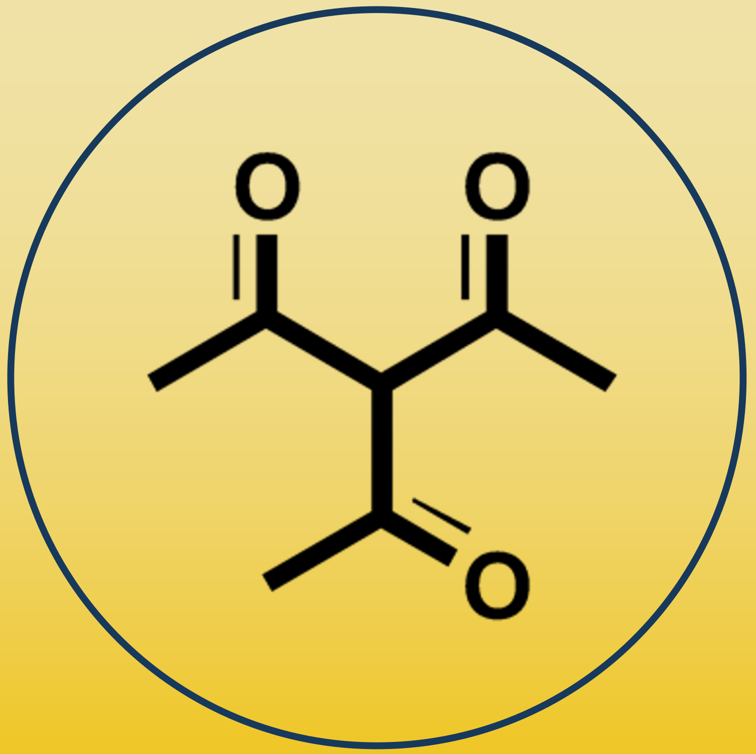
DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

Design and Development of Bio-Advantaged Vitrimers as Closed-Loop Bioproducts



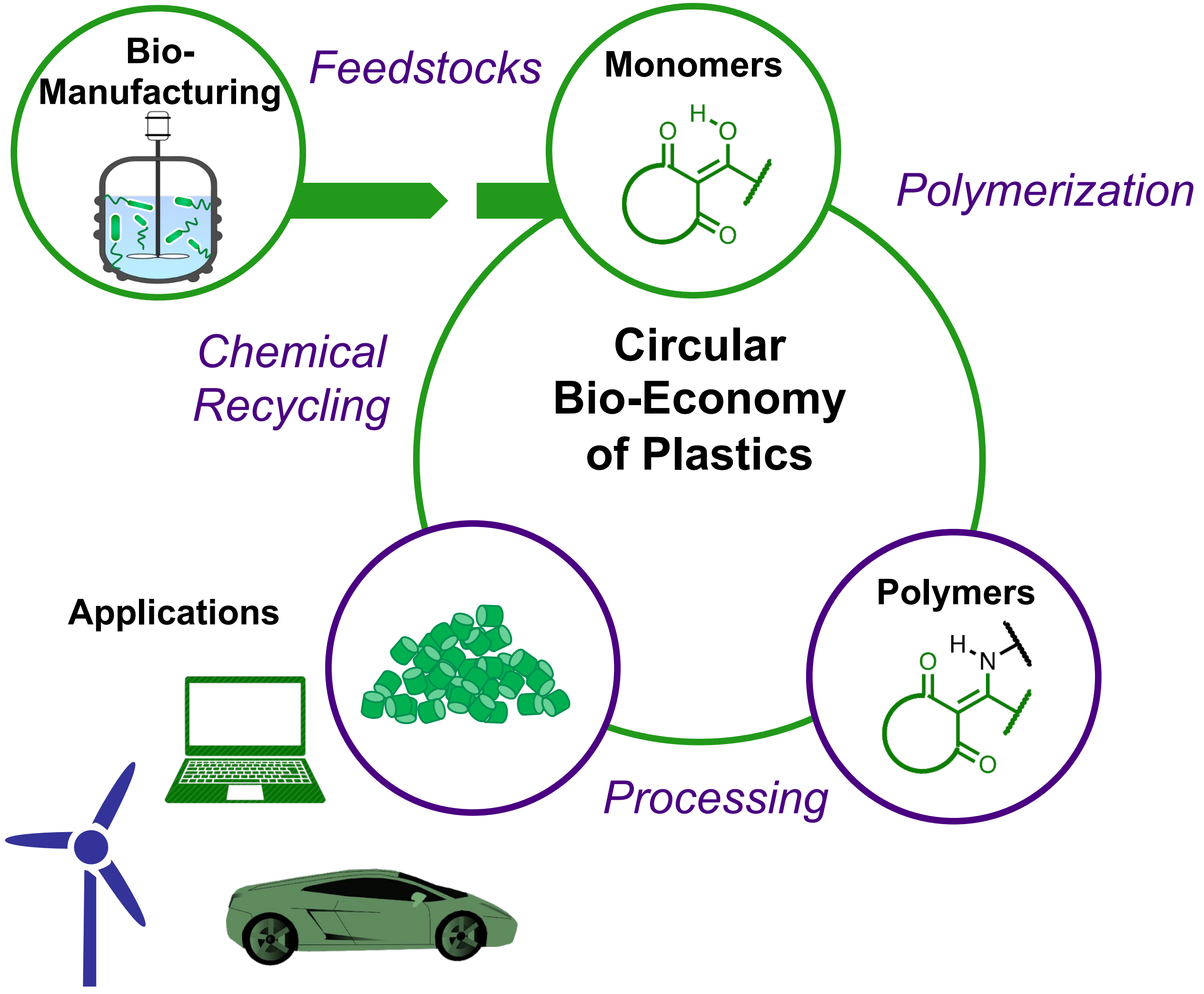
Apr 7, 2023
Technology Area Session

UC Berkeley: Jay Keasling & Kristin Persson

Lawrence Berkeley National Lab: Brett Helms, Tom Russell, Corinne Scown

Project Overview

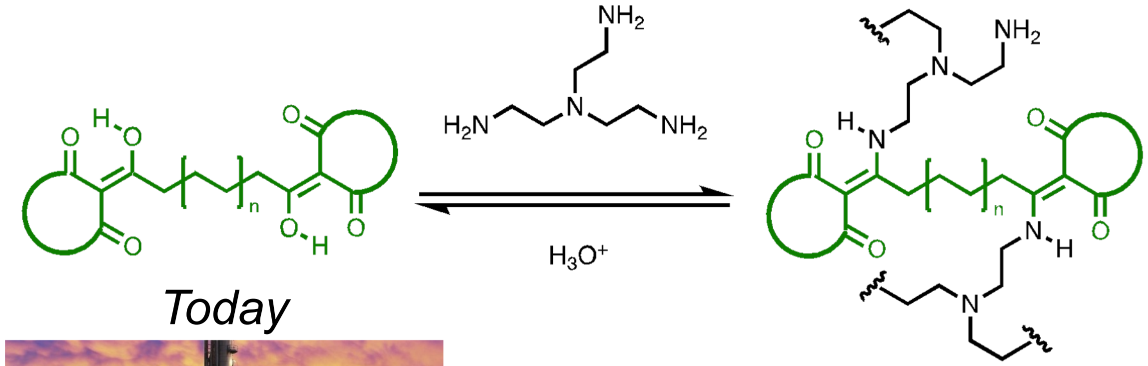
Vision



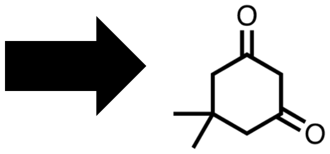
Advancing Beyond State-of-the-Art

Triketone Monomers

Infinitely Recyclable Polydiketoenamines

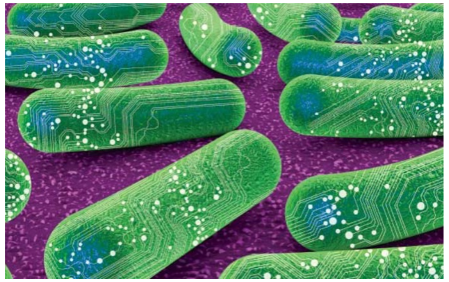


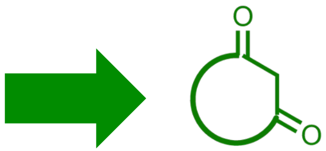
Today



Limited Functionality

Future

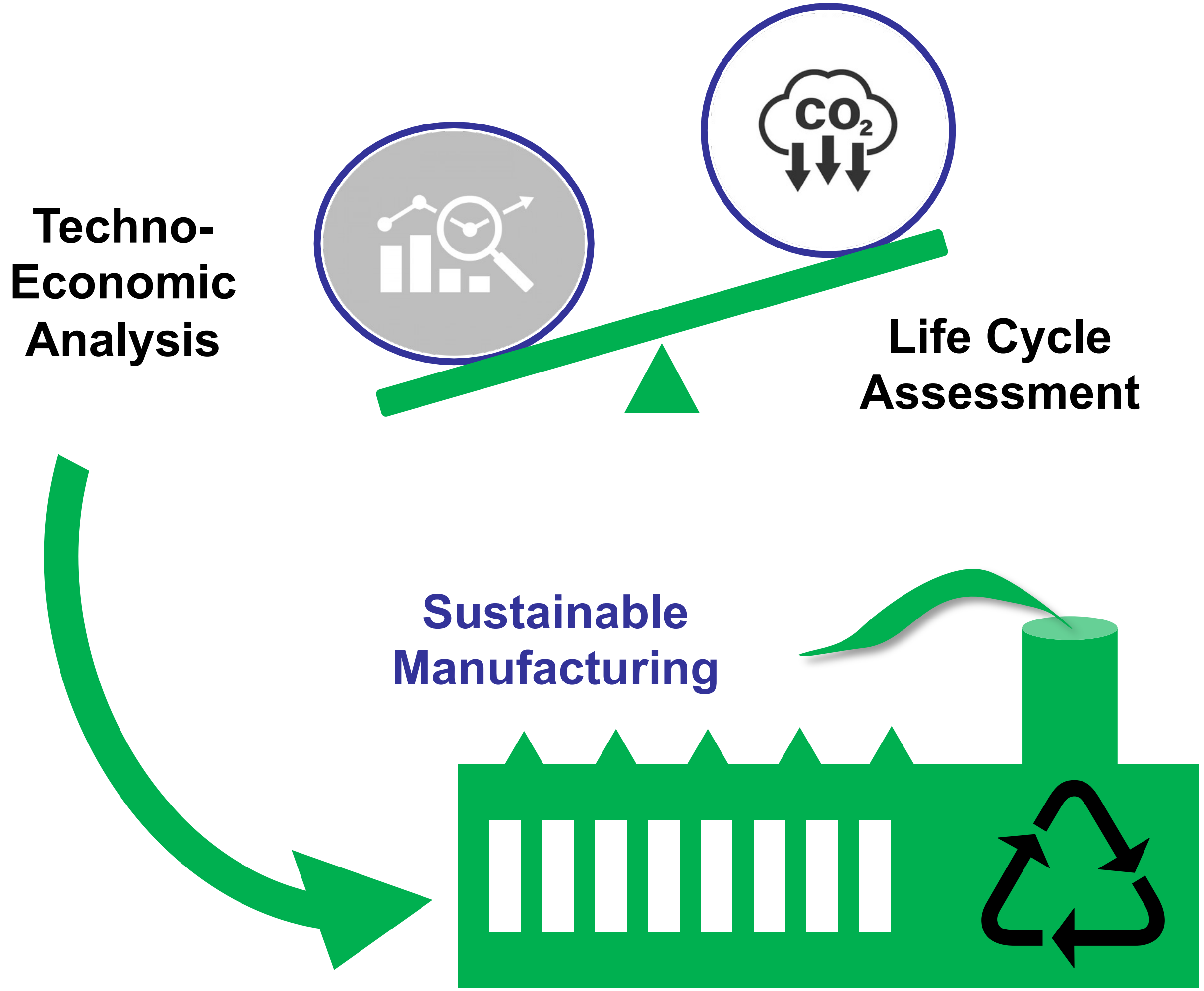




Bio-Advantaged Functionality

Project Overview

Potential Impacts



Potential Risks

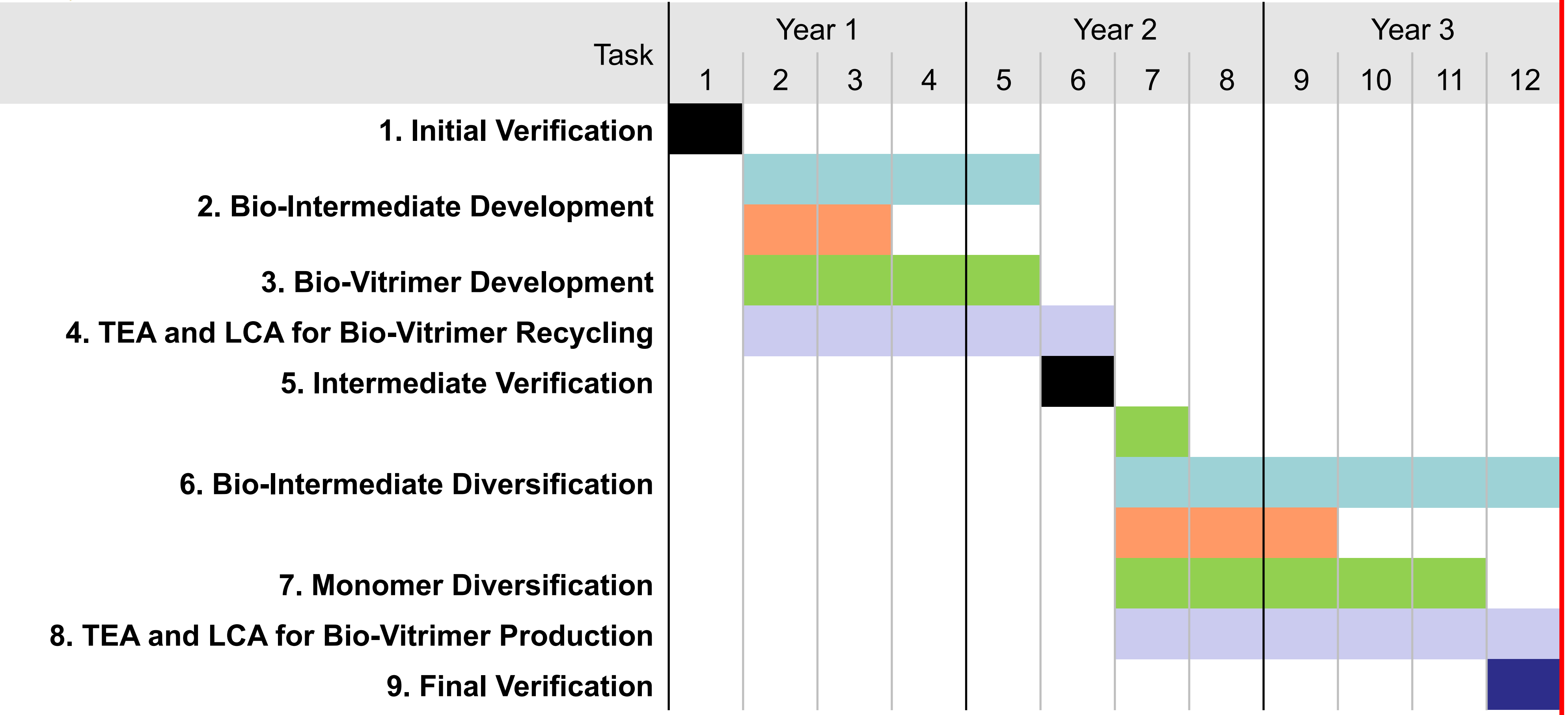
Poor scalability of either bio- or chemical synthesis processes

Bio-Monomers fail to deliver market-differentiating performance advantages

Minimum selling price too high for widespread adoption in the market

1 – Approach

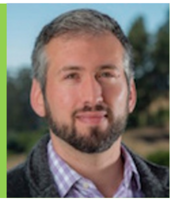
BETO review



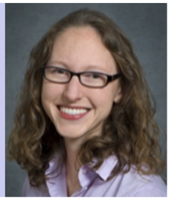
Keasling Group
Biology
UCB

Persson Group
Computational
UCB

Helms Group
Chemistry
LBNL



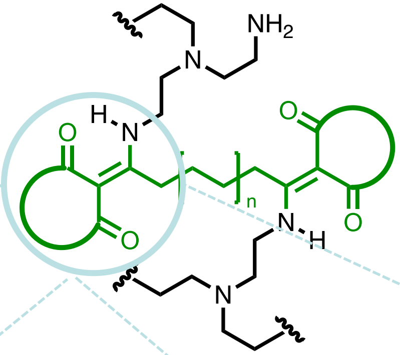
Scown Group
Energy/ Environmental
LBNL



Risk	Mitigation
Scalability of chemically recyclable polymer bio-products.	Techno-economic analysis and life-cycle assessment of key processes.
Market adoption as a performance-advantaged and sustainable bio-product.	Work with industry to tailor performance for specific uses. Demonstrate biosynthetic route to key feedstocks and minimize losses in recycling.

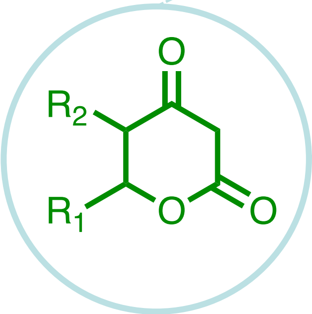
1 – Approach

Budget Period 2–3



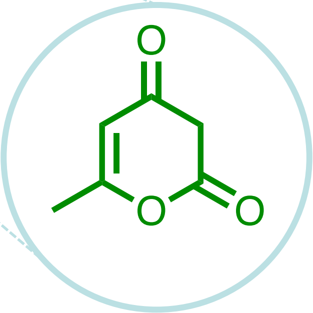
Aliphatic BKDL

R_1 and R_2 BKDL Dictate PDK Resin Properties

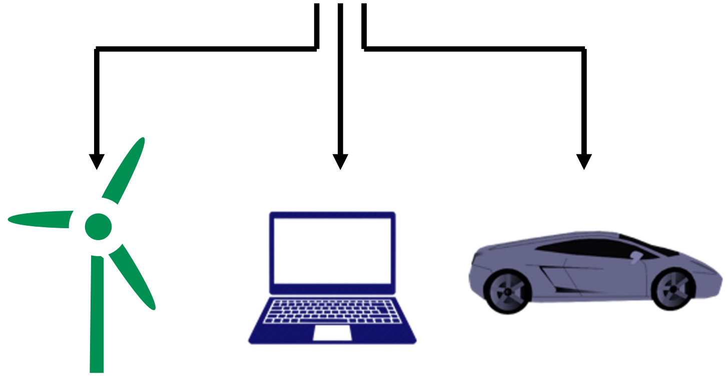


Bio-Synthesis Targets

Aromatic BKDL



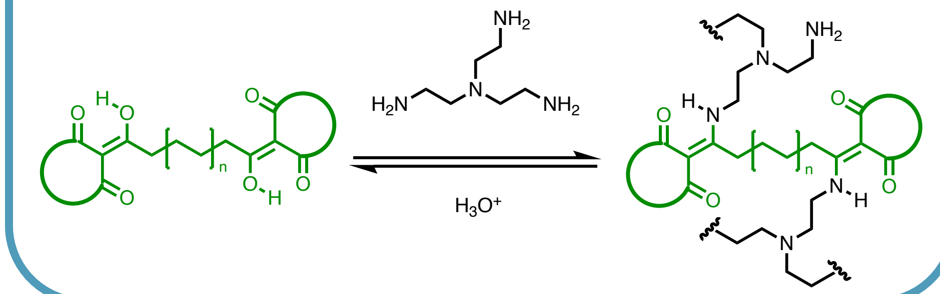
Double-bond BKDL Provide new Thermal Properties



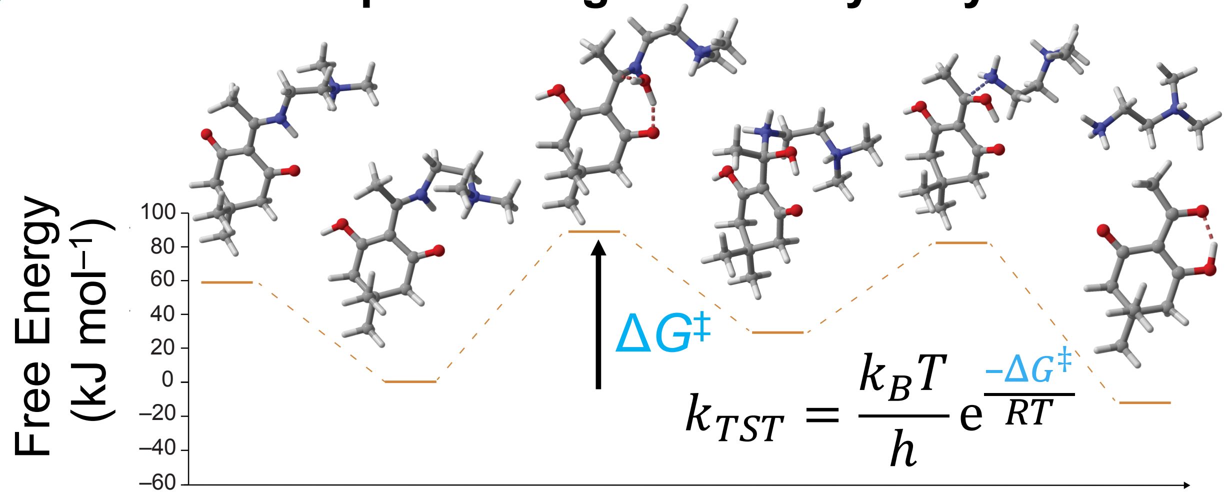
Objective: Co-Design Bio-PDK Resins for Properties AND Chemical Recycling

1 – Approach

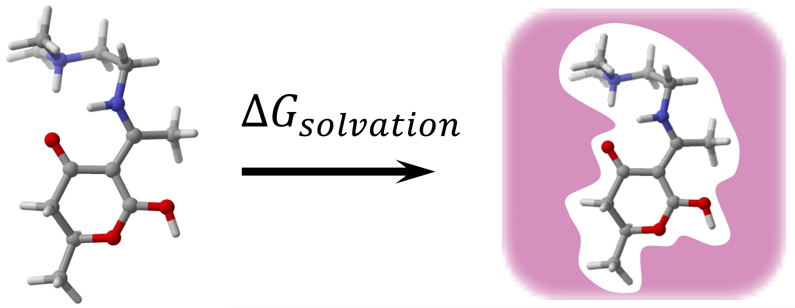
Diketoenamine Hydrolysis in Acid Unlocks Chemical Recycling



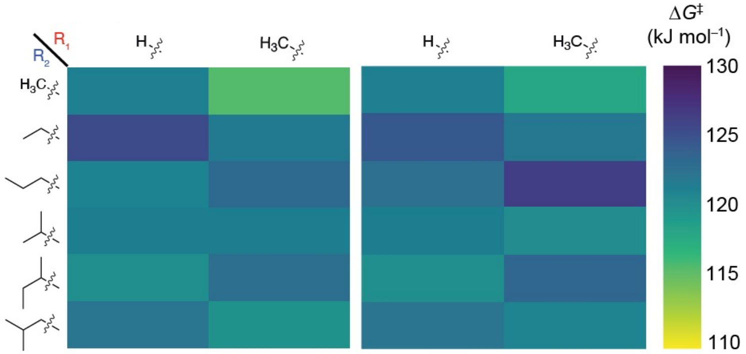
Compute Energetics for Hydrolysis



$$k_{TST} = \frac{k_B T}{h} e^{\frac{-\Delta G^{\ddagger}}{RT}}$$



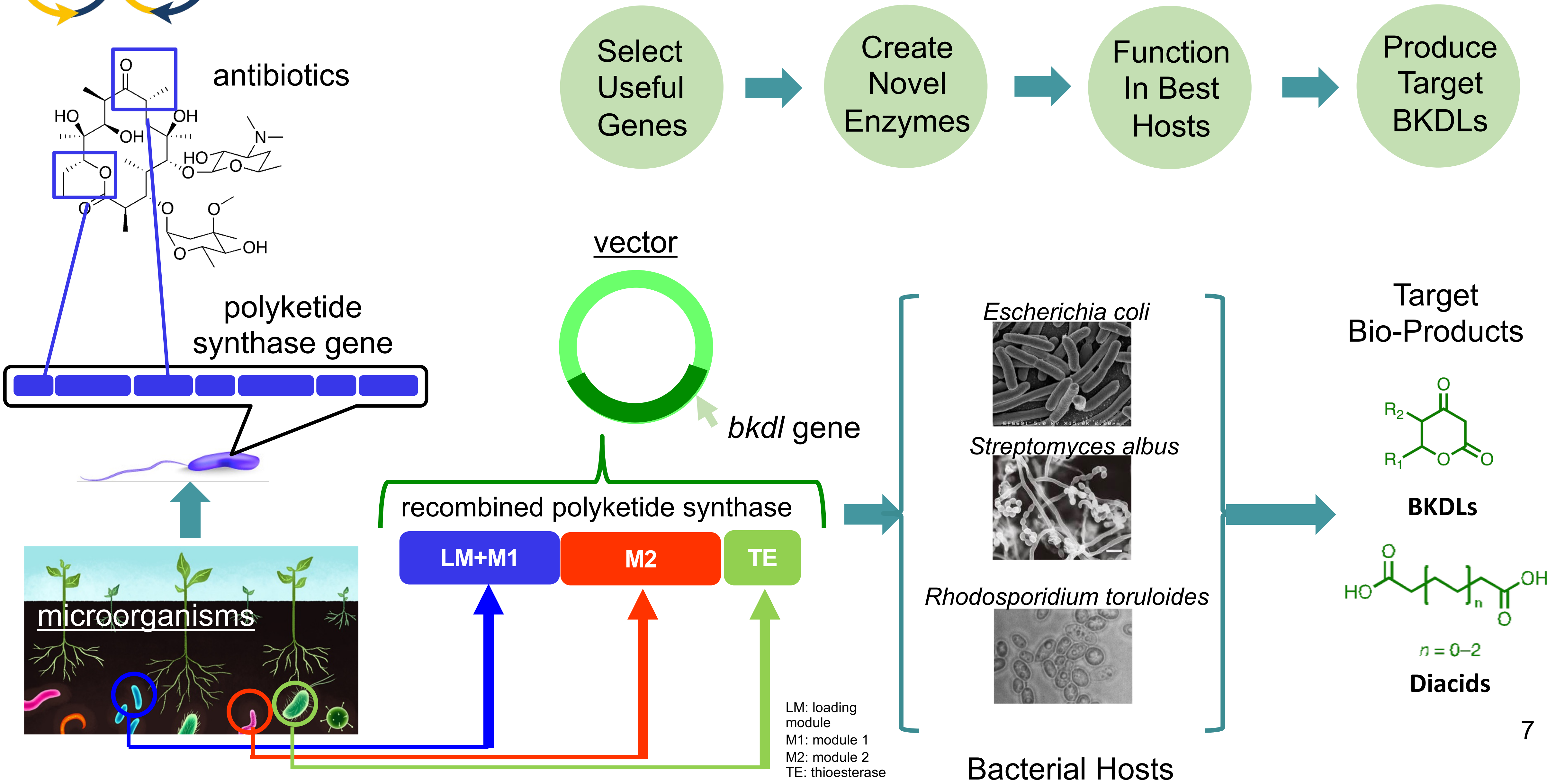
HT Screens Predict Variants with Most Favorable Recycling Rates



Validate with Experiment

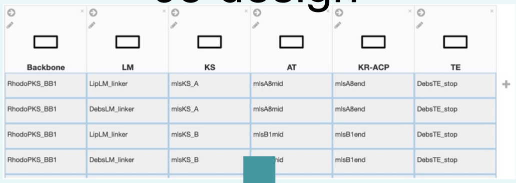
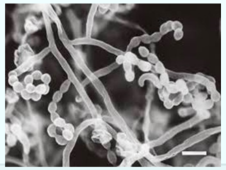
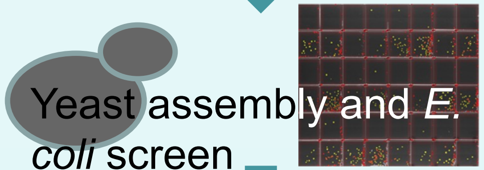
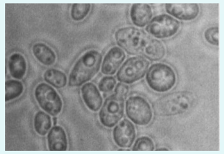
Recommend Specific BKDLs for Bio

1 – Approach


Select Useful Genes
Create Novel Enzymes
Function In Best Hosts
Produce Target BKDLs
antibiotics
polyketide synthase gene
microorganisms
vector
bkdl gene
recombined polyketide synthase
LM+M1
M2
TE
LM: loading module
M1: module 1
M2: module 2
TE: thioesterase
Escherichia coli
Streptomyces albus
Rhodosporidium toruloides
Bacterial Hosts
Target Bio-Products
BKDLs
Diacids
n = 0–2

1 – Approach

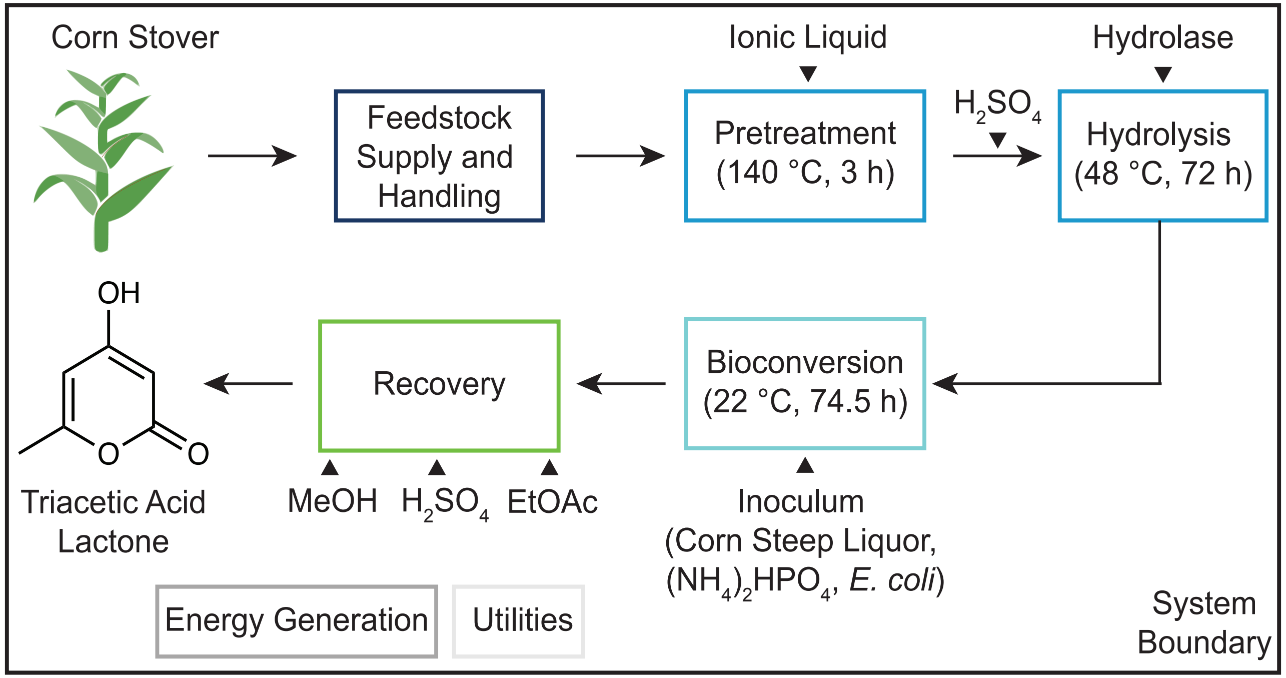
BETO review

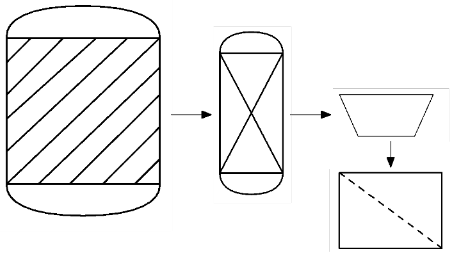
Design and Build	Host Development	Fermentation	Test	Learn
J5 design 	*E. coli* 	 1~5 mL	LC-MS	Substrate Specificities
 PCR & ZAG analysis	*S. albus* 	 10~50 mL	GC-MS	Functional Fusion Boundaries
 Yeast assembly and *E. coli* screen	*R. toruloides* 	 1~5 L	Metabolomics Go/No-Go: > 1 g/L	Product Toxicity
DIVA NGS sequencing 		 100~300 L	Proteomics	Protein-Protein Interactions

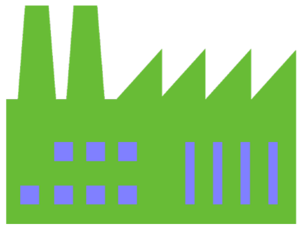
Automation / High-throughput platform

1 – Approach

Bio production of TAL





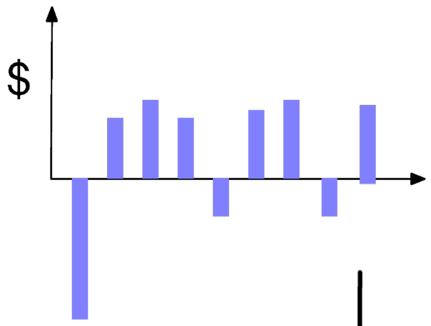


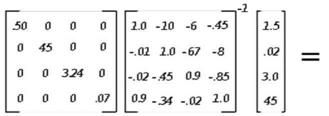
CAPEX & OPEX

Mass & Energy Balance

Cash Flow Analysis

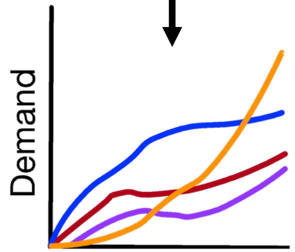
Life-Cycle GHG Analysis





Compute LC inventory

System-Wide Impacts



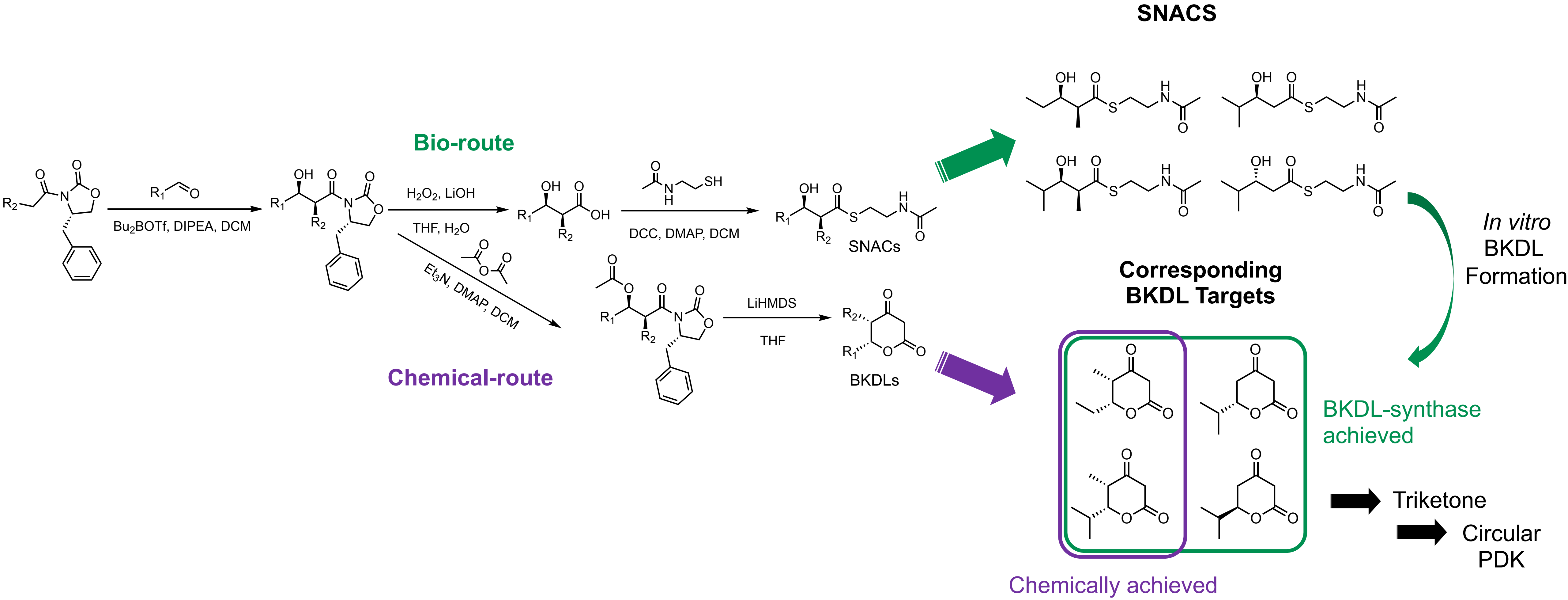
Potential Waste Reduction

Source: Demarteau et al. ***2023.***

2 – Progress and Outcomes

Milestone 6.1.1: Explore which alternative BKDL structures are accessible using SNACs	LBNL supplies UCB with >3 SNACs. Produce >3 add. BKDL structures

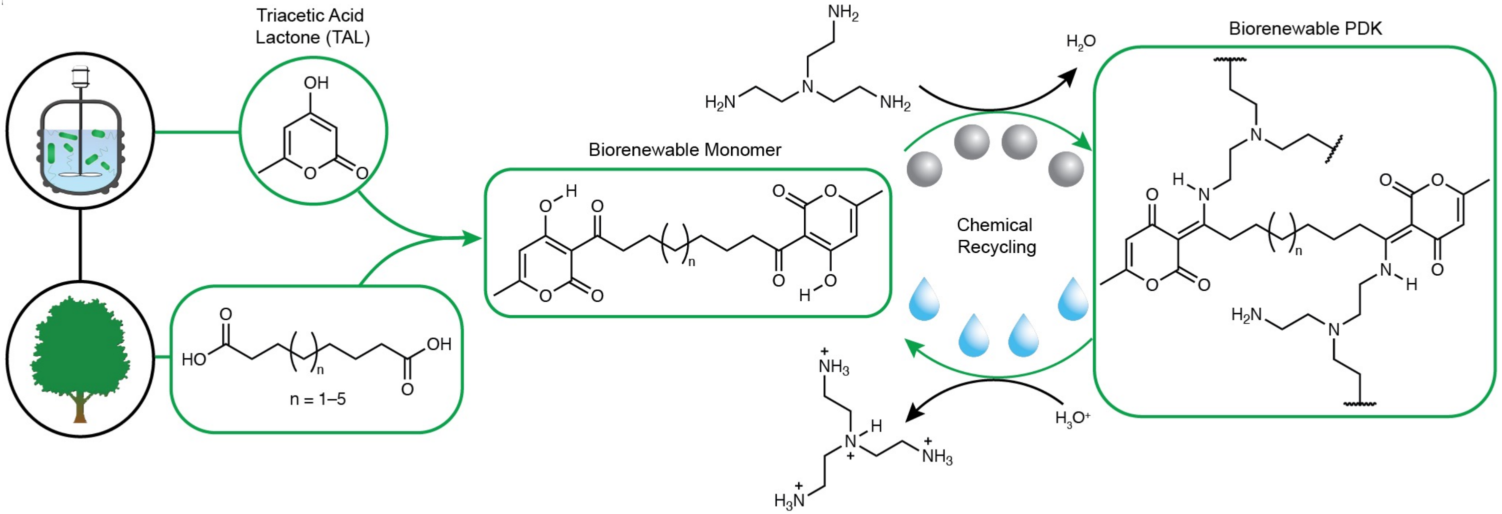
In vitro Alternative BKDL Structures Synthesis



2 – Progress and Outcomes

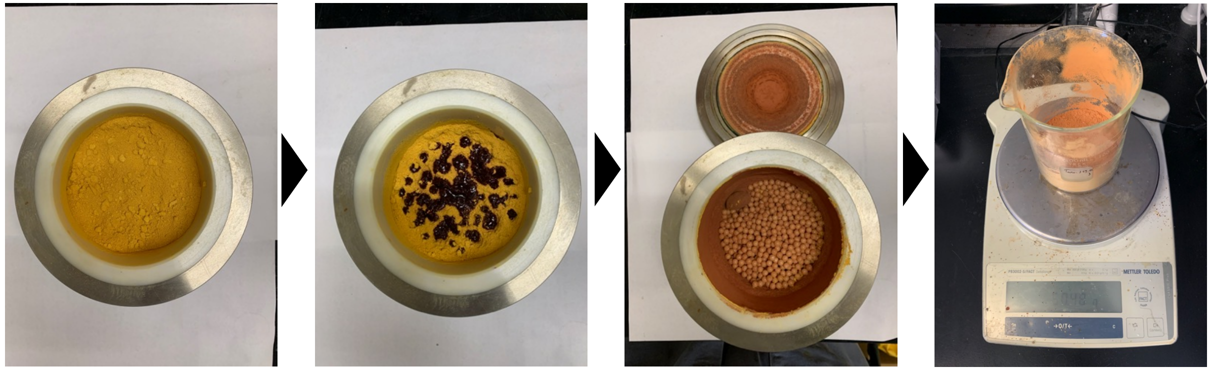
Milestone 7.2.1: Demonstrate a 50-g vitrimer batch size with >75% biomass content and <1% VOC content	Polymerize bio-derived DKLs with amine monomers at LBNL; show <1% mass loss upon heating to 150 ˚C

Biorenewable Circularity in Polydiketoenamine Plastics



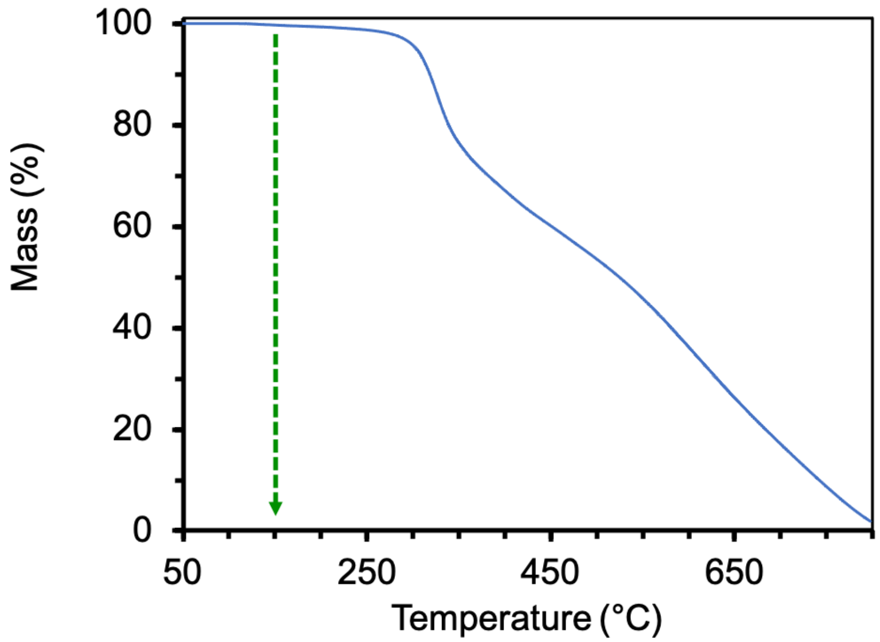
Bio-Content (C10 diacid) = 26%
Bio-Content (C10 diacid + BKDL) = 80%

50 g C10 TAL TK | Addition of TREN | After-Ball Milling | Polymer recovery



m = 50.5 g ✓

Mass Loss at 150 °C = 0.32% ✓

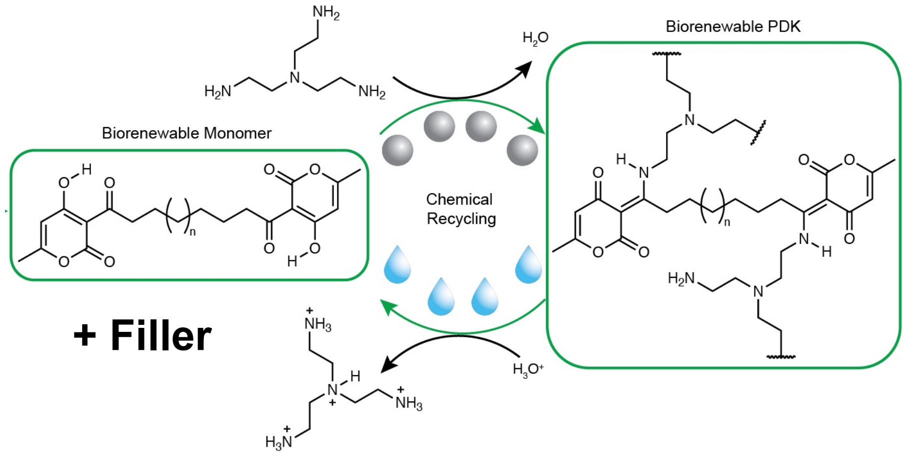


Nature Sustainability **2023**, Manuscript Accepted

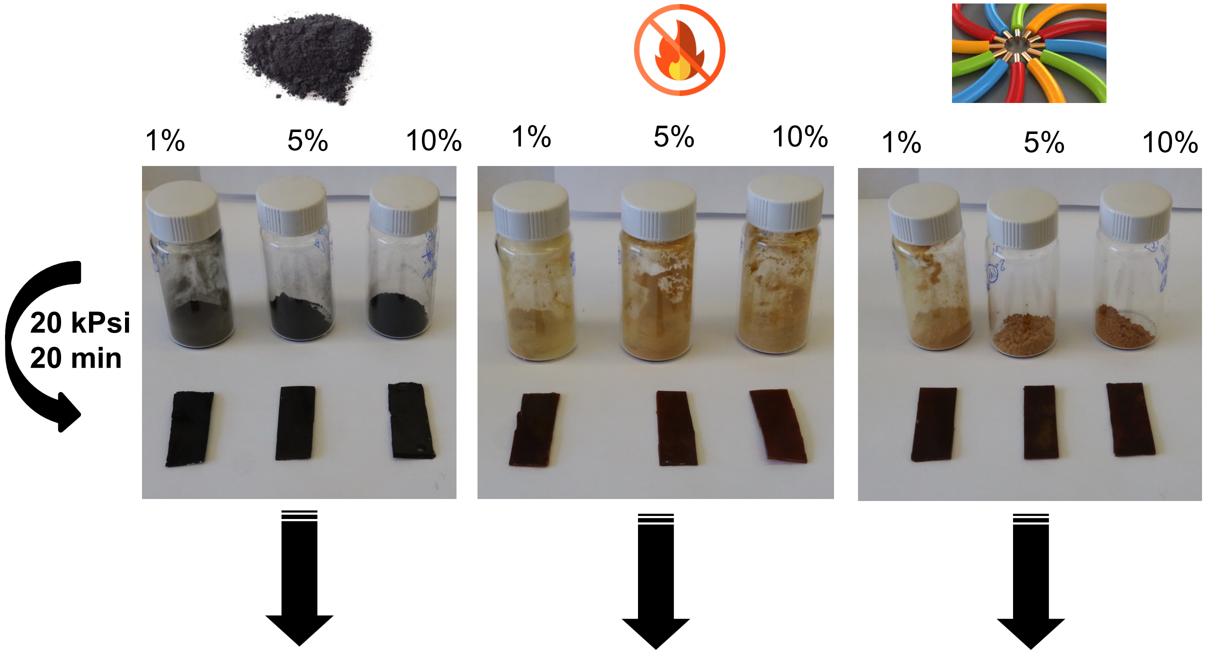
2 – Progress and Outcomes

Milestone 7.4.1: Demonstrate chemical depolymerization of molded vitrimers ≥1 g	Chemically recycle >10 PDK vitrimers with 0–30% w/w filler; recover DKL in >95% yield, >95% purity

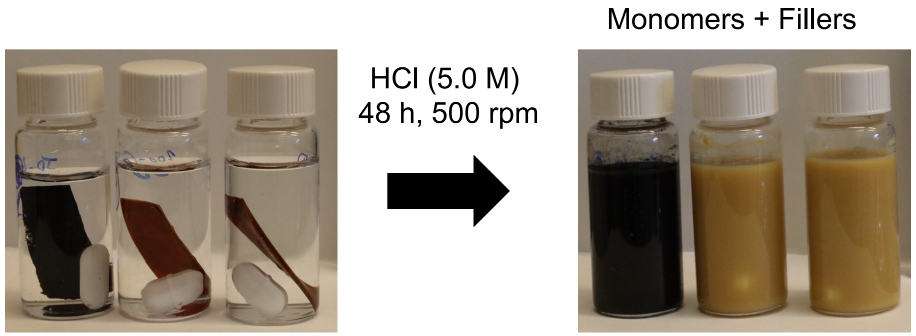
Synthesis of Bio-Vitrimer Composites



Carbon Black (Color) | **Triphenyl Phosphate (Fire-retardant)** | **Dioctyl Phthalate (Plasticizer)**



Depolymerization in Acid



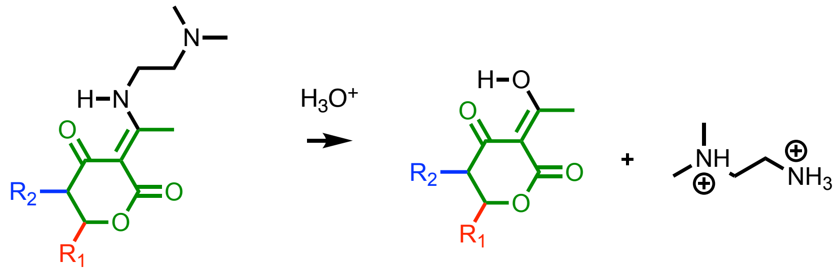
	/	Carbon Black			Triphenyl Phosphate			Dioctyl Phthalate		
	0%	1%	5%	10%	1%	5%	10%	1%	5%	10%
Isolated Yield (%)	90	58	78	80	62	77	75	55	63	83
Purity (%)	95	/	95	97	/	96	98	/	93	96

2 – Progress and Outcomes

BETO review

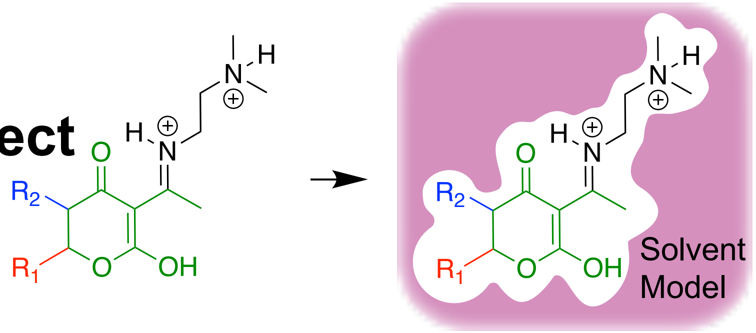
Sub-Task Progress	Outcome
Budget Period 2: Screen >100 γ, δ substituted BKDLs for hydrolysis energy barrier	• Screened 108 BKDLs varying in R_1 and R_2 • Predicted a **strong** effect on the solvation free energy, up to 35 kJ mol^{-1} • Predicted a **weak** effect on the hydrolysis free energy barrier, less than 5 kJ mol^{-1} • **Significance:** Recycling rates can be controlled by choice of R_1 and R_2

Screens for Post-Consumer Chemical Recycling to Monomer



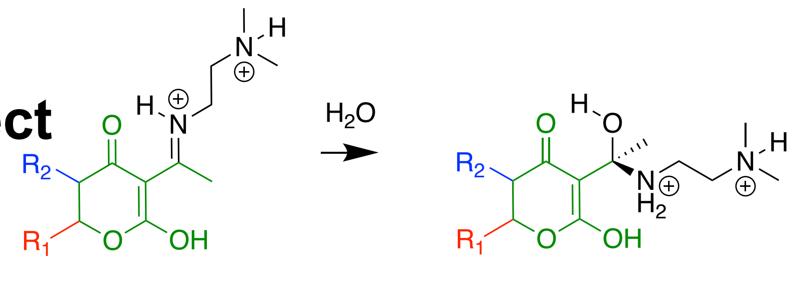
Solvation Free Energy

Strong Effect



Hydrolysis Free Energy Barrier

Weak Effect



2 – Progress and Outcomes

BETO review

Sub-Task Progress	Outcome
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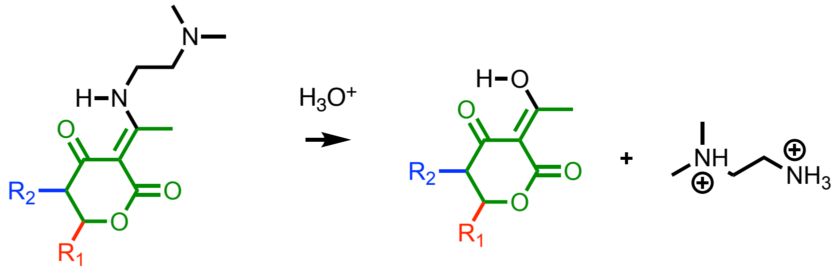
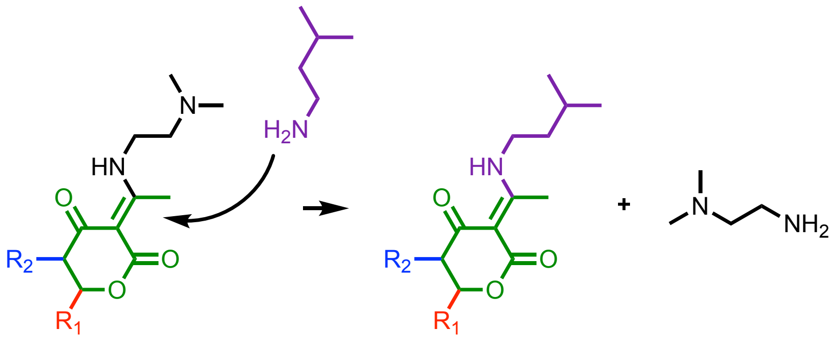
Budget Period 3: Screen >100 γ,δ substituted BKDLs for amine-bond exchange energy barrier	• Screened 16 BKDLs varying in R_1 and R_2 • Predicted a **negligible** effect on the amine-bond exchange energy barrier, < 5 kJ mol^{-1} • **Significance:** Energetics of re-processing PDKs is low and not strongly dictated by R_1 and R_2

Screens for Post-Consumer Chemical Recycling to Monomer

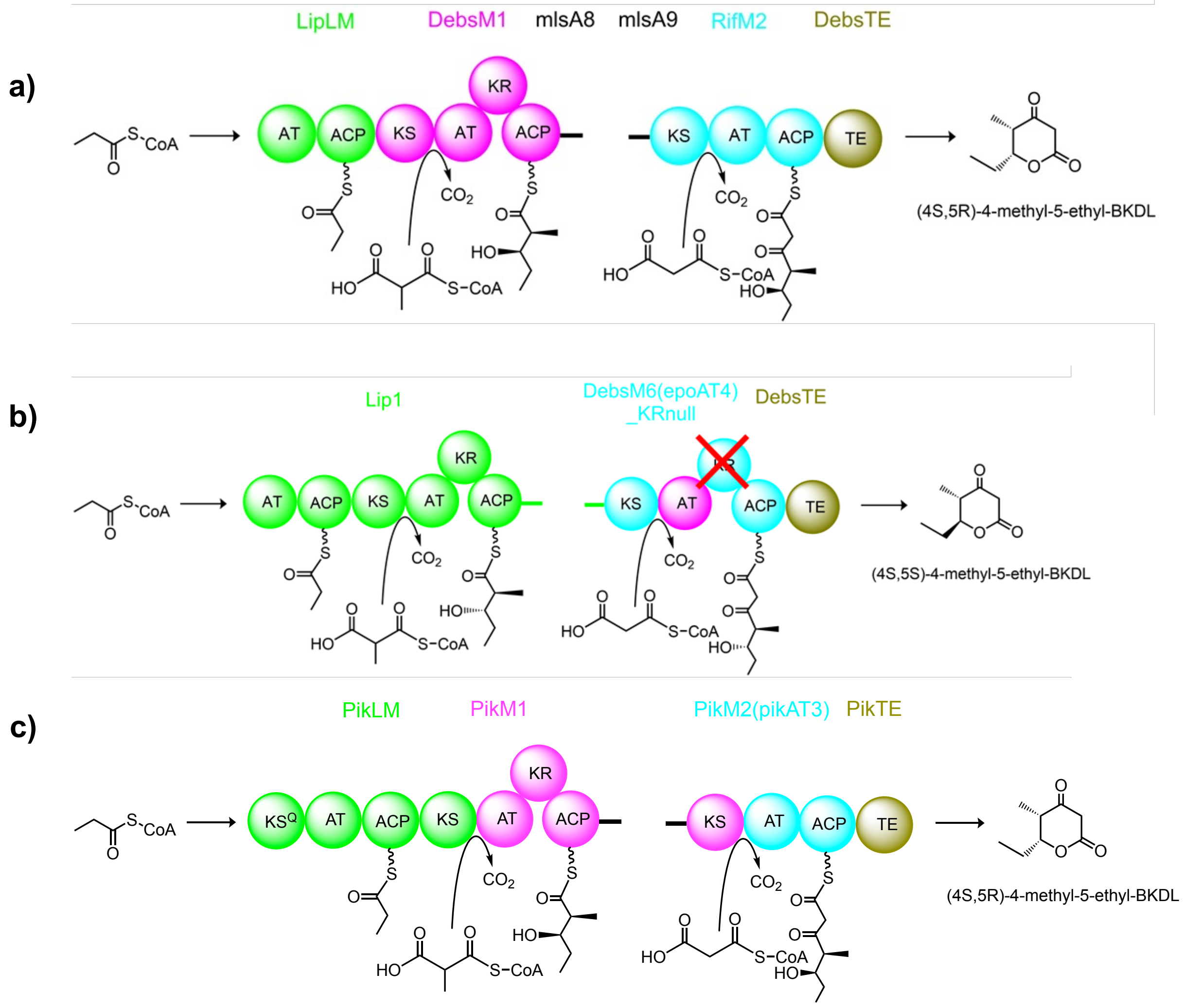


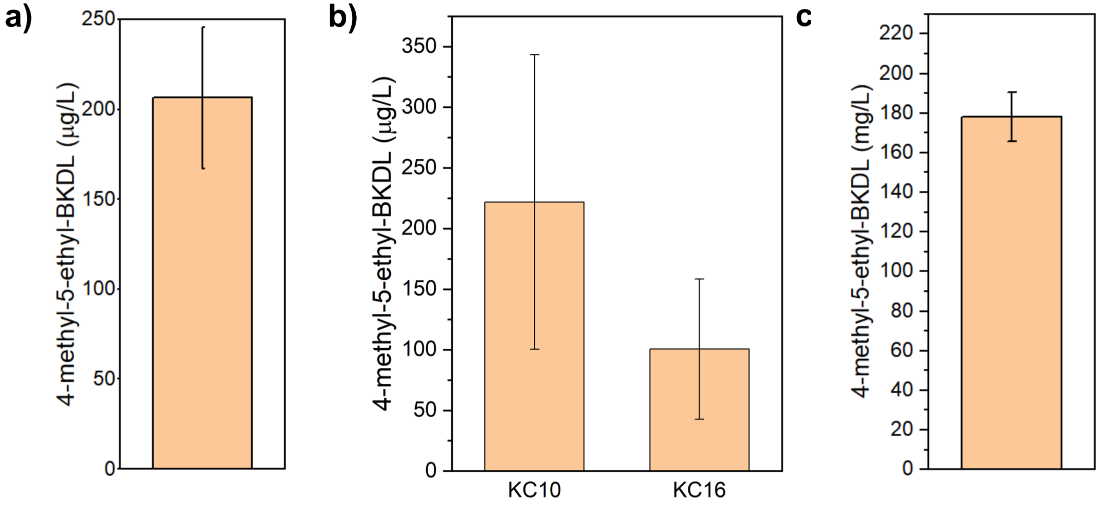
Screens for Post-Industrial Recycling via Scrap Recovery



2 – Progress and Outcomes

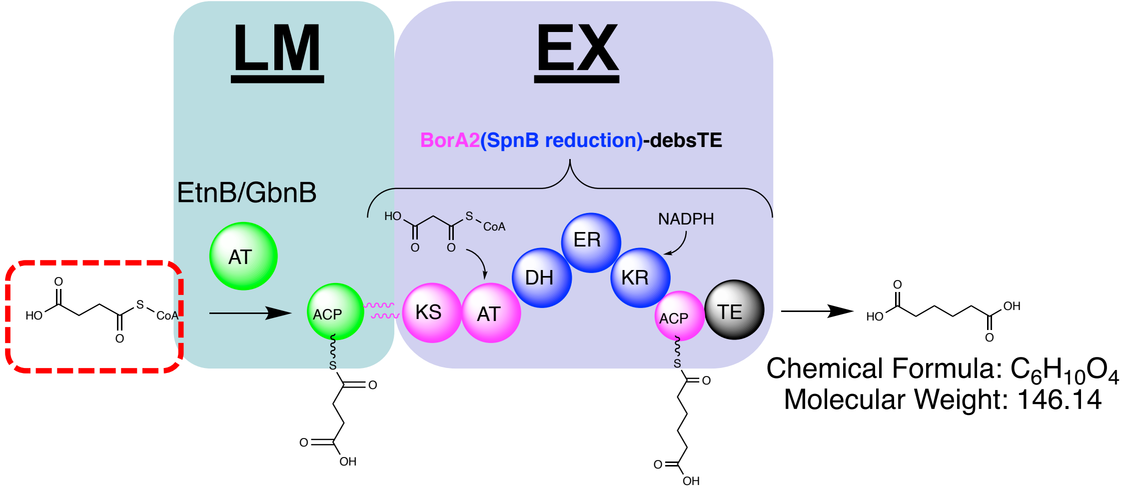
Q8	M6.2.1	UCB reports to LBNL alternate BKDLs that are accessible, to direct LBNL's experimental validation efforts for circularity.	√



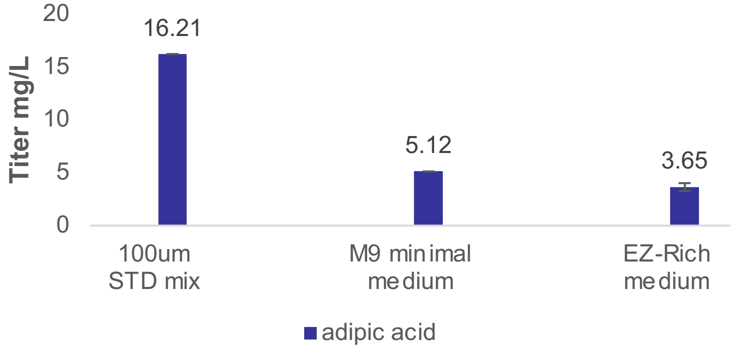


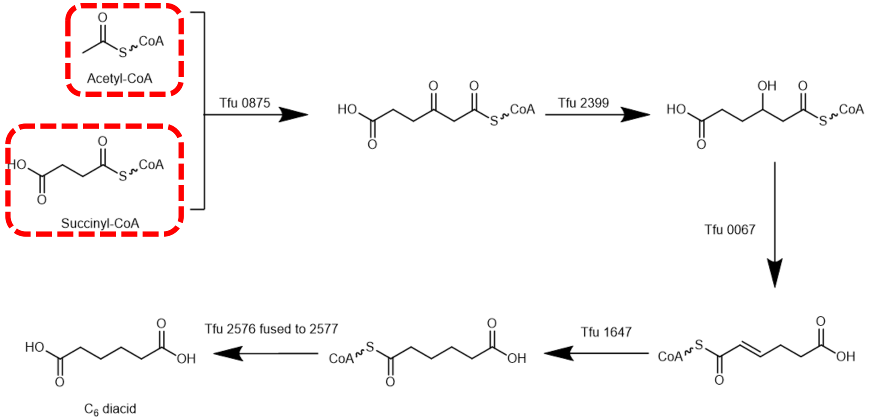
2 – Progress and Outcomes

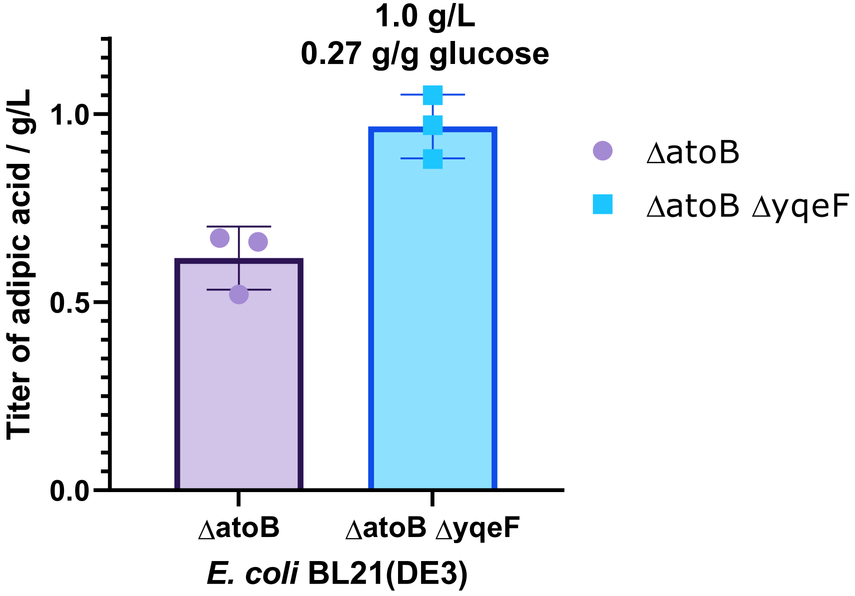
Q10	M6.3.1	UCB measures TRY of C6 diacid production in three hosts. Must confirm production of >10 mg/L in 50 mL shake flasks.	√
BP3	End of Project Goal	UCB will measure the TRY of the C6 diacid at >1 L scale, which must exceed 1g/L and 0.1 g/g based on cellulosic sugars.	√

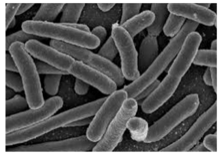
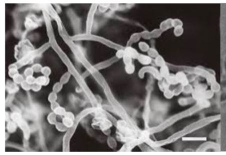
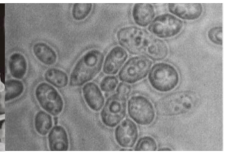
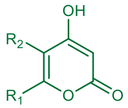
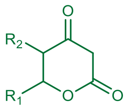
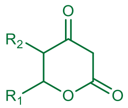
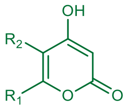
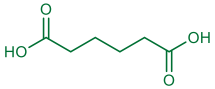


LM: Loading system **EX**: Extension system



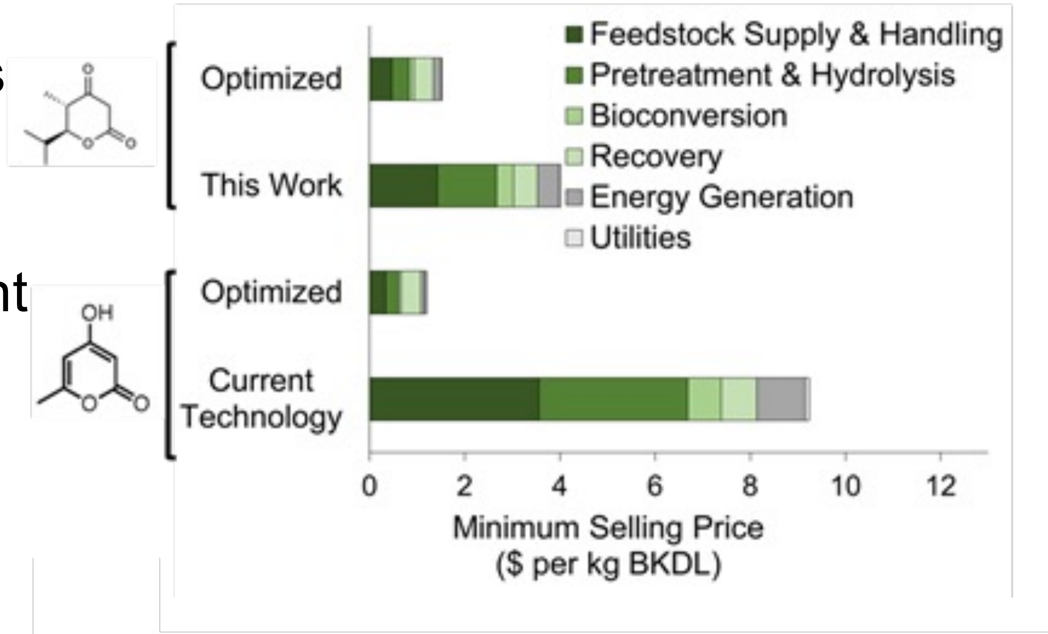


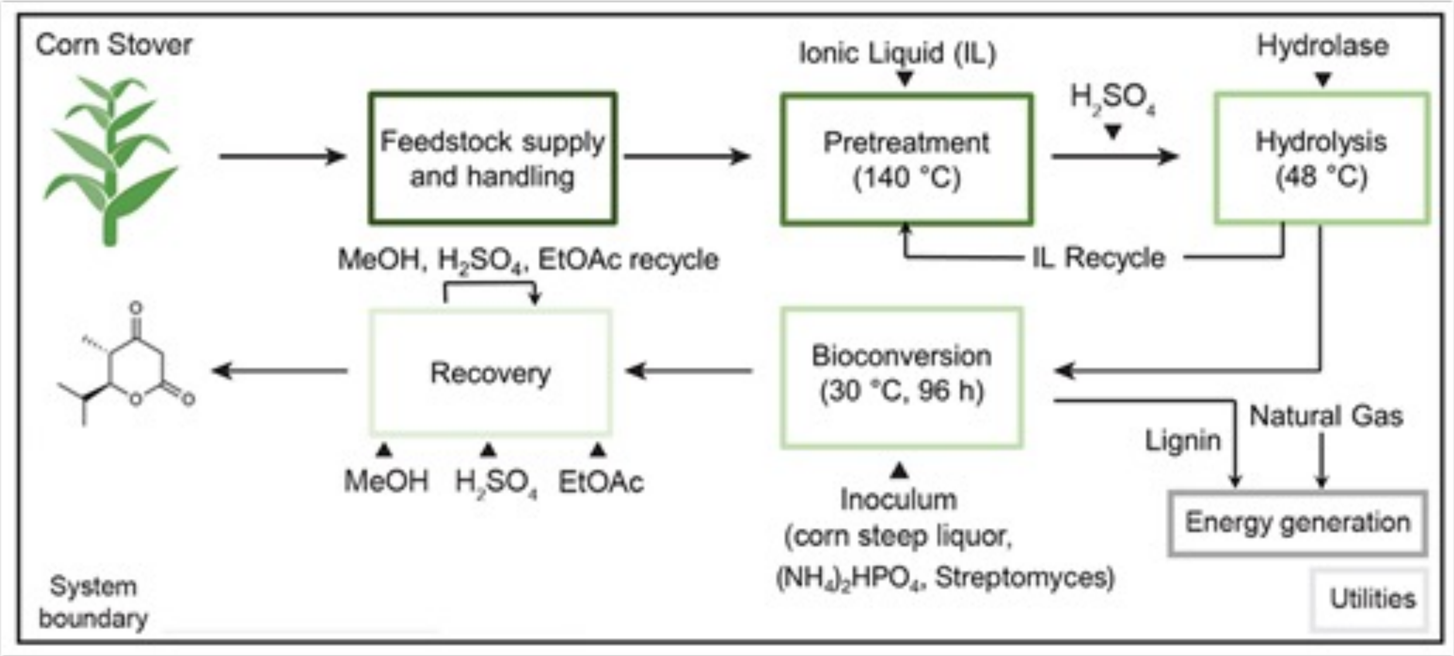


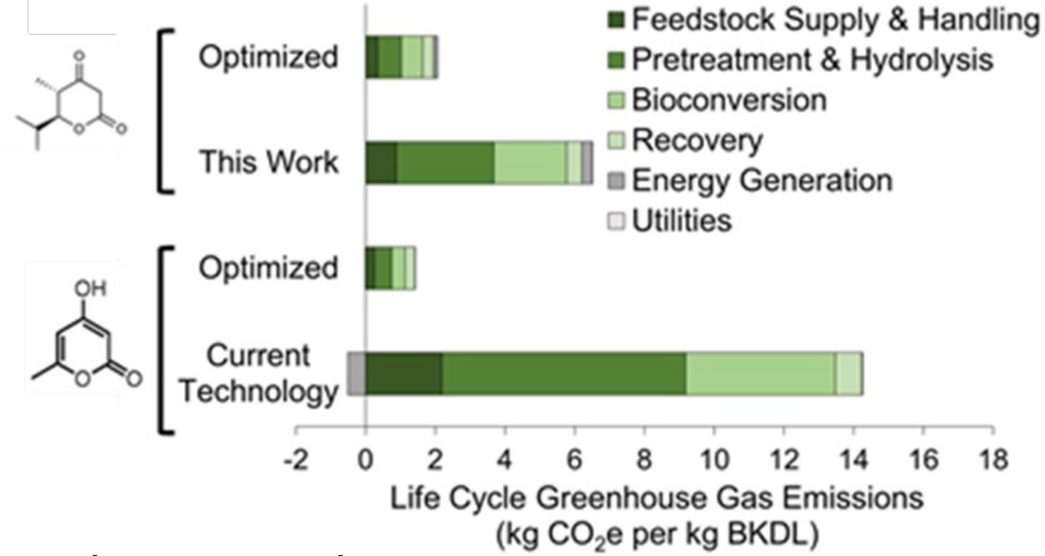
		E. coli 		*S. albus* 	*R. toruloides* 
Task 6.1: Diversification of BKDL ● More BKDLs were synthesized with substrate analogue SNACs *in vitro*					
Task 6.2: Alternate BKDL synthase construction ● Seven different BKDLs produced		2.7 g/L	178 mg/L	78 mg/L	4.7 g/L
		aromatic	aliphatic	aliphatic	aromatic
					
Task 6.3: *In vivo* production of C6 diacid ● Successfully produced in *E. coli*		1.0 g/L			
Task 6.4: Pathway discovery for C8 diacid ● A novel pathway designed and developed in *E. coli* and *S. albus*		*Not tested*		*Not tested*	

2 – Progress and Outcomes

- Technoeconomic analysis & life-cycle GHG emissions of bio production of aliphatic/aromatic BKDL
- TEA/LCA-informed potential of BKDL as a replacement of dimedone, with moderate improvement in yield and utilizing a co-fermenting host.



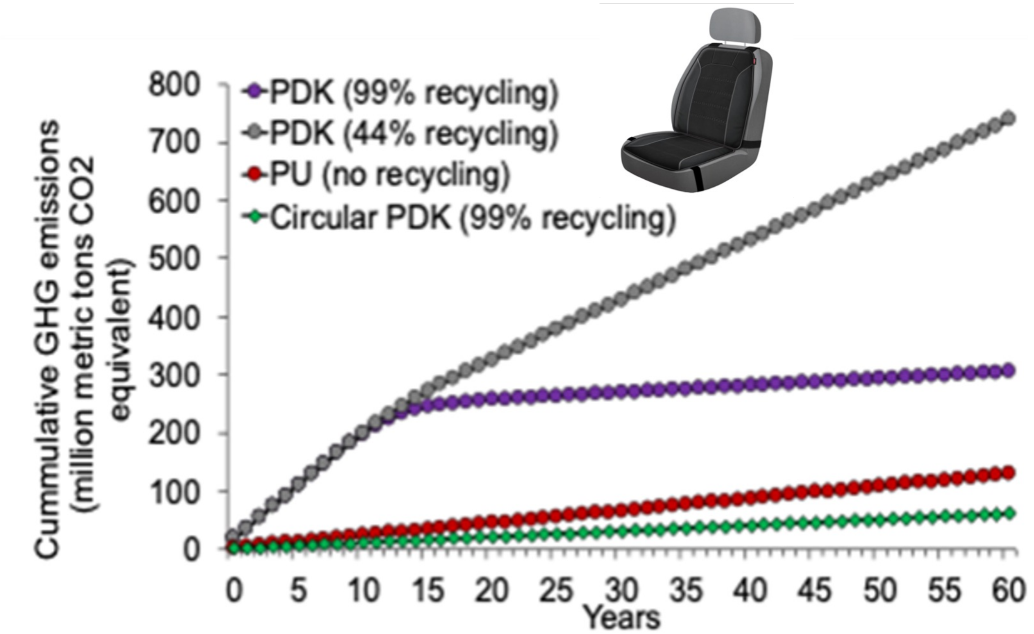




Source: Wang et al. manuscript under preparation

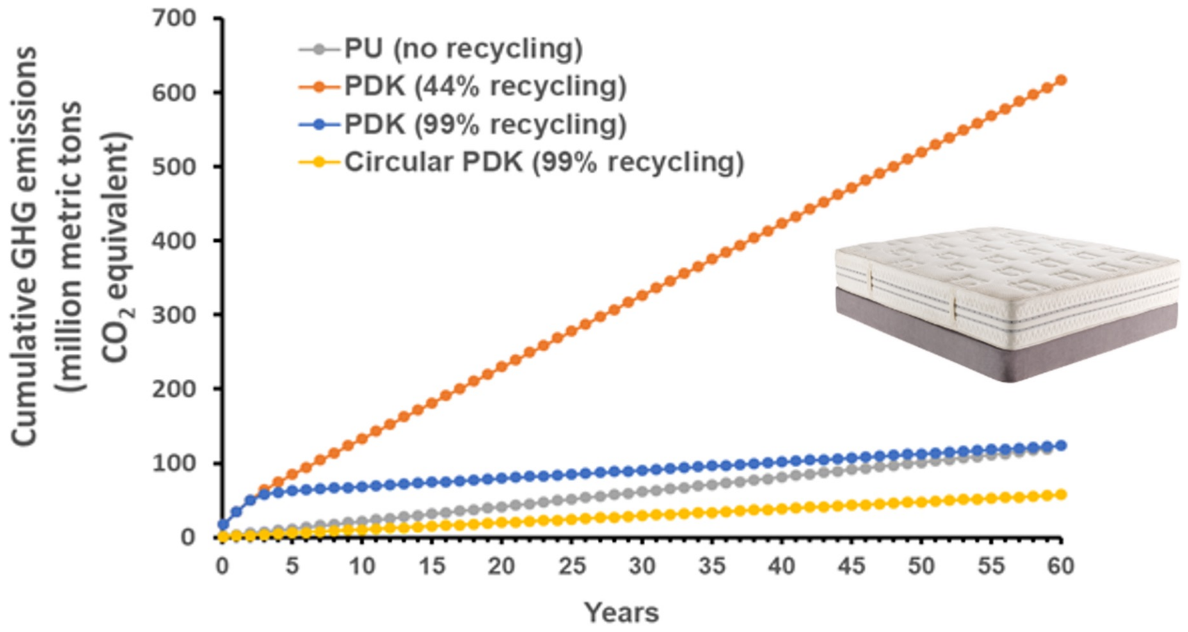
2 – Progress and Outcomes

Milestone 8.2.1: Report life-cycle cost results based on at least 2 end-use functional units, incorporating EOL differences from base case.	Automotive seat cushions and bed mattresses chosen as end-use functional units.



Source: Demarteau et al. (2022) *ACS Sust Chem. & Engg*

Based on the incorporation of PDK as a replacement for polyurethane foam in passenger vehicles.

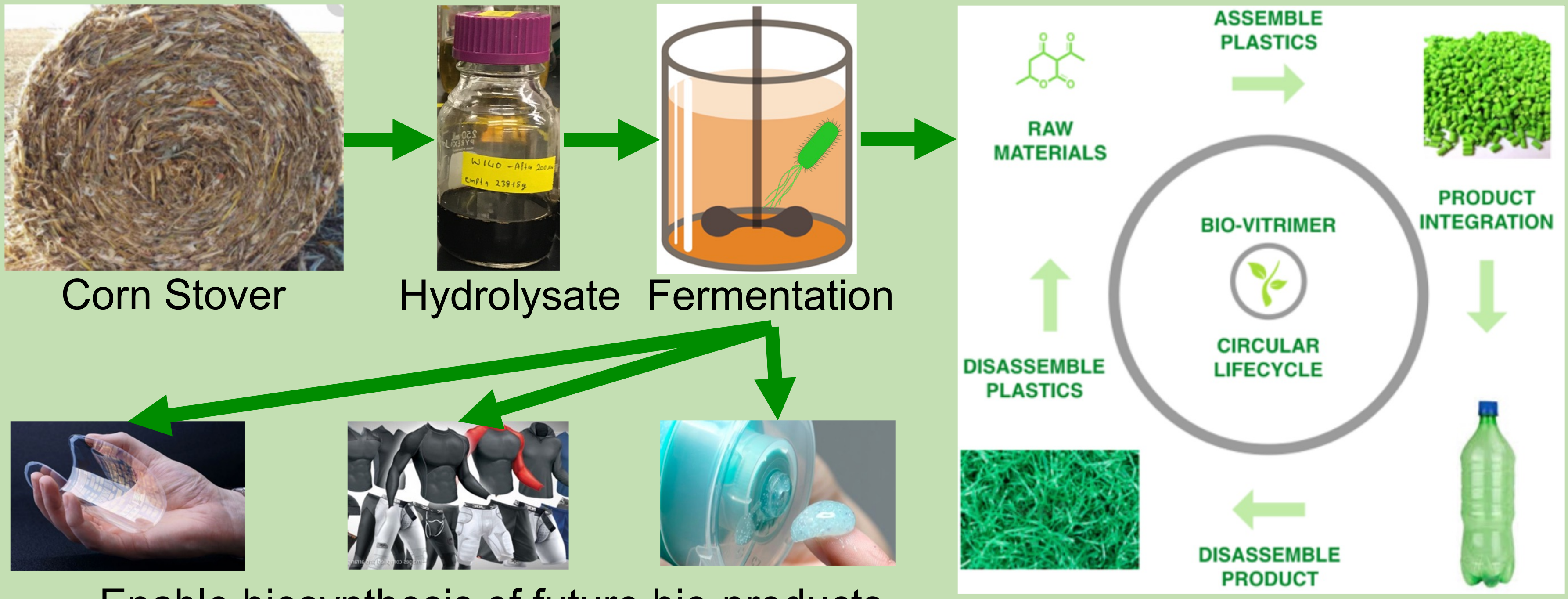


Source: Bose et al. Manuscript under compilation

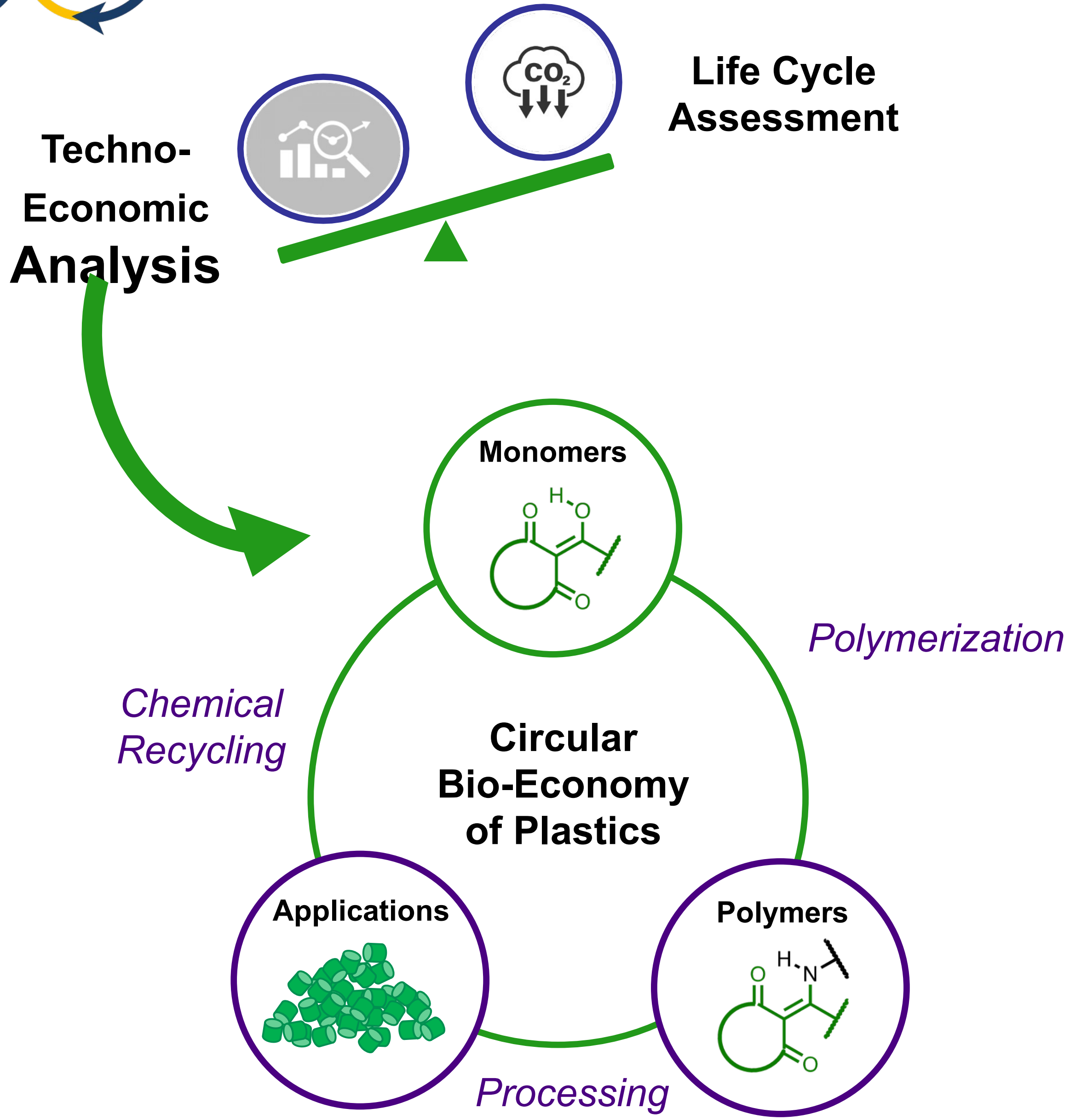
Based on the incorporation of PDK as a replacement for polyurethane foam in bed mattresses.

3 – Impact

BETO review

Biosynthesis lowers intensity of feedstock production and refinement and enables resilience in manufacturing supply chains	 Enable biosynthesis of future bio-products
High-throughput DNA assembly	A platform for design and building *bkdl* genes & testing in high-throughput.
Proper hosts for biosynthesis	Host optimization for biosynthesis of diverse polyketide products

3 – Impact



Removal of fillers from composites with circular PDK towards a more sustainable manufacturing

Feasibility of Bio-PDK Resins production that is cost-competitive in the market

Reduction in GHG emissions through introduction of circular PDK

Applications of PDK in durable goods that currently lack plastic recycling initiatives

Summary

1. Approach:
- Identify BKDL targets via screens of hydrolysis activation barrier for using DFT and MD
- Close the loop in Design–Build–Test–Learn for BKDL production with high-throughput platform.
- Integrate BDKLs into Bio-Based PDK resins and validate predictions for performance and recyclability.
- Model of process chemistry and assess impact of bio-products on sustainability targets for circularity

2. Progress and Outcomes:
- Demonstrated PDK vitrimer production with >80 % bio-content and >95% resource recovery.
- Diversify the BKDLs with 7 different structures and produce adipic acid > 0.15g/L.
- Built model for bio production of BKDL.
- Built model for prediction of replacement of PUF with circular PDK in application-specific case studies.

3. Impact:
Vitrimers can be synthesized from sustainable resources with a reduced environmental impact. Vitrimers can be predicted and designed to be recyclable and non-toxic. Techno-economic analysis and life-cycle assessment informs best path to commercialization.

Quad Chart Overview

Timeline
- 07/01/2019
- 03/31/2023

	FY22 Costed	Total Award
DOE Funding	*(10/01/2021 – 9/30/2022)* *$524,001*	*(negotiated total federal share)* *$1,017,861*
Project Cost Share *	$140,687.89	$499,466

TRL at Project Start:
3. Proof-of-Concept Research

TRL at Project End:
8. Final Testing and Evaluation

*Only fill out if applicable.

Project Goal
Design and develop infinitely recyclable and therefore closed-loop polymeric bio-based materials, specifically focusing on a new class of polymers called vitrimers that combine the processing and recycling ease of thermoplastics with the performance advantages of thermosets.

End of Project Milestone
Demonstrate 1g/L of C6 diacid in fed-batch fermenter. Demonstrate PDK vitrimer platform technology readiness wrt formulation and circularity: both chemical recyclability and scrap recovery for 10-g vitrimer samples with >75% biomass content, <1% VOC content, 0–30% w/w filler.

Funding Mechanism
DE-FOA-0001916, Topic 3a. Performance Advantaged Bioproduct Identification

Project Partners*
- Lawrence Berkeley National Laboratory

Additional Slides

Responses to Previous Reviewers' Comments

- 1. No connections to industry advisors and yet this will be required to deliver an impact with clear commercialization potential.

Response: We have deeply developed a network of industry advisors, including C-level executives of major chemical companies (Jean Sentenac, CEO, Axens; Hartwig Michels, President of Petrochemicals, BASF; etc.). We also have NDAs and MTAs with BASF, Arkema, Proctor and Gamble, Clorox, Ford, and others. We were not asked to provide this information in the 15-minute talk. Nevertheless, we have done this. We are also pursuing funded collaborations with these partners to scale-up the research products from this BETO project.

- 2. Without significant improvements in material properties, the potential market penetration of circular PDK polymers likely will be limited vs. low-cost and well-known properties of HDPE and PET in major markets.

Response: The reviewer misunderstood our directions; we are not expecting to displace PET or HDPE. We are expecting to displace non-recyclable polyamides and polyurethanes. We have substantially demonstrated performance improvements over those materials in bio-based formulations and have maintained lossless circularity in recycling outcomes. We have further carried out detailed analysis of the economics and pricing to assess potential roadblocks to commercialization.

- 3. Can they clarify whether they will narrow the number of candidates for microbial host strain development?

Response: Regarding the host development, we will focus on one or two hosts which are good for the BKDL production. The hosts working well with PKS genes and supplying a rich amount of necessary CoA esters will be preferred. The future strain engineering will focus on these aspects.

Publications, Patents, Presentations, Awards, and Commercialization

- Publications

Leveling the cost and carbon footprint of circular polymers that are chemically recycled to monomer. *Sci. Adv.* **7**, eabf0187 (2022).
Lower-Cost, Lower-Carbon Production of Circular Polydiketoenamine Plastics. *ACS Sustain. Chem. Eng.* **10**, 2740–2749 (2022).
Circularity in mixed-plastic chemical recycling enabled by variable rates of polydiketoenamine hydrolysis. *Sci. Adv.* **8**, eabp8823 (2022).
Helms, B. A. Polydiketoenamines for a Circular Plastics Economy. *Acc. Chem. Res.* **55**, 2753–2765 (2022).
Biorenewable circularity in triacetic acid lactone polydiketoenamine plastics. *Nat. Sust.* Manuscript under review (2023).

- Patents

Bio-Renewable Polymers and Uses Thereof
Microbial Production Of Monomers For Recycling Of Plastic Polymers LBNL 2022-001-01
Triacetic Acid Lactone Production by Thiolase BktB from Burkholderia B23-032; LBNL 2022-151-01