ResIn: Responsible Innovation for Highly Recyclable Plastics

U.S. DEPARTMENT OF ENERGY

DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

March 9, 2021

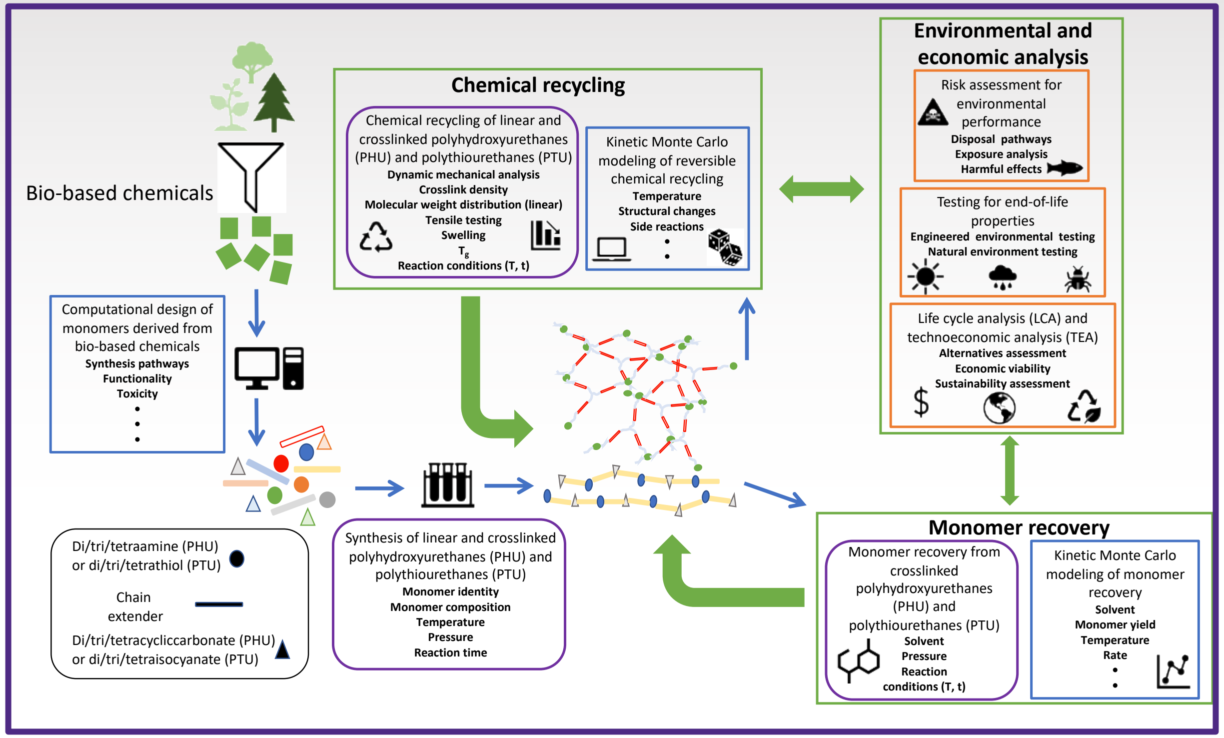
Performance Advantaged BioProducts Review Panel

Linda J. Broadbelt

Northwestern University

FY19 Bioenergy Technologies Office Multi-Topic Funding Opportunity Announcement DE-FOA-000209

Area of Interest: 8a: Designing Highly Recyclable Plastics



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Project Overview

Goals

- Achieve 25% monomer recovery of polyhydroxyurethanes (PHU) and polythiourethanes (PTU)

State of the Art is 0%

- Deliver PHU and PTU materials using a minimum of 50% biobased content

Biomass is not currently used as a PU feedstock

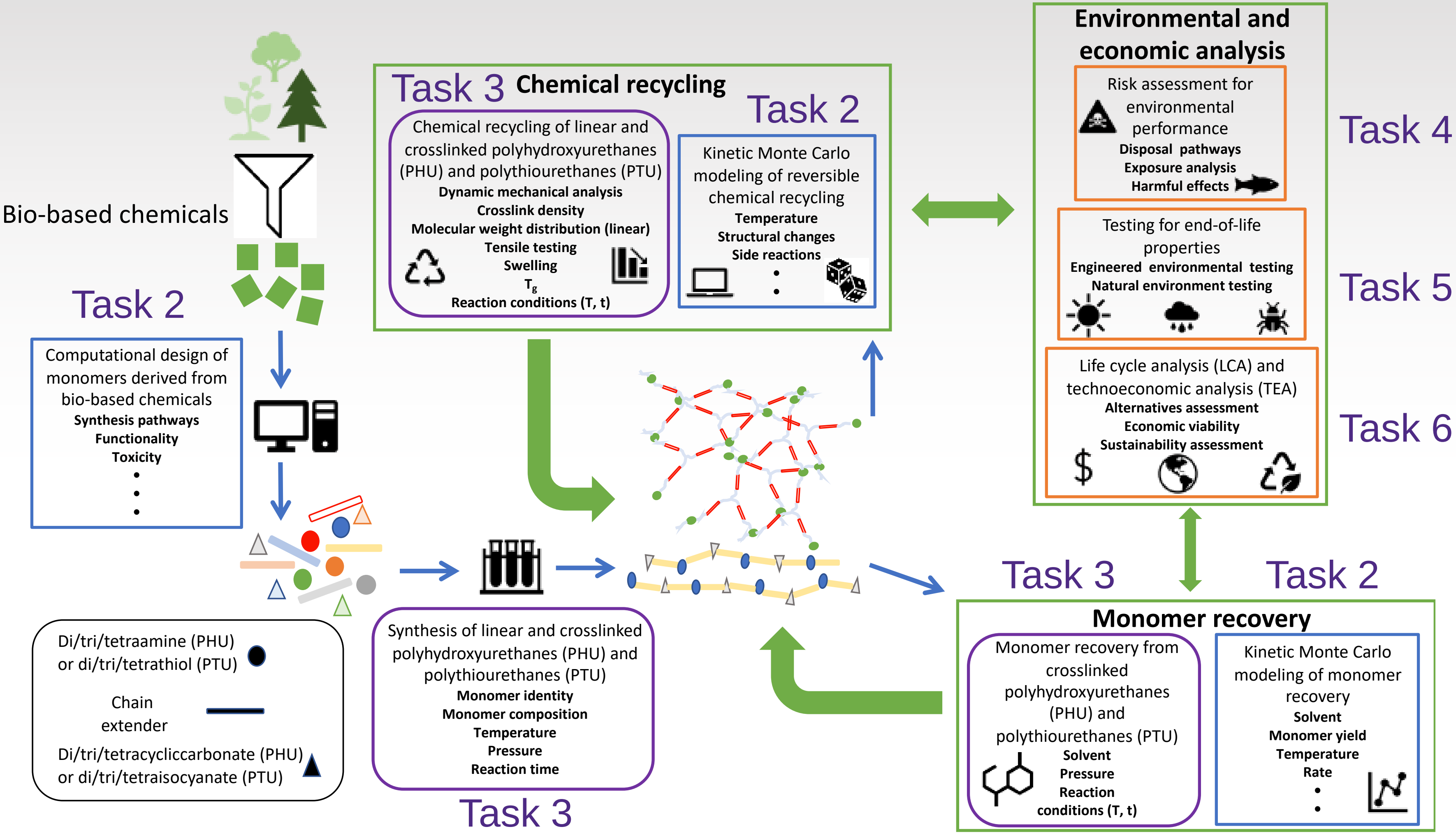
Aligned with BETO's mission of ensuring our nation's competitive advantage in the emerging bioeconomy by funding research and development of technologies to produce advanced bioenergy from terrestrial and algal biomass, biogas, and other waste streams

- Deliver kinetic Monte Carlo (kMC) framework that predicts conditions for chemical recycling/monomer recovery from PHU and PTU
- Demonstrate economic viability and sustainability of approach through TEA and LCA
- Deliver risk assessment framework to enable responsible design of polymers
- Deliver insights into end-of-life fate of polyurethanes in different scenarios

Context

- **Aim:** recover monomers from PHU and PTU replacements for polyurethanes
- **Today:** state-of-the-art is 0% recovery of monomers from this important class of materials
- **Important:** design of novel materials that can be recycled considering all aspects of the lifecycle provides potential environmental and economic benefits
- **Risks:** broad range of applications demands specific material properties and end-use may require additives

Project overview and tasks



Management: Task Structure

Task 2.0: Computational Design of Monomers and PHUs and PTUs for Recyclability

Lead: L. Broadbelt (NU)

Milestones: monomer and pathway design, kMC framework development and application

Task 3.0: Synthesis, Testing, Monomer Recovery, and Recycling of Non-Biobased and Bio-based PHU and PTU

Lead: J. Torkelson (NU)

Milestones: synthesis of new materials, monomer recovery studies, property testing

Task 4.0: Risk Assessment Framework

Lead: C. Negri (ANL)

Milestones: quantification of fate and transport in environment, scenarios for risk assessment

Task 5.0: End-of-Life Property Testing

Lead: M. Urgun-Demirtas (ANL)

Milestones: evaluation of biodegradation, degradation analysis and prediction

Task 6.0: Systems Economic and Sustainability Analysis

Lead: J. Dunn (NU)

Milestones: material flow analysis, TEA, LCA, GREET^{TM} model enhancement

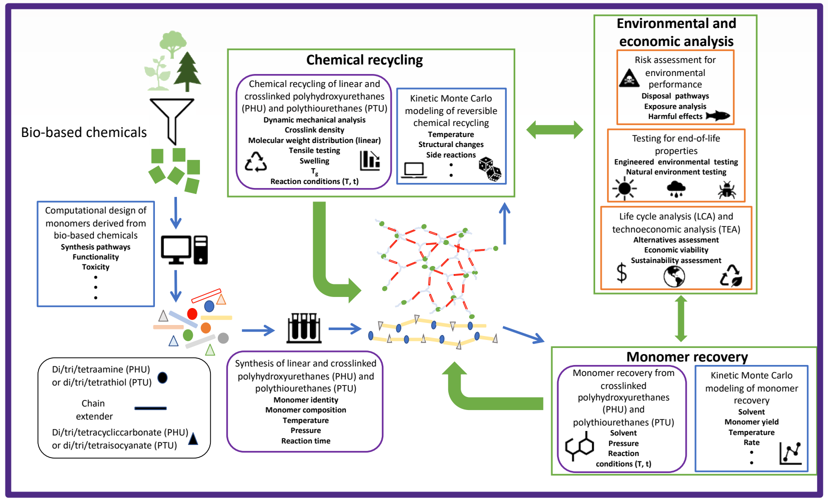
Management

Project organization

- Monthly team meetings with all PIs, students, postdocs, and industrial collaborators
- Quarterly attendance of team meetings by DOE project managers
- *Ad hoc* meetings with various combinations of team members, including industrial partners
- **Box** site for document sharing and communication

Risks and mitigation strategies

- COVID delays of experimental work
  - ➢ Focused on computational approaches, literature research, and project planning
- Potential number of monomers to synthesize and characterize is large
  - ➢ Computational screening weights experimental needs in screening protocol
  - ➢ Industrial collaborators provide materials
- Integration of tasks may rely on progress in monomer prediction and synthesis
  - ➢ Literature sources provide data for computational framework development
  - ➢ Industrial partners offer baseline PU information



Approach

- Use **automated pathway design tools** to identify routes to known and novel monomers from biobased starting molecules
- **Synthesize novel PHU and PTU** linear and network materials and test for properties and monomer recovery
- Assemble **risk assessment framework** that evaluates environmental performance
- Carry out **end-of-life degradation testing** using standard and newly developed methods
- Build **TEA and LCA** of the bio-based and baseline PU systems supply chain
- Consider the **material flows** of PU associated with its production and use in the U.S. and how these will change as a bio-based, circular economy scales up. Assess the potential economic and environmental effects of highly recyclable PU
- Integrate all stages of the PU supply chain from at least 50% biomass and **generate TEA and LCA results, a** Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies (**GREET) module for the PU circular economy, and an evaluation of potential supply chain disruption when PU is designed for 25% monomer recovery**

Partner with industrial collaborators for technology impact

Approach: Challenges and Milestones

Challenges

- Monomer design space is vast, and testing all potential leads from computation is prohibitive

Experimental accessibility can be used as screening metric

Exploring partnerships through Scientific Discovery through Advanced Computing (SciDAC) for HPC

- Standard degradation tests have long feedback cycle and require significant amount of material

Capability for parallel testing and supply by industrial partners

- Risk assessment framework and TEA/LCA advance in absence of knowledge of leading PHU and PTU candidates

Opportunity for TEA/LCA and risk assessment framework to lead

Major milestones, Go/No-Go Decisions

- FY20: Go/No-Go (Initial verification) – synthesis of PHU and PTU with property characterization targets established
- FY21: Major milestone - Identify and quantify disruption of PU supply chain (Task 6)
- FY22: Go/No-Go - Synthesis and quantitative, basic property characterization of one linear and one network PHU or PTU made from model compounds and one biobased monomer identified from Task 2

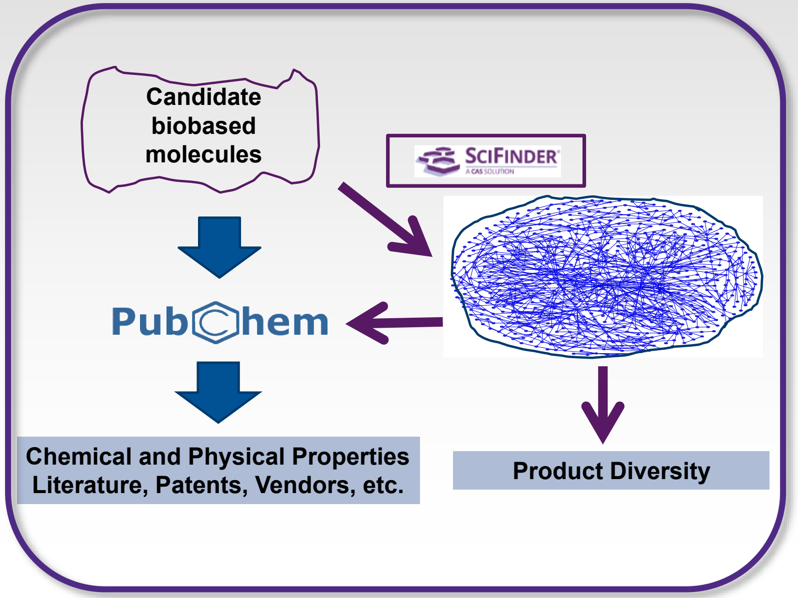
Technology Impact

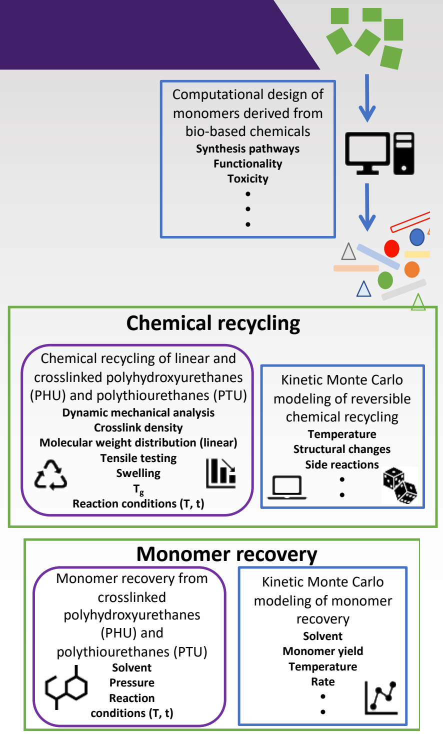
- Among all polymers, PU ranks **sixth** in annual **worldwide production**
- Potential to **advance bioeconomy** by moving to bio-based PU replacements
- Focused efforts on responsible recycling of biobased polyurethane (PU)-like materials, namely biobased polyhydroxyurethanes (PHUs) and polythiourethanes (PTUs), that offer the possibility of recovering value and improving sustainability in two ways:
  - **Recovery of monomer** from spent materials, whether thermoplastics or thermosets
  - **Reprocessability** of spent networks with full recovery of crosslink density and associated properties after reprocessing due to the excellent dynamic character of the crosslinks
- In addition, an **overall framework/methodology** for the responsible design of polymers that will be test driven for the case of PHU and PTU will be developed

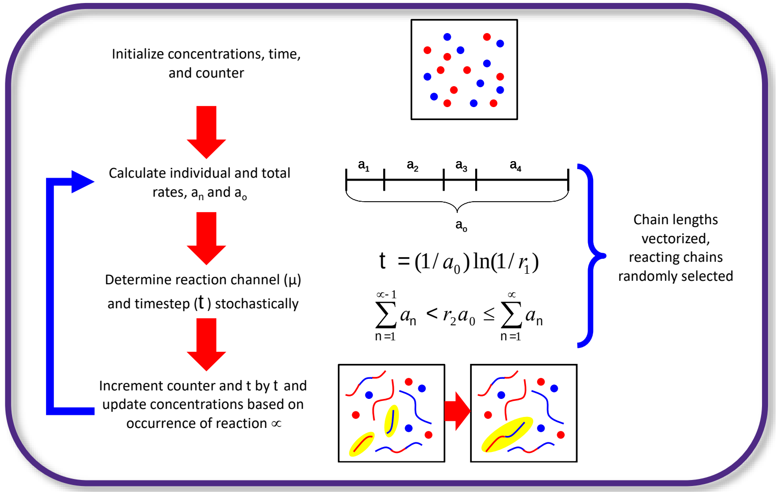
Task 2: Computational Design of Monomers and PHUs and PTUs for Recyclability

Approach

- Automatically generate progeny from molecules summarized by Biddy et al. based on chemocatalytic operators
  - Identify monomer candidates with desired functionality
  - Compare to databases to identify novel molecules and commercially available candidates
- Develop kinetic Monte Carlo code for synthesis and degradation of PU
  - Model synthesis of linear and network PHU and PTU
  - Model monomer recovery of same materials



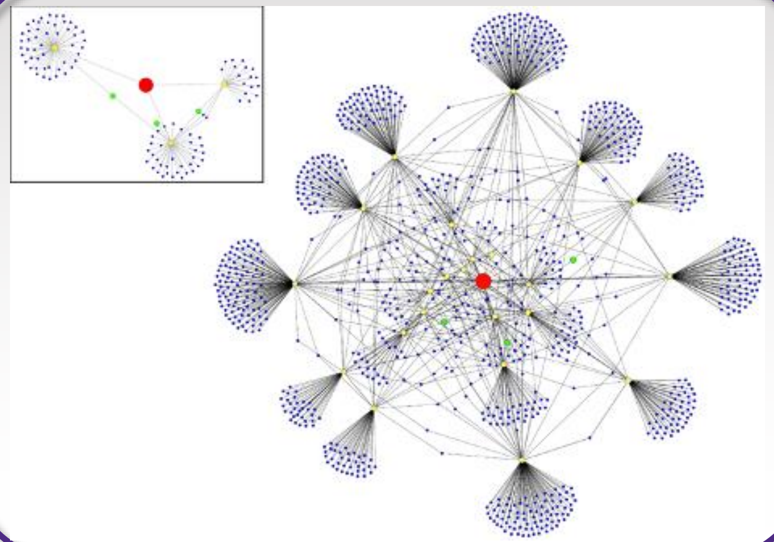


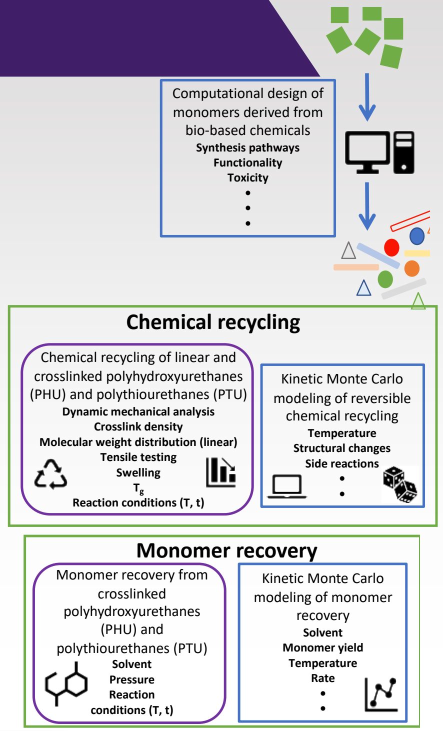


Task 2: Computational Design of Monomers and PHUs and PTUs for Recyclability

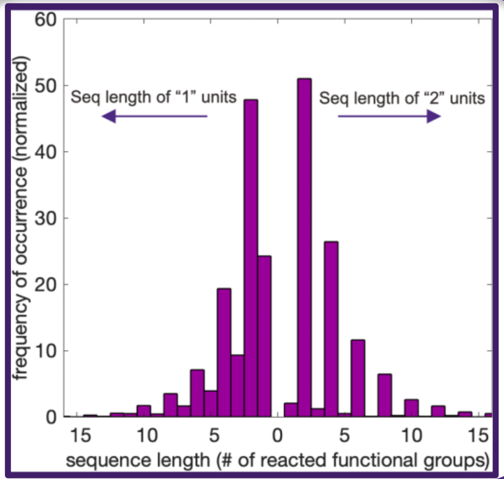
Progress and Outcomes

- Pathway design for PHU monomers successfully completed
  - > 40,000 molecules were generated from 15 starting molecules
  - 15 commercial molecules were identified with biobased origins
  - Numerous novel molecules were created





- Kinetic Monte Carlo code for synthesis of linear PHU and PTU completed
  - Allows sequence to be explicitly calculated for multi-monomer recipes
  - Adapted for modeling of monomer recovery via alcoholysis
  - Leveraged in related projects for degradation of other condensation polymers



Task 3: Synthesis, Testing, Monomer Recovery, and Recycling of non-Biobased and Biobased PHU and PTU

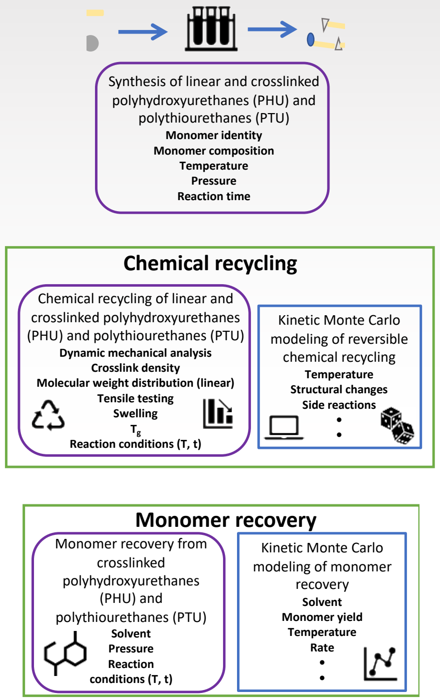
Approach

- Tune and optimize the step-growth syntheses of linear and network, non-biobased and biobased polyhydroxyurethane (PHU) and polythiourethane (PTU)

- Achieve and further improve properties to levels equal to or exceeding those of selected, conventional polyurethanes (PUs), both linear PU and network PU

- Achieve effective chemical recycling of network PHU and PTU, both non-biobased and biobased, by exploiting inherent dynamic covalent crosslinks allowing for melt-state reprocessing with full crosslink density recovery and performance characteristics associated with networks made with permanent crosslinks

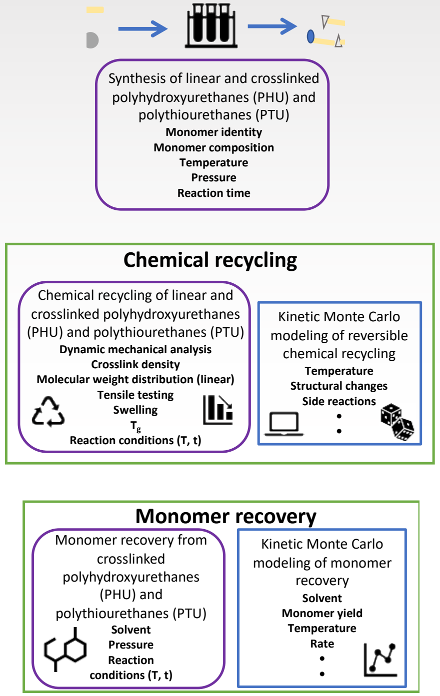
- Demonstrate routes to monomer recovery from linear and network PHU and PTU, both non-biobased and biobased, and engineer one or more routes to achieve 25% or more monomer recovery



Task 3: Synthesis, Testing, Monomer Recovery, and Recycling of non-Biobased and Biobased PHU and PTU

Technical Challenges

- Identifying and obtaining or synthesizing appropriate biobased monomers to be used in PHU and PTU synthesis
- Overcoming perceived major stumbling blocks for effective chemical recycling of PHU and PTU networks containing dynamic covalent crosslinks
  - achieving full crosslink density recovery after reprocessing
  - achieving excellent elevated-T creep resistance
- Going from proof-of-principle monomer recovery to effective, 25%+ recovery



Go/No-Go Decision Points

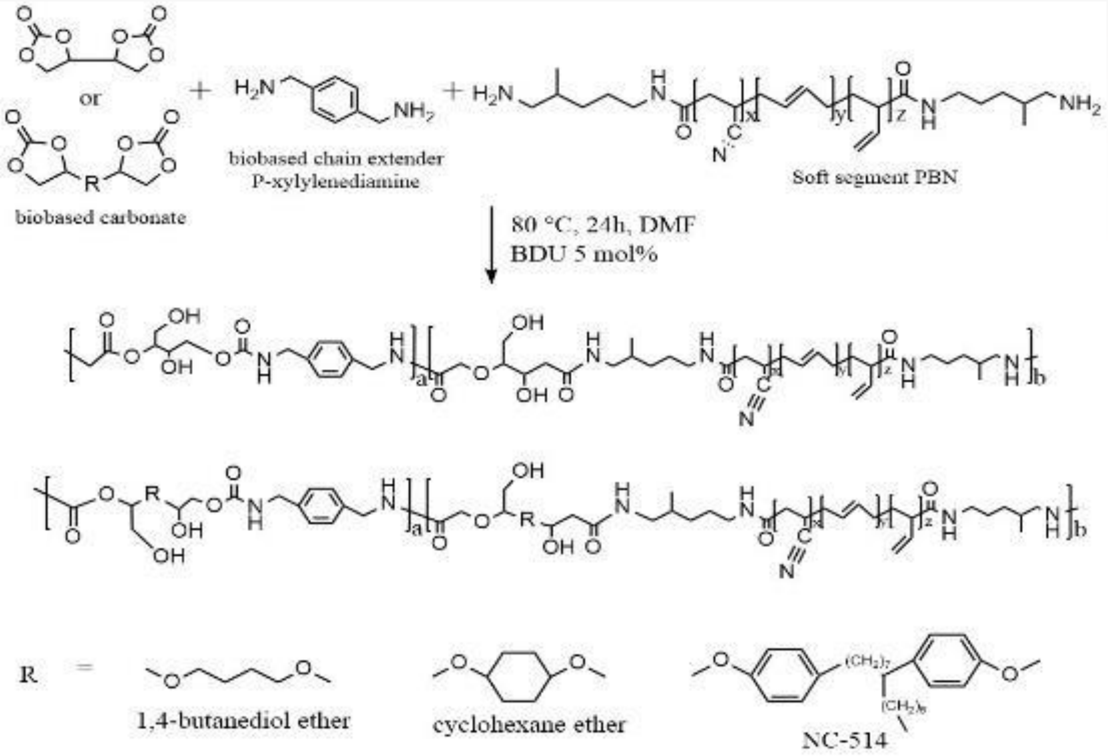
- Successful syntheses of selected PHUs and PTUs with appropriate properties (completed)
- Monomer recovery from PHU and/or PTU at 10% (study in progress)

Task 3: Synthesis, Testing, Monomer Recovery, and Recycling of non-Biobased and Biobased PHU and PTU

Progress and Outcomes

Synthesis of partially bio-based, linear segmented PHUs as a key accomplishment

Bio-based epoxies $\xrightarrow{CO_2 \text{ fixation}}$ Bio-based cyclic carbonate $\xrightarrow{\text{Cyclic carbonate aminolysis}}$ Bio-based PHUs



Synthesis of linear and crosslinked polyhydroxyurethanes (PHU) and polythiourethanes (PTU)
Monomer identity
Monomer composition
Temperature
Pressure
Reaction time

Chemical recycling

Chemical recycling of linear and crosslinked polyhydroxyurethanes (PHU) and polythiourethanes (PTU)
Dynamic mechanical analysis
Crosslink density
Molecular weight distribution (linear)
Tensile testing
Swelling
T_g
Reaction conditions (T, t)

Kinetic Monte Carlo modeling of reversible chemical recycling
Temperature
Structural changes
Side reactions
:

Monomer recovery

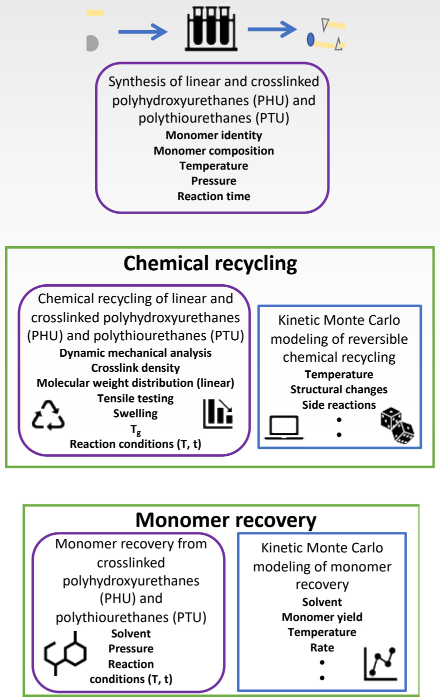
Monomer recovery from crosslinked polyhydroxyurethanes (PHU) and polythiourethanes (PTU)
Solvent
Pressure
Reaction
conditions (T, t)

Kinetic Monte Carlo modeling of monomer recovery
Solvent
Monomer yield
Temperature
Rate
:

Task 3: Synthesis, Testing, Monomer Recovery, and Recycling of non-Biobased and Biobased PHU and PTU

Other key accomplishments

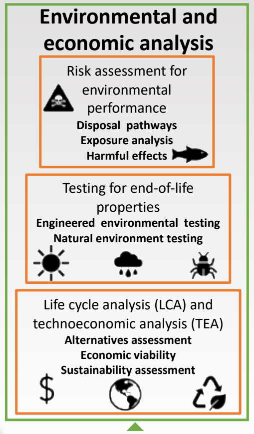
- Synthesis of fully biobased, linear PHUs
- Excellent tunability of properties of partially biobased, linear segmented PHUs
  - extent of nanophase separation is easily tuned leading to dramatic property tunability
  - utility as thermoplastic elastomers (substitutes of thermoplastic PU elastomers)
  - in some cases, excellent broad-T range acoustic noise/vibration damping that is not observed in conventional PU elastomers
- Demonstration that PHU networks exhibit not only full recovery of crosslink density recovery after reprocessing but also long-time creep resistance at 80 and 100 °C
- Synthesis of reprocessable PHU network nanocomposites with full crosslink density recovery after reprocessing along with mechanical property enhancements and long-time creep resistance at 80 and 90 °C

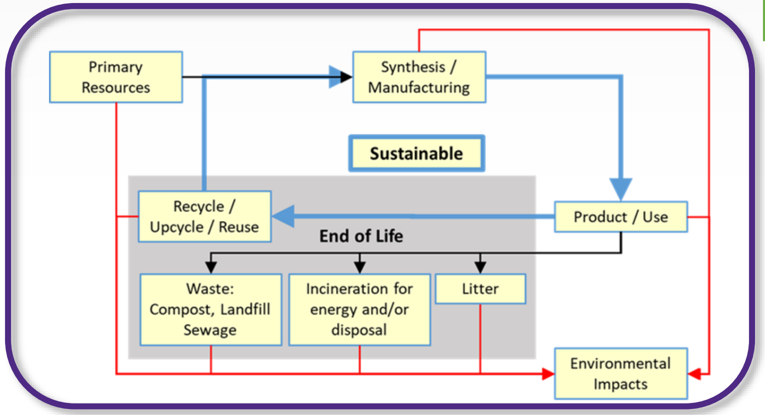


Task 4: Risk Assessment Framework

Approach

- A risk assessment framework will be designed to provide stakeholders a methodology to guide product design to minimize environmental impacts (supports responsible innovation)
  - Hazard identification, exposure assessment, effects identification, risk evaluation
  - Account for differences in material chemical composition and structure on potential EOL impacts
- Challenges posed by evaluation of polyhydroxy- and polythiourethanes
  - Unlimited potential polymer composition and additives
  - Undetermined industrial and environmental conversion products and rates (proximate exposure species)
  - Meaningful evaluation of scenario risks
  - Sufficient sensitivity for scenario differentiation
- Decision Points
  - Scenario risk evaluation is **meaningful**
  - Scenario risk evaluation is **discerning**
- Metrics for qualitative/quantitative evaluation of materials in the environment and their hazards
  - Suite of scenarios to be evaluated (range of leading chemistries and EOL options)
  - Relative hazards (exposure / toxicity) associated with functional groups and general classes of PUs and their components
  - Relative behavior of PU functional groups under different physical, chemical, and biological stressors and rates (e.g., ether more easily cleaved by light than ester)

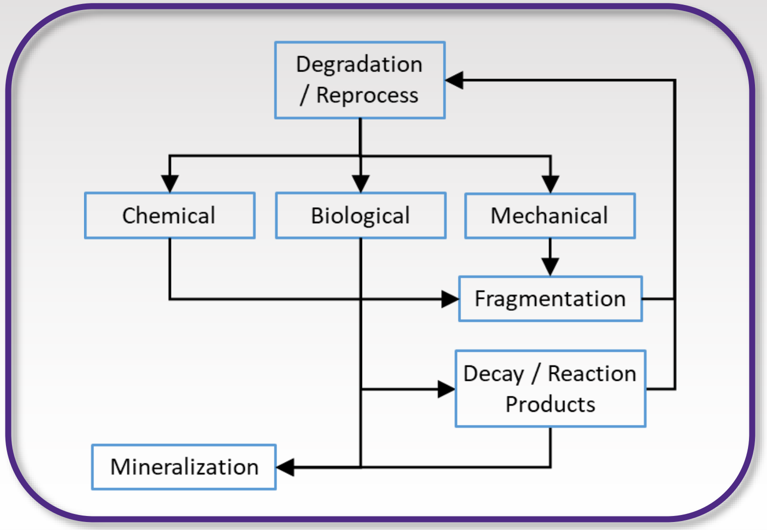


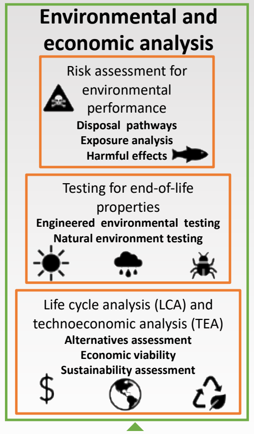


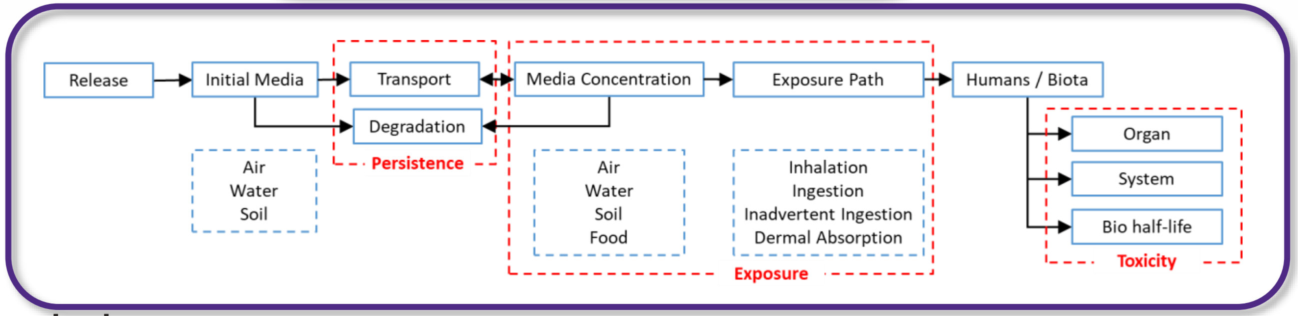
Task 4: Risk Assessment Framework

Progress and Outcomes

- Developed a draft risk assessment exposure schema
  - EOL release options and pathways through the environment
  - Routes of exposure through the environment
- Developed preliminary ranking criteria for the risk assessment framework
  - Relative risk: 1. persistence, 2. exposure, 3. toxicity / impairment
  - Framework foundation
  - Guides remaining development and evaluation
- Identified 4 EOL scenarios for evaluation (Task 4.1 milestone)
  - 1. litter, 2. incineration, 3. landfill, 4. recycle/reuse
  - Encompass wide range of potential outcomes
- Ongoing literature search – functional group characteristics
  - Feeds into Task 4.2 milestone as to determining degradation processes and the relative stability of soft and hard segment polymer chains
  - Needed for the framework decision matrix





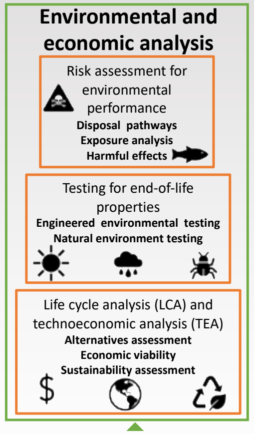


Task 5: End-of-life Property Testing

Approach

- End-of-life testing scenarios
  - engineered environments: landfill, AD and composting facilities
  - natural environments: soil, fresh and marine water
- Test biodegradation of PHU and PTU under different environmental conditions
  - Side-by-side systematic assessment of both synthetic and new PHU and PTU in natural and engineered environments
- Target validation of model results and provision of a more holistic picture of the fate of PHU and PTU in the environment
  - Determine % carbon conversion to CO_2, rate of conversion, and changes in mechanical properties
  - Conceptual understanding of steps involved in biodegradation

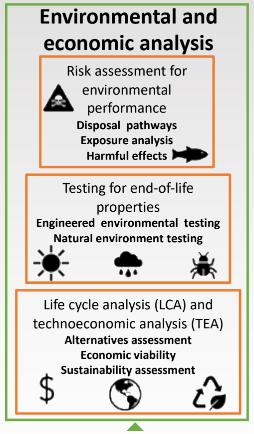
https://www.ieabioenergy.com/wp-content/uploads/2018/10/Standards-and-Labels-related-to-Biobased-Products-2016-to-2018.pdf



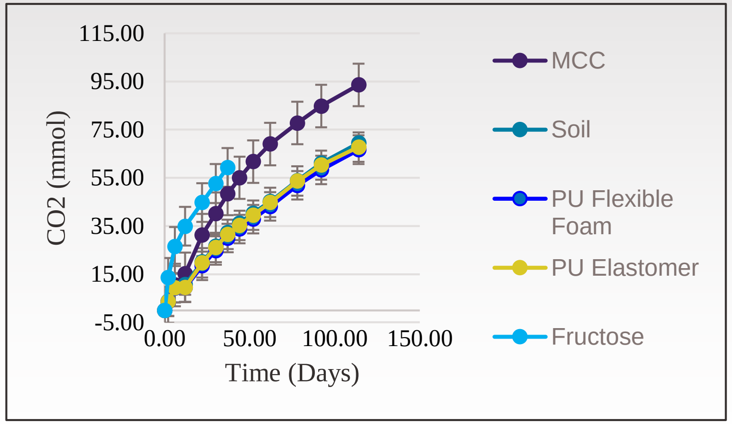
Task 5: End-of-life Property Testing

Approach: Standard Methods Used for Biocertification

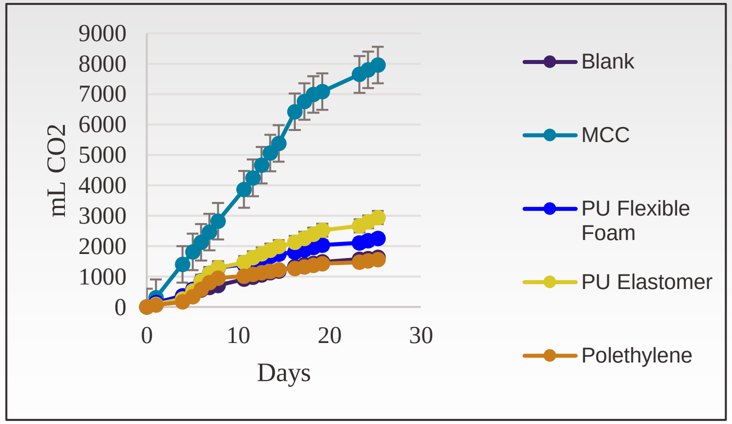
Method Name	Temperature	Inoculum	Sample Size	Reactor size	Duration	Measurement
ISO 14851 - *Aerobic biodegradability of plastic materials in an aqueous medium*	23 °C ± 1 °C	Activated sludge taken from a WWTP	25 mg	300 mL	Min 28 days	BOD over time or CO_2
ASTM 5988 - *Aerobic Biodegradation of Plastic Materials in Soil*	23± 2 °C	Natural Soil	1 g	2L	Max 2 years	Volume of CO_2
ASTM 5338 - *Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions*	58 ± 2 °C	Mature compost	20 g	500 mL	Min 45 Days	Volume of CO_2
ASTM 5511 - *Anaerobic Biodegradation of Plastic Materials Under High-Solids Anaerobic Digestion Conditions*	37 ± 2 °C	Activated sludge taken from a stand-alone food waste digester	3.75 g	500 mL	15-30 Days	Volume of CO_2 and CH_4



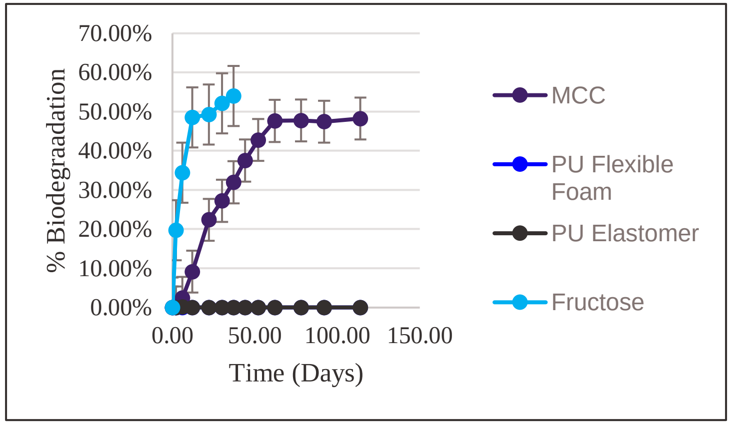
Progress and Outcomes



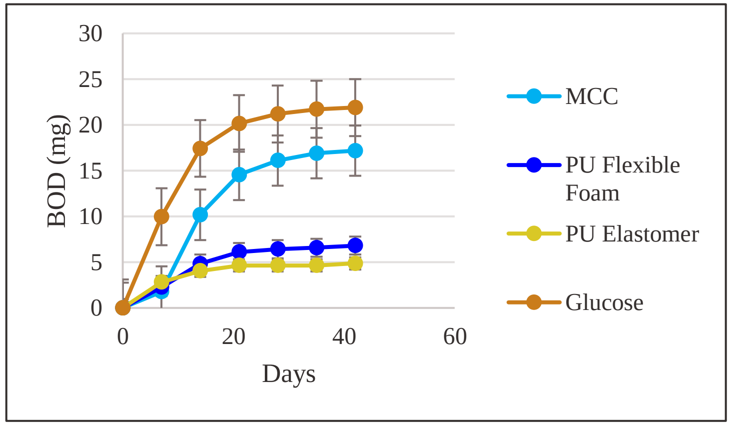
Soil environment



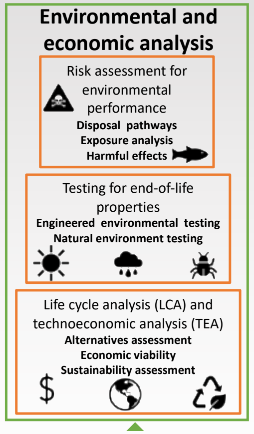
Composting environment



Soil environment



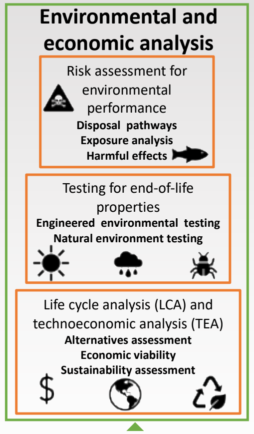
Freshwater environment



Task 6: Systems Economic and Sustainability Analysis

Approach

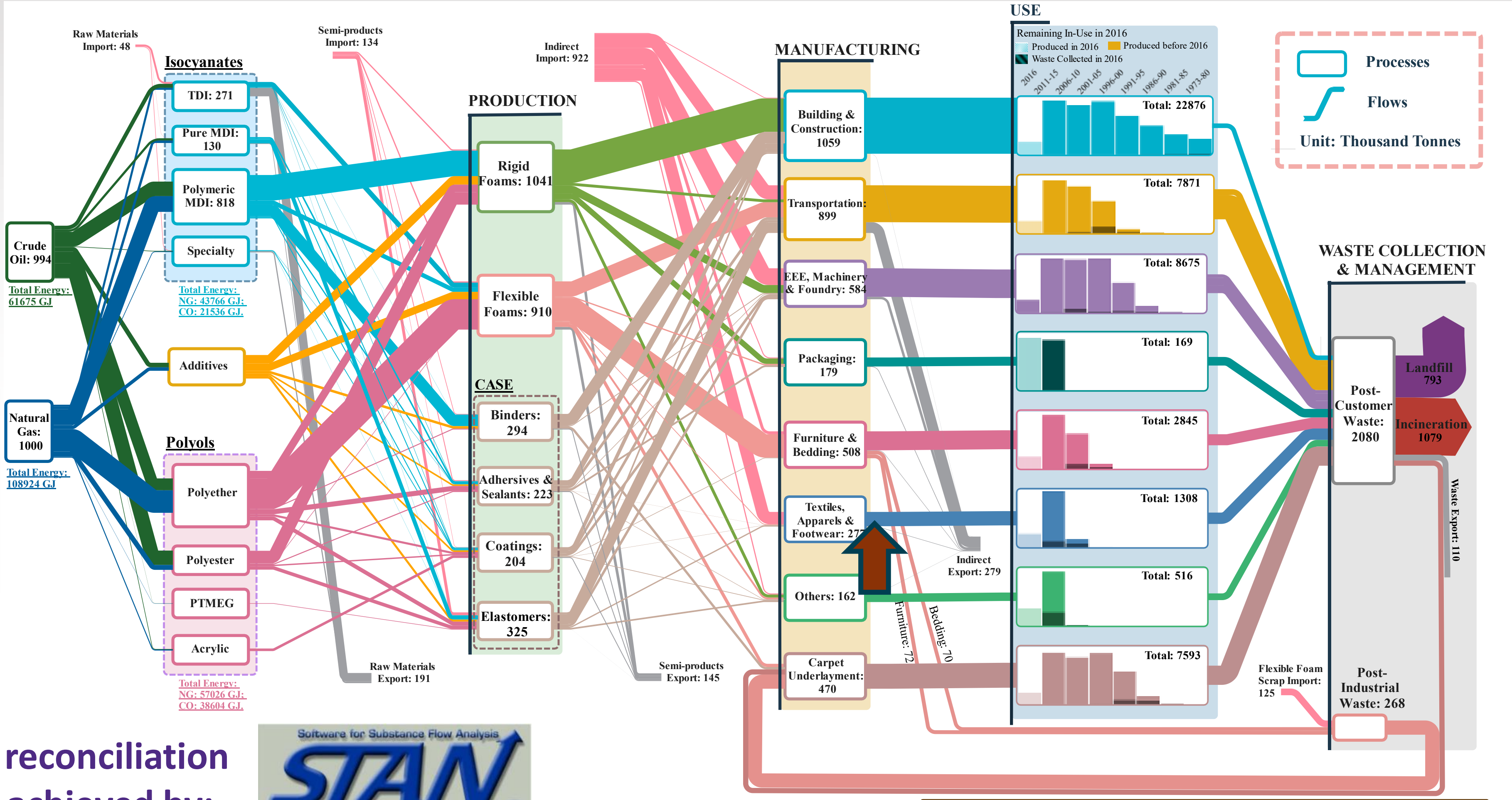
- Process modeling in AspenPlus that leverages existing BETO design cases and prior work.
- Modeling informs techno-economic analysis
- Material and energy flows inform life cycle analysis with Argonne's Greenhouse gases, Regulated Emissions and Energy use in Technologies (GREET™) model
- Material flow analysis used numerous data sources and STAN software for data reconciliation

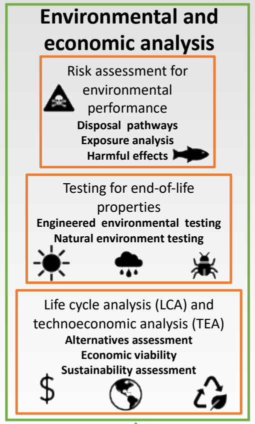


Task 6: Systems Economic and Sustainability Analysis

Progress and Outcomes

Completed materials flow analysis of PU in the US for 2016 from raw material to end-of-life





Data reconciliation was achieved by: STAN 2 — Software for Substance Flow Analysis, Vienna University of Technology

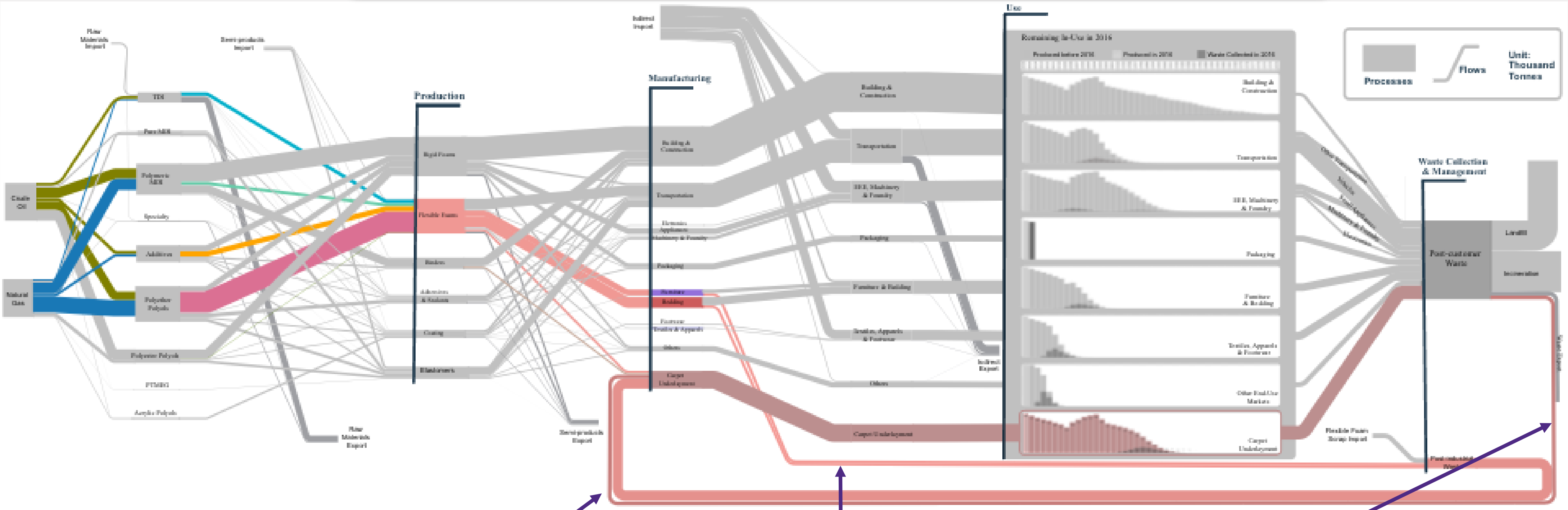
Sankey diagram was drawn by: e!sankey — show the flow

EEE: Electrical and Electronic Equipment;
MDI: Methylene Diphenyl Diisocyanate;
TDI: Toluene Diisocyanate;
PTMEG: Polytetramethylene Ether Glycol

Task 6: Systems Economic and Sustainability Analysis

Progress and Outcomes

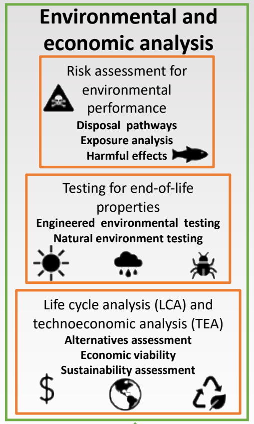
Circularity is currently limited to carpet underlayment



Carpet underlayment

Post-industrial waste

Post-consumer waste



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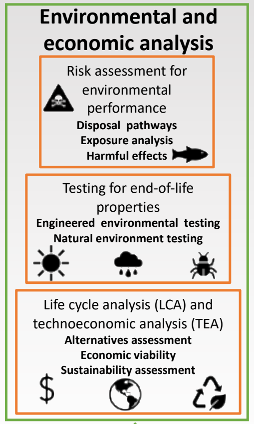
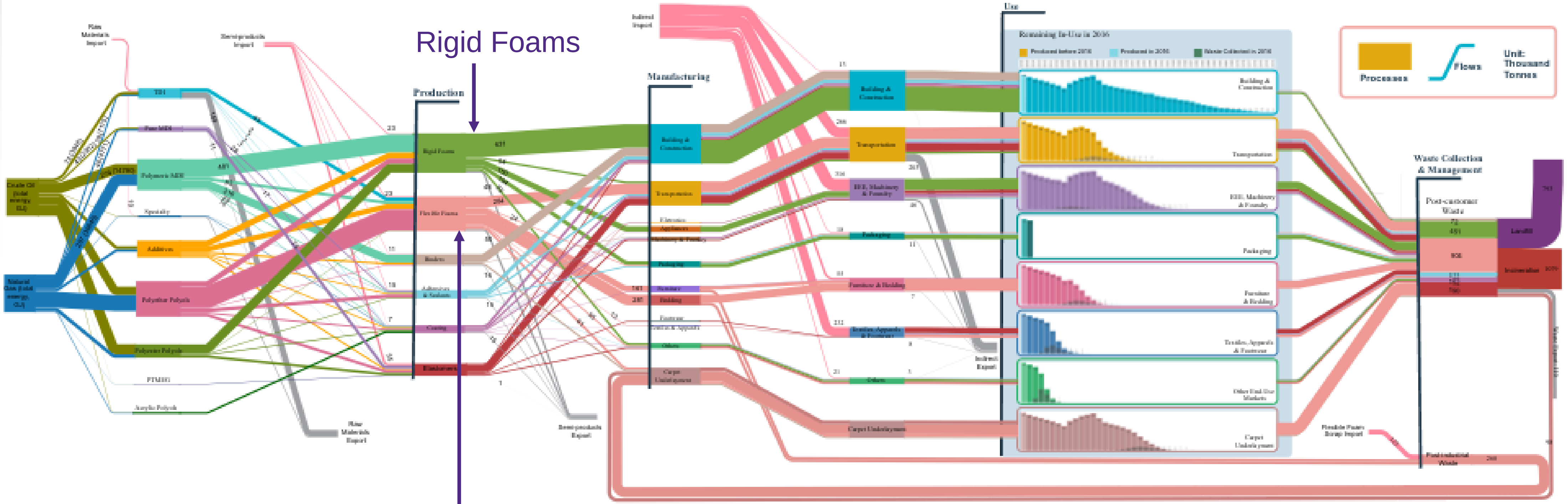
Task 6: Systems Economic and Sustainability Analysis

Progress and Outcomes



Flexible foams dominate flows to end of life



Milestone 6.1 Completed: Identify and quantify disruption of PU supply chain, including emerging or potential new PU uses, resulting from development of highly-recyclable PU. Present results to ResIn team and BETO in preparation for dissemination in the public domain

Summary and Key Takeaways

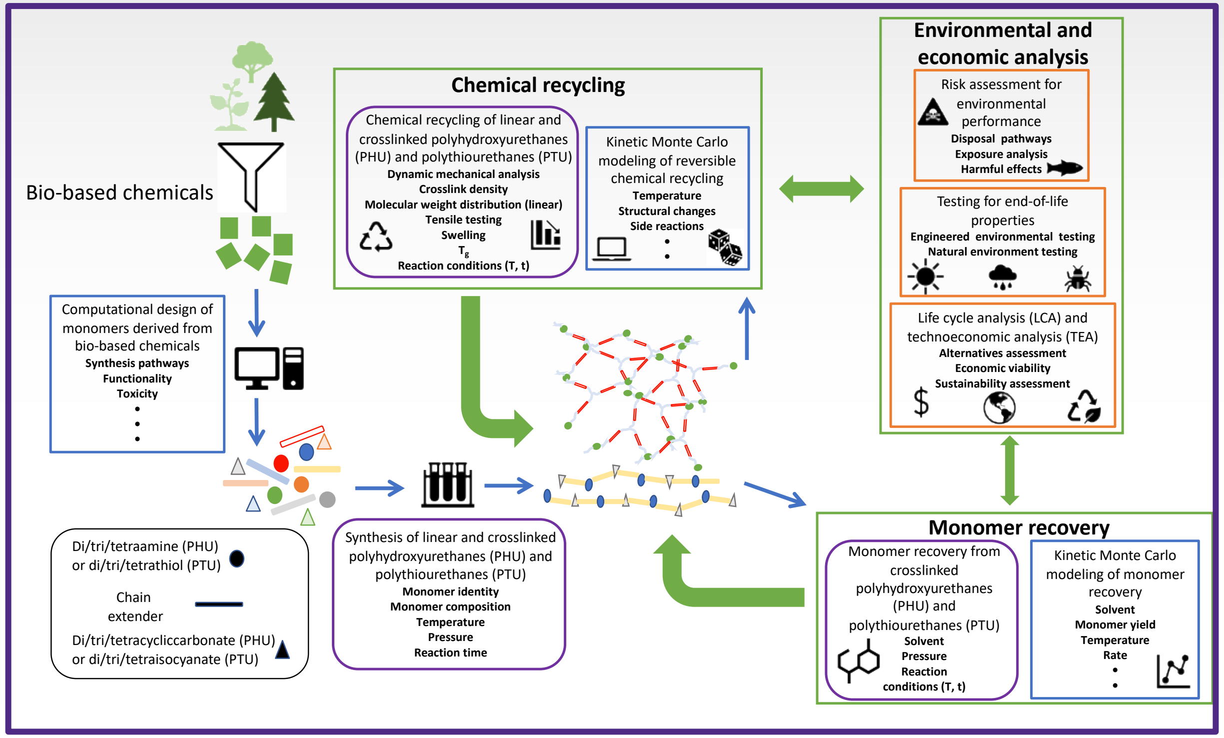
Polyurethanes (PU) are currently not recycled

PU are currently produced from a supply chain originating from fossil fuels

Key deliverables

New bio-based polyhydroxyurethanes (PHU) and polythiourethanes (PTU), linear and crosslinked, that can be recycled to original use or monomer recovery

A design framework that includes kinetic Monte Carlo simulations, LCA, TEA, risk assessment and end-of-life testing



Quad Chart Overview

Timeline
- Project start date: 10/1/2019
- Project end date: 12/31/2022

	FY20 Costed	Total Award
DOE Funding	$239,008	$2,499,998
Project Cost Share	$261,378	$656,485

Project Partners
- Fenner Precision
- The Dow Chemical Company
- Michelin

Project Goal
Our project goal is to achieve chemical recyclability, as measured by 25% or more of recovered monomers, of polyhydroxyurethanes (PHUs) and polythiourethanes (PTUs) through production routes that are economically viable and are at least 50% biomass-derived.

End of Project Milestones
Milestone 2.6: Computational prediction of end-of-life fate as a function of monomer identity, material topology, and chemical recycling conditions

Milestone 3.7: Optimized quantitative details on recovery of crosslink density and recovery of other properties after recycling of spent PHU and PTU networks (from subtasks 3.7 and 3.9) by reprocessing enabled by several dynamic chemistries

Milestone 4.5: Release of complete set of information as report to team members and BETO on critical properties of environmentally benign target products

Milestone 5.4: Definition of key analytical approaches beyond CO_2 generation that correlate with mechanisms responsible for biodegradation of plastics under different environmental conditions

Milestone 5.5: Model results (Task 2) are validated with experimental data

Milestone 6.5: Finalize cost and sustainability metrics for highly-recyclable, 50% bio-based PU (e.g., $/kg, kg CO2e/kg) and characterization of influence of highly-recyclable, 50% bio-based PU on PU and associated supply chains in the United States

Funding Mechanism
FY19 Bioenergy Technologies Office Multi-Topic Funding Opportunity Announcement DE-FOA-000209

Area of Interest: 8a: Designing Highly Recyclable Plastics

Additional Slides

Publications, Patents, Presentations, Awards, and Commercialization

- Liang, C., Gracida, U. R., Gallant, E., Hawkins, T. R., & Dunn, J. B. (November 16–20, 2020). The Influence of Increasing Polyurethane Recyclability and Renewable Content on Material Flows [Conference presentation]. 2020 Virtual AIChE Annual Meeting.
- Dunn, J. B., Liang, C., Gracida, U. R., Gallant, E., Hawkins, T. R. (December 10, 2020). Materials flow analysis in support of circular plastics economy development: Polyurethane in the United States. Northwestern University Institute on Sustainability and the Environment Program on Plastics, Ecosystems, and Public Health Seminar Series. https://isen.northwestern.edu/materials-flow-analysis-supporting-a-circular-plastics-economy
- "Methods for making recyclable and depolymerizable polymer network materials via thiourethane dynamic chemistry", J.M. Torkelson, L. Li, and X. Chen, U.S. Patent App. 16/913,635.
- Torkelson, J.M., "Transforming Thermosets into Thermoplastics: Dynamic Covalent Bonds Enable the Sustainable Chemical Recycling of Traditionally Non-recyclable Polymer Materials", Inaugural Seminar Series for the Biodesign Center for Sustainable Macromolecular Materials and Manufacturing, Arizona State University, October 15, 2020.
- Guanhua Wang, Lauren Lopez, Matthew Coile, Yixuan Chen, John M. Torkelson, and Linda J. Broadbelt, Identification of Known and Novel Monomers for Poly(hydroxyurethanes) from Biobased Materials, submitted to *Ind. Eng. Chem. Res.*, **2021**.

Acronym guide

PHU: polyhydroxyurethane
PTU: polythiourethane
PU: polyurethane
kMC: kinetic Monte Carlo
TEA: technoeconomic analysis
LCA: life cycle assessment
NU: Northwestern University
ANL: Argonne National Laboratory
GREET^{TM}: Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies
SciDAC: Scientific Discovery through Advanced Computing
HPC: High performance computing
EOL: End of life
AD: anaerobic digestion
ISO: International Organization for Standardization
ASTM: American Society for Testing and Materials
BOD: biological or biochemical oxygen demand
STAN: subSTance *flow* ANalysis

Material Flow Analysis Data Sources

Name	Time	Source	Summary
Trade Data	2016	USITC, CCC	Import and export data of raw materials for PU, PU products, end-use products, PU wastes
PU Concentration Data	2016	ISOPA, WRAP, PlasticsEurope, peer-reviewed literature, market report, experts' estimates	Content of PU in end-use products and wastes (kg PU/kg commodity)
Production Data	2016	PU Magazine, ICIS	PU production amount
Transfer Coefficient Data	2016	PU Magazine, ACC, peer-reviewed literature	Distribution of PU by end use, distribution of PU by product type
Waste Data	2016	EPA, CCC, peer-reviewed literature, experts' estimates	PU waste amount
Raw Material Data	2014, 2018	ACC, ISOPA, market report	Isocyanate, polyols, and additives production amount, distribution of raw materials to PU products

USITC: United States International Trade Commission
ACC: American Chemistry Council
ISOPA: European Diisocyanate & Polyol Producers Association
CCC: Carpet Cushion Council
EPA: Environmental Protection Agency
ICIS: Independent Commodity Intelligence Services

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