Performance Advantaged Bioproducts from Catalytic Fast Pyrolysis

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Performance-Advantaged Bioproducts and Separations Consortium

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Goal Statement

Goal: Identify and synthesize novel, performance advantaged polymers from catalytic fast pyrolysis (CFP) products

- Survey potential polymers that could be derived from CFP products and industrial needs
- Synthesize polymers from products identified in CFP bio-crude and test for improved performance
- **Unique opportunities and challenges for CFP**

Outcome: A report describing opportunities for Performance Advantaged Bioproducts (PABP) from CFP

- Unique polymers that can be prepared from CFP bio-crude
- Experimental results demonstrating performance enhancement relative to polymers from fossil sources

Relevance: Advance bioeconomy through bioproducts

- Pathway to reach BETO goal of $2.50 GGE biofuels from CFP
- Use unique molecular functionality in CFP products
- Diversify revenue streams for CFP biorefineries
- Higher value product streams

Quad Chart Overview

Timeline

Start Date: October, 2018
End Date: September, 2020
Percent Complete: 25%

	Total Costs Pre FY17	FY17 Costs	FY18 Costs	Total Planned Funding (FY19 – End Date)
DOE Funded	–	–	$200K	$400K

Partners:

BETO Projects: Performance-Advantaged Bioproducts via Selective Biological and Catalytic Conversion, Inverse Biopolymer Design through Machine Learning and Molecular Simulation, Analysis in Support of Novel Biobased Products and Functional Replacements, Catalytic Upgrading of Pyrolysis Products

Industrial contacts: Luna, Sumitomo Bakelite, Patagonia, Tolmar, Gore

Barriers addressed

Ct-J. Identification and Evaluation of Potential Co-products

- Novel polymers are evaluated and compared to conventional polymers

Ct-K. Developing Methods for Bioproduct Production

- Pathways to novel polymers are demonstrated from catalytic fast pyrolysis (CFP) products.

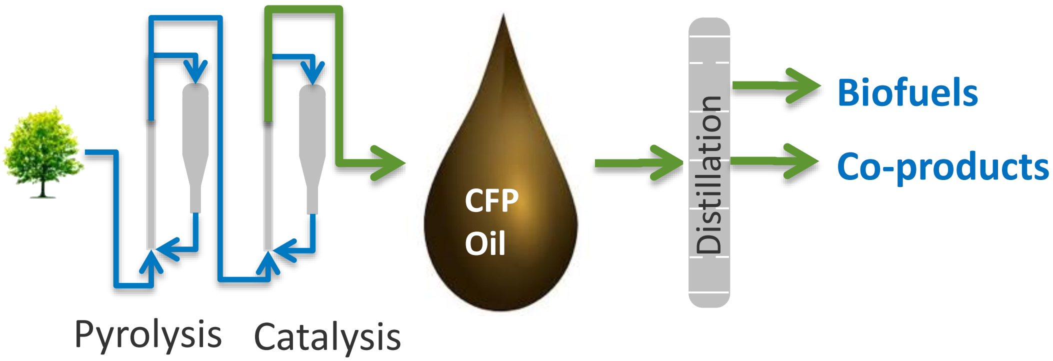
Objective

Identify performance advantaged biomass-sourced polymers that can be prepared from CFP products

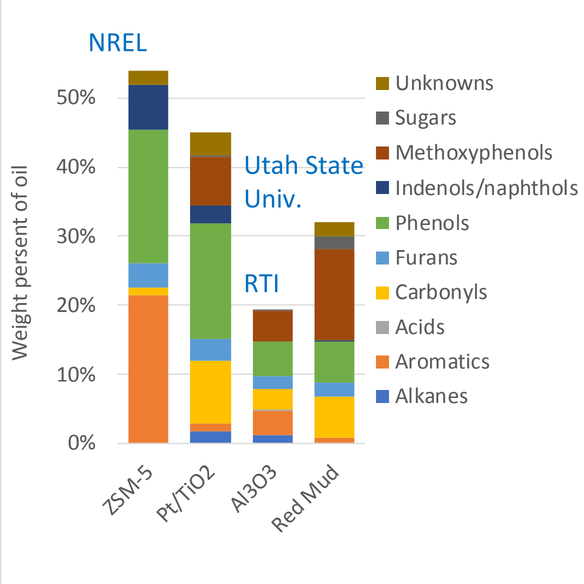
End of Project Goal

Demonstrate to stakeholders the superiority of CFP performance advantaged polymers by publishing a roadmap that outlines commercial viability and demonstrated, clear production pathways. The roadmap will be supported by experimental results, literature studies and technoeconomic models

1-Project Overview



Detailed Product Analysis



Characteristics of Catalytic Fast Pyrolysis

- High throughput/low cost
- Diversity of products
- Low selectivity – focus has been hydrocarbons
- Preliminary TEA suggests > 1% selectivity could improve CFP economics

Top 10 Products

Compounds	ZSM-5	Compounds	Pt/TiO_2	Compounds	Red Mud	Compounds	Al_2O_3
m-cresol	3.5%	phenol	3.1%	2-MeO-4-propenyl-phenol,	2.8%	Furfural	1.9%
phenol	3.2%	m-cresol	2.4%	2-MeOH-4-methyl-phenol	2.3%	4-Et-2-MeO-phenol	1.6%
xylene	2.9%	3-Me-2-Cyclopenten-1-one	2.2%	levoglucosan	1.6%	2-MeO-phenol	1.6%
2-Me-naphthalene	2.8%	2-cyclopenten-1-one	2.1%	2-OH-3-Me-2-cyclopenten-1-one	1.4%	1,2-diEt-benzene	1.4%
2,4-diMe-phenol	2.5%	2-MeO-4-(1-Pr)-phenol	1.6%	4-Et-2-MeO-phenol	1.3%	2-butanone	1.3%
naphthalene	2.1%	3-Et-phenol	1.6%	guaiacol	1.2%	p-cresol	1.2%
o-cresol	2.1%	Pr-phenol	1.5%	2-MeO-3-propeyl-phenol	1.1%	2,4-diMe-phenol	1.2%
2-Et-5-Me-phenol	1.9%	o-cresol	1.4%	catechol	1.1%	2-MeO-4-(1-prop-1-en-1-yl)-phenol	1.2%
toluene	1.6%	2-Me-2-cyclopenten-1-one	1.3%	furfural	0.9%	o-cresol	1.0%
2-Me-indene	1.4%	unknown	1.2%	2-MeO-4-Pr-phenol	0.9%	phenol	0.9%

1-Project Overview

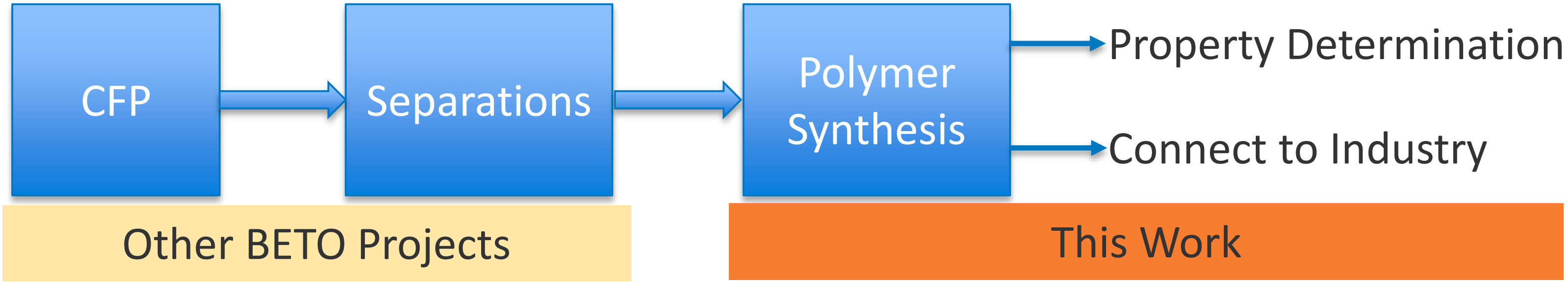
Project History

- In FY18 part of "Analysis in Support of Novel Biobased Products and Functional Replacements" Project - Split off in FY19

Background: Products from CFP?

- CFP biocrude optimally contains 20% oxygen – Opportunity for PABP
- Significant previous work using phenolics from Fast Pyrolysis for phenol resins
- Novel polymers from CFP have not been considered
- **PABP Challenges**: Selectivities, Separations and **Unknown Material Performance**

PABP Polymer Pathway for CFP



Polymer Synthesis Challenge: Route Unclear – Performance Unknown

- Demonstrate industrially relevant polymer synthesis pathways
- Measure properties of polymers
- Benchmark against commercial and other biomass-derived polymers
- Work with industrial partners to deploy polymers

2- Management Approach

Team:

- Extensive experience with CFP
- Polymer synthesis
- Polymer properties, engineering and commercialization

Project interfacing:

- Biweekly meetings of Polymer Team at NREL (five BETO projects)
- Monthly meeting with BETO technology manager
- Weekly meetings with CFP projects and our PABP team

Industrial Liaison:

- Interviews with industrial contacts
- Regular visits by interested companies
- Conference attendance:
  - *Thermal and Catalytic Sciences Symposium – Auburn 2018*
  - *Gordon Research Conference: Polymers – Mount Holyoke 2017*

Milestones

Developed to track and demonstrate progress.

i.e.

Q1, 2019

Demonstrate that initial synthetic steps in performance advantaged polymer synthesis can be accomplished (**Monomer Synthesis**).

Go/No-Go:

Synthesis and characterization of three potentially performance advantaged polymer from CFP products.

2-Technical Approach

Survey CFP Products FY18

Critical success factor: Identify products from CFP that can be used to make novel, performance advantaged polymers of interest to industry

Challenge: Insufficient data concerning CFP products, routes to novel polymers and interest in industry

Approach: Survey data from literature and NREL, interview industrial stakeholders

Filter molecules:
- Reasonable selectivity (> 1%)
- Reasonable route to novel polymer
- Polymer with enhanced performance
- Address needs for industry

Polymer Synthesis

Critical success factor: Demonstrate reasonable synthetic routes for preparing novel polymers using unique starting molecules

Challenge: Synthetic routes not developed for these feeds and polymers

Approach: Test similar synthetic pathways

Measure Properties (Glass Transition Temperature, Barrier Properties, Young's Modulus, Recyclability, etc.)

Critical success factor: Measure properties that are improved over commercial polymers and that impact industrial applications

Challenge: Properties of these polymers are unknown

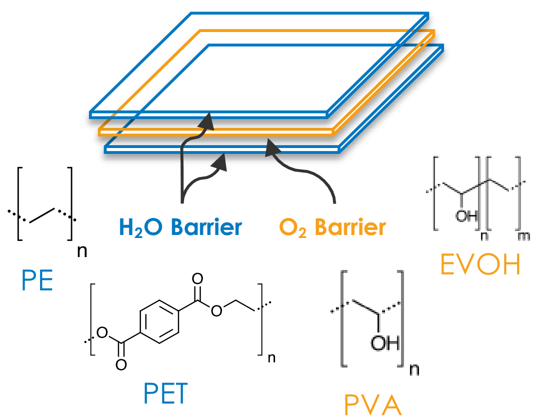
Approach: Measure properties for synthesized polymers, use machine learning to predict properties

2-Technical Approach
Example: Barrier Properties

Industrial Need: *Simplify packaging material for reduced cost and reduced complexity – ease of recycling*

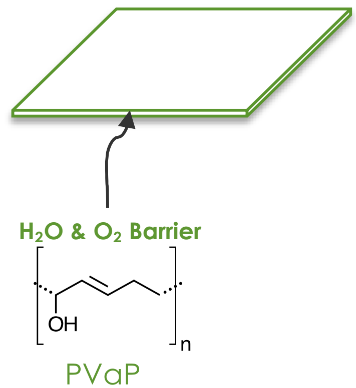
Existing Materials

Multi-layer Packaging



Polymer from cylopentenone

Single-layer Packaging



Easier to recycle

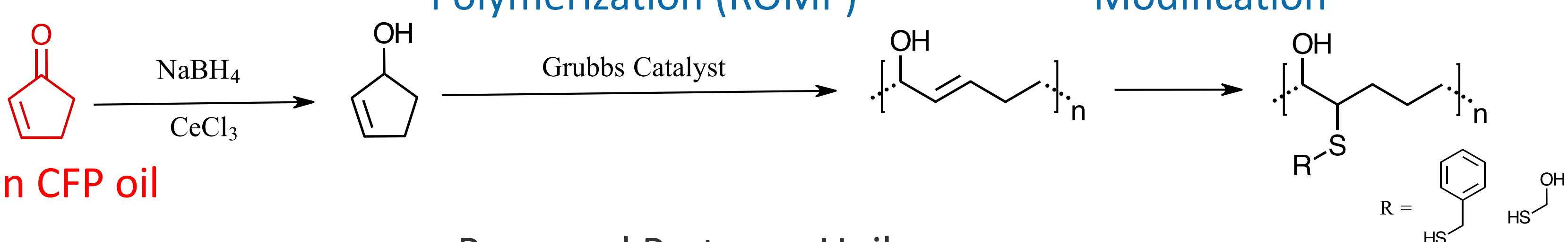
CFP product could lead to enhanced performance, addressing packaging need

Synthesis route from CFP product – cyclopentenone

Reduction

Ring Opening Metathesis Polymerization (ROMP)

Post Polymerization Modification



3% in CFP oil

Proposed Partners: Unilever, Sealed Air, Braskem

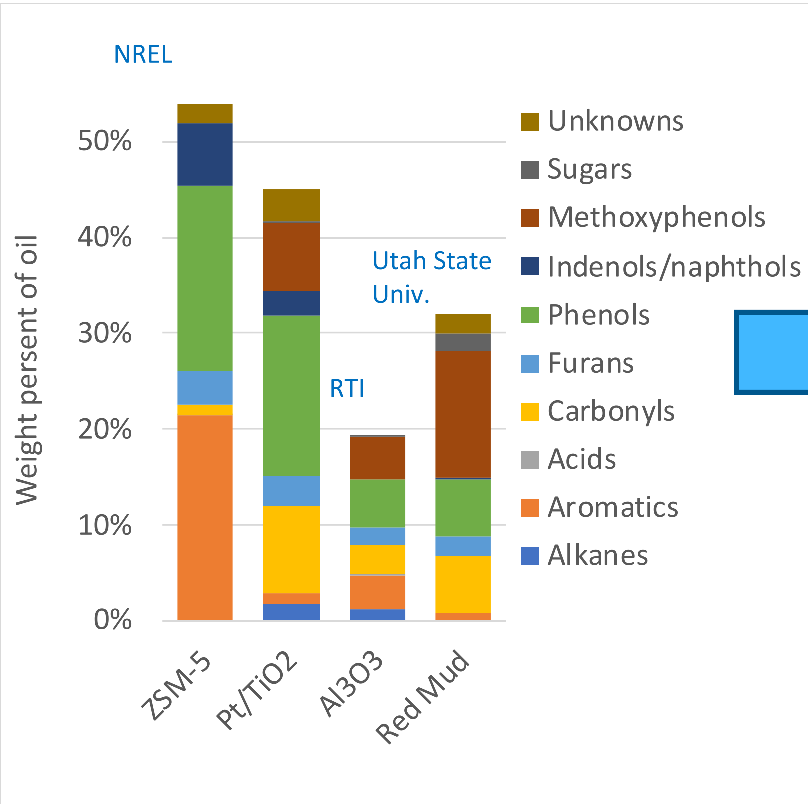
3-Technical Accomplishments – Overview

- **Survey of chemical products from CFP – FY18**
  - Handful of studies where oil and carbon balance measured
  - Small scale experiments in literature provide potential innovation for new catalytic pathways
  - Separations being developed in CFP project
- **Material needs and performance limitations – FY18**
  - Industrial stakeholder interviews
  - Polymers and opportunities
- **Identify potential novel polymers – FY18**
- **Identify 10 polymers that are the lowest hanging fruit – FY18**
  - Products found in CFP oils at reasonable concentrations (> 1wt%)
  - Reasonable strategies for separation
  - Identify polymers that can potentially have enhanced performance – based upon empirical knowledge.
  - Working with inverse design to predict properties of polymers with machine learning
- **Synthesize monomers from CFP products – FY19**
  - Address synthesis challenges associated with novel polymers and unique CFP products

3-Technical Accomplishments
Survey of Products from CFP

CFP State of Technology

Detailed Product Analysis

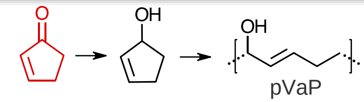


Example Polymer Classes

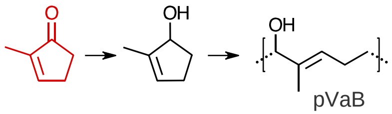
CFP Product	Potential Polymer Classes
Phenols	Polycarbonates, polysulfones, PF resins, PEEK
Carbonyls	Polyethers, polyketals, polyvinyl alcohols
Methoxyphenols	Polyurethanes, Polycarbonates
Furans	Polyethers
Indols/Naphthols	Polycarbonates
Sugars	Polylactones, polyurethanes, polyethers

- Using these catalysts, similar products are formed
- Wide range of polymer classes can be synthesized
- We will focus on **novel** polymers – NOT phenolic resins!

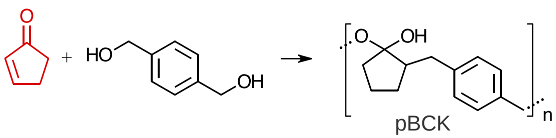
3-Technical Accomplishments
Ten Polymers Selected



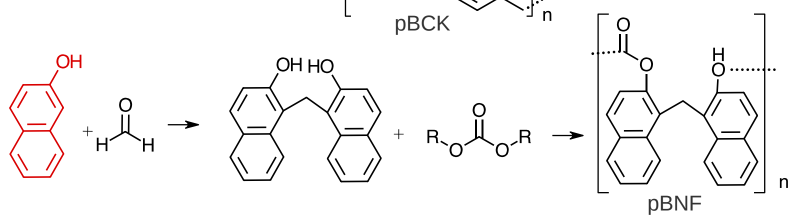
Barrier properties



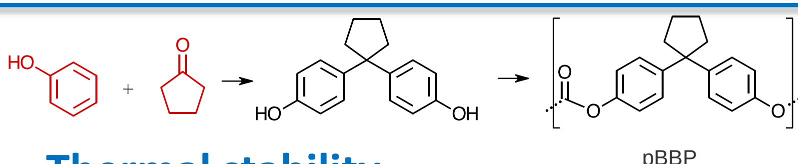
Barrier properties



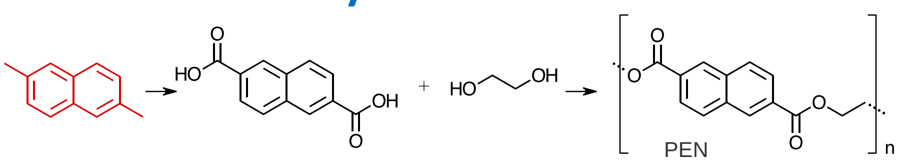
Recyclable



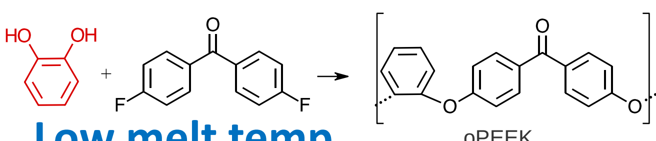
Thermal properties



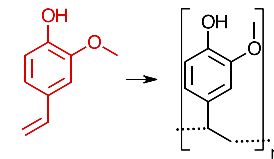
Thermal stability



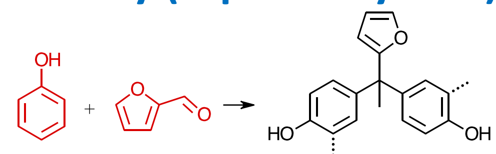
Thermal stability and barrier properties



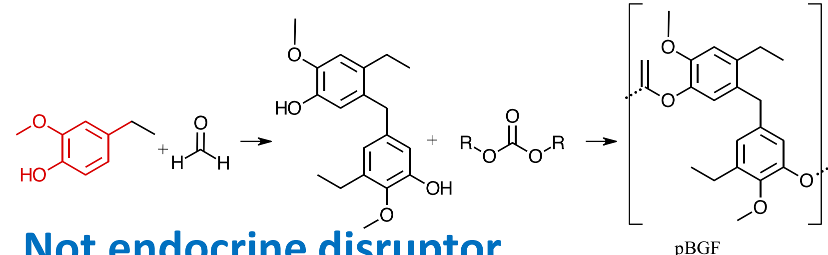
Low melt temp



Toxicity (replace styrene)



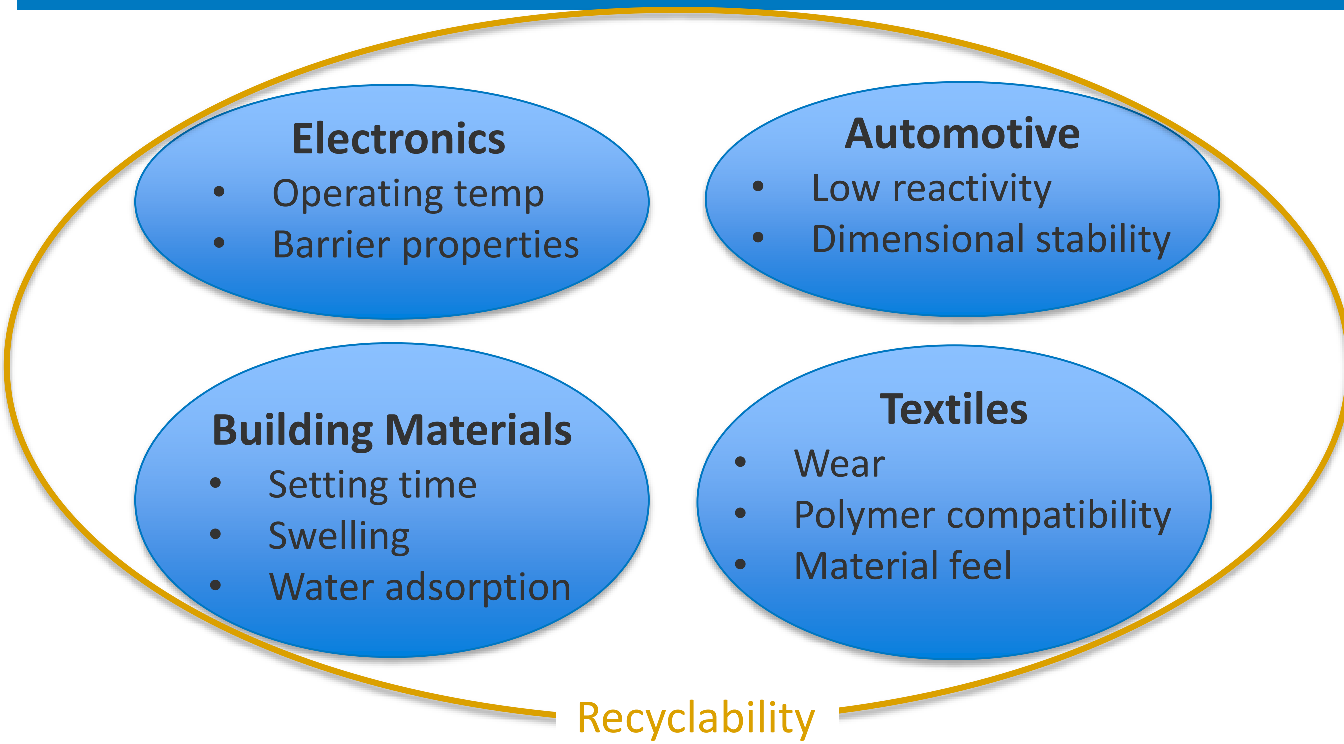
Toxicity (replace formaldehyde)



Not endocrine disruptor

- Filtered for yields, synthesis routes, enhanced performance, industrial needs
- Provides guide for future work
- First four polymers will be focus of year two work

3-Technical Accomplishments
Polymer Properties and Industrial Needs



Performance Gaps in Industrial Polymers

- Thermal properties
- Barrier properties
- Recyclability
- Renewable content

Industrial stakeholder interviews helped identify goals for property enhancement

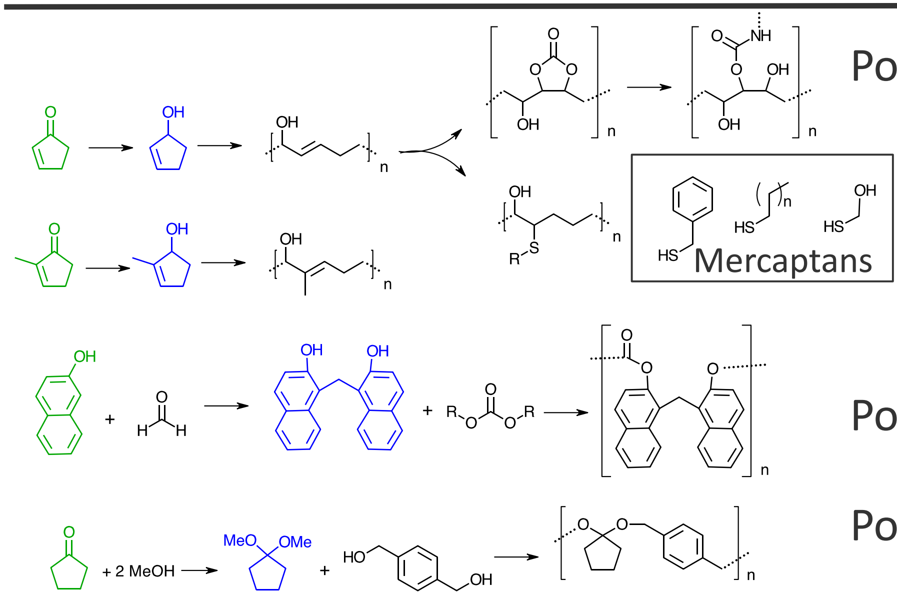
3-Technical Accomplishments
Synthesis of Monomers

Oxygenate | Monomer | Polymer

1. Ketone Reduction

2. Naphthol Condensation

3. Ketone Methoxylation



Polyurethanes

Coatings

Polycarbonates

Polyketals

We were able to synthesize and separate all four monomers

Challenges in monomer structure:

1. Low ring strain
2. Monofunctional
3. Water interference

Approaches:

1. Reduction to alcohol
2. Dimerization
3. Methoxylation

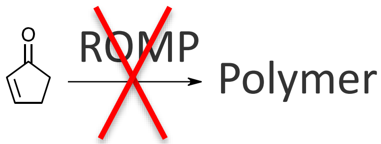
Challenges in monomer synthesis:

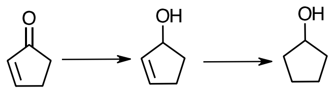
1. Product selectivity
2. Selectivity for ring substitution
3. Reversibility

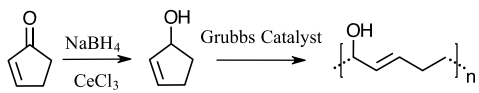
Approaches:

1. Use $CeCl_3$
2. Selected most thermodynamically favored product
3. Optimized reaction and separation conditions

3-Technical Accomplishments
Monomers Synthesized





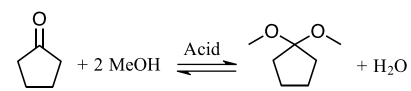


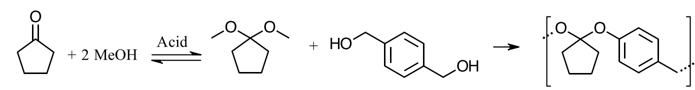
Ring open polymerization of cyclopentenone

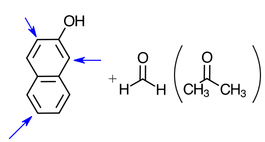
- Challenge: not enough ring strain
- Solution: reduce carbonyl group to alcohol
- Challenge: Stopping reaction at cyclopentenol
- With added $CeCl_3$ yields of 97%
- ROMP catalysis to polyvinyl alcohol

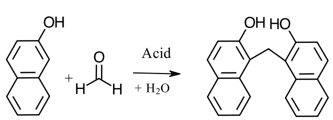
Prepare polyketals from cyclopentanone

- Tried enone (cyclopentenone) – did not work
- Cyclopentanone with acid and methanol to make dimethoxy
- Reversible 70 – 80% pure – polymerization to pull reaction









Prepared BPA – like monomer from naphthol

- Tried other positions- acid or bases, protecting groups, Gringard reagents
- Tried other bridging groups
- The 1-1’ methylene linkage gave the best yields

4-Relevance for Bioeconomy

Bioplastics are one of the fastest growing sectors of the plastics industry, 20-30% annual growth rate [*Plastics Industry Association*]

- Co-products are an important component of a successful bioeconomy and the economics of a biorefinery (BETO – draft MYP). **Similar to petroleum refinery (16% of the petroleum, ~50% of the revenues)**
- Co-products can improve economics of CFP biorefineries
  - Increase revenue streams
  - High-value co-products that are not economically accessible by other routes
- Performance advantaged polymers take advantage of the unique chemical composition and structure of biomass
- There is little work on co-products from CFP, even though it is perhaps the most cost advantaged conversion technology for biofuels
- We will demonstrate **high value products** that will help improve the economics of CFP biorefineries
- We are demonstrating **reasonable synthetic pathways** for novel polymers and measuring their improved performance.
- We will **work with our industrial partners** to help commercialize these materials

4-Relevance for BETO

BETO Draft MYP Biofuels Cost

Year (FY)	Target (GGE)	Methods to achieve target with CFP
2022	$3.5	Catalyst Development
2030	$2.5	Will include co-products

- We identified co-products from CFP
- Performance advantage and industrial relevance will help commercialization
- Economic analysis will determine impact on biofuels cost

BETO draft MYP Barriers

Ct-J. Identification and Evaluation of Potential Co-products

- Properties to be measured: Thermal, Mechanical, Barrier, Recyclability
- Collaborate with Inverse Design Project: provide data on CFP polymers for machine learning and molecular dynamics

Ct-K. Developing Methods for Bioproduct Production

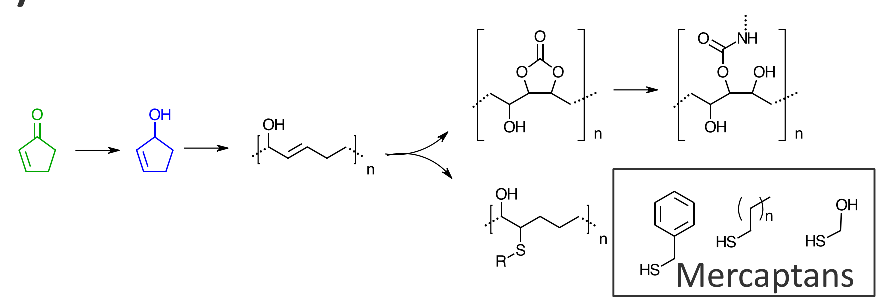
- Demonstrate pathways for conversion of CFP bio-crude products into high value products
- Provide targets for catalyst modifications to improve selectivity and yields for co-products

5-Future Work
Polymer Synthesis

- Synthesize polymers from monomers made in Q1
- Post polymerization modification to improve properties
- Go/No Go (Q2FY19) Synthesize three polymers and measure properties. Demonstrate performance advantage in one property. If properties are not improved over existing materials, use machine learning to guide additional synthesis.
- Synthesis of five additional polymers in FY20

Post polymerization to improve properties of polyvinyl alcohols

- Carbonates to form polyurethane linkages
- Mercaptans to add hydrophobicity
- Radical cross linking

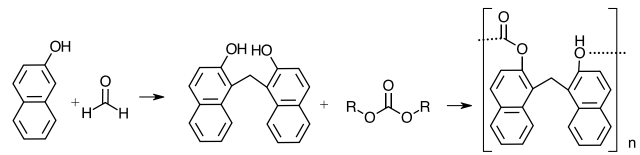


Produce a polymer with low O_2 and H_2O permeability

5-Future Work
Polymer Synthesis

Polycarbonates from bisnaphthols

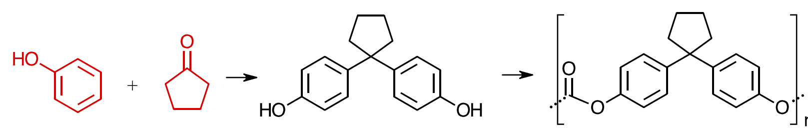
- Try using alkyl carbonates
- Avoid phosgene



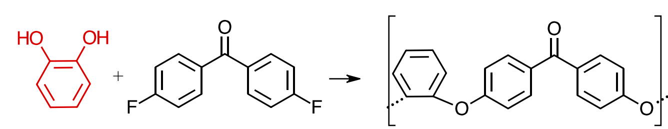
Polycarbonate with improved thermal properties

Examples of other polymers

- Using other molecules identified in CFP bio-crude



pBPC



oPEEK

Produce at least 5 novel polymers to test for performance advantage

5-Future Work
Polymer Properties and Industrial Engagement

- Polymer Properties
  - Thermal properties
  - Barrier properties
  - Mechanical properties
- Provide polymer properties to inverse design team
- Use machine learning to predict properties of CFP polymers
- Work with our industrial partners to help commercialize polymers
- Publish a report on the performance advantaged products from CFP, which outlines commercial viability and demonstrated synthesis pathways. (Q4 milestone, FY20)

Summary

Overview: Novel polymers can be made from CFP products that could solve important industrial problems and that could improve economics of biorefineries

Approach: We are synthesizing and testing polymers that could be prepared from CFP products and that could have improved properties

Progress:

- Identified realistic products from CFP
- Interviewed industrial stakeholders
- Identified ten polymers that could impact these industries
- Completed synthesis of monomers

Relevance: The work is critical for success of CFP biorefineries and for creating markets for valuable co-products

Future Work: We will finish synthesis of several polymers and measure their properties. We will provide data to inverse design team who will use machine learning molecular dynamics to predict properties. Look for commercialization opportunities with our industrial partners.

Acknowledgements

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BETO Projects:

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Gregg Beckham, PI "*Performance-Advantaged Bioproducts via Selective Biological and Catalytic Conversion*"

Phil Pienkos, PI "Fully Renewable Polyurethane Resins Produced from Algae and other Feedstocks"

Josh Schaidle, PI "*Catalytic Upgrading of Pyrolysis Products*"

Andrew Sutton, "Tailored Polymers Through Rational Monomer Development", Los Alamos National Laboratory

Matthew Yung, PI "*Gas Phase Selective Partial Oxidation of Lignin for Co-products from Biomass Conversion*"