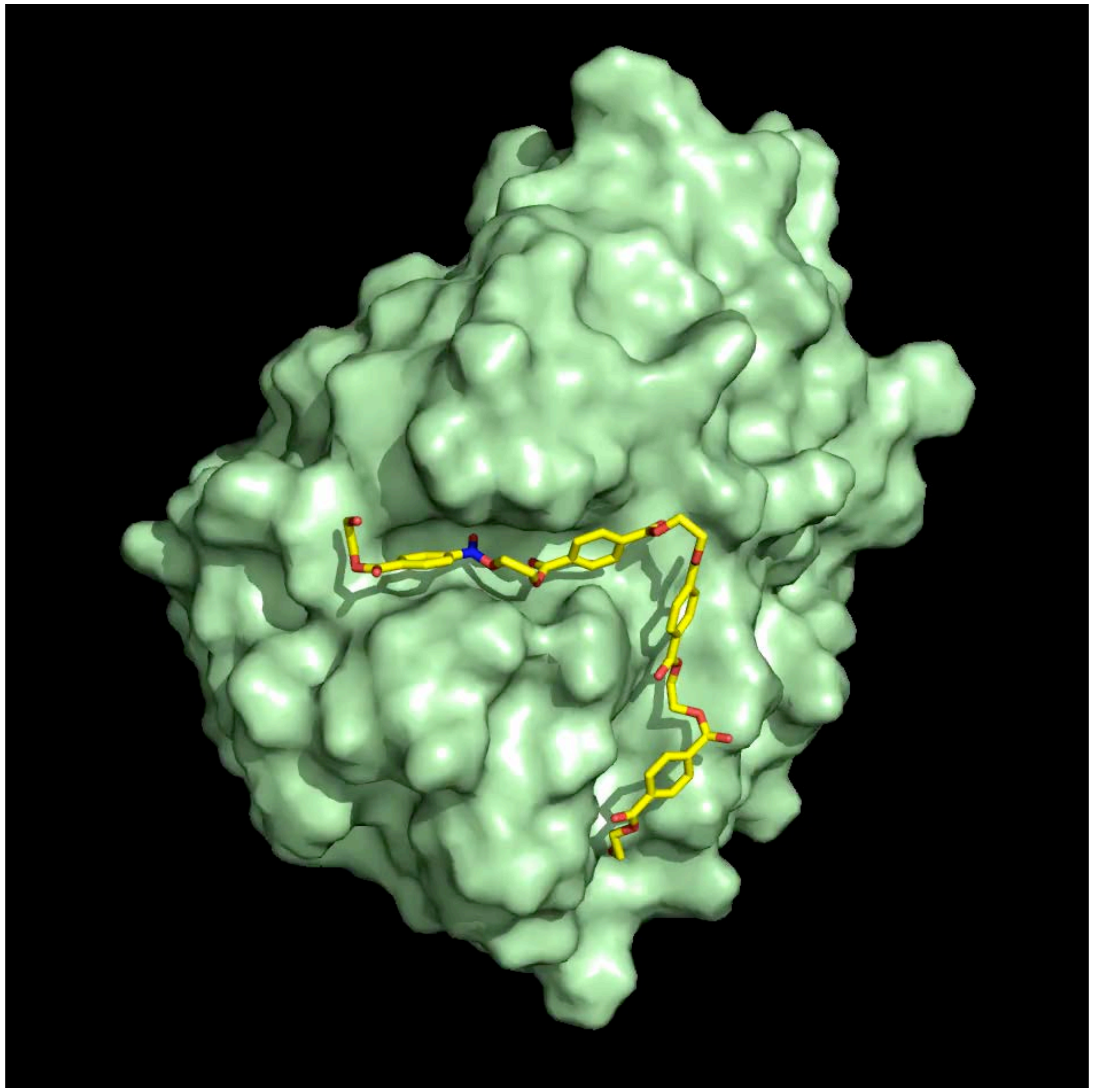
What does PETase look like at the molecular level?



Austin, Allen, Donohoe, Rorrer, Kearns *et al.*, *PNAS* 2018

How does the PET polymer bind to PETase?





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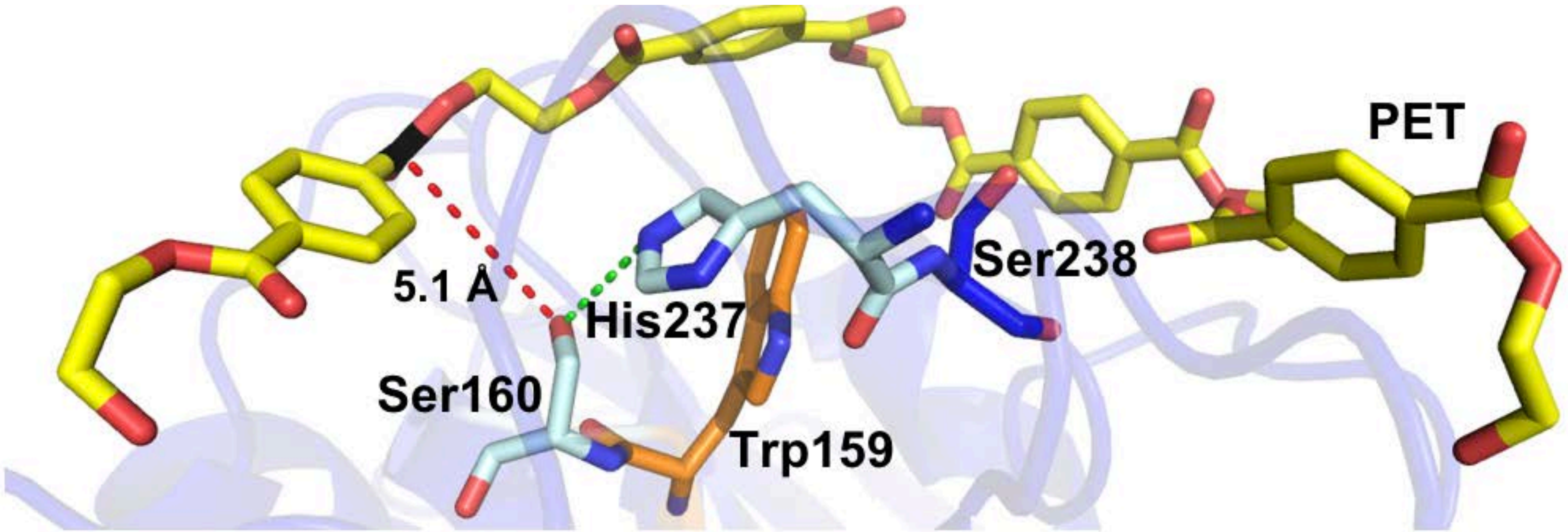

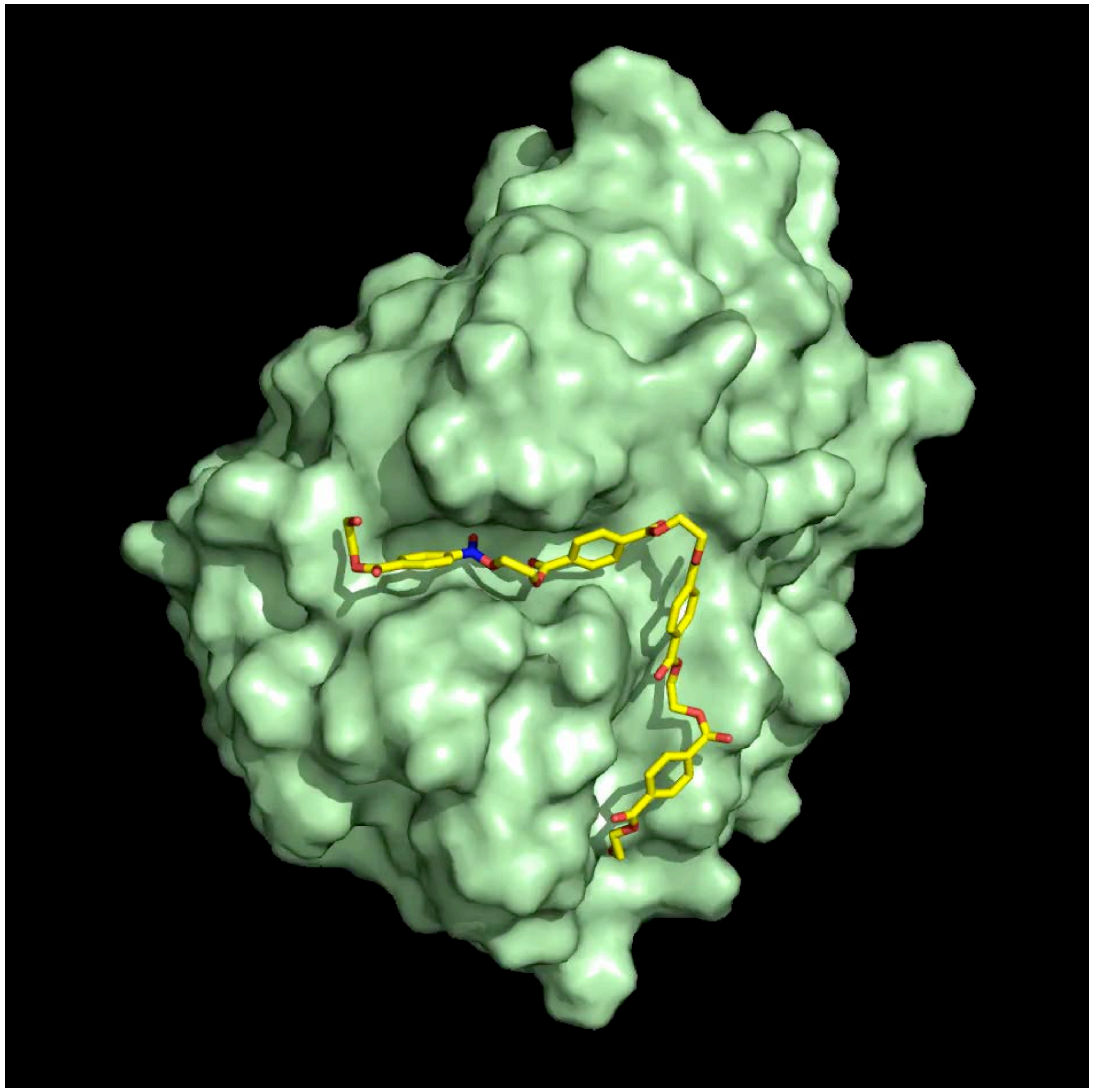

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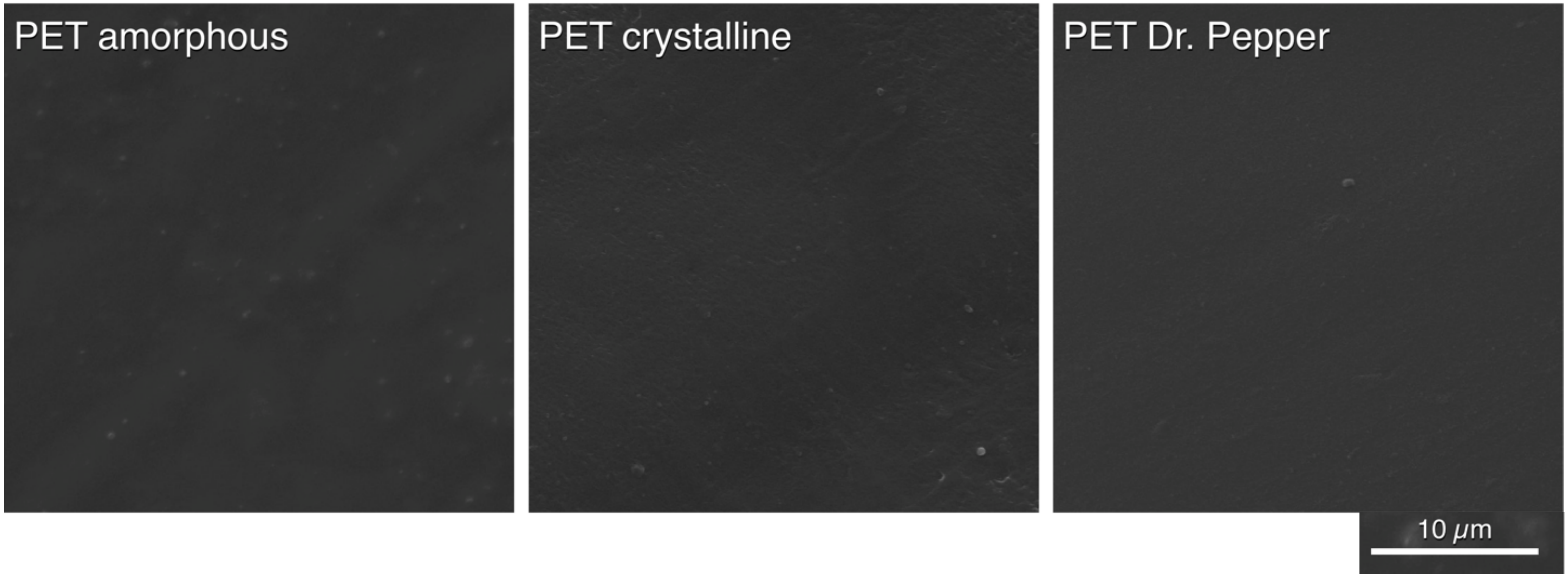
PETase assays on solid polymers



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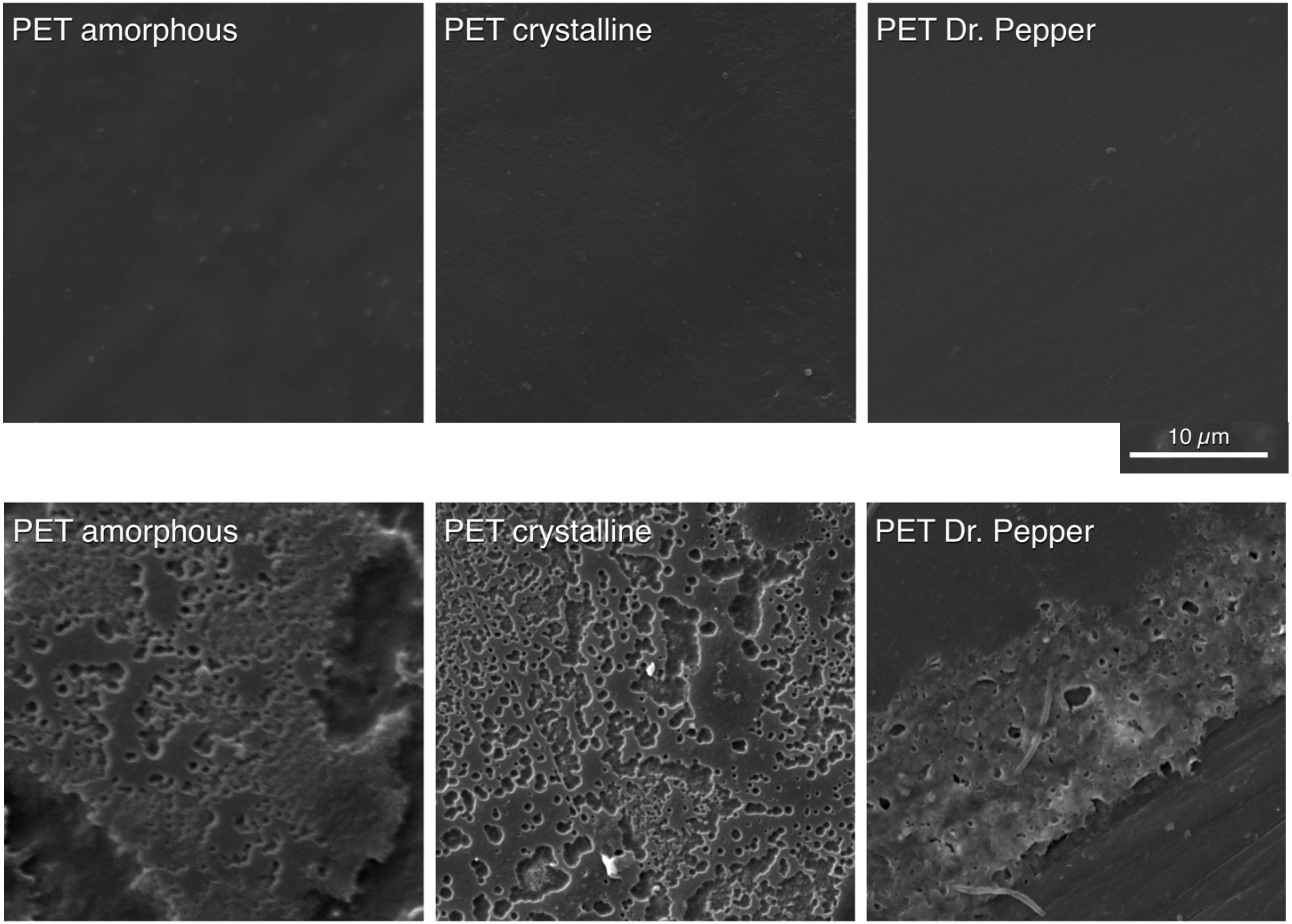
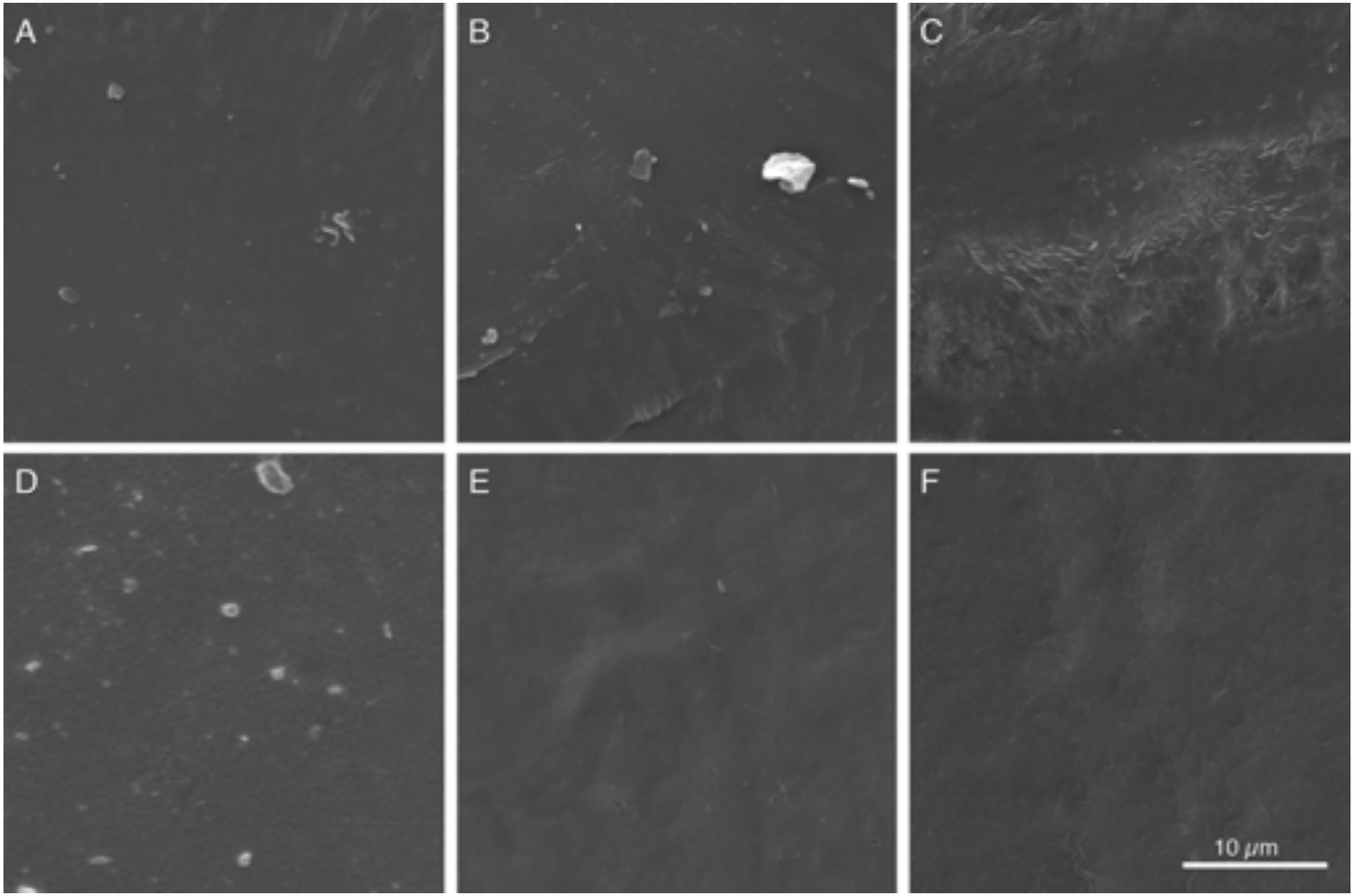


Austin, Allen, Donohoe, Rorrer, Kearns *et al.*, *PNAS* 2018

PETase does not digest PLA or PBS

Polybutylene succinate (as-synthesized, buffer control, with PETase)

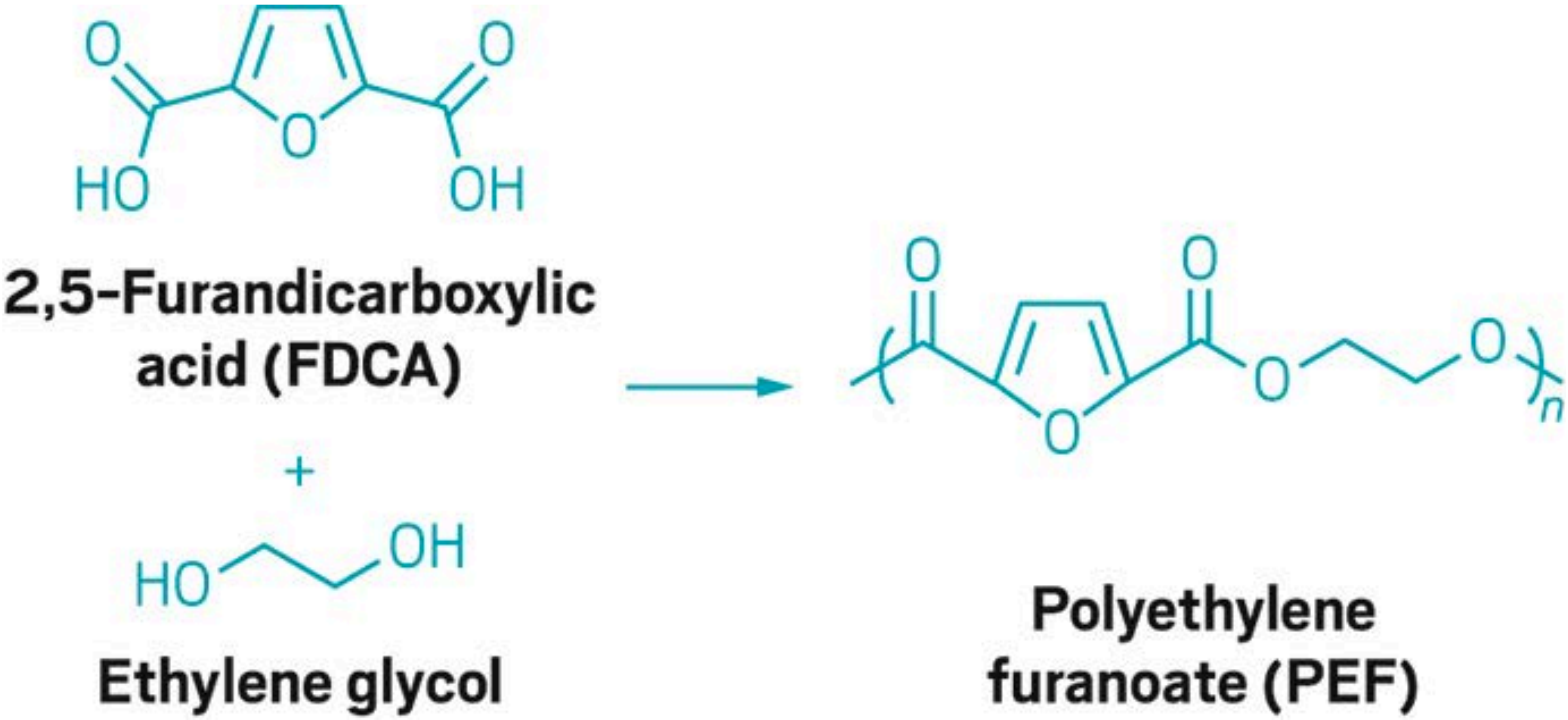
Polylactic acid (as-synthesized, buffer control, with PETase)



Austin, Allen, Donohoe, Rorrer, Kearns *et al.*, *PNAS* 2018

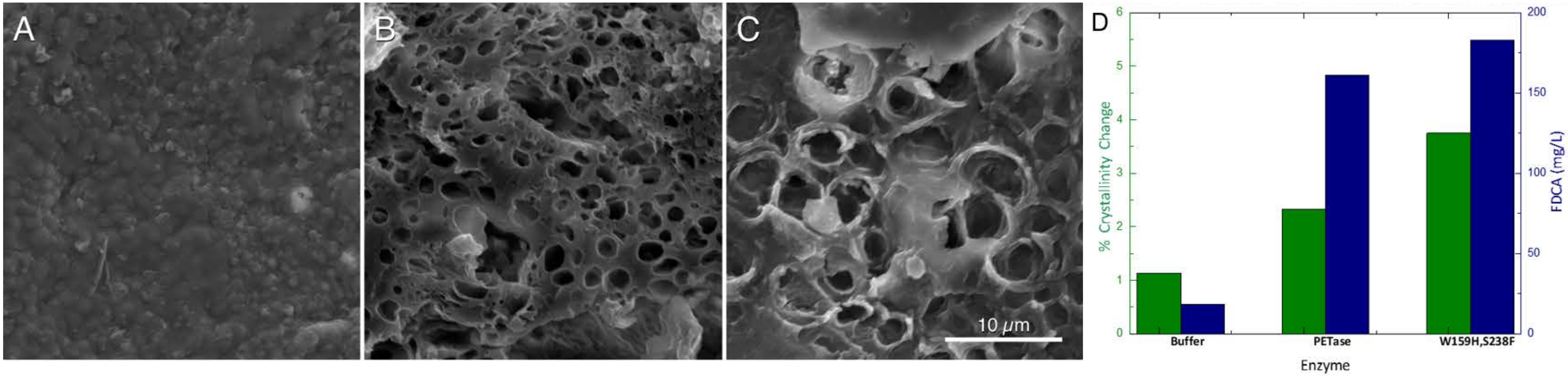
Bio-based semi-aromatic polyester

C&EN, 2016



Austin, Allen, Donohoe, Rorrer, Kearns *et al.*, *PNAS* 2018

PETase digests PEF as well



Control PEF coupon

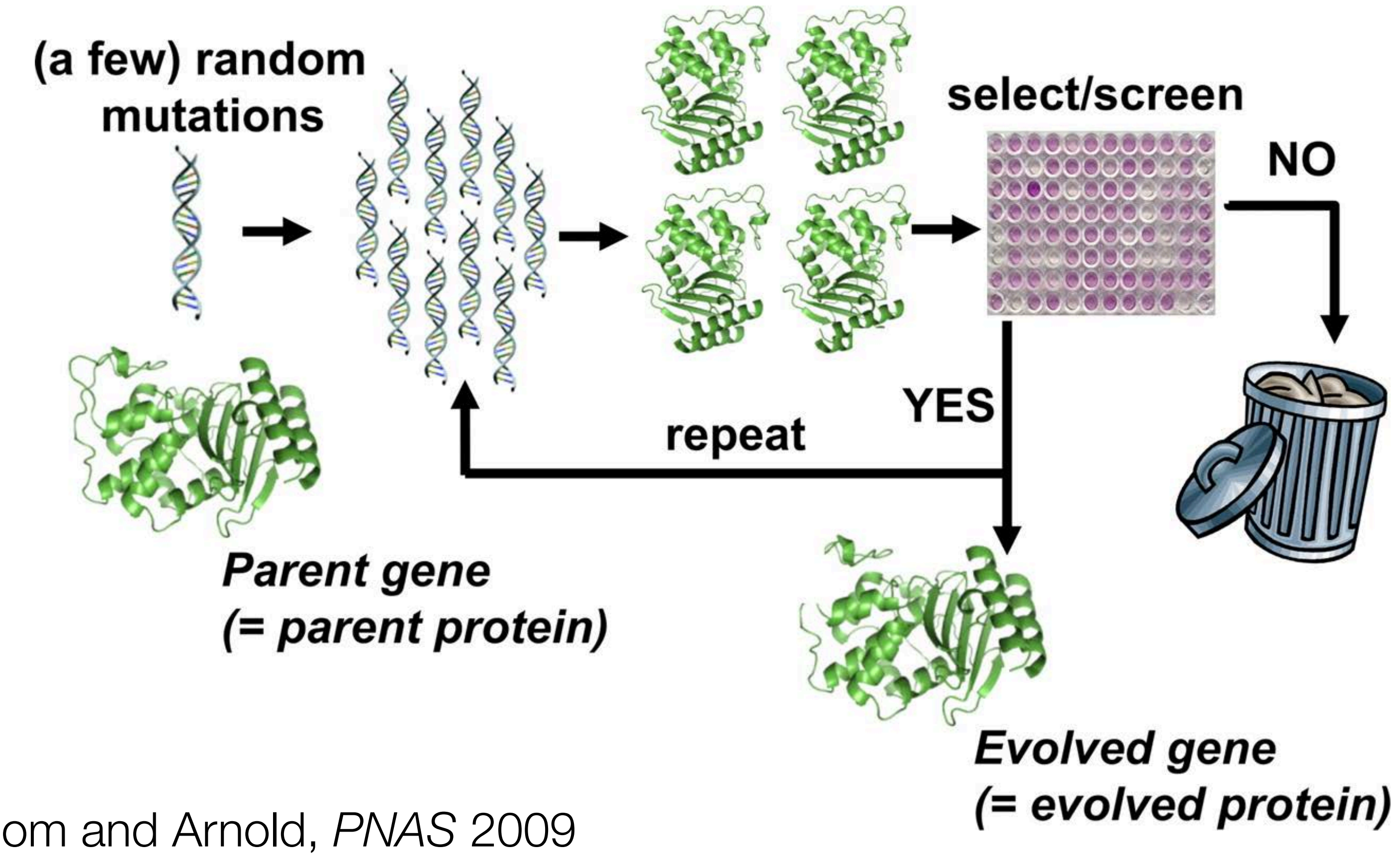
PEF coupon treated w/ PETase!

PEF coupon treated w/ double mutant PETase!

Austin, Allen, Donohoe, Rorrer, Kearns *et al.*, *PNAS* 2018

What’s next for PET bioconversion?

Directed evolution of PETase enzymes



Bloom and Arnold, *PNAS* 2009

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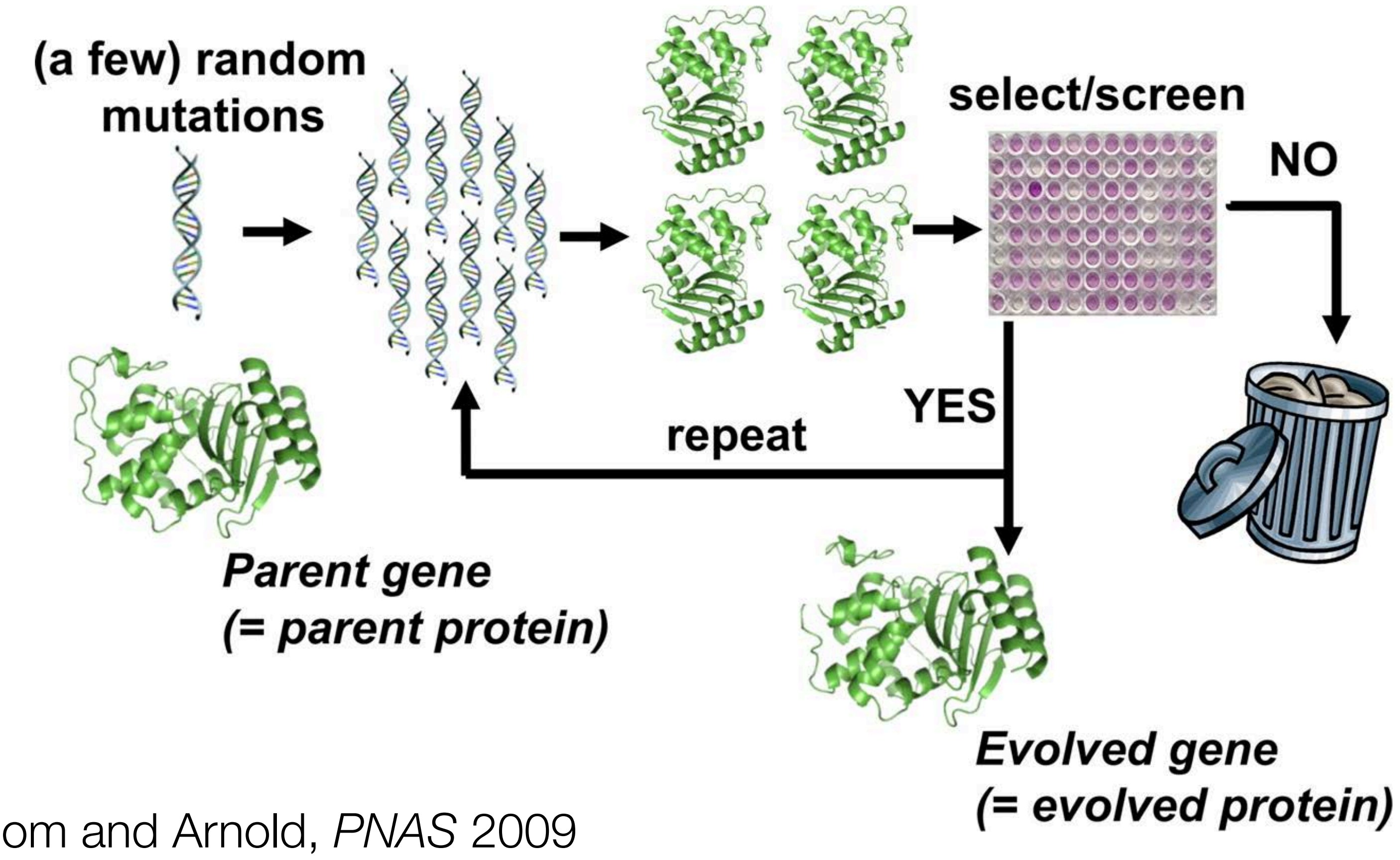

Bloom and Arnold, *PNAS* 2009

Prospecting for hyperthermophilic PETases

UNIVERSITY OF PORTSMOUTH

MONTANA STATE UNIVERSITY
1893
BOZEMAN - MONTANA

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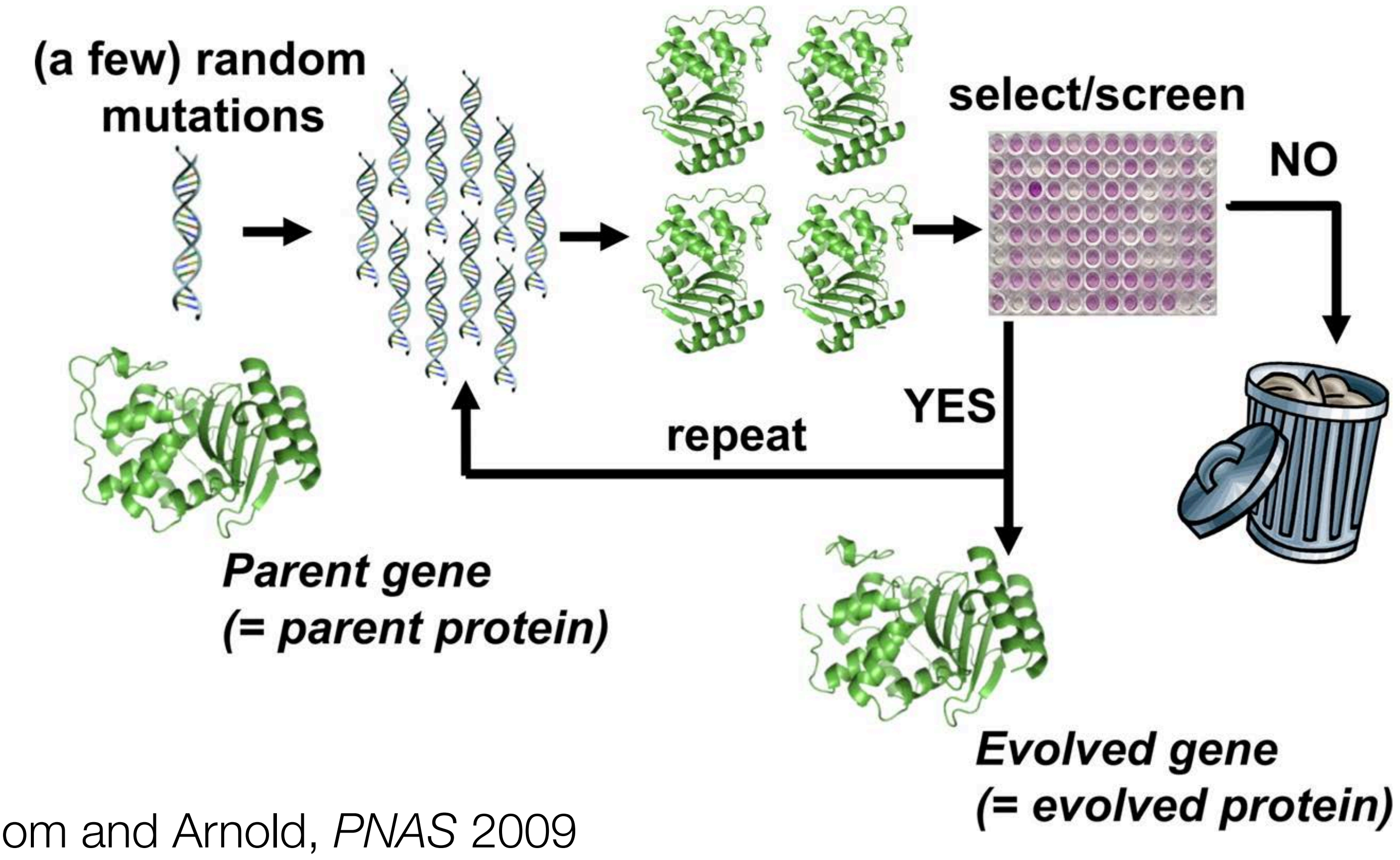
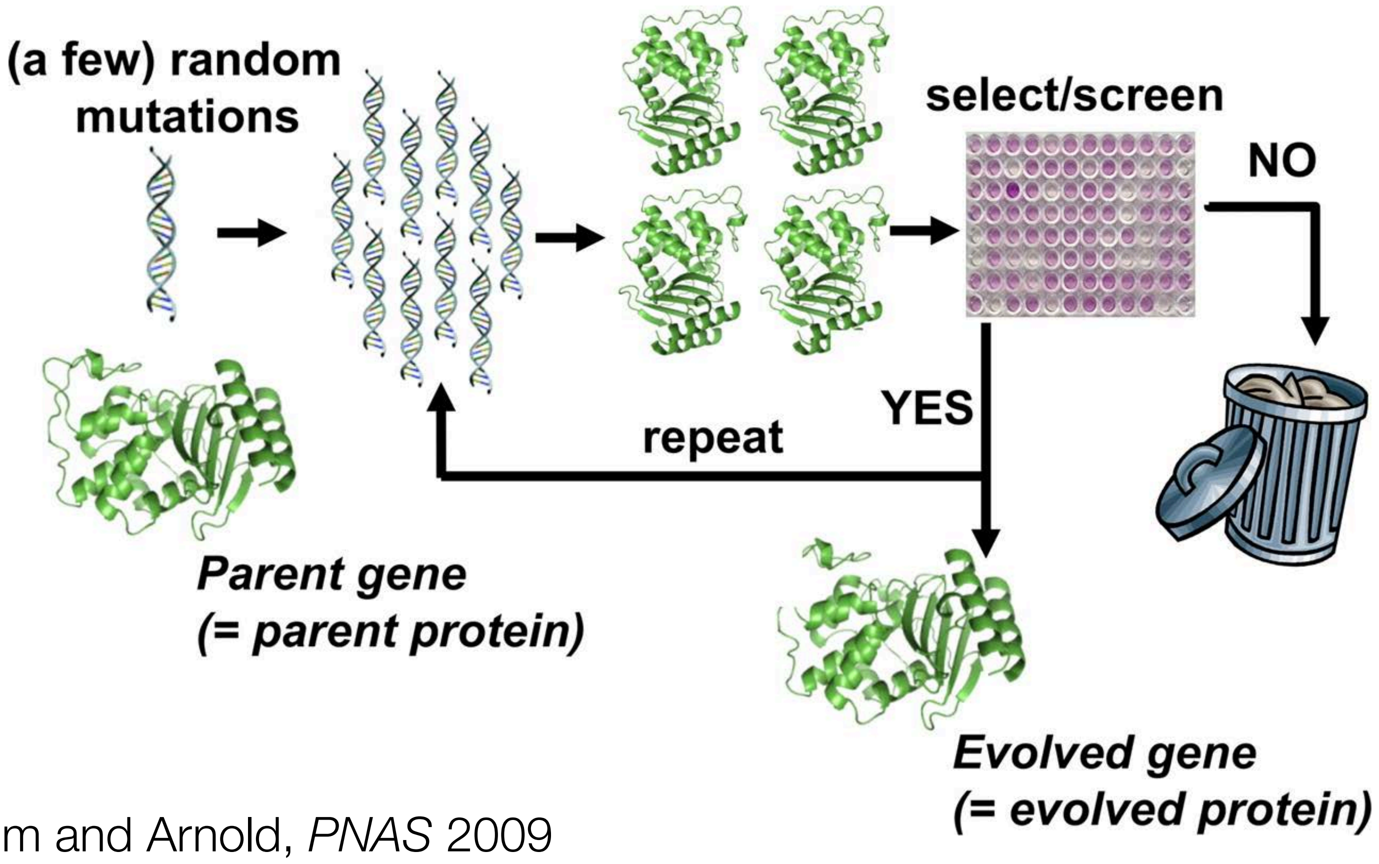


Bloom and Arnold, *PNAS* 2009

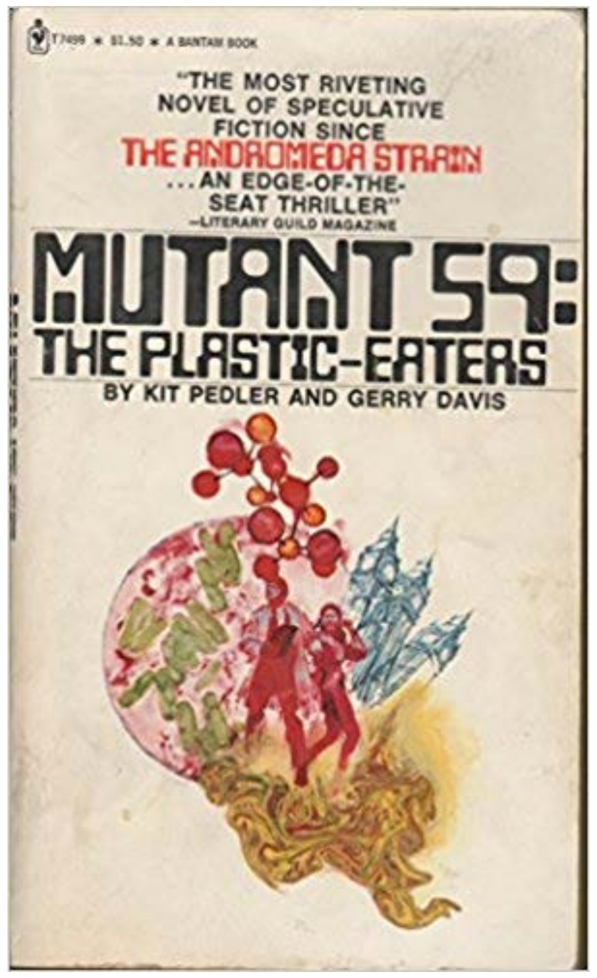
Prospecting for hyperthermophilic PETases

What's next for PET bioconversion?

Directed evolution of PETase enzymes



Bloom and Arnold, *PNAS* 2009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MUTANT 59: THE PLASTIC-EATERS

BY KIT PEDLER AND GERRY DAVIS

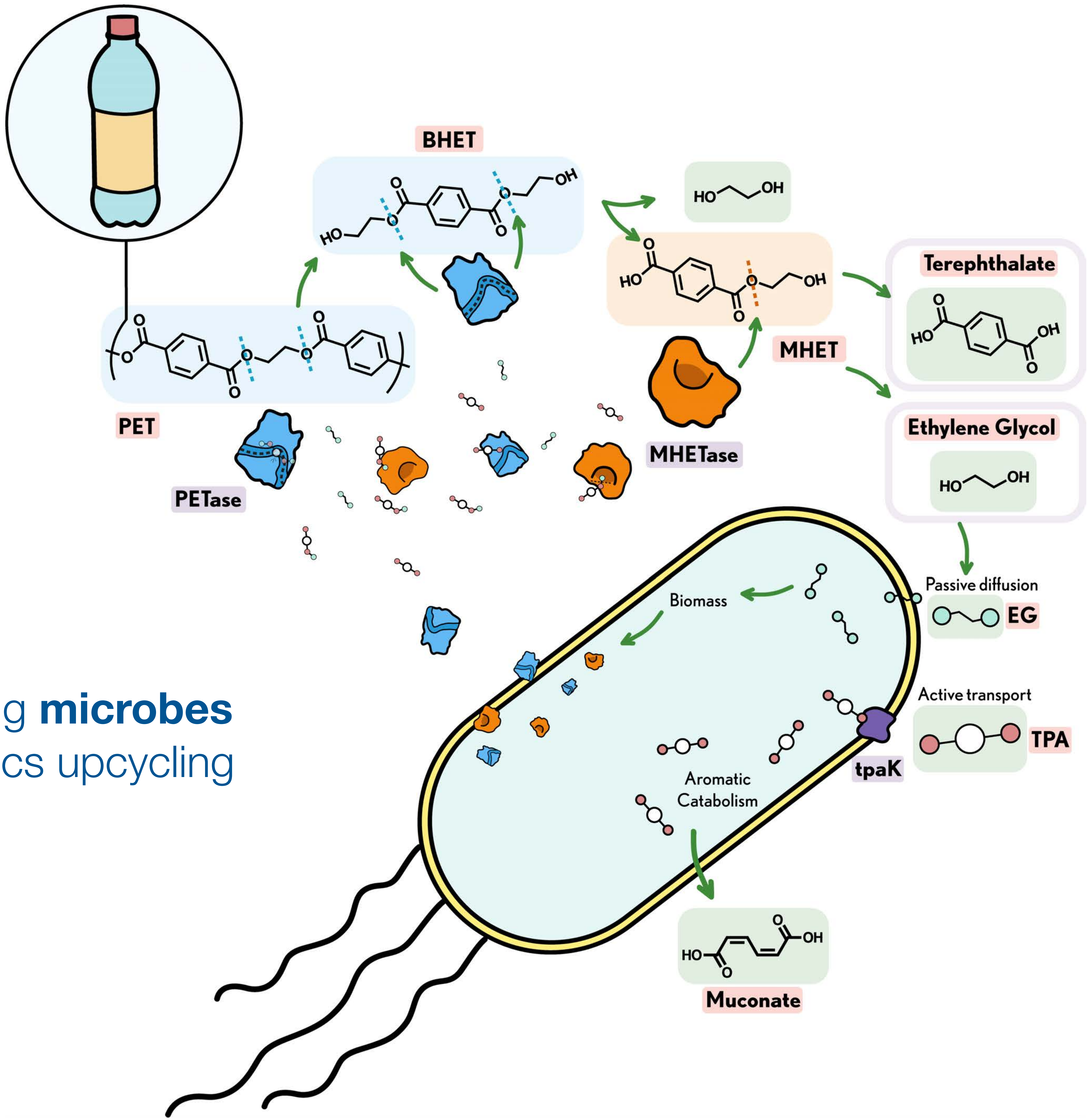
gsk

Prospecting for hyperthermophilic PETases

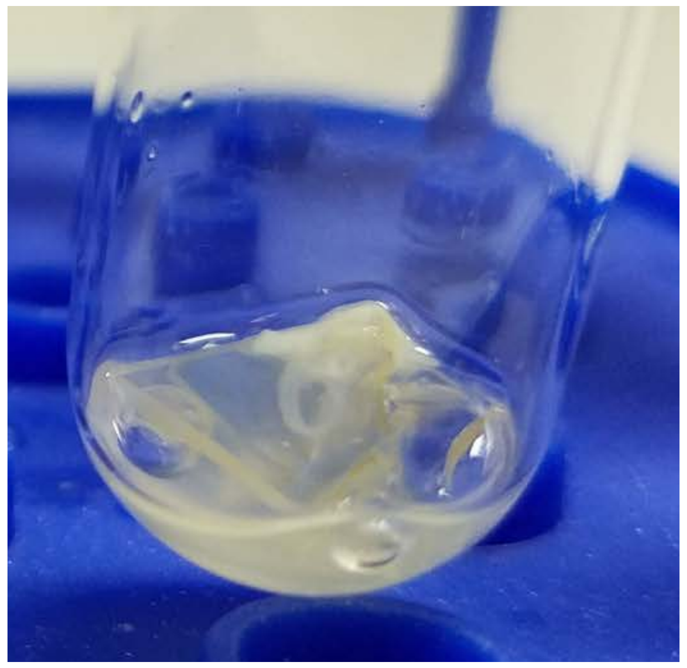
UNIVERSITY OF PORTSMOUTH

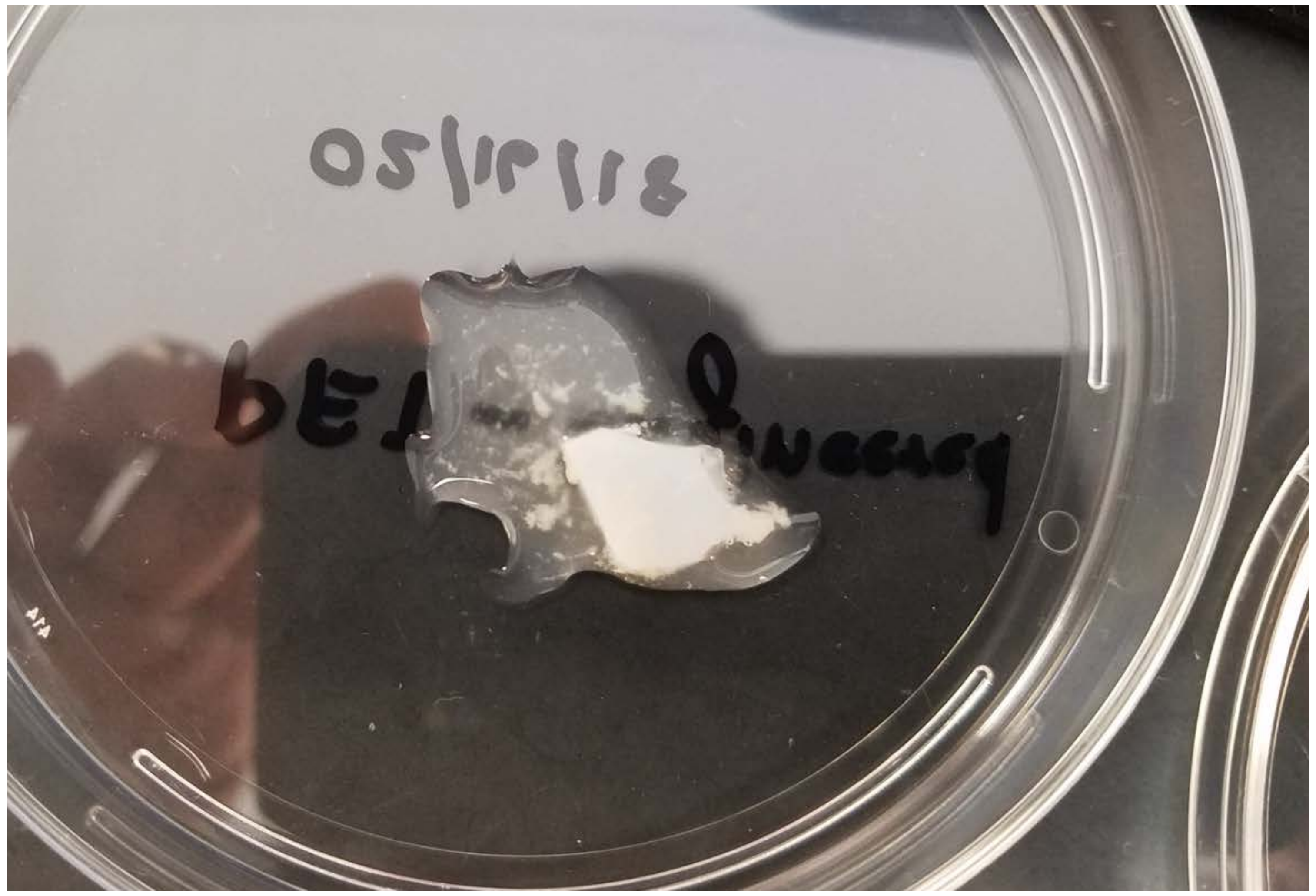
MONTANA STATE UNIVERSITY
1893
BOZEMAN - MONTANA

Designing **microbes** for plastics upcycling



Microbial PET degradation is within sight now





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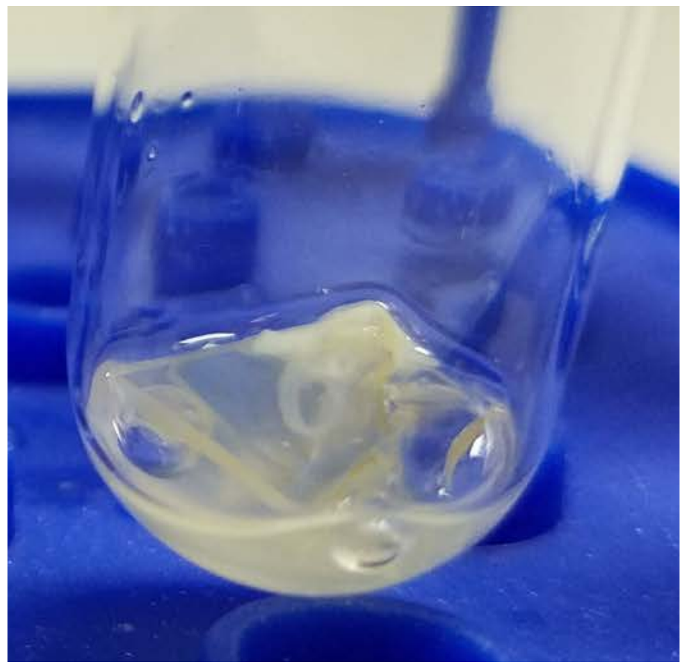
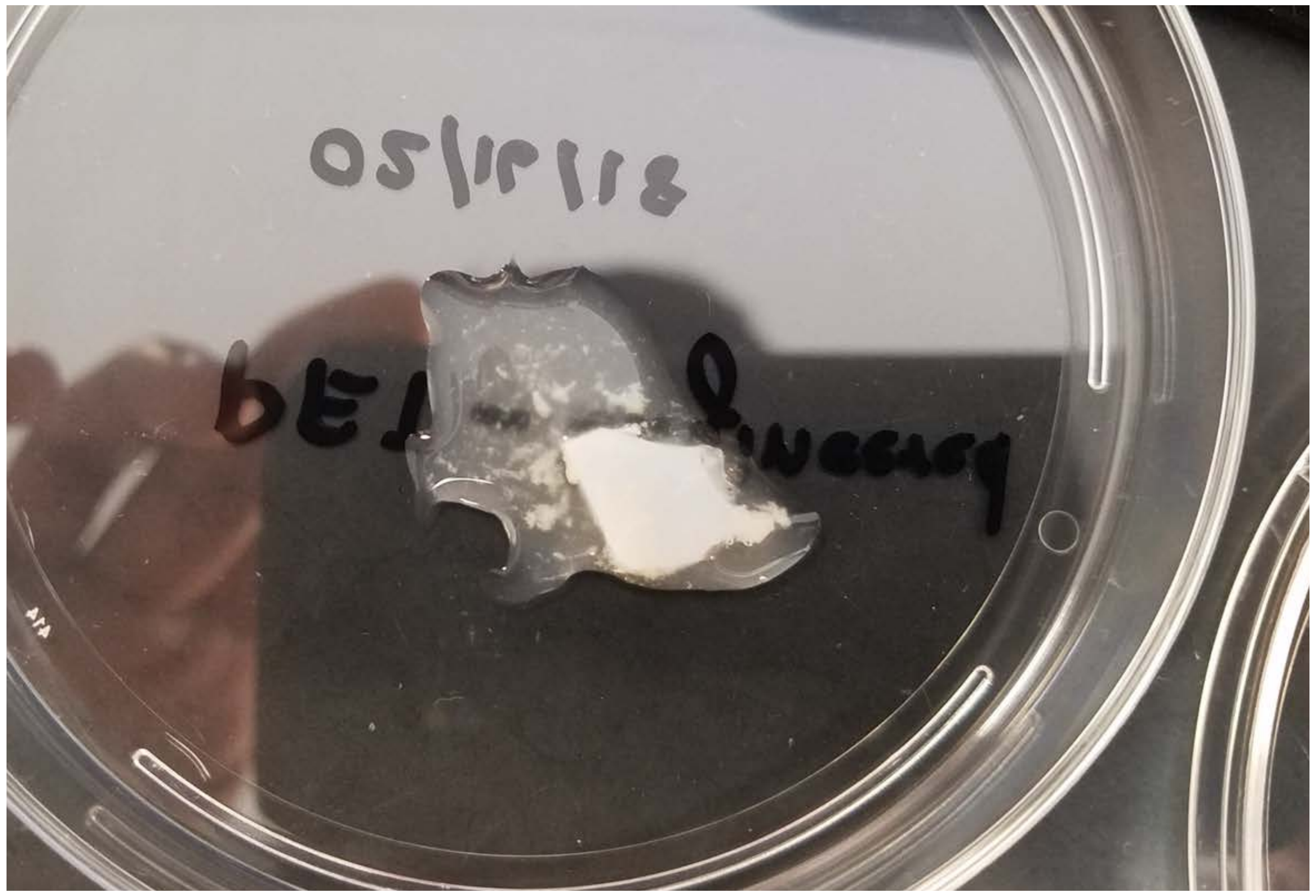
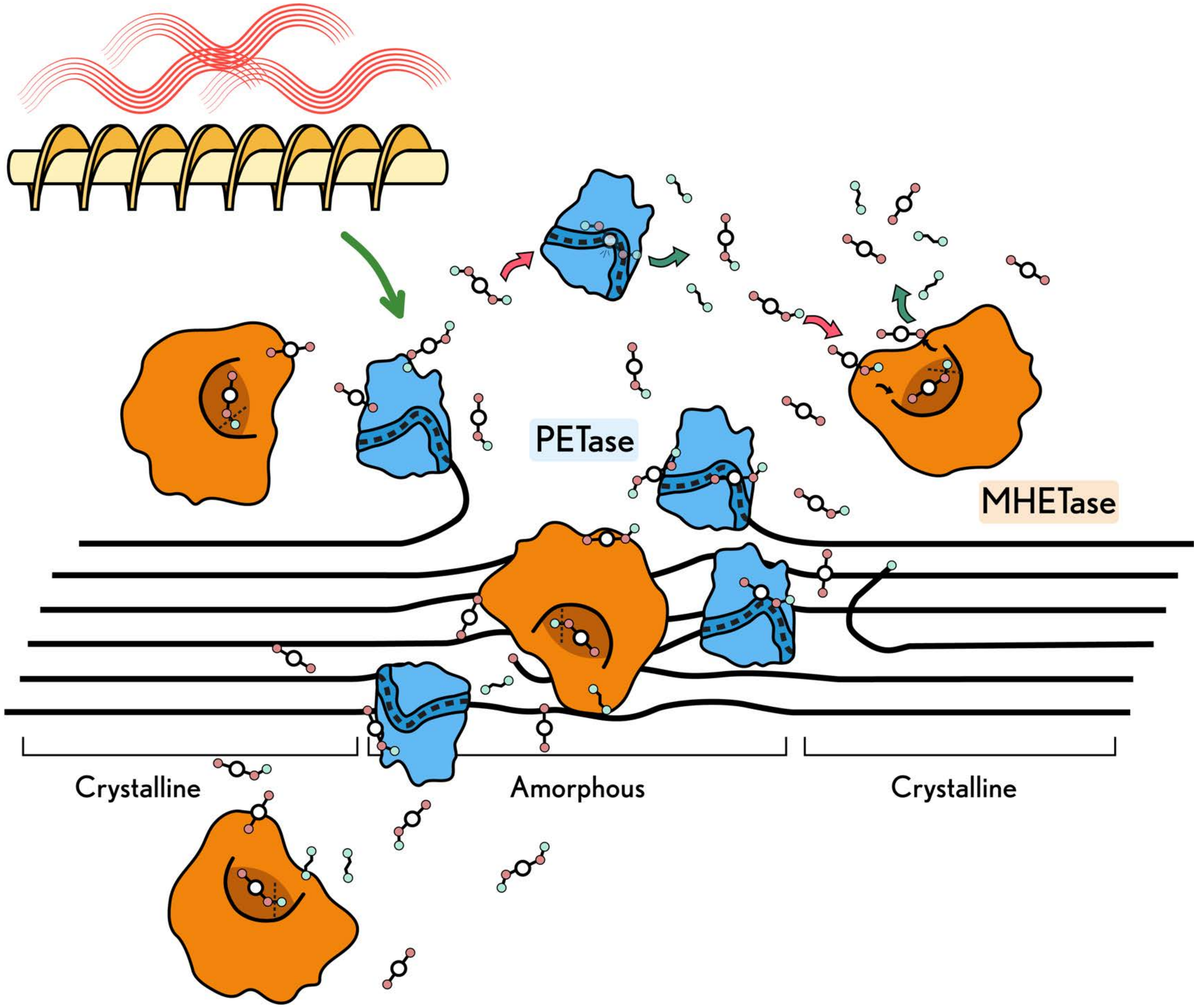


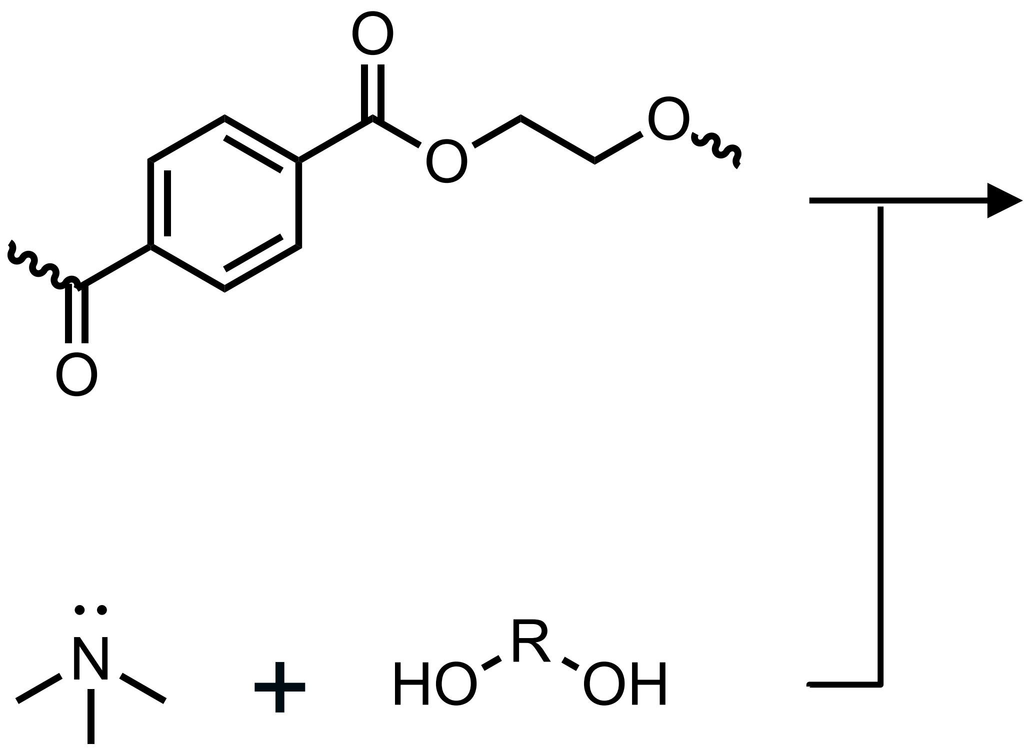


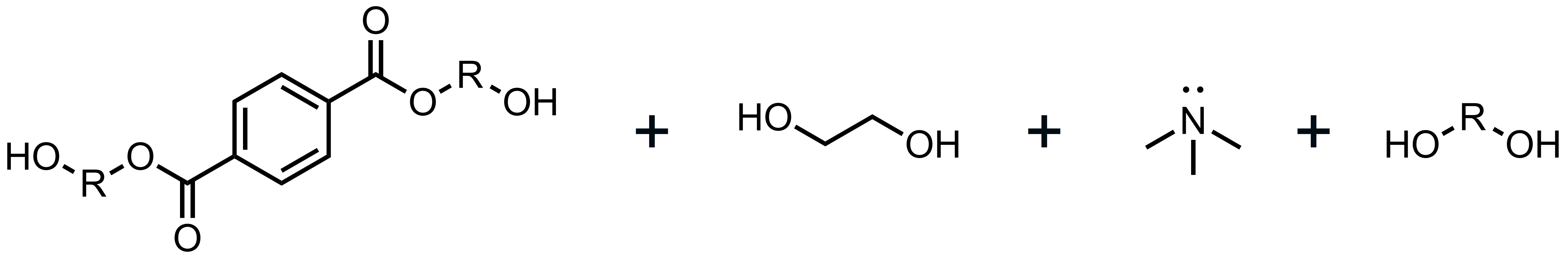
Hybrid chemical and biological processing



Using chemistry to breakdown PET faster

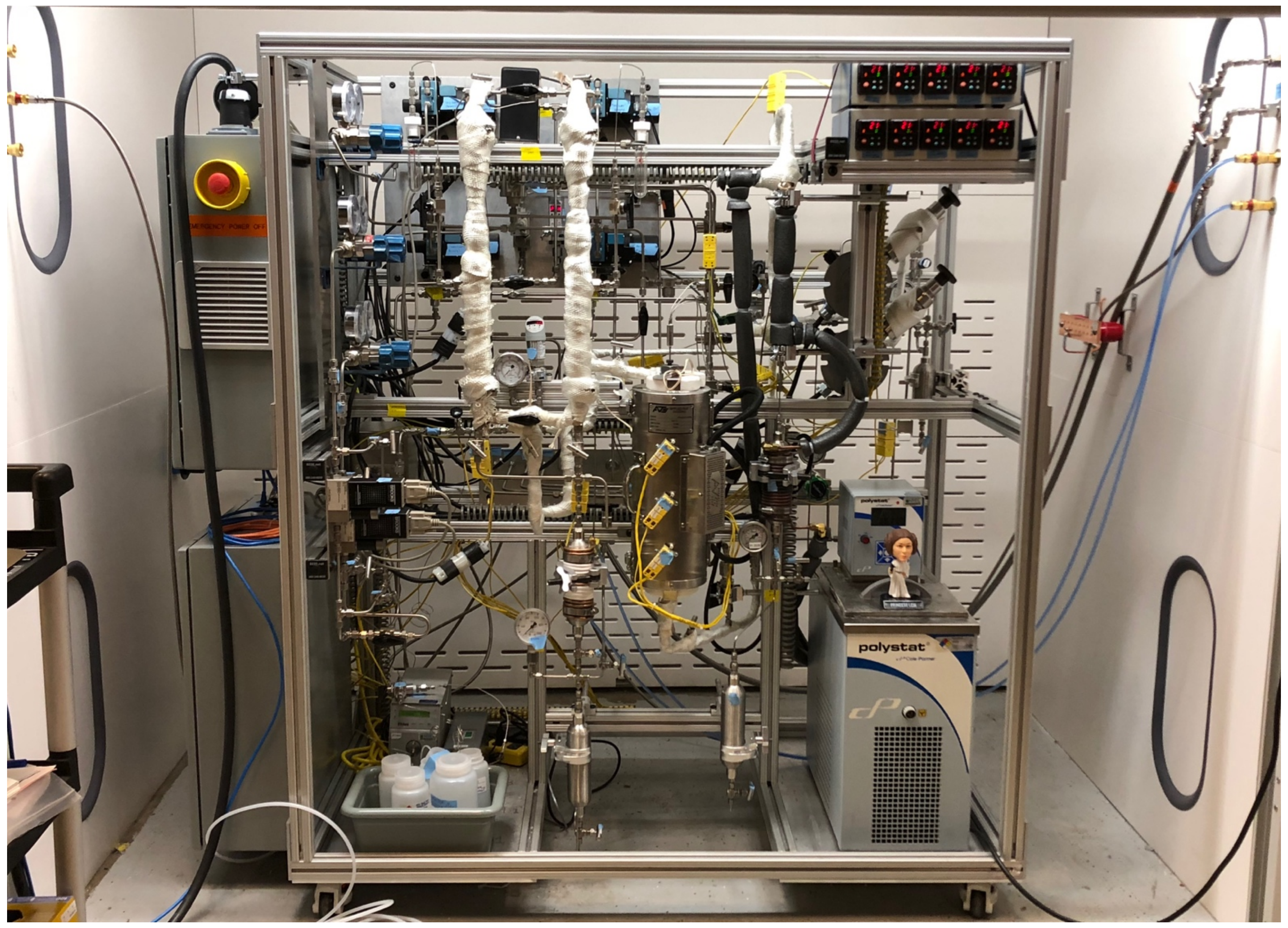
Collaboration with Greg
Breyta and Bob Allen, IBM



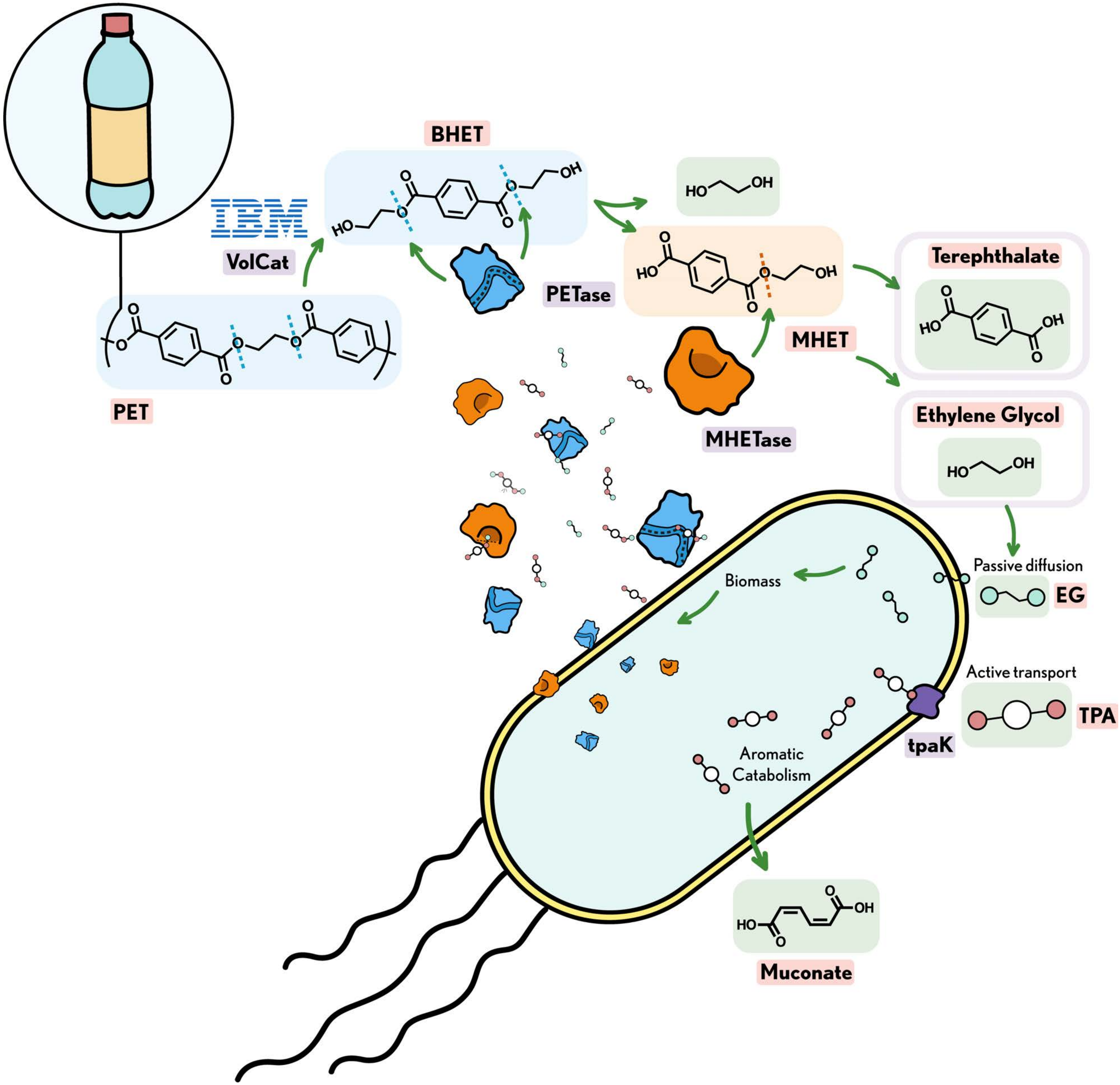


IBM

“give biology a hand”

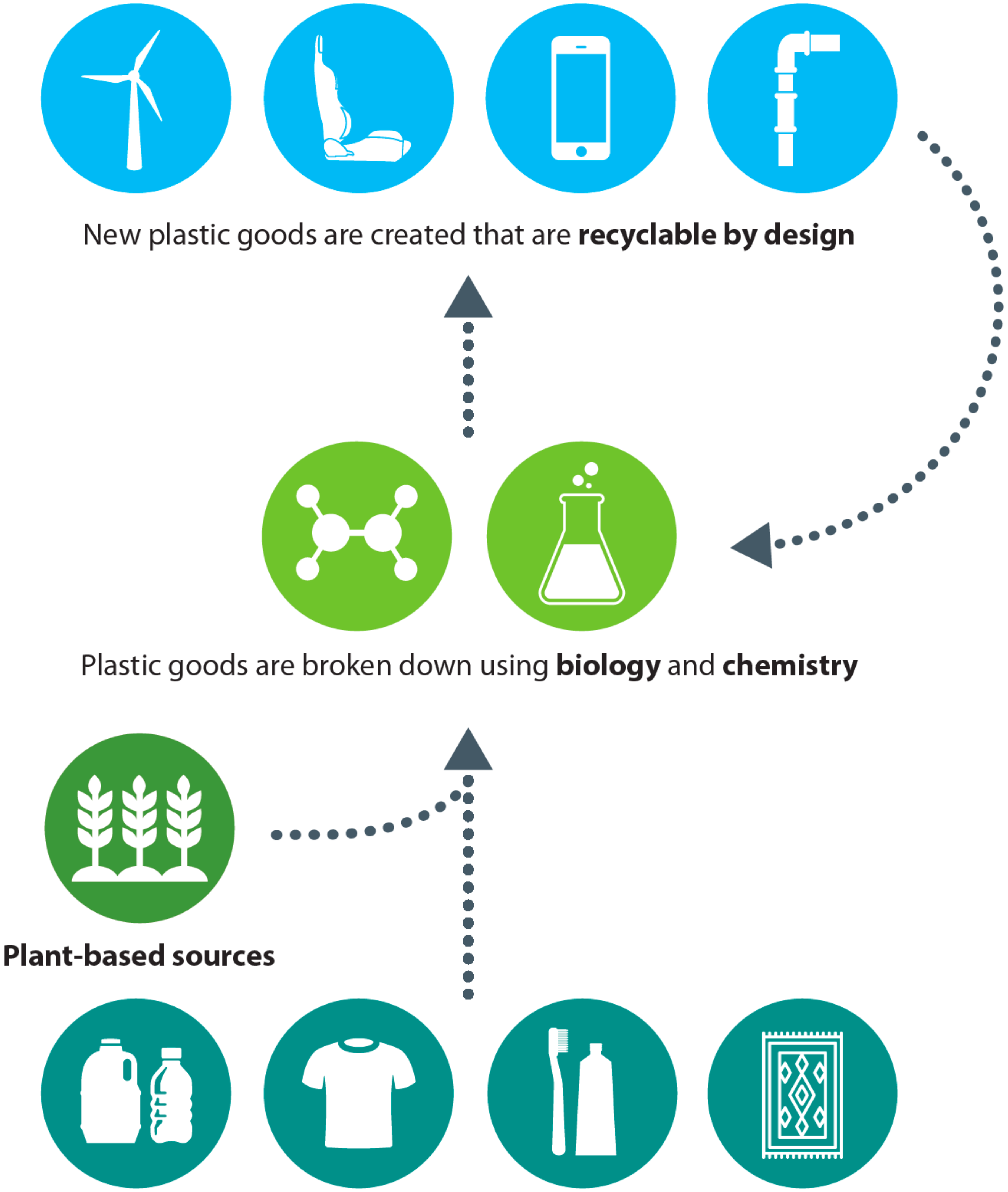


Now the PET breakdown product is the biological substrate



Challenge 2: What do we do with the breakdown products of plastics?

Concept of plastics upcycling



New plastic goods are created that are **recyclable by design**

Plastic goods are broken down using **biology** and **chemistry**

Plant-based sources

Exemplary upcycled products – high-strength composites

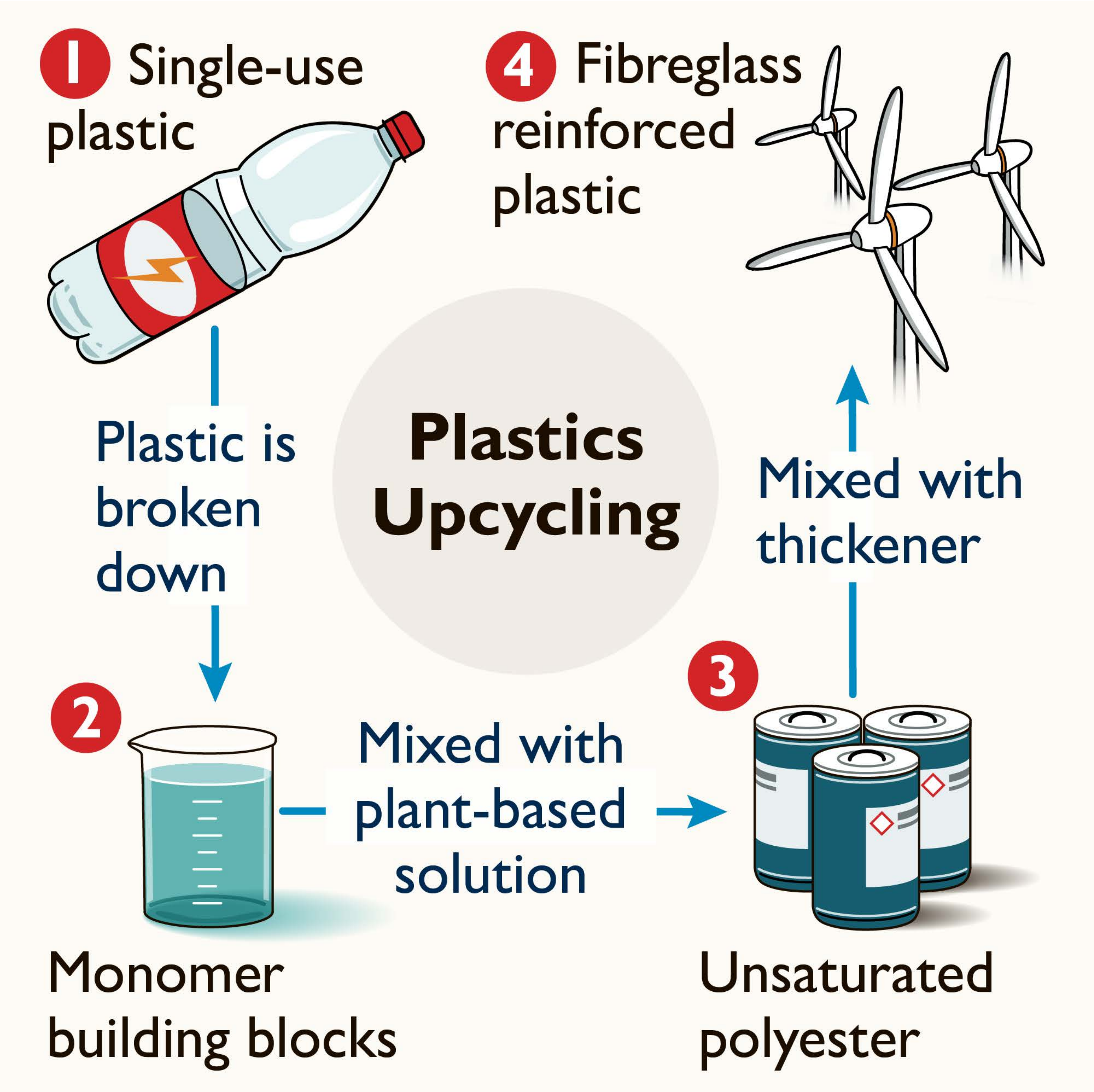
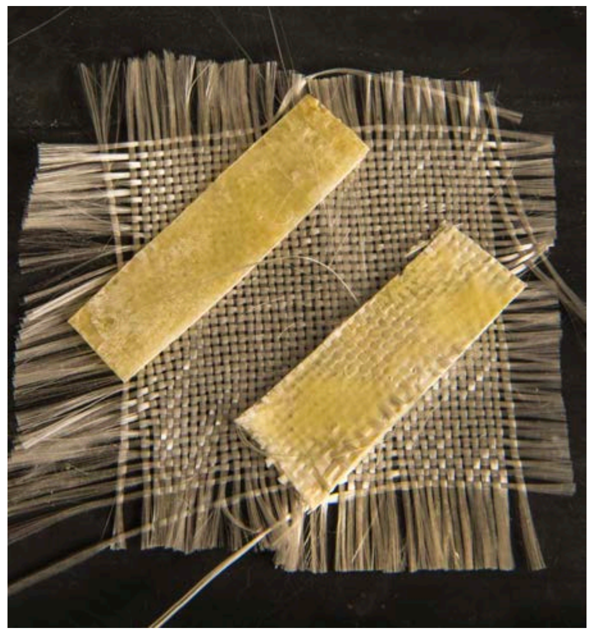


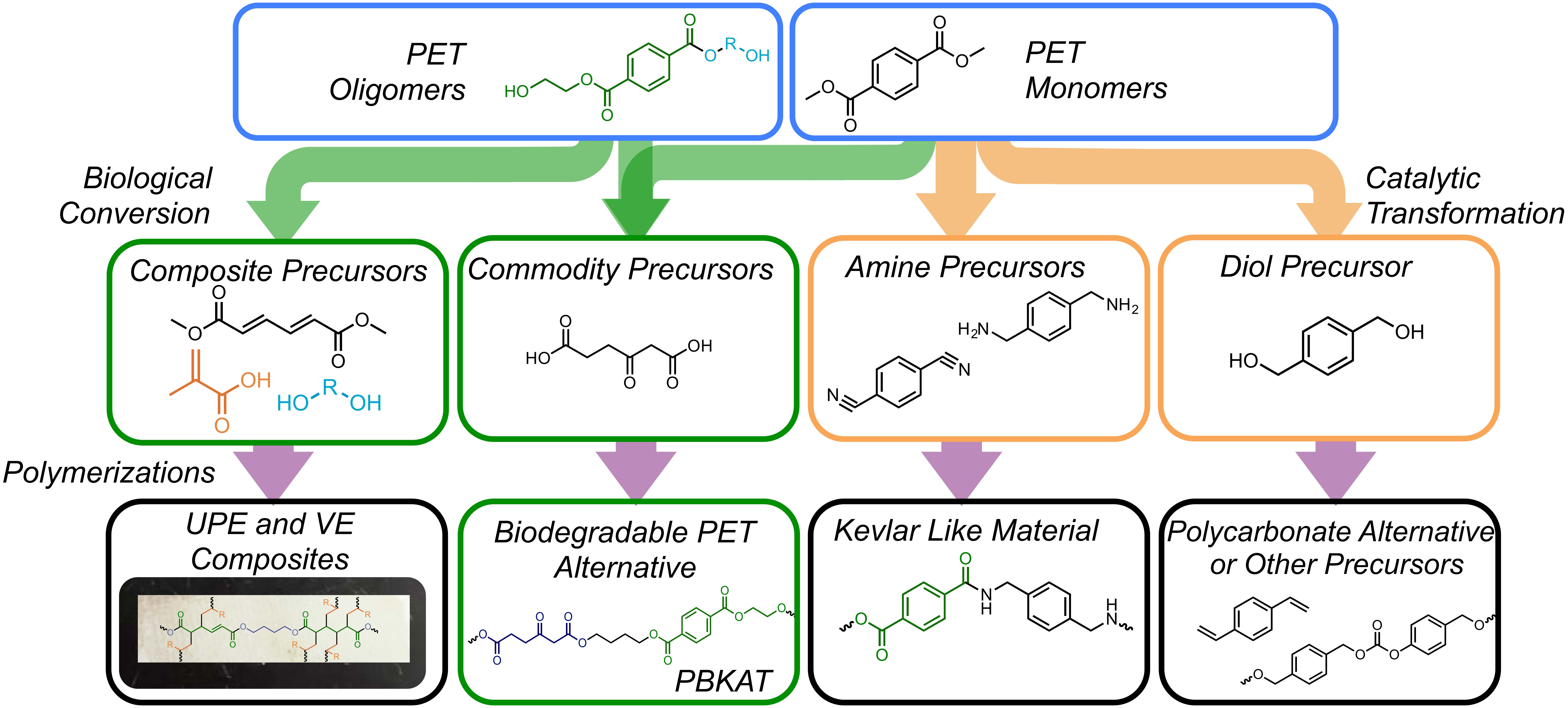
Image from the *Guardian*



Materials Flows through Industry

rPET + bio-based monomers enable 57% reduction in supply chain energy, 40% GHG emissions reduction for composites manufacturing and a ~5x value addition to rPET

What else can we do with the depolymerization product?



PET Oligomers

PET Monomers

Biological Conversion

Catalytic Transformation

Composite Precursors

Commodity Precursors

Amine Precursors

Diol Precursor

Polymerizations

UPE and VE Composites

Biodegradable PET Alternative

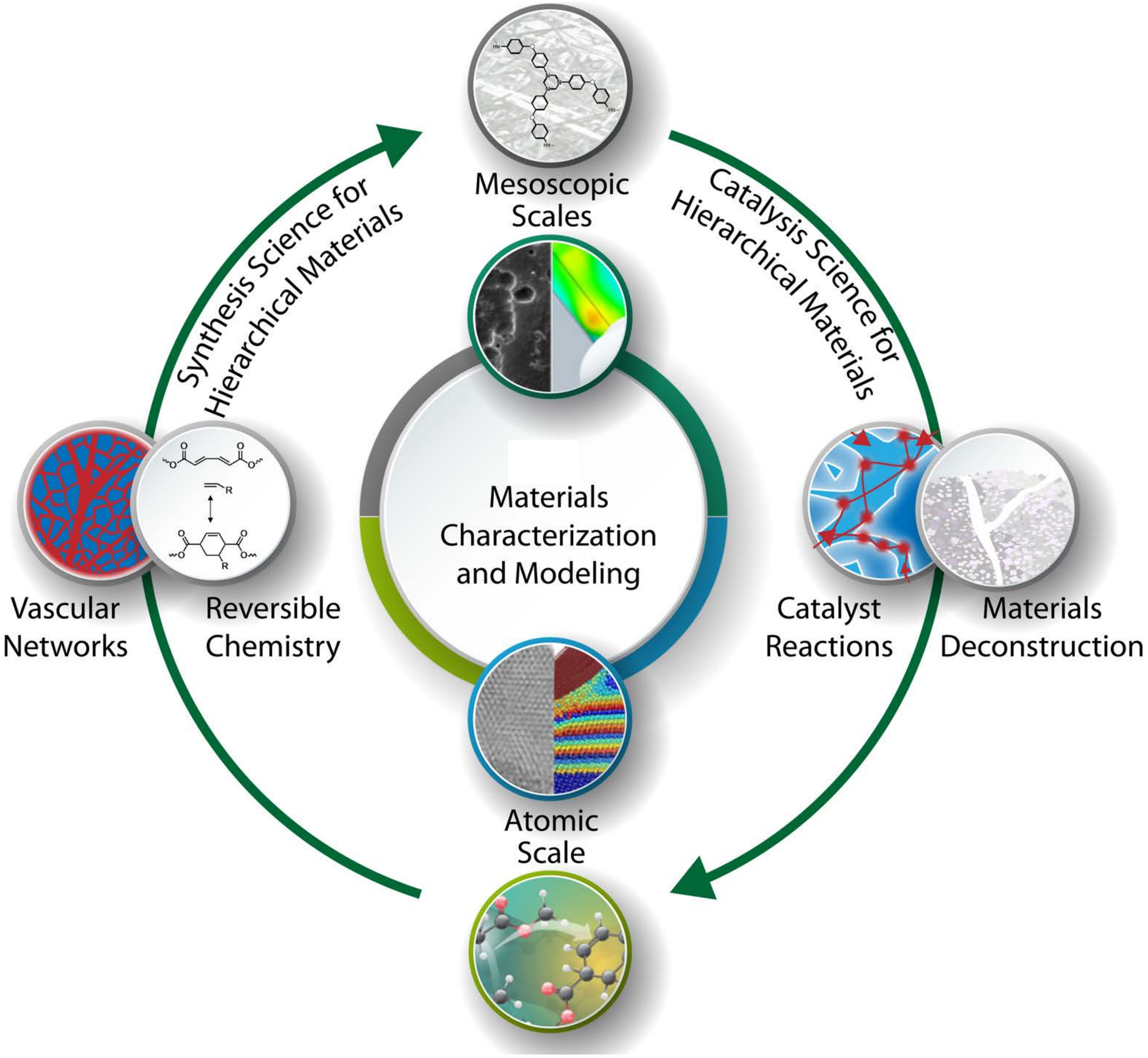
PBKAT

Kevlar Like Material

Polycarbonate Alternative or Other Precursors

Rorrer *et al.* in preparation

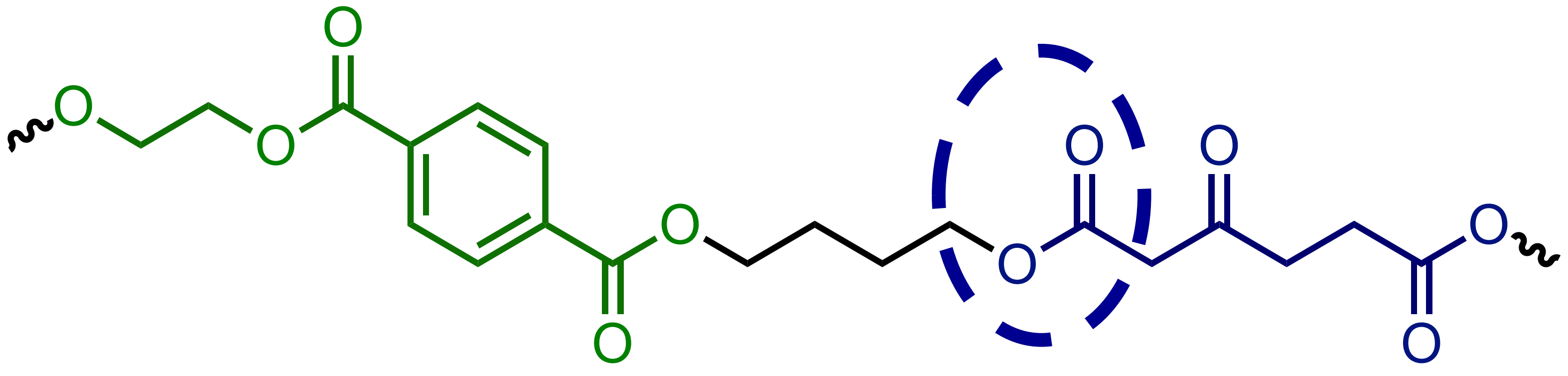
Challenge 3: Can we make plastics recyclable-by-design?



Co-design for material performance and end-of-life catalytic processing

Poly(butylene β-ketoadipate-*co*-terephthalate), PßKAT

Polymer	T_g	T_m	H_2O Permeability (g 25μ/m^2/day)
PET	70	260	20
PßKAT – 5%	70	260	18
PßKAT – 10 %	70	260	22
PßKAT	70	--	--



Labile subunit

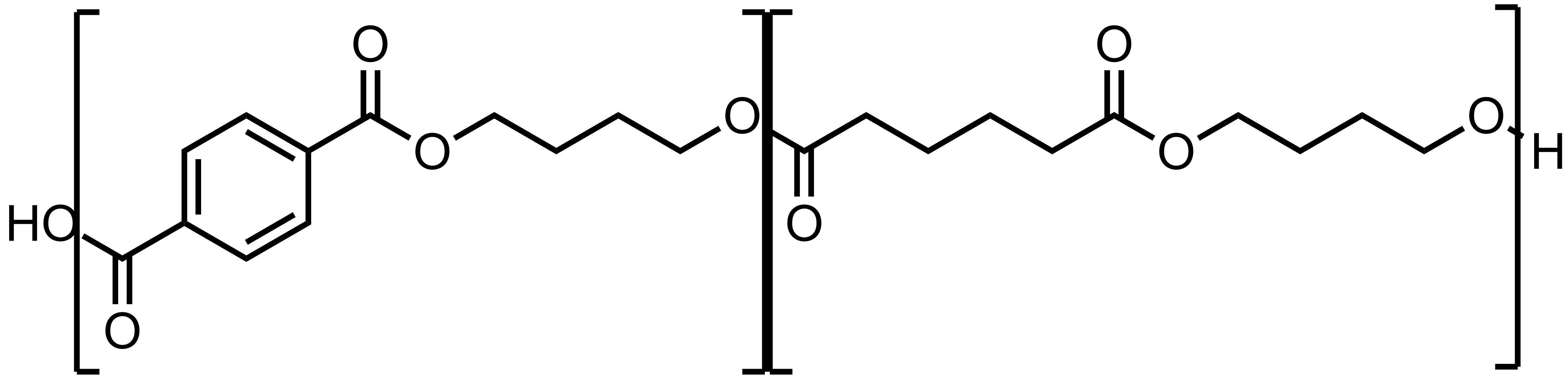
PßKAT predicted to last ~6 y in the environment relative to 450 y for PET

PßKAT is likely more inherently chemically recyclable — ongoing work

Comparison to existing biodegradable plastic

Polybutylene-adipate-*co*-terephthalate (PBAT)

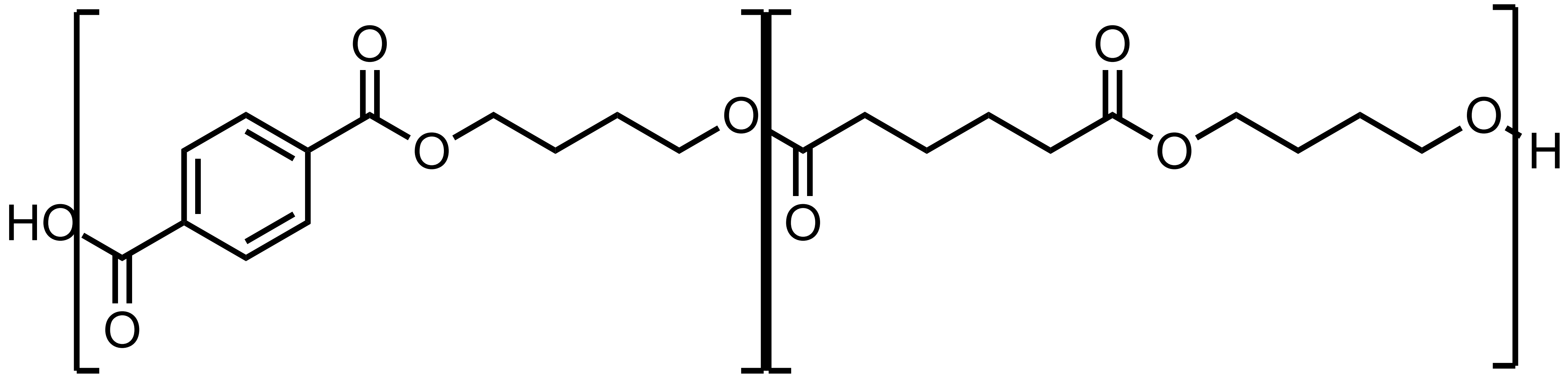
ecoFLEX®



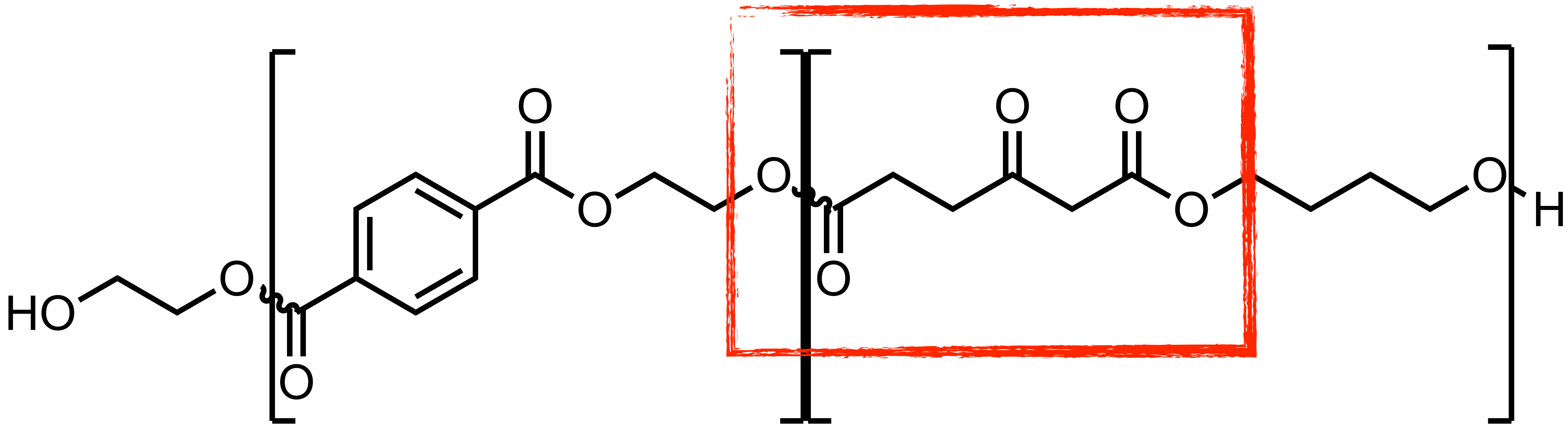
Rorrer *et al.*, in preparation

Comparison to existing biodegradable plastic

Polybutylene-adipate-*co*-terephthalate (PBAT)



Polybutylene-ß-ketoadipate-*co*-terephthalate (PßKAT)



ß-ketoadipate

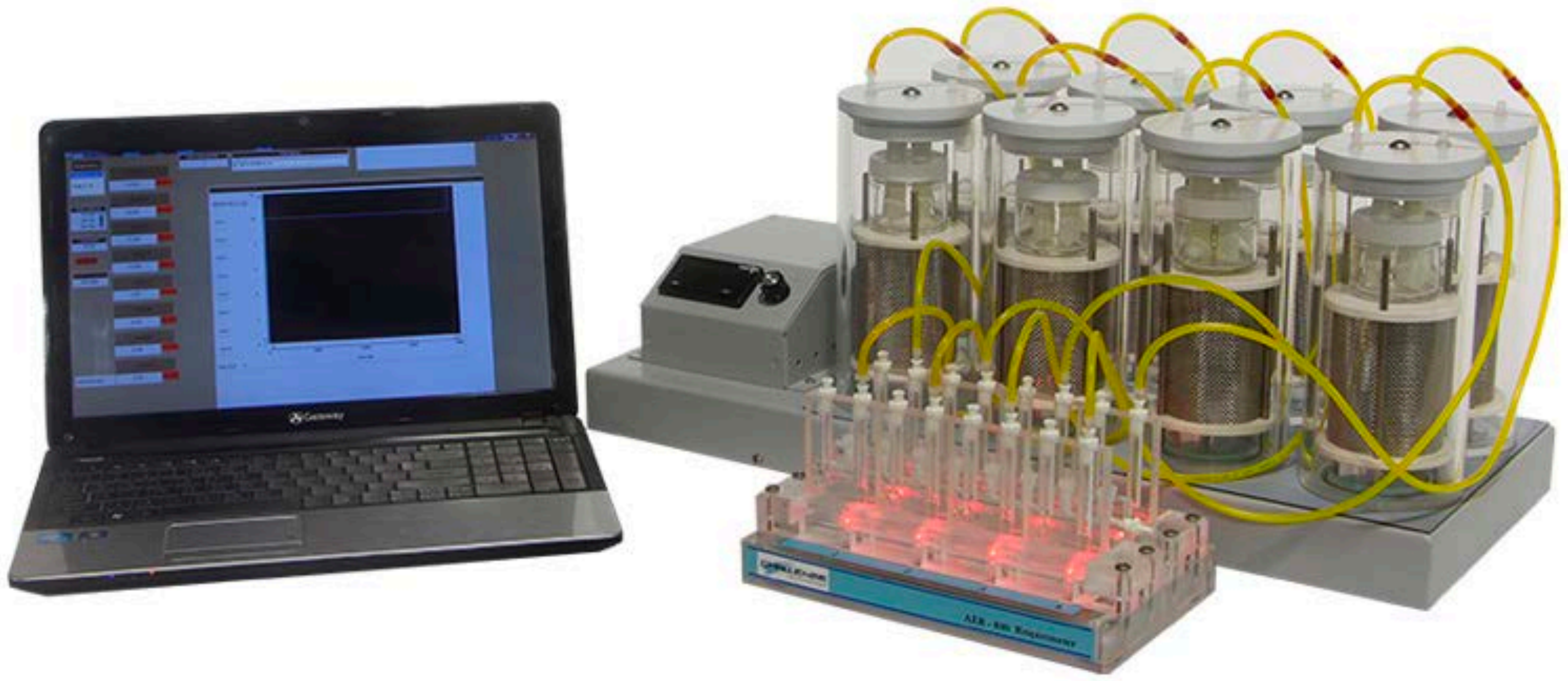
Rorrer *et al.*, in preparation

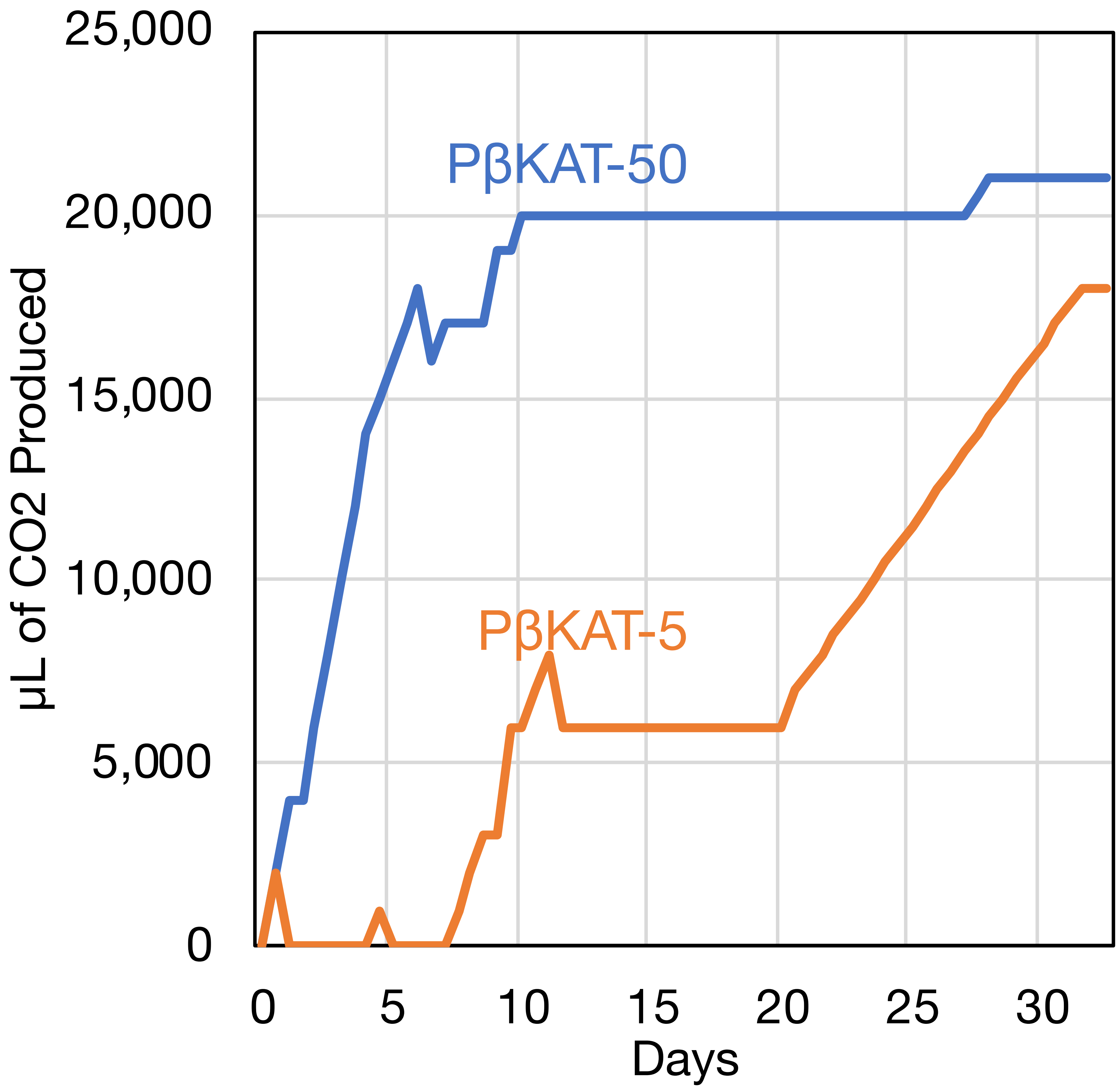
PßKAT has similar properties to PET even at 10% ßKA loading

BKA Loading	T_g (°C)	T_m (°C)	Permeability (g 25μ/m^2/day)	E’ (0.1 Hz,35°C)
PET	69	262	20	4.1 GPa
PBKAT – 1%	72	265	18	4.3 GPa
PBKAT – 5%	73	257	22	4.5 GPa
PBKAT – 10 %	71	261	21	4.1 GPa
PBKAT – 50 %	68	254	--	--
PBKAT	70	--	--	--

Rorrer *et al.*, in preparation

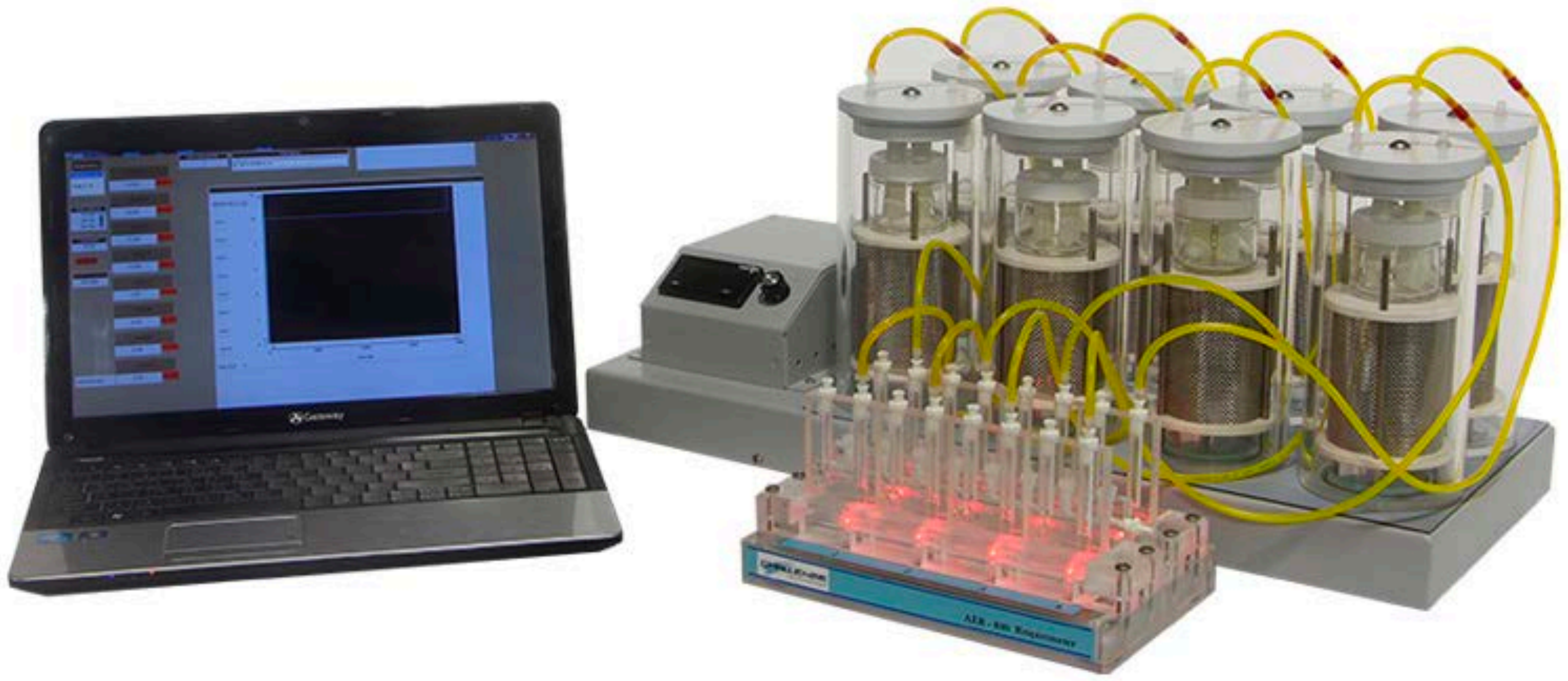
PβKAT is more amenable to hydrolysis than PET



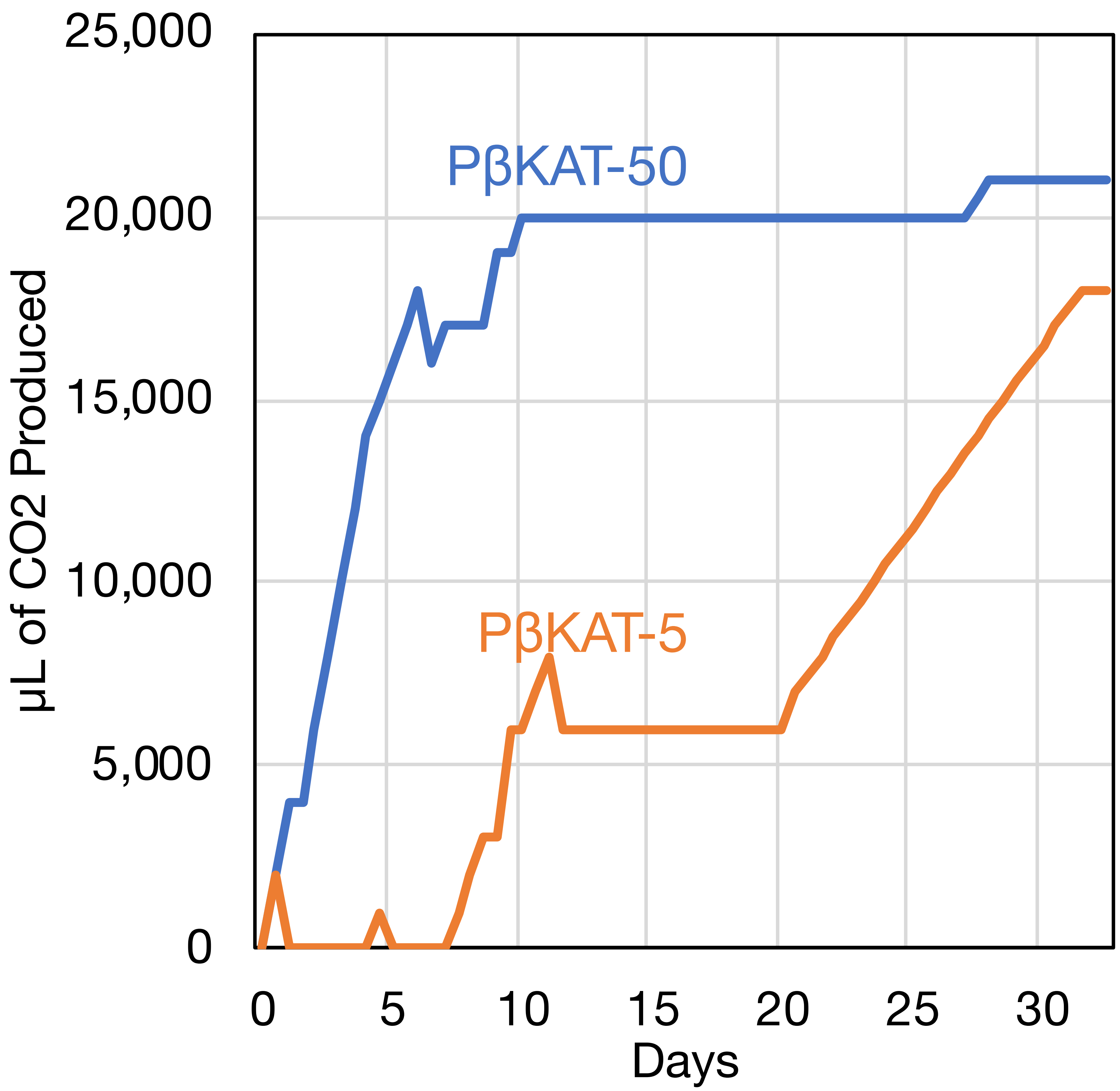


Rorrer *et al.*, in preparation

PβKAT is more amenable to hydrolysis than PET



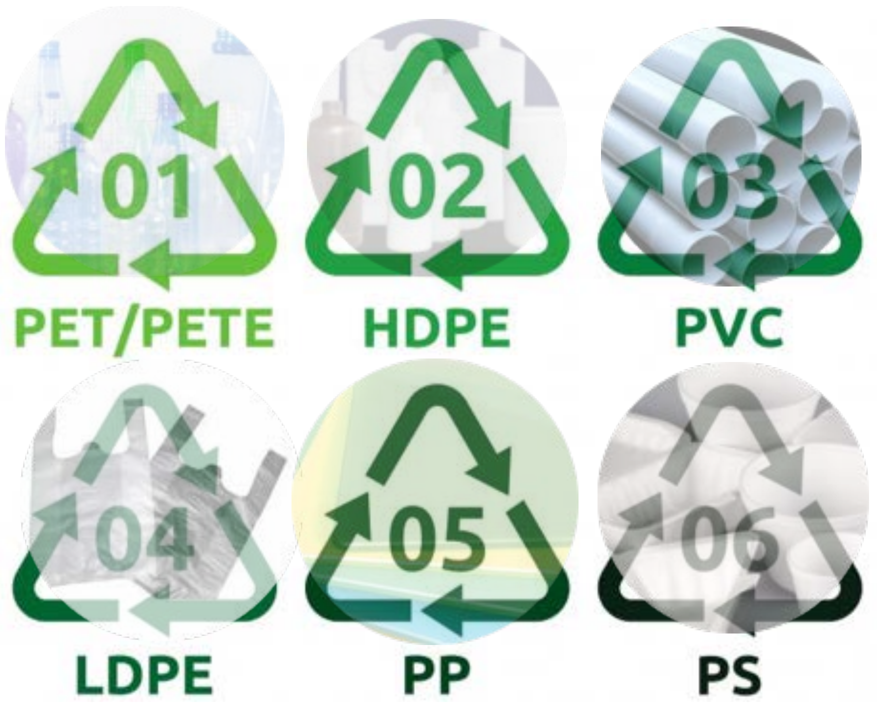
PET ~ 450 years
PβKAT ~ 6 years

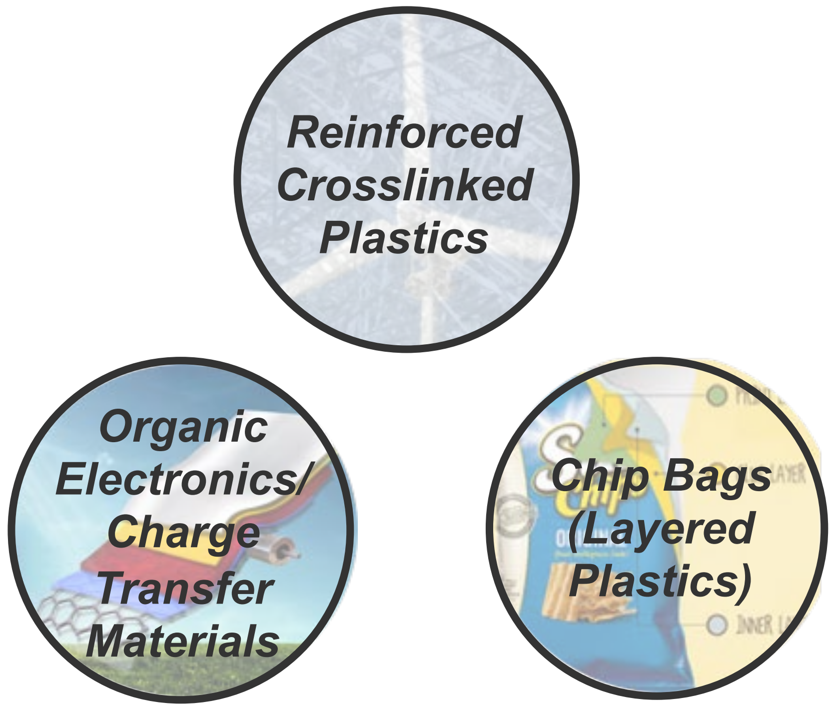


Rorrer *et al.*, in preparation

Challenges and opportunities in the Circular Plastics Economy

Upcycling Existing Plastics





Reinforced Crosslinked Plastics

Organic Electronics/ Charge Transfer Materials

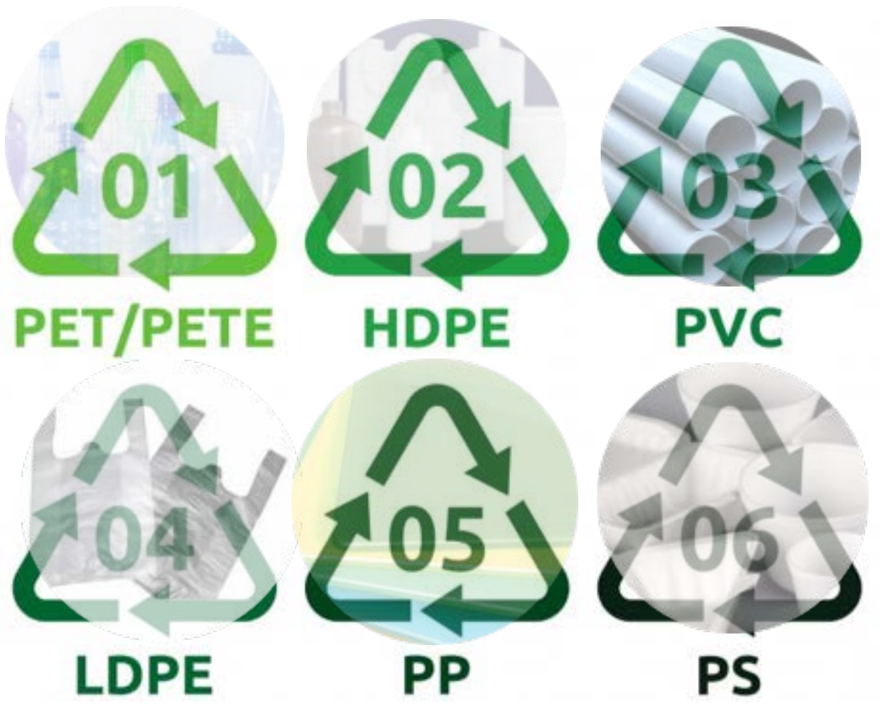
Chip Bags (Layered Plastics)

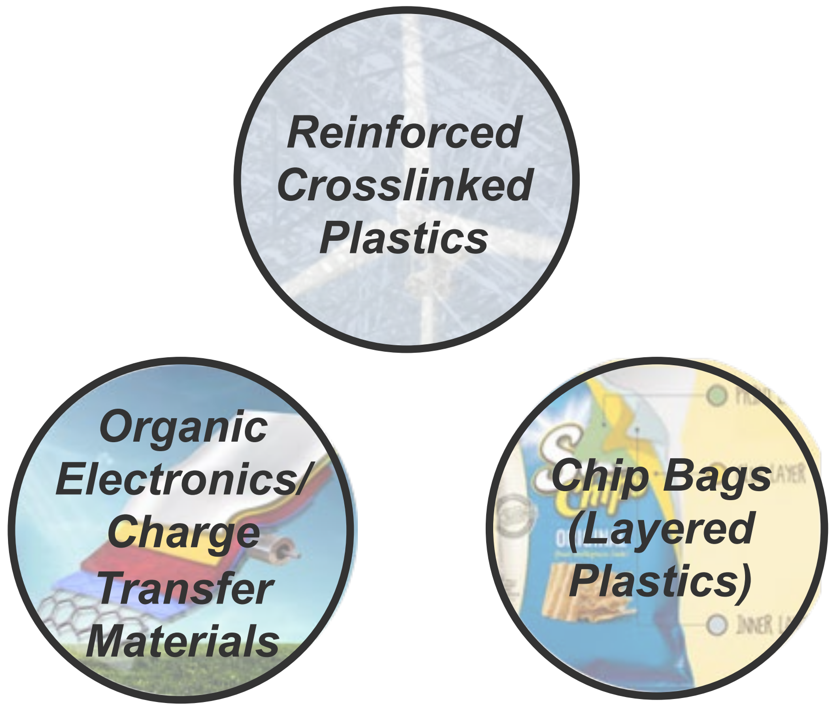
Opportunities:

- Combine biological and chemo-catalytic transformations for efficient upcycling
- Rich area for enzyme, microbe, and chemical catalyst discovery and design
- Leverage decades of investment in biomass conversion R&D

Challenges and opportunities in the Circular Plastics Economy

Upcycling Existing Plastics





Opportunities:

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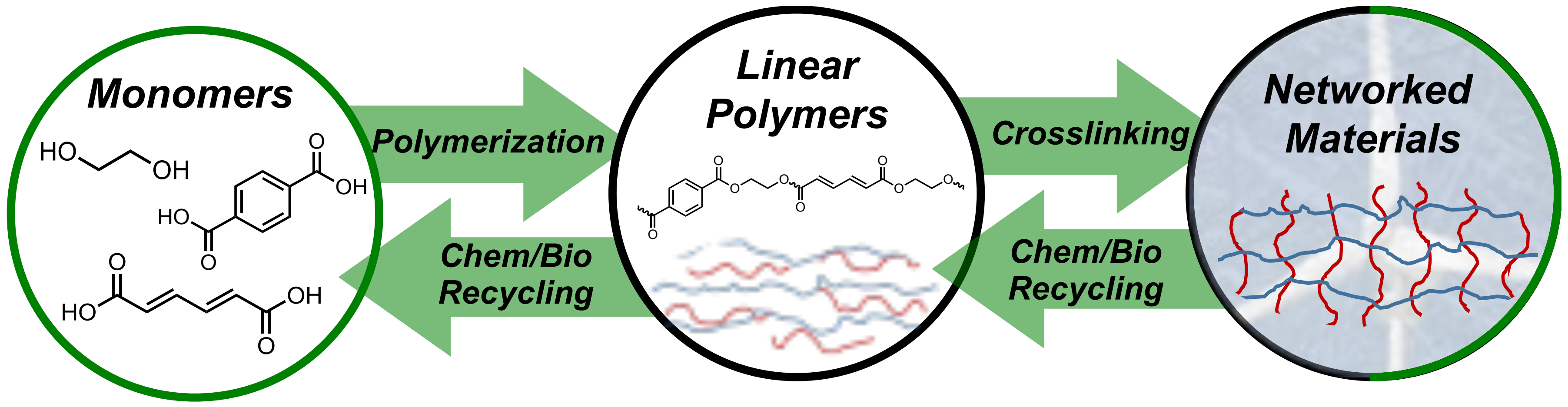
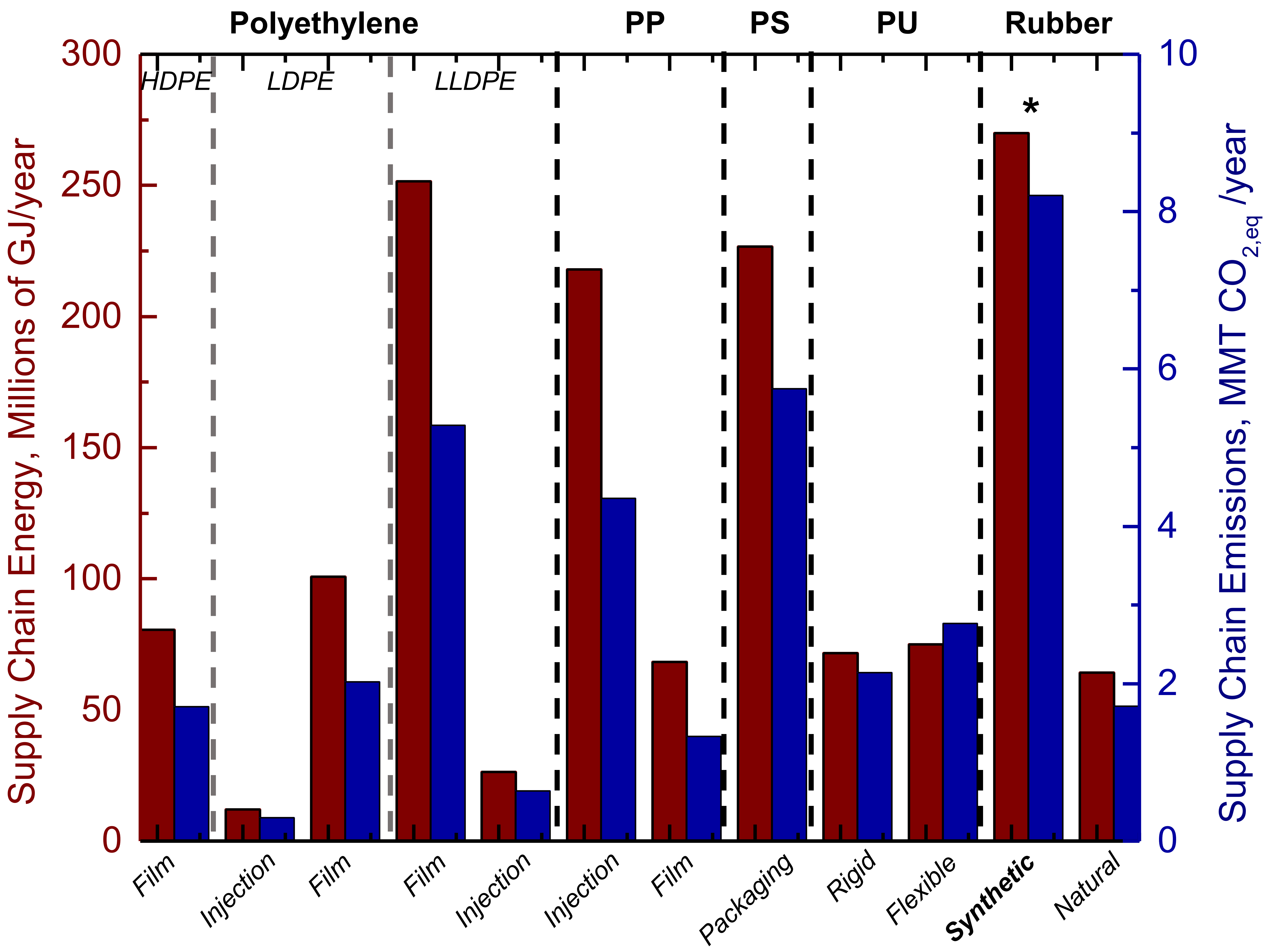
Recyclable-by-design



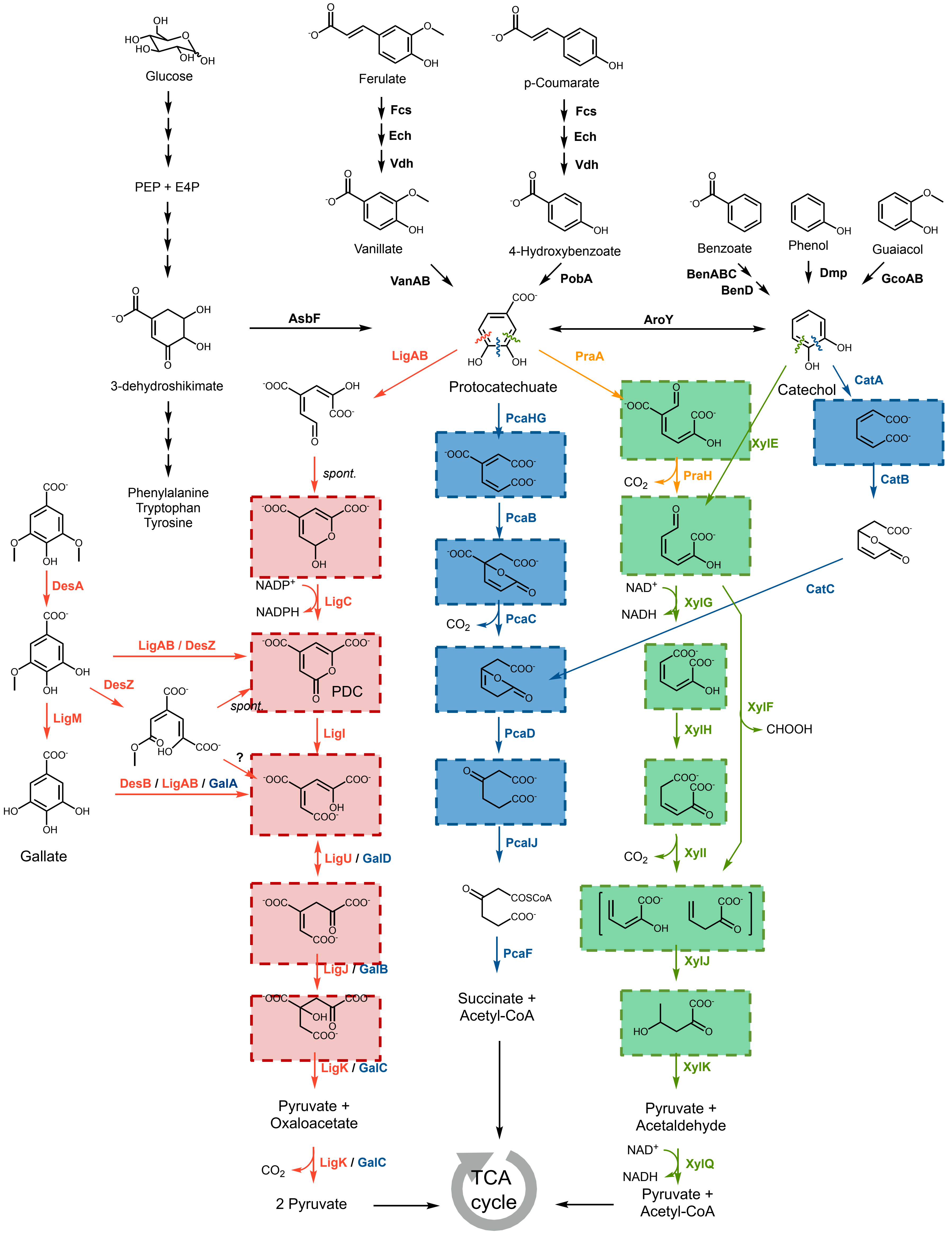
Opportunities:

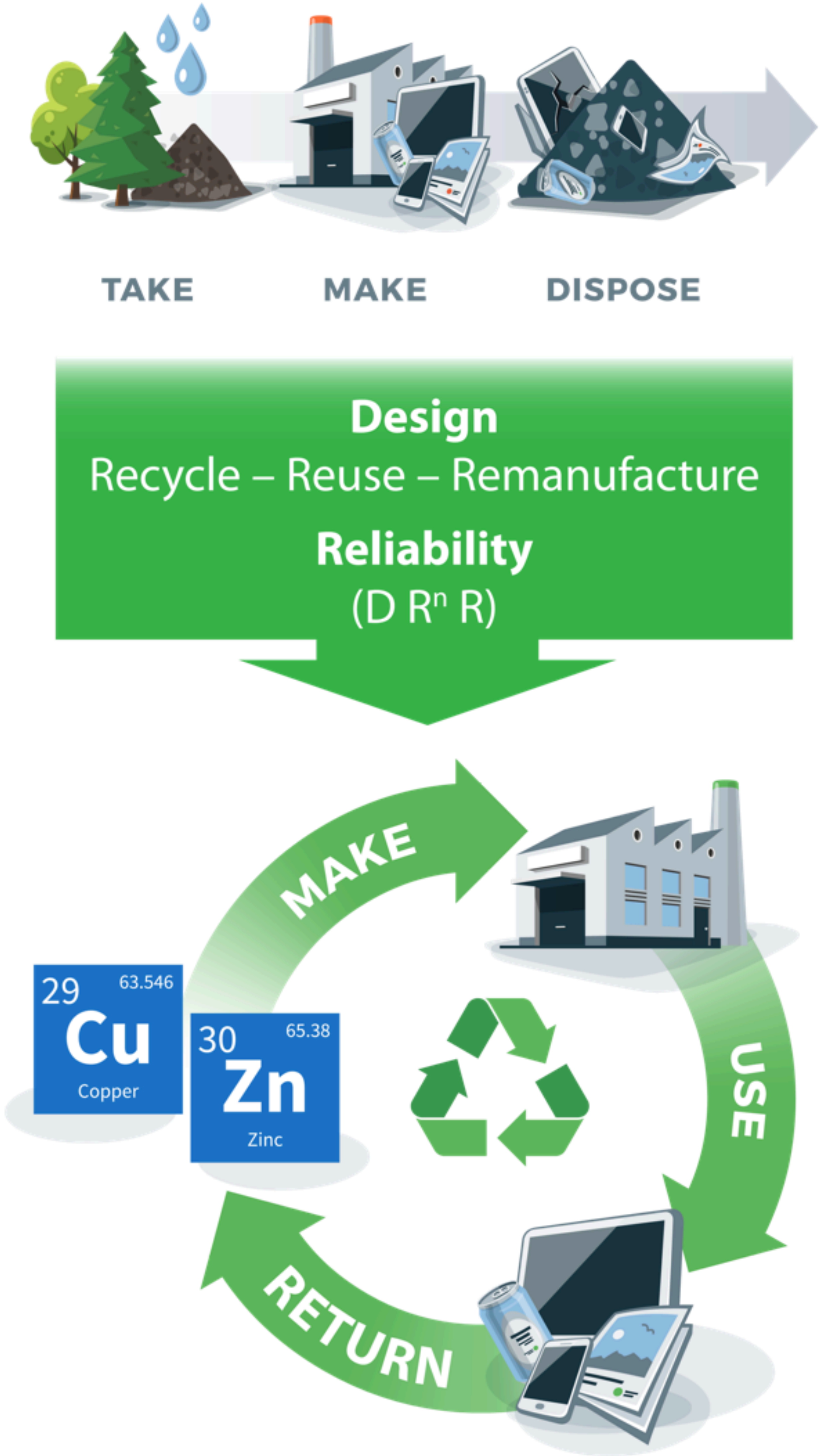
- Novel material formulations and designs with new building blocks
- Co-design of materials performance and end-of-life recycling processes
- Nexus of synthesis science, catalysis science, modeling, and process research



What plastics are the most energy and greenhouse gas intensive?

Nicholson *et al.* in preparation





Design
Recycle – Reuse – Remanufacture
Reliability
(D R^n R)

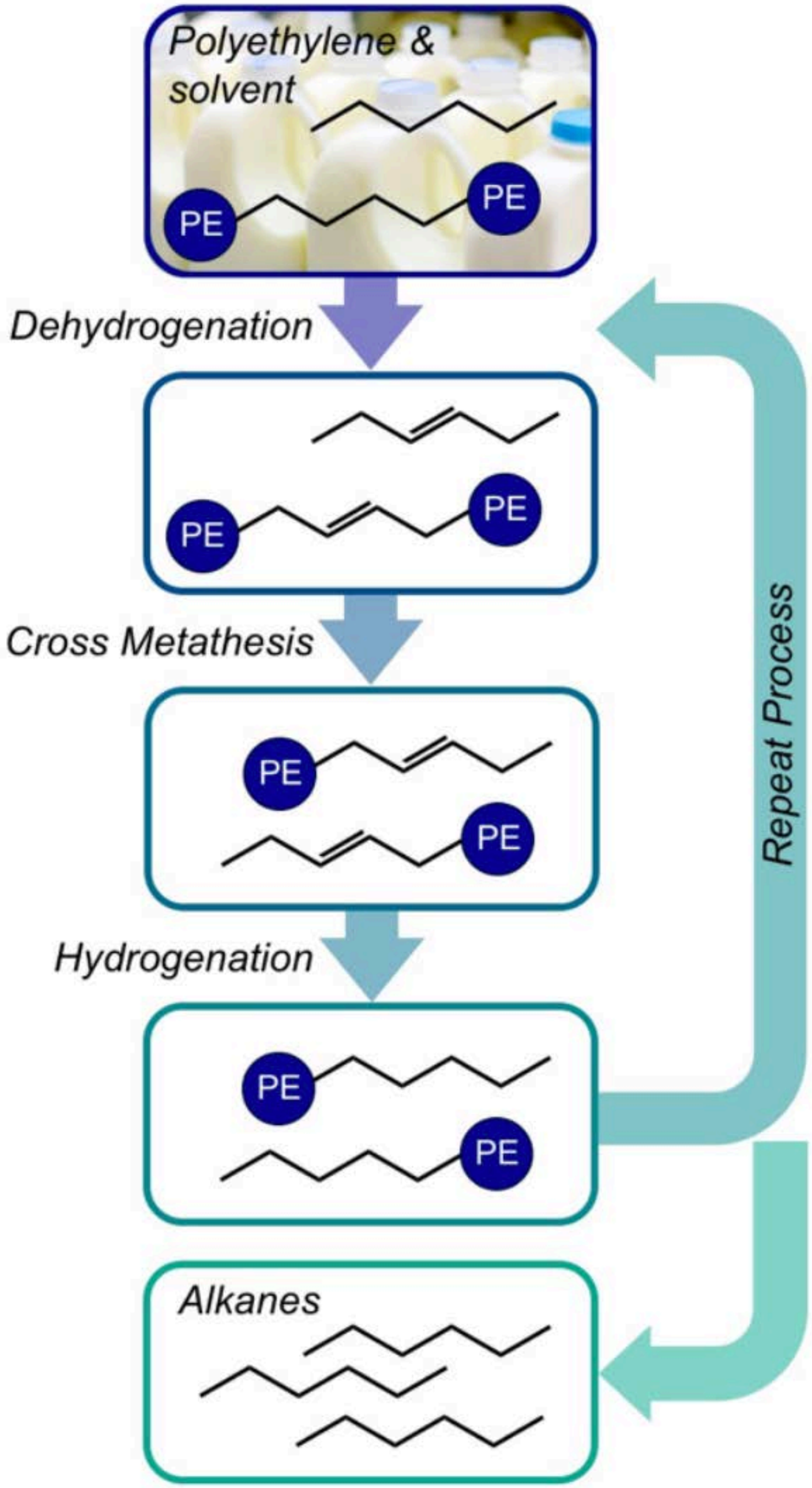
The bioeconomy can let us rethink plastics from the bottom up

We can hunt for new biocatalysts…

Work from Rita Clare

We can hunt for new biocatalysts…

Work from Rita Clare



And new chemical catalysts too!

Work from Lucas Ellis

Acknowledgements

NREL NATIONAL RENEWABLE ENERGY LABORATORY

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BIOENERGY TECHNOLOGIES OFFICE

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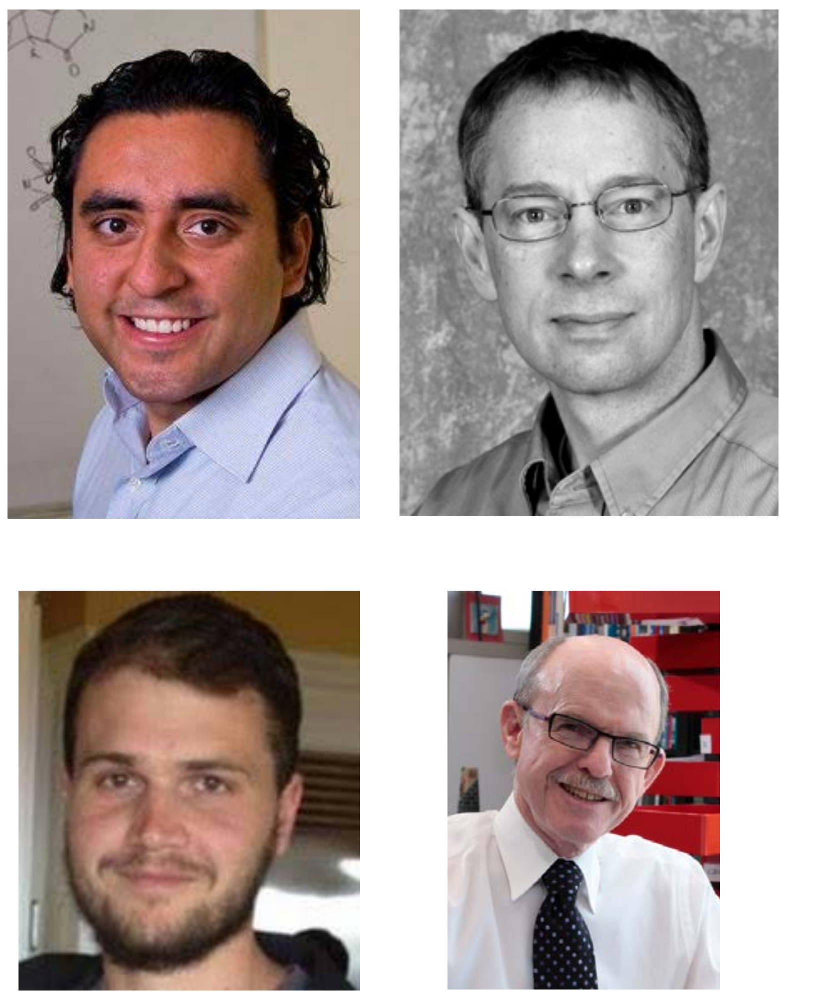

Let’s discuss!