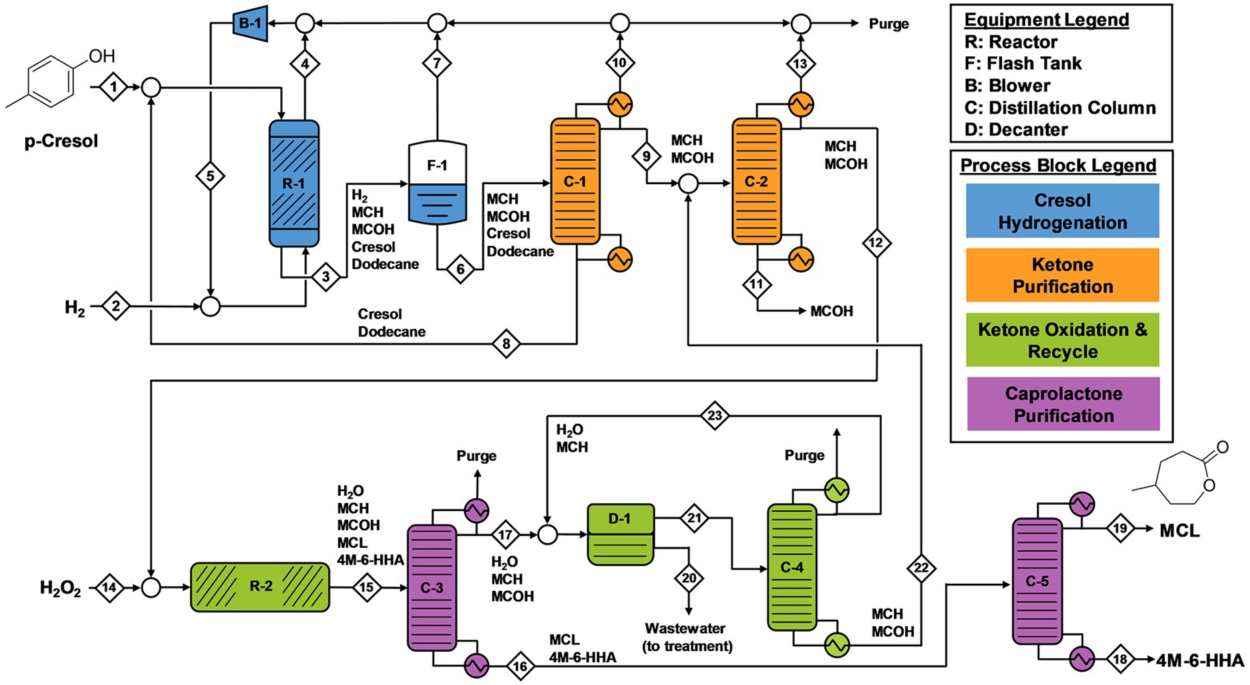
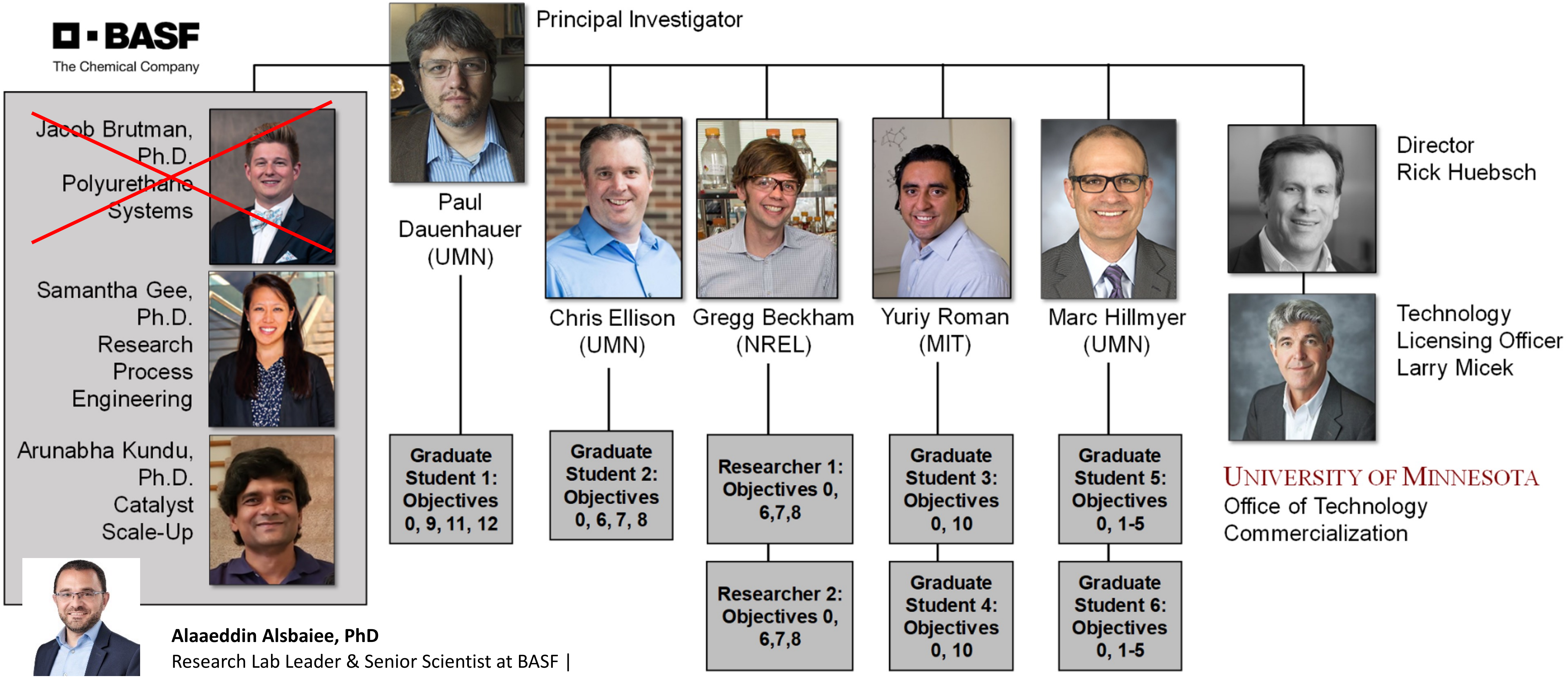
Recyclable and Biodegradable Manufacturing and Processing of Plastics and Polymers based on Renewable Branched Caprolactones

Paul J. Dauenhauer, University of Minnesota

Summary. A chemical process is proposed of parallel closed loops of renewable polymers based on alkyl-caprolactone monomers, allowing for a broad range of materials and applications while also providing flexibility in material end-of-life options without long-term waste. A ‘lignin first’ approach converts lignin (derived from trees and grasses) to aromatic monomers using the existing MIT and NREL Reductive Catalytic Fractionation (RCF) process. These alkylated aromatic monomers then undergo tandem reduction to cyclic ketones and Baeyer-Villiger oxidation to alkyl-caprolactones for use in multiple classes of polymeric materials. These polymers can biodegrade to CO_2 and H_2O and are eventually converted back to lignin or other biomass via photosynthesis (loop #1). Alternatively, chemical processes convert the polymers back to their base monomers (loop #2).



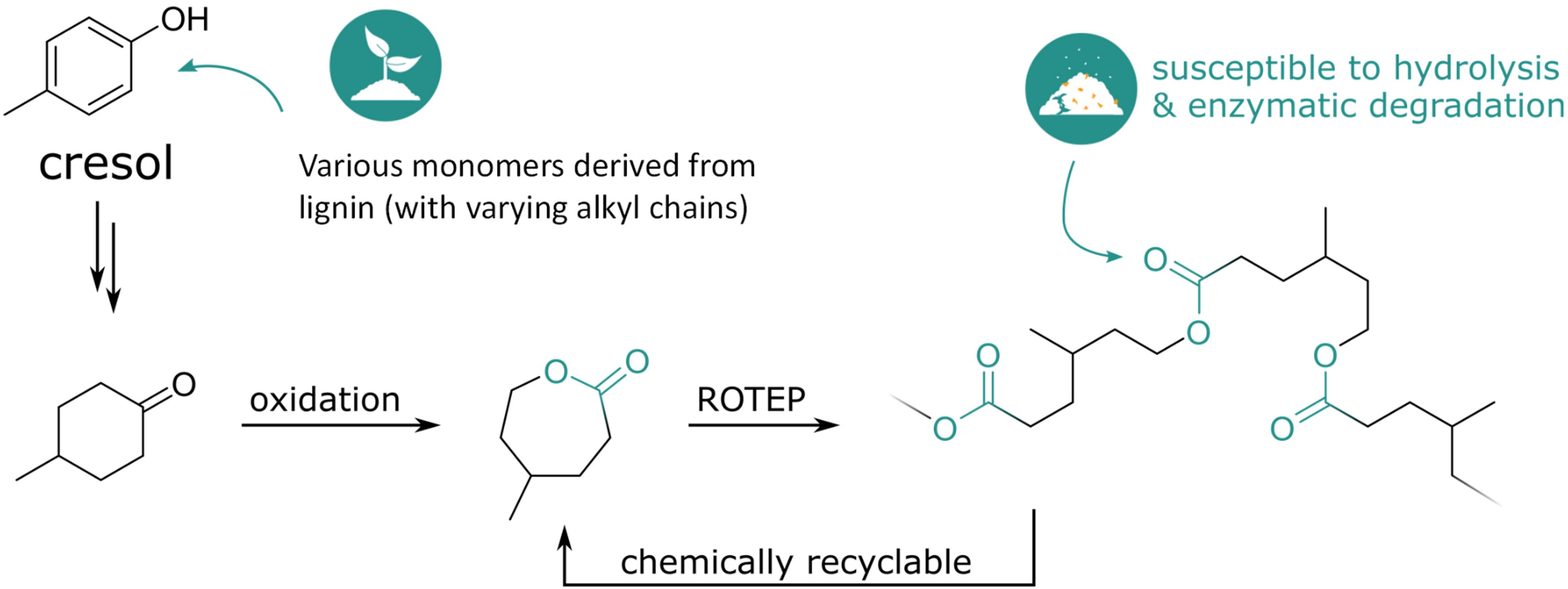
Project Team and Organization



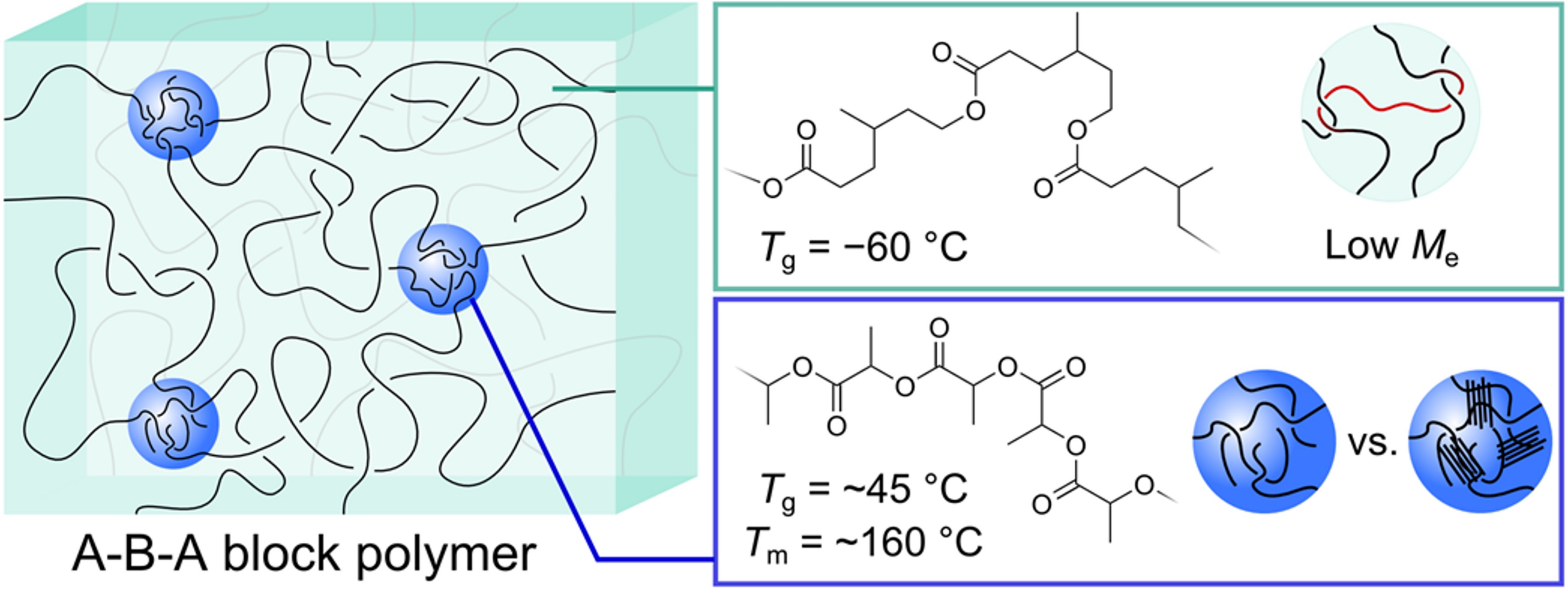
Student Researchers

- Jimmy Soeherman: University of Minnnesota
- Michaela Pfau-Cloud: University of Minnesota
- Aristotle Zervoudakis: University of Minnesota
- Jamison Watson: MIT
- Abhay Athaley: NREL

Approach: Technology Overview: Monomers & Polymers



Approach: Caprolactone Polymer: Advanced Properties, Temperature



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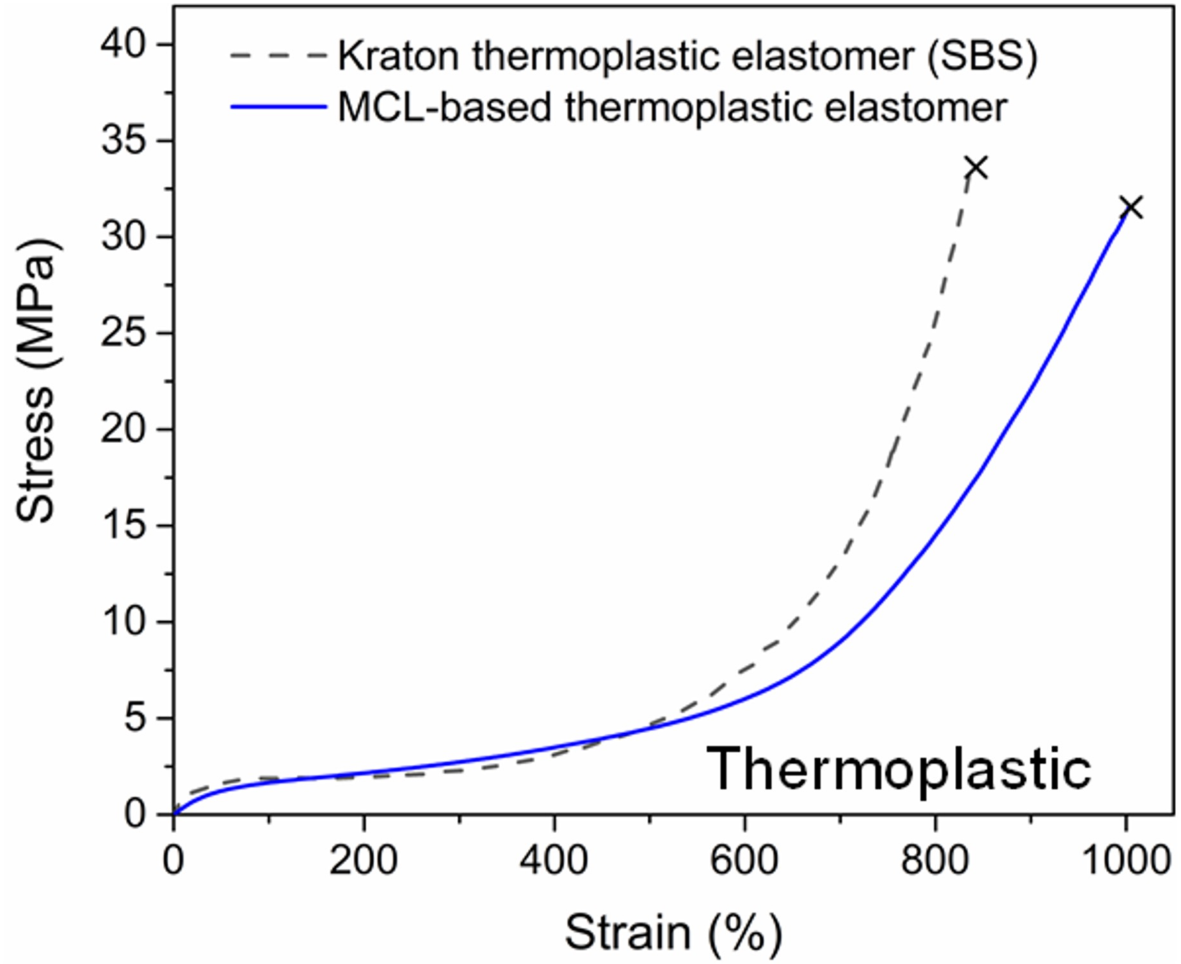
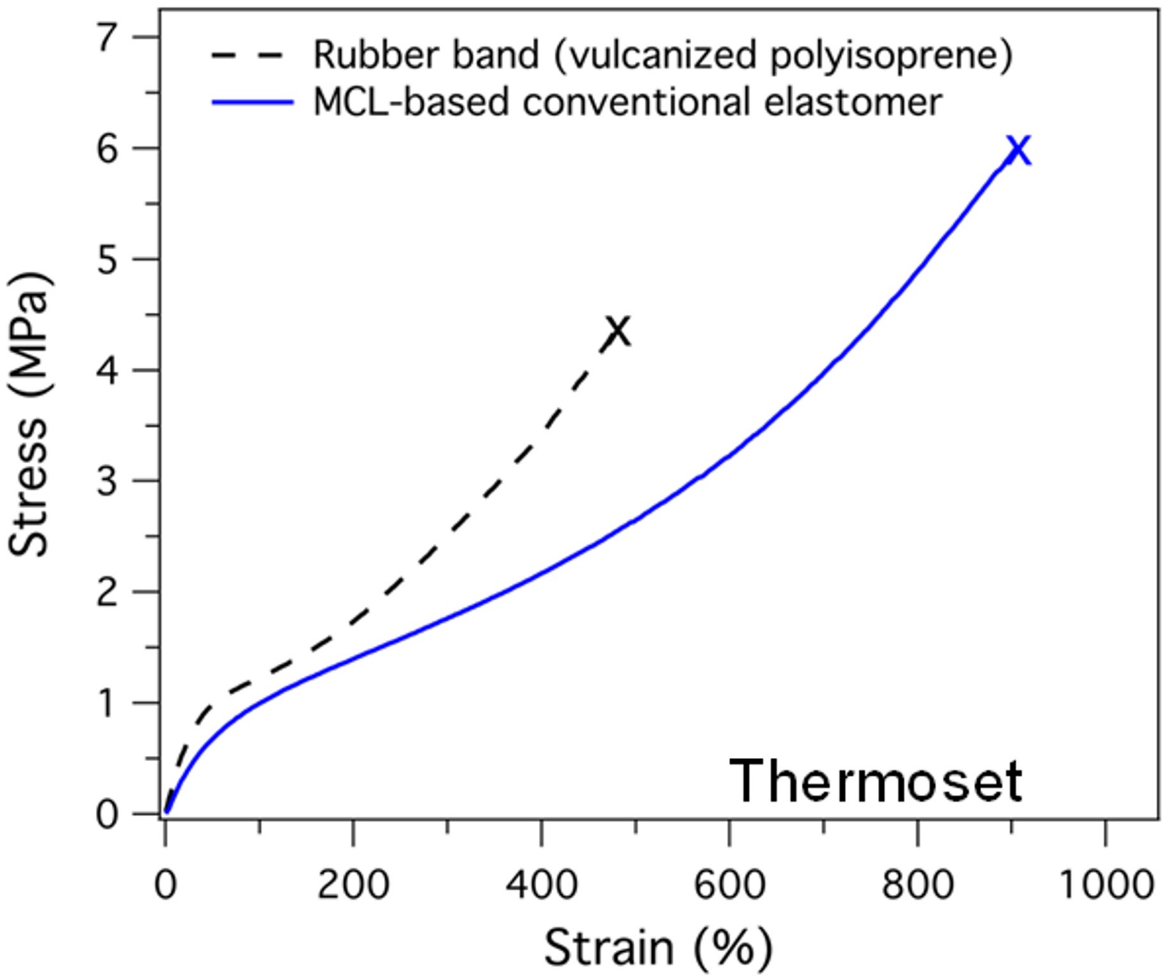
Impact: Caprolactone Polymer: Advanced Properties, Strain





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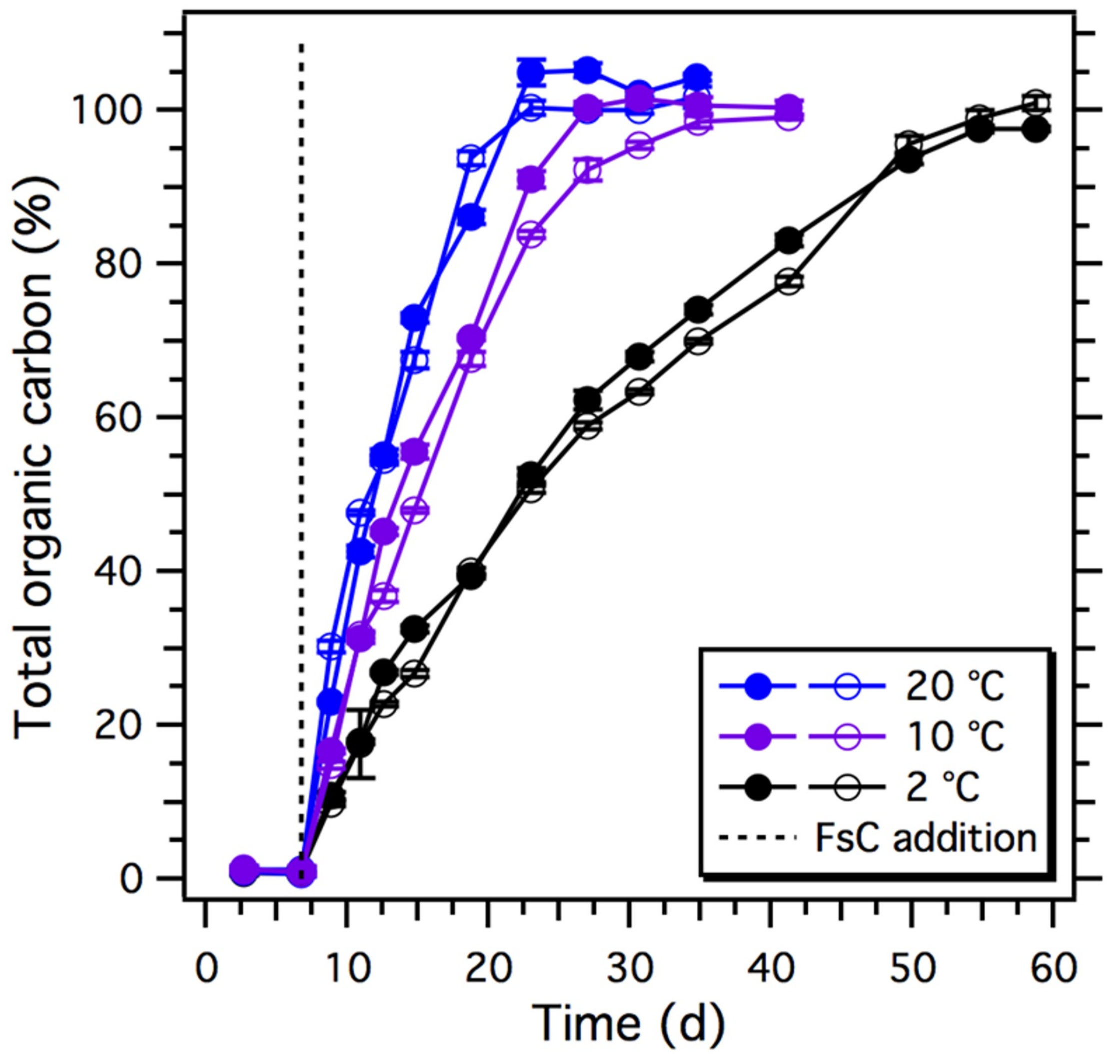
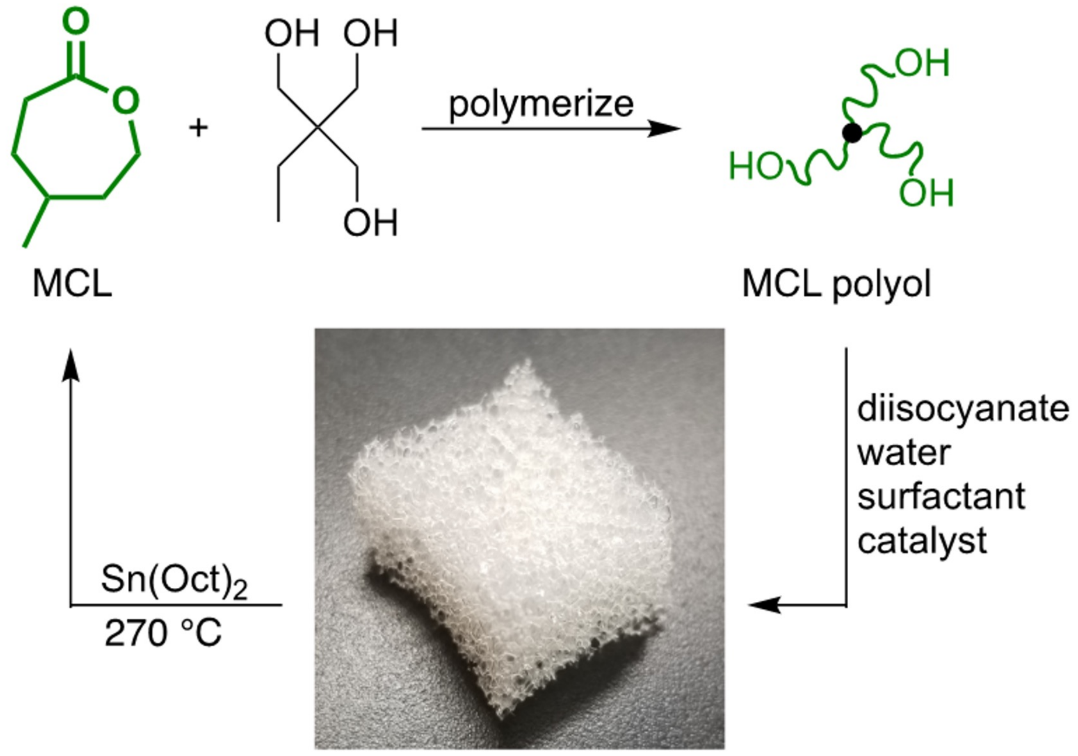
Impact - Caprolactone Polymer: Chemical Recycling





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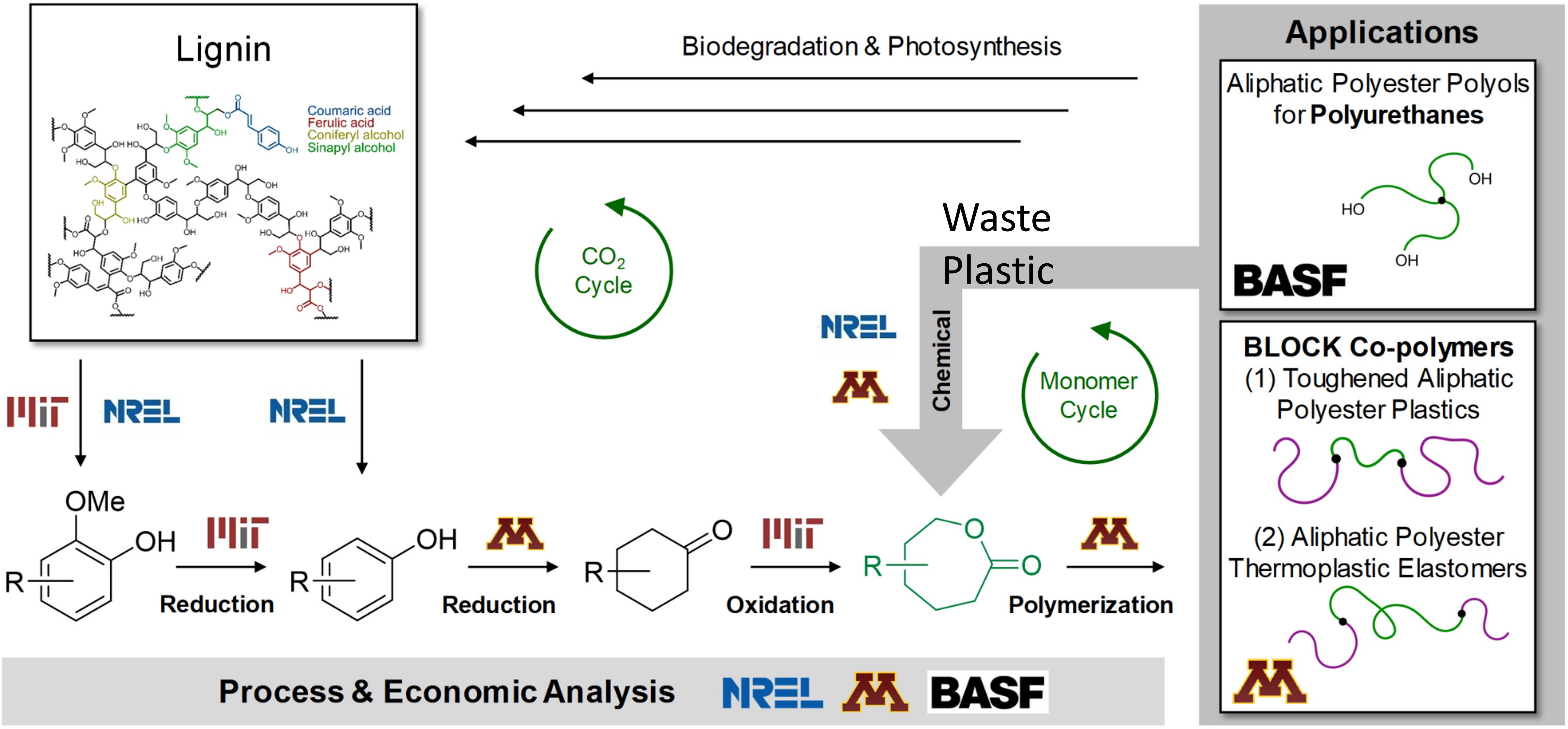
Approach: Renewable Caprolactone-based Plastic Cycles

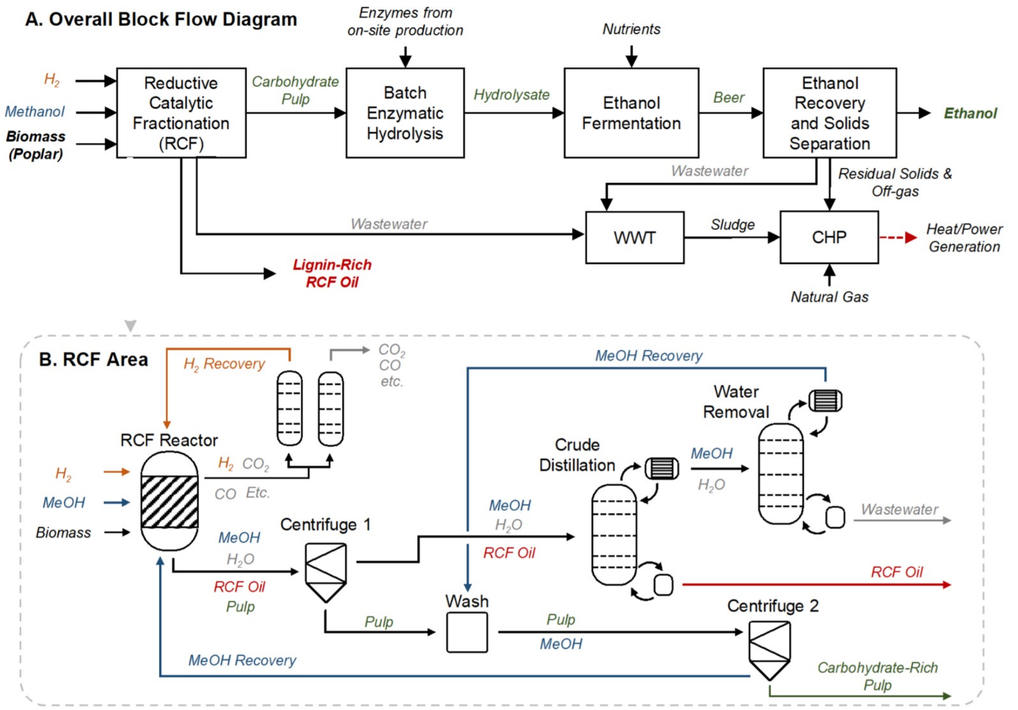


Metrics & Primary Targets

- Energy: ≥50% energy savings relative to virgin material production for upcycled plastics;
  - Basis: Compare energy of recycling to entire monomer production process of biomass production, RCF process, and hydrogenation/oxidation/purification
  - **Ratio = (Energy of Recycling) / (Energy of RCF, Hydrogenation, Oxidation)**
  - Note: This ratio will also increase if we include biomass production, harvesting, and pre-processing
- Carbon: ≥75% carbon utilization from waste plastics in an upcycled product; and
  - Basis: Evaluate polymer decomposition yield using extruder reactor with catalyst and recycled monomer purification
- Economics: ≥2x economic incentive for upcycled products relative to today's standard recycling.
  - Basis: Work backwards from monomer value + costs of recycling to determine feedstock breakeven price of waste plastic

Lignin Sourcing via RCF Process

NREL Transforming ENERGY



Existing RCF process at NREL converts woody biomass to lignin monomers

Existing design with accompanying TEA and LCA

Will provide propyl-phenols in sufficient quantity to conduct caprolactone synthesis experiments

Not a focus of the current project, but it will supply feedstock

Lignin RCF → Hydrogenation → Oxidation → Polymerization → Recycle

TEA and LCA

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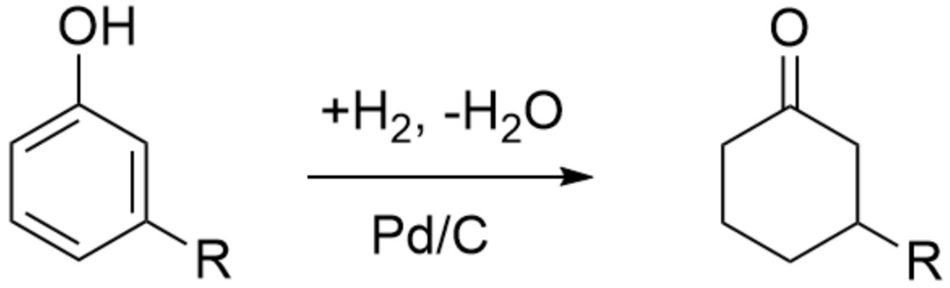
Hydrogenation to Cyclic Ketones



Hydrogenation of alkyl-phenol reactant selectively makes cyclic ketones

Experiments utilize existing Parr reactors and flow reactors at the University of Minnesota (photograph)

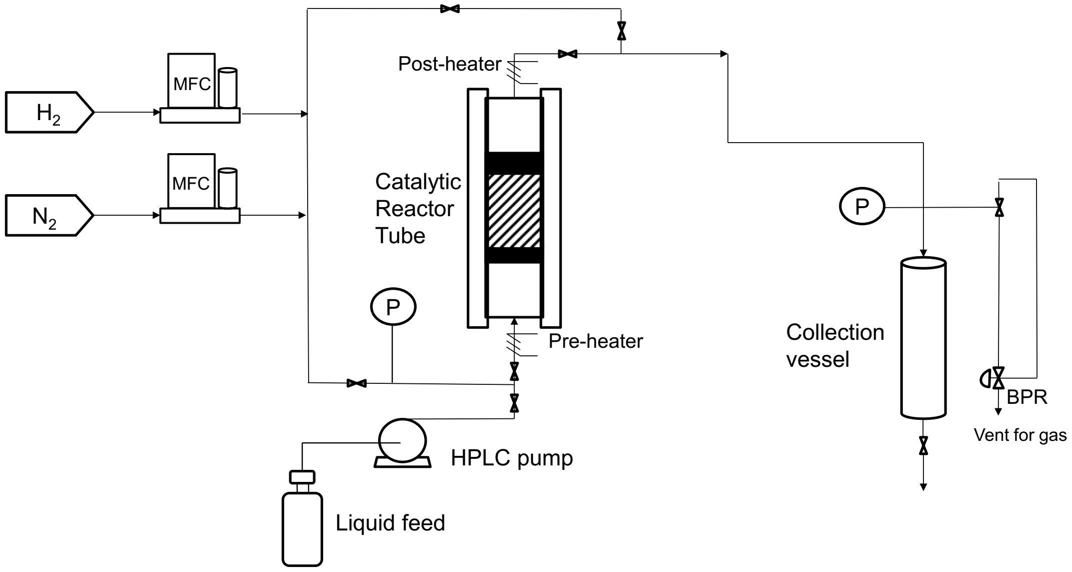
Experiments aim to maximize selectivity to ketone products without over hydrogenation

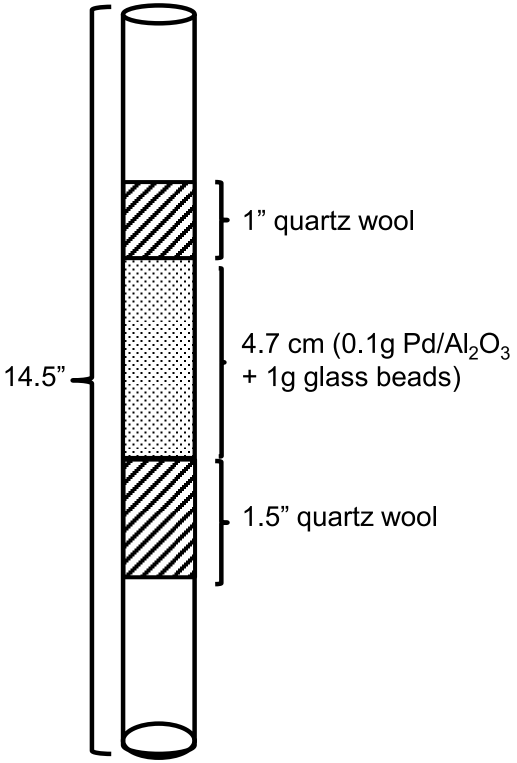
Lead: Paul Dauenhauer

Lignin RCF → **Hydrogenation** → Oxidation → Polymerization → Recycle

TEA and LCA

Hydrogenation to Cyclic Ketones



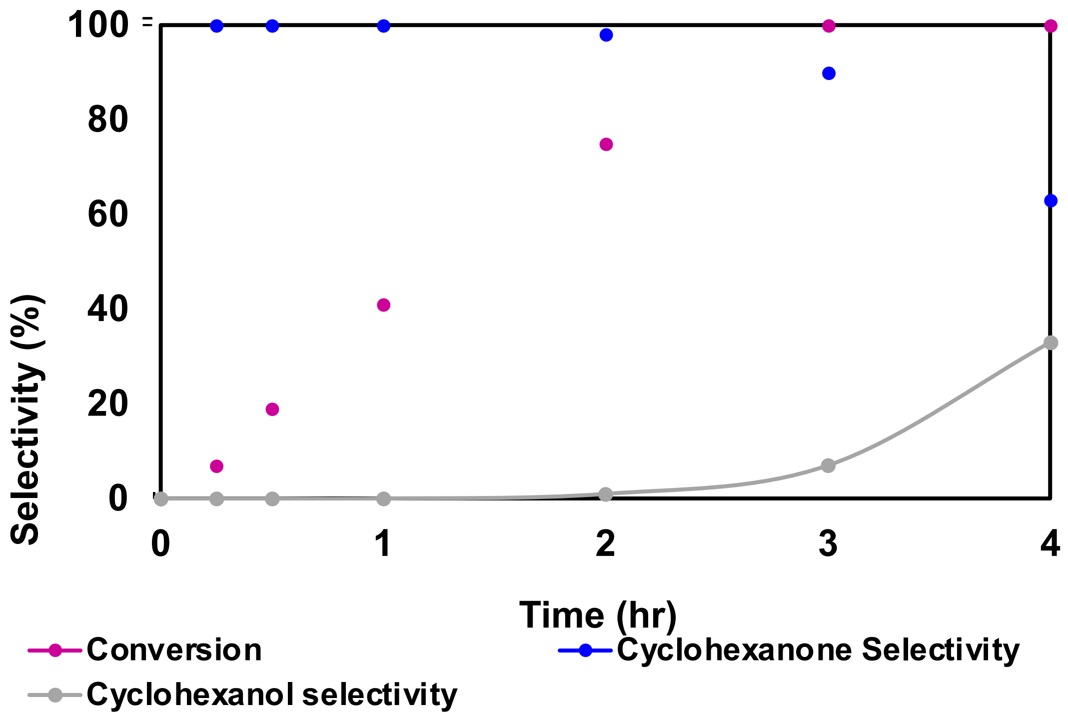


Completed: Reactor three-phase parameter optimization, gas – liquid – solid contacting

Lignin RCF → **Hydrogenation** → Oxidation → Polymerization → Recycle

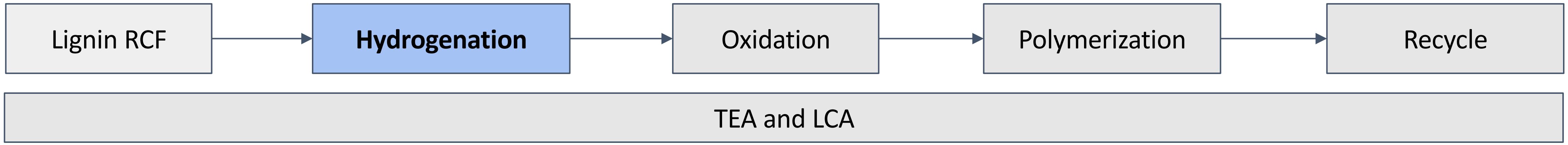
TEA and LCA

Hydrogenation to Cyclic Ketones

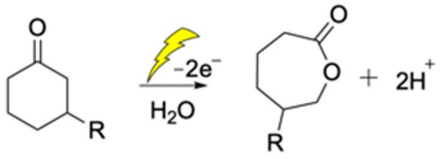


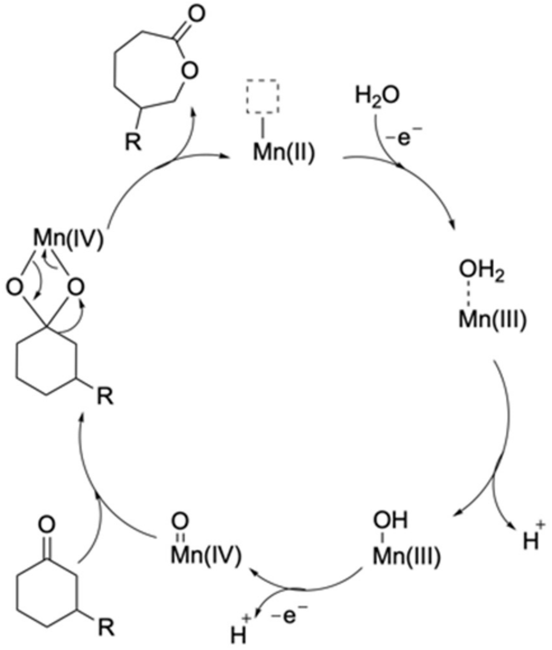
Identified: Supported metal catalyst that gives >99% selectivity to cyclohexanone

In Progress: Reactor optimization for activity and kinetic measurements for process model



Oxidation of Cyclic Ketones





Electrochemical Baeyer-Villiger oxidation converts cyclic ketones to alkyl-caprolactones

Experiments utilize existing electrocatalytic reactors at MIT

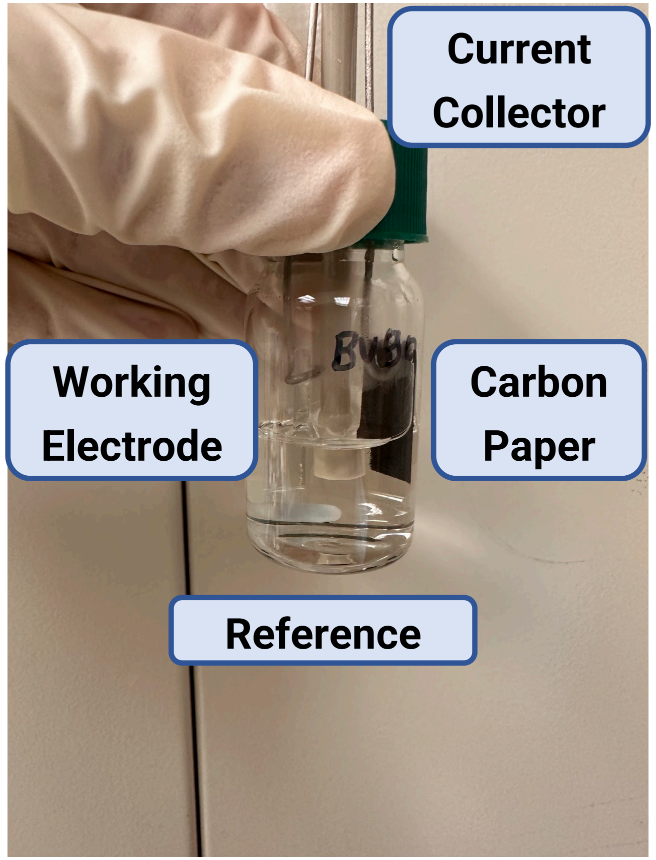
Experiments aim to maximize selectivity to caprolactone products without over oxidation

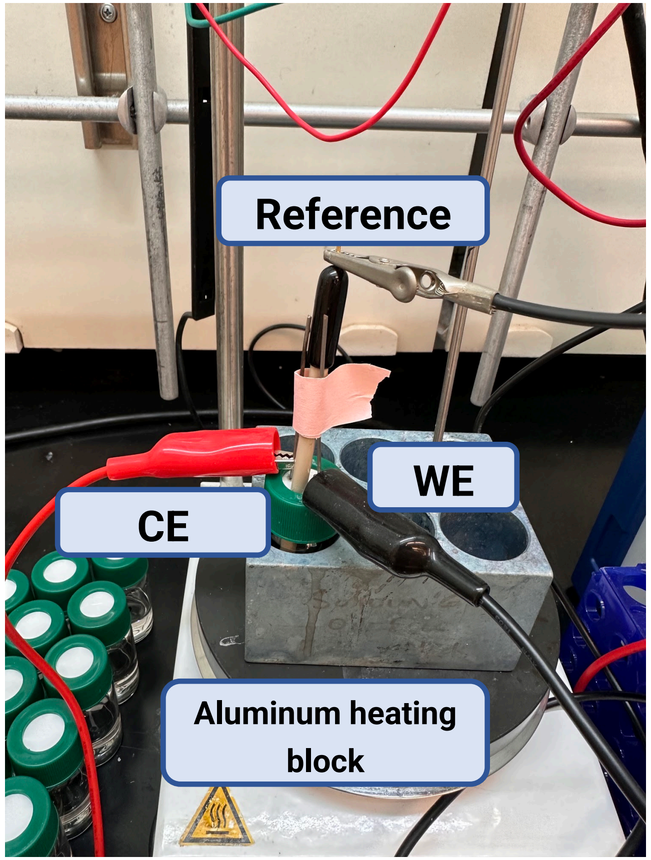
Lead: Yuriy Roman, MIT

Lignin RCF → Hydrogenation → **Oxidation** → Polymerization → Recycle

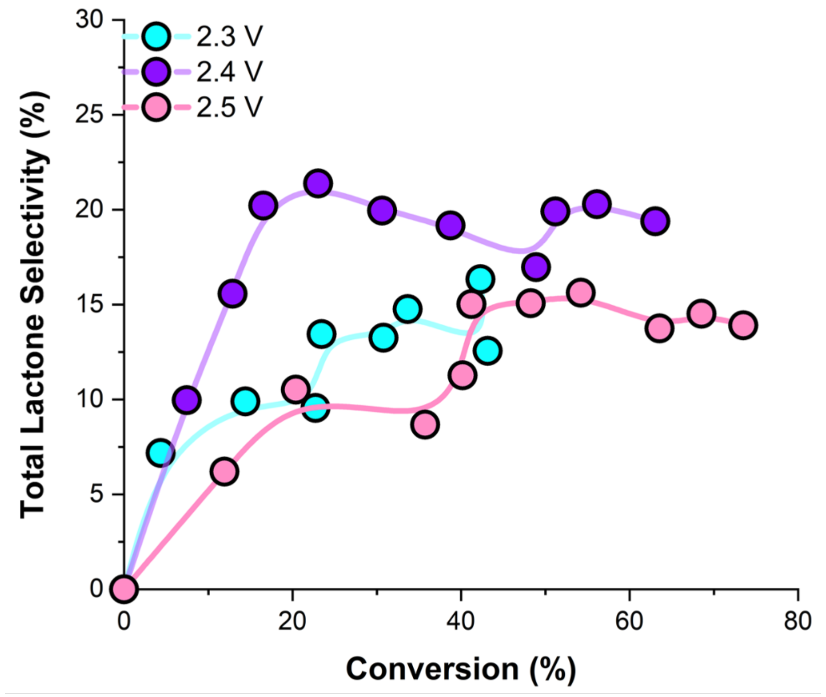
TEA and LCA

Oxidation of Cyclic Ketones – H_2O





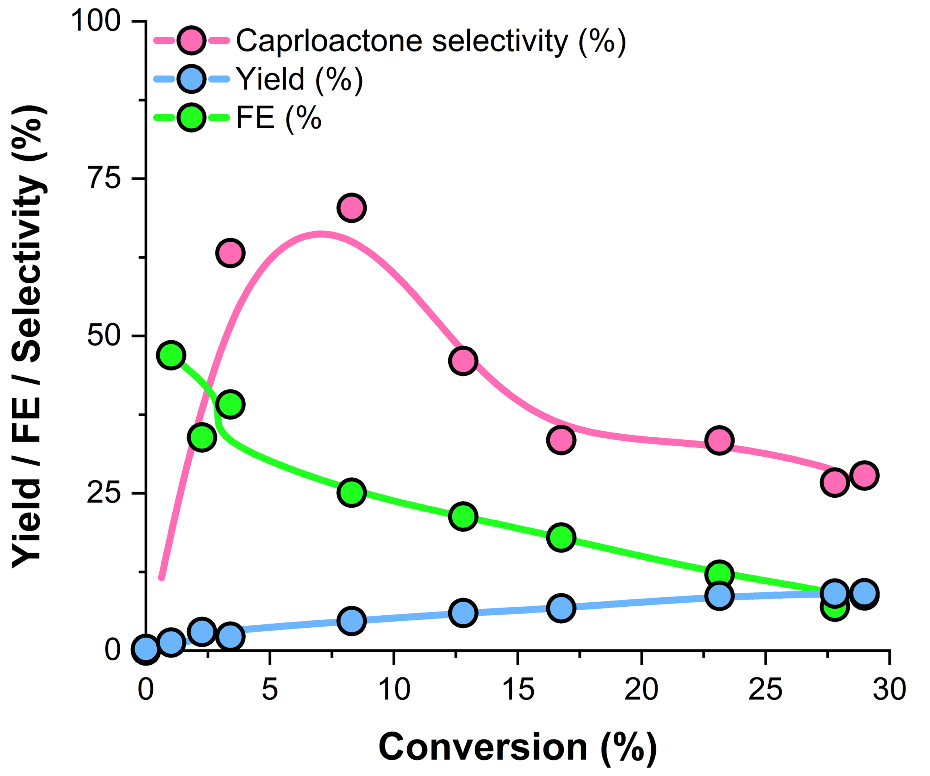
Low selectivity with Pt electrocatalyst and H_2O reactant



Lignin RCF → Hydrogenation → **Oxidation** → Polymerization → Recycle

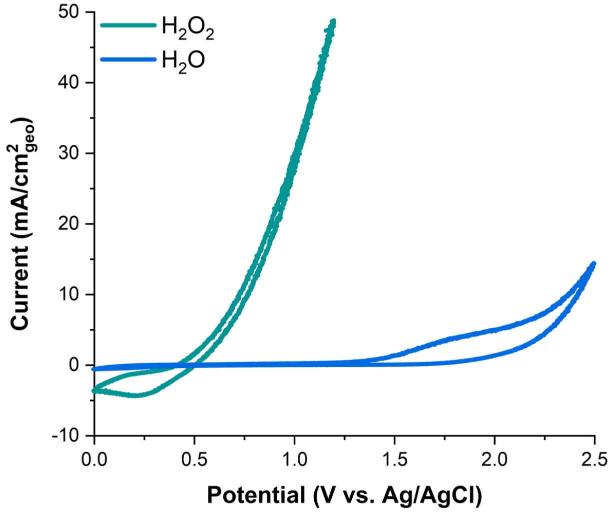
TEA and LCA

Oxidation of Cyclic Ketones – H_2O_2



Alternative: Oxidize with H_2O_2

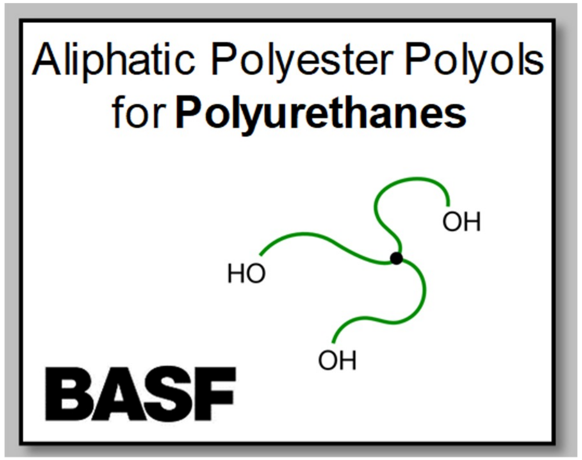
Result: High selectivity condition at ~10% conversion of 75% of target molecule

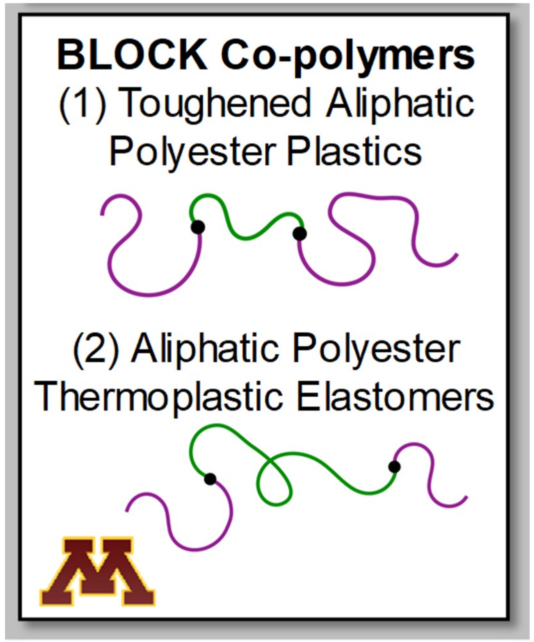


Lignin RCF → Hydrogenation → **Oxidation** → Polymerization → Recycle

TEA and LCA

Polymerization of Caprolactones





Polymerize alkyl-caprolactones to polyurethane and block co-polymers

Experiments utilize existing reaction equipment at the University of Minnesota and BASF

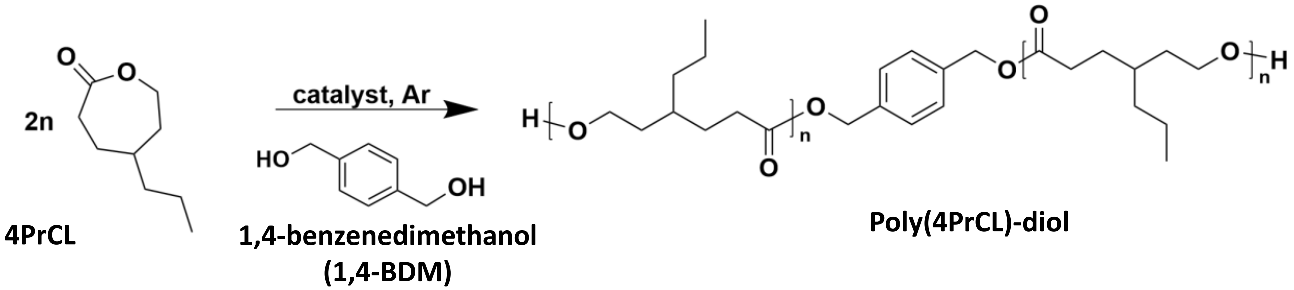
Experiments aim to controllably tune the properties of polymers for PU and TE applications

Leads: Jake Brutman (BASF), Marc Hillmyer (UMN)

Lignin RCF → Hydrogenation → Oxidation → **Polymerization** → Recycle

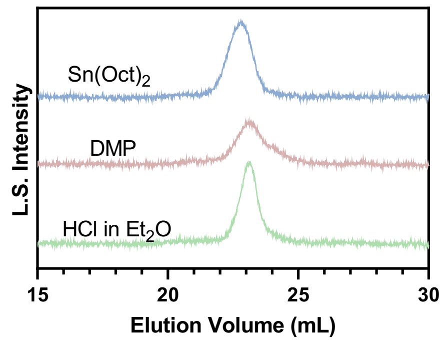
TEA and LCA

Polymerization of Caprolactones



Entry	Catalyst	4-PrCL (g)	Cat. (mol%)	Target M_n (kg/mol)	Initiator (mol%)	Temp. (°C)	Time	Conv. (%)	$M_{n,\ NMR}$ (kg/mol)	Observed Rate Constant (K_{obs}, h^{-1})
1	$Sn(Oct)_2$	3.0	0.2	50	0.31	150	1 h	96	40.4	3.6 ± 0.2
2		3.0	0.05	100	0.16	180	1 h	95	108	3.8 ± 0.4
3		3.0	0.05	10	1.56	180	30 min	95	11.0	6.7 ± 0.8
4	Dimethyl Phosphate (DMP)	2.0	5	10	1.56	100	1 h	96	10.1	1.8 ± 0.4
5		2.0	5	5	3.12	100	30 min	95	5.2	7.9 ± 0.6
6	Diphenyl Phosphate (DPP)	2.0	1	10	1.56	100	20 min	96	10.4	9.8 ± 3.0
7	Hydrochloric Acid in Ether (HCl in Et_2O)	2.0	2	10	1.56	RT	24 h	97	9.7	0.4 ± 0.02

SEC of P4PrCL (THF, 1.0 mL/min)

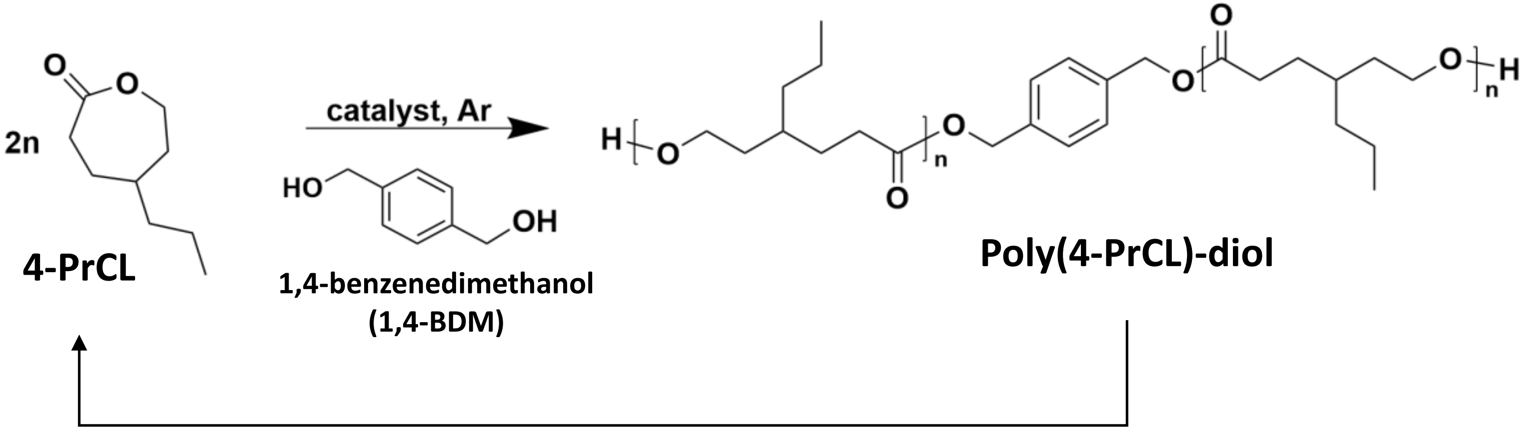


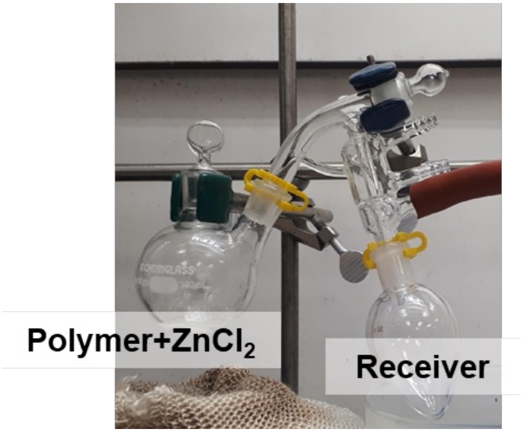
Catalyst	M_n (kg/mol)	M_w (kg/mol)	Dispersity (Đ)
$Sn(Oct)_2$	13.7	15.9	1.1
DMP	11.6	13.4	1.2
HCl in Et_2O	10.8	12.1	1.1

Lignin RCF → Hydrogenation → Oxidation → **Polymerization** → Recycle

TEA and LCA

Polymerization of Caprolactones





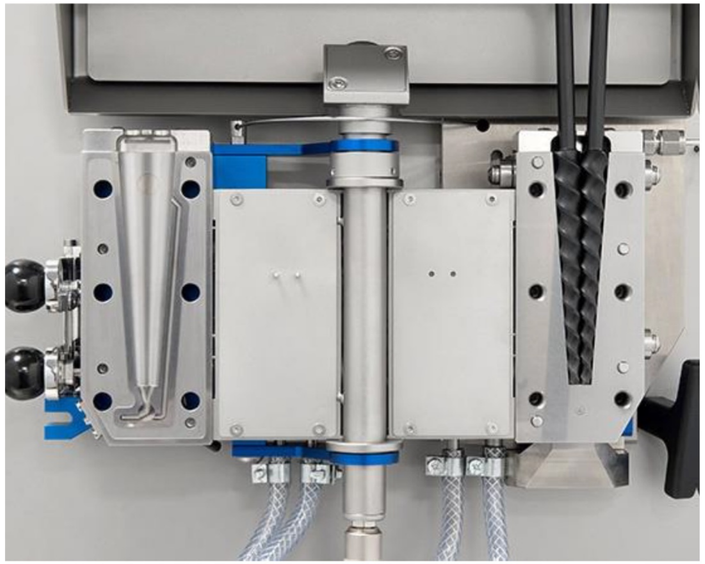
Entry	Catalyst	Cat. (mol%)	Yield (%)	Reaction Temp (°C)	Time (h)
1	$Sn(Oct)_2$	1	89	250-270	~ 20
2		5	91	250-270	~ 20
3		9	93	250-270	~ 20
5	Zinc Chloride ($ZnCl_2$)	1	91	250-270	~ 20

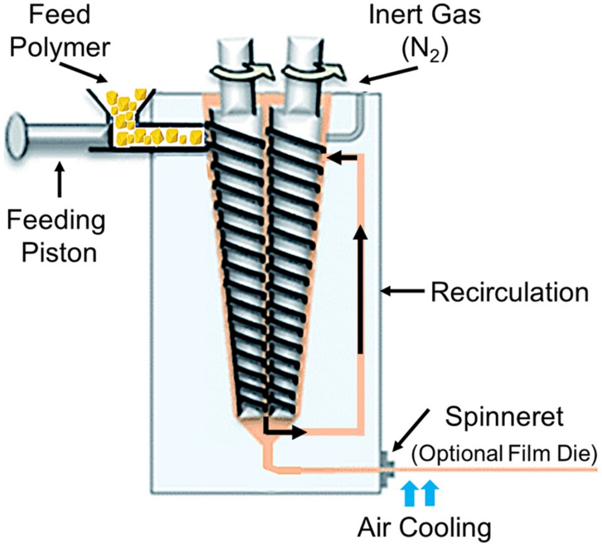
The depolymerization of P4PrCL to 4PrCL monomer using $Sn(Oct)_2$ or $ZnCl_2$ was successful. The long reaction time was attributed to the reactive distillation set-up

Lignin RCF → Hydrogenation → Oxidation → **Polymerization** → Recycle

TEA and LCA

Polymer Chemical Recycling





Depolymerize alkyl-caprolactone polymers back to monomers

Experiments utilize existing extruder at the University of Minnesota (photo)

Experiments aim to selectively recover only the monomer

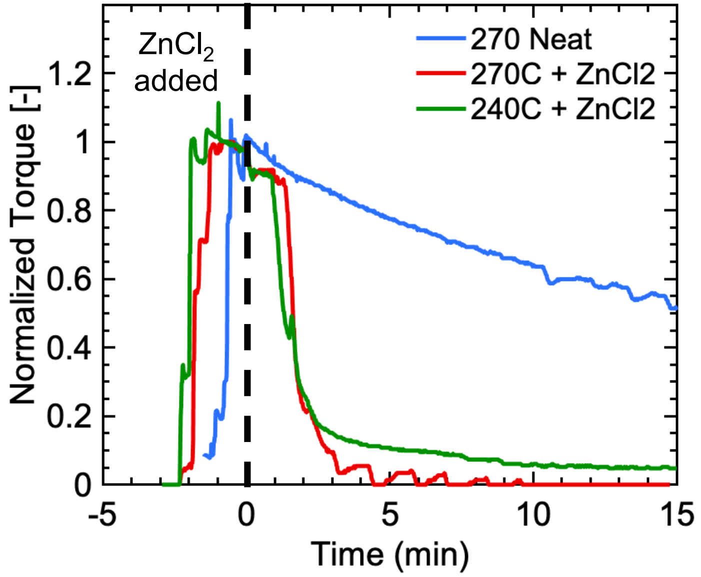
Leads: Chris Ellison (UMN)

Lignin RCF → Hydrogenation → Oxidation → Polymerization → **Recycle**

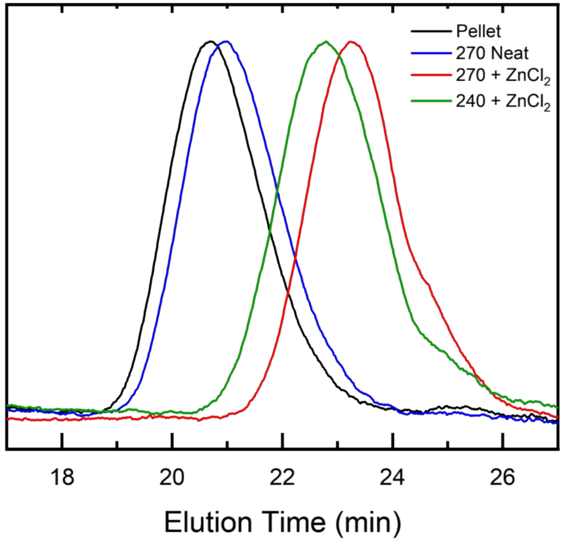
TEA and LCA

Polymer Chemical Recycling

Monitor Reaction Progress through Torque Readings



Determine Extent of Depolymerization with SEC



*Note: All samples dissolved in $CHCl_3$ and precipitated in MeOH before running

Sample	M_n (g/mol)	Đ
Pellet	94,000	1.65
270ºC Neat	69,000	1.68
270ºC + $ZnCl_2$	5,300	1.86
240ºC + $ZnCl_2$	14,900	2.10

Processing Conditions:

Temperature: 270ºC, Screw Speed: 100 RPM

Residence Time: 15 minutes

Neat PCL allowed to mix for 1.5 minutes before adding concentrated PCL + $ZnCl_2$ pellets, 1 mol% $ZnCl_2$ (1.1 wt%)

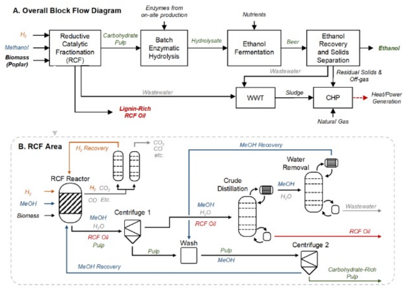
Lignin RCF → Hydrogenation → Oxidation → Polymerization → **Recycle**

TEA and LCA

Progress & Accomplishments

TEA and LCA

RCF Process



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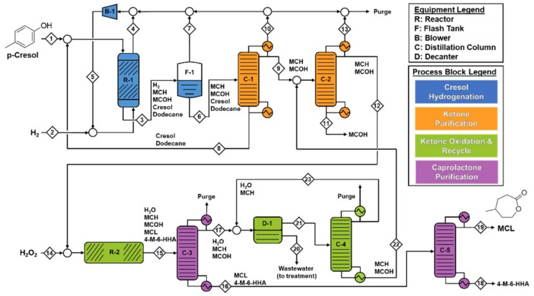
Monomer Process



Polymer Process

Design in Progress

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Recycle Process

Design In Progress

Combine TEA and LCA of four process elements: (1) RCF, existing, (2) monomer production, existing, (3) polymerization, new, (4) recycling, new

Refine the monomer production process and invent/optimize the polymerization and recycling processes

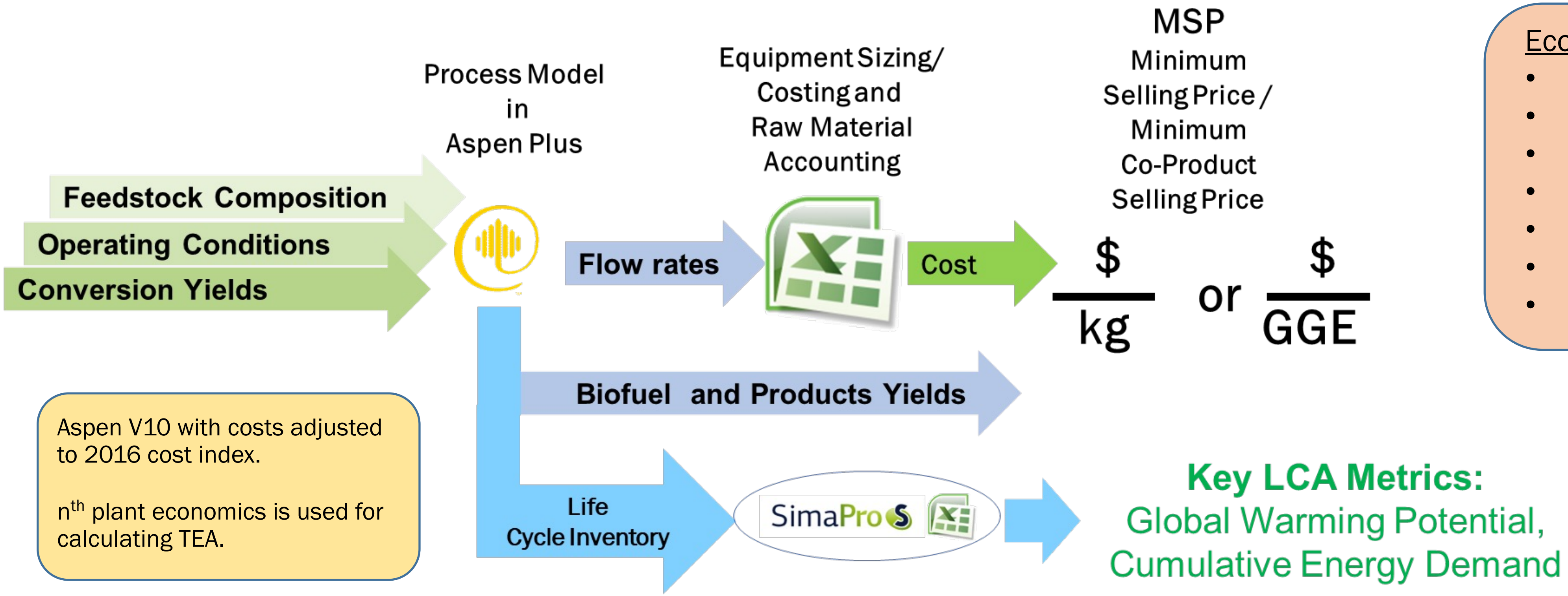
Leads:

- TEA, Samantha Gee (UMN)
- LCA, Gregg Beckham (NREL)

Lignin RCF → Hydrogenation → Oxidation → Polymerization → Recycle

TEA and LCA

TEA and LCA



Economic Assumptions:

- Internal rate of return= 10%
- 30 year plant life
- Equity/Debt = 40/60
- Interest rate= 8%
- Loan term= 10 years
- Income tax rate= 21%
- Salvage value- none

Aspen V10 with costs adjusted to 2016 cost index.

n^{th} plant economics is used for calculating TEA.

Lignin RCF → Hydrogenation → Oxidation → Polymerization → Recycle

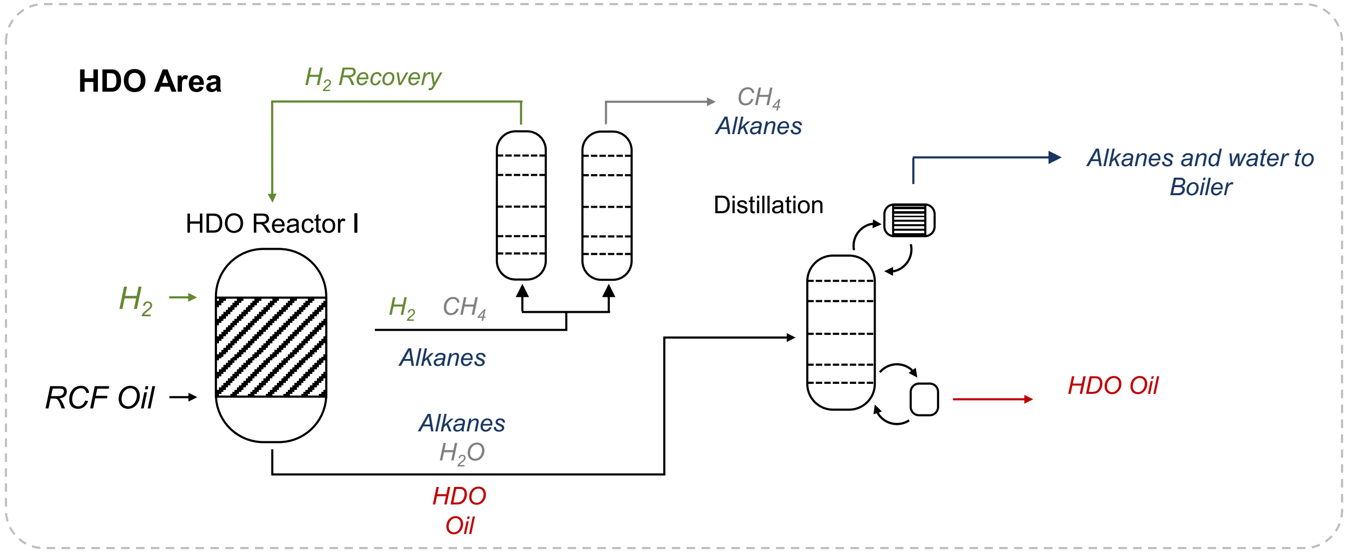
TEA and LCA

Bartling *et al. Energy Environ. Sci.*, 2021,14, 4147-4168
Davis *et al.*, NREL Technical Report, 2018

Progress & Accomplishments

TEA and LCA

Abhay Athalay at NREL is building the process section by section for optimization in BP3



- Solvent free process using MO_2C catalyst
- Near quantitative carbon yields, stably removing methoxy groups from lignin compounds
- Leveraging experimental data from fully integrated catalytic deoxygenation process for converting lignin into aromatic blendstocks and saturated cycloalkane for sustainable aviation fuel (SAF)

Lignin RCF → Hydrogenation → Oxidation → Polymerization → Recycle

TEA and LCA

Bartling *et al. Energy Environ. Sci.*, 2021,14, 4147-4168
Davis *et al.*, NREL Technical Report, 2018

Progress toward Goals & Milestones

Task	Description	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Verification													
O0-1	Verify catalytic recycling of PU / PEI using $Sn(Oct)_2$												
O0-2	Verify reduction of cresol as feedstock for oxidation chemistry												
O0-3	Verify synthesis of polyester polymer from caprolactone monomer												
Polymer Synthesis and Evaluation													
O1-1	Explore organocatalysts for promoting ring-opening polymerization												
O1-2	Develop streamlined method for polymerization kinetics/thermodynamics												
O2-1	Expand to industrially relevant polymerization practices												
O2-2	Explore PU catalysts for ROTEP												
O3-1	Use dynamical mechanical analysis of high molar mass polymers												
O3-2	Use differential scanning calorimetry to evaluate Tg												
O3-3	Identify thermal decomposition profiles of new polycaprolactones												
O4-1	Determine which PCLs represent drop-in replacements for PU												
O4-2	Explore which PCLs can be used for new applications in PU												
O5-1	Use sequential addition to prepare ABA copolymers												
O5-2	Use mechanical property testing for physical properties												
Polymer Chemical Recycling													
O6-1	Measure baseline $Sn(Oct)_2$ catalyst performance for PU/PEI recycling												
O6-2	Characterize a breadth of Sn-based and non-Sn catalysts												
O6-3	Evaluate catalyst stability and feedstock form for accessibility												
O7-1	Measure batch kinetics for catalytic PU decomposition reactive distillation												
O7-2	Measure PU decomposition with twin screw extrusion												
O7-3	Measure polyester elastomer catalytic kinetics in screw extrusion												
O8-1	Evaluate performance of PU decomposition in auger-type reactor												
O8-2	Evaluate performance of polyester elastomer in auger-type reactor												
Overall Process Development and Techno-economic Development													
O9-1	Evaluate the batch kinetics of RCF-derived lignin-monomers.												
O9-2	Develop a continuous flow catalytic reduction reactor												
O10-1	Develop electrochemical Baeyer-Villiger oxidation to avoid peroxides:												
O10-2	Obtain kinetic parameters governing the Baeyer-Villiger oxidation process												
O10-3	Investigate the mechanism of electrochemical Baeyer-Villiger oxidation												
O11-1	Design the polyurethane recycle sub-process												
O11-2	Design the polyester elastomer recycle sub-process												
O12-1	Develop scenarios for combining lignin, synthesis, and polymerization												
O12-2	Integrate data for fit-for-purpose simulations												
O12-3	Evaluate overall techno-economics of full integrated process												

Q1: Met verification requirements

- Demonstrated key chemistries of polymer synthesis, recycling, and hydrogenation

Q6: Midterm verification approved for continuation into BP3

- **Go / No-GO:** Produce a sufficient amount of polymer to allow for all recycling and analysis experiments in BP3.
- Made major progress in Q2-Q6 tasks and milestones

Completed Milestones

- 6.1.1
- 9.1.1
- 1.1.1
- Go/No-Go #2