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Bio-Optimized Technologies to keep Thermoplastics out of Landfills and the Environment

Bio-Optimized Technologies to keep Thermoplastics out of Landfills and the Environment (BOTTLE)

Technology Session Review Area: Performance-Advantaged Bioproducts, Bioprocessing Separations, and Plastics

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Adam Guss, Oak Ridge National Laboratory
Christopher Tassone, SLAC National Accelerator Laboratory
Meltem Urgun-Demirtas, Argonne National Laboratory
Linda Broadbelt, Northwestern University
Eugene Chen, Colorado State University
Jennifer DuBois, Montana State University
John McGeehan, University of Portsmouth
Yuriy Román-Leshkov, MIT

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BOTTLE Project Overview

- The plastics pollution problem
- Context for the BOTTLE Consortium
- Brief history of BOTTLE to date
- Project goals
- Framing BOTTLE via the Heilmeier Catechism

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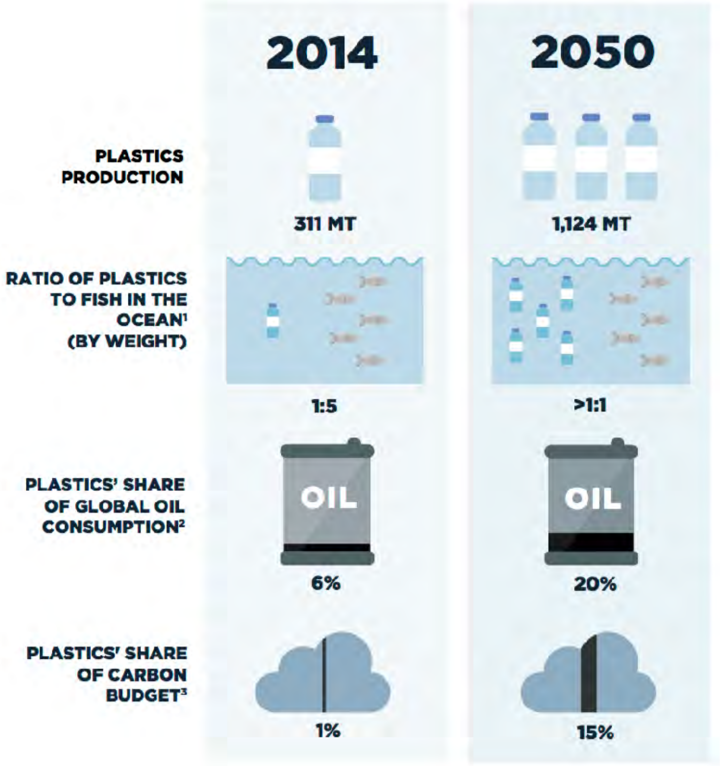
Plastics pollution

- Growing awareness of the plastics waste problem in the last decade
- Plastics pollution is basically found everywhere researchers look



Data from Jambeck *et al*. *Science* 2015;
Image from Ellen MacArthur Foundation

Images from Fortune, Huffington Post, BBC

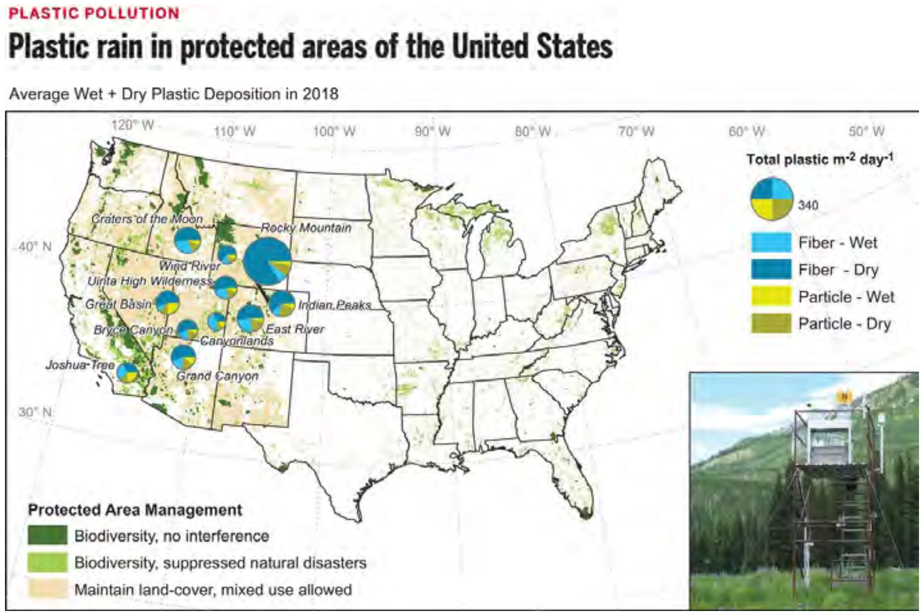


Image from Brahney *et al.* *Science* 2020

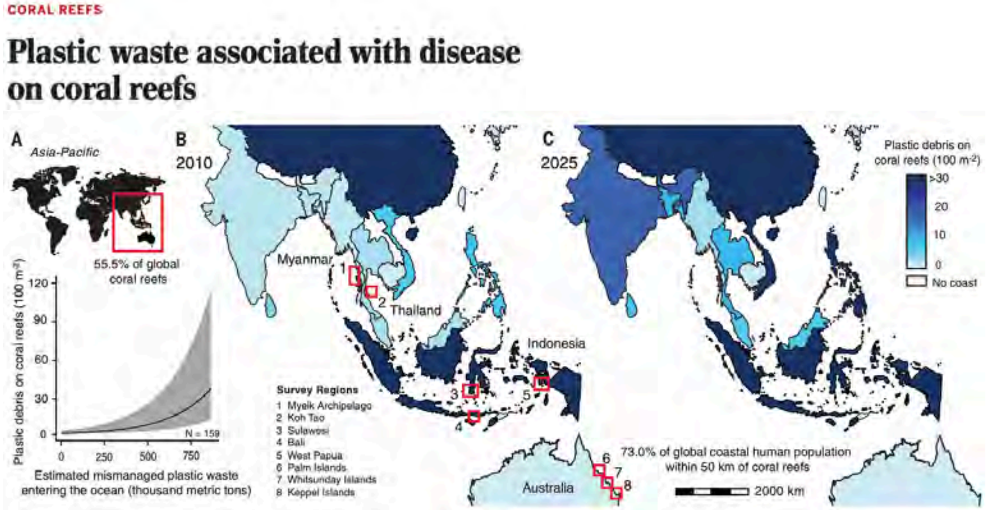
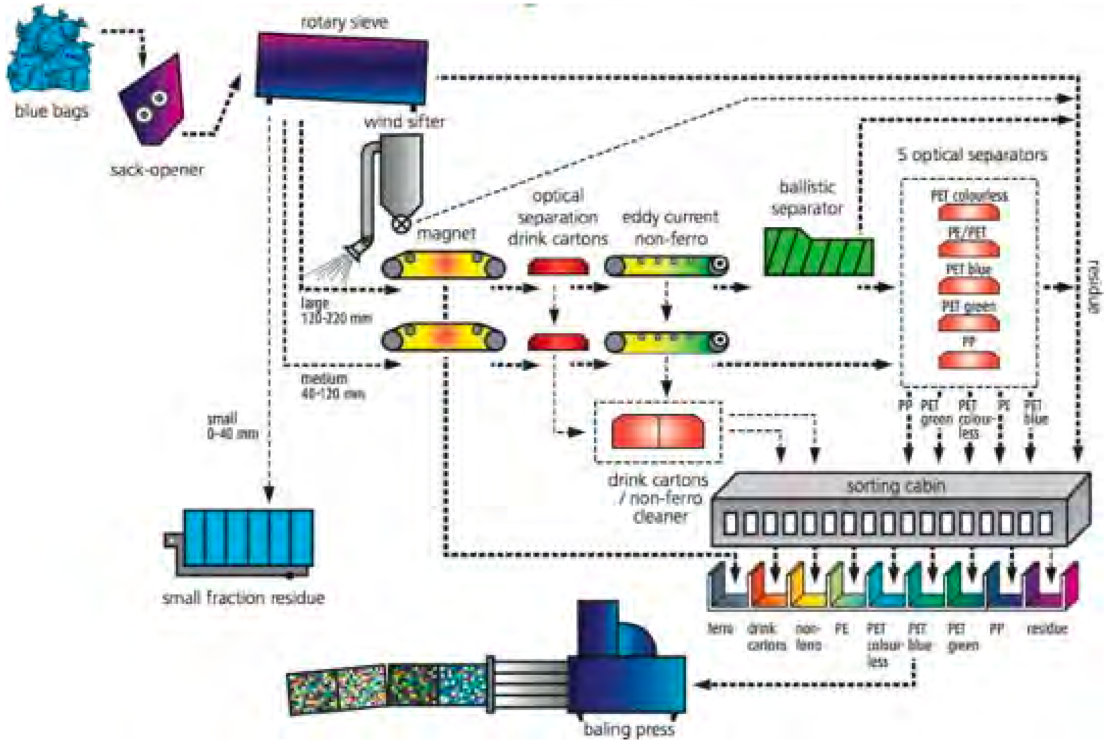


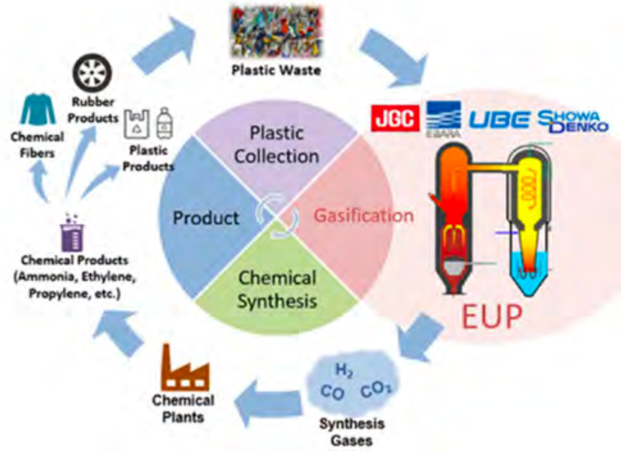
Image from Lamb *et al.* *Science* 2018

Current recycling approaches

Current plastics waste management and recycling approaches are limited:

- Recycled plastics often lower quality and value
- Mech. recycling not applicable to all polymers
- Little economic incentive for plastics reclamation





Methods "beyond" mechanical recycling for waste plastics: energy recovery, pyrolysis, and gasification

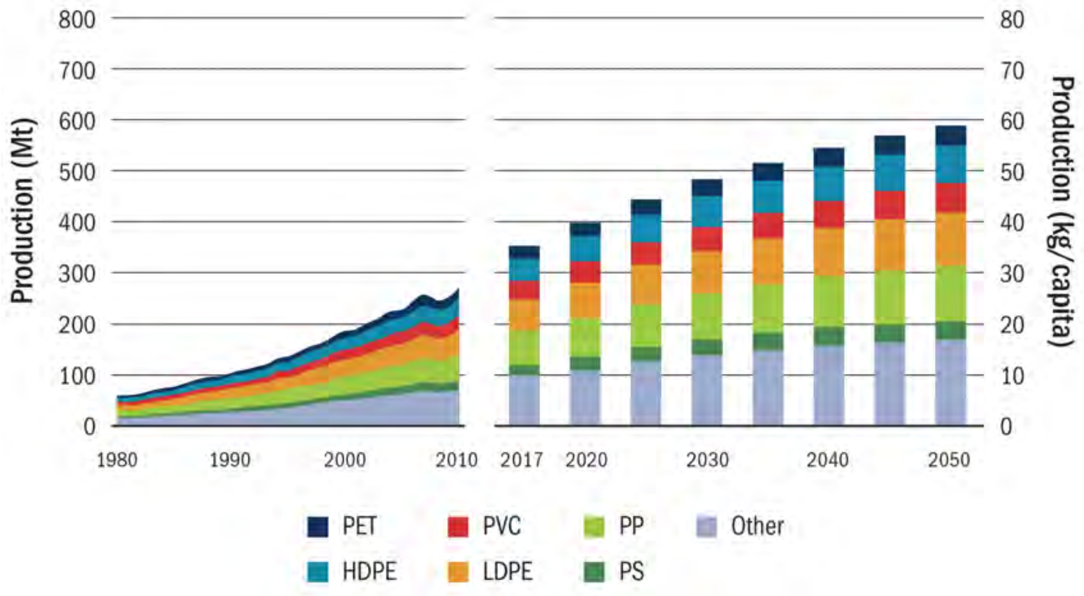
Image from Van Geem *et al*. *Waste Management* 2017

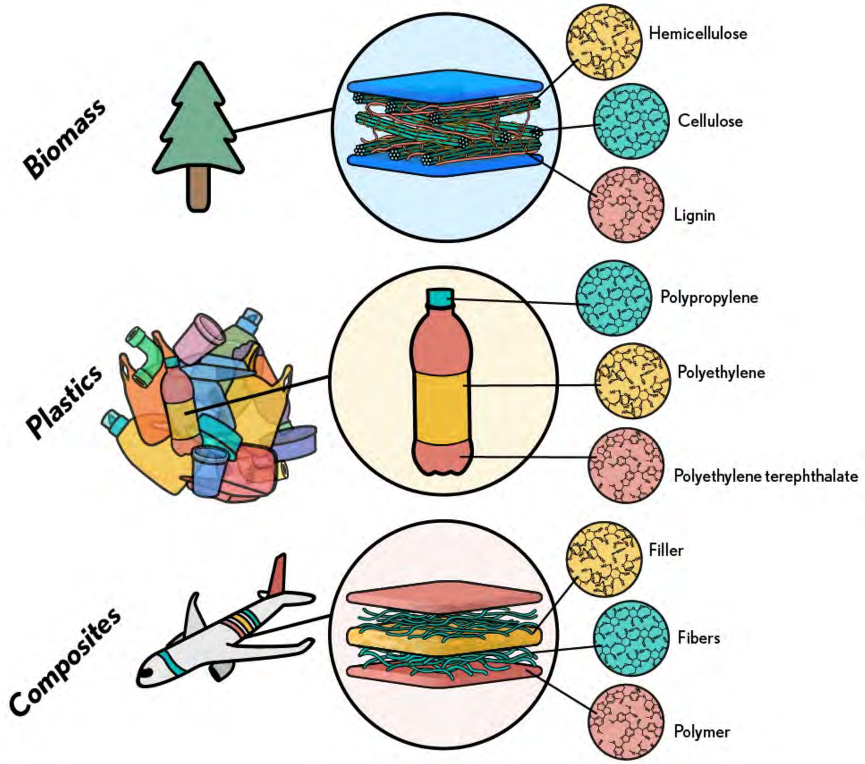
Images from ChemWeek, Plastics News Europe, C&E News

Context for the BOTTLE Consortium

Why should DOE labs work on waste plastics?

- ~6% of world fossil fuel consumption used to make polymers (equivalent to global aviation sector)[1]
- Projected to increase to 20% global fossil consumption by 2050[1]
- US likely generates most plastic waste globally[2]





Biomass and plastics share a few key attributes:

- Low-value, disperse, heterogeneous, solid polymers

Can we apply expertise in biomass conversion to develop economically viable, sustainable solutions for plastic waste that go beyond conventional approaches?

Image from DOE Plastics Innovation Challenge Roadmap, 2021 (Data from IEA 2018)

1. *EMF The New Plastics Economy*, 2016; 2. K Lavender Law *et al. Science Advances* 2020

Project history

- DOE issued Plastics Innovation Challenge
- FY20 seed project jointly funded by BETO and AMO to establish the BOTTLE Consortium
- Aimed to establish a *complementary* team to conduct *analysis-guided* R&D in plastics upcycling
- BOTTLE aimed to be complementary to other DOE activities in this space: REMADE, EFRCs, etc.
- DOE Lab Call expanded team in mid-FY20
- Began 3-year project in FY21 (October 2020)

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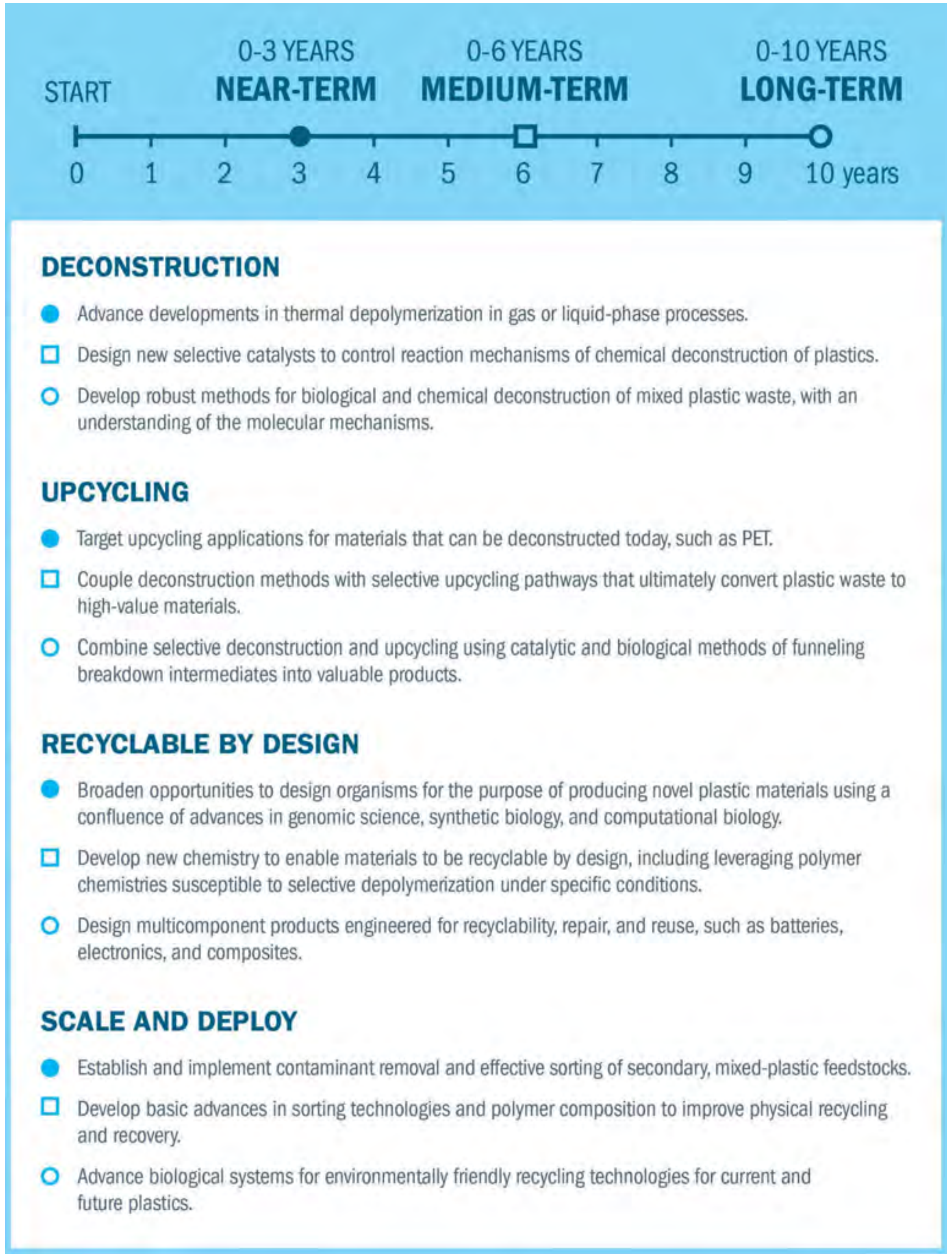


Image from DOE Plastics Innovation Challenge Roadmap, 2021

Project overview: BOTTLE vision, mission, and goals

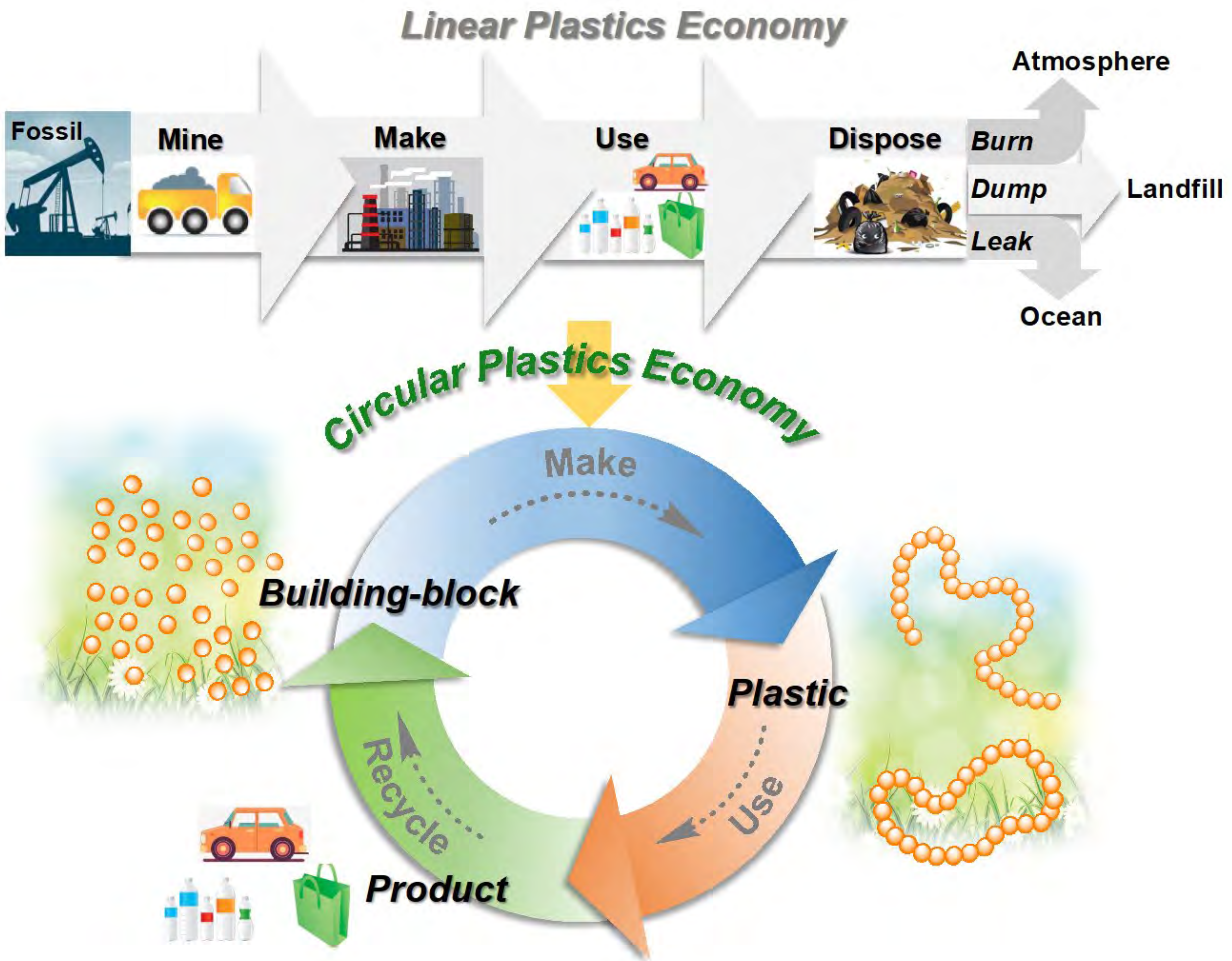
The vision for BOTTLE is to deliver selective and scalable technologies that enable cost-effective recycling, upcycling, and increased energy efficiency for plastics

The mission of BOTTLE is to:

- Develop robust processes to upcycle existing waste plastics, and
- Develop new plastics and processes that are recyclable-by-design

The goals of BOTTLE are:

- Develop chemical/biological processes to deconstruct and upcycle today's plastics
- Design chemistries and recycling processes for tomorrow's plastics that are recyclable-by-design
- Work with industry to catalyze a new upcycling paradigms
- Leverage DOE investments in process development, catalysis, materials, and analysis-driven R&D



Hong & Chen, *Trends Chem*. 2019, 1, 148

Project overview: Heilmeier Catechism framing

What are you trying to do?

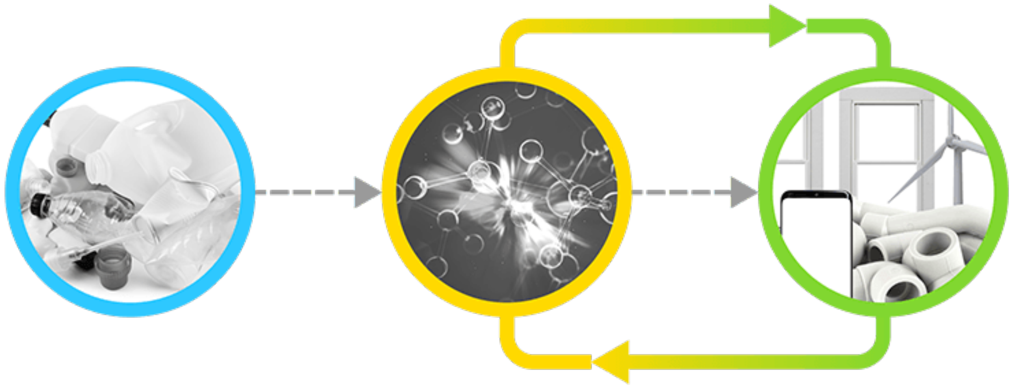
- Develop selective, scalable processes to deconstruct and upcycle today's plastics and thermosets
- Redesign tomorrow's plastics to be recyclable-by-design (RBD) and derived from bio-based feedstocks

How is it done today?

- Most plastics that are recycled are down-cycled and many are not recyclable at all
- Energy recovery and thermochemical conversion methods have substantial limitations

Why is this problem important:

- Waste plastics are both an energy & environmental problem



What are the risks?

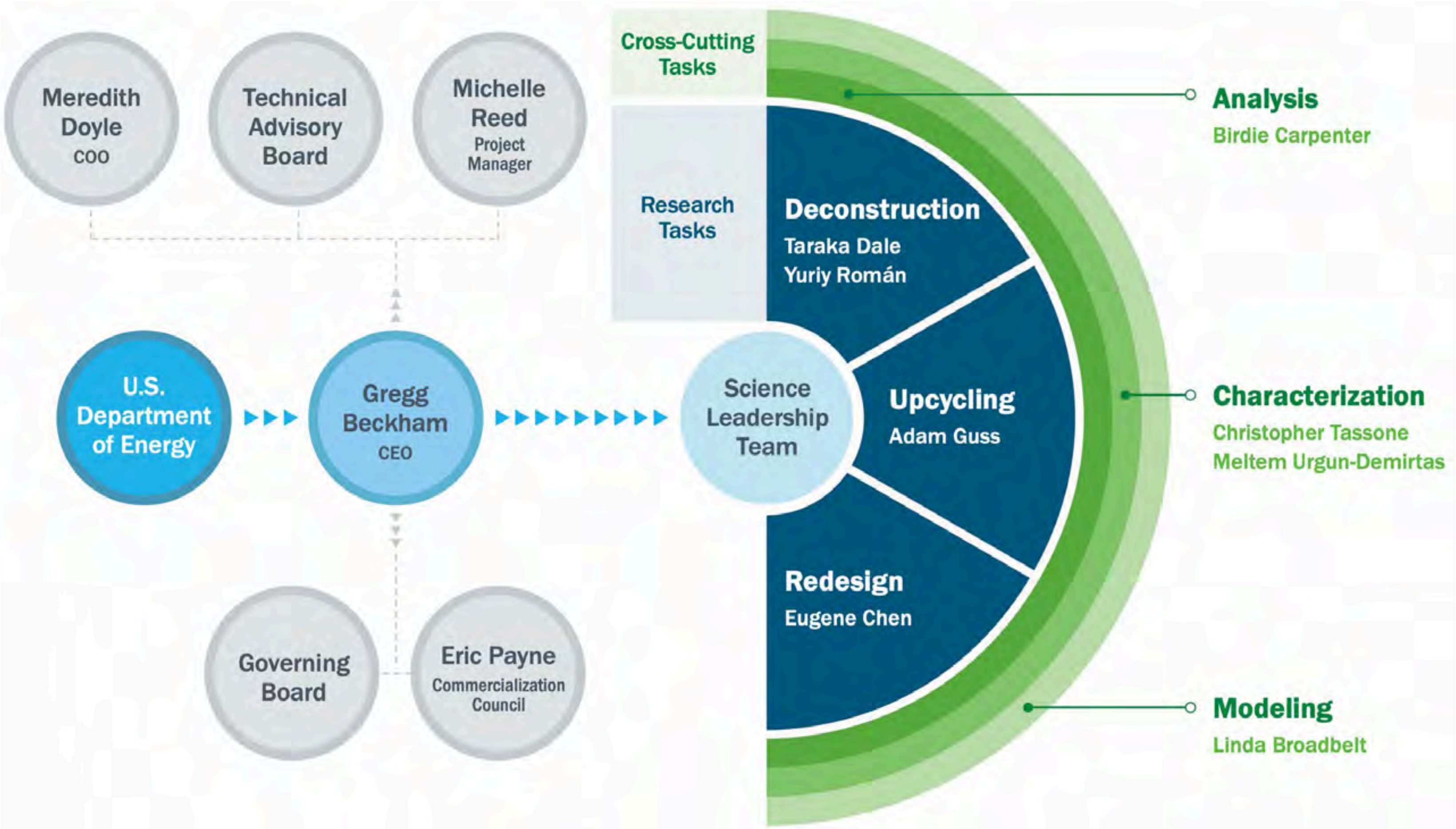
There are *many* risks, including (but not limited to):

- challenges deconstructing and upcycling realistic plastic waste,
- unable to develop technologies that out-perform energy recovery and/or pyrolysis,
- unable to redesign tomorrow's plastics with cost/performance that incentivize adoption

BOTTLE Management

- Project team
- Organizational leadership
- Research task structure
- Industry engagement and communications plans
- Reporting and decision making
- Collaboration and communication
- Project risks and mitigation plans

Team structure



Argonne NATIONAL LABORATORY

Colorado State University

Los Alamos NATIONAL LABORATORY EST. 1943

MIT

NREL NATIONAL RENEWABLE ENERGY LABORATORY

MONTANA STATE UNIVERSITY

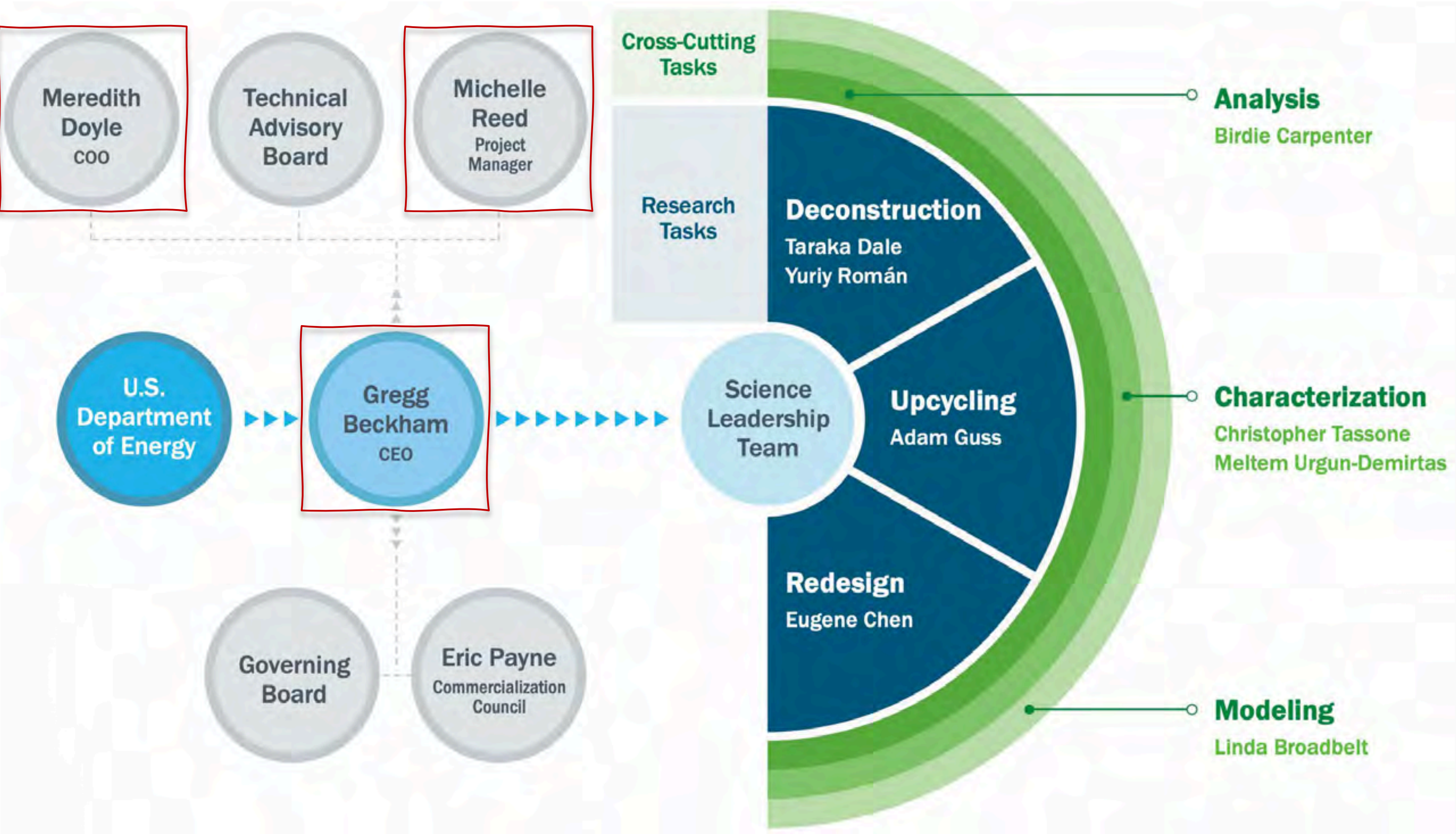
OAK RIDGE National Laboratory

Northwestern University

SLAC NATIONAL ACCELERATOR LABORATORY

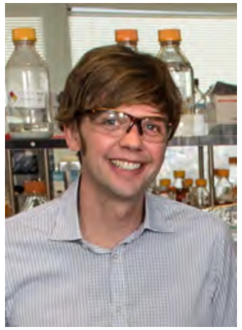
UNIVERSITY OF PORTSMOUTH

Leadership Team



BOTTLE Leadership Team (LT):

- CEO, COO, & PM
- Oversee the Management task
- Weekly meetings
- *Role focused on leadership of BOTTLE*

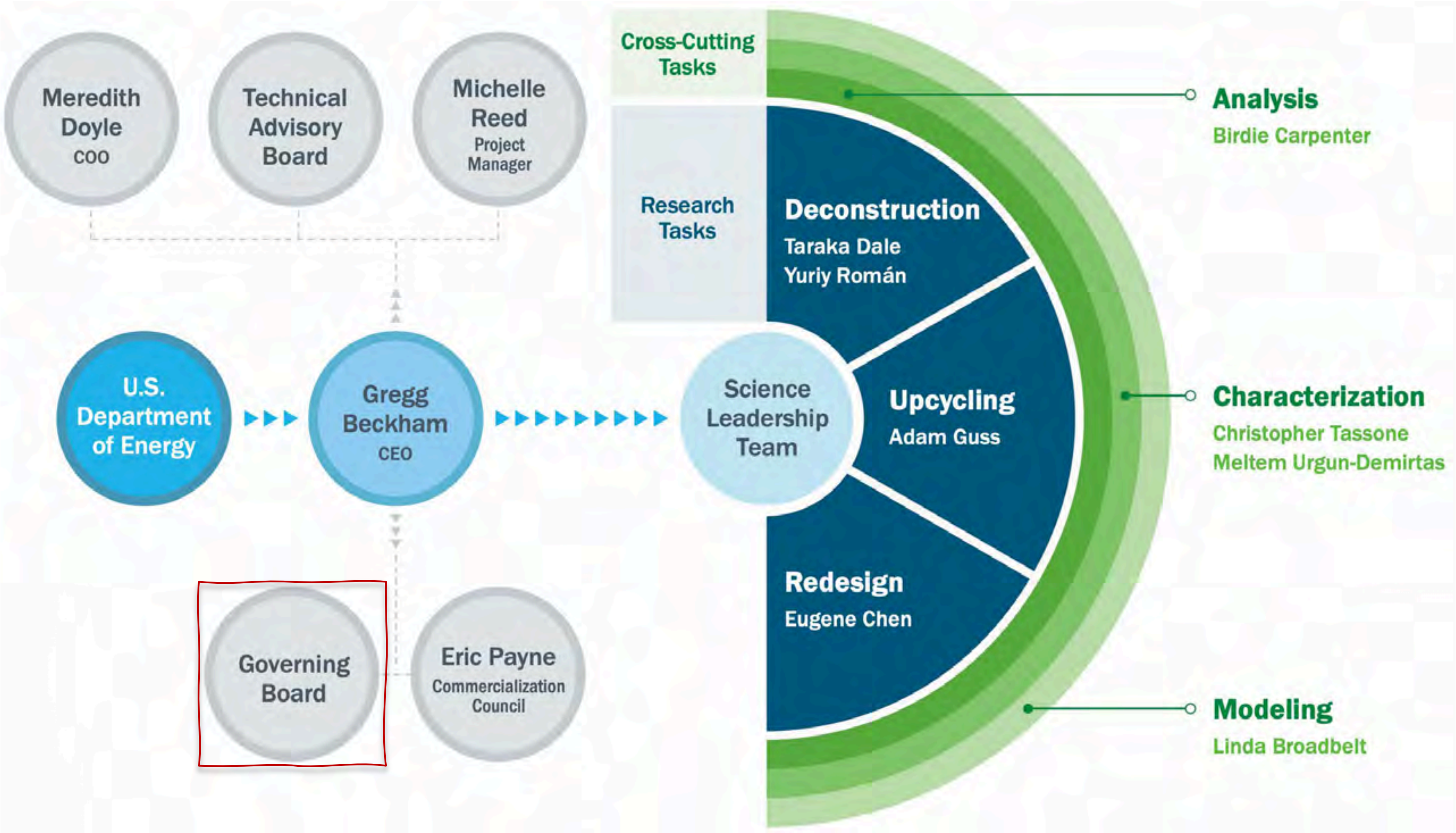


CEO

COO

PM

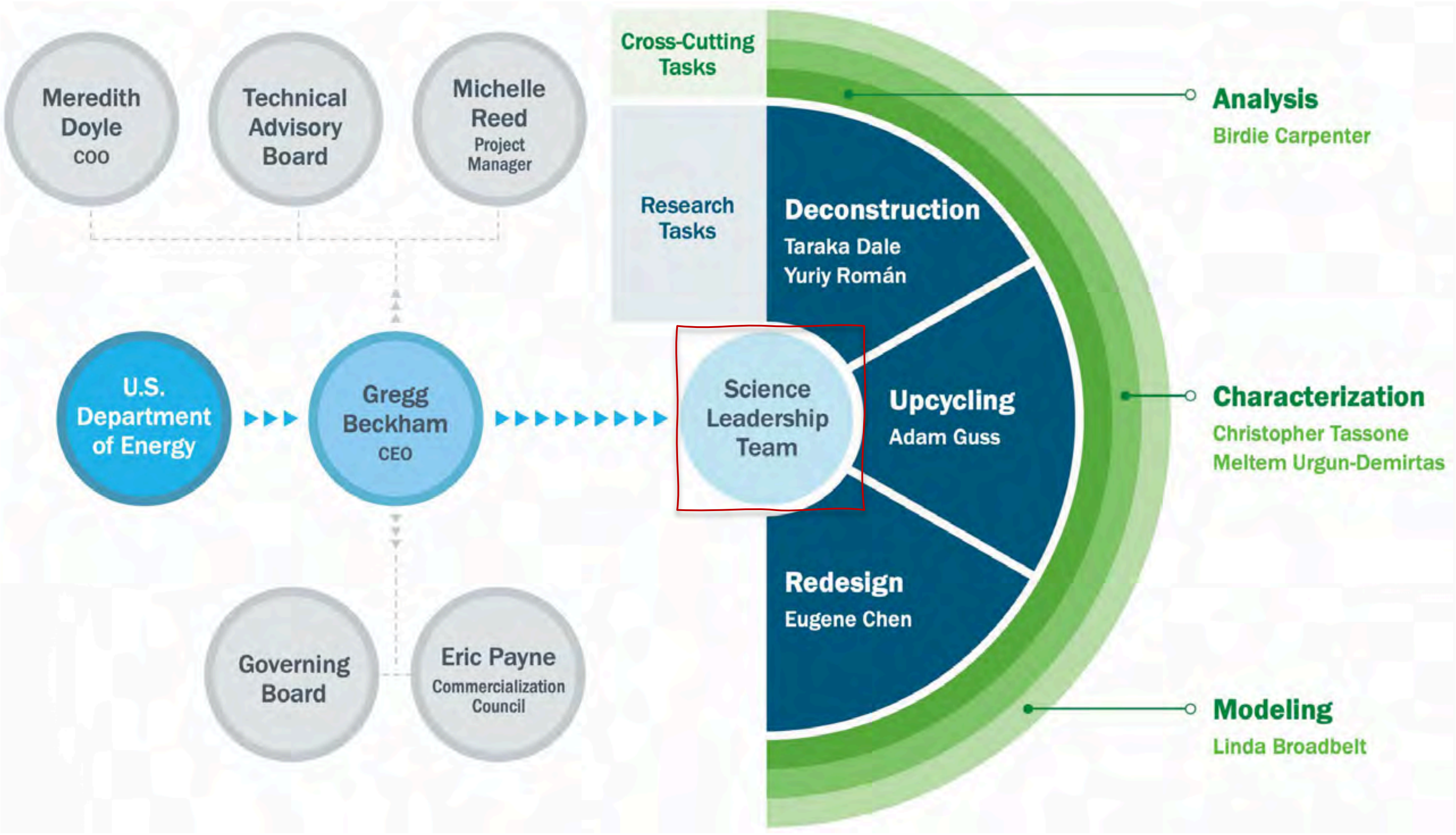
Governing Board



Governing Board (GB):

- BOTTLE LT, lab and several univ. leads, DOE
- Yearly strategic planning meeting
- *Role focused on management, strategy*
- Provide advisory input on:
  - BOTTLE priorities,
  - maintaining the BOTTLE mission in alignment with DOE,
  - industrial engagement,
  - finances and project management,
  - facilities and operations, and
  - management concerns

Science Leadership Team



Science Leadership Team (SLT):

- CEO, all institutional leads, DOE
- Yearly planning meeting, teleconferences every other month
- *Role focused on research execution*
- Establish key technical challenges, including annual review of BOTTLE R&D portfolio
- Implement and supervise research projects at each institution
- Foster inter-institutional collaborations
- Recommend future projects within each Consortium area

BOTTLE SLT team and expertise

ANL – Meltem Urgun-Demirtas
- End of life testing (EOL) and toxicity studies

Colorado State – Eugene Chen
- Bio-based plastics and redesign
- New building blocks
- Homogeneous catalysis

LANL – Taraka Dale
- Computational protein design
- Strain and enzyme evolution
- Biosensor development

MIT – Yuriy Román
- Heterogeneous catalysis
- Reaction engineering
- Electrochemistry

Montana State – Jen DuBois
- Enzyme biochemistry

Northwestern – Linda Broadbelt
- Computational modeling including DFT and chemical operators/retrosynthesis

NREL – Bob Allen
- Process development
- Biological and chemical catalysis
- Polymer chemistry

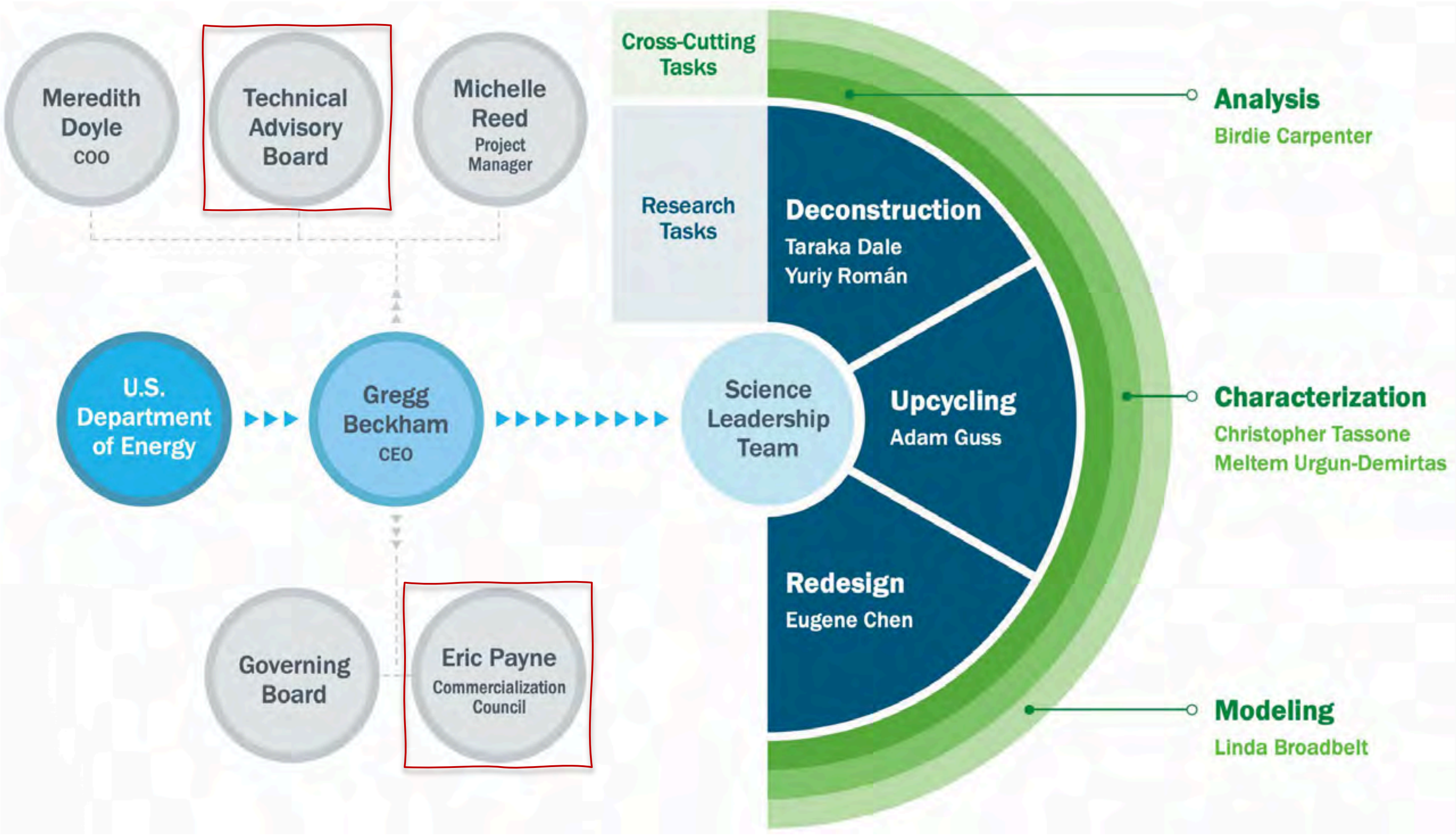
NREL – Birdie Carpenter
- Analysis including TEA, LCA, MFI, and EEIO modeling

ORNL – Adam Guss
- Prospecting and gene hunting
- Synthetic and systems biology
- Genetic tool development

SLAC – Chris Tassone
- Time-resolved and space-resolved *in situ*/operando experiments
- Polymer physics and chemistry
- Chemical catalysis

U of Portsmouth – John McGeehan
- Structural biology
- Protein biophysics
- Centre for Enzyme Innovation (CEI)

Technical Advisory Board and Comm. Council



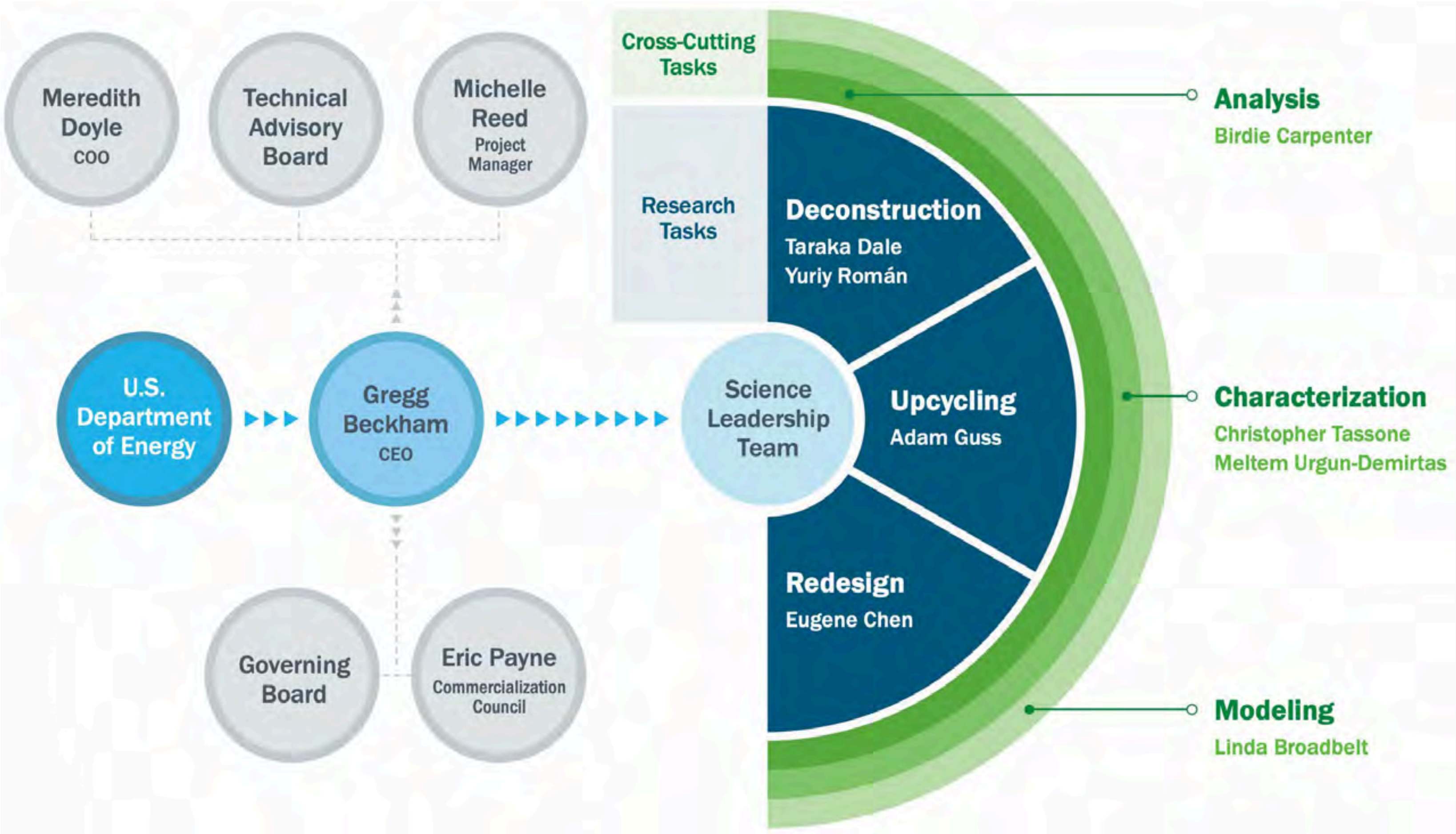
Technical Advisory Board (TAB):

- Feedback on R&D, operations, management
- Invited diverse group of thought leaders from academia, government, industry, non-profits
- TAB represents key points in the plastics value chain to ensure robust assessment of BOTTLE
- Convene annually (virtually or in-person)
- Provide written evaluations to DOE, BOTTLE LT
- Includes leads of complementary large R&D efforts in this space

Commercialization Council:

- Representative from each partner institution
- Central “storefront” for accessing BOTTLE IP through partnership and licensing
- Promote rapid deployment of BOTTLE IP

Research Tasks



Deconstruction:

- Led by experts in biocatalysis (T. Dale, LANL) and chemical catalysis (Y. Román, MIT)
- Focus: selective depolymerization of today's plastics

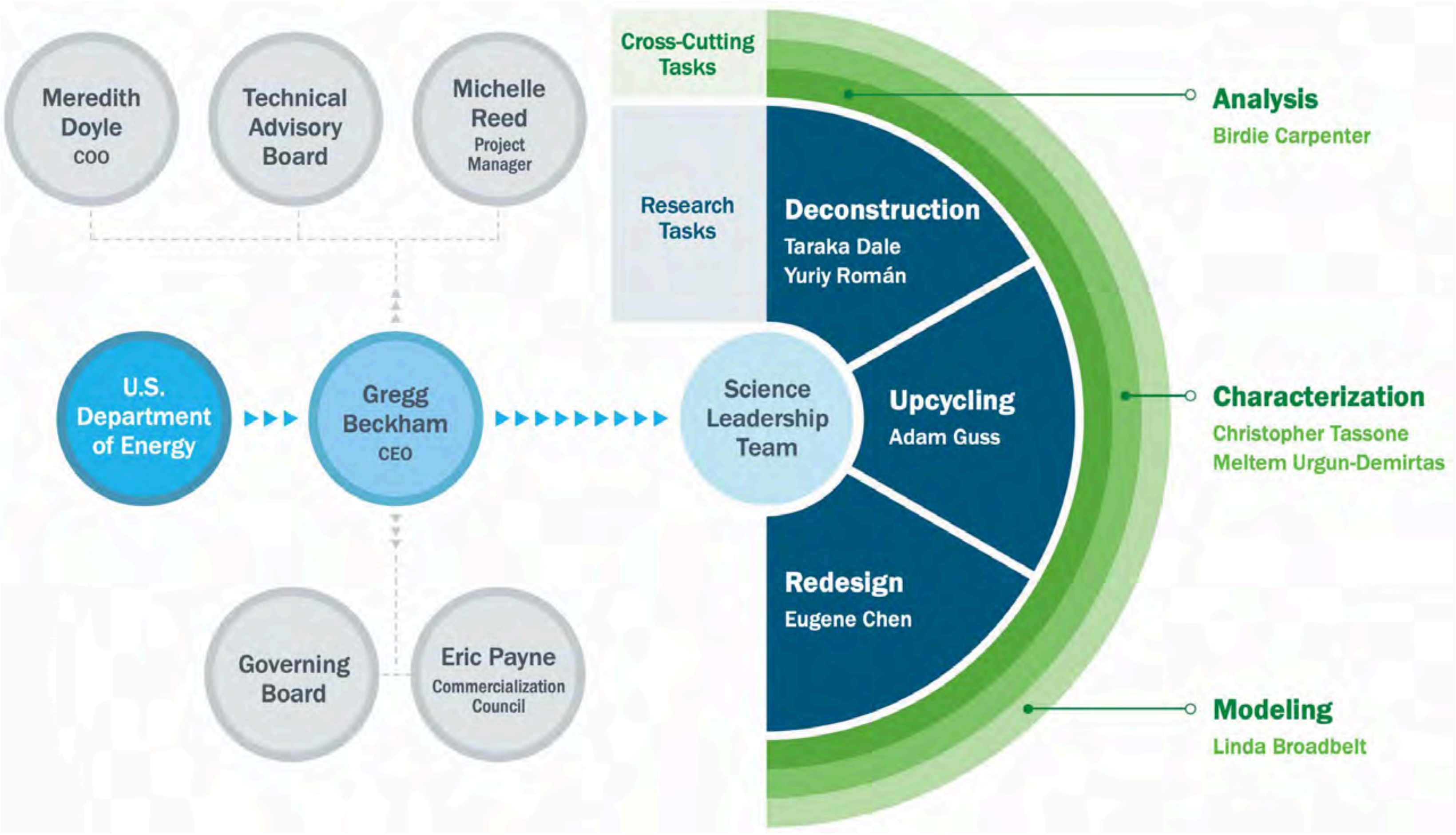
Upcycling:

- Led by expert in genetics and metabolic engineering (A. Guss, ORNL)
- Focus: converting intermediates from today's plastics to high-value materials
- Bridging task between Deconstruction and Redesign

Redesign:

- Led by expert in circular polymers (E. Chen, CSU)
- Focus: creating recyclable-by-design (RBD) polymers to replace commodity plastics

Cross-Cutting Tasks



Analysis:

- Led by **analysis** expert (B. Carpenter, NREL)
- Focus: TEA, LCA, EEIO, and other analysis tools to map to BOTTLE key metrics

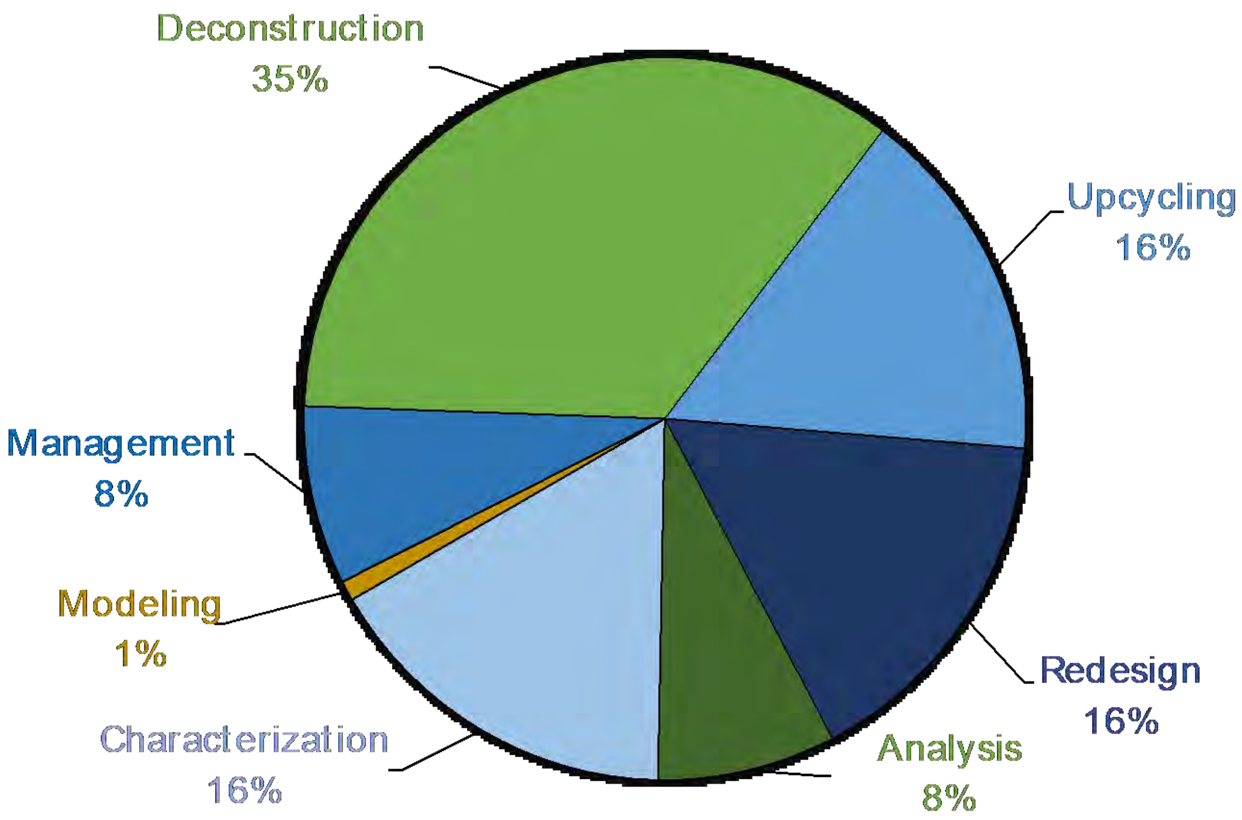
Characterization:

- Led by experts in materials biodegradation (M. Urgun-Demirtas, ANL) and synchrotron-based characterization (C. Tassone, SLAC)
- Focus on polymer end-of-life testing and *in situ/in operando* characterization of catalytic processes and new materials

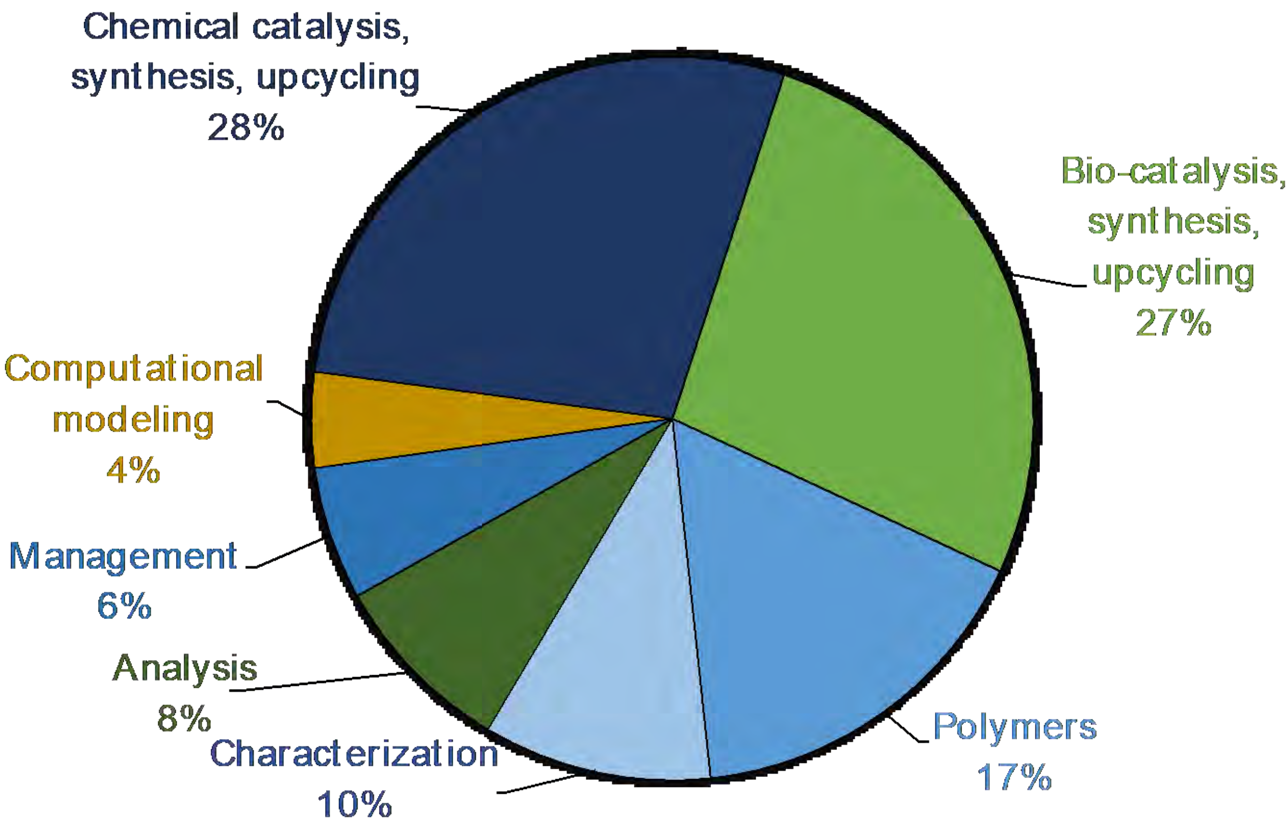
Modeling:

- Led by expert in polymer kinetics, theory, and retrosynthesis (L. Broadbelt, NU)
- Focus on deconstruction modeling and polymer redesign via machine learning and pathway predictions

Funding allocations by task and discipline



By task



By discipline

Industry engagement and communication plans

- Both plans established at the FY20 BOTTLE all-hands meeting
- <u>Centralized</u> industry engagement effort
- BOTTLE GB developed plans in FY21 and received positive feedback

Industry Engagement:

- Led by Bob Baldwin and Ron Schoon
- Coordinated outreach guided by industry landscape analysis
- Developed standard promotional documents
- Progress updates provided monthly
- Responsible for monitoring the BOTTLE.org e-mail address
- IPMP, CRADA and NDAs coordinated by Eric Payne

<u>Industry Engagement and Outreach</u>
Bob Baldwin & Ron Schoon

<u>Commercialization Council Lead</u>
Eric Payne

Communications:

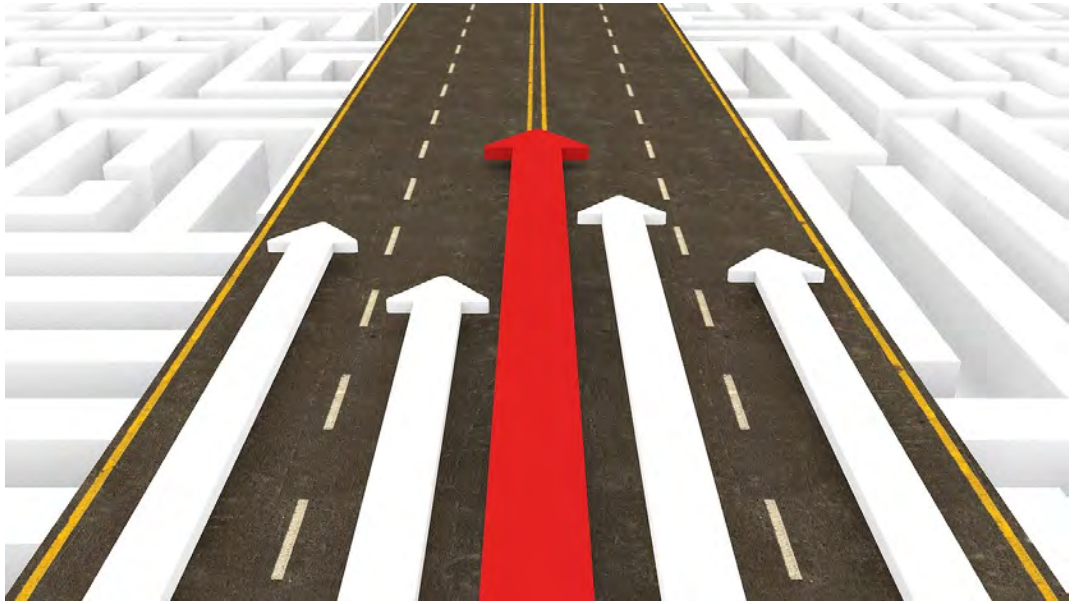
- Led by Kathy Cisar
- POC for www.BOTTLE.org content
- Coordinates news stories with BOTTLE partners and DOE
- Organized development of logos, templates, etc.
- Working on webinars and social media presence
- Meets regularly with BOTTLE LT

<u>Communications Lead</u>
Kathy Cisar

Reporting and decision making

Progress tracking & reporting

- Use PM software for operational efficiency
- Developed templates for reports and milestones
- Frequent communication ensures timely milestone adjustment, if needed
- Annual *BOTTLE Research Review* (FY21 milestone)



On- and off-boarding projects:

- BOTTLE conducts <u>analysis-guided</u> R&D
- All major projects benchmarked to our key metrics
- Advisory input for our R&D portfolio from the TAB

Resource allocation:

- BOTTLE GB assesses resource allocations annually using active PM principles, SLT input, tracking deliverable contribution and completion metrics, and progress towards analysis-guided research impact

Collaboration and communication

Fortnightly BOTTLE R&D meetings:

- Purpose: communication and collaboration for each project in BOTTLE
- Attendance: all BOTTLE members
- Recorded via Dropbox Paper

Monthly meetings with DOE Technology Managers

- Purpose: updates on BOTTLE progress
- Attendance: AMO and BETO TMs, technical presenter(s) from BOTTLE, and BOTTLE LT
- Recorded via Box Note

Annual all-hands meeting

- Purpose: foster collaboration, develop the next FY project plan
- Attendance: all BOTTLE members

Data Management Plan (DMP):

- Created and approved by SLT in FY20
- Meets the DOE Public Access Plan criteria
- Utilizes Dropbox for transparency and access to all BOTTLE members

Project risks and mitigation plans

Risk: Geographically-distributed partner institutions adversely impact research coordination

Mitigation: Frequent, documented R&D meetings ensure active collaboration. Slack for daily interactions.

Risk: Research priorities unclear and resources not used effectively

Mitigation: Project priority documents created at start of FYs to outline priorities.

Risk: Industry engagement will be mostly virtual, limiting our ability to develop projects

Mitigation: Developing virtual tours and content to showcase BOTTLE's capabilities. Planning several virtual webinars with DOE.

Risk: Merit Review of BOTTLE identified a critical gap of material science expertise

Mitigation: BOTTLE on-boarded an industrial polymer chemist (Bob Allen, formerly IBM), via institutional investments at NREL.

Risk: COVID-19 will impact both near- and long-term activities

Mitigation: Developed a 'COVID-19 Contingency Plan' with SLT, including: all meetings using a virtual platform, frequent COVID-19 check-ins with SLT, and utilization of a cloud-based folder for all materials

BOTTLE Approach

- Carbon, economic, and energy metrics
- BOTTLE R&D approach
- Analysis efforts
- Substrate considerations
- Milestones
- Task descriptions, approach, primary projects, and risks

Metrics for BOTTLE projects

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The mission of BOTTLE is to:

- Develop robust processes to upcycle existing waste plastics, and
- Develop new plastics and processes that are recyclable-by-design

BOTTLE projects will aim to meet 3 key metrics:

Energy:

- ≥50% energy savings relative to virgin material production
- Closed-loop recycling estimated to save 40-90% energy[1]

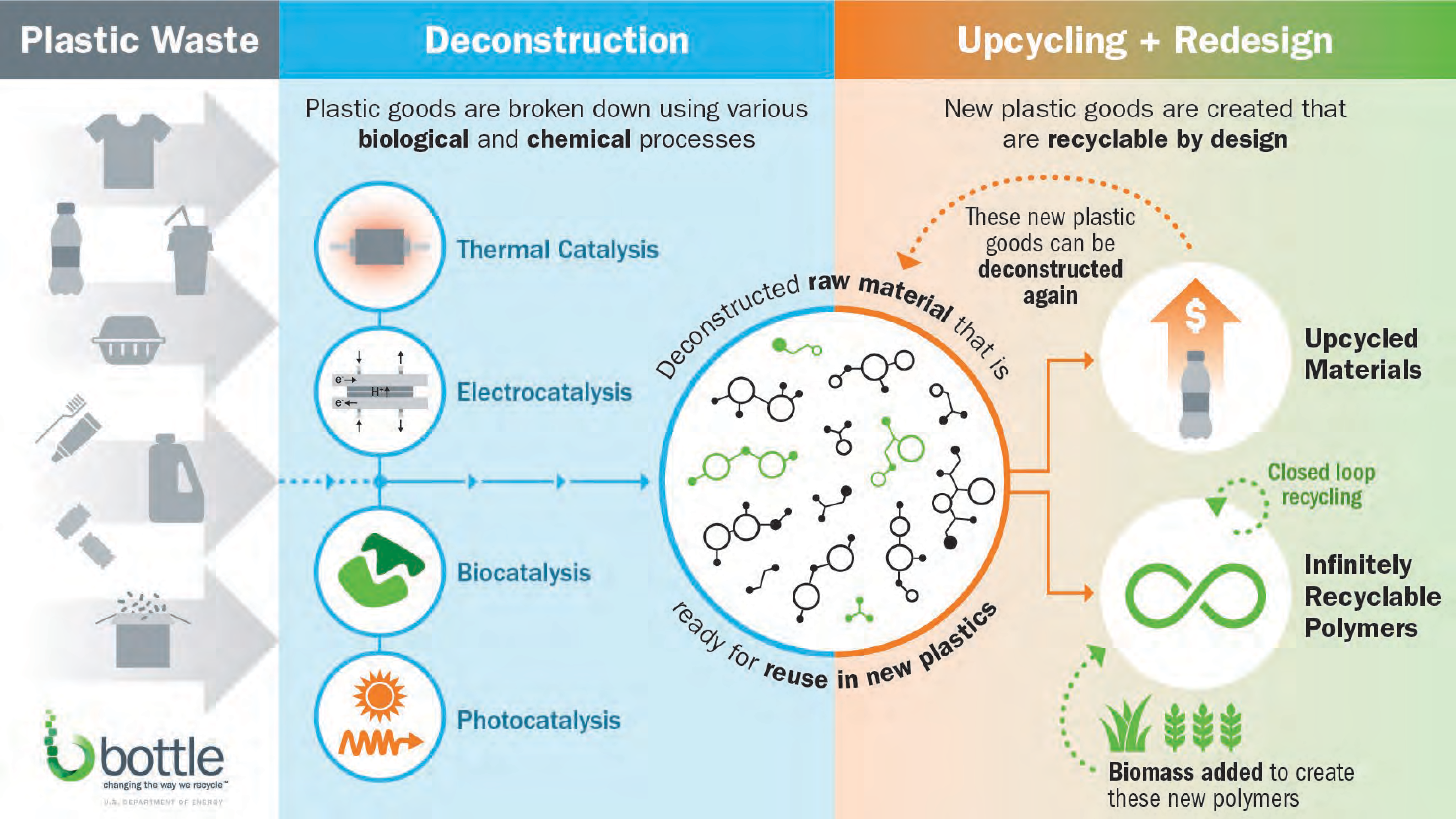
Carbon:

- ≥75% carbon utilization from waste plastics
- Estimated based on recycling of commodity thermoplastics

Economics:

- ≥ 2x economic incentive over reclaimed materials

1. Rahimi and Garcia, *Nature Reviews Chemistry*, 2017


Plastic Waste
Deconstruction
Upcycling + Redesign
Plastic goods are broken down using various biological and chemical processes
New plastic goods are created that are recyclable by design
Thermal Catalysis
Electrocatalysis
Biocatalysis
Photocatalysis
Deconstructed raw material that is ready for reuse in new plastics
These new plastic goods can be deconstructed again
Upcycled Materials
Closed loop recycling
Infinitely Recyclable Polymers
Biomass added to create these new polymers
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Analysis-guided R&D

- Analysis guides which polymers we work on
- Techno-economic analysis (TEA) using Aspen Plus
- Energy/GHG assessment via Materials Flows through Industry (MFI)
- All major BOTTLE projects evaluated for C, $, and E metrics
- Economics and sustainability assumptions follow transparent practices in EERE-funded R&D

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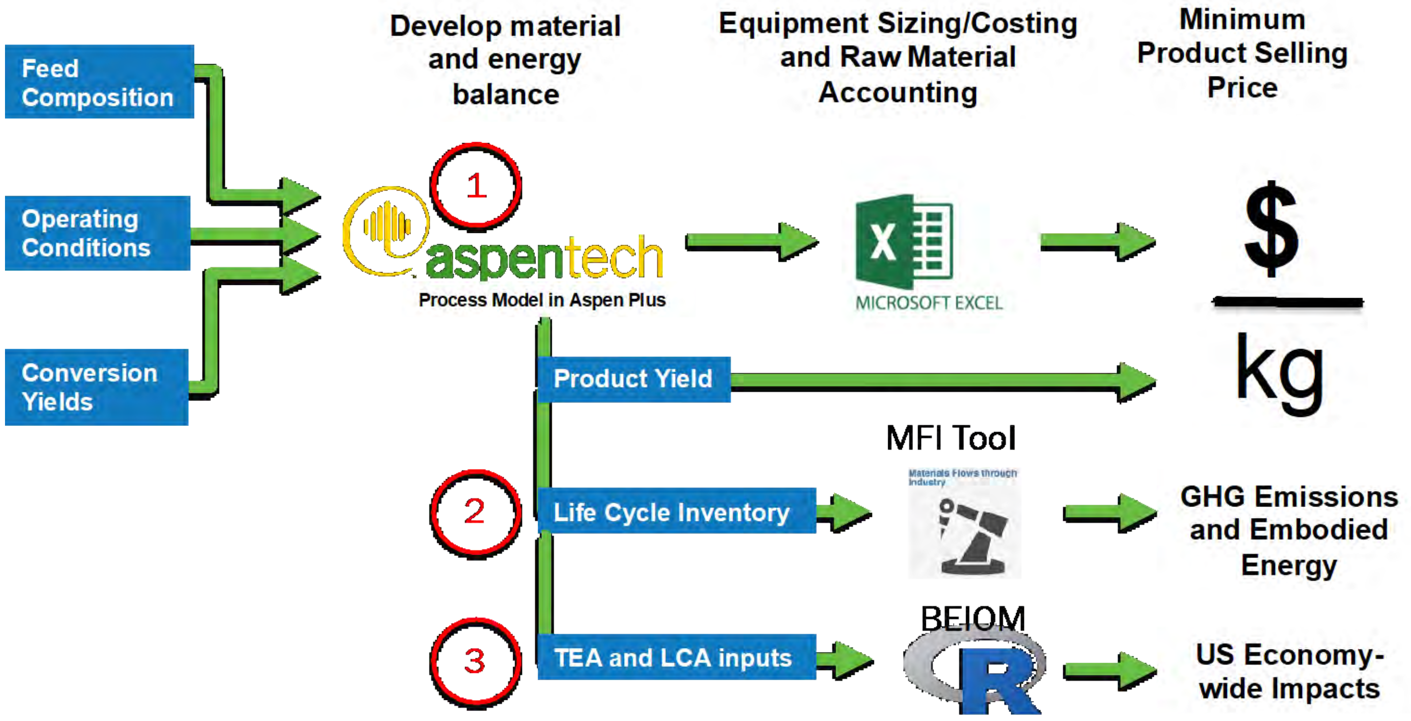


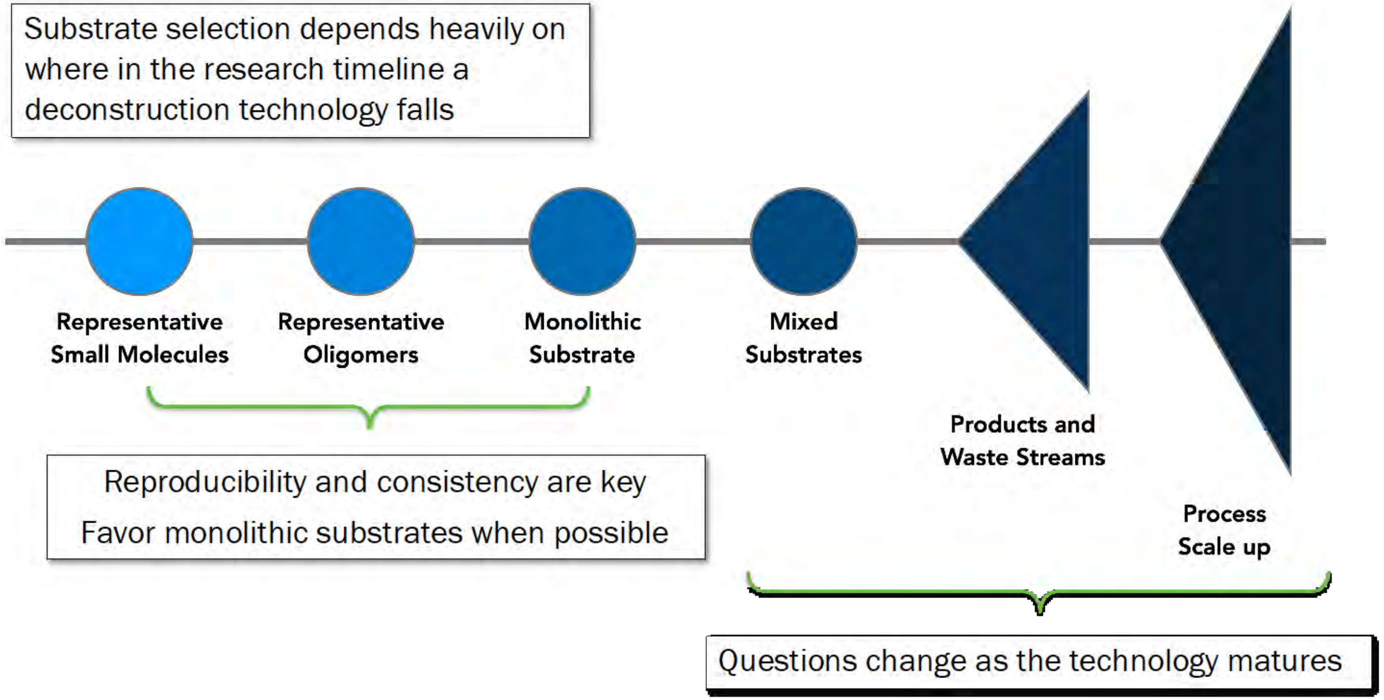
Approach to analysis

- Work with Analysis in parallel to lab R&D
- Mass & energy balances early in projects
- Evaluate ability to meet key metrics based on "theoretical maximum" case
- As projects increase in TRL, they merit more in-depth analysis
- Analysis is a primary risk mitigation tool to focus R&D

Substrates

Substrates present several challenges:

- Realistic substrates contain additives that may influence upcycling feasibility
- Rigorous polymer characterizations are key
  - Lessons from biomass: Poor characterization leads to failures and lack of confidence in the field
- Ensure reproducibility of BOTTLE research and be a positive example for the field



- Use model substrates (for reproducibility) and real substrates (for feasibility)
- BOTTLE appointed a “Substrate Czar” for substrate procurement and characterization

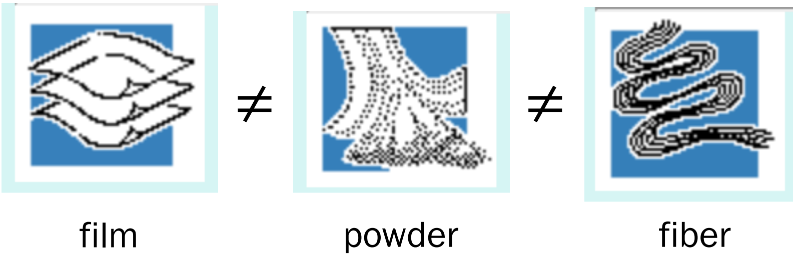


Image from GoodFellow website

Milestones, Go/No-Go decisions

Abbreviated milestones:

- FY21: ML pipeline to predict the T_g of RBD polymers, analysis on ≥2 RBD polymers
- FY22 G/NG: Down-select C-C bond cleavage strategies using analysis
- FY23: Deconstruction/Upcycling: 3 methods to cleave C-C bonds and upcycle intermediates
- FY23: Redesign: 10 RBD polymers able to be produced at ≤$2.50/lb
- FY23: Analysis: ≥10 analyses for BOTTLE processes to achieve C, $, and E metrics
- FY23: Modeling: Computational pipeline to predict RBD polymers with target properties
- FY23: Characterization: 3 Laboratory Analytical Procedures

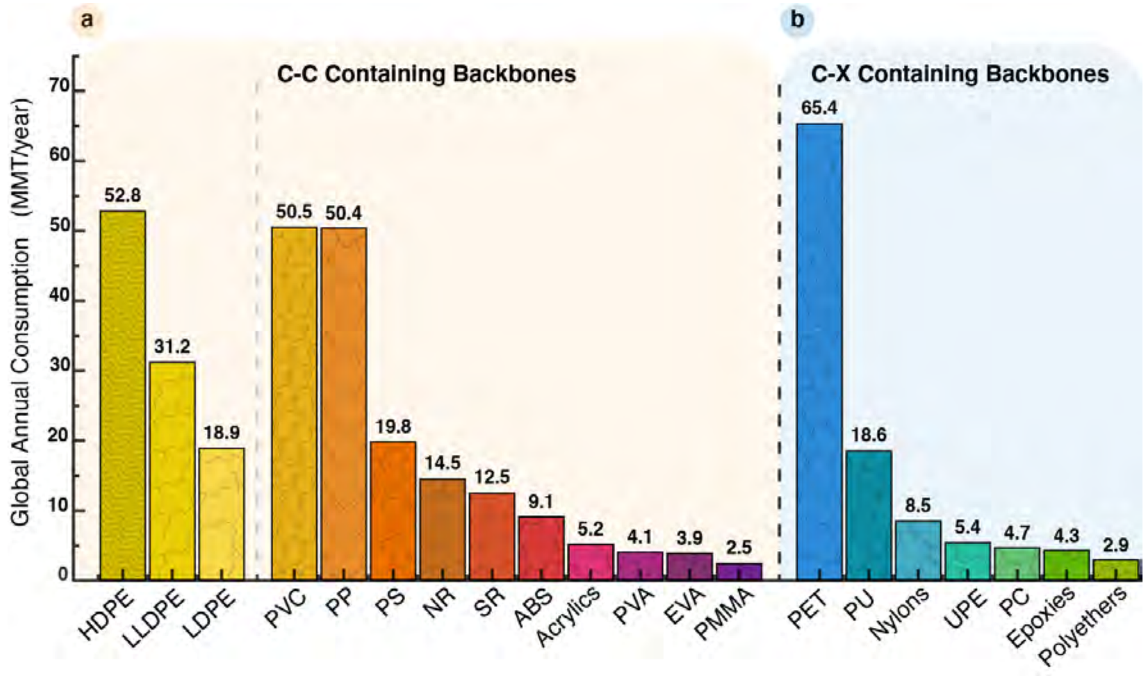


Image from Ellis, Rorrer, Sullivan, Otto, McGeehan, Román, Wierckx, Beckham, in revision at *Nature Catalysis*

Annual Review for BOTTLE projects:

Yearly portfolio review to on-board and off-board projects as dictated by analysis conducted the previous year

FY21 Industry Engagement:

Establish new industry-led, funds-in partnerships to tackle pressing commercial challenges

Deconstruction

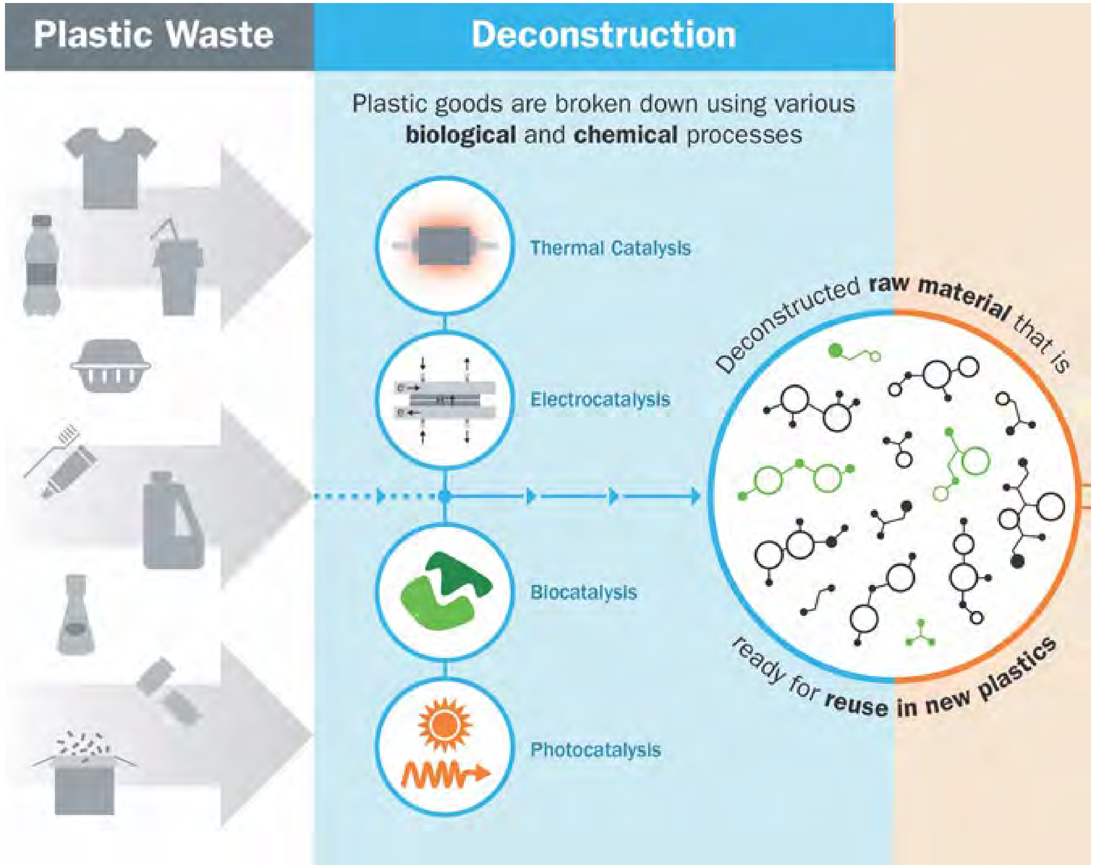
- Led by Taraka Dale (LANL) and Yuriy Román (MIT)
- Thermal, electro, bio, photo-catalysis
- Participants: LANL, MIT, MSU, NREL, ORNL, SLAC, UoP

Primary projects:

- C-C bond cleavage catalysis via thermal, electro-, and photo-catalytic methods
- Selective deconstruction of mixed plastics
- Enzymatic and organocatalytic process development for C-O and C-N-linked polymers

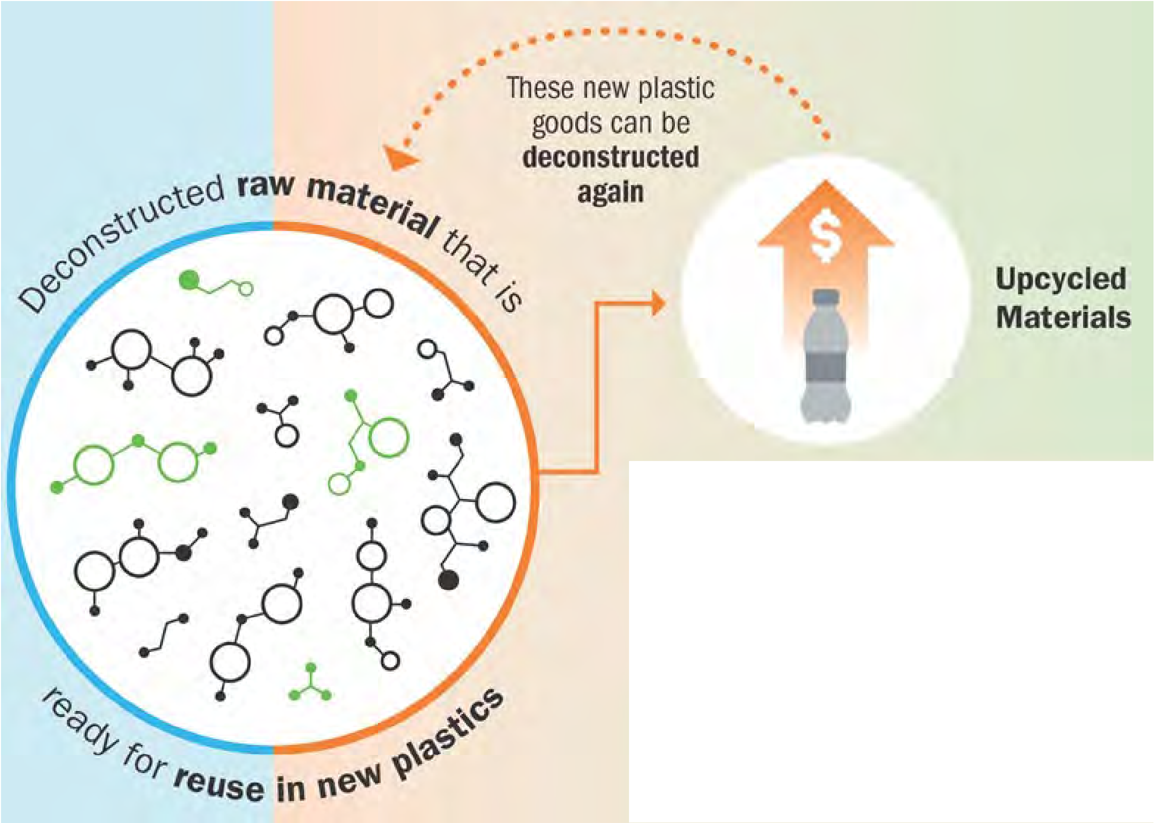
Risks:

- Catalytic deconstruction of plastics as solids will scale with surface area – may inherently limit rates
- Additives may deactivate or inhibit catalysts



Upcycling

- Led by Adam Guss (ORNL)
- Biological and chemo-catalytic conversion
- Participants: NREL and ORNL



Primary projects:

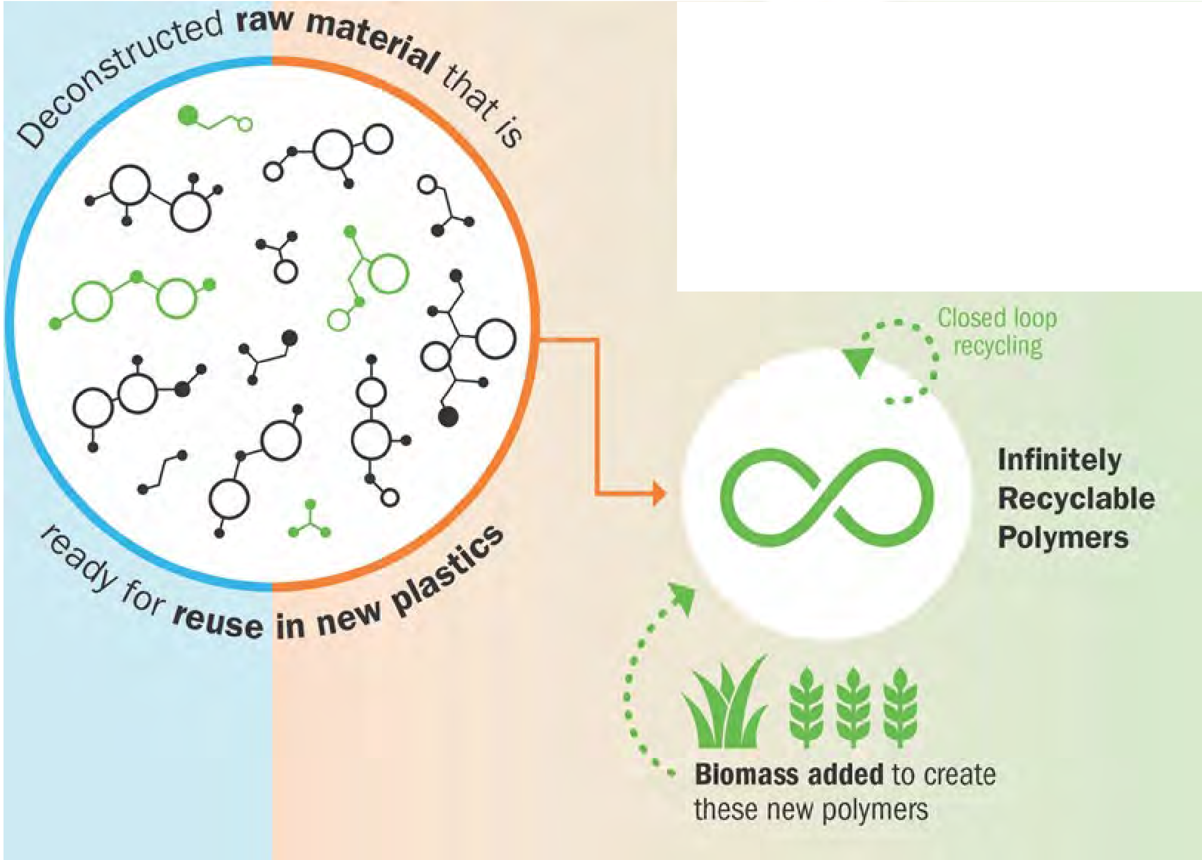
- Bioconversion of Deconstruction intermediates
- Discovery of new pathways to assimilate new intermediates from Deconstruction, and
- Consolidated biological deconstruction and upcycling of C-O and C-N-linked polymers

Risks:

- We are unable to identify metabolic pathways for some deconstruction products and/or additives
- Bio-upcycling approaches are too slow to be economical and/or unable to meet carbon goals

Redesign

- Led by Eugene Chen (CSU)
- This task will create RBD polymers to replace today's plastics with Deconstruction and Upcycling
- Participants: ANL, CSU, MIT, NREL, ORNL, SLAC



Primary projects:

- Redesign projects include new routes to replace PE, PP, PS, PET, nylons, PU, and more
- Modeling and analysis used to design atom-efficient, cost-effective routes for new monomer syntheses

Risks:

- We are unable to produce RBD polymers at commodity prices and achieve >50% energy savings relative to today's materials
- Performance of RBD circular polymers cannot match that of today's commodity plastics

Analysis, Characterization, and Modeling

Task Leads:

- Analysis: Birdie Carpenter (NREL)
- Characterization: Chris Tassone (SLAC) & Meltem Urgun-Demirtas (ANL)
- Modeling: Linda Broadbelt (NU)
- Cross-cutting Tasks integrated into Research Tasks

Primary projects:

- Analysis: TEA, LCA, and EEIO to guide R&D
- Characterization: analytics and characterization including wet chemistry, catalyst, polymer, biodegradation, and synchrotron-based characterizations
- Modeling: Chemical operators for synthesis predictions, machine learning to predict polymer properties, DFT, and kinetic modeling

Risks:

- Monomer design space is vast, testing all potential leads from computation is prohibitive
- Analysis tools may not be able to access reliable global supply chain data for baseline analyses

BOTTLE Impact

- Scientific
- Industrial

Image from https://www.altmetric.com/details/91362881 (BOTTLE 2020 paper)

Impact

Scientific:

- Analysis-guided R&D distinguishes BOTTLE from basic science efforts – able to compare approaches in a self-consistent, rigorous, agnostic manner

- Focus on impactful publications and patents that encompass inter-disciplinary science, engineering, and analysis

- Standards development for both substrate characterization and analysis-guided R&D benchmarks to enable consistency within BOTTLE research tasks and across other plastics deconstruction scientific efforts

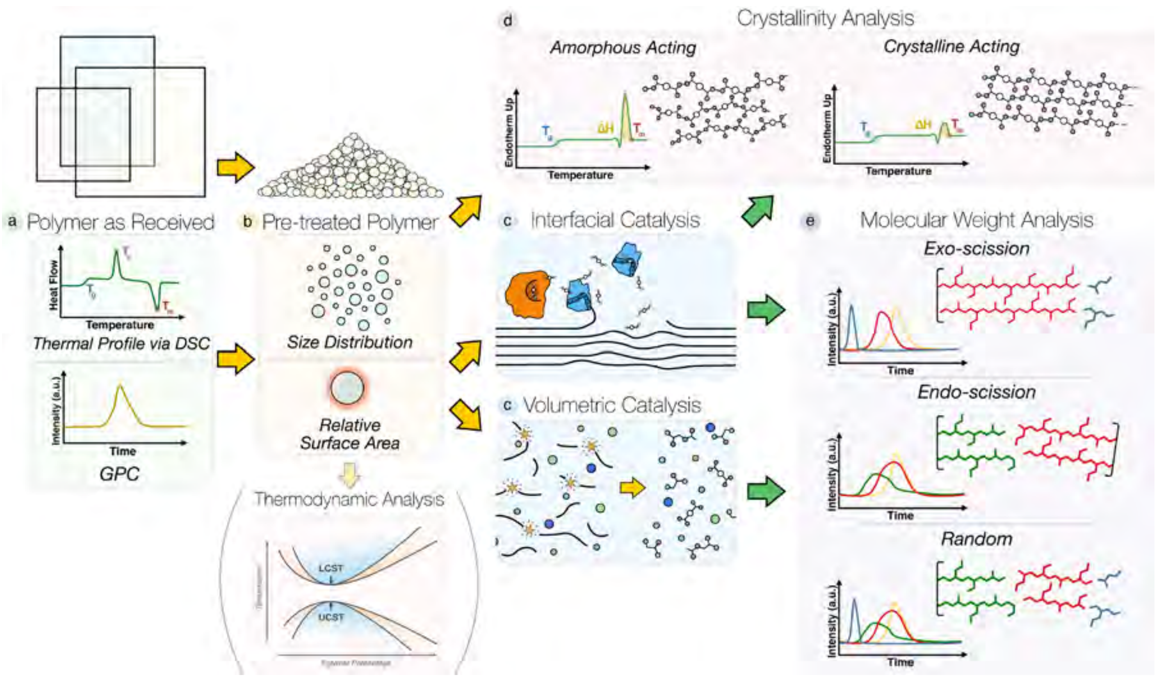


Image from Ellis, Rorrer, Sullivan, Otto, McGeehan, Román, Wierckx, Beckham, in revision at *Nature Catalysis*

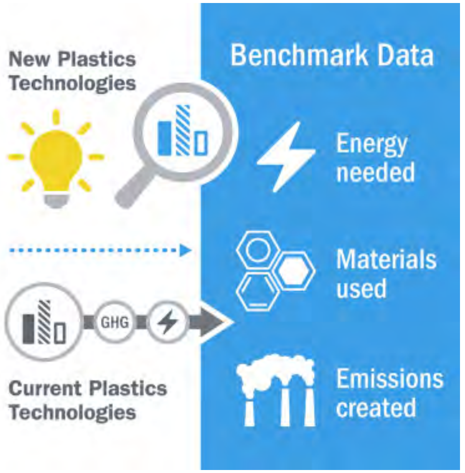


Image from Nicholson, Rorrer, Carpenter, Beckham, *Joule* 2021

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Impact

Industrial:

- Analysis-guided R&D to inform viability of both BOTTLE and external technologies to ensure relevance
- Working with industry via CRADAs – provides feedback to DOE-funded efforts to guide R&D
- Comm. Council setup for facile tech. transfer
- TAB includes industry leaders to ensure robust assessment of BOTTLE technologies
- Business Development investments from institutions to solve industry's most critical problems
- Industrial collaboration through BOTTLE FOA awards

Overall: BOTTLE conducts interdisciplinary, industry-relevant, and process-enabling research to deconstruct and upcycle today's plastics and redesign tomorrow's plastics

BOTTLE Progress and Outcomes: Setting up BOTTLE

- Foundational documents
- Industry engagement
- Communication materials
- FOA and Lab Call proposals
- Consortium launch

Foundational Documents

- **IPMP** – **I**ntellectual **P**roperty **M**anagement **P**lan
  - Document that enables industry access to BOTTLE innovations
  - Agreed to by all Academic Partners
- **Governance plan:** outlines BOTTLE management structure
- **CRADA:** Developed standard set of pre-approved CRADA documents for BOTTLE engagements
- **MMTA:** Allows for materials transfer between BOTTLE members
- **NDA:** Protects confidential information to promote free exchange of information among BOTTLE members
- Data Management Plan
- FOA US Manufacturing Plan

Industry Engagement

- Developed pre-approved CRADA documents for BOTTLE engagements that are available on the BOTTLE website
- Streamlined access to BOTTLE innovations to maximize industrial impact
  - Rights to Subject Inventions in CRADA – address option terms, royalties, cooperation among joint IP owners, publications, etc.
- Over <u>80</u> companies engaged to date
- We are placing an emphasis on contacting companies that span the **Plastics Value Chain**
  - Primary plastics production
  - Raw material production
  - Manufacture and use
- Identified key companies using an industry landscape analysis
- Currently negotiating five separate proposals

Communication and Messaging

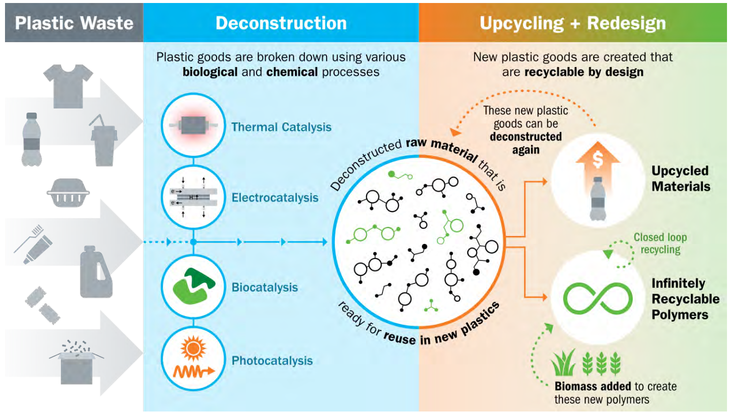
Goal: Develop uniform BOTTLE messaging materials for one cohesive message across 10 institutions

Developed www.BOTTLE.org

- Provides updates to external parties on recent publications & news
- ‘Contact Us’ page for direct engagement
- ‘Join Us’ page contains CRADA documents for transparent partnership mechanisms

Presentation Materials

- Slide templates for uniform presentations (used for this presentation)
- Icons: provide visual context to Research Tasks
- Placemat slide: conveys BOTTLE’s approach in a single image



Communication and Messaging

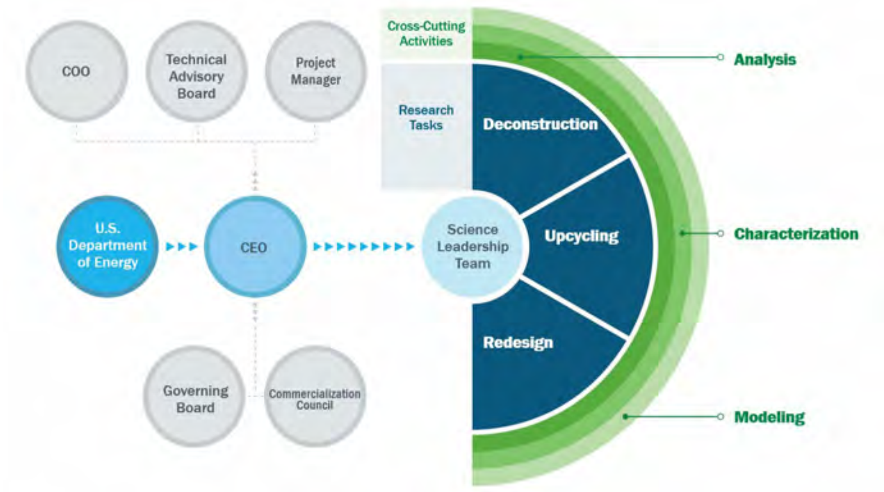
Branding Materials

- Designed a BOTTLE logo to show the monomer breakdown products upcycled into new product s
- Inspired the tagline “Changing the way we recycle”

bottle
changing the way we recycle
U.S. DEPARTMENT OF ENERGY

Industry Engagement

- Created a ‘1-pager’ for initial industry engagement
- Designed overview slides for industry presentations to streamline pre-NDA conversations
- Developed an Org chart as a visual representation of BOTTLE structure



Proposals

Lab Call:

- Hosted webinar with DOE labs to solicit input and develop complementary partnerships in BOTTLE
- Participated in two rounds of Lab Calls in FY20
- First round onboarded ANL, NU, and SLAC
- Second round finalized 3-year AOP for BOTTLE

BOTTLE FOA: Topic Area 3 (TA3) designed to allow applicants to propose work with BOTTLE Consortium

- All potential TA3 applicants sent inquiries via www.BOTTLE.org
- Documented all interactions via the BOTTLE email/website
- All TA3 inquiries discussed with BOTTLE SLT to determine scope fit and appropriate BOTTLE partners
- 9 full TA3 proposals submitted, 3 selected for awards:
    - University of Wisconsin-Madison, University of Minnesota, and University of Delaware

Joint FY20 Bioenergy and Advanced Manufacturing FOA
BOTTLE: Bio-Optimized Technologies to keep Thermoplastics out of Landfills and the Environment

Funding Opportunity Announcement (FOA) Number:
DE-FOA-0002245

Official FY21 launch of BOTTLE project

- BOTTLE officially started on October 1st, 2020
- Two-day kickoff meeting held on Oct. 20 & 21
- Have an executed IPMP
- 10 AOPs were submitted to AMO and BETO
- 7 R&D meetings have been held
- A SLT meeting held in December
- All-hands meeting will be scheduled in Q3
- Paper and patent application pipeline starting to increase substantially

Future Work in FY21: Finalize TAB and hold inaugural meeting (summer), finalize CRADAs with BOTTLE FOA TA3 partners, and expand website content to highlight partnerships and capabilities

bottle
changing the way we recycle
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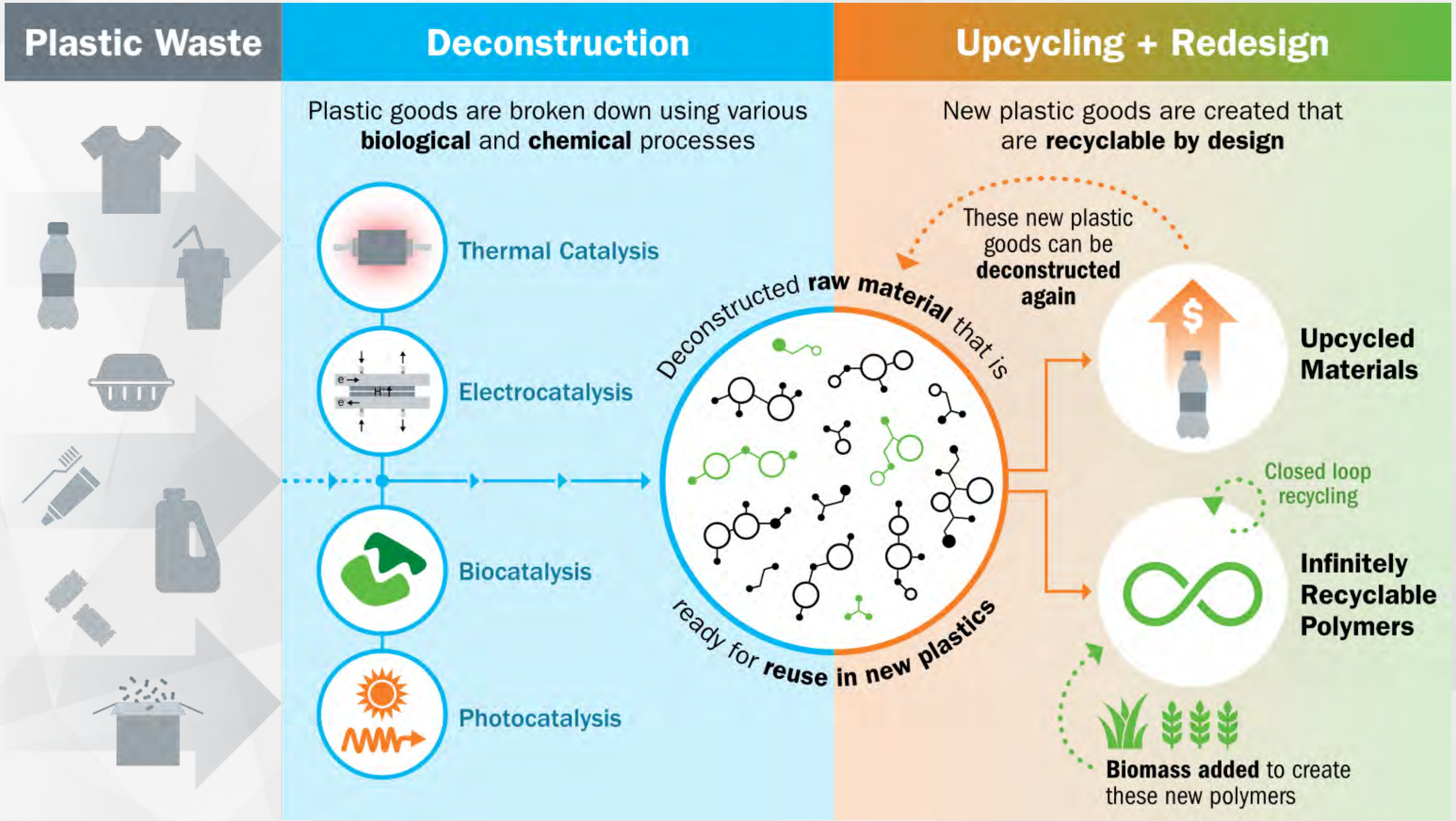
Bio-Optimized Technologies to keep Thermoplastics out of Landfills and the Environment

First Q&A section



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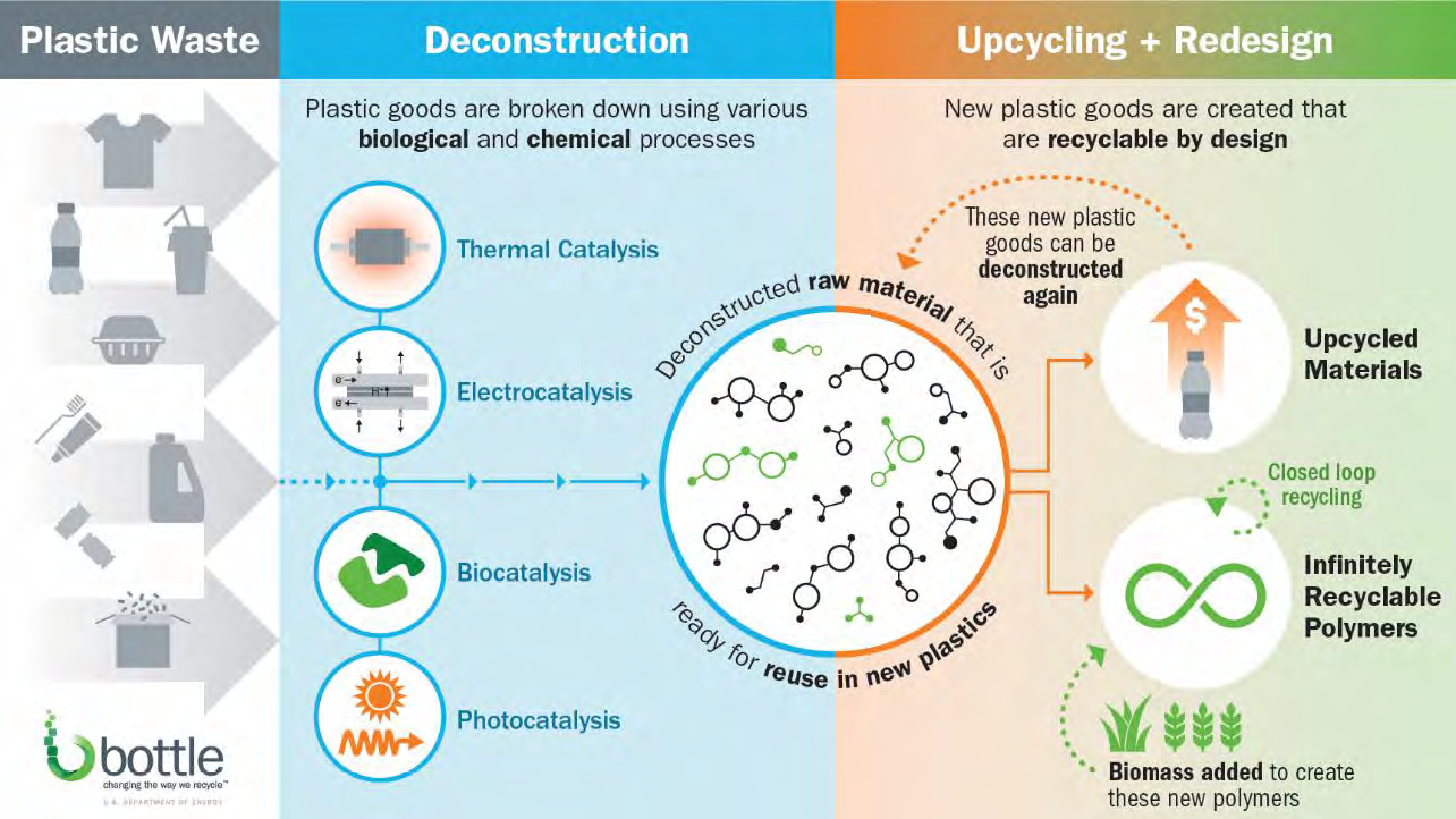
BIOENERGY TECHNOLOGIES OFFICE
ADVANCED MANUFACTURING OFFICE

BOTTLE Progress and Outcomes: R&D

- Analysis
- Characterization
- Deconstruction
- Upcycling
- Redesign & Modeling



Plastic Waste
Deconstruction
Upcycling + Redesign
Plastic goods are broken down using various biological and chemical processes
New plastic goods are created that are recyclable by design
Thermal Catalysis
Electrocatalysis
Biocatalysis
Photocatalysis
Deconstructed raw material that is ready for reuse in new plastics
These new plastic goods can be deconstructed again
Upcycled Materials
Closed loop recycling
Infinitely Recyclable Polymers
Biomass added to create these new polymers
bottle
changing the way we recycle™
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Analysis

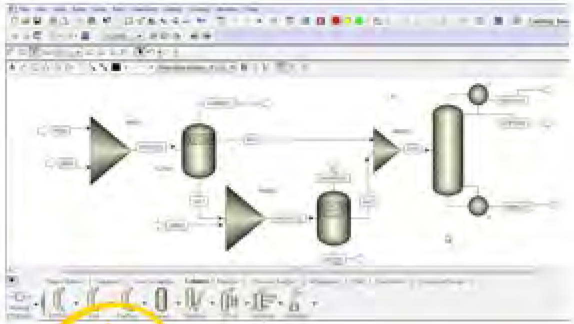
- Analysis scope and tools
- Benchmarking today's plastics manufacturing
- Ongoing analysis in thermal recycling methods
- Ongoing analysis in PET chemical recycling
- Illustrative analysis for enzymatic PET recycling

Analysis Scope – TEA, MFI, and EEIO Modeling

Three complementary analysis scopes:

- **T**echno-**E**conomic **A**nalysis (TEA): economics of prospective technology at the <u>plant level</u>
- **M**aterials **F**lows through **I**ndustry (MFI): environmental impacts at the <u>supply chain level</u>
- **E**conomically-**E**xtended **I**nput-**O**utput (EEIO): economic and environmental impacts at the <u>economy level</u>

TEA



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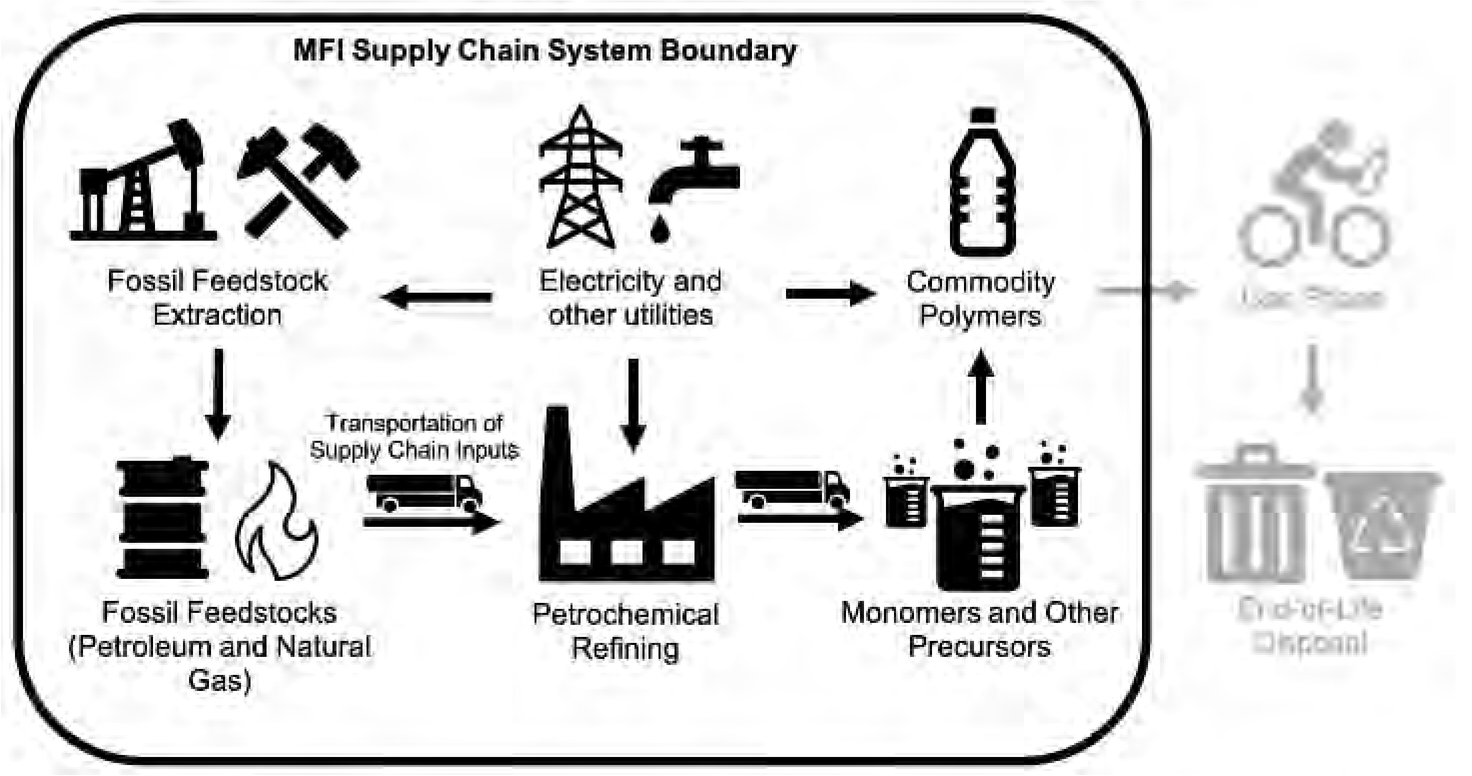
MFI

EEIO (BEIOM)

Higher Resolution ⟵⟶ Wider Scope

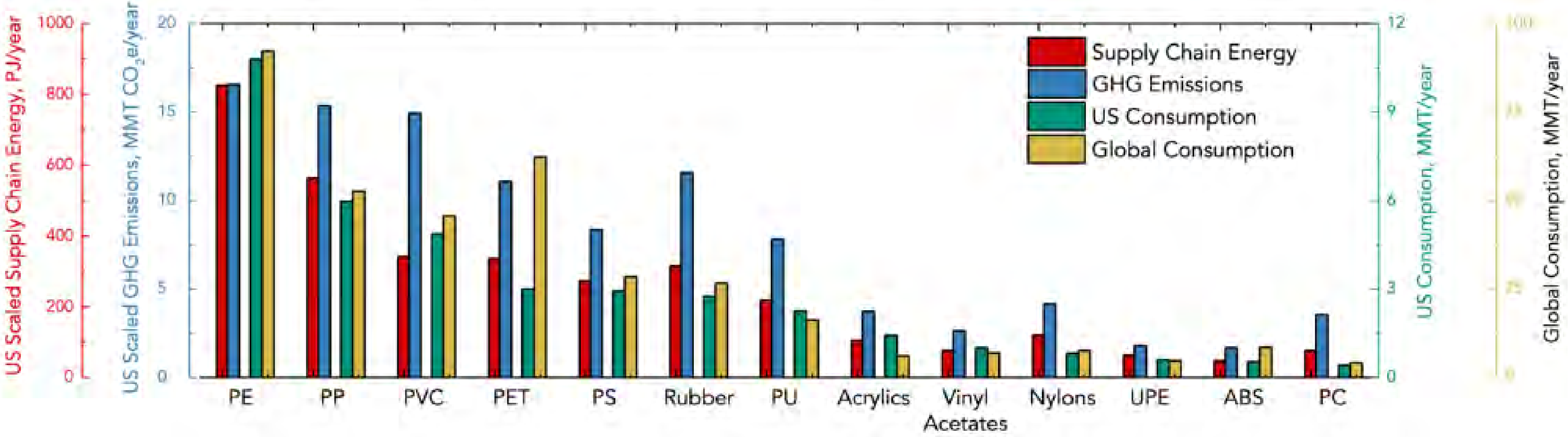
BOTTLE technologies require accurate baselines

- Goal: Estimate supply chain energy and greenhouse gas (GHG) emissions from US-based plastics consumption
- Scope: Polymers with global consumption of ≥1 MMT per year
- Output: Estimates of energy and GHG emissions from MFI supply chain analyses



SR Nicholson, NA Rorrer, AC Carpenter, GT Beckham, *Joule* 2021

Supply chain energy and GHG emissions analysis

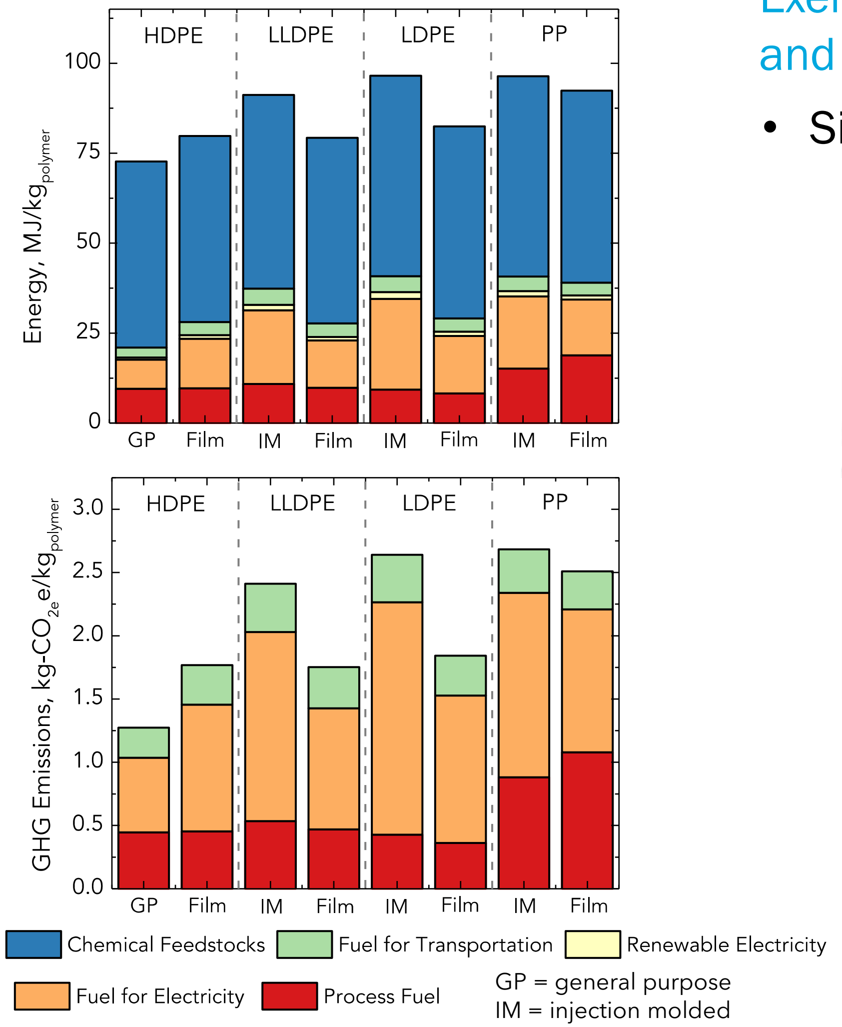


Plastics consumption accounts for 3.2 Quads/yr and 104 MMT CO_2e/yr in the US

- Metrics enable comparison of new recycling technology for today's plastics or replacements
- If an organization has candidate recycling, circular, or bio-based technologies to compare business-as-usual, these data serve are a baseline
- MFI is publicly available for use so anyone can access this tool to compare their candidate processes
- Ongoing work: extending this analysis to MFI Global

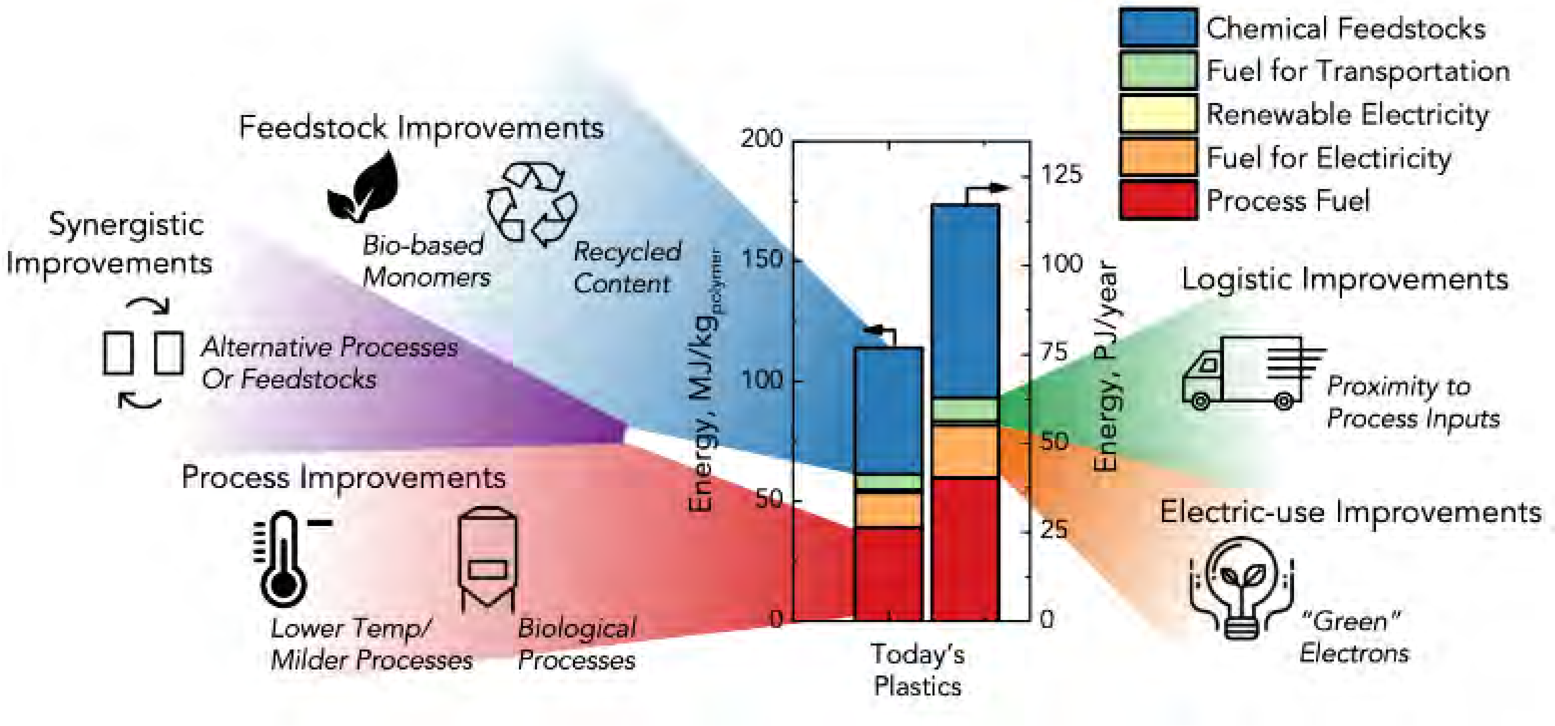
SR Nicholson, NA Rorrer, AC Carpenter, GT Beckham, *Joule* 2021

Enabling outcomes of benchmarking analysis



Exemplary case study on polyolefins highlights both the per kg and total energy and GHG emissions in the US annually

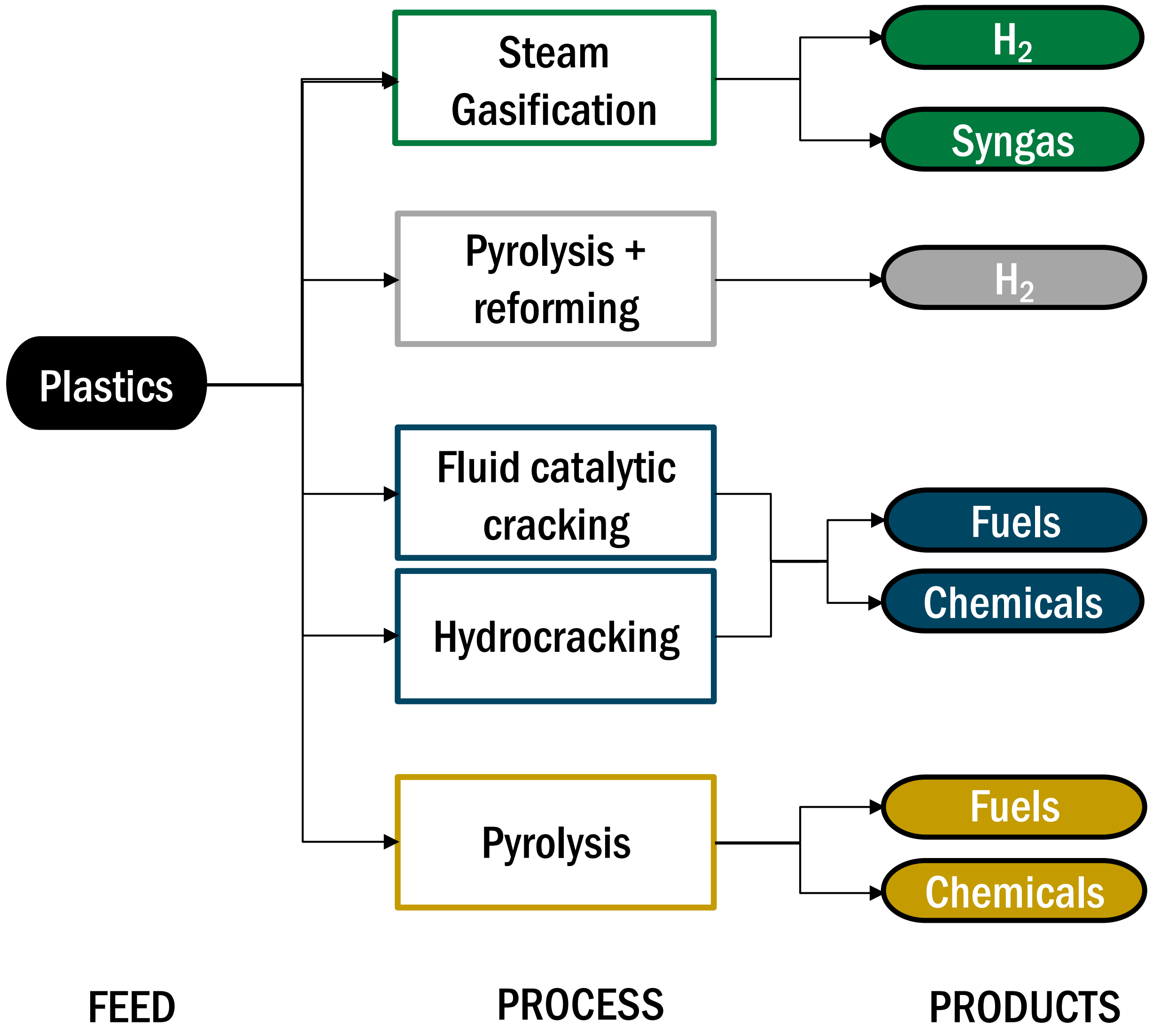
- Similar case studies included for all 18 polymers



SR Nicholson, NA Rorrer, AC Carpenter, GT Beckham, *Joule* 2021

Ongoing analysis: Benchmarking pyrolysis and gasification

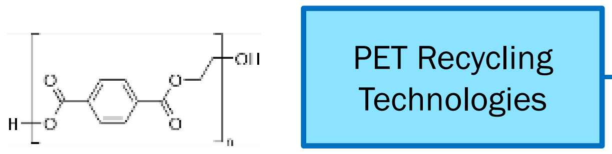
- Goal: Evaluate pyrolysis and gasification of mixed plastic waste to benchmark new recycling technologies against them
- Scope: Use literature and patent data to inform mass & energy balances
- Output:
  - Transparent, peer-reviewed design cases for plastics pyrolysis and gasification available for the community
  - Baseline estimates of carbon, economics, and energy metrics for these processes

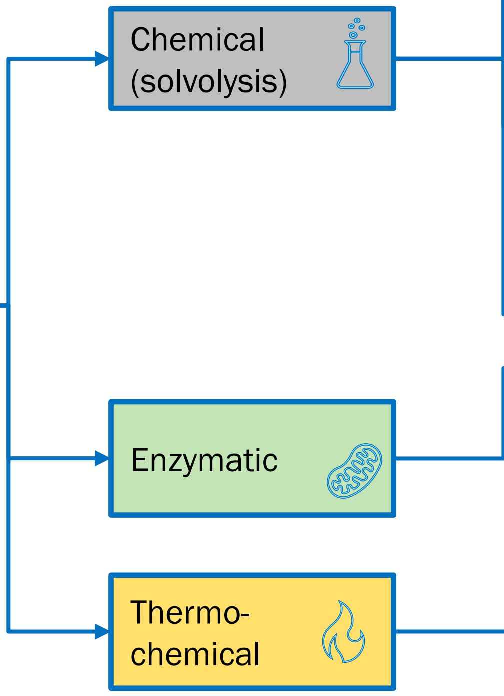


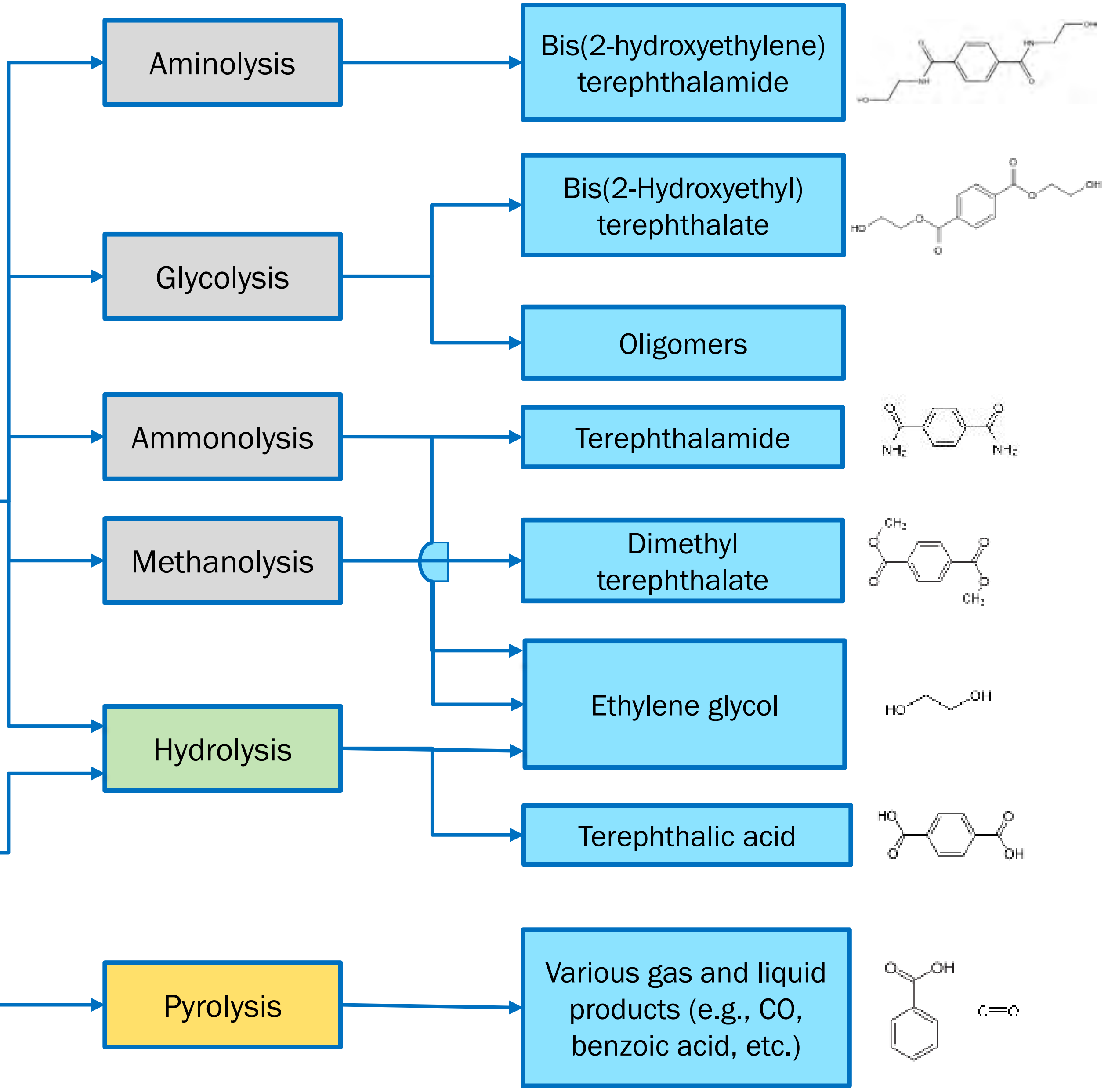
G Yadav, A Singh *et al.* in preparation; S Afzal, A Singh *et al.* in preparation

Ongoing analysis: PET Recycling

- Goal: Evaluate and compare proposed PET chemical recycling strategies
- Scope: Use literature and patent data to inform mass & energy balances







- Output: Transparent cases for PET chemical recycling, estimates of C, $, and E metrics for these processes

Example: PET enzymatic hydrolysis

Goals:

- Determine key drivers for community to enable enzymatic PET depolymerization
- Provide base model to compare enzyme-based approaches for PET recycling to chemo-catalytic and thermal methods
- Highlight areas for further impactful development of biocatalysis-enabled plastics recycling

Methods:

- TEA, MFI, EEIO (BEIOM)
- Process data from patent and peer-reviewed literature

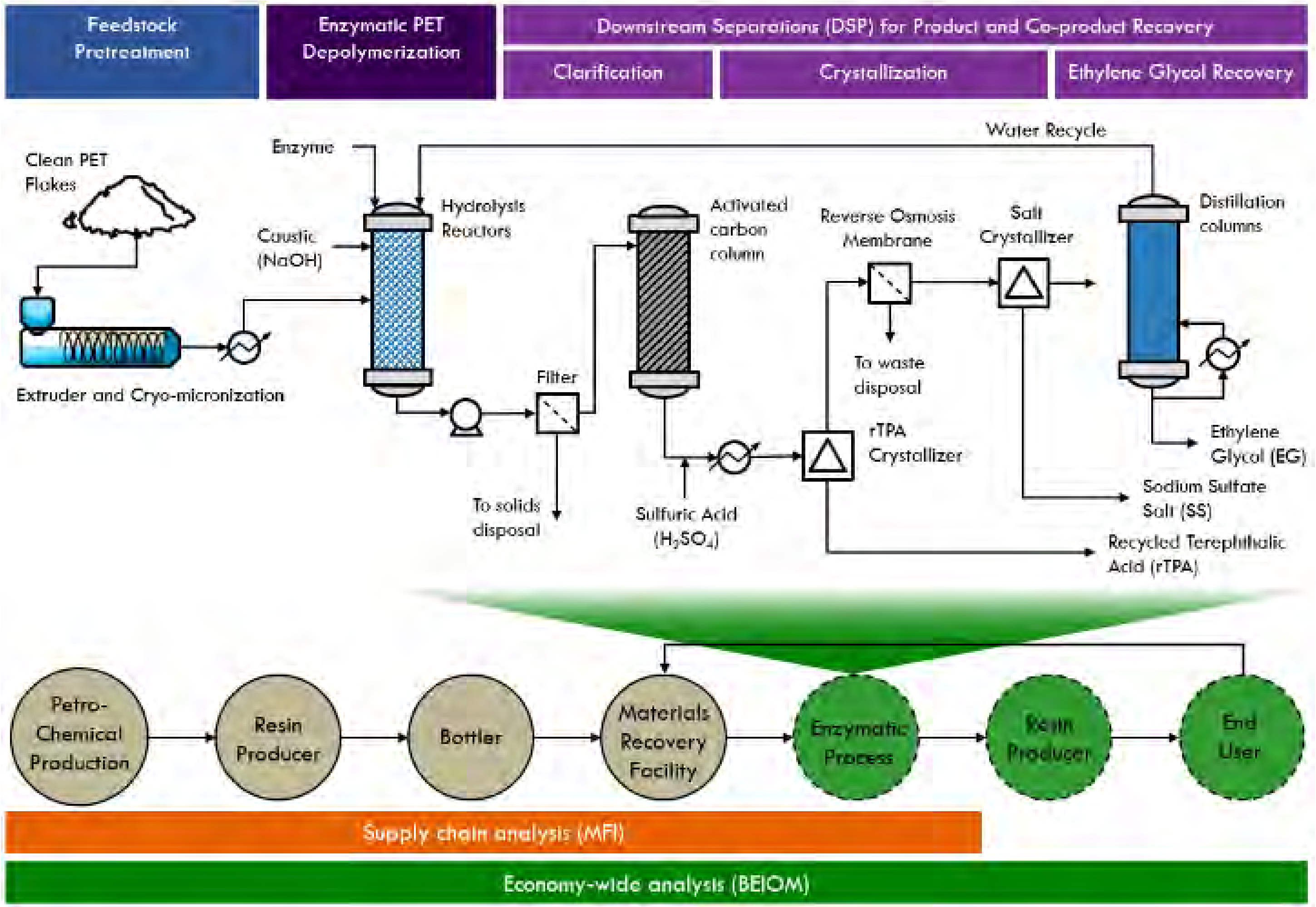
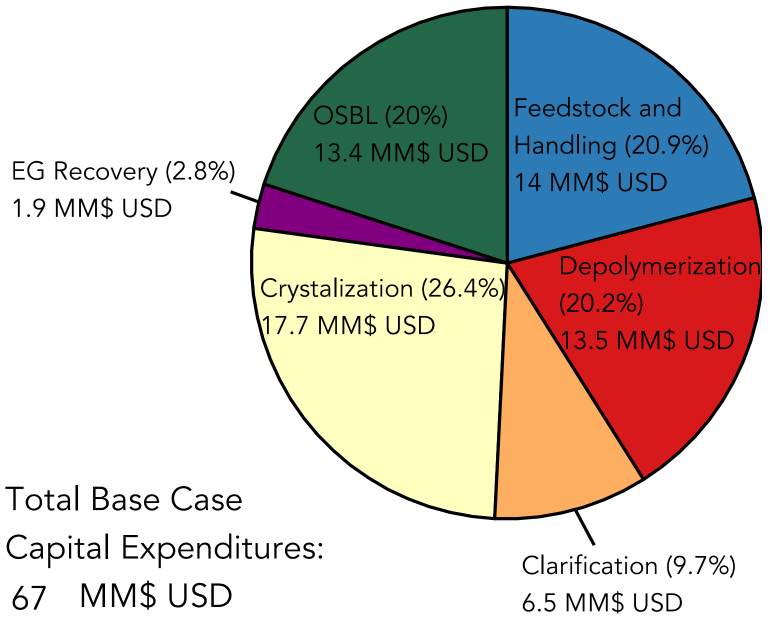


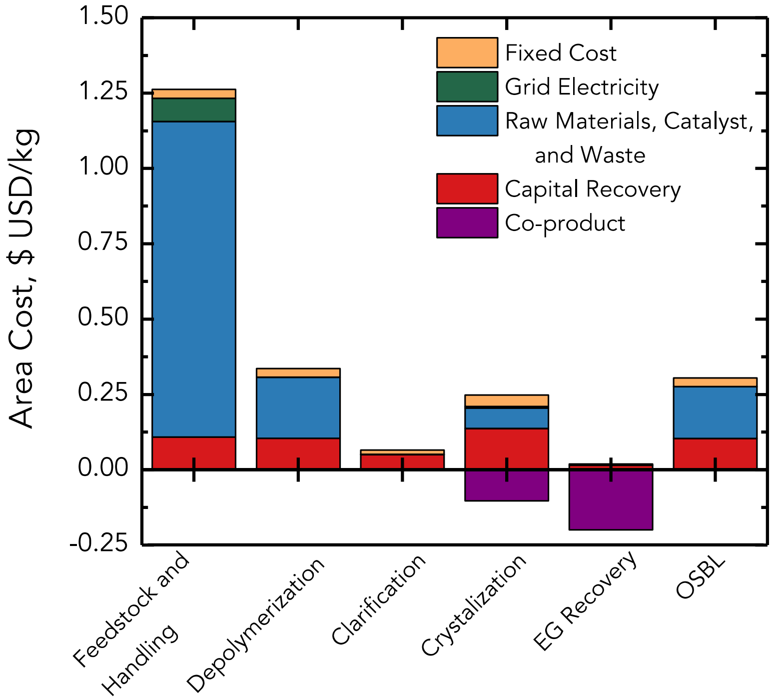
Figure: (*Top*) Simplified process flow diagram of the PET enzymatic depolymerization process (*Bottom*) A representation of the bottom-up supply chain model (MFI tool) scope and top-down environmentally-extended input-output (BEIOM model) scope

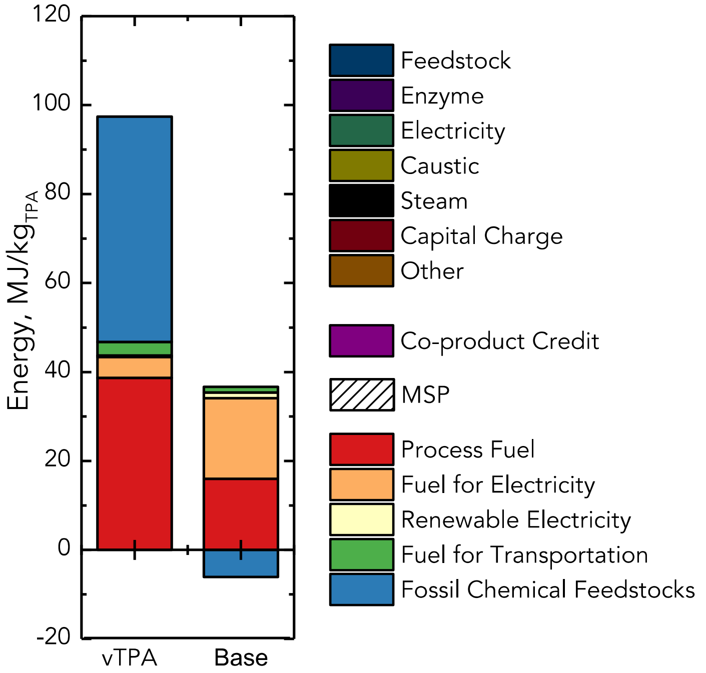
A Singh, NA Rorrer, SR Nicholson, E Erickson, J DesVeaux *et al.* in review

EEIO = environmentally-extended, input-output, rTPA = recycled terephthalic acid

Example: Analysis results for PET enzymatic hydrolysis







A Singh, NA Rorrer, SR Nicholson, E Erickson, J DesVeaux *et al.* in review

Enzymatic PET recycling shows substantial promise relative to virgin polyester manufacturing:

- TEA Impacts (Aspen) :
  - Recycled TPA from enzymatic recycling predicted to be $1.93/kg from processed, clean flake ($0.66/kg)
  - Cheaper feedstock enables cost parity; TPA price $0.50 – $1.50/kg
  - Other major drivers: solids loading and process yield
- Supply Chain Impacts (MFI) :
  - Supply-chain energy reduced by 69-83%
  - GHG emissions by 17-43% per kg of TPA
  - Major drivers: mechanical pretreatment and EG recovery
- EEIO Impacts (BEIOM) :
  - Reduce broader environmental impacts up to 95%
  - Up to 45% more socio-economic benefits

Characterization

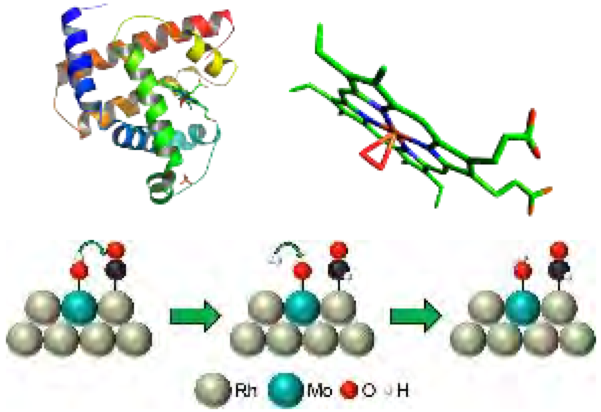
- Characterization Scope
- Characterization Capabilities
- Advanced synchrotron-based characterization
- Biodegradation capabilities for polymers from Redesign

Characterization Scope –Mechanisms, structure and EOL

Three complementary characterization scopes:

- **Mechanistic Determination**, quantification of products, and elucidating kinetics enables us to improve process efficiency, product selectivity, and process compatibility
- **Polymer structure** characterization used to determine relationships between polymer chemistry, and its associated structure and performance to improve redesigned polymers
- **End-of-Life (EOL)** determines environmental impacts of redesigned polymers in natural (soil and fresh water) and engineered environments (landfill, composting, and anaerobic digester)

Mechanism Determination



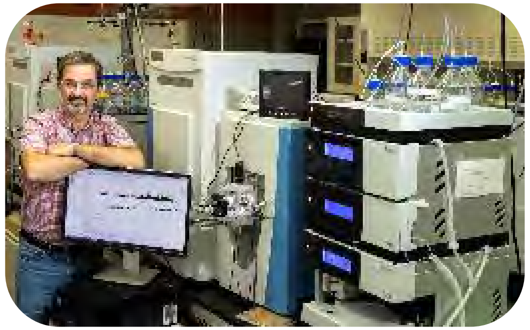
Polymer Structure

End-of-Life

Analytics, catalyst, and polymer characterization capabilities

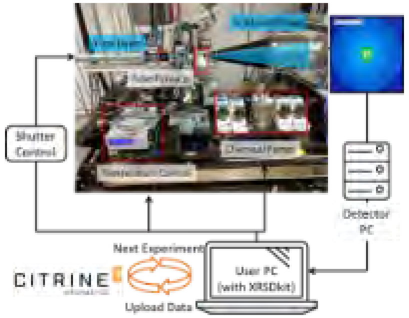
Analytical chemistry:

Multiple high-resolution GC-MS, LC-MS instruments for small-molecule identification and proteomics



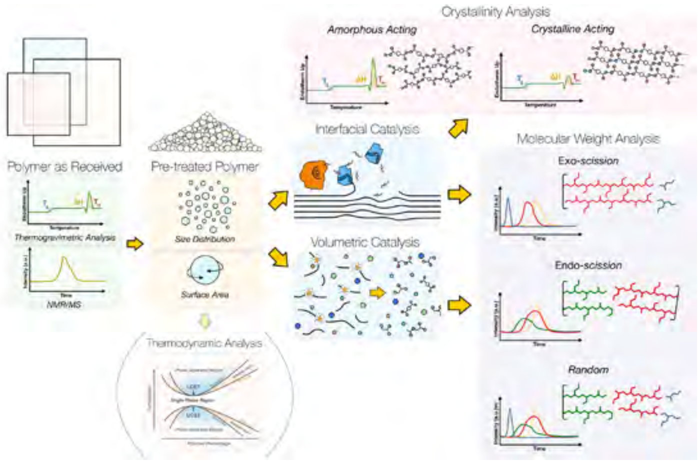
Laboratory-scale catalyst characterization:

Automated ML-driven catalyst synthesis, catalyst characterization tools (BET, EPR, TPR/TPD, ICP-MS, etc.)



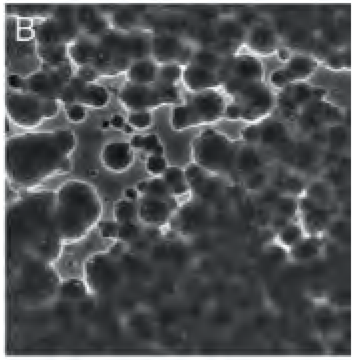
Laboratory-scale polymer characterization:

GPC, HT-GPC, thermal, mechanical, barrier, particle size measurements, multiple spectroscopies, etc.



Laboratory-scale microscopy:

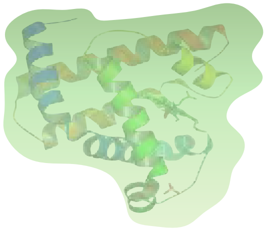
AFM, FT-IR, Raman, SEM, TEM, cryoEM (SLAC), including *in situ* capabilities with heating stages

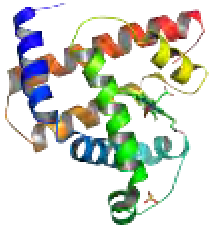


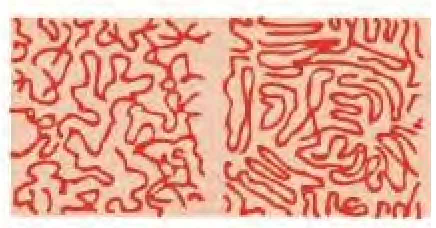
Advanced characterization capabilities

X-ray scattering:

Multiple beamlines to characterize polymer substrate evolution during deconstruction, substrate-catalyst interactions, and structure-property relationships in redesigned polymers

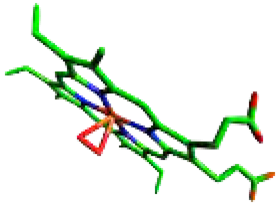


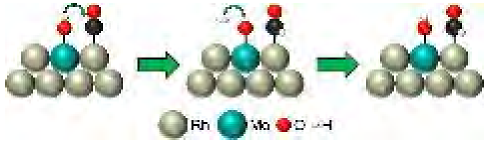




X-ray Spectroscopy

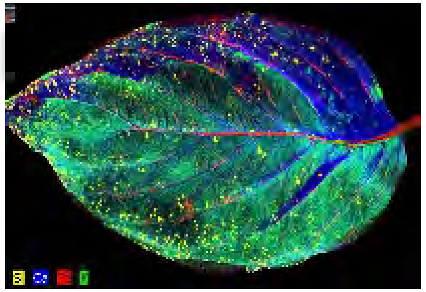
Multiple beamlines to characterize the structural trajectory during reactions with fs resolution. Elucidate mechanisms and describe the substrate-catalyst active electronic coupling





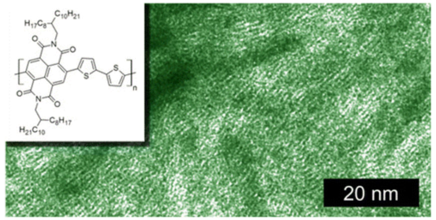
X-ray imaging

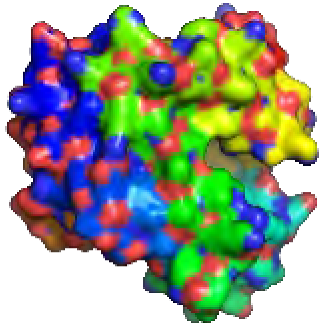
Imagine capabilities with resolution from nm to μm scales. Full spectral-tomographic reconstruction to visualize catalyst-substrate interaction to inform process design



Cryo-EM

World leading cryo-EM capabilities with atomic resolution to determine structure in non-crystalline samples. Imaging of amorphous polymers and structural work on biocatalysts.





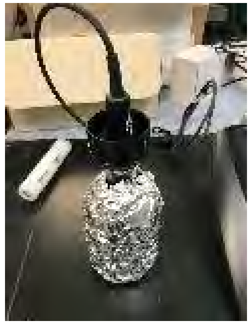
End-of-Life (EOL) Testing Capabilities

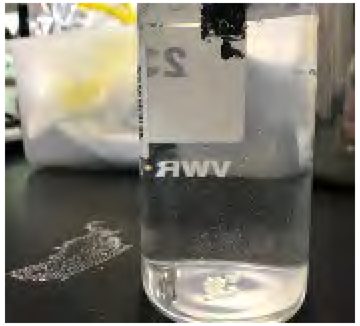
Soil Biodegradation (ASTM D5988)

CO_2 produced over time is captured via desiccators (incubated in dark) containing CO_2 trap (0.5 N KOH)

Freshwater Biodegradation (ISO 14851)

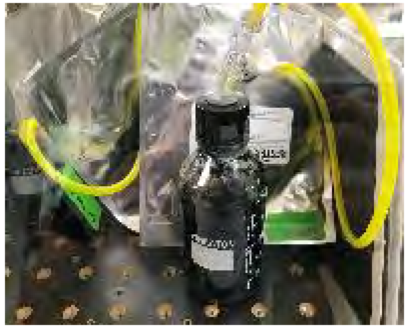
Samples placed in freshwater medium and % biodegradation tracked via dissolved oxygen over time





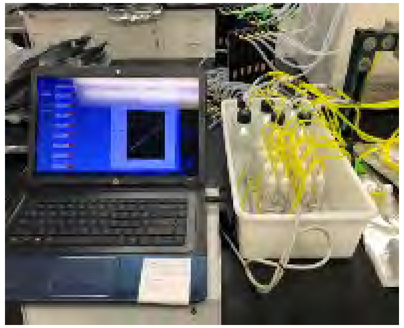
High Solids Anaerobic Biodegradation (ASTM D5511)

High solids (20%) inoculum degrades sample and gas produced is measured via GC and gas bag volume



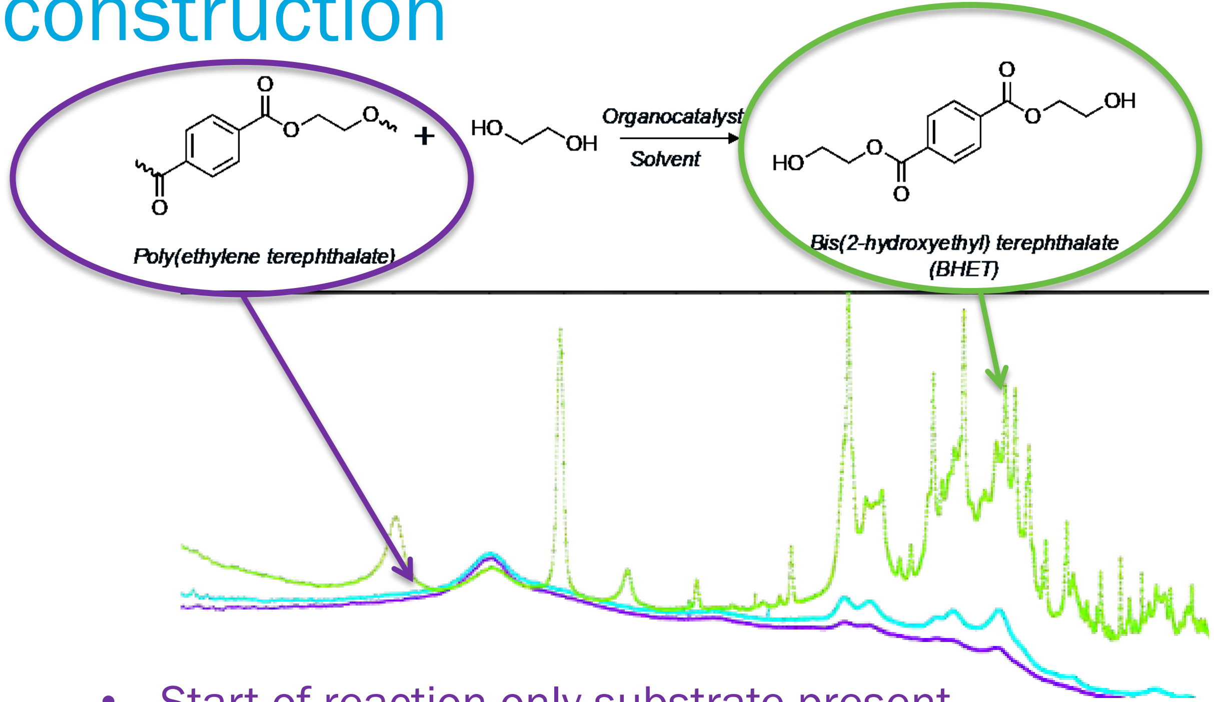
Composting Biodegradation (ASTM D5338)

Compost degrades samples and gas is measured via GC, gas bag volume, and/or on-line gas volume system

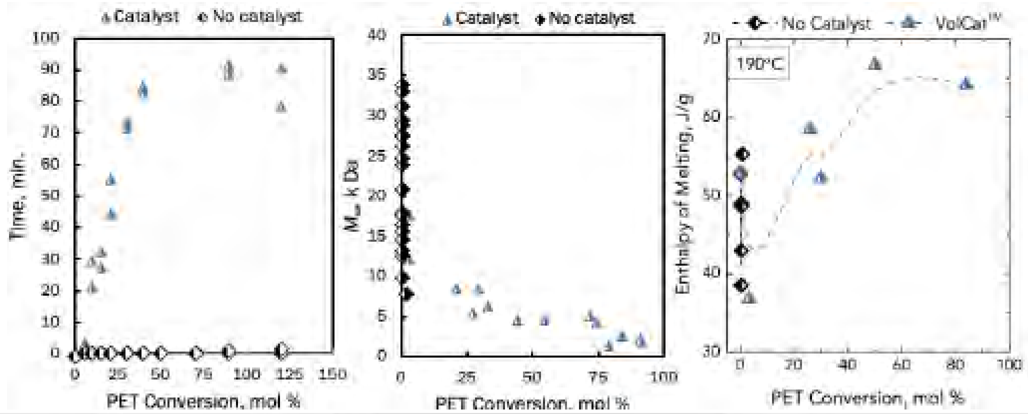


Ongoing characterization: PET Deconstruction

- Goal: Determine deconstruction mechanisms of homogeneous catalytic PET deconstruction
- Scope: Utilize *operando* scattering to follow the reaction kinetics, disentangle solvent effects, temperature, and catalyst on the evolution of the substrate
- Output: Reduced process intensity, optimized catalyst loading, increased selectivity to desired products, increased reactivity



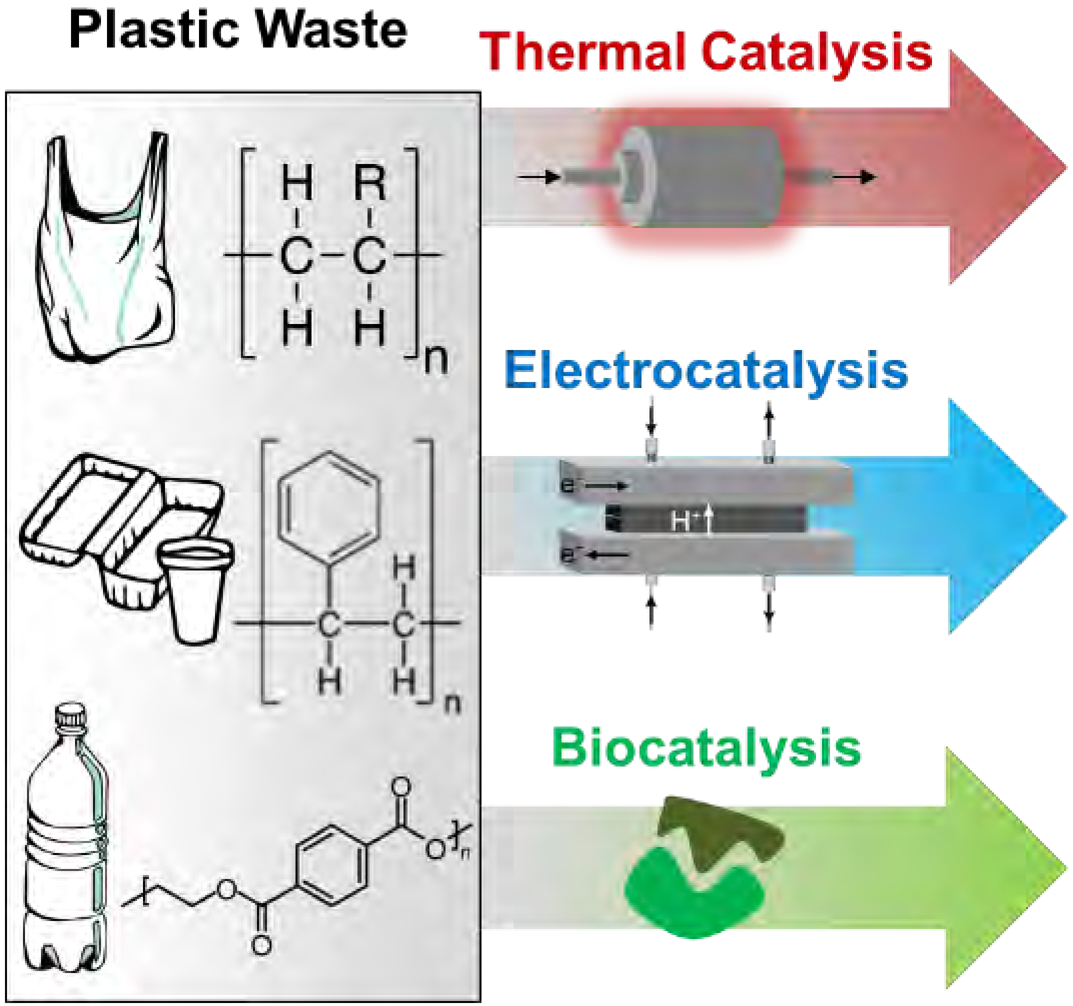
- Start of reaction only substrate present
- After 20 minutes the substrate recrystallizes
- After 40 minutes product crystallizes



Deconstruction

- C-C bond cleavage via alkane hydrogenolysis
- C-C bond cleavage via tandem chemistries
- Electrochemical oxidative C-C bond cleavage
- Enzymatic polymer deconstruction via two-enzyme systems
- Rapid assays for polyesterases
- HTP assays for enzymatic polyester deconstruction

Deconstruction scope

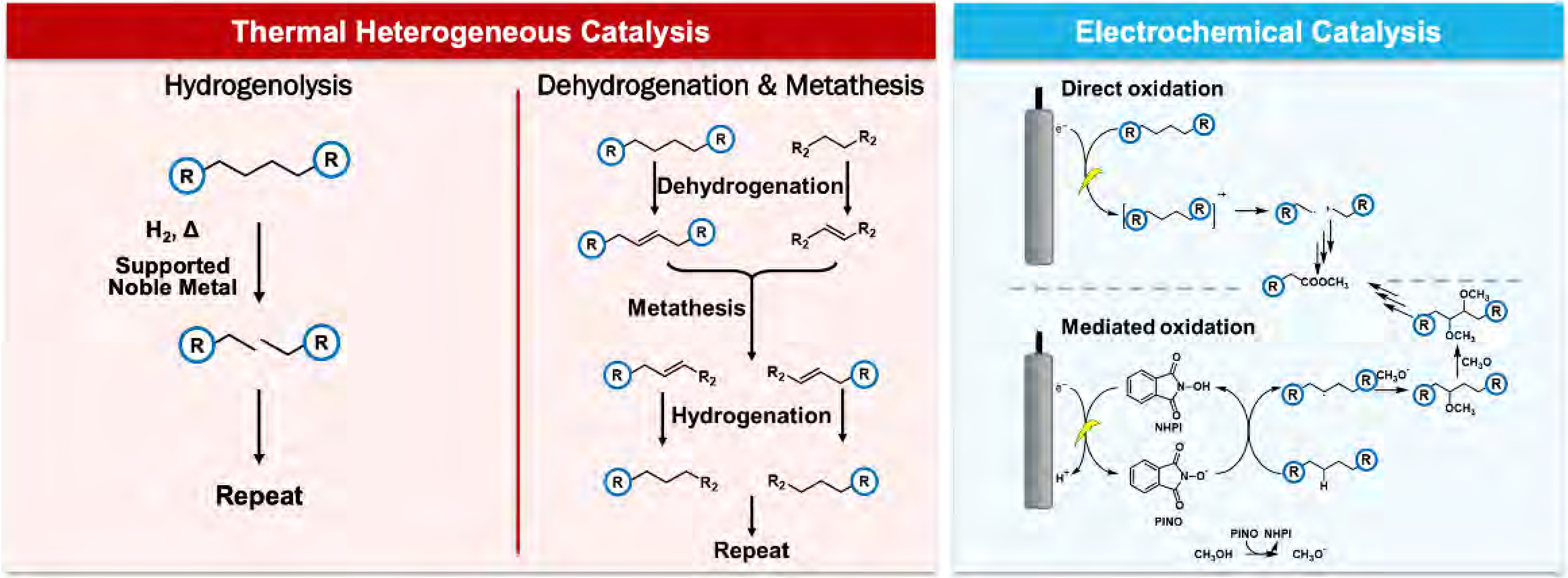


- C-C bond cleavage via alkane hydrogenolysis
- C-C bond cleavage via tandem chemistries

- Electrochemical oxidative C-C bond cleavage

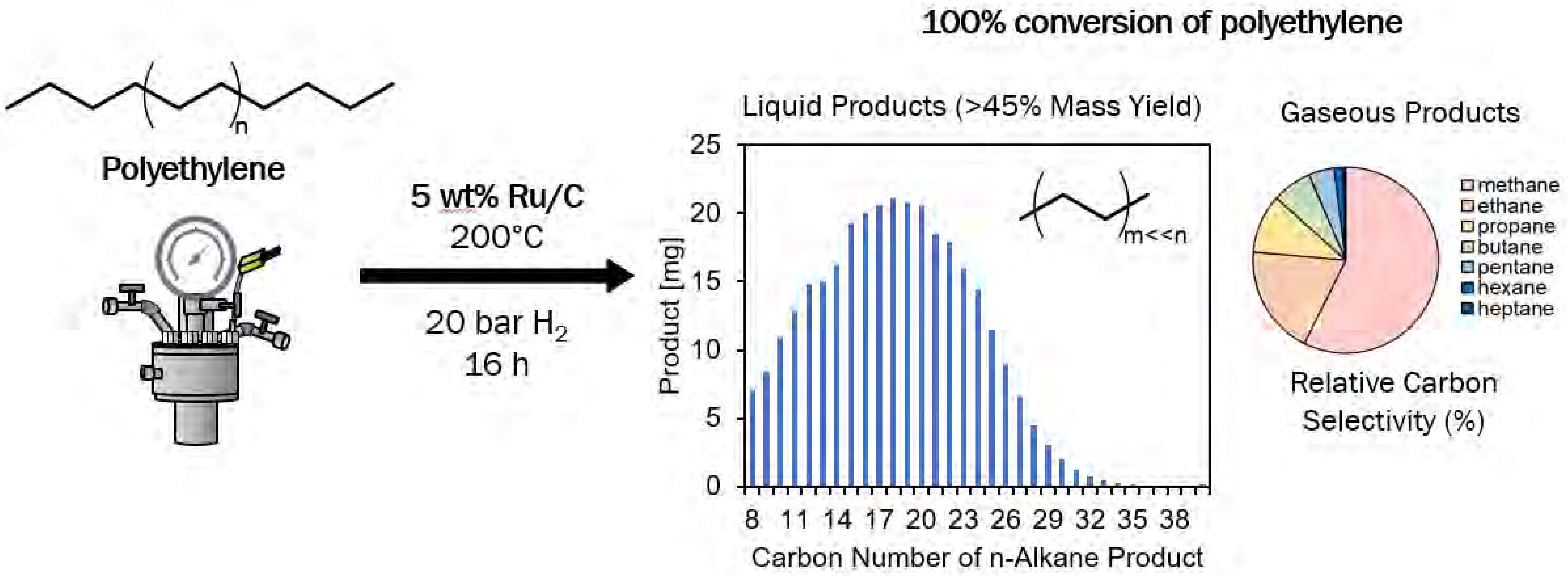
- Enzymatic deconstruction via two-enzyme systems
- Rapid assays for polyesterases
- HTP assays for enzymatic polyester deconstruction

C-C bond cleavage for plastics deconstruction



C-C bond cleavage is among the most important areas in deconstruction R&D that will require new catalysis innovation

Alkane hydrogenolysis of PE



5 wt% Ru/C effective for depolymerization of PE to liquid *n*-alkanes

- Demonstrates potential for alkane hydrogenolysis over supported metal catalysts
- No solvent needed – catalysis conducted in the melt phase
- Key upcycling challenge/future work is valorization of alkane products

JE Rorrer, GT Beckham, Y Román-Leshkov, *JACS Au* 2021

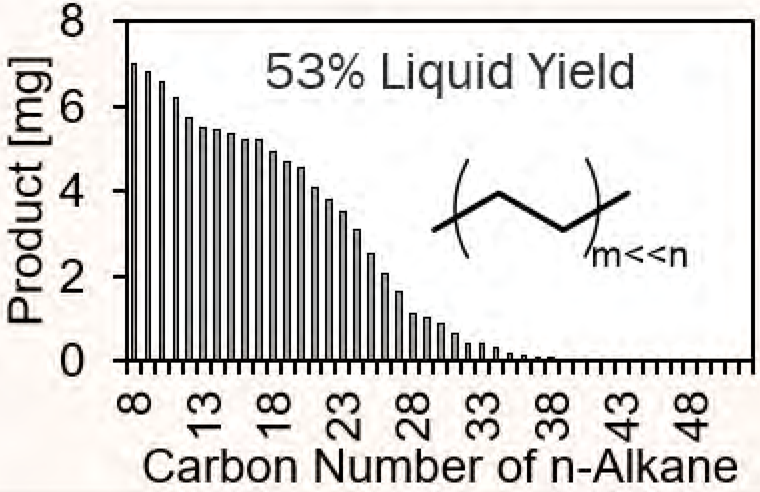
Post-consumer LDPE and PP hydrogenolysis

Post-Consumer LDPE Plastic Bottle

5wt% Ru/C

16 h

225°C, 22 bar H_2



Polypropylene (M_w ~340 kDa)

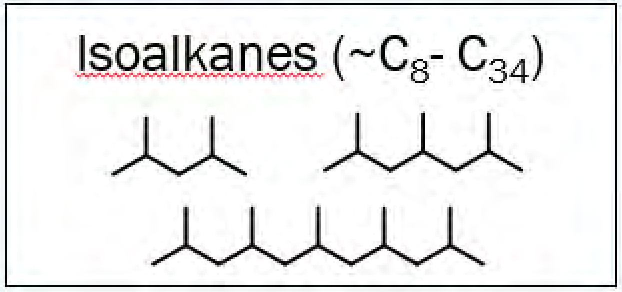
5wt% Ru/C

24 h

225°C, 50 bar H_2

100% Conversion

~64% Liquid Yield



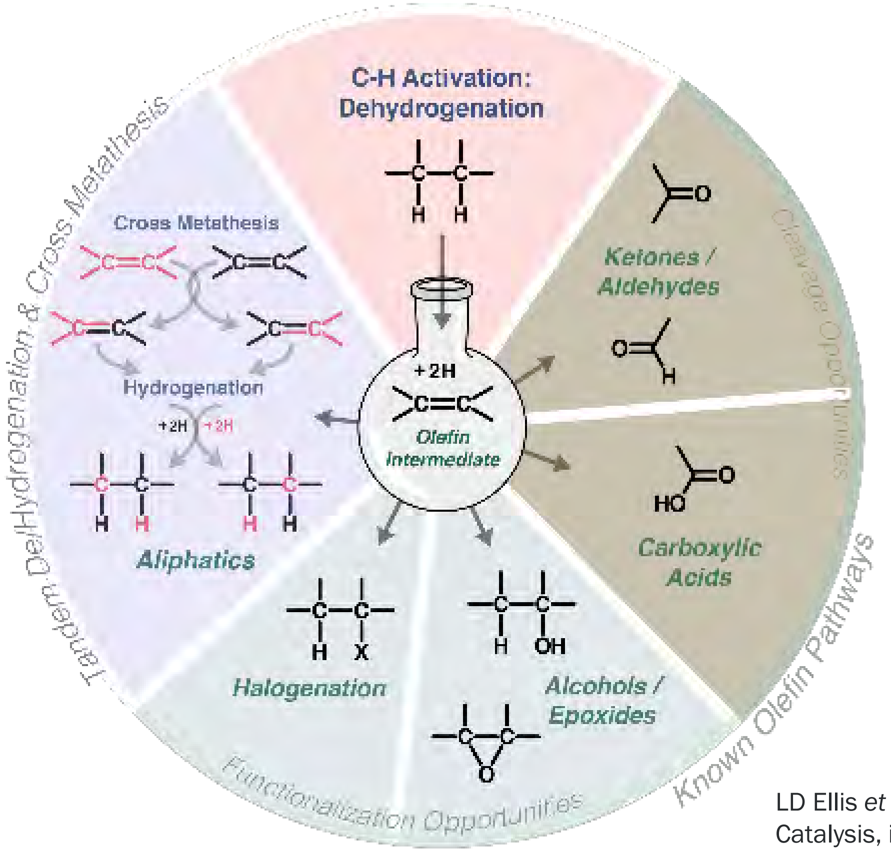
5 wt% Ru/C is also effective for depolymerization of LDPE and PP to liquid alkanes

JE Rorrer *et al.* in preparation

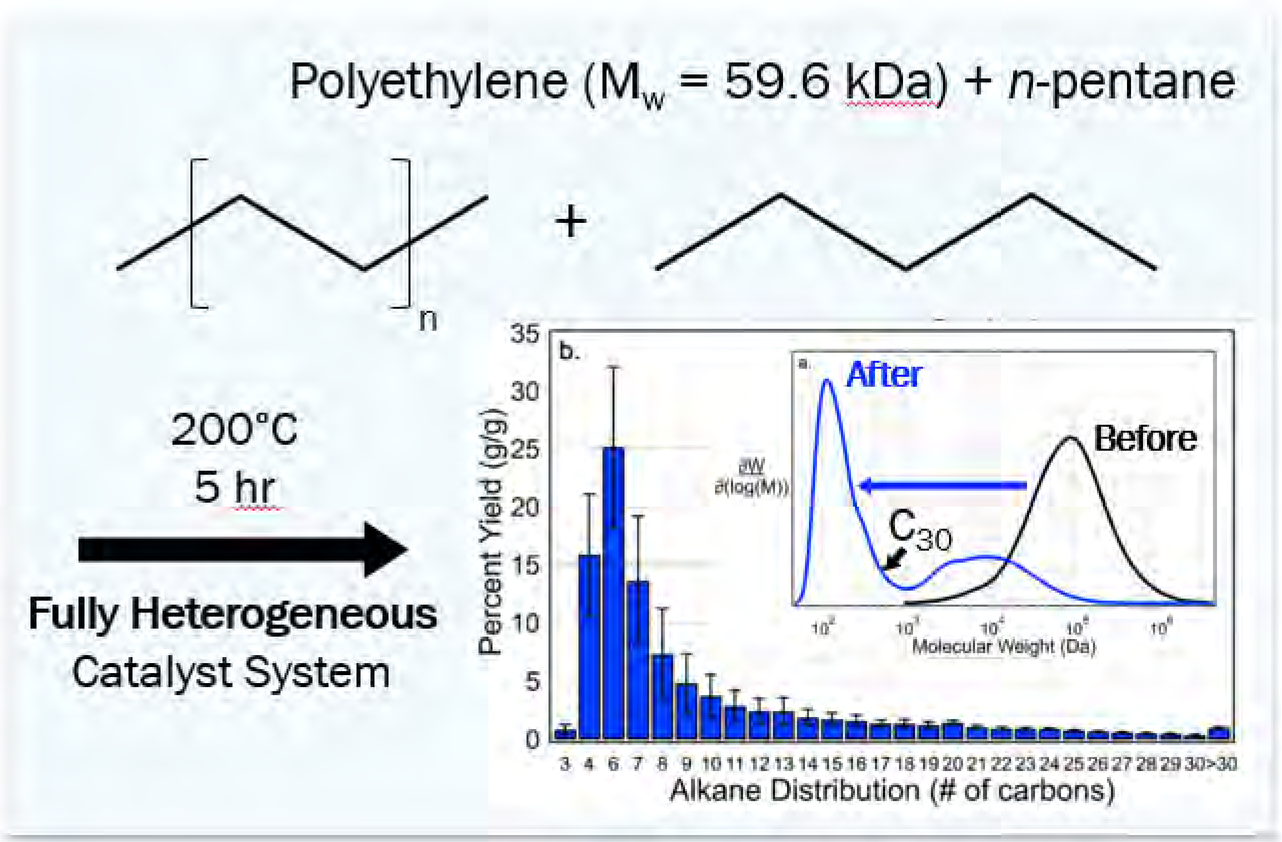
- Ongoing work examining PS, PET, and other materials, including mixtures
- Ongoing work with Analysis team to understand the potential of alkane hydrogenolysis

Olefin-intermediate processes for C-C cleavage

Olefin-intermediate processes offer multiple pathways for polyolefin deconstruction and upcycling



LD Ellis *et al.*, *Nature Catalysis*, in revision



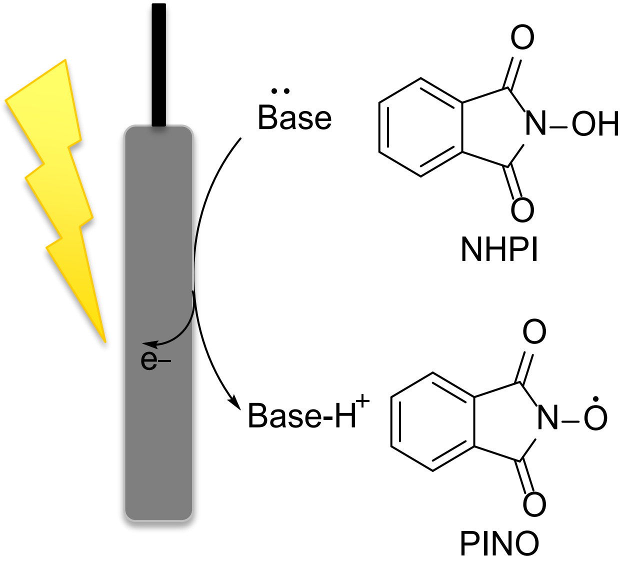
LD Ellis *et al.*, *ACS SusChemEng* 2021

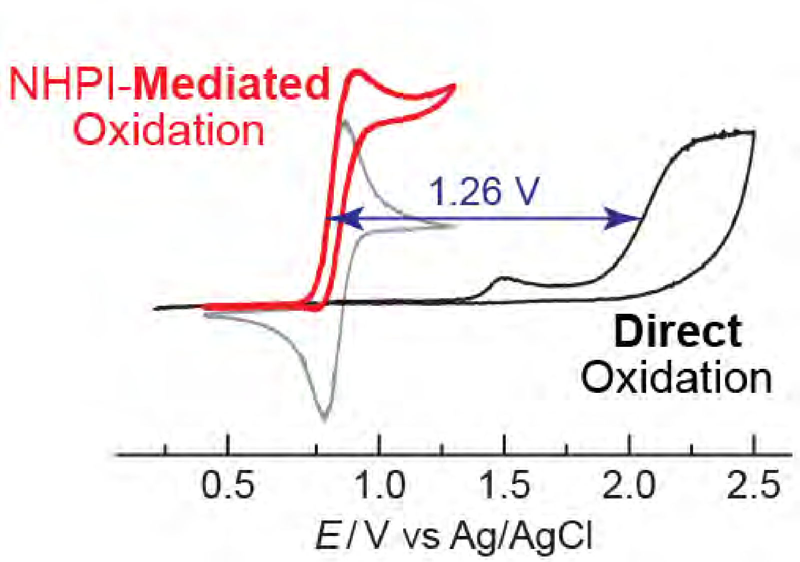
Baseline activities demonstrate potential for the olefin-intermediate process

- Ongoing work focused on upcycling of reaction products through additional chemistries and alternative solvents
- Additional ongoing work with the analysis team to understand the potential of olefin-intermediate processes

Electrochemical oxidative C-C bond cleavage

Goal: Develop a redox mediator system to oxidatively cleave C-C bonds at ***room temperature***

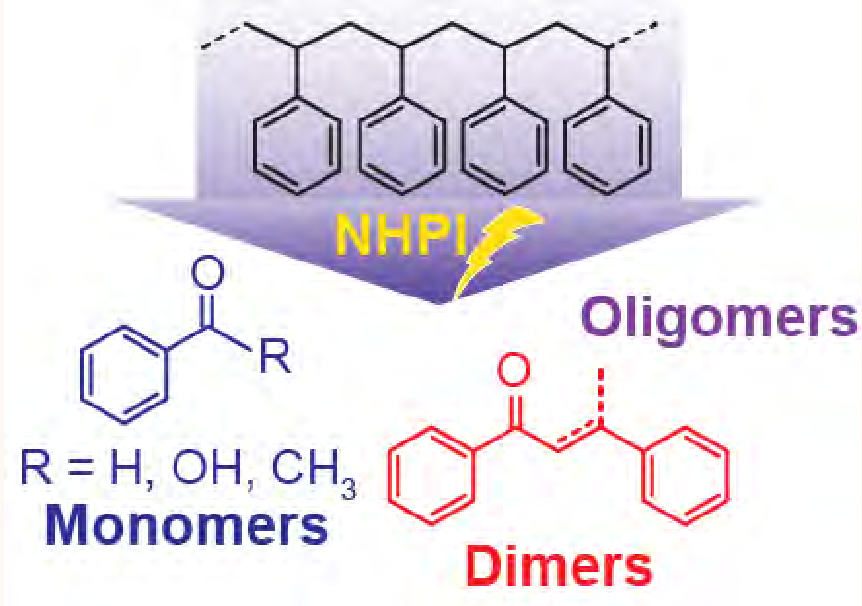




Outcome:

- Mediated oxidation reduces the driving force (oxidation potential) by 1.26 V
- Enabled C-C bond cleavage for model compounds (bibenzyl, 1,3-diphenylpropane, 1,4-diphenylbutane, and their derivatives)

Polystyrene (10,000 Da) can be completely deconstructed



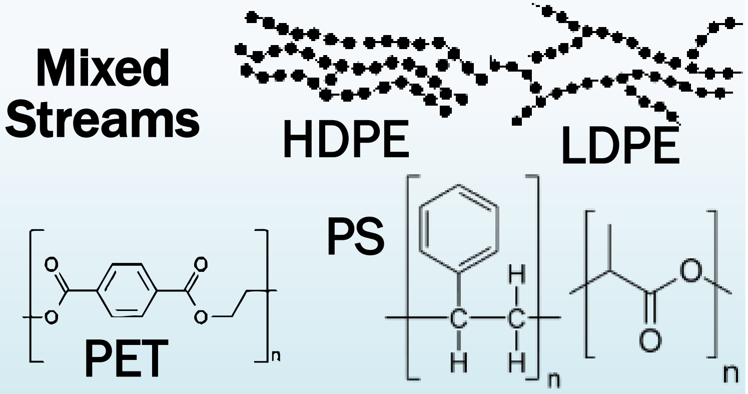
Mass yield = 7.5% 4.8%

Ongoing and future work in chemo-catalytic Deconstruction

C-C Cleavage Thermal Catalysis

Substrate Scope

Mixed Streams



Analysis

- What are realistic selectivity/activity/yield targets?

Additive Study

- Effect of common additives on Ru-catalyzed hydrogenolysis

Electrochemical C-C Bond Cleavage

Substrate Scope

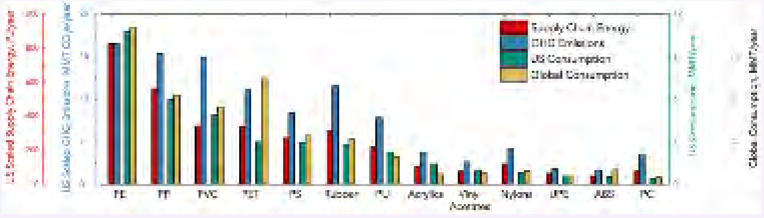
- Expand polymer substrates
- Stable mediators for e-chem
- Upcycling products into bio-compatible feeds or directly to high-value products

Characterization

- Characterization of PS products
- Decomposition mechanism of PINO
- Spectroscopy e.g. in situ EPR, UV-vis

Additional efforts

- Photocatalytic and thermal catalytic deconstruction of polyolefins via homogeneous catalysis
- Organocatalysis for C-O and C-N linked plastics (polyesters, polyamides, etc.)
- Expansion to other substrates guided by analysis efforts

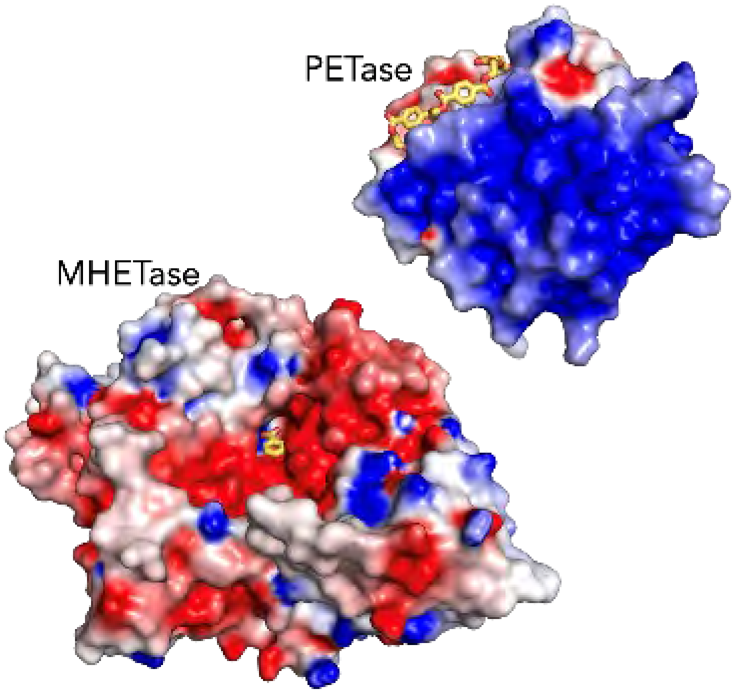


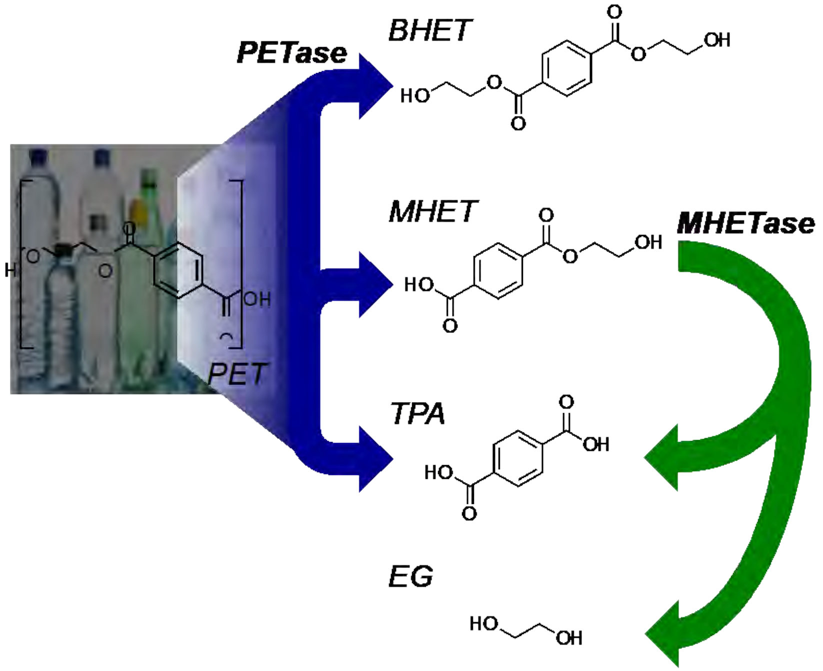
Enzymatic PET deconstruction

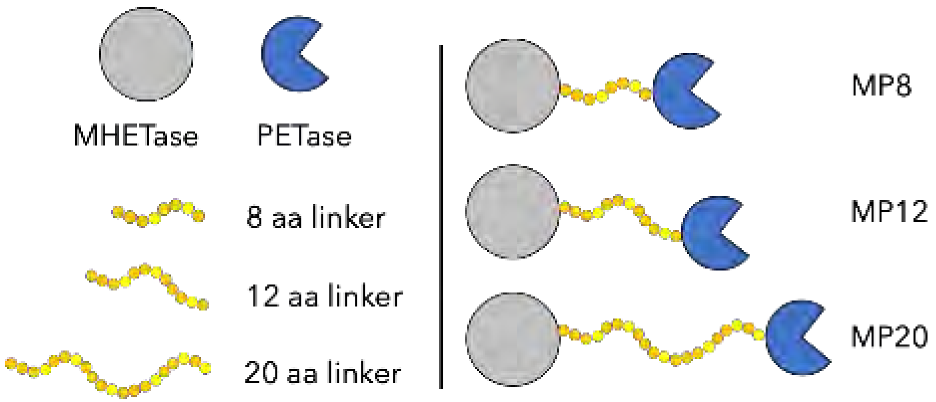
Goal: Understand multi-component enzyme systems for polyester deconstruction and engineer enzymes for accelerated PET deconstruction

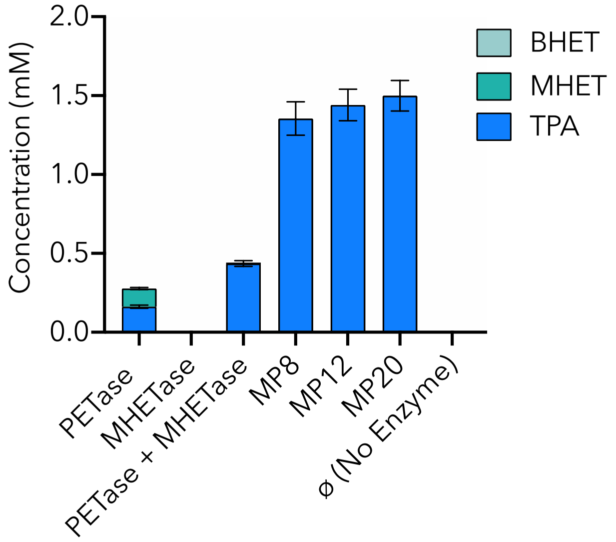
Scope: *Ideonella sakaiensis* PETase and MHETase enzymes[1]

Outcome: 6-fold higher activity when linking enzymes with tandem depolymerization functions[2]



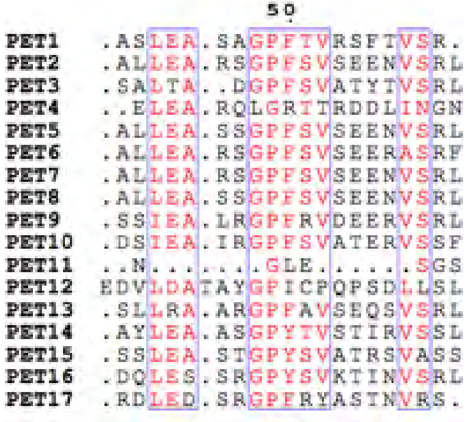


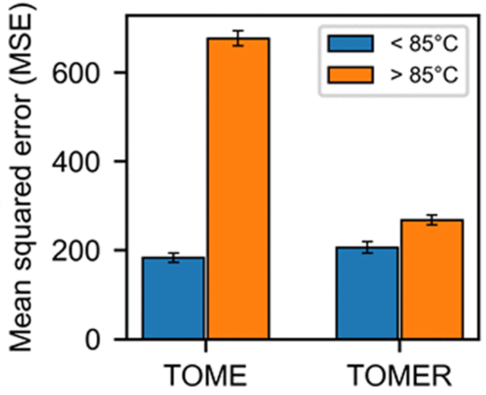


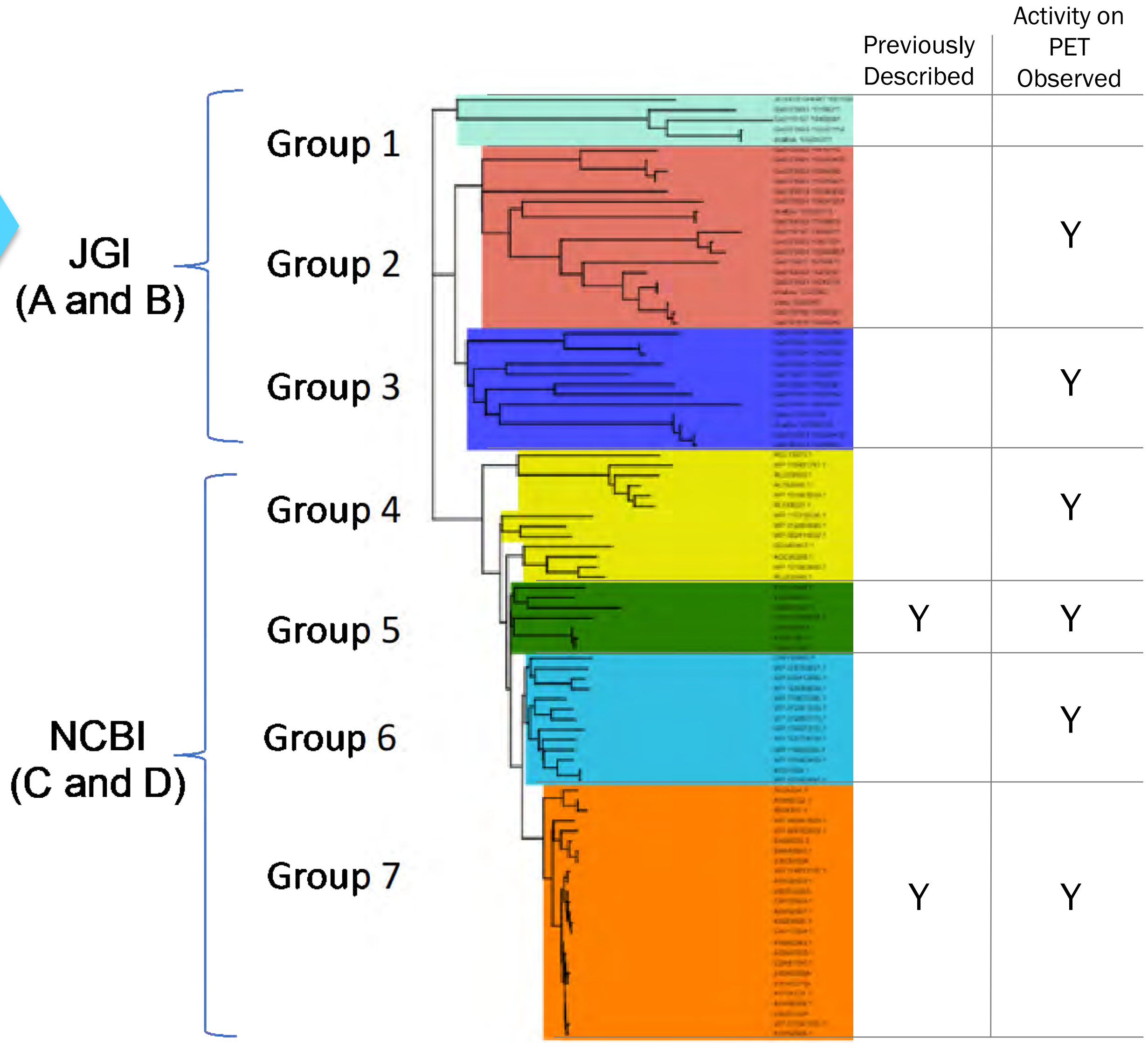


1. Yoshida *et al. Science* 2016
2. Knott, Erickson, Allen, Gado *et al. PNAS* 2020

Process concept for identification of diverse PET hydrolases







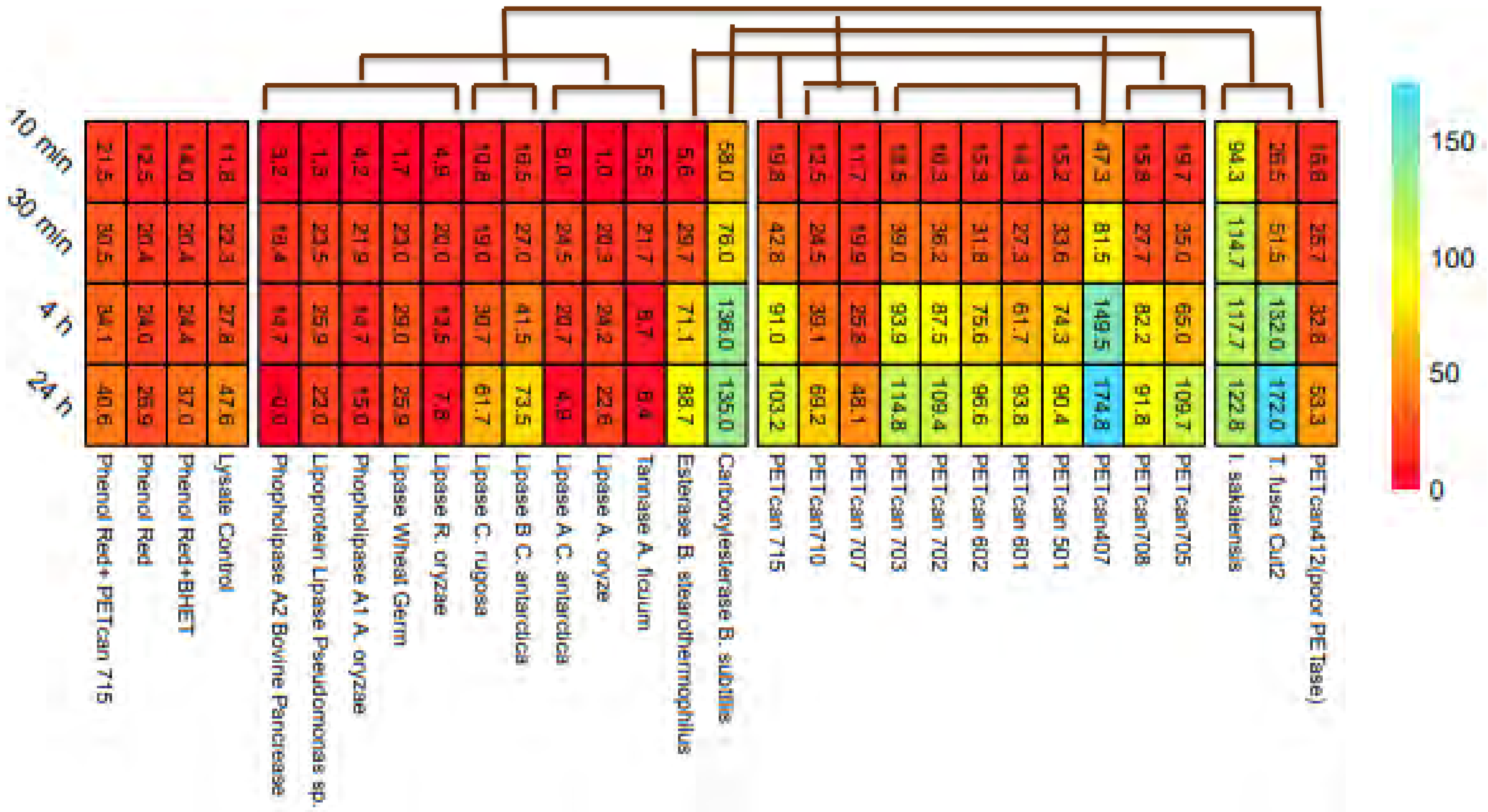
- Goal: Use known PET hydrolases to build a predictive model and explore natural diversity to identify additional candidates
- Method: Predict protein thermal stability using a machine learning strategy
- Ongoing: Identified thermotolerant candidates show a wide sequence diversity – previously reported PETases are only found in 2 of the clades
- Ongoing: Assay 74 candidates for activity on PET

TOMER algorithm from Gado, Beckham, Payne *J. Chem. Inform. Model.* 2020

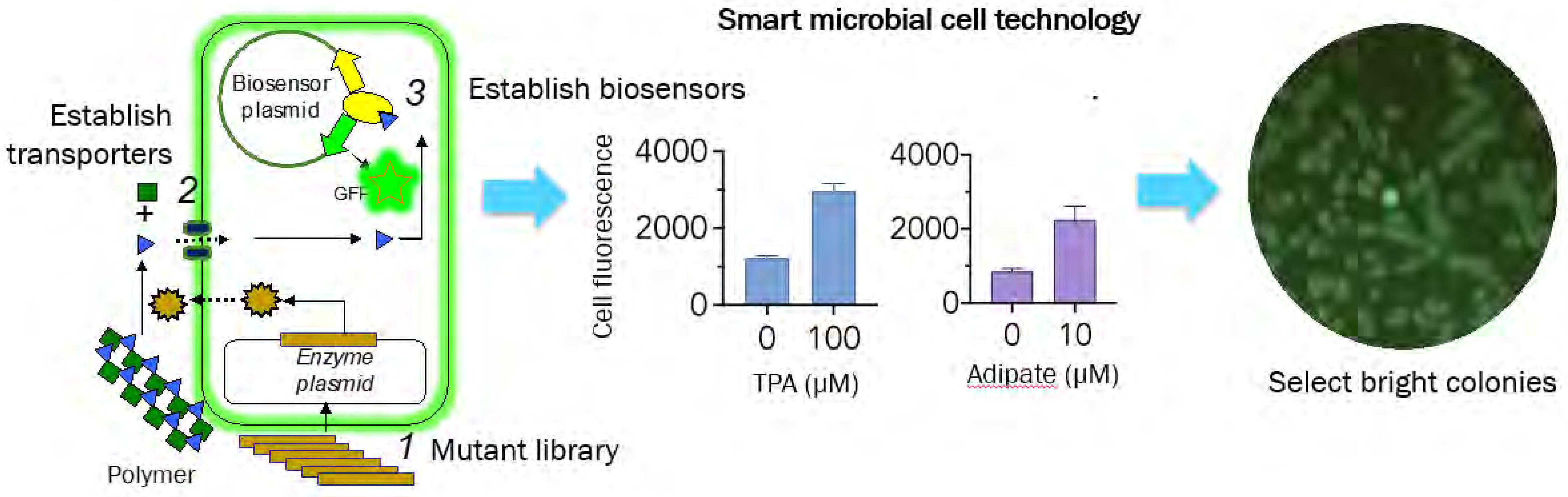
Developing rapid assays for polyesterases

- Goal: Develop flexible kinetic assay for binning candidate biocatalysts
- Method: Solution-phase, colorimetric, hydrolysis assay. Suitable for range of enzyme purities, substrates, and test conditions
- Outcome: A standardized enzyme assay with broad utility for polyesterase field – deploying to candidate PET hydrolases now

38 enzymes: 1 day reaction with BHET → 4 groups



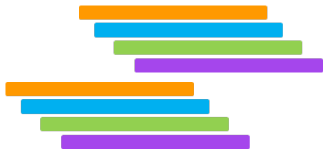
High throughput screening for polymer degradation



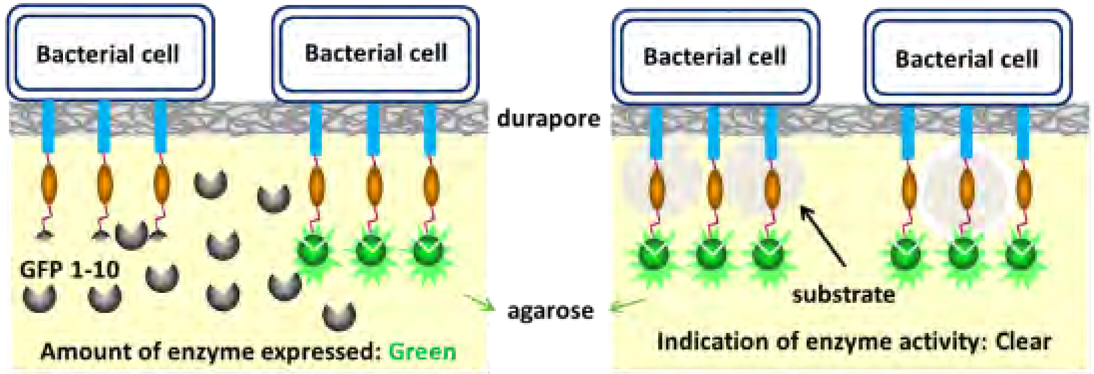
- Goal: Develop ultra-high throughput approaches for generating and screening mutant libraries
- Method #1: Custom biosensors used for rapid isolation of enzymes with increase degradation activity
- Outcome: Whole cell screening assays using fluorescent reporters permits a “one-tube” analysis of thousands (10s-100s) of enzyme variants in one experiment.

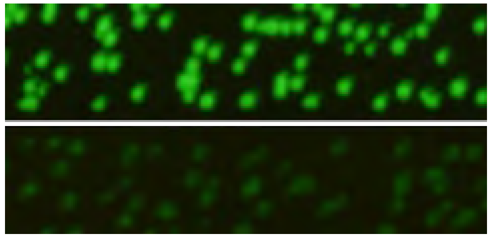
High throughput screening for polymer degradation

Mutant library



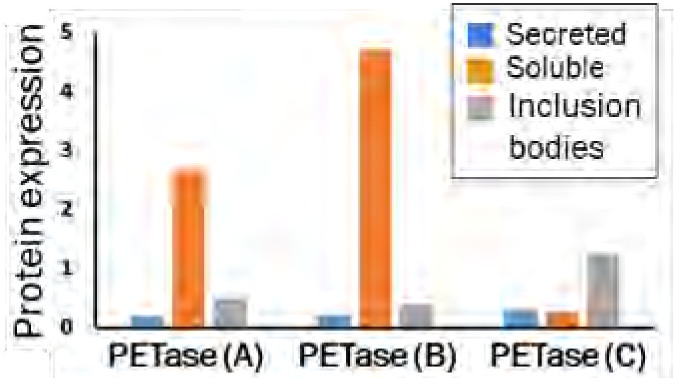
DNA shuffling

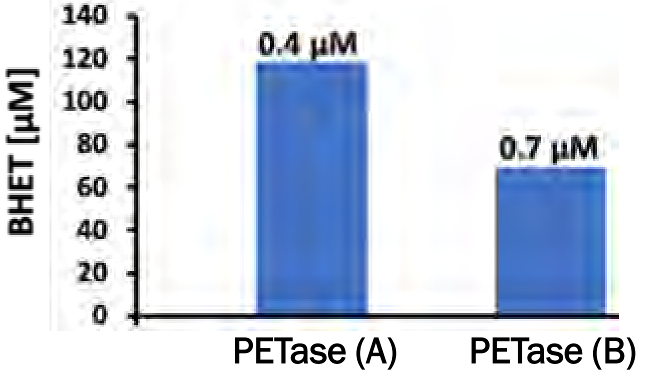




In vivo screening for improved expression, solubility, & activity

Enzyme characterization



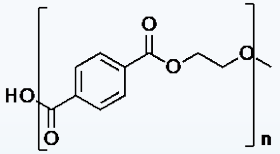


- Method #2: Use mutagenesis and directed evolution approaches to increase expression and solubility, as well as enzymatic activity
- Outcome: Suite of ultra-high throughput assays to accelerate identification of improved enzyme variants
- Ongoing: PETase and then move to enzymes for other polymers – Can also further improve thermostability

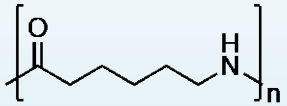
Ongoing and future work in biocatalytic Deconstruction

Substrate choice

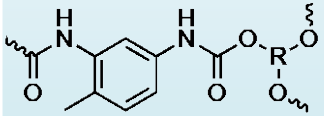
Model Substrates



PET
- PET powder
- BHET



PA
- Nylon 6



PU
- Flexible Foams

Realistic Substrates

- Films
- Textiles: clothing, carpets, fibers
- Foams, insulation
- Mixed streams

Enzyme identification & engineering

Computation

- Machine learning based algorithms for identifying new, naturally occurring, thermotolerant deconstruction enzymes
- Computational protein engineering (ROSETTA) for creating libraries of enzyme variants

Performance Improvement Targets

- Activity on highly crystalline polymers
- Stability (shelf-life), temperature tolerance, and solvent tolerance
- Tolerance to additives, dyes, and contaminants

Enzyme screening & characterization

High throughput screening

- HT (100s) to ultra-HT (1000s+) methods for screening activity of natural enzymes & mutant libraries
- New biosensors for degradation products of interest across polymers
- Transition to high-temperature assays

Advanced Characterization

- Imaging/microscopy for surface studies and interfacial catalysis
- Structural analyses:
  - X-ray crystallography
  - Cryo-EM
  - SAXS

Upcycling

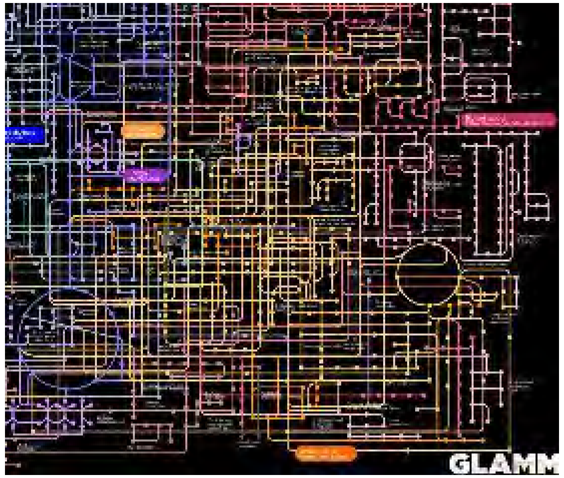
- Biological PET upcycling
- Identification of new metabolic pathways for plastics upcycling
- Consolidated Bioprocessing of PET

Upcycling Scope

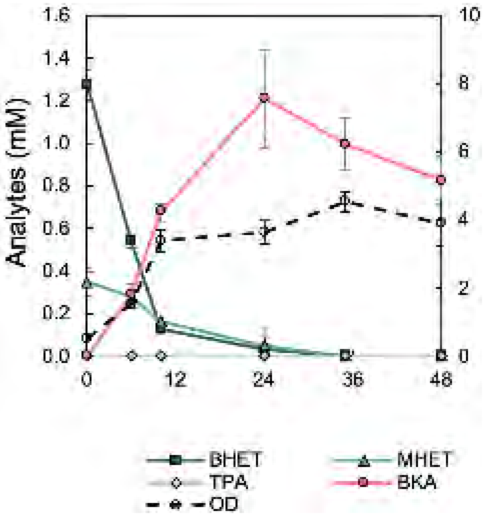
Three complementary upcycling scopes:

- Pathway discovery integrates with Deconstruction and allows us to identify novel metabolic pathways for microbial consumption of plastic deconstruction products
- Metabolic engineering allows us to biologically synthesize monomers for “recyclable-by-design” polymers
- Chemical upcycling provides a complement to biological routes by targeting applications directly

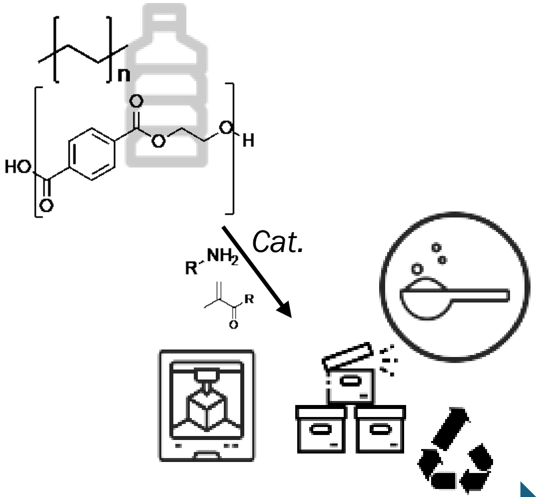
Metabolic pathways



Bioproduction



Chemical Upcycling



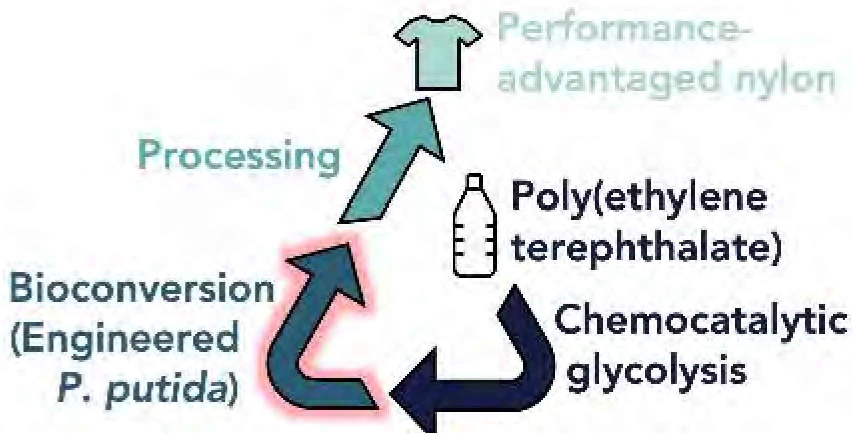
Conversion of incumbent plastics ⟷ Production of new building blocks and products

Biological PET upcycling

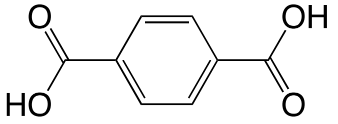
Goal: Enable PET upcycling to β-ketoadipate, a precursor to a performance-advantaged nylon-6,6[1]

Method: Metabolically engineer *Pseudomonas putida* for:

1) Catabolism of the BHET, the PET monomer released by chemocatalytic glycolysis
2) Bioconversion of depolymerized PET to β-ketoadipate



Outcome 1: TPA catabolism by engineered *P. putida*



terephthalic acid (TPA)

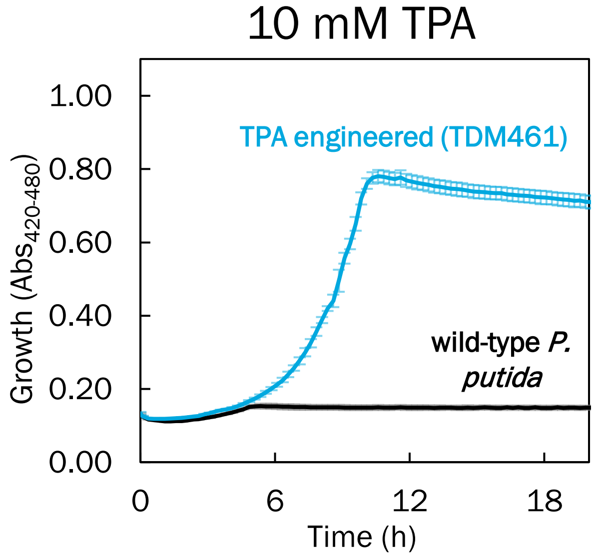
↓ $TpaK_{RHA1}$

↓ $TphA_{E6}$

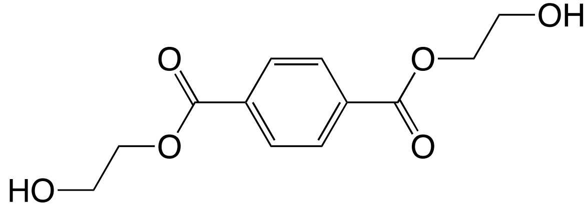
↓ $TphB_{E6}$

⇣

growth



Outcome 2: BHET catabolism by engineered *P. putida*



bis(2-hydroxyethyl)TPA (BHET)

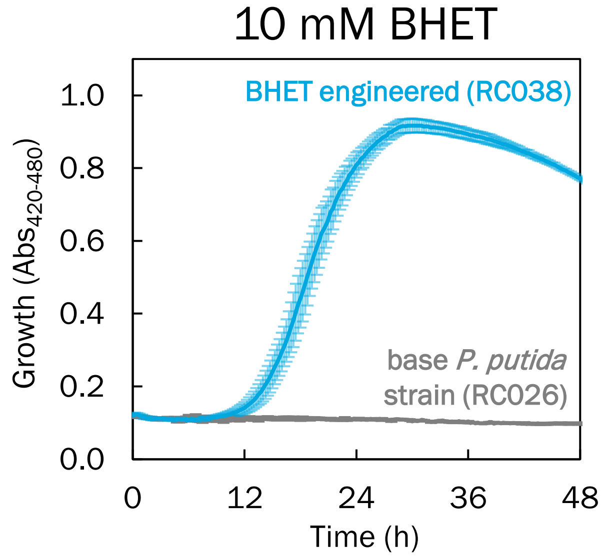
↓ $PETase_{Is}$

↓ $MHETase_{Is}$

TPA

⇣

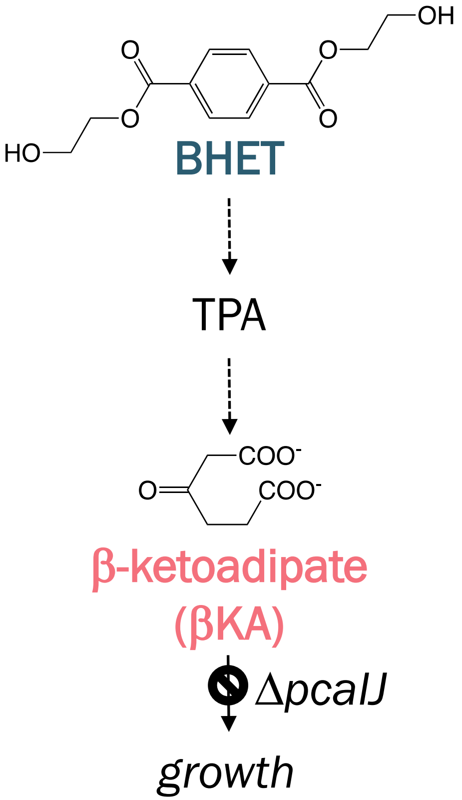
growth

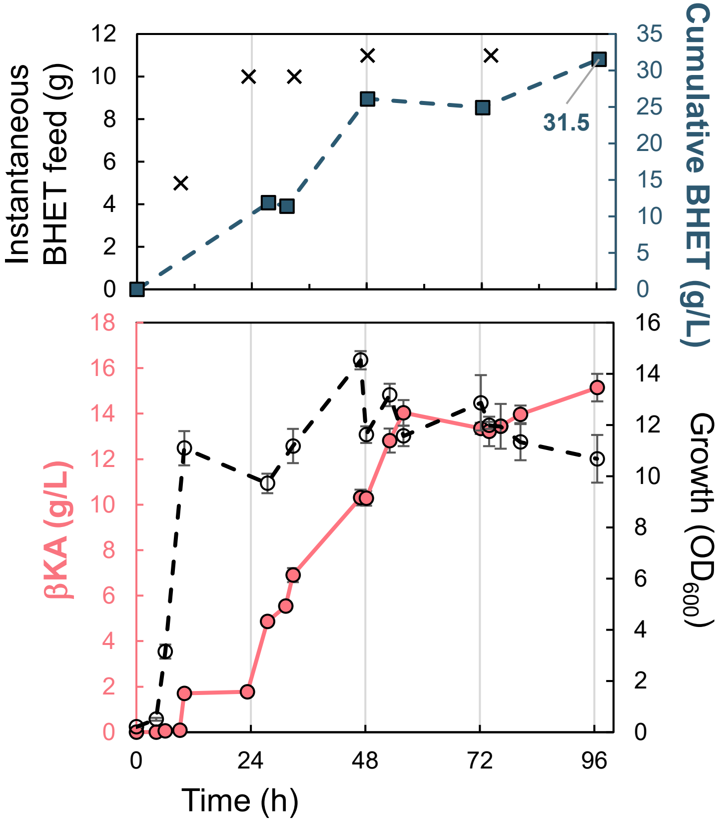


1. CW Johnson *et al. Joule* 2019
2. AZ Werner et al., *in review* 2021

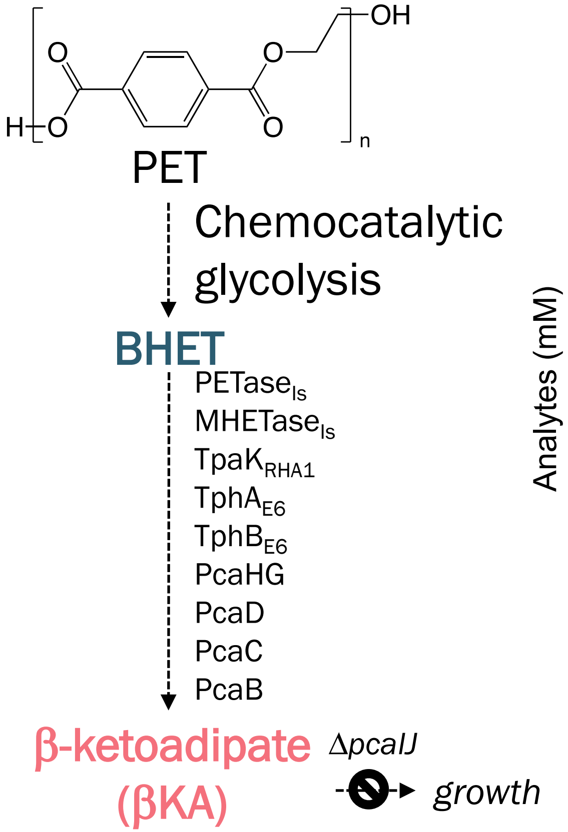
Tandem chemical and biological PET upcycling

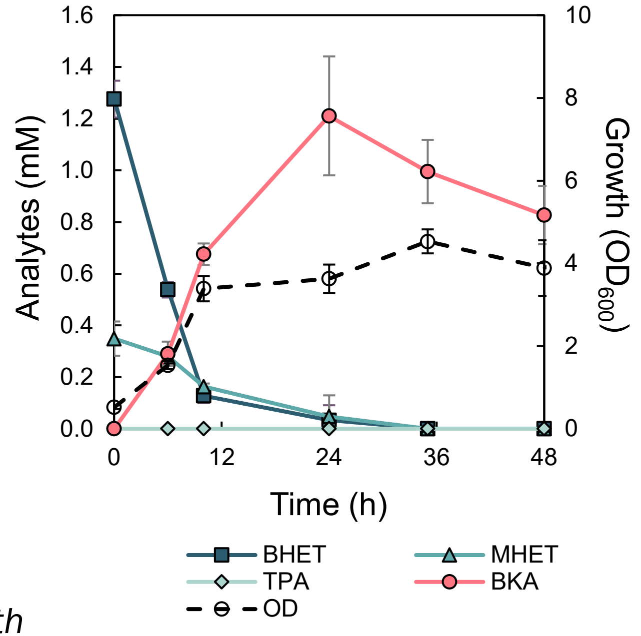
Outcome 3: Production of 15.1 g/L βKA from BHET at 76% (mol/mol) and 0.16 g/L/h





Outcome 4: Proof-of-concept demonstration of βKA production from crude PET glycolysis product

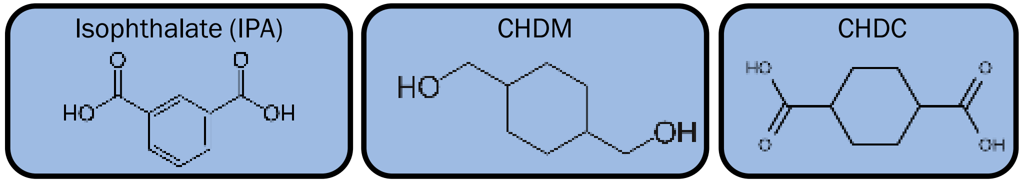




Future work: improve titer, rate, yield (TRY) and interface between deconstruction & bio-upcycling

Discovery of metabolic pathways for deconstruction products

PET co-monomers



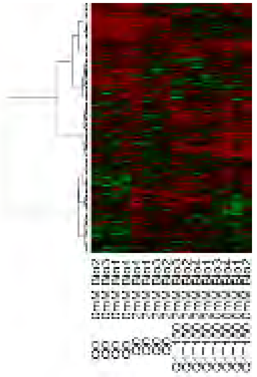
Environmental sources

Enrichment

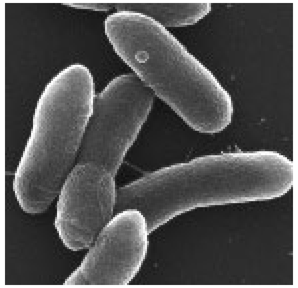
Isolation

Genome sequencing

Systems biology for pathway discovery



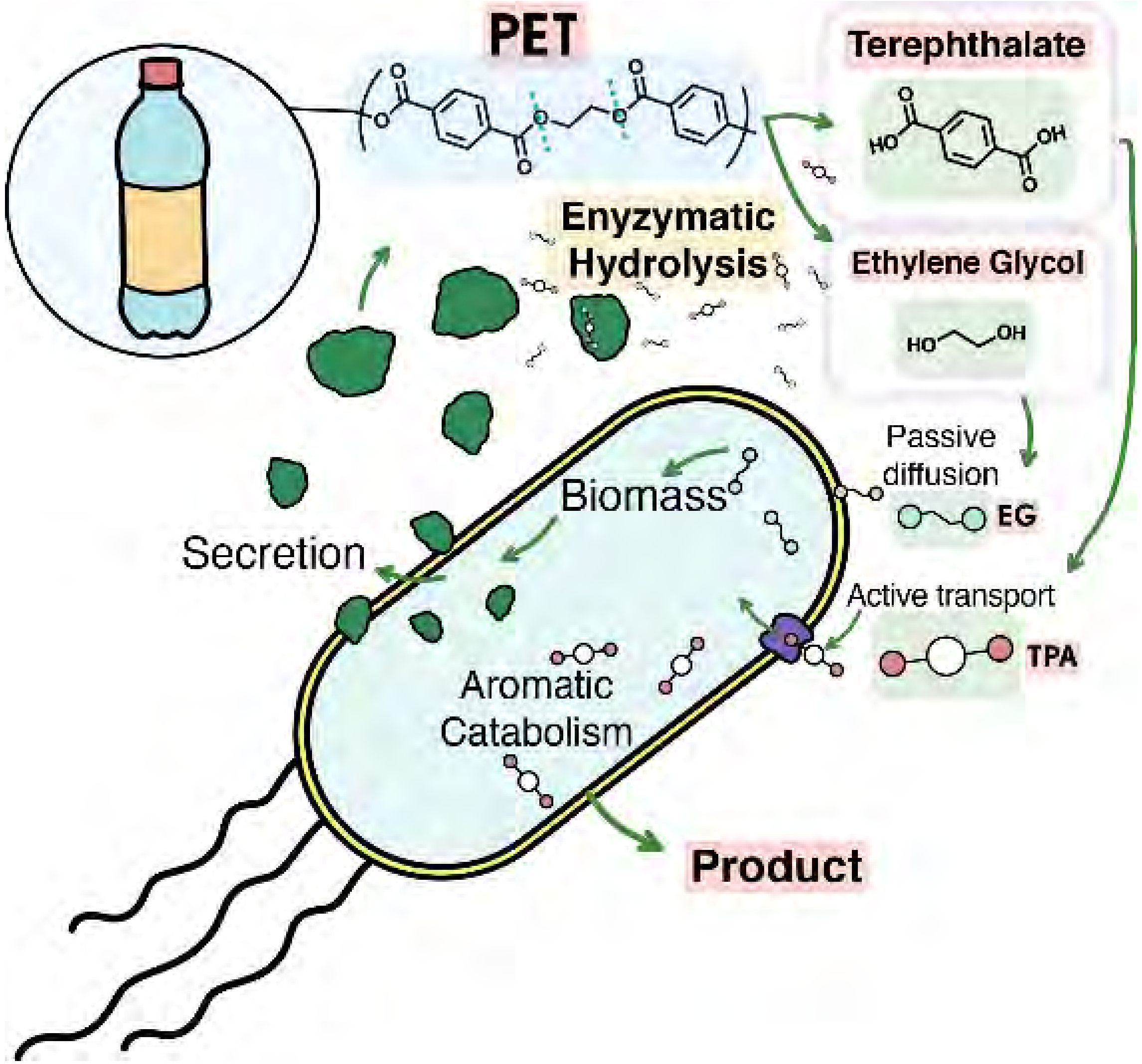
Engineer *P. putida*



- Goal: Identify novel isolates that grow on plastic deconstruction products (for example IPA, CHDM, and CHDC) and elucidate corresponding metabolic pathways
- Methods: Systems biology to identify the responsible genes and pathways
- Ongoing: Discovery of the suite of genes needed for growth on target substrate
- Future work: Move pathways into *P. putida* to “expand the funnel” of substrates that can be consumed for conversion of commercial PET, other plastics

PET-CBP: Deconstruction and bioconversion near the T_g

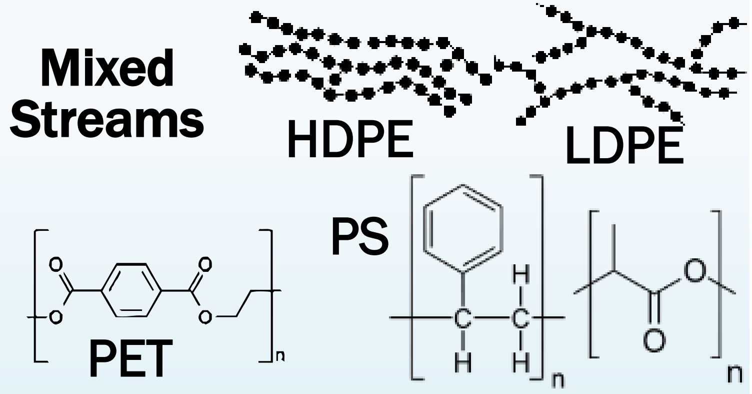
- Goal: Develop high temperature bioconversion approaches for consolidated deconstruction and bioconversion of PET near the T_g , where enzymatic PET deconstruction greatly improves
- Methods: Isolating organisms and pathways that function at higher temperatures
- Outcome #1: Isolated organisms that grows on EG at 65˚C and sequenced corresponding genomes
- Outcome #2: Isolated organism that grow on TPA at 55˚C and identified corresponding pathway genes
- Future directions: Develop genetic tools for thermophilic EG-degrader and engineer it for consolidated bioprocessing (CBP) of PET



Ongoing and future work in Upcycling

Expanded substrate bioconversion

P. putida



- Metabolic engineering for conversion of mixed, deconstructed feedstocks

High temperature

- Engineered organisms for simultaneous deconstruction and upcycling

New products

Monomers

- Making building blocks for the next generation of “recyclable-by-design” polymers
- Focus on enhancing titer, rate, yield

Oligomers

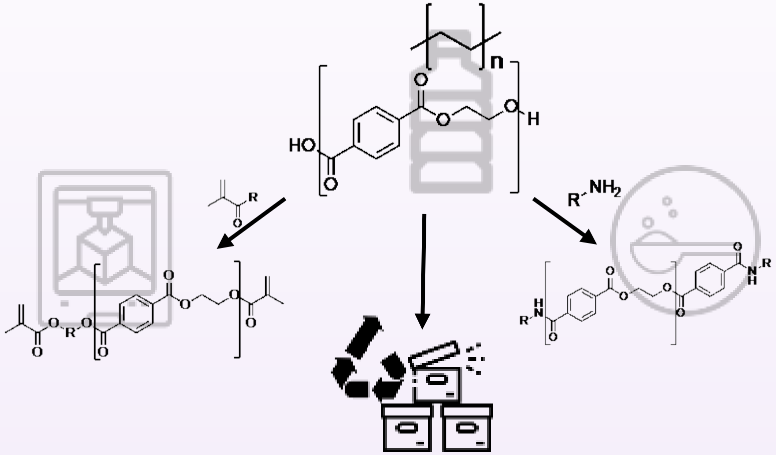
- Functional oligomers for block copolymer applications (e.g., telechelics)
- Use of glycolysis products in high value applications (e.g., FRPs, PUs, etc.)

Biosensors

- Enhanced tools can accelerate bioengineering efforts

Chemical upcycling

- PET to 3D Printing Resin
- Aminolysis of polyesters to polymer additives
- Oxidative processes to yield long chain carboxylates for polyamide/polyester applications



Redesign and Modeling

- Prediction of recyclable-by-design polymers
- Designer PHAs
- Acrylic plastics
- Crystalline, high-performance RBD circular polymers
- HCT/LCT hybrid polymers

Redesign Scope – Recyclable-by-Design (RBD) Circular Polymers (CPs)

- ## RBD-CP project goal

  The Redesign task will create tomorrow's plastics to be RBD, economically viable, energy efficient, and derived from bio-based sources and today's plastics, and processes to recycle redesigned materials.

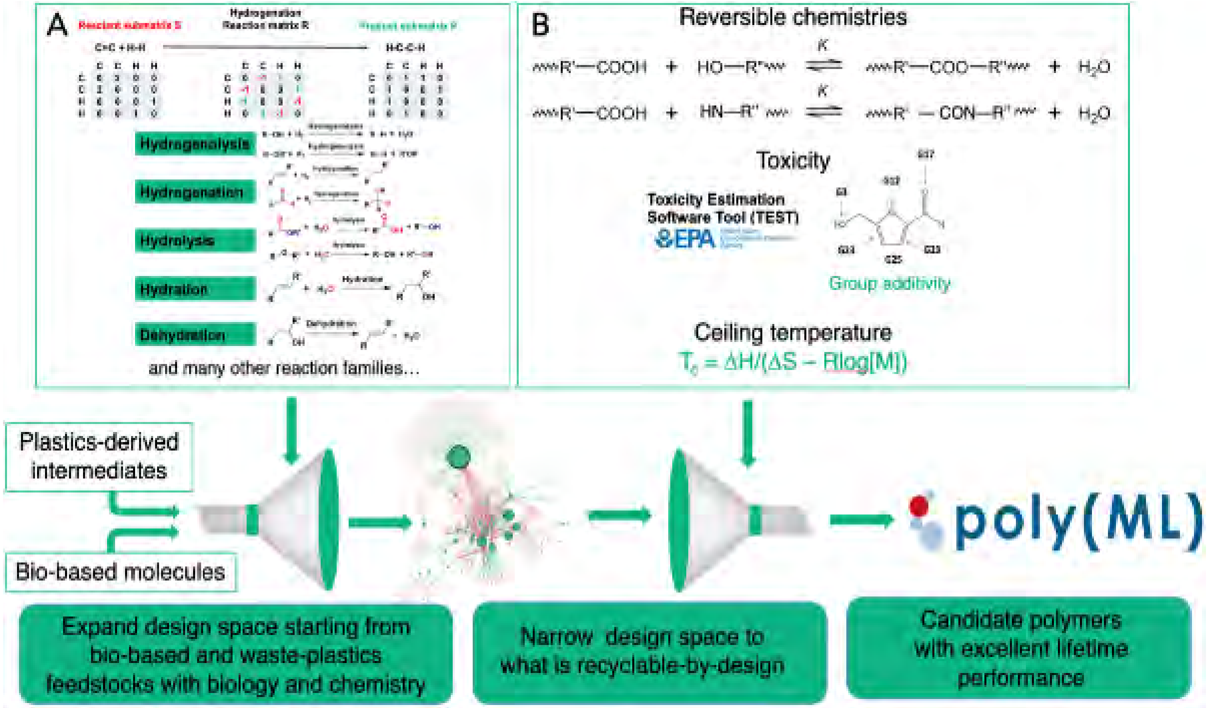
- ## Scopes of RBD-CPs

  - Expanding training database to improve domain of validity for RBD-CPs and develop new polymer chemistries and structures for RBD-CPs and their performance
  - Designer high-performance biodegradable polyhydroxyalkanoates (PHAs)
  - Crystalline high-performance RBD-CPs with intrinsic crystallinity and chemical recyclability
  - Acrylic bioplastics with low ceiling temperature (LCT)-enabled chemical recyclability
  - HCT/LCT hybrid monomer design for CPs that can unify conflicting properties

- ## Approaches

  Establishing CP design principles and high-throughput computational pipelines for selecting RBD monomer structures, identifying polymerization conditions, and predicting polymer properties.

Predicting RBD polymers



Overall goal:

- Deliver a computational pipeline to predict RBD polymers with target thermal and mechanical properties

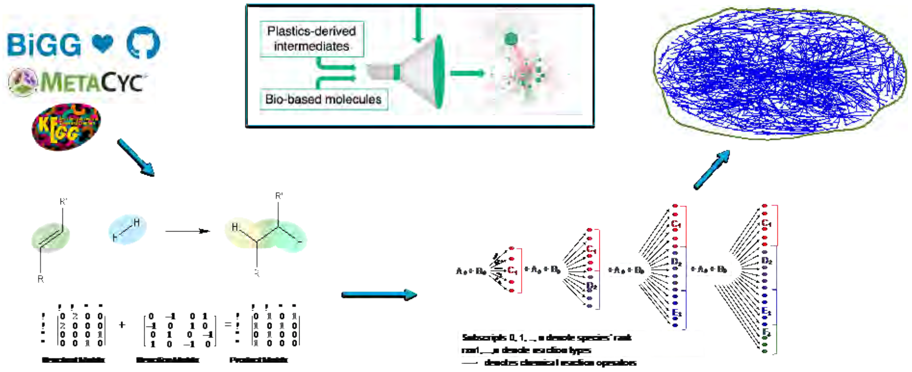
Specific goals:

- Build a library of millions of accessible bio/waste plastics-derived monomers
- Apply cheminformatics to build polymers *in silico*
- Use DFT to predict ceiling temperature (T_c)
- Use PolyML to predict mechanical and thermal properties

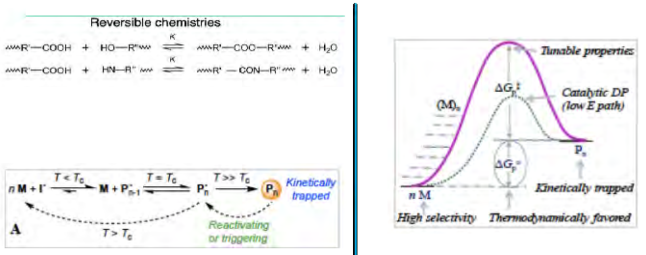
Impact:

- Narrow design space from 10^6 potential polymers that we *could* make to 10^1 polymers that we *should* make

Generation of monomers



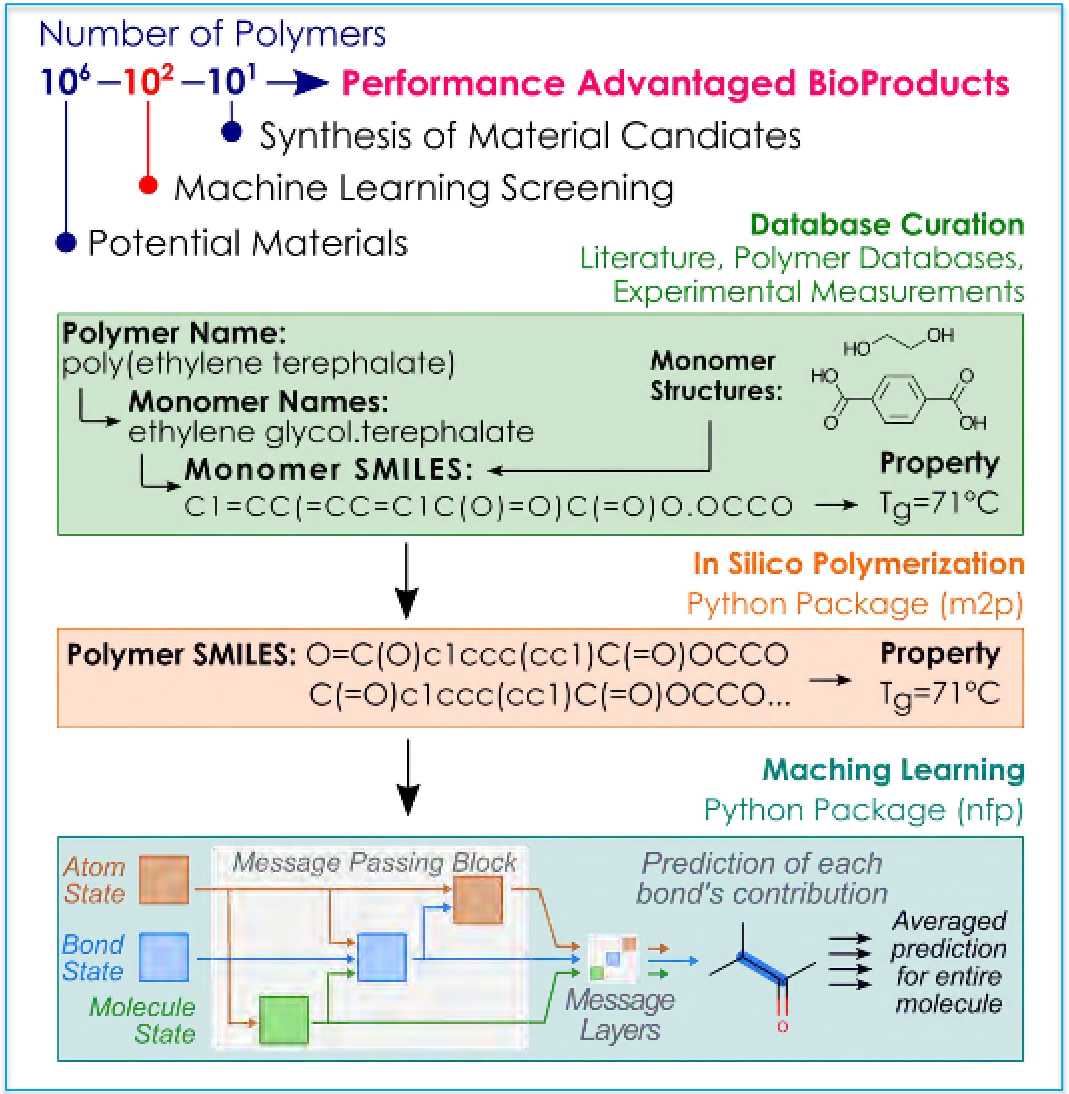
Screening of monomers



$T_c = \Delta H_p/(\Delta S_p - R\log[M])$

PolyML for materials design

Poly(ML)



Overall goal:

Use high throughput ML methods to down select material candidates based on predicted performance

Specific goals:

- High fidelity structural generation
- End-to-end learning (graph neural nets)

Impact:

- Explore vast material design space and avoid inefficient Edisonian approach

Prediction Rate	10^2 predictions s^{-1}
Properties	T_g, T_M, ρ, E, $P_{M\text{-}O2}$, $P_{M\text{-}N2}$, $P_{M\text{-}CO2}$, $P_{M\text{-}H2O}$
Polymer Classes	Olefins, Acrylates, Esters, Amides, Carbonates, Imides

PolyML+BOTTLE

Poly(ML)+

Goal:

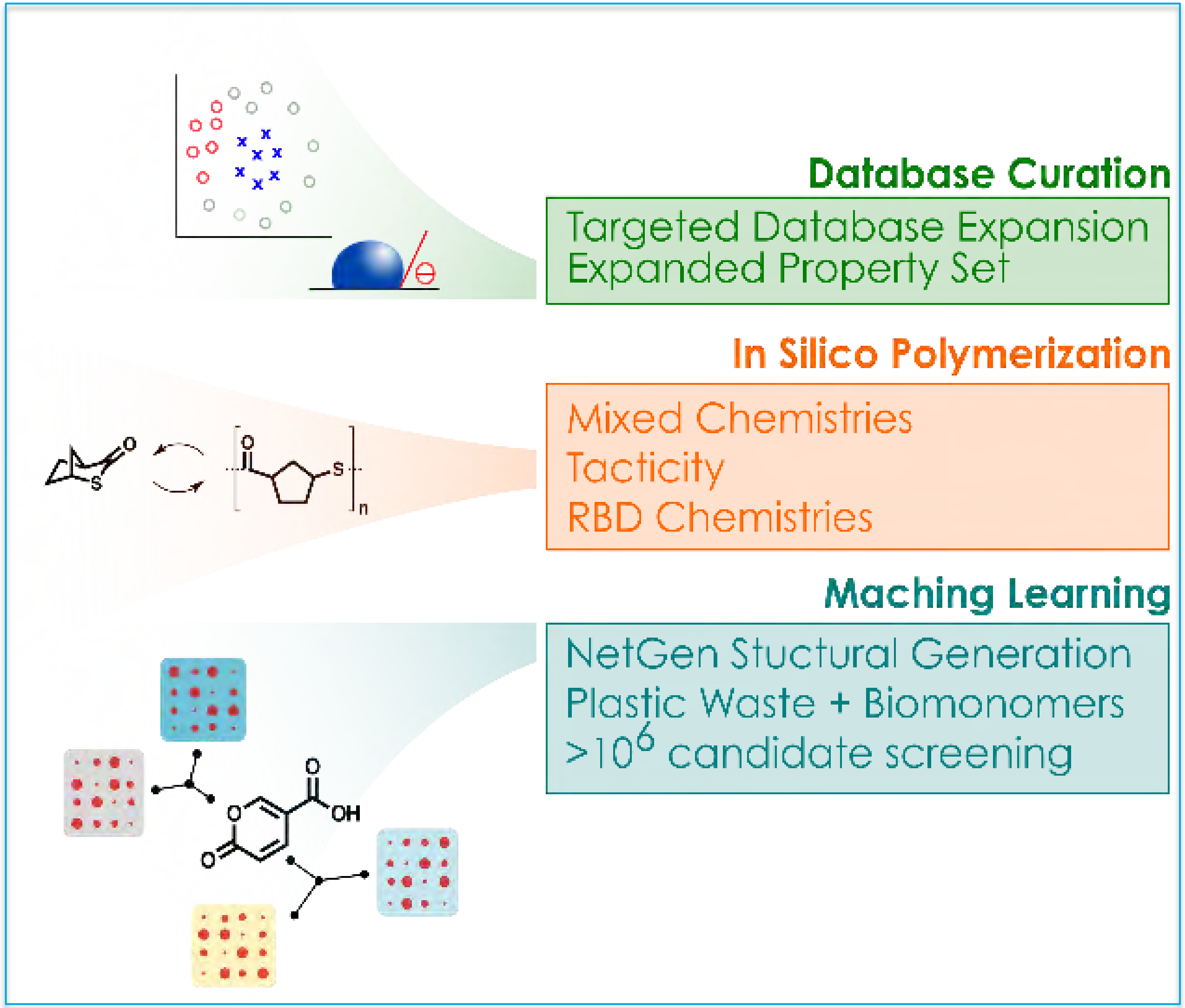
- Expansion of polyML for RBD polymers

Scope:

- Training database to be expanded to improve domain of validity for RBD polymers
- New polymer chemistries (*e.g.*, vitrimer linkages) and structures (*e.g.*, tacticity) for RBD and performance

Future directions:

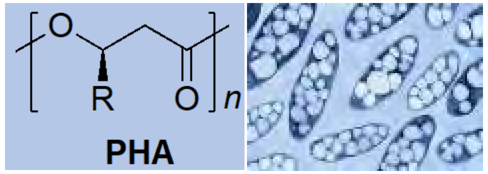
- HTP prediction, screening, and feedback between experiment and computation with incorporation of pathway generation tools



Designer PHAs: platform for HP biodegradable polymers

Features

- Natural polymers (>150 structures) by bacteria or other microbes
- Biorenewable carbon and energy storage material
- The best end-of-life option for biodegradable plastics

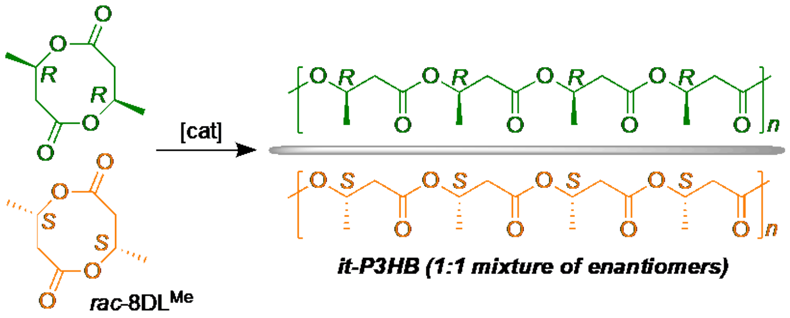


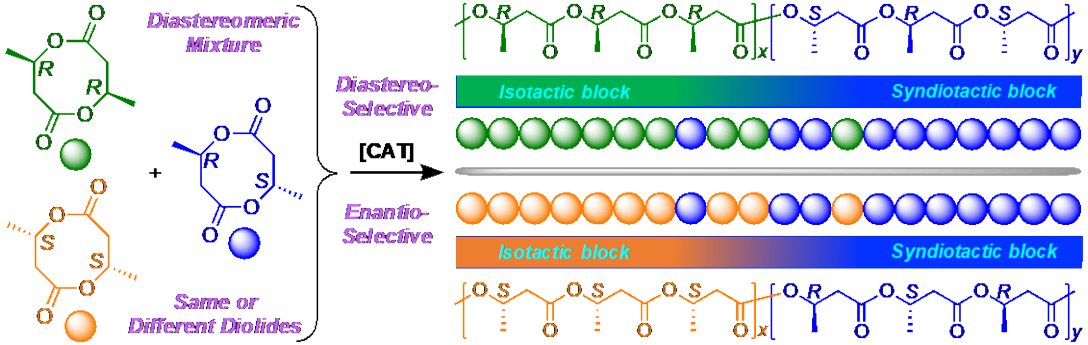
Problems

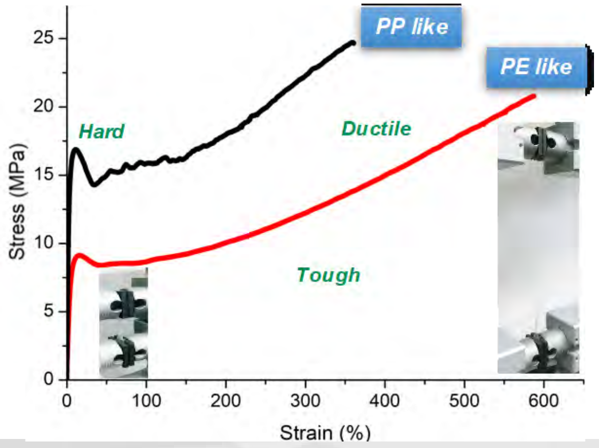
- Current biosynthesis: slow kinetic, low volume, high cost
- Poor mechanical properties (R = Me, P3HB, 3% elongation)
- PHA copolymers with enhanced ductility but diminished crystallinity

Solutions

- Catalyzed chemical synthesis: chemocatalytic pathway for *speed, scale, & efficiency*
- Precision synthesis to access novel PHA microstructures inaccessible by bacteria
- Microstructure-rendered high-performance PHAs to replace non-degradable PE and *it*-PP







X Tang, *et al. Nat. Commun.* 2018

X Tang, *et al. Science* 2019

X Tang, *et al. Angew. Chem.* 2020

Chemo/biocatalytic pathway to circular PHAs

Biological

- Synthesized within a bacterial cell for carbon & energy storage (step-growth mechanism)
- Perfectly isotactic
- Linear
- Polymer properties tuned by choice of feed & metabolic engineering
- Copolymers are *random/statistical*
- Feeds include sugars, fatty acids, various waste streams

Biodegradable
Biocompatible
Tunable

Chemical

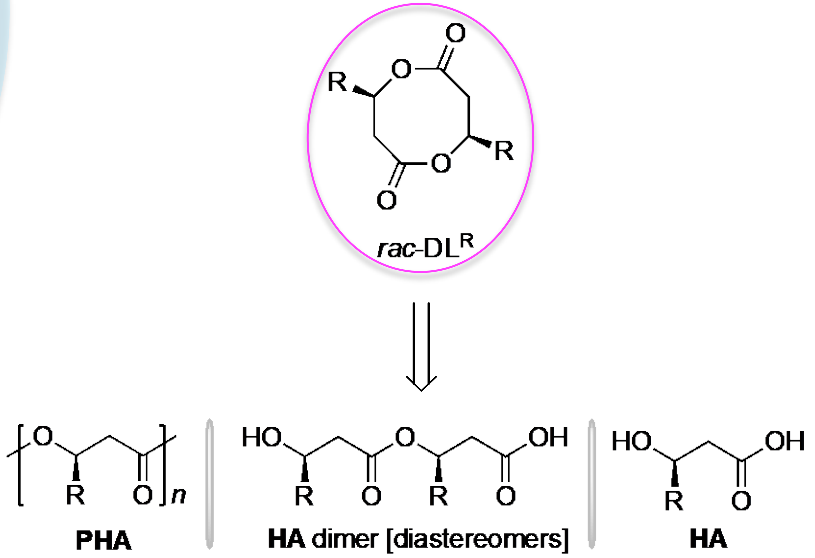
- Synthesized by catalyzed, scalable, and rapid ring-opening polymerization (chain-growth mechanism)
- Unnatural tacticities and side chains available
- Linear, cyclic, star architectures
- Polymer properties tuned by choice of monomers and catalysts
- Copolymers can be random, gradient, or blocks

Multi-institutional & multi-pronged Approaches:

Retrosynthetic computational tools (NREL, NWU)

Metabolic engineering (NREL, ORNL)

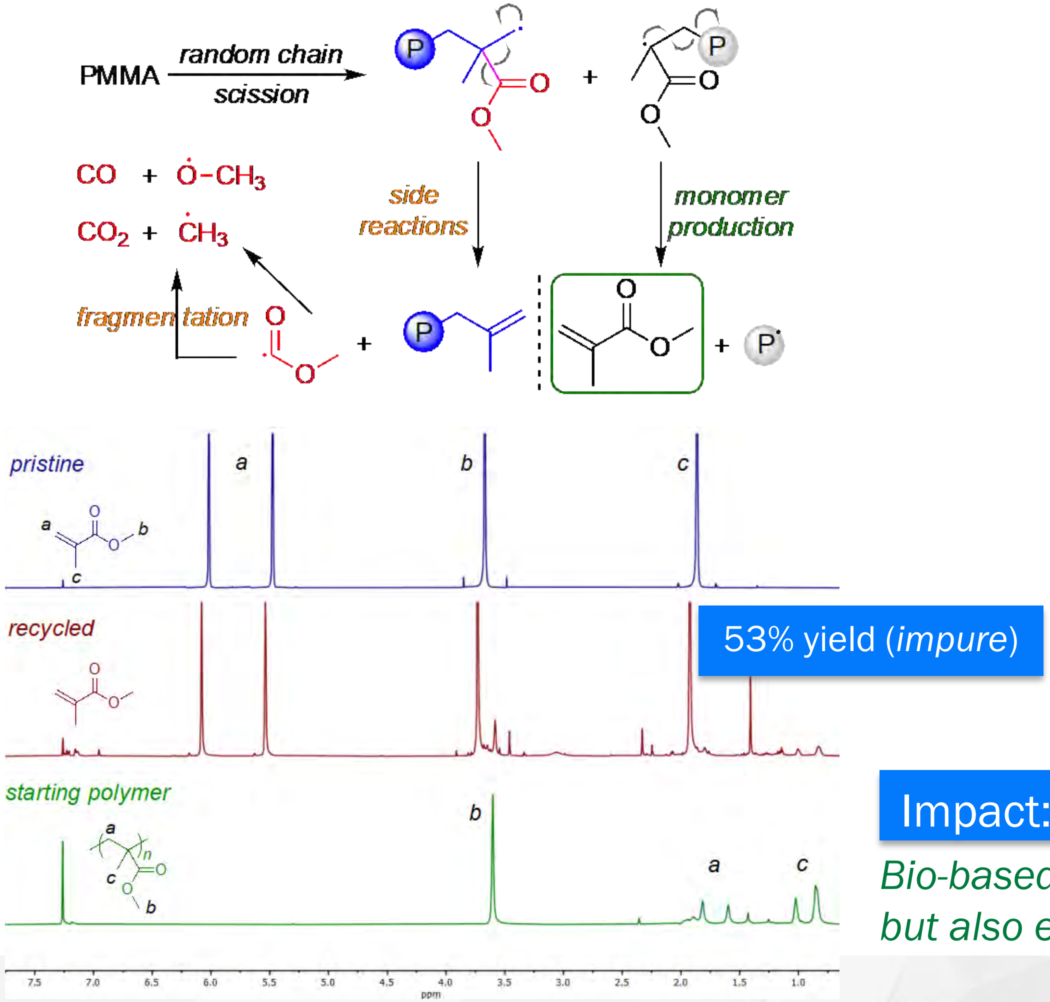
Chemical catalysis (CSU, MIT)



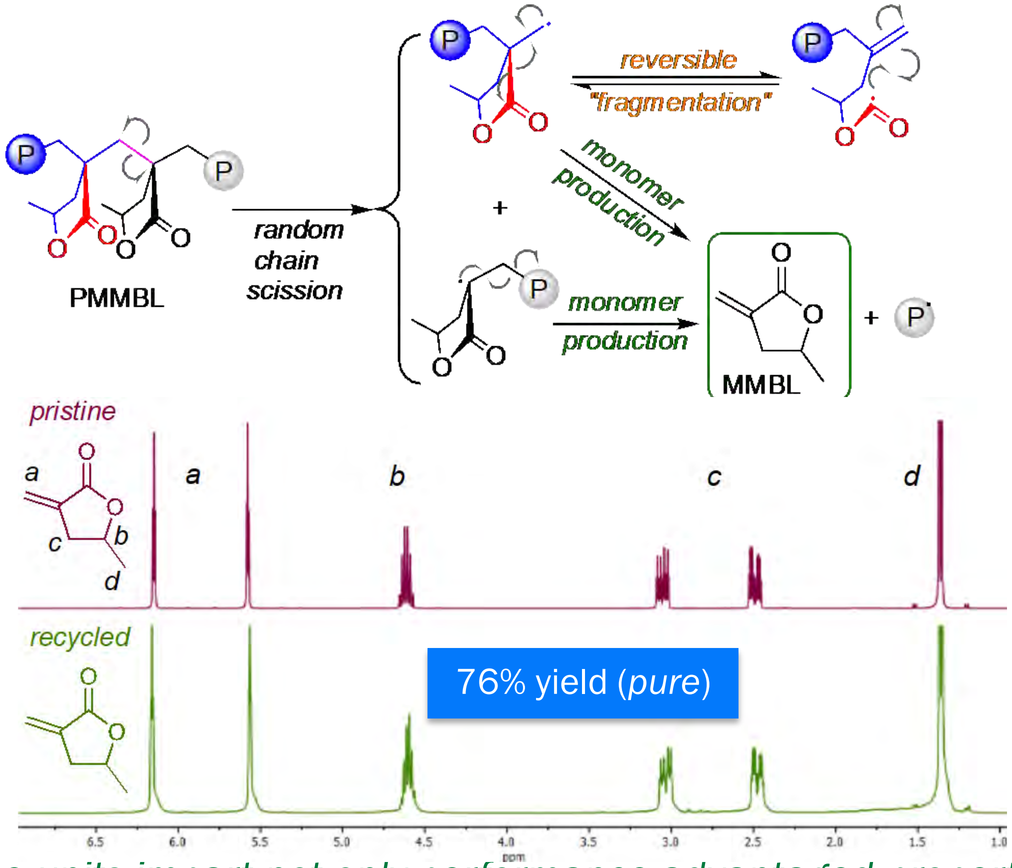
Impact: *Biologically sequestered PHAs from waste plastics are to be transformed into building blocks for high-performance designer PHAs with catalysis-enabled chemical circularity*

Recyclability: petroleum vs bio-based acrylic plastics

- Petroleum PMMA: T_g ~110°C, T_d ~300°C, solvent non-resistant, limited monomer recovery in recycling due to fragmentation side reactions



- Bio-based PMMBL: superior thermal properties and solvent resistance (T_g ~225°C, T_d ~400°C) *and* better recyclability with pure monomer recovery



Impact:

Bio-based vinyl lactone units impart not only performance-advantaged properties but also enhanced chemical recyclability!

R Gilsdorf, *et al. Polym. Chem.* **2020**

Crystalline high-performance RBD-CPs

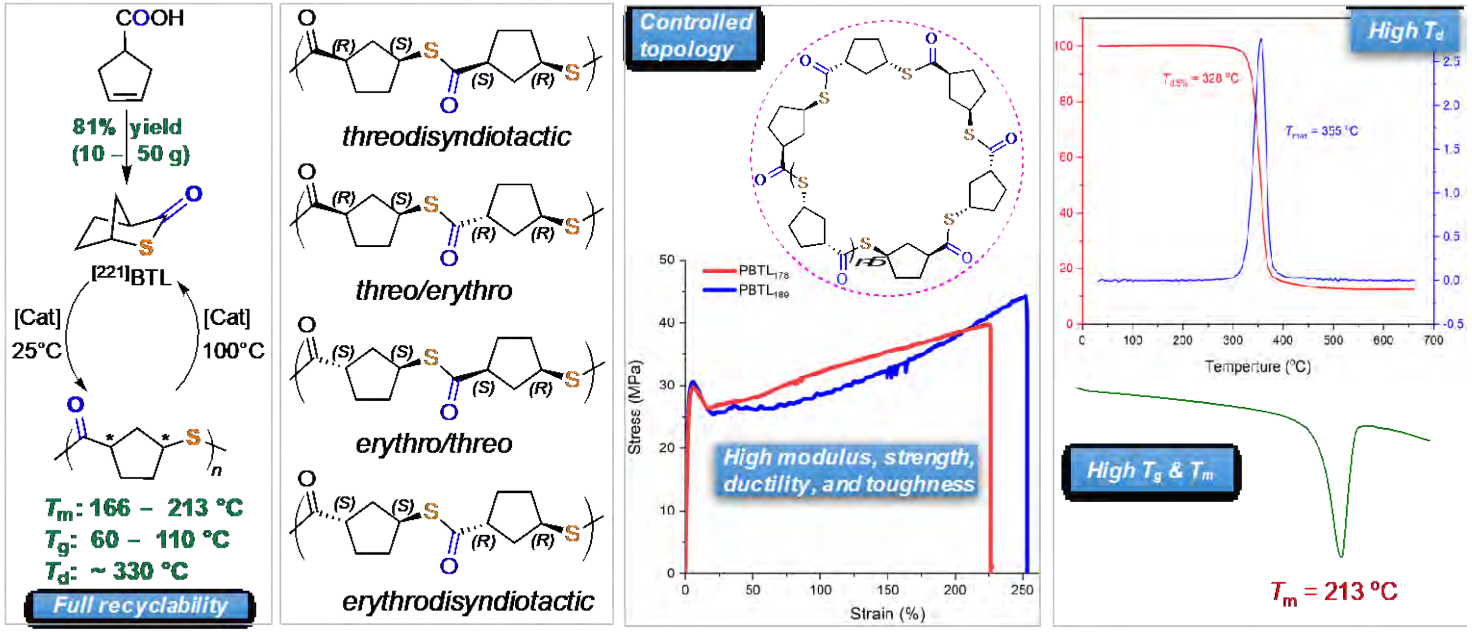
Problems

Tradeoffs challenge the design of CPs with high chemical recyclability *and* high-performance properties:

- Depolymerizability–performance
- Crystallinity–ductility
- Stereo-disorder–crystallinity

Solutions

- A bridged [2.2.1] bicyclic thioester ring for high polymerizability and selectivity for monomer recovery, as well as high-recovery, as well as high-performance properties and tacticity-independent crystallinity



Impact:

- RBD-CPs can be designed to defy the three common types of property tradeoffs
- Circular PBTL exhibits intrinsic crystallinity and an unusual set of desired high-performance properties, as a promising alternative to PET and *it*-PP

C Shi, *et al. Sci. Adv.* **2020**

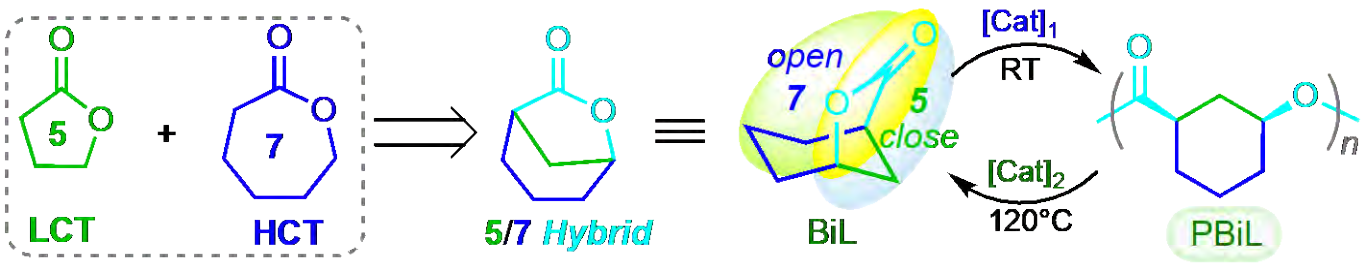
HCT/LCT hybrid monomer design

Problems

- HCT polymers exhibit high-performance properties but are difficult to chemically recycle
- LCT polymers are readily recyclable but lack robust performance properties
- These contrasting properties are conflicting in a single monomer structure

Solutions

- Structural hybridization between HCT and LCT parent monomers into a hybrid structure containing both sub-structural units to achieve both high de/polymerizability and performance properties



LCT	HCT		5/7 Hybrid
Very low	*High*	← Polymerizability →	*High*
Low	*Medium*	← Performance →	*High*
High	*Low*	← Recyclability →	*High*

T_g = 114–135 °C
T_m = 150–263 °C
$T_{d,5\%}$ = 320–330 °C

Impact:

- A powerful approach for RBD-CPs where conflicting properties must be exploited and unified
- Radically altering properties of the resulting RBD-CP polymers
- Overcoming traditional polymers' structure/property tradeoffs
- As a promising alternative to PET, PC, and *it*-PP

C Shi, *et al. in review* 2021

Ongoing and future work in Modeling and Redesign

Redesign

RBD-CPs

- Monomers derived from bio-based building blocks and waste plastic deconstruction
- RBD acrylic bioplastics
- Architecturally complexed CPs

Designer PHAs

- High T_g and T_d PHA thermoplastics
- PHA thermoplastic elastomers
- Recyclable PHA thermosets

Modeling for RBD

Monomer and polymer discovery

- Expand pool of starting molecules and chemistries
- T_c calibration
- Expansion of property domain of PolyML

Deconstruction modeling

- Expand kMC framework for condensation polymers
- Couple intrinsic kinetics with phase behavior and transport

Closed-loop upcycling

- Chemical circularity for designer PHAs through integrated chemo- and biocatalytic processes
- Closing the upcycling loop via integration of upcycling of mixed waste plastics, coupled with biological funneling, into the circular designer PHA scheme consisting of (monomer) capture – redesign – recycle

Summary

Overview

- BOTTLE focuses on analysis-guided R&D to upcycle today's plastics and redesign tomorrow's plastics

Management

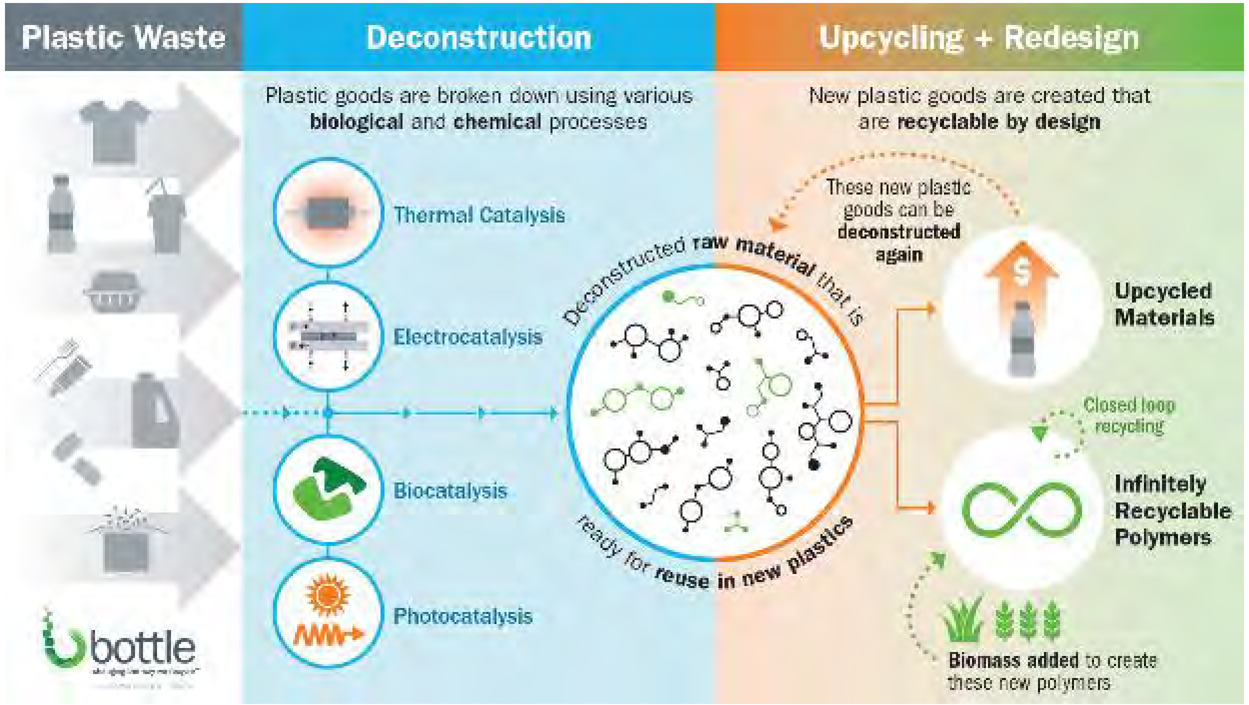
- We have a world-class, interdisciplinary, complementary team with a transparent collaborative approach to manage R&D

Approach

- Interdisciplinary team with analysis as our foundation provides agnostic view of realistic solutions to solving the plastics waste problem

Progress and Outcomes

- Made substantial progress across the R&D portfolio with high-impact publications emerging from seed project
- Initiating active collaborations with industry to derisk and scale BOTTLE technologies to real world problems



Quad Chart

Timeline

- Active Project Duration: 10/1/2020 – 9/30/2023
- Total Project Duration: 10/1/2019 – 9/30/2023

	FY20	Active Project (FY21-23)
DOE Funding	$2,000,000	$30,000,000

Project Partners

- ANL, CSU, LANL, MIT, MSU, NREL, NU, ORNL, SLAC, UoP

Barriers addressed

- Ct-D Advanced Bioprocess Development
- Ct-J Identification and Evaluation of Potential Bioproducts
- CT-K Developing Methods for Bioproduct Production

Project Goal

- Develop selective, scalable processes to deconstruct and upcycle today's plastics and thermosets
- Redesign tomorrow's plastics to be recyclable-by-design (RBD) and derived from bio-based feedstocks

End of Project Milestone

- Deconstruction/Upcycling: Deliver 3 catalytic methods to cleave C-C bonds and upcycle intermediates.
- Redesign: Produce 10 new RBD polymers able to be produced at ≤$2.50/lb over a range of large-volume applications. Demonstrate ≥50% predicted energy savings relative to incumbent materials.
- Analysis: Deliver 10 designs analyses to ensure BOTTLE metrics are achieved.
- Modeling: Deliver a computational pipeline to predict RBD polymers with target thermal and mechanical properties.
- Characterization: Publish 3 LAPs for plastics deconstruction products.

Funding Mechanism

Bioenergy Technologies Office FY21 AOP Lab Call (DE-LC-000L079) – 2020

Thank You

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BIOENERGY TECHNOLOGIES OFFICE

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bottle

changing the way we recycle

U.S. DEPARTMENT OF ENERGY

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- Jay Fitzgerald, Nichole Fitzgerald, Gayle Bentley, Joel Sarapas (BETO)

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Additional Slides

Publications

In preparation

Avantika Singh, Nicholas A. Rorrer, Scott R. Nicholson, Erika Erickson, Jason DesVeaux, Andre F.T. Avelino, Patrick Lamers, Arpit Bhatt, Yimin Zhang, Chao Wu, Greg Avery, Ling Tao, Andrew R. Pickford, John E. McGeehan, Alberta C. Carpenter, Gregg T. Beckham, Analysis of the enzymatic recycling of poly(ethylene terephthalate), in preparation.

Allison Z. Werner, Rita Clare, Thom Mand, Isabel Pardo, Kelsey J. Ramirez, Christopher W. Johnson, Nicholas A. Rorrer, Davinia Salvachúa, Adam M. Guss, Gregg T. Beckham, Tandem chemical deconstruction and biological upcycling of poly(ethylene terephthalate) to b-ketoadipic acid by *Pseudomonas putida* KT2440, in preparation.

In review or revision

Benjamin C. Pollard, Brandon C. Knott, Heather B. Mayes, Tucker Burgin, Michael F. Crowley, John E. McGeehan, Gregg T. Beckham, H. Lee Woodcock, The reaction mechanism of the PETase enzyme, in revision at *Nature Comm*.

Lucas D. Ellis‡, Nicholas A. Rorrer‡, Kevin P. Sullivan‡, Maike Otto, John E. McGeehan, Yuriy Román-Leshkov, Nick Wierckx, Gregg T. Beckham, Chemical and biological catalysis for plastics upcycling, in revision at *Nature Catalysis*.

Robin M. Cywar, Nicholas A. Rorrer, Caroline Hoyt, Gregg T. Beckham, Eugene E.Y.-X. Chen. Bio-based Polymers with Performance-advantaged Properties. In revision at *Nat. Rev. Mater*.

Shi, C.; McGraw, M. L.; Li, Z.-C.; Cavallo, L.; Falivene, L.; Chen, E. Y.-X., Hybrid Monomer Design for Unifying Conflicting Polymerizability/Recyclability/Performance Properties. Chem 2021, in review.

In press

Lucas D. Ellis, Sara V. Orski, Andrew G. Norman, Kathryn L. Beers, Yuriy Román-Leshkov*, and Gregg T. Eugene Kuatsjah, Anson C. K. Chan, Rui Katahira, Gregg T. Beckham, Michael E. P. Murphy, and Lindsay D. Eltis*, Elucidating the repertoire of lignostilbene dioxygenases of Sphingomonas sp. SYK-6 and their role in the catabolism of lignin-derived aromatic compounds, in revision at J. Biol. Chem, in press at *ACS SusChemEng*.

Publications

2021

Lucas D. Ellis, Sara V. Orski, G.A. Kenlaw, Andrew G. Norman, Kathryn L. Beers, Yuriy Román-Leshkov, Gregg T. Beckham. Tandem heterogeneous catalysis for polyethylene depolymerization via an olefin intermediate process. *ACS Sustainable Chemistry & Engineering* (2021). 9, 2, 623–628

Julie E. Rorrer, Gregg T. Beckham, Yuriy Román-Leshkov, Conversion of polyolefin waste to liquid alkanes with Ru-based catalysts under mild conditions, *JACS Au*. (2021) 1, 8-12.

Scott R. Nicholson, Nicholas A. Rorrer, Alberta C. Carpenter, Gregg T. Beckham, Manufacturing energy and greenhouse gas emissions associated with plastics consumption, *Joule* (2021).

2020

Brandon C. Knott‡, Erika Erickson‡, Mark D. Allen‡, Japheth E. Gado‡, Rosie Graham, Fiona L. Kearns, Isabel Pardo, Ece Topuzlu, Jared J. Anderson, Harry P. Austin, Graham Dominick, Christopher W. Johnson, Nicholas A. Rorrer, Caralyn J. Szostkiewicz, Valérie Copié, Christina M. Payne, H. Lee Woodcock, Bryon S. Donohoe, Gregg T. Beckham, John E. McGeehan, Characterization and engineering of a two-enzyme system for plastics depolymerization, *PNAS* (2020), 117, 25476-25485.

Gilsdorf, R. A.; Nicki, M. A.; Chen, E. Y.-X. High Chemical Recyclability of Vinyl Lactone Acrylic Bioplastics, *Polym. Chem*. (2020). 11, 4942-4950.

C. Shi, M. L. McGraw, Z.-C. Li, L. Cavallo, L. Falivene and E. Y.-X. Chen, “High-Performance Pan-Tactic Polythioesters with Intrinsic Crystallinity and Chemical Recyclability”. *Sci. Adv.* (2020) eabc0495.

Japheth E. Gado, Gregg T. Beckham, Christina M. Payne, Improving enzyme optimum temperature prediction with resampling strategies and ensemble learning, *J. Chem. Inform. Model*. (2020), 60, 4098-4107.

Patents and patent applications

- Bio-derived Epoxy-Anhydride Thermoset Polymers for Wind Turbine Blades and Anti-Static Coatings: 20-59, U.S. provisional patent application 63/087,547
- PET upcycled to 3D printing materials: 20-37, U.S. provisional patent application 63/050,912
- Universal reactive additives for biodegradable olefinic polymers: 20-77, Forthcoming
- PETase/MHETase enzyme chimera: 20-86, U.S. provisional patent application 63/022,784
- Upcycling mixed waste plastic through chemical depolymerization and biological funneling: 20-123, U.S. provisional patent application 63/126,153
- Catalysts and methods for depolymerizing plastics: 20-22, U.S. provisional patent application 63/050,209

Presentations

2020

Understanding the Origin of Long-Chain Alkane Hydrogenolysis Selectivity for the Chemical Upcycling of Waste Polyolefins, *2020* American Institute of Chemical Engineers (AIChE) National Conference, Session: Catalytic Upcycling of Waste Plastics, Catalysis and Reaction Engineering Division, Monday, Nov. 16th, 2020.

A heterogeneous system for alkane rearrangement: A means to depolymerize polyethylene at low temperature (< 200°C). Oral Presentation. Catalytic Upgrading of Waste Plastics Session, American Institute of Chemical Engineering Annual Meeting, November 11, 2020.

Towards sustainable performance-advantaged bioproducts and plastics upcycling, Michigan Technological University (via webinar), November 6th, 2020

Efforts towards selective and sustainable plastics upcycling, Trash-Free Seas Alliance and ReSource Annual Meeting, Sponsored by the World Wildlife Fund and The Ocean Conservancy (via webinar), October 20th, 2020.

Tackling the Waste Plastics Problem – Plastics Supply-Chain Modeling and Chemical Catalysis Efforts in the BOTTLE Consortium. Invited Oral Presentation. Global Symposium on Waste Plastics, October 14, 2020.

Efforts towards sustainable performance-advantaged bioproducts and plastics upcycling, Materials Life-Cycle Management Mini-Symposium, University of Delaware (via webinar), October 1st, 2020

Bacterial aromatic catabolism for lignin and plastics conversion, BioDiscovery Institute, University of North Texas (via webinar), August 20th, 2020

Computational Investigation of the PETase Reaction Mechanism. ACS Fall 2020 Virtual Meeting & Expo, Virtual Poster, August 17th-20th, 2020.

Tackling the Waste Plastics Problem – Plastics Supply-Chain Modeling and Chemical Catalysis Efforts in the Bottle Consortium. International Congress on Sustainability & Engineering. August 4th, 2020

Computational Investigation of the PETase Reaction Mechanism. NIH LCB Seminar Series, Virtual Seminar, July 23rd, 2020.

Challenges and opportunities in plastics upcycling: Highlights from the BOTTLE Consortium, MIT Plastics and the Environment Program workshop (via webinar), June 18th, 2020

Challenges and opportunities in sustainable packaging, Sustainable Packaging Coalition (via webinar), May 26th, 2020

Upcycling waste polyesters to performance thermoplastics and thermosets. 24th Annual Green Chemistry & Engineering Conference, virtual, May 29th, 2020.

Bio-derived Carboxylic Acid. Radtech UV+EB conference 2020, March 2020, Orlando, FL.

Biological processes for lignin and plastics conversion, University fo California Riverside (via webinar), January 7th, 2020

Presentations

2018-2019

Introduction to the BOTTLE consortium, DOE AMO-BETO Plastics for a Circular Economy Workshop, December 11th, 2019

Using selective chemical and biological catalysis to upcycle lignin and plastics, ExxonMobil Research and Engineering, October 25th, 2019

Challenges and opportunities in upcycling and redesigning plastics, ISMR 2019, October 9th, 2019

Challenges and opportunities in plastics upcycling: the role of biological and chemical recycling, Sustainable Packaging Coalition Advance 2019, October 8th, 2019

Biological recycling and upcycling, Mars Technology Committee Meeting, October 2nd, 2019

Enzymes for lignin and plastics conversion, Enzymes, Coenzymes and Metabolic Pathways, July 23rd, 2019

New approaches to manufacture and recycle plastics, University of Wisconsin Madison, May 13th, 2019

Hybrid biological and catalytic processes to manufacture and recycle plastics, Boise State University, March 27th, 2019

Interfacial biocatalysis to break down plants and plastics, Colorado State University, February 15th, 2019

Challenges and opportunities in plastics upcycling, 2019 Polymer Upcycling Workshop, UCSB, January 24th, 2019

Hybrid biological and catalytic processes to manufacture and recycle plastics, USC, January 14th, 2019

Hybrid biological and catalytic processes to manufacture and recycle plastics, Princeton University, November 28th, 2018

Opportunities and challenges in plastics upcycling, ABLC Global, November 8th, 2018

Awards

Top 100 Altmetric paper 2020 (#39)

Characterization and engineering of a two-enzyme system for plastics depolymerization

Brandon C. Knott[a,1], Erika Erickson[a,1], Mark D. Allen[b,1], Japheth E. Gado[a,c,1], Rosie Graham[b], Fiona L. Kearns[d], Isabel Pardo[a], Ece Topuzlu[a,e], Jared J. Anderson[a], Harry P. Austin[b], Graham Dominick[a], Christopher W. Johnson[a], Nicholas A. Rorrer[a], Caralyn J. Szostkiewicz[a], Valérie Copié[e], Christina M. Payne[c], H. Lee Woodcock[d], Bryon S. Donohoe[f], Gregg T. Beckham[a,2], and John E. McGeehan[b,2]

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High Attention Score compared to outputs of the same age and source (99th percentile)

In the top 5% of all research outputs scored by Altmetric

https://www.altmetric.com/details/91362881

Consortium value

Why choose a consortium model?

- The dire global plastics pollution problem will not be solved by one institution
- The world needs many minds working together to enable the plastics circular economy
- Using an integrated science approach and analysis-guided research, we have built a diverse team of leading experts at world-class facilities to solve problems faster
- BOTTLE partners have an inventory of innovations that can inform the design of industry-specific collaborative projects with the highest probability of producing novel IP and provides access to chemists, biologists, material and environmental scientists, and engineers able to tackle a variety of problems