# Synthesis and Analysis of Performance-Advantaged Bioproducts

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

PI: Gregg T. Beckham, National Renewable Energy Laboratory

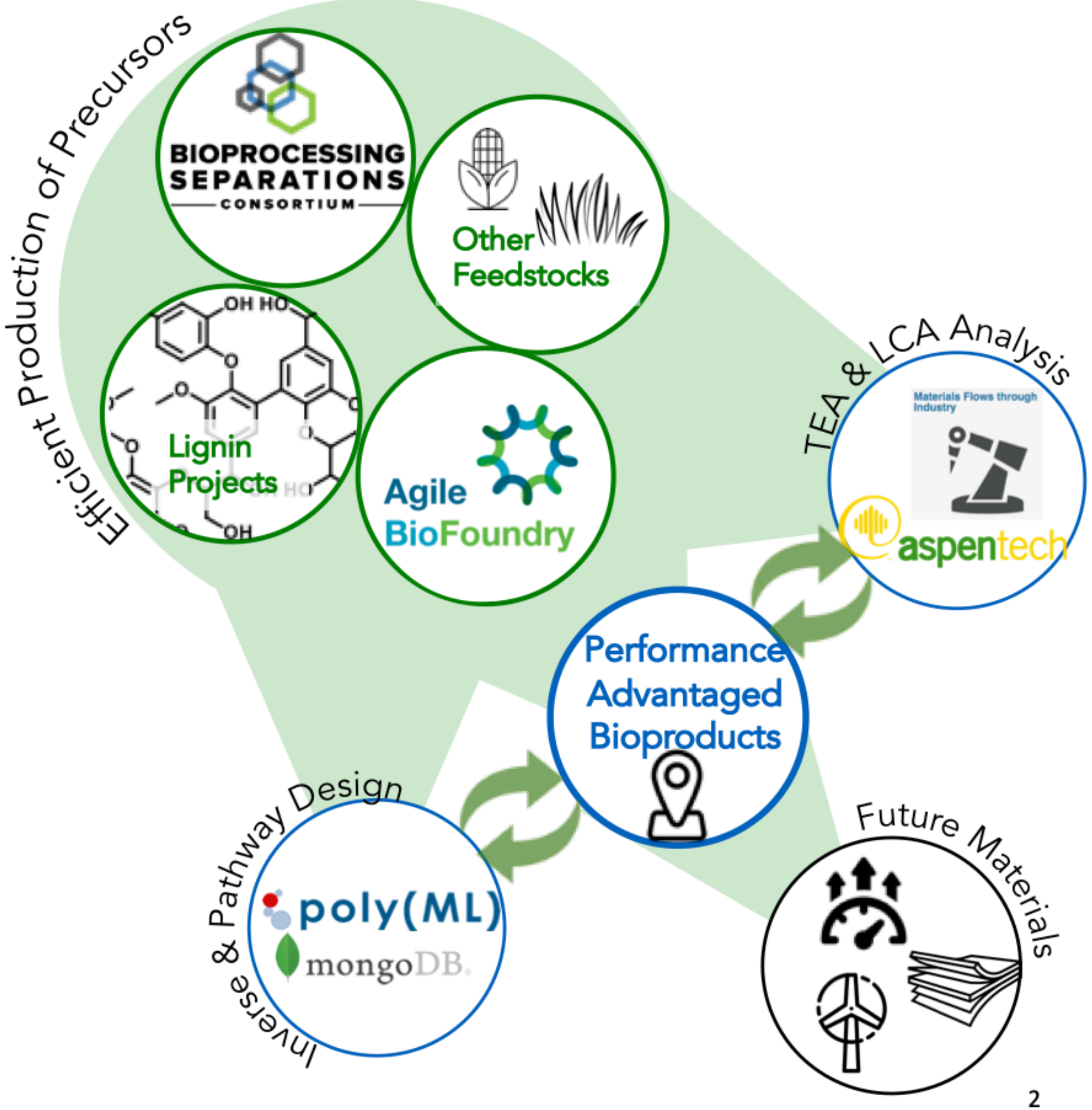
# Project overview

**Goal**: Synthesize, characterize, and conduct analysis for economic, sustainable performance-advantaged bioproducts (PABPs)

- ≥50 candidates in 3-year cycle, ≥10 PABPs
- Work with Inverse Design (ID) *et al*. to develop a computational-experimental framework for PABPs
- Subcontract with Northwestern & Iowa State
- Project started in FY18

**Heilmeier Catechism:**

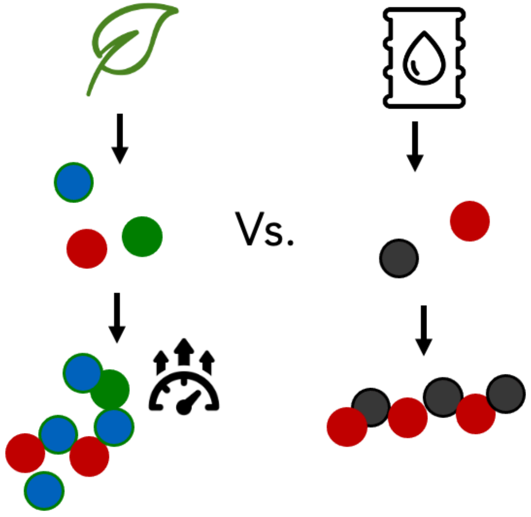
- **Aim**: incentivize bioeconomy investments via PABPs
- **Today**: Huge field of biochemicals, Edisonian methods to develop PABPs is resource-intensive
- **Important**: PABPs can accelerate the bioeconomy
- **Risks**: Full PABP characterization not always obvious – requires early collaboration; syntheses often time consuming when building blocks are unavailable



# Management

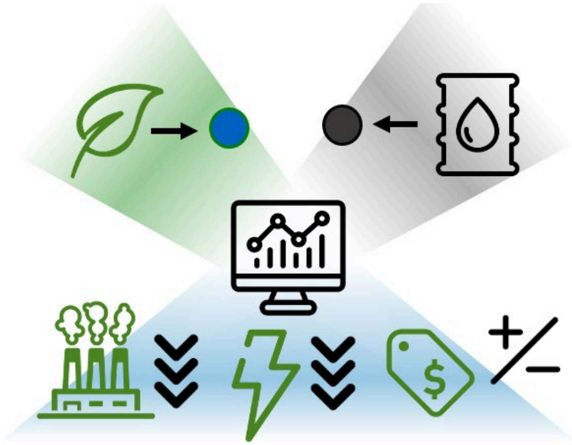
## Task 1: PABP Synthesis and Characterization

- Experts in synthesis and characterization: R. Cywar, C. Hoyt, N. Rorrer
- Milestones: **PABP synthesis, characterization**
- Collaborate with BETO projects and universities including E. Chen (CSU) Y. Román (MIT), G. Huber and S. Stahl (U Wisconsin)



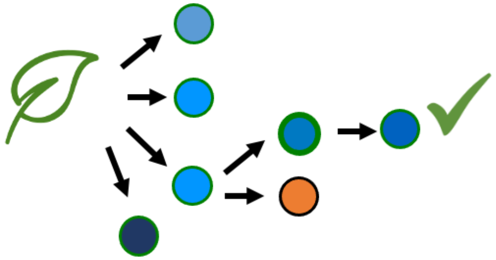

## Task 2: PABP Analysis

- Experts in TEA and LCA: S. Nicholson, A. Singh
- Milestones: **Analysis of PABPs, supply-chain modeling of incumbents and PABPs**



## Task 3: PABP Pathway Design

- Led by **Linda Broadbelt** (Northwestern) **Brent Shanks** (Iowa State)
- Milestones: **computational tool development** with Inverse Design and analysis efforts



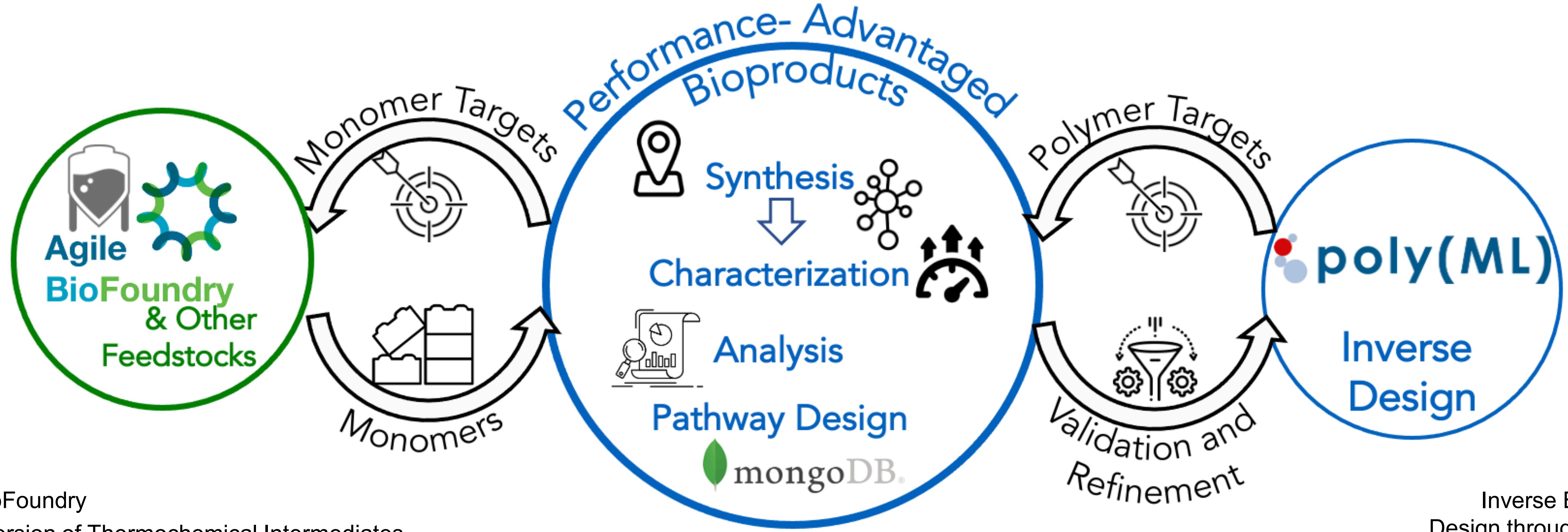
## Project organization:

- Fortnightly meeting with ID project
- Monthly mtgs with PI-staff, PI-postdocs
- *Ad hoc* meetings with metabolic engineering, lignin, SepCon projects
- Ops & Project Mgrs – labs, equipment, reporting, finances

## Risks:

- Bio-based building blocks for PABPs are often not commercially available
- Potential number of PABPs to synthesize and characterize is vast
- Industrial performance metrics are not fully known
- Current TRL rarely includes prototype production

# Management: Project interactions




**Projects:**

- Agile BioFoundry
- Bioconversion of Thermochemical Intermediates
- Biological Lignin Valorization, Lignin-First Biorefinery Development, Lignin Utilization
- Separations Consortium
- Multiple academic collaborators

**Projects:**

Inverse Biopolymer Design through Machine Learning and Molecular Simulation

**This project resides at the nexus of multiple projects**

- Projects in BETO portfolio and external collaborators provide building blocks for PA chemicals and polymers
- This project receives predictions for target polymers from ID and provides feed back to enhance datasets

# Approach

## Technical approach:

- Work with ID project to narrow design space and explain experimental observations
- Experiments focus on PABP syntheses & characterizations
- AspenPlus and Materials Flows through Industry (MFI) for analysis
- Report new PABPs via integrated publications and patents

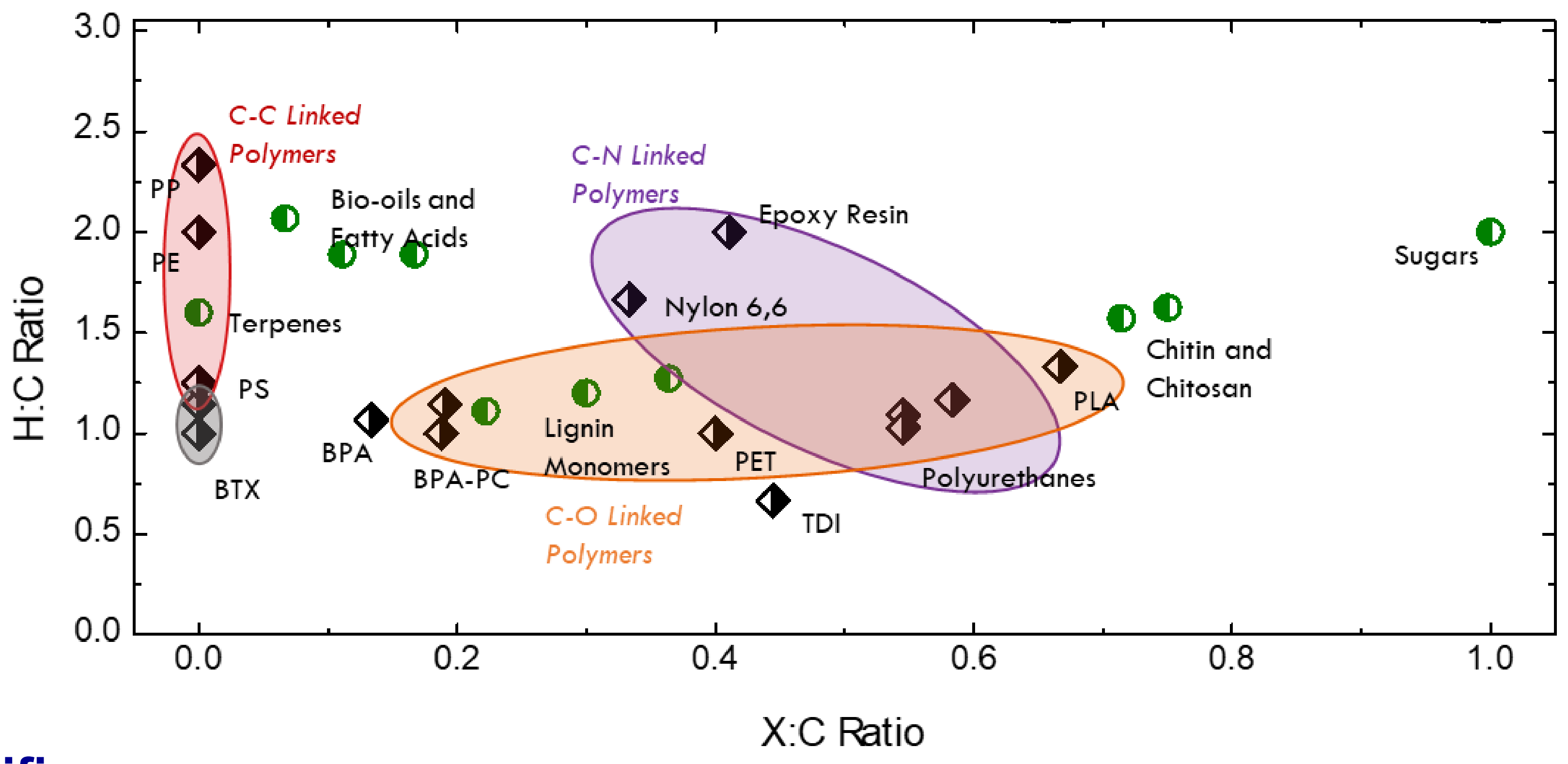
## Challenges:

- Comprehensive characterizations not always obvious – requires collaborations with end-users
- Syntheses for new molecules or polymers are often time-consuming
- Tech. transfer often requires kg quantities of PABPs

## Major milestones, Go/No-Go Decisions:

- FY21: Produce ≥ 5 polymers from PolyML predicted to be PABPs
- FY21: Quantify the energy and GHG emissions of commodity chemical consumption in the US
- FY22: Conduct TEA and MFI for ≥2 non-polymer PABPs
- FY23: Produce ≥50 PABPs, demonstrate ≥10 as PABPs w/in 25% cost of incumbent

# Impact




Van Krevelen diagram showing chemical distances of feedstocks to polymers (X is a heteroatom, typically oxygen or nitrogen)

**Scientific:**

- The heteroatom functionality of biomass makes it ideal for PABPs, including polymers
- Combine computation (ID) & experiment to narrow design space to target PABPs we *should* produce
- TEA and MFI (LCA) to compare cost and sustainability of PABPs to their fossil counterparts
- Field-leading publications in PABPs (e.g. Johnson *et al. Joule* 2019; Cywar *et al. Nature Reviews Materials*, 2021)
- Ultimate goal – set of analysis, computation, and experimental tools to narrow PABP design space

# Impact

**Industrial:**

- Actively pursuing proposals via Technology Commercialization Funds for tech. transfer
- Tech. transfer and industry engagement ongoing via Energy I-Corps
- Experimental R&D coupled with analysis can de-risk technology prior to industry collaboration
- Scaling up polymer production in several cases for industrial partner testing

ENERGY I-CORPS U.S. Department Of Energy

biolyst renewables

NITRICA RENEWABLE ACRYLONITRILE

Cycle

**Overall:**

The two PABP projects *together* aim to deliver rigorous tools to **design, produce, and analyze PABPs** in collaboration with BETO projects and with academic and industrial partners

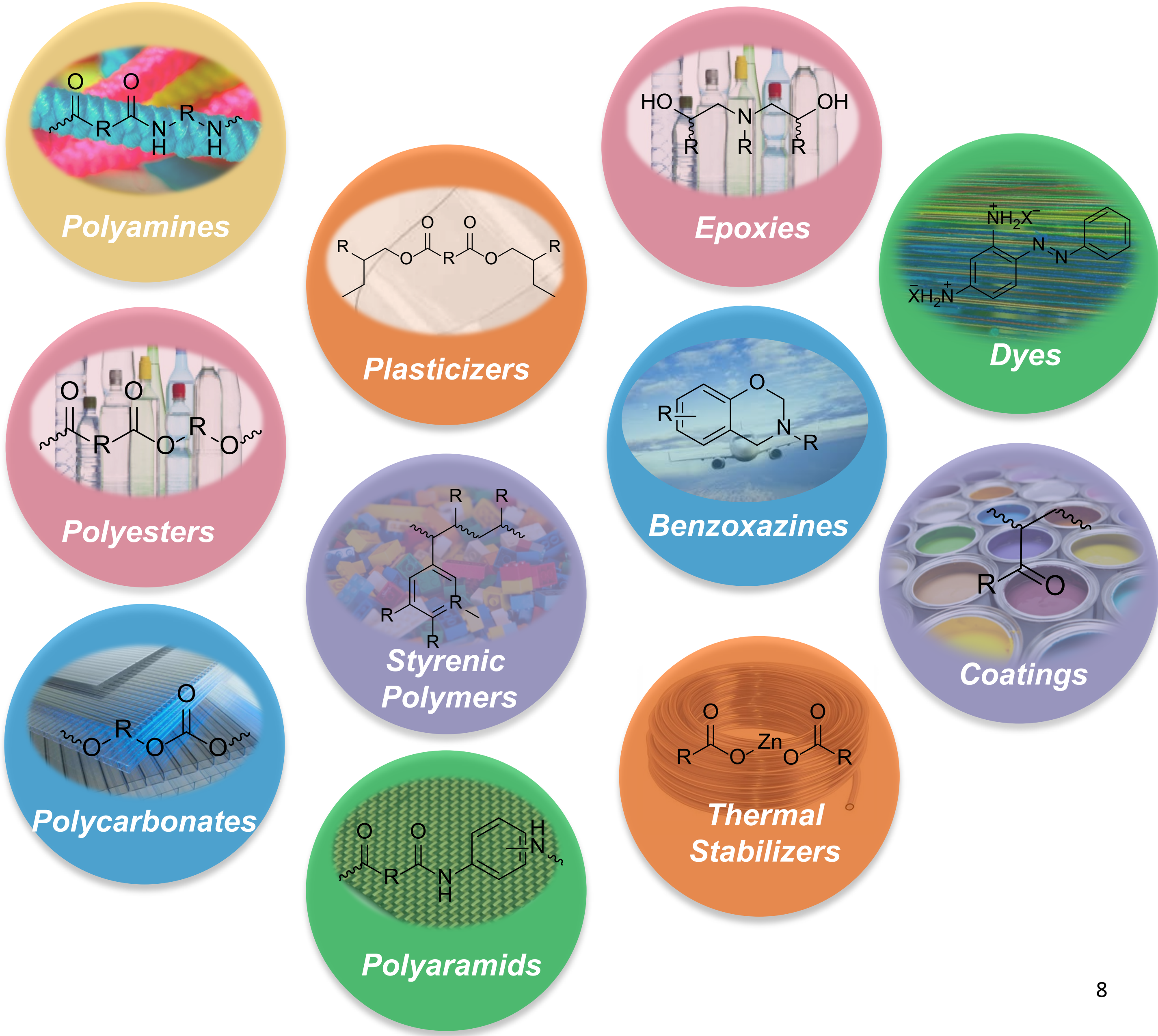
# Progress and Outcomes

## Synthesis/characterization progress:

- Performance-advantaged nylons enabled by β-keto acids
- New thermosets from aromatic amines and corresponding TEA/LCA
- New directions in plasticizers and stabilizers
- Summary of PABP syntheses
- Synthesis of polymers from ID project

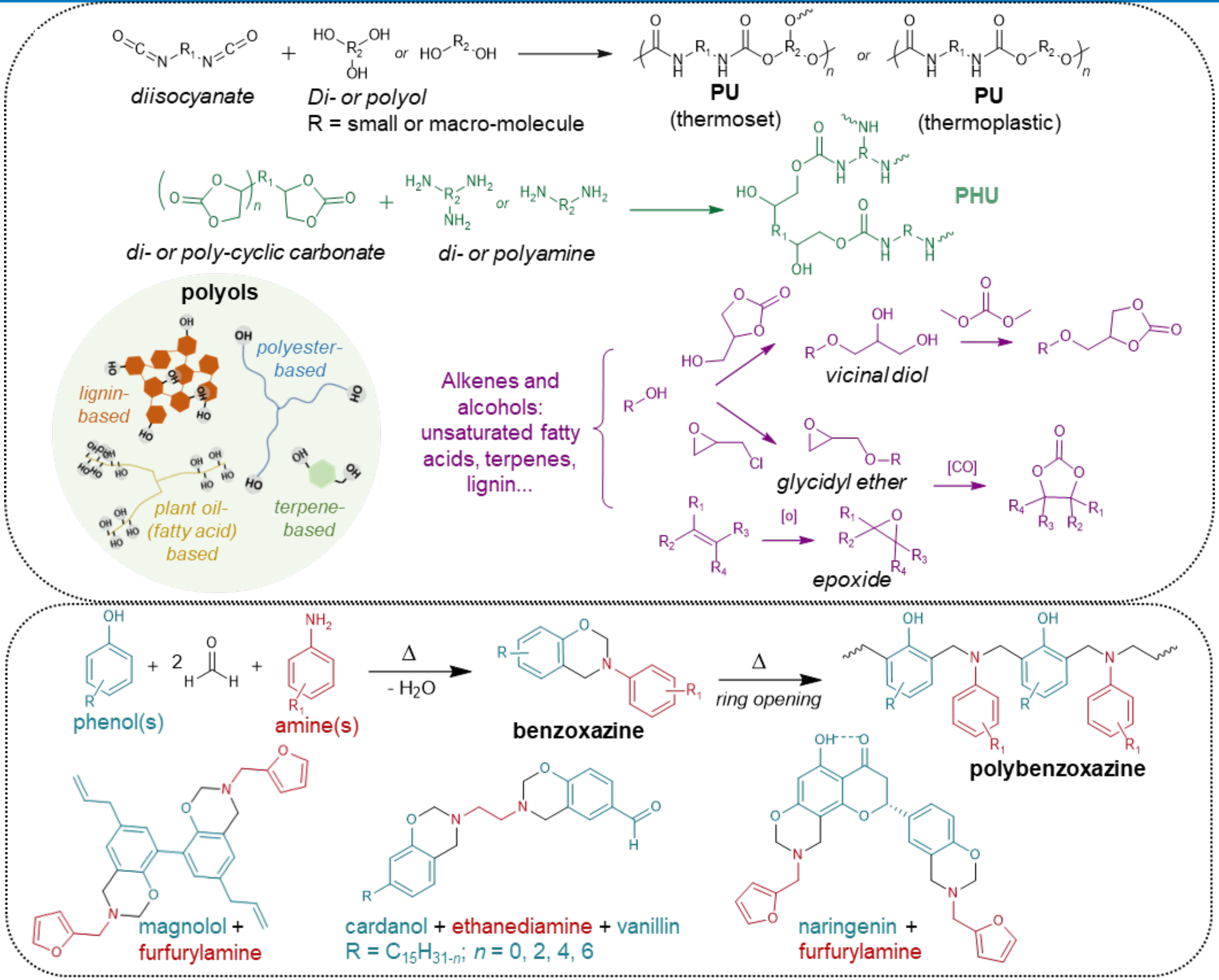
## Analysis

- New directions in analysis and computational modeling with ID project



# Forthcoming review on performance-advantaged bio-based polymers

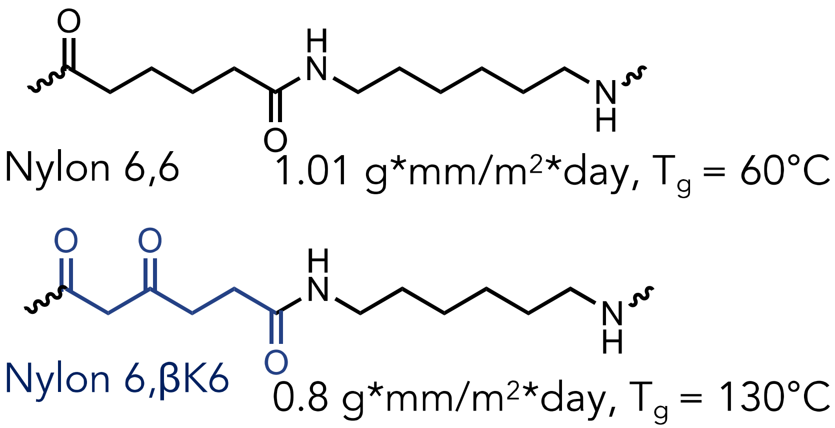
- PA properties, derived from bio-based functionality, are critical to commercial success (vs. direct replacements)
- Scope: C-O and C-N linked backbone polymers with demonstrated performance advantages in **Manufacturing, In-Use, End-of-life**

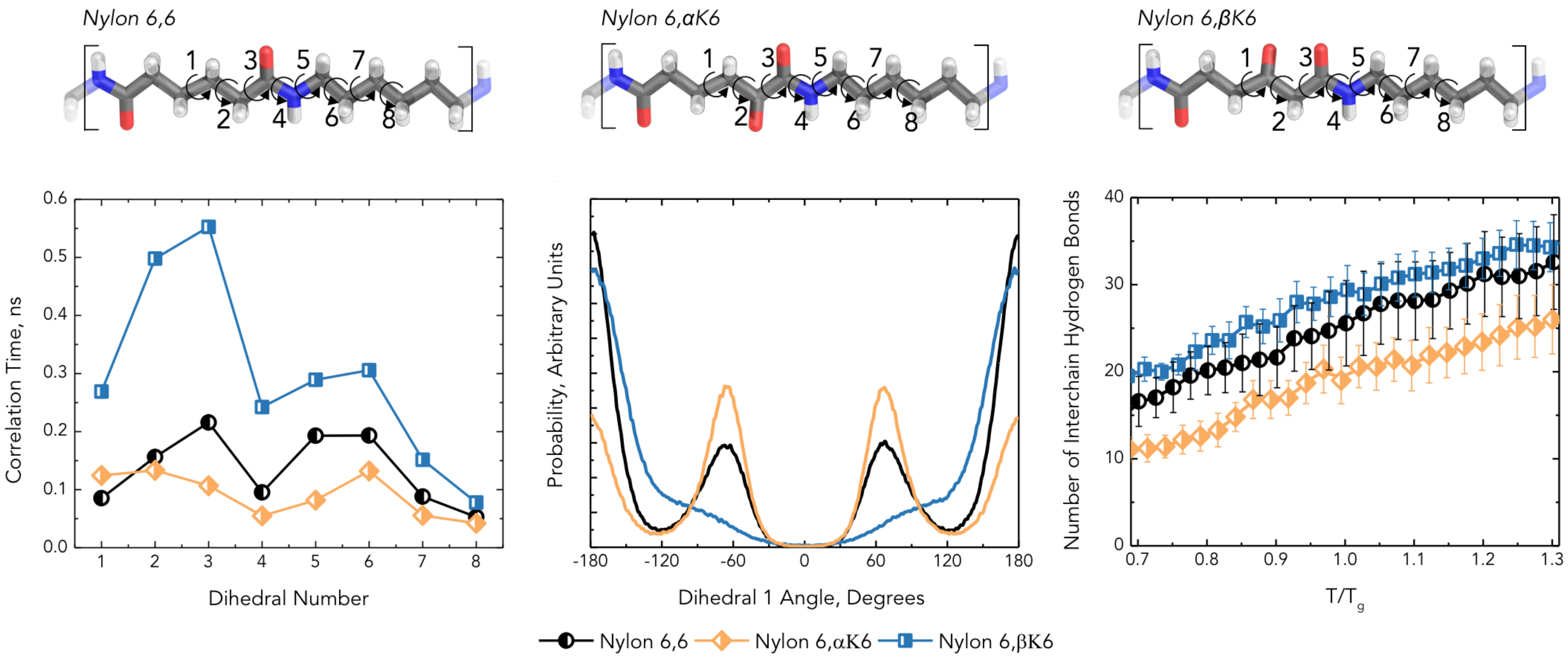



Cywar, Rorrer, Hoyt, Beckham, Chen, *Nature Review Materials*, in press

*Example figure panels showing how bio-derived functionality (polyols, alkenes, phenols, amine) results C-N polymers (performance-advantages described in-text)*

# Performance-advantaged nylons enabled by β-keto diacids



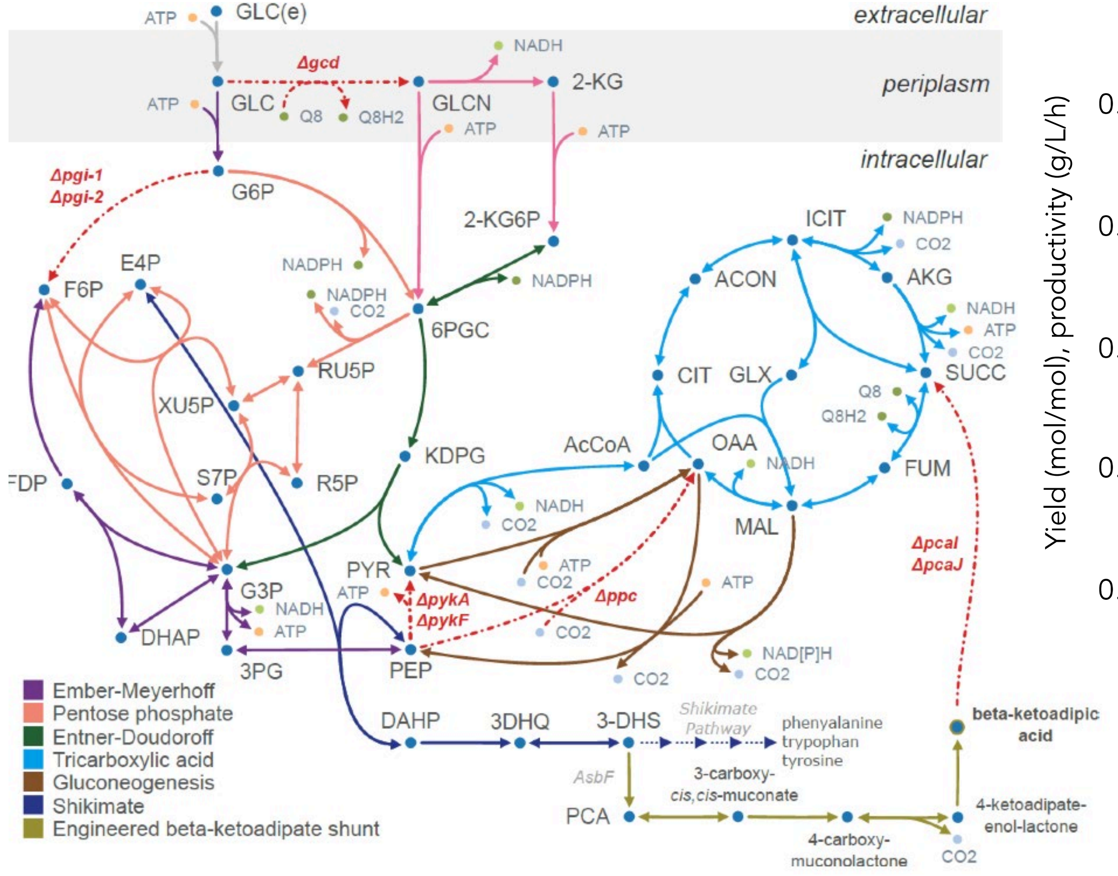



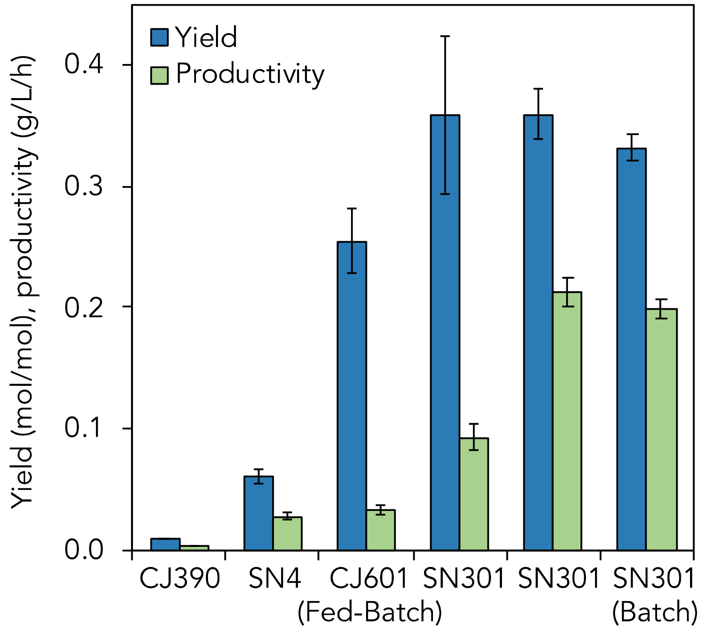

### C6 dicarboxylic acids with β-ketone enable enhanced nylon performance

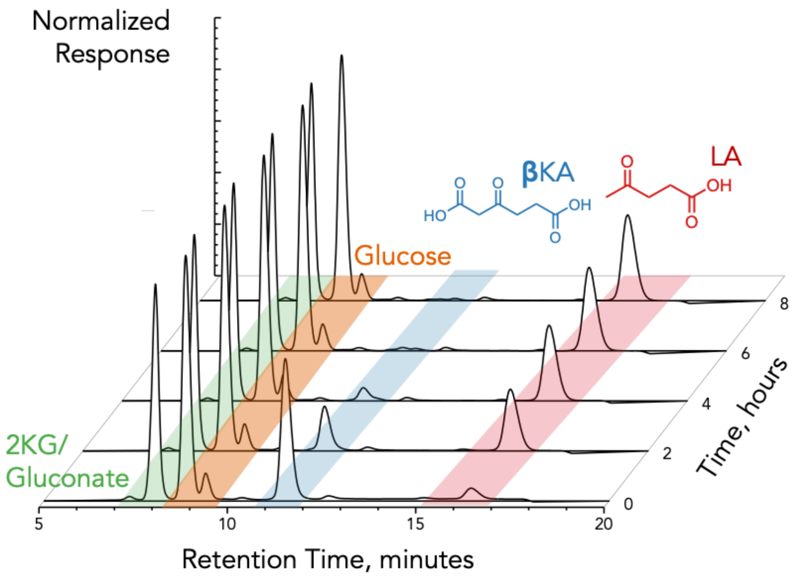
- Nylon 6,6, absorbs water, providing a target for improvement
  - Improved thermal properties can provide robust material performance for automotive and textile applications
- The β-ketone reduced water permeability by 20% while simultaneously increasing the T$_g$ by 216%
- Molecular simulations (ID) used to understand β-ketone properties

Rorrer *et al.*, in review

# Performance-advantaged nylons: an interdisciplinary approach



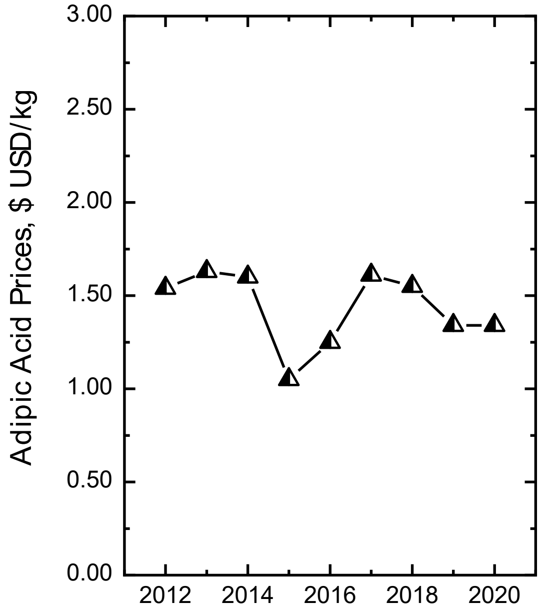

## βKA investigation spans disciplines

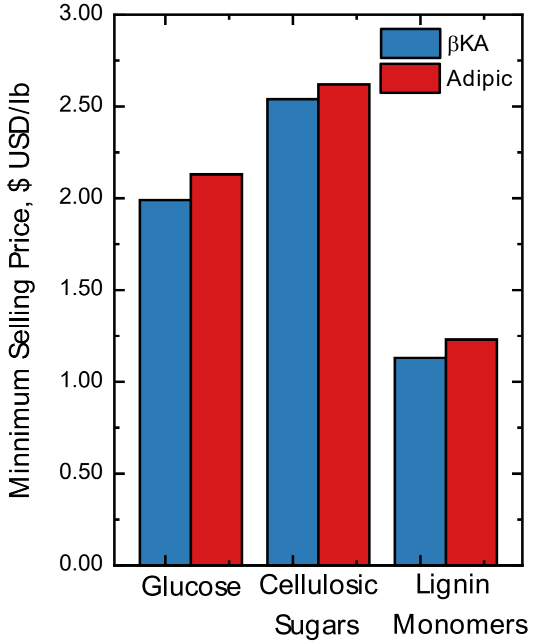
- Strains engineered to produce βKA from sugars (Agile BioFoundry and Biological Lignin Valorization projects)
- Standardized analysis procedures developed for βKA (Lignin Utilization)
- Collaboration with other projects enables de-risking of technology along the entire manufacturing process

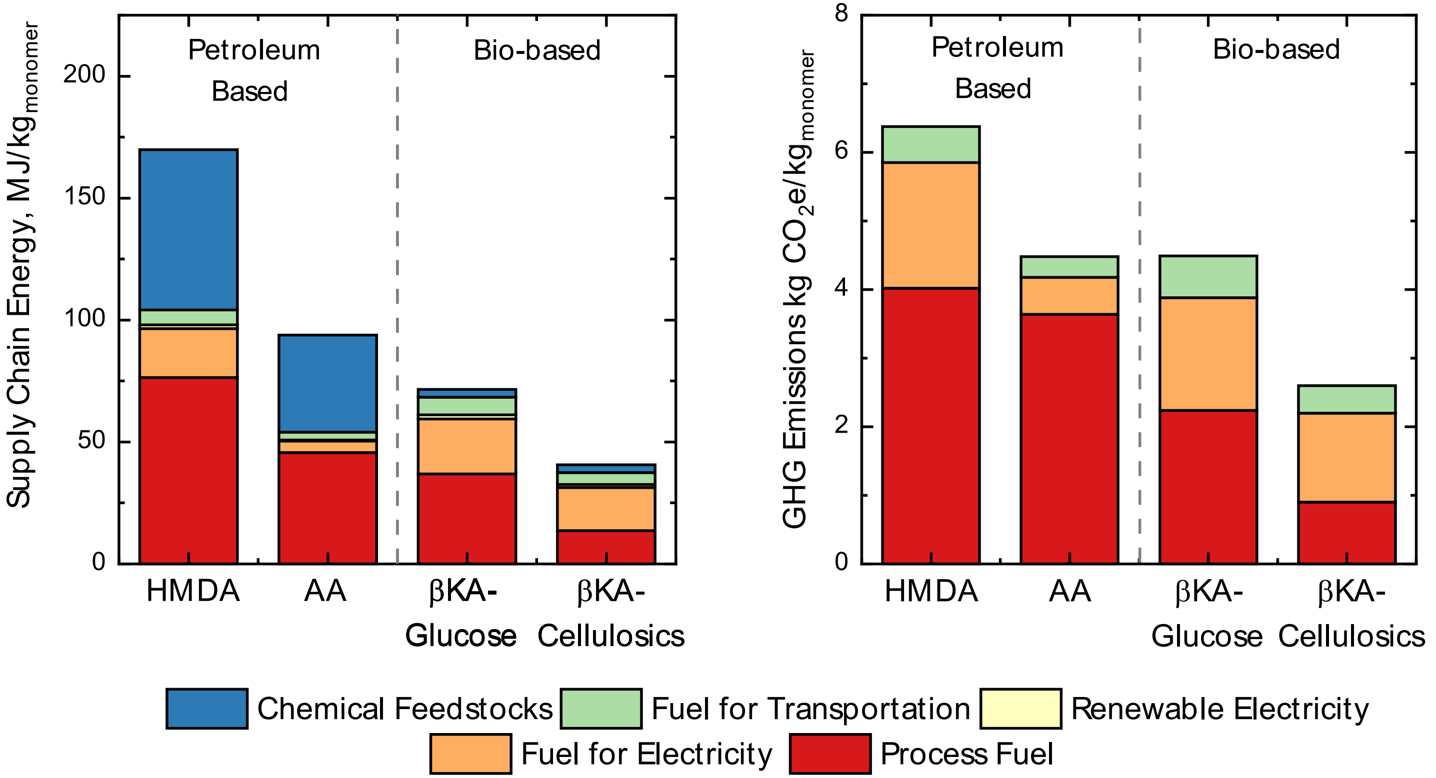


Rorrer *et al.*, in review

# Performance-advantaged nylons – advantages in manufacturing




Abbreviations: HMDA, Hexamethylenediamine; AA, Adipic acid; βKA, β-ketoadipic acid

**βKA can cost as low as $1.13/kg with a 22% reduction in GHG emissions**

- Lowest cost achieved from lignin feedstock
- Supply chain energies and GHG emissions depend on feedstock: ***in all cases***, they are lower for bio-based monomers
- Significant potential to target N-containing monomers in future work (HMDA)

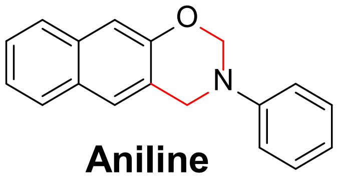


Rorrer *et al.*, in review

# Thermosets from bioderived amines enable multiple performance options

## Biologically produced 4APAA bifunctionality ideal for catalytic benzoxazine thermosets

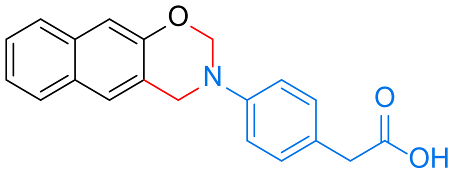
- 4APAA *reduces the processing temperature* for polybenzoxazines by >100°C




**Aniline**

**249 °C**

*Bio-based amine* **4APAA** provides *built-in catalytic functionality*



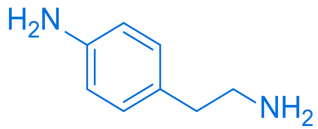

**4-aminophenyl acetic acid (4APAA)**

**135 °C**

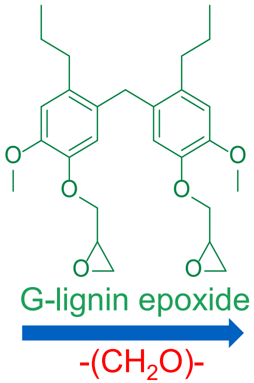
Curing Temperature

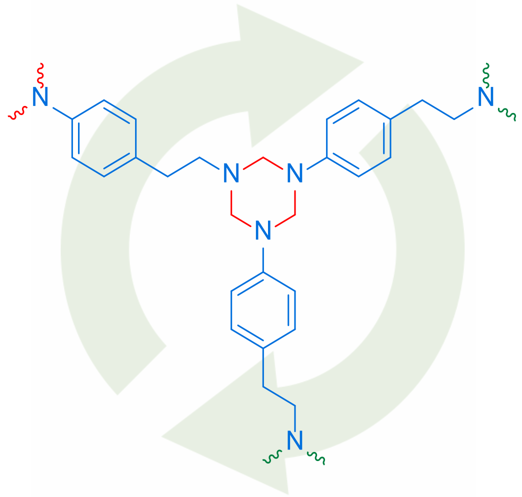
Benzoxazine

Functionalized Benzoxazine



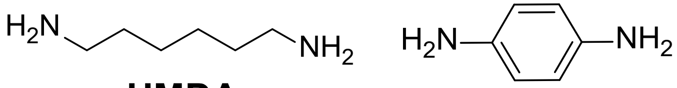

**2-(4-aminophenyl)ethylamine (4APEA)**




*Bioderived epoxy triazine network*

vs.




**HMDA** **PDA**

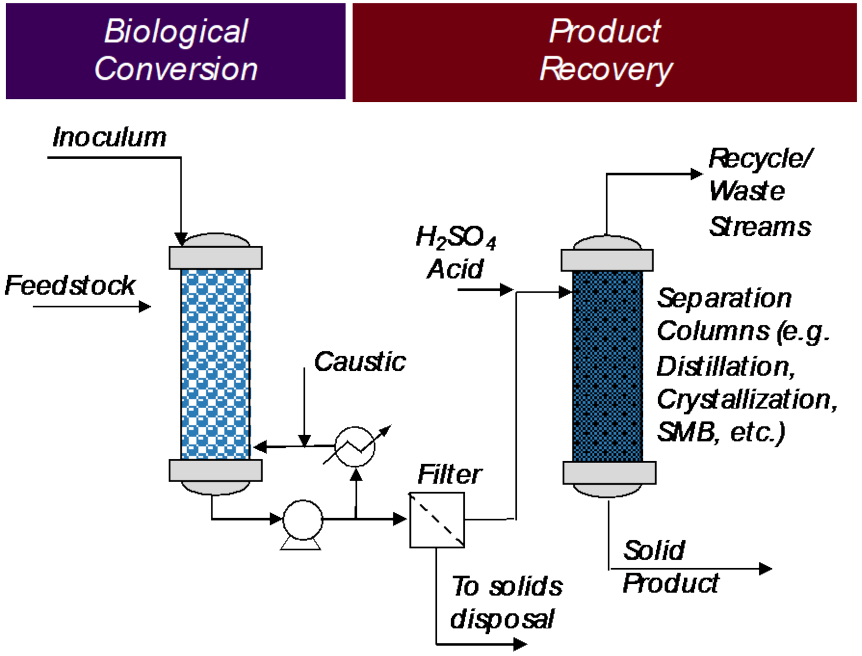
Petroleum Standards

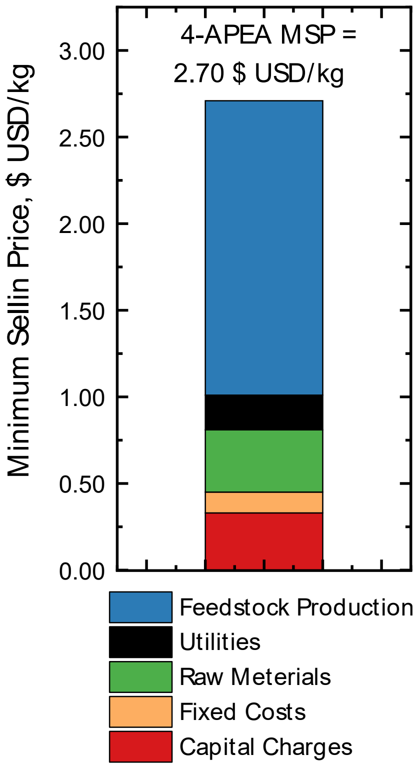
## Bio-based 4APEA introduces end-of-life recycling for epoxy thermosets

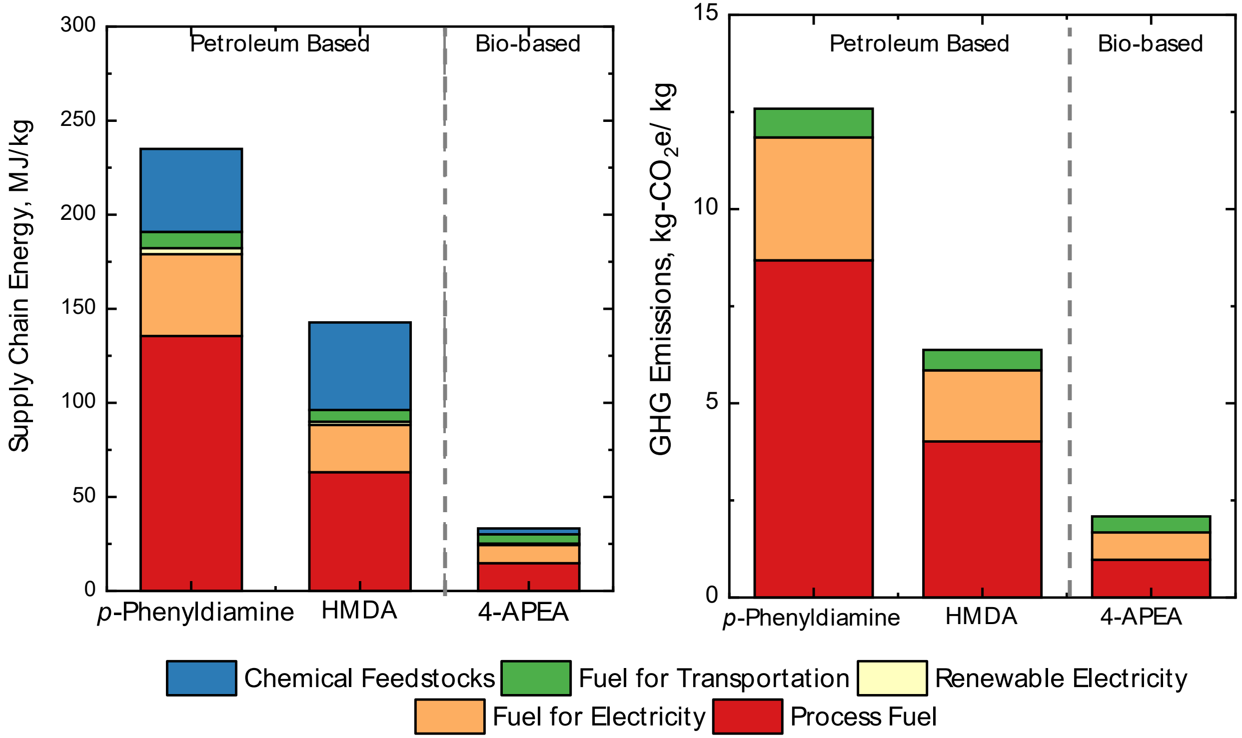
- Recyclable by acid hydrolysis because of 4APEA triazine linkages incorporated into epoxy network
  - When lignin monomers are used, health risks are reduced compared to BPA epoxy resins
  - With Lignin-First Biorefinery Development, Agile BioFoundry

Hoyt *et al.* in preparation

# Biomass-derived amines exhibit reduced environmental impacts



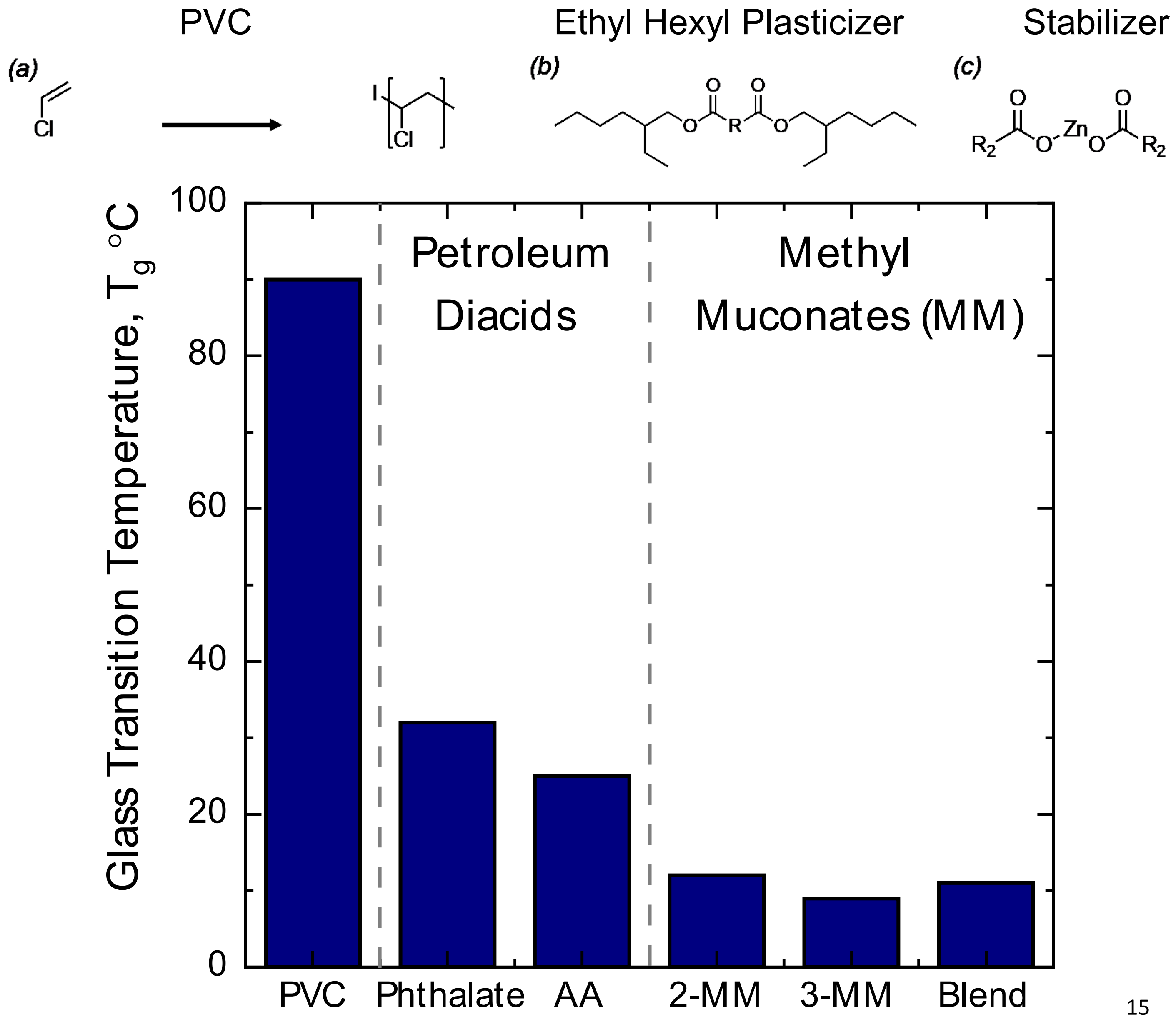




**Amines from biomass offer ≥85% reduction in supply chain energy and GHG emissions**

- Amines can be used in multiple PA applications (e.g. benzoxazines, nylons, etc.)
- Feedstock is a key contributor to cost – analysis is ongoing for reducing feedstock contribution

Hoyt *et al.* in preparation

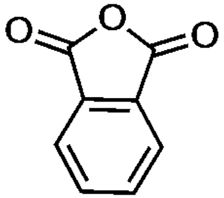
# PVC plasticizers



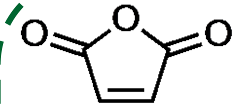

**Methyl muconates are highly effective at PVC plasticization**

- Methyl muconates (*Bioconversion of Thermochemical Intermediates project*) can be used in plasticizers
- When blended with PVC (10 wt%), bio-plasticizers lead to a 75-83% reduction in $T_g$, *a 12-20% improvement over the petroleum standard*
- Methyl muconates are potentially safer – testing and analysis ongoing

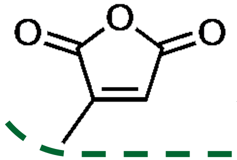
# PVC thermal stabilizers



Phthalate Anhydride *(Petro. Std.)*



Maleic Anhydride



Citraconate Anhydride

Agile BioFoundry

| Sample | TGA, $T_{d, 50}$ °C | % Change to PVC | Other Notes |
|---|---|---|---|
| PVC | 300 | -- | -- |
| Lead- Phthalate | 360 | 20% Improvement | *Petroleum Standard* |
| Tin Malate | 310 | | |
| Tin Citraconate | 290 | | |
| Zinc-Phthalate | 370 | 23% Improvement | -- |
| Zinc-Malate | 390 | 30% Improvement | Soluble in THF, no thermal mixing needed |
| Zinc-Citraconate | 420 | 40% Improvement | Soluble in THF, no thermal mixing needed |

## Stabilizers from anhydrides use safer metals and improve stabilization

- PVC stabilizers often contain metals (lead, tin) to manage HCl emitted in PVC processing
- Additives are an ideal market for PABPs as they can be used in material formulations at low loadings, are coupled with high volume products, and can sell for high prices – analysis ongoing
- **Current efforts:** understanding mechanistic basis for this performance enhancement (ID)

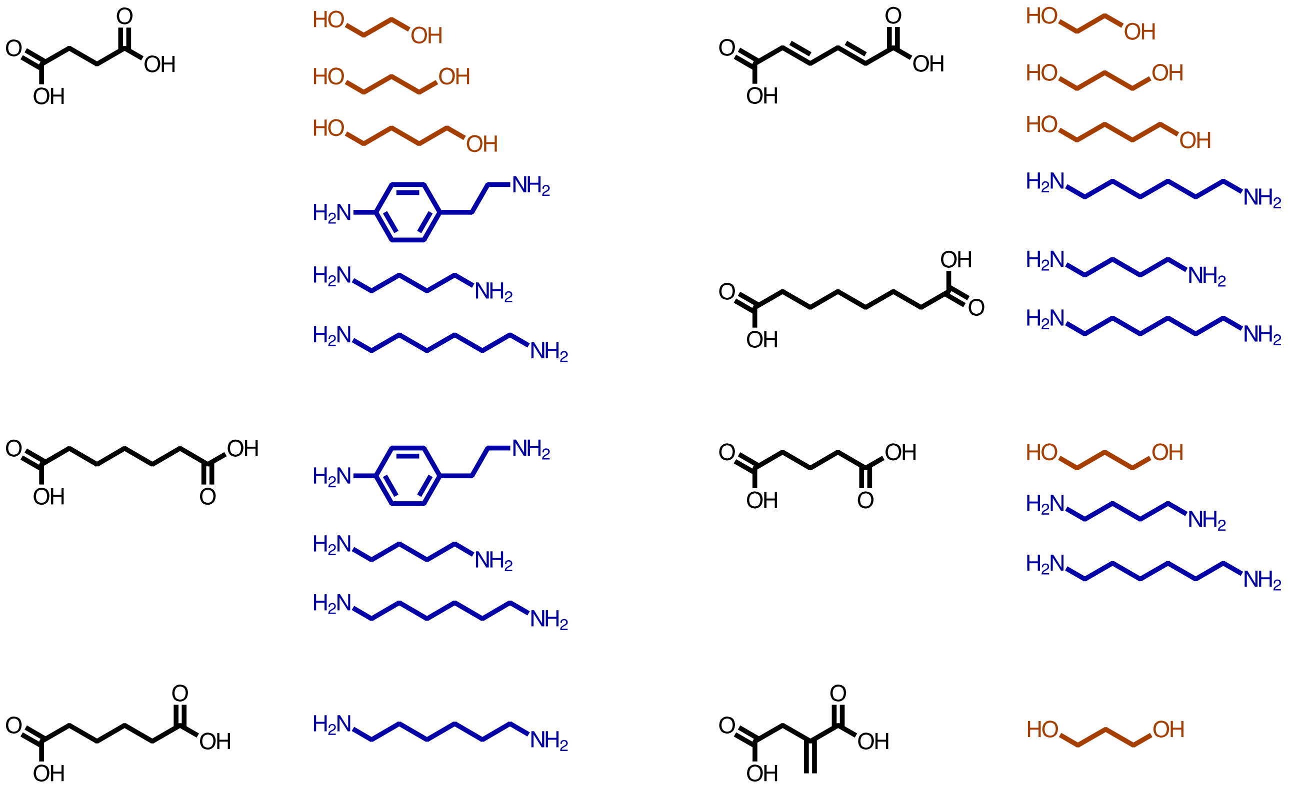
# Cumulative PABP syntheses

| *Petroleum Polymer* | *Bio-based Monomer* | *Metric* | *Property Change* | *Formulations* |
|---|---|---|---|---|
| ***Polyamines/Polyaramids*** | | | | |
| Nylon 6,6 | **BKA** | **Permeability/$T_g$** | 20% Reduction/110% Increase | 4 |
| | **BKG** | **$T_g$** | 105% Increase | 4 |
| | **Muconic** | **$T_d$/Flame Resistance** | 10% Increase | 4 |
| | Methyl-muconates[a] | Permeability | 15% Reduction, Large $T_g$ Reduction | 9 |
| | ML Monomer Suite[b] | $T_g$ | -- | 20 |
| Nomex | **PDC** | **Processability** | Reduction in $T_g$ | 4 |
| ***Polyesters*** | | | | |
| PET *(amorphous)* | **PDC** | **$T_g$/Biodegradability** | 10% Increase/ Acid/Base Reduction Increased | 4 |
| ***Polycarbonates*** | | | | |
| BPA-PC | **5-5' Linked Dimers** | **Endocrine Disruption** | Reduction | 2 |
| | **Lactide** | **Recyclability** | Enabled | 6 |
| **Styrenic Polymers** | | | | |
| ABS | **Lignin Monomers** | **Toxicity/Separation Reduction** | 80%/60% Reduction | 6 |
| **Epoxy Resins** | | | | |
| Thermosetting Epoxies | **Lignin Monomers/Aromatic Amines** | **$T_g$/Recyclability** | Maintained/ Acidic Recycling Introduced | 11 |
| | Multiple Dimers and Diamines | $T_g$, Mechanical | Properties Maintained | 12 |
| **Polymer Additives** | | | | |
| Benzoxazines | **Aromatic Amines** | **$T_g$, Processibility** | Properties Maintained, $T_p$ reduced | 10 |
| Phthalate Plasticizers | **Methyl Muconates/ Citraconates** | **Plasticization/ Thermal Stabilization** | 50% Reduction at same loading | 6 |

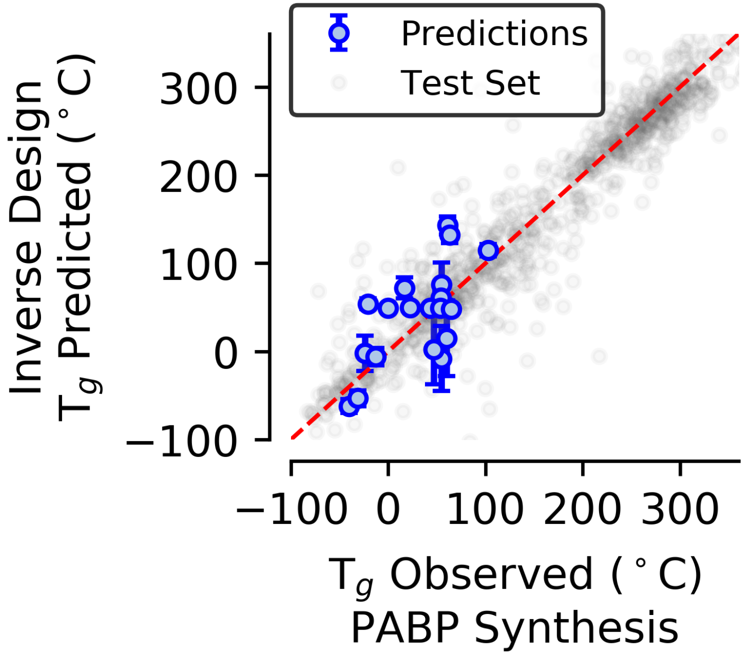
**Total: 110 new formulations to date from target 50 (first 3-year cycle), at least 10 are PABPs**

- Overall, this project seeks to achieve advantages in manufacturing, performance, and end-of-life
- PA often achieved via elevated $T_g$, lower permeabilities, higher thermal stabilities, etc.
- Table outlines brief descriptions of PABPs synthesized in the project to date

# Synthesis of new polymers predicted from PolyML



poly(ML)




**Experimental syntheses corroborate PolyML predictions**

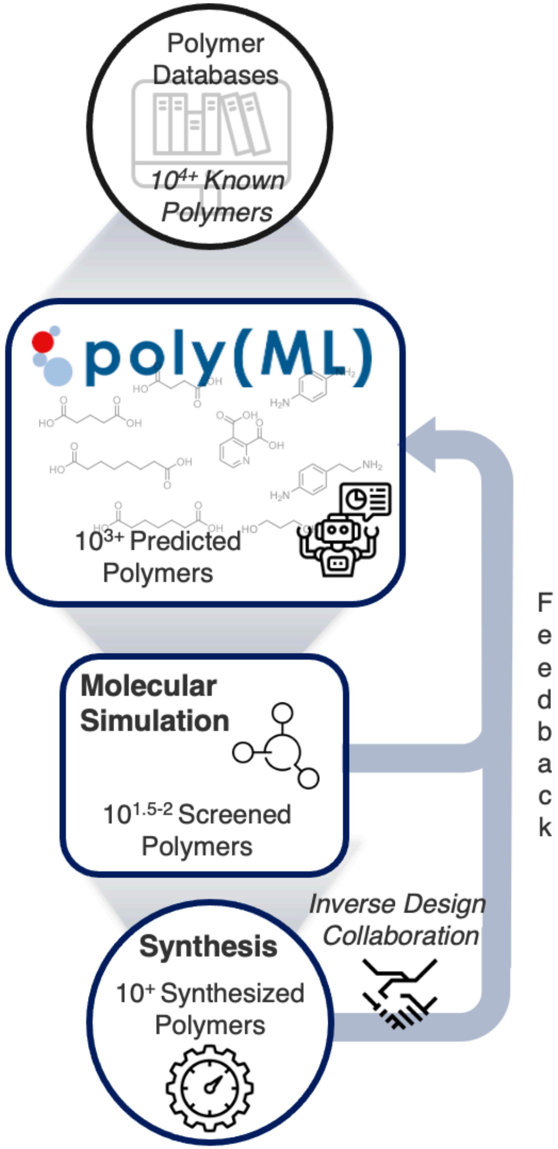
- Synthesized **8 polyesters** and **12 polyamides** to provide validation of PolyML predictions
- The initial syntheses were for heteroatom monomers that can be obtained from biomass
- **Current efforts:** Leveraging new predictions from PolyML to target new high-performance polymers (e.g. high $T_g$ with low permeability)



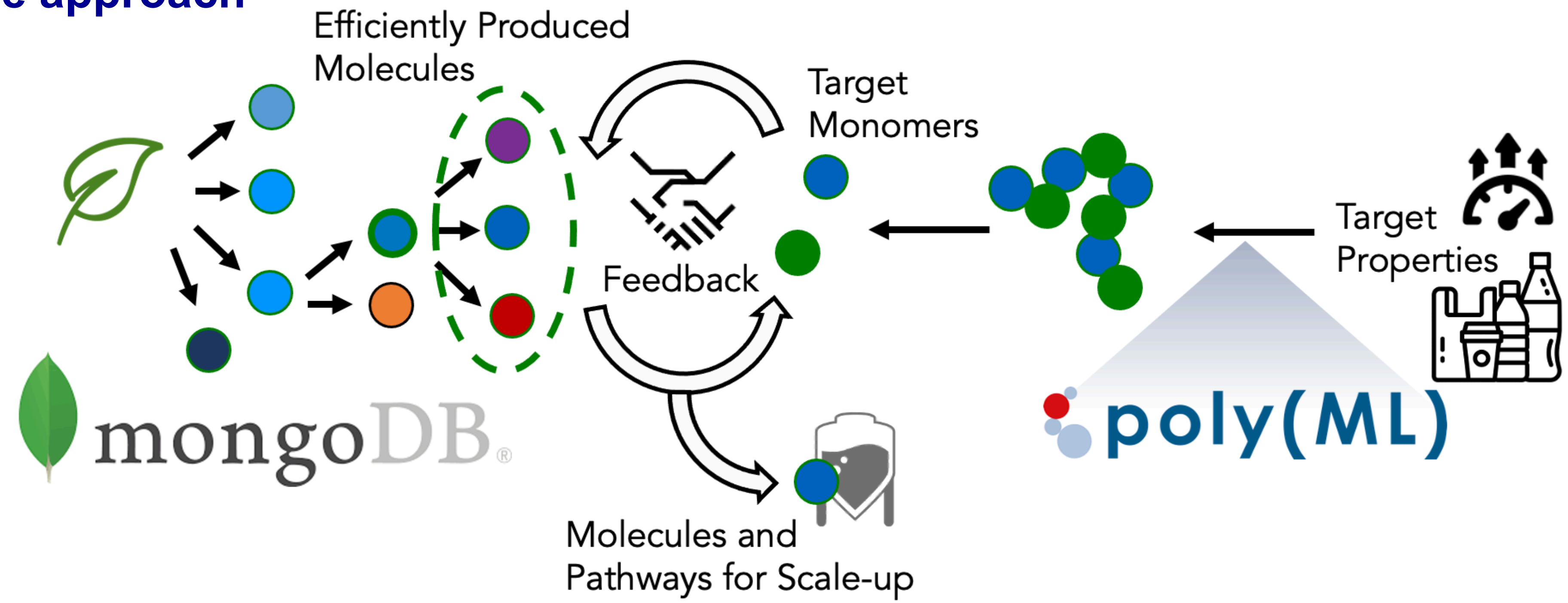
Wilson *et al.* in preparation

# Identifying pathways to PABPs via PolyML and mongoDB

## Current approach




## Future approach

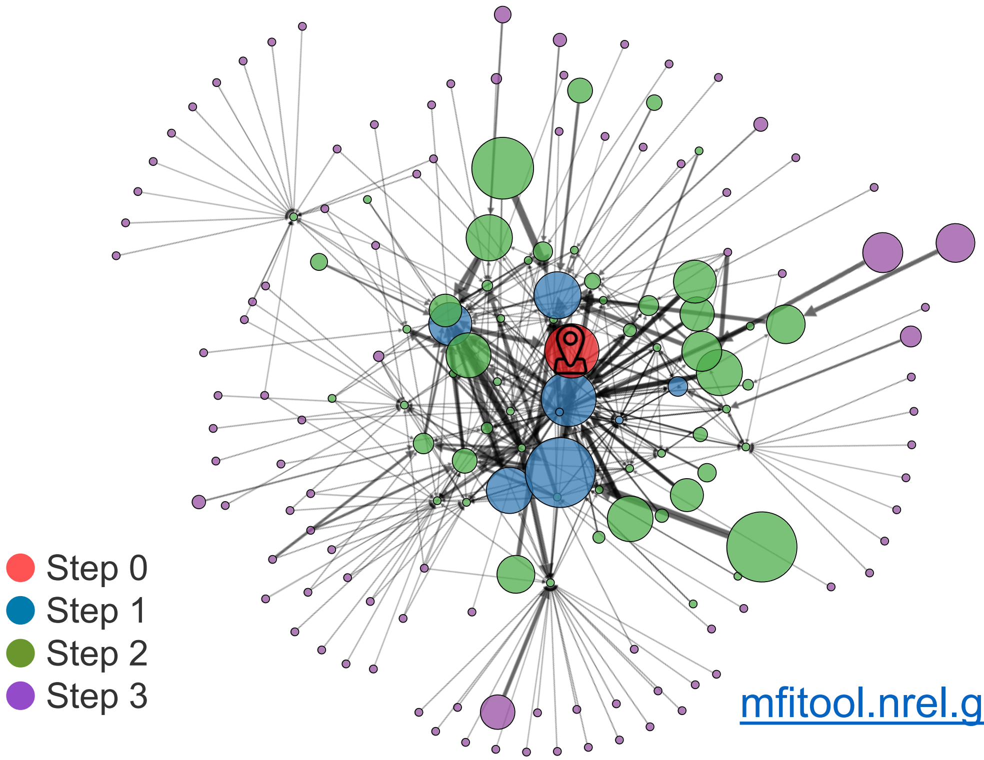



**Pathway prediction coupled with polymer prediction aimed at narrowing synthesis and polymer design space**

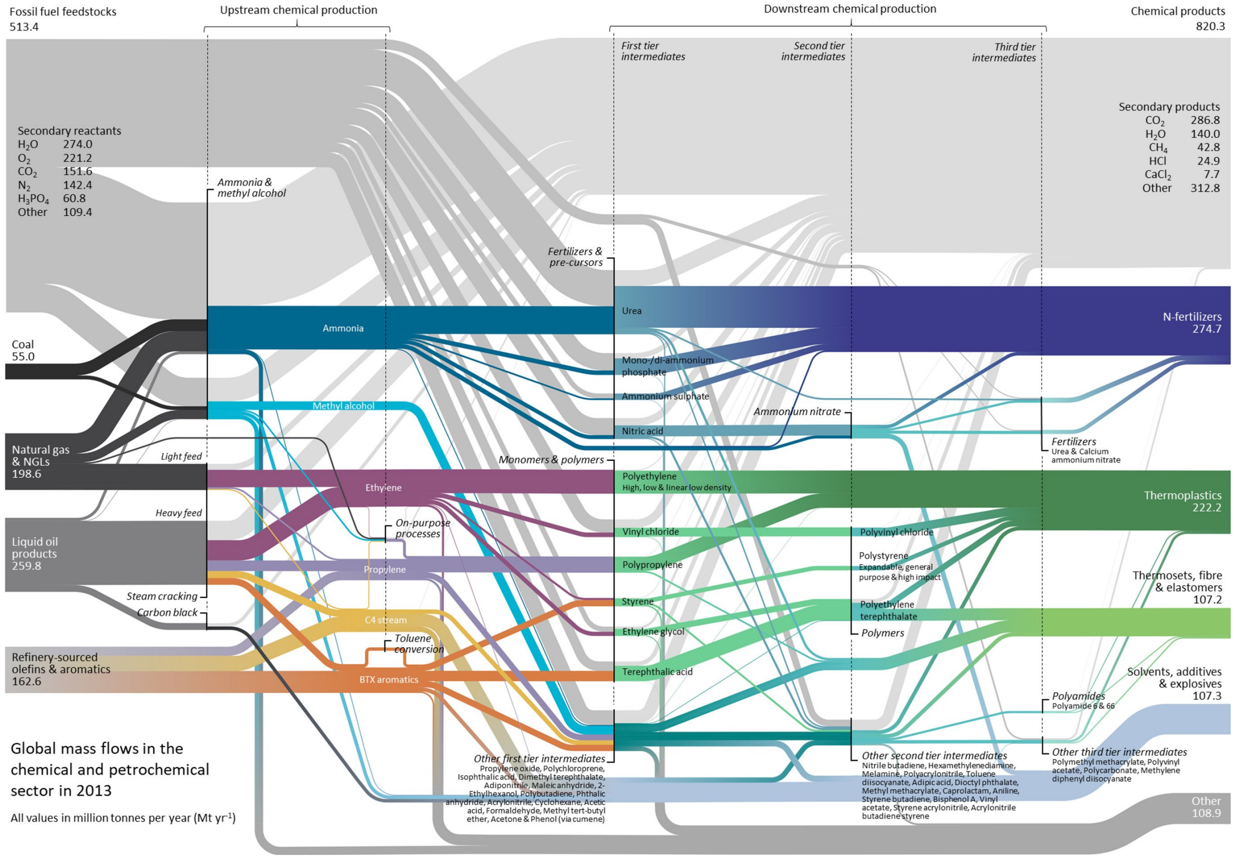
- PolyML identifies target molecules for PA polymers (*what molecule we should make*)
- MongoDB identifies and ranks hybrid chemical and biological pathways to target molecules, including considering rate, selectivity, thermodynamics, & separations (*how to best make the molecule*)

# Benchmarking chemicals production to identify PABP targets

**MFI models chemicals production as steps of supply chain inputs to the final product**




mfitool.nrel.gov




Levi, P. G., & Cullen, J. M. (2018). *Env. Sci. Tech.*, *52*(4), 1725-1734

**Using MFI to estimate supply chain energy & GHG emissions of today's commodity chemicals**

- Analogous to plastics benchmarking analysis in BOTTLE (Nicholson *et al. Joule* 2021)
- Currently identifying case studies based on market size; PABP targets can be benchmarked against these baseline data for supply chain energy and GHG emissions

# Summary

## Overview

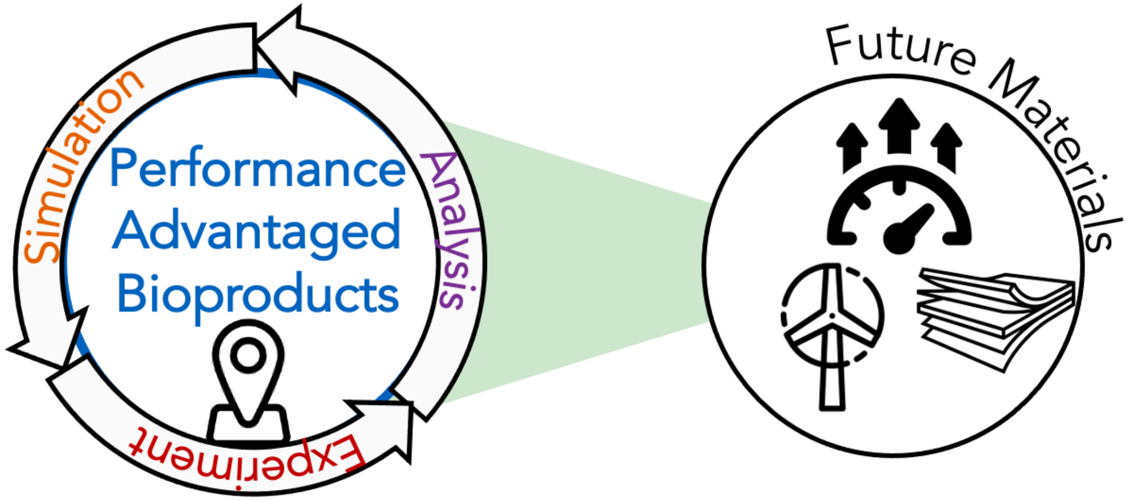
- This project – with Inverse Design – seeks to combine analysis, computation, and experiment to efficiently identify, synthesize, and characterize a suite of cost-effective, sustainable PABPs

## Management

- Key collaborations with Agile BioFoundry, BETO lignin projects, SepCon, among others to source monomers and with Inverse Design to narrow design space

## Approach

- Experimental efforts focus on PABP syntheses & characterizations
- Employ Aspen Plus and Materials Flows through Industry for analysis
- Disseminate new PABPs via integrated, high-impact publications and patents




## Impact and Progress

- Key outputs to date include >100 PABP formulations and multiple bio-based, performance-advantaged polymers

## Future Work

- Include additives as a key focus area expand project reach and distinguish work from other BETO projects in polymer design

# Quad charts

## Timeline

- Active Project Duration: 10/1/2020 – 9/30/2023
- Total Project Duration: 10/1/2017 – 9/30/2023

| | FY20 | Active Project (FY21-23) |
|---|---|---|
| **DOE Funding** | PABP - $450,000<br>PABP analysis - $250,000 | $1,560,000 |

## Project Partners

**BETO Projects**: Biologial Lignin Valorization (2.3.2.100), Separations Consortium (2.5.5.502), Biochemical Platform Analysis (2.1.0.100), Inverse Biopolymer Design through Machine Learning and Molecular Simulation (2.5.1.500), Agile BioFoundry (2.5.3.105), Bioconversion of Thermochemical Intermediates (2.3.2.301), Lignin Utilization (2.3.4.100), Lignin-First Biorefinery Development (2.2.3.106)

**University Partners:** Iowa State, Northwestern University, Colorado State University, MIT, University of Wisconsin-Madison

## Barriers addressed

Ct-J Identification and Evaluation of Potential Bioproducts
Ct-K Developing Methods for Bioproduct Production
At-D Identifying New Market Opportunities for Bioenergy and Bioproducts

## Project Goal

Synthesis, characterization, and analysis of performance-advantaged bioproducts

## End of Project Milestone

Produce ≥50 bioproducts hypothesized to offer a performance advantage. Demonstrate ≥10 bioproducts with a performance advantaged property >10%. Demonstrate that these bioproducts can be produced within 25% of the cost of the petro-derived counterpart.

## Funding Mechanism

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

**Acknowledgements**

DOE Technology Managers Andrea Bailey and Nichole Fitzgerald

**NREL Contributors:**

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# Q&A

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# Additional Slides

# Responses to previous reviewer comments

- Excellent work results and progress on polymers. I would have liked to see some end uses that are watersoluble oligomers potentially useful in many consumer goods products and industrial applications; however, I'm glad to see future work on other applications. ß–ketoadipic acid work is exceptional and I'm glad to see results here as I feel this may be a first work moving forward in industry. Don't rely on weak links and biodegradability of polymers. Better to focus on recyclability because the European Union may in the future ban weak-link polymers and U.S. policy usually takes time to adjust, but often follows stiffer guidelines in the future.
    - We appreciate the positive comments from the reviewers. We agree that it would be ideal to expand beyond the current applications to include others, which additional funding would enable to increase bandwidth. The comment regarding biodegradability is excellent and we fully agree. We are attempting to make polymers that can be more easily chemically recycled.
- It seems like bioproducts do have great potential to deliver better properties. The question becomes how does this reach an innovation level great enough to bring sufficient investment to make a commercialized product.
    - We agree that the bio-based materials need to reach a level of innovation to catalyze industrial investment. To that end, we are in close coordination with industry regarding the innovations coming from this project to offboard them as we reach a sufficient technical readiness level.
- This is an interesting project to build and test new polymers from bio-based monomers and measure their properties. Very good progress on synthesis of new formulations have been reported, some of which exhibit enhanced properties. This program has received extensive input from industry on worthwhile performance characteristics and is nicely synergistic to the inverse learning program, as it will generate novel information to augment databases and improve predictive tools for new polymers.

# Responses to previous reviewer comments (Analysis)

- The project must filter down choices quickly to focus on few chemicals to move forward. Two years seems long to filter down. Suggest that they should group materials together in terms of similar functionality to target mixtures that could replace things like chelants, aqueous viscosity modifiers for consumer products, or even lower molecular weight, water-soluble-type oligomers may be easier targets for functional materials in the 20,000 molecular weight average range or lower. This could avoid costly separation of single materials in some cases while providing a bigger cost reduction to fuel cost/GGE and a bigger chance to be successful overall.
- This has potential to be a very valuable publication when completed. Would be good if it could somehow identify pointers to next-generation molecules.
- The project is addressing a core goal in biorefinery development—understanding the properties and performance that are the true products of the chemical industry. Incorporating this understanding with a definition of the technology needs to derive these properties from bio-based building blocks will need to be a key component of any report or white paper resulting from this work.
- The project aims to generate a list of desirable bio-based targets, differing from prior work by including more performance and characteristics criteria to prioritize performance-advantaged bioproducts. With the pressing need to improve biorefinery economics via better valorization of streams, this effort is of strategic importance and, if successful, can be a guiding decision tool to focus valuable R&D time on better target choices.
- Great integrated approach to share information, results, and resources. Very well presented and the explanation of the framework for analysis of evaluating performance-advantaged bioproducts was clear. External advisory panel with eleven advisors provides a wide variety of industry perspectives. This is very thorough research and analysis to outline the value proposition and market pull.
    - We thank the reviewers for their helpful feedback and comments. We will work to incorporate these suggestions in the project going forward.

# Publications, patents, presentation, awards, and commercialization

**In review or revision:**

To be filled in by February 19th, 2021

Robin M. Cywar, Nicholas A. Rorrer, Caroline B. Hoyt, Gregg T. Beckham*, Eugene Y.X. Chen*, Bio-based polymers with performance-advantaged properties, in review at *Nature Rev. Materials*.

**In press:**

Christopher W. Johnson‡, Davinia Salvachúa‡, Nicholas A. Rorrer‡, Brenna A. Black‡, Derek R. Vardon‡, Peter C. St. John‡, Nicholas S. Cleveland, Graham Dominick, Joshua R. Elmore, Nicholas Grundl, Payal Khanna, Chelsea R. Martinez, William E. Michener, Darren J. Peterson, Kelsey J. Ramirez, Priyanka Singh, Todd A. Vander Wall, A. Nolan Wilson, Xiunan Yi, Mary J. Biddy, Yannick J. Bomble, Adam M. Guss, Gregg T. Beckham*, Innovative chemicals and materials from bacterial aromatic catabolic pathways, *Joule*. (2019) 3, 1523-1537.

# Publications, patents, presentation, awards, and commercialization

**Presentations**

Performance-advantaged bioproducts from lignin, BioEnergy Society of Singapore (via webinar), December 14th, 2020

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

Performance-advantaged bioproducts from lignin and carbohydrates, 8th Fuel Science Center International Conference (via webinar), June 24th, 2020

Bacterial aromatic catabolism for lignin and plastics conversion, University of Minnesota BioTechnology Institute, March 5th, 2020

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

Engineering non-model cell factories to produce novel polymer precursors, Biomass to Biobased Chemicals and Materials, July 17th, 2019

Challenges and opportunities in plastics upcycling, Plenary Invited Lecture, 26th BioEnvironmental Polymers Meeting, June 5th, 2019

Interfacial biocatalysis for breaking down plants and plastics, Boise State University, March 27th, 2019

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

**Patent applications**

Thioester and Thioaldehydes of Lignin Monomers for Reversible Crosslinked Applications: ROI-19-107, pending