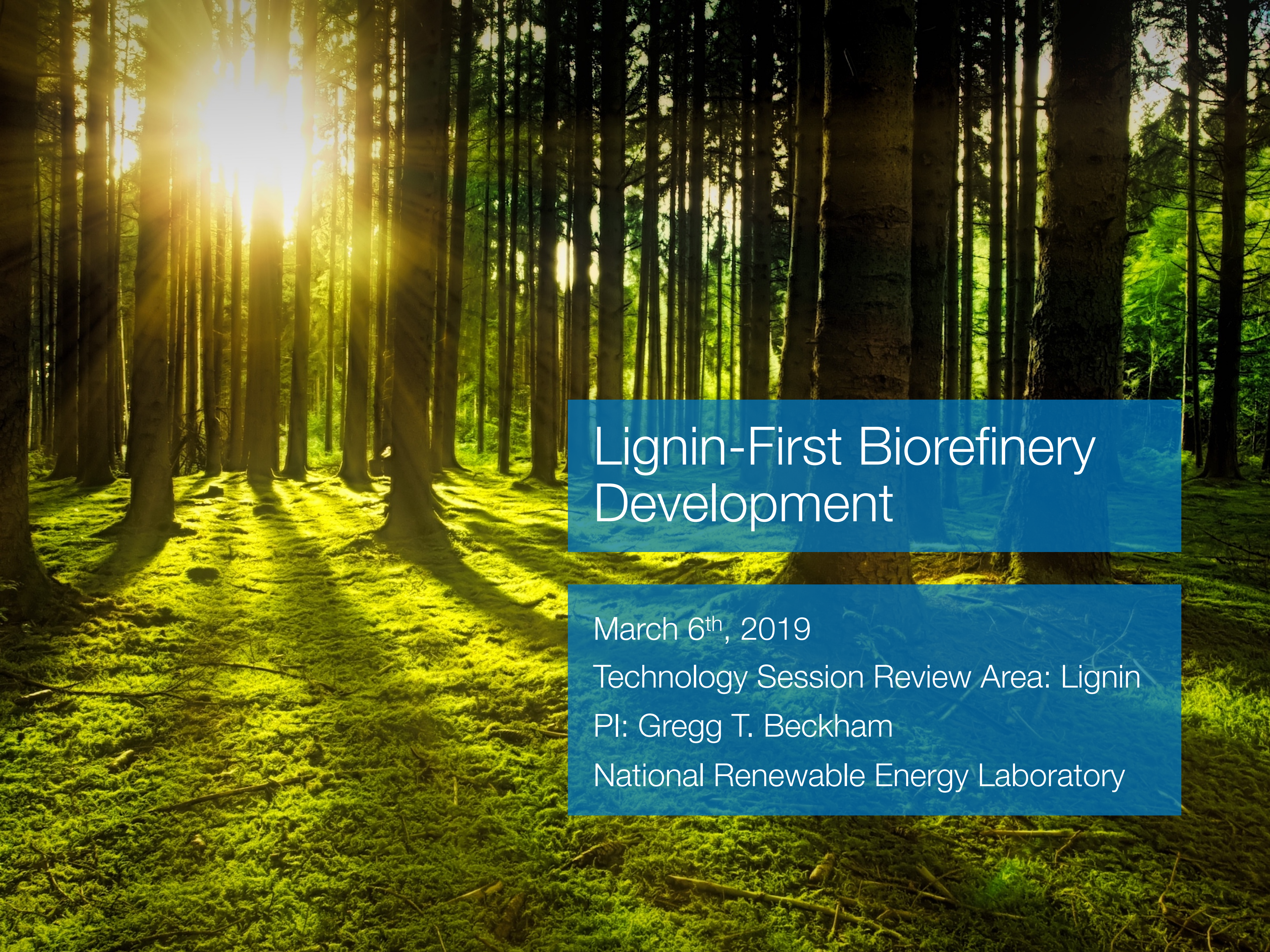


Lignin-First Biorefinery Development

March 6th, 2019

Technology Session Review Area: Lignin

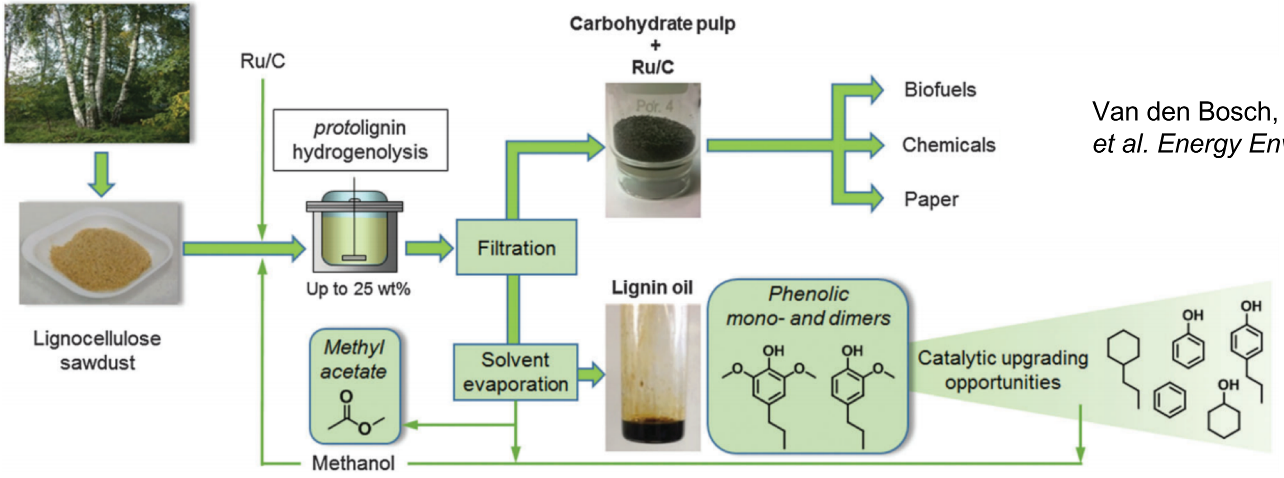
PI: Gregg T. Beckham

National Renewable Energy Laboratory

Goal statement

Goal: Develop a lignin-first biorefining concept to fractionate lignin and polysaccharides via Reductive Catalytic Fractionation (RCF)

- Active stabilization method to cleave lignin C-O bonds and stabilize reaction products
- Bench-scale demonstration of $2-3/gge modeled cost of biofuels and co-products
- Alternative to polysaccharide-centric pretreatments
- **Collaboration with Yuriy Román at MIT**



Van den Bosch, Schutyser *et al. Energy Env. Sci* 2015

Outcome: new catalytic fractionation process for lignin and polysaccharide valorization

- RCF is "catalytic funneling" to a few monomeric products

Relevance: process enables lignin valorization and biomass fractionation simultaneously

Quad chart overview

Timeline

- Start date: October 2017
- End date: September 2020
- Percent complete: 50%

	Total Costs Pre FY17	FY17 Costs	FY18 Costs	Total Planned Funding (FY19-Project End Date)
DOE funded	--	--	$547k	$1,400k

Partners:

BETO Projects: Lignin Utilization, Separations Consortium, Performance-Advantaged Bioproducts via Selective Biological and Chemical Conversion, Direct Catalytic Conversion of Cellulosics, Enzyme Engineering and Optimization

Universities: MIT (Yuriy Román), UCSB, Imperial College London, KU Leuven, University of Stockholm, Dalian Institute of Technology, EPFL, U. Groningen, U. Stockholm

Other DOE projects: Center for Bioenergy Innovation (CBI, ORNL)

Barriers addressed

Ct-B Efficient preprocessing and pretreatment

- Developing new catalytic fractionation process for integrated biomass conversion

Ct-C Process development for conv. of lignin

- Developing process to produce lignin monomers and valuable lignin oils

Objective

Demonstrate that RCF can be a viable alternative to standard thermochemical pretreatment and can produce upgradable, high yielding streams from lignin and polysaccharides

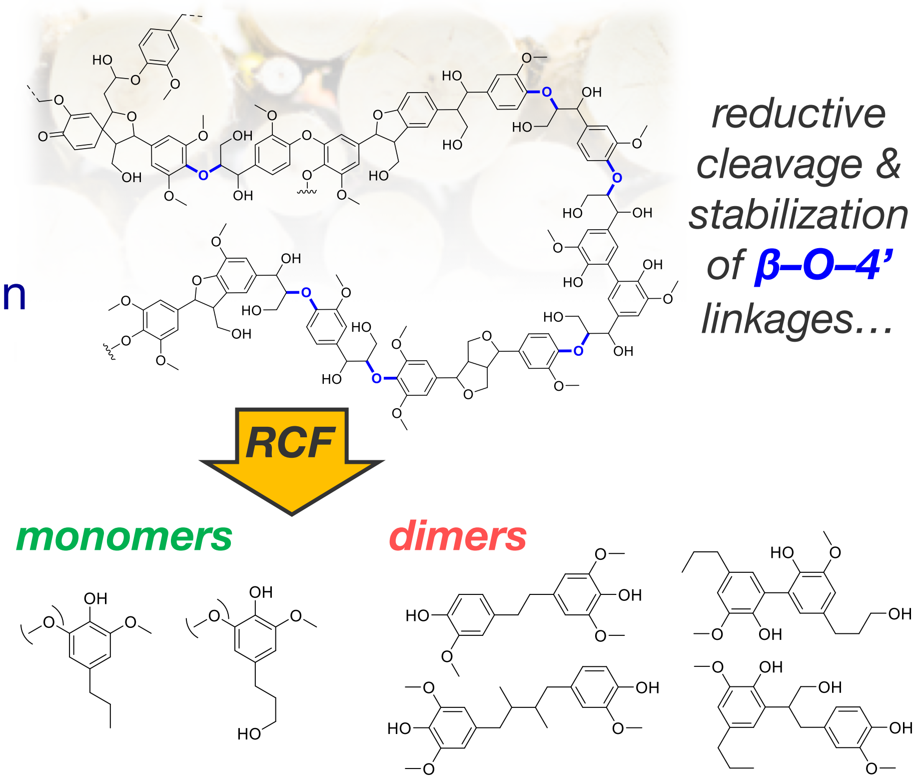
End of Project Goal

Develop a strategy that can **enable < $3/gge MFSP based on a lignin-first biorefinery concept using RCF**, valorizing both lignin (60% target) and polysaccharides

Project overview

History: RCF originally developed in 1960s as an analytical method

- Recent resurgence as a valorization strategy
- Primarily conducted in batch systems
- Project started in FY18



Context: Most fractionations condense lignin

- E.g., acid cleaves ethers and condenses lignin
- RCF stabilizes C-O cleavage products
- Retains polysaccharides
- Enables hardwoods in biochemical conversion

Goals:

- **Develop an industrially relevant RCF process to meet $2-3/gge MFSP targets**
- **Transition RCF to flow** with highly active, stable catalysts
- Separate RCF oil into monomer and oligomers streams
- Valorize oligomers and robust analytics for oil characterization
- Employ TEA to identify cost drivers

Management approach

Team assembled with expertise to enable lignin-first biorefining:

- Jake Kruger – Chemist, heterogeneous catalysis
- Nick Thornburg – Reaction engineer, modeling
- Brenna Black, Bill Michener - Analytical chemists, LC-MS/GC-MS
- MIT: Yuriy Román – expert in catalysis, reaction engineering

Collaborations:

- **Joint meetings with MIT every two weeks**
- **Separations Consortium:** fractionate lignin oil into monomers, oligomers
- **Enzyme Engineering/Optimization, Direct Cat. Conv. of Cellulosics** for polysaccharide valorization
- Leverage modeling developed in **Consortium for Computational Physics and Chemistry**
- **Work with RCF community towards best practices for analytics, mass balances**

Dedicated **project manager** to track milestones and budget

Working with Biochemical Platform Analysis to conduct TEA and identify cost drivers to focus R&D activities

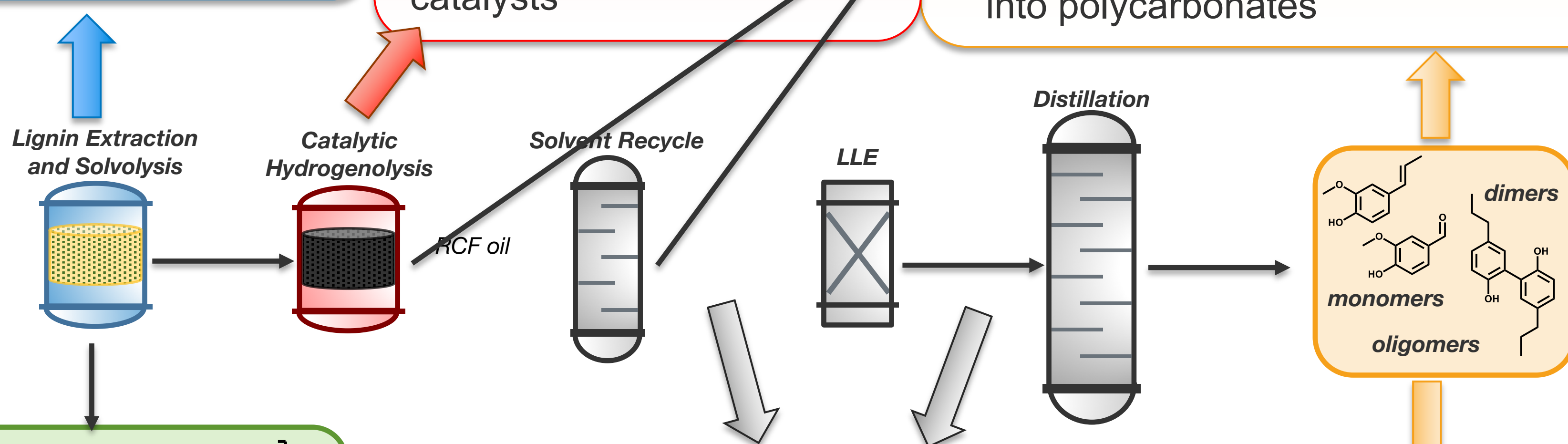
Milestones: **focus towards process improvements**

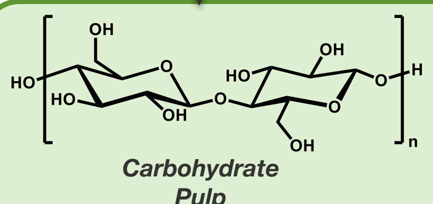
Project interactions

CCPC
Lignin solvolysis supported by first-principles modeling to inform design criteria

ChemCatBio
Advanced characterization to understand deactivation modes and design better catalysts

Performance-Advantaged Biopolymers
- Unsaturated RCF monomers can be used as styrene replacements
- RCF 5-5’ dimers can be incorporated into polycarbonates





SepCon
Novel technology to improve efficiency and selectivity of RCF oil separations

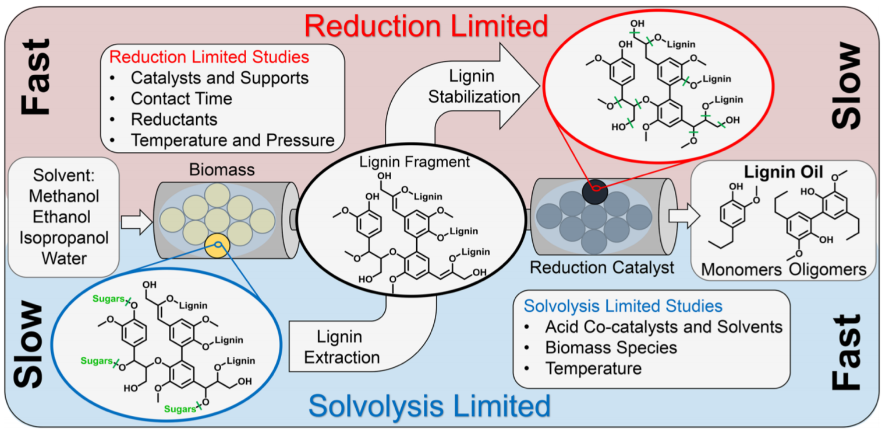
Lignin Utilization
RCF oligomers can be oxidized to monomers or made into bioproducts

Direct Catalytic Conversion of Cellulose
Residual carbohydrates can be catalytically converted to fuels

Enzyme Engineering and Optimization
Residual carbohydrates can be enzymatically hydrolyzed to sugars

Technical approach

Aim 1: Develop RCF **reactor/catalyst** to produce high lignin monomer yields



Critical success factors: Stable catalysts, fast reaction times, high lignin oil/monomer yields

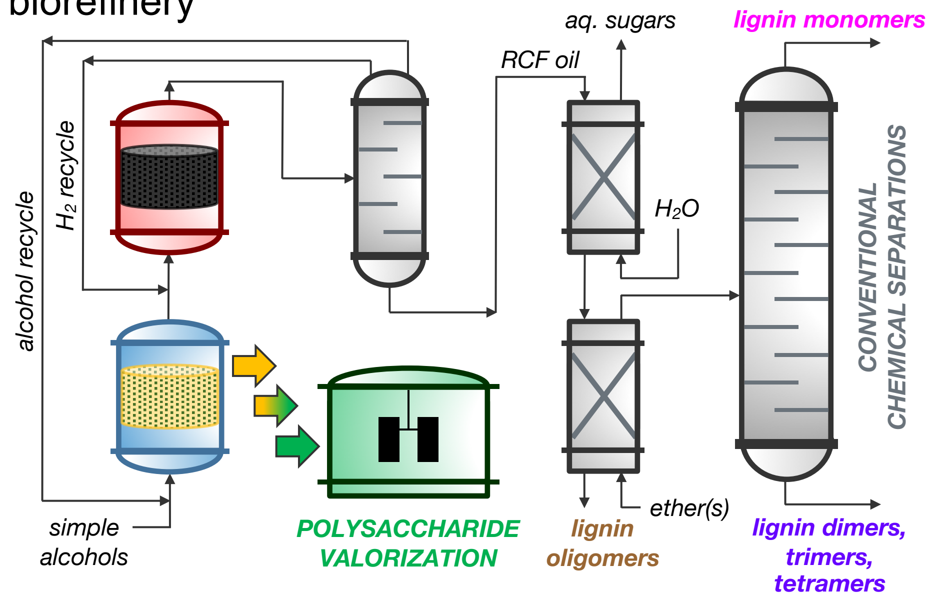
Challenges: high lignin extraction, polysaccharide retention

Approach:

- Flow systems to separate hardwood feedstock and catalysts
- Biomass modeling and imaging for solvolysis
- Catalyst stability via advanced characterization

Anderson, Stone *et al.*, *ACS SusChemEng* 2017

Aim 2: Develop the RCF **process** for the integrated biorefinery



Critical success factors: Solvent minimization, polysaccharide retention, oil separations, oligomer valorization

Challenges: monomer purity, solvent recycle

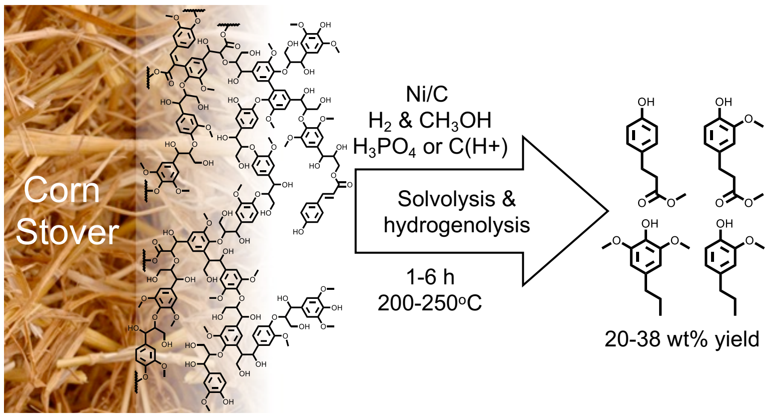
Approach:

- Flow-around/continuous RCF reactors
- Separations of RCF oil via LLE/distillation
- Polysaccharide and lignin oligomer valorization via collaborations

Outline of technical accomplishments

Initial results on RCF

- RCF of corn stover
- Initial flow-through demonstrations



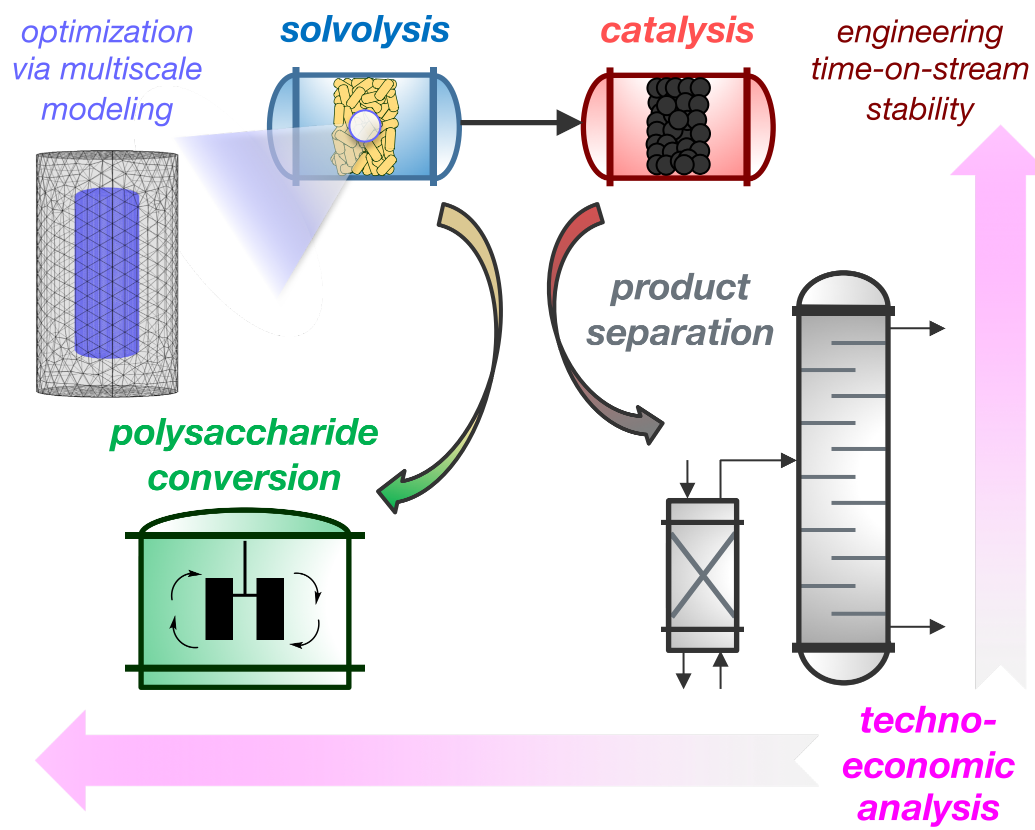
Aim 2: Develop the RCF **process** for the integrated biorefinery

- RCF oil separations
- Enzymatic hydrolysis of residual polysaccharides
- Preliminary techno-economic analysis

Anderson *et al.*, *ACS SusChemEng* 2016

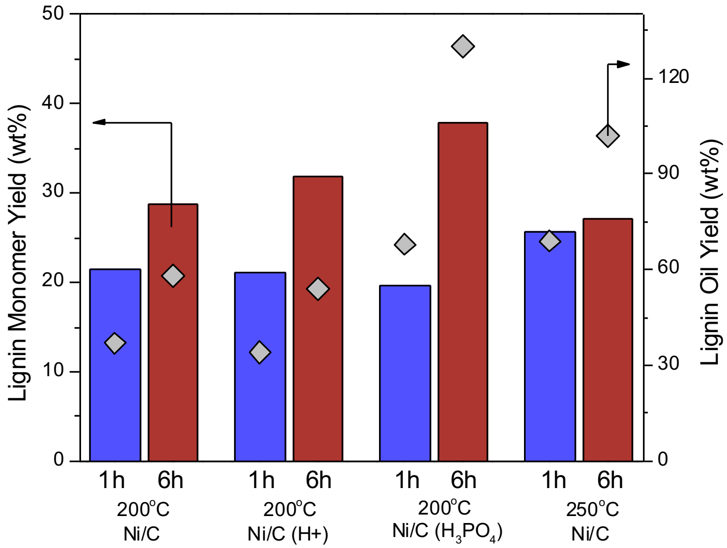
Aim 1: Develop RCF **reactor/catalyst** to produce high lignin monomer yields

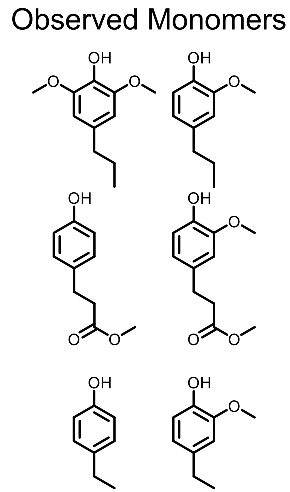
- Separating solvolysis and catalysis
- Modeling solvolysis reactions
- Commissioning, initial runs on flow system



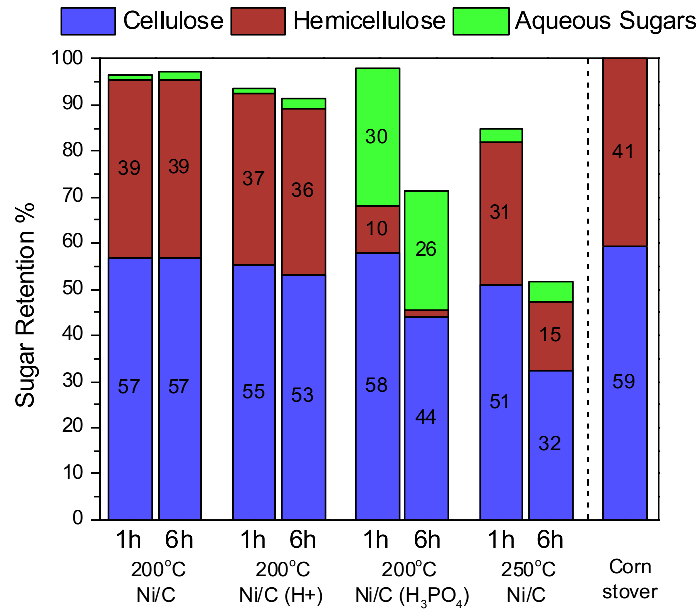
Initial batch RCF runs on corn stover

Lignin monomer and oil yields





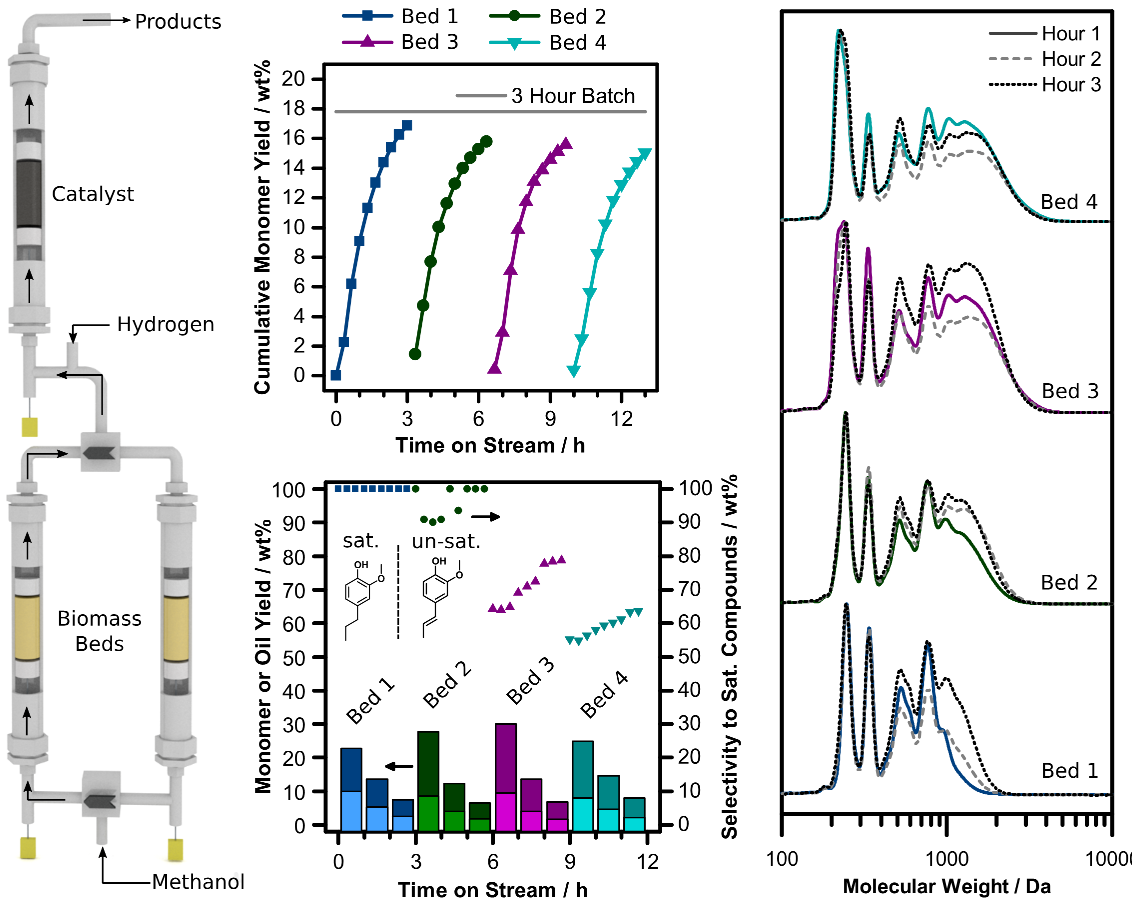
Sugar retention after RCF



- Tested RCF on corn stover as a function of co-catalyst, residence time, temperature
- Achieved up to 38% monomer yield with acid co-catalysts
- Ester and ether bond cleavage products in lignin oil
- **Outcome: Demonstrated high yields of aromatic monomers with excellent polysaccharide retention and digestibility**

Anderson *et al.*, *ACS SusChemEng* 2016

Initial flow-through system to separate biomass and catalyst

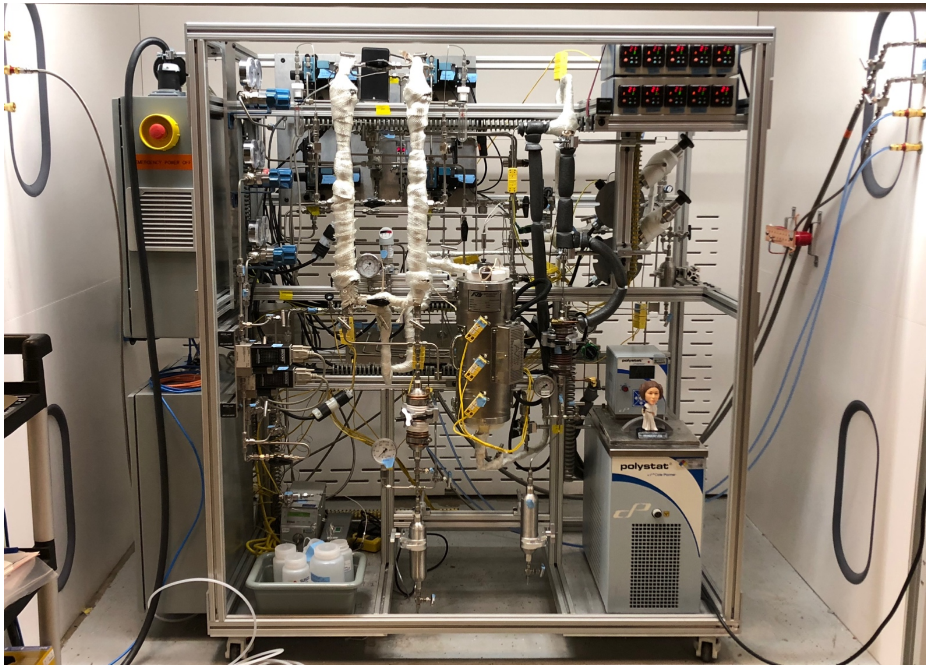


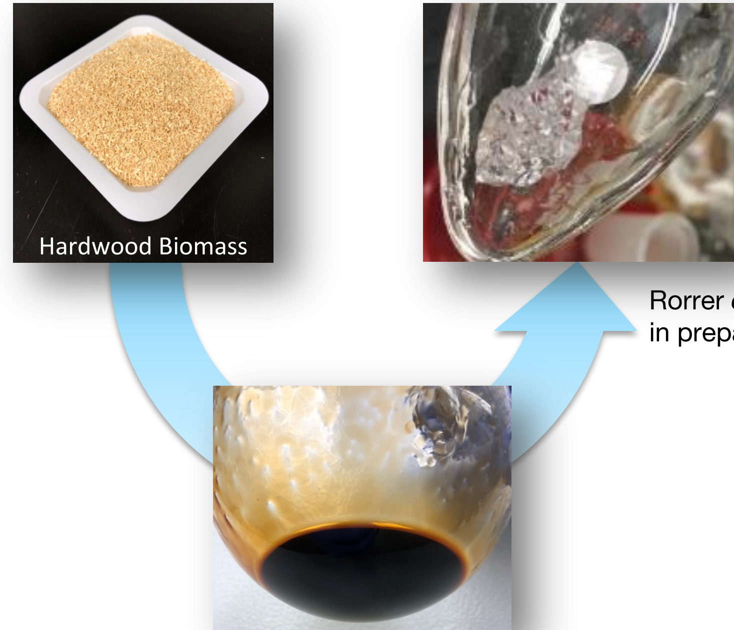
Anderson, Stone *et al.*, *Joule* 2017

Anderson, Stone *et al.*, *ACS SusChemEng* 2018

- Batch RCF does not allow for detailed biomass or catalyst studies because they are mixed
- Led by Yuriy Román at MIT, inspired by flowthrough pretreatment literature
- **Outcome: Physical separation of biomass and catalyst – enables study of solvolysis and catalyst activity/stability independently**

Aim 1: Commissioning a new flow system





Rorrer *et al.*, in preparation

Features

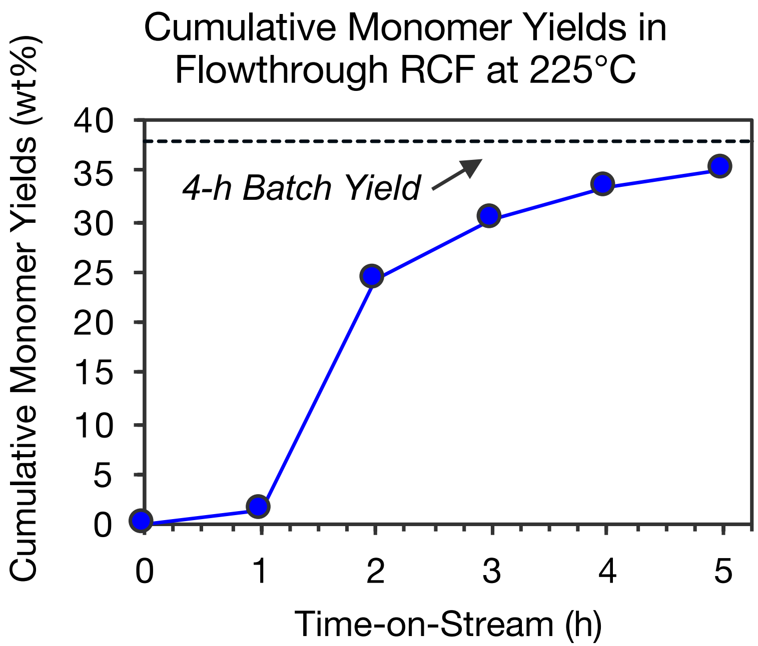
- Reaction temperatures up to 300°C
- Nine independently-controlled heat zones
- Operating pressures up to 2000 psig
- Biomass beds up to 5 g
- Gas flow rates up to 4000 sccm
- Liquid flow rates up to 2 x 10 mL/min
- Designed/interlocked for safe operation

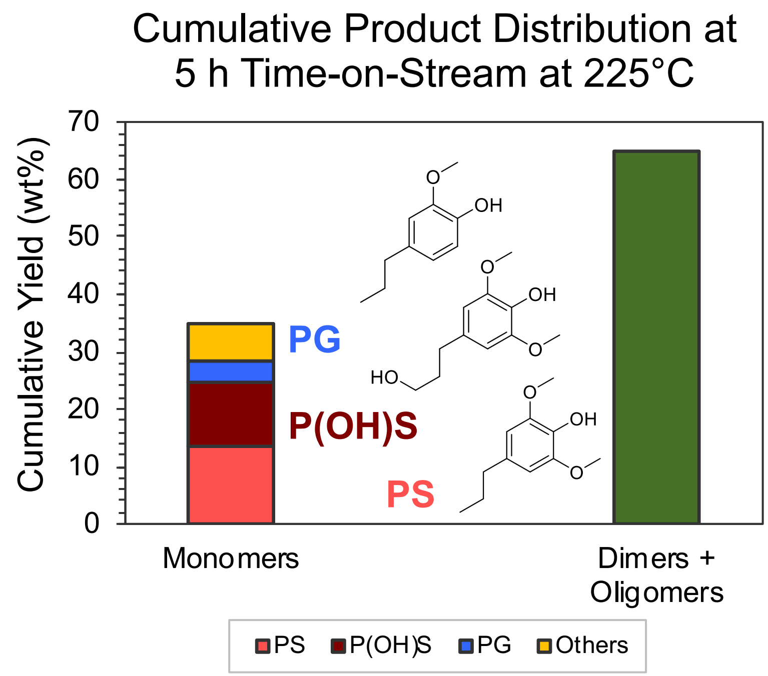
Capabilities

- Decoupled solvolysis and catalysis, across many lignin upgrading strategies
  - Supercritical alcoholysis
  - Acid (co-)catalyzed fractionation
  - Base (co-)catalyzed depolymerization
- Integrate multiple processing steps, e.g. low-temperature *in situ* extractives recovery

Outcome: Flexible, flow-through catalytic lignin reactor system for RCF optimization

Aim 1: Initial RCF on hardwoods and polysaccharide digestions





Enzymatic hydrolysis yields (testing at higher solids loadings ongoing now)

RCF Reaction Temperature	**Glucan Conversion (wt%)**		**Xylan Conversion (wt%)**	
	24 h	*121 h*	*24 h*	*121 h*
225°C	67.2 ± 2.5	92.4 ± 3.6	71.3 ± 2.6	92.2 ± 3.8

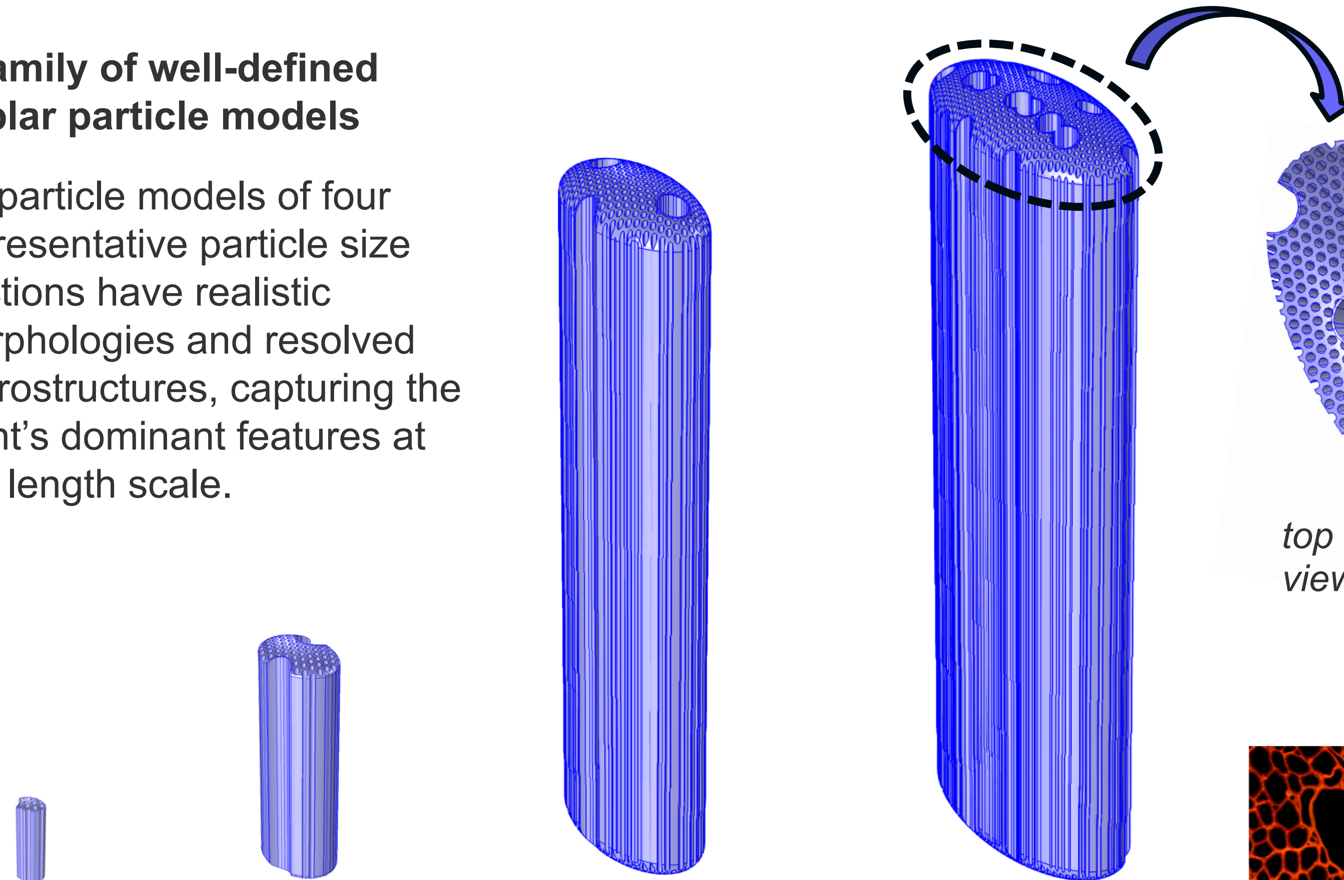
1% solids loadings, CTec3 at 40 mg/g enzyme loading

- RCF monomer yields on birch approach 35% monomers
- Enzyme digestions on residual biomass show excellent conversion
- **Outcome: Demonstrated ability to fully convert lignin and polysaccharides in a hardwood**

Aim 1: Modeling the solvolysis process for improved RCF

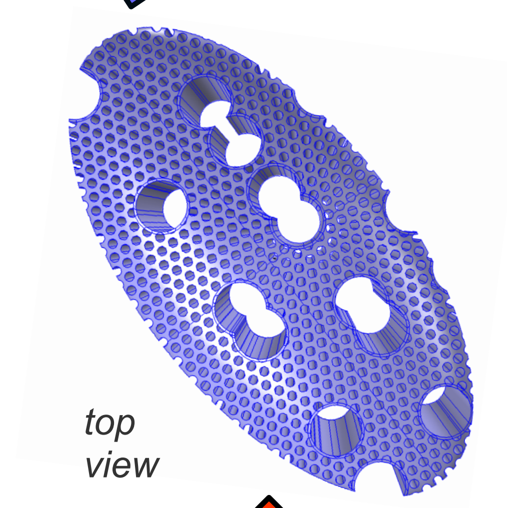
A family of well-defined poplar particle models

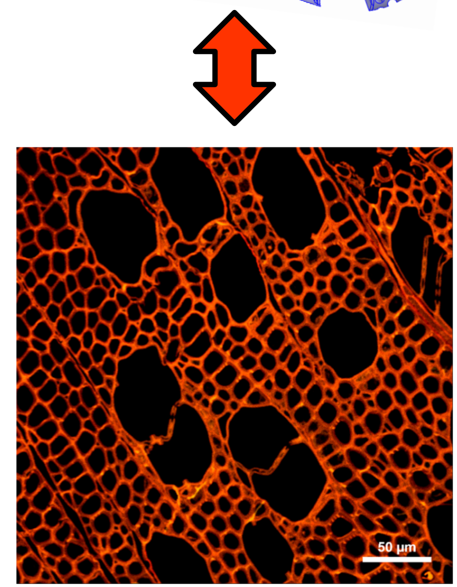
3D particle models of four representative particle size fractions have realistic morphologies and resolved microstructures, capturing the plant's dominant features at this length scale.



<125 µm | 125–250 µm | 250–500 µm | 500–1000 µm

Thornburg *et al.*, in preparation





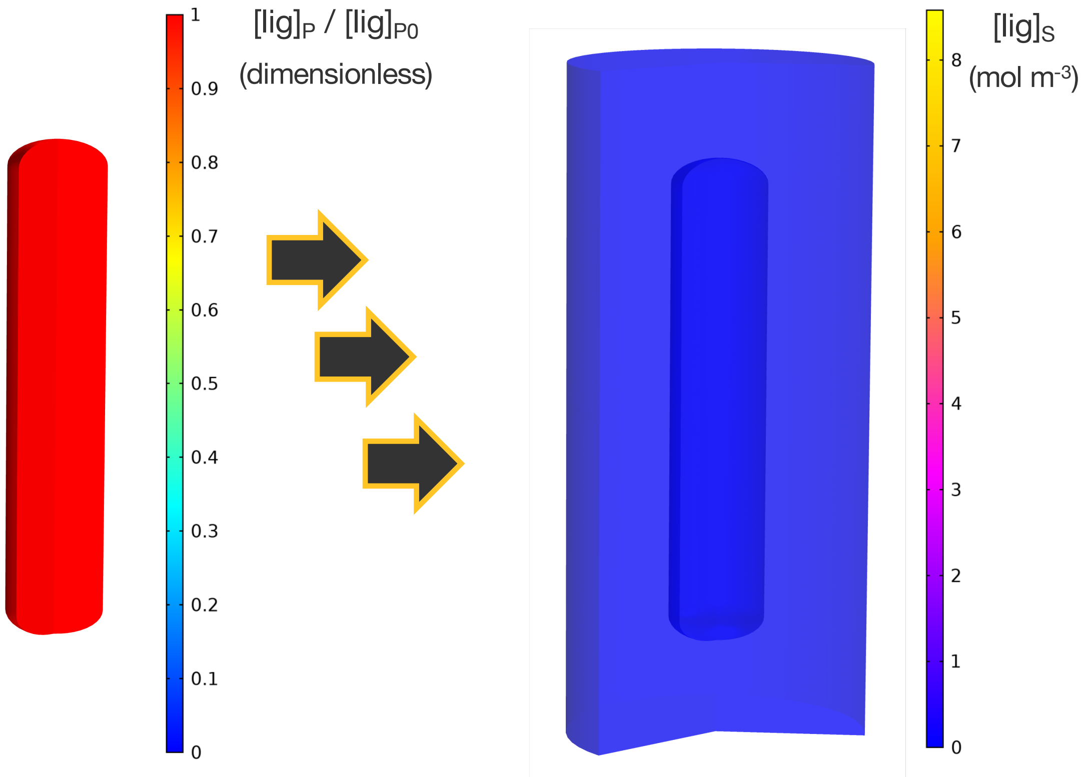
Fluorescence micrograph of 300 nm-thin hybrid poplar cross-section

Outcome: Building predictive models of lignin solvolysis with realistic geometries of biomass particles

Aim 1: Modeling the solvolysis process for improved RCF

Lignin Concentration Profile in Particle Cell Walls

Lignin Concentration Profiles in Particle Pores and in Free Methanol

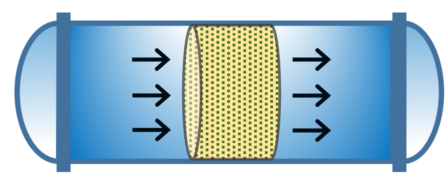


lignin transport **FROM** *cell wall* **TO** *pores and* **INTO** *free solution…*

Outcome: Capturing reactive transport phenomena in real lignin extraction processes

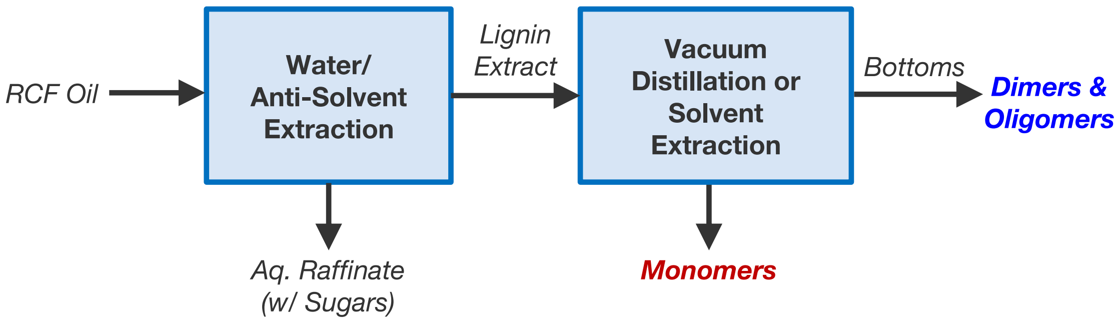
- Rapidly converging ***reduced-order 2D axisymmetric models*** enable rapid testing of rate law hypotheses while accounting for heat and mass transfer
- Best fits observed with a pseudo-first order reversible rate law, capturing extraction plus redeposition events
- ➢ ***Intrinsic kinetic parameters*** may be decoupled from transport effects for ensembles of differently-sized particles

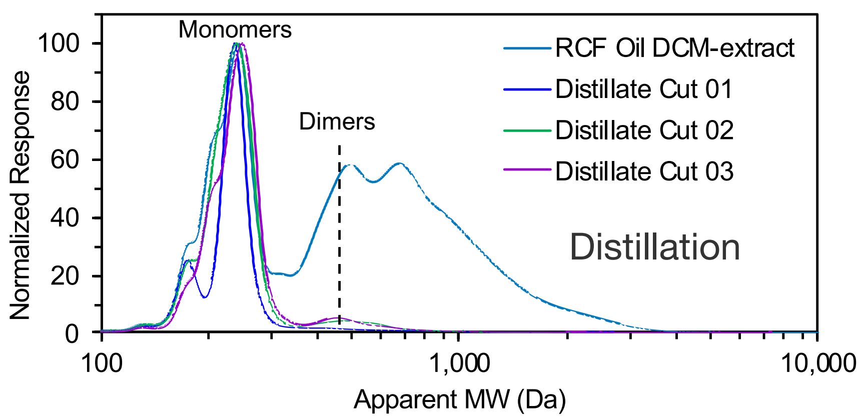
…with straightforward extensions to RCF reactor-scale modeling….

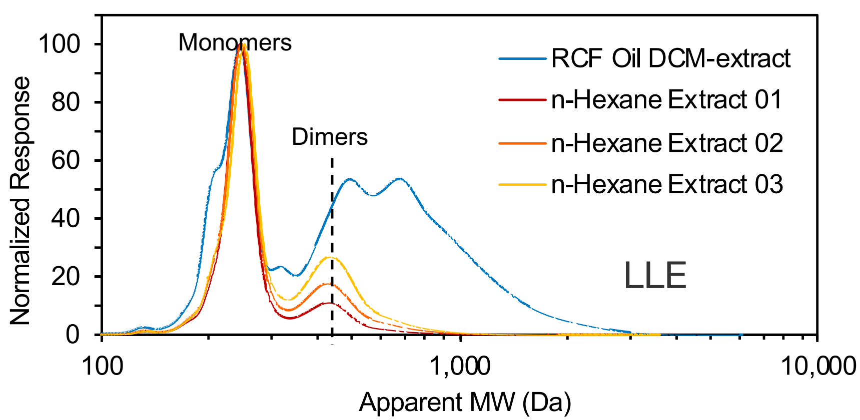


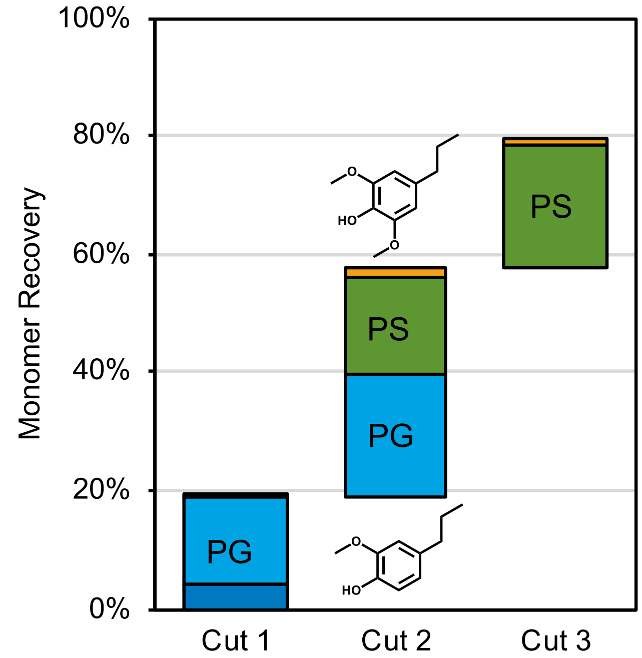
Thornburg *et al*., in preparation

Aim 2: Separations of RCF oil





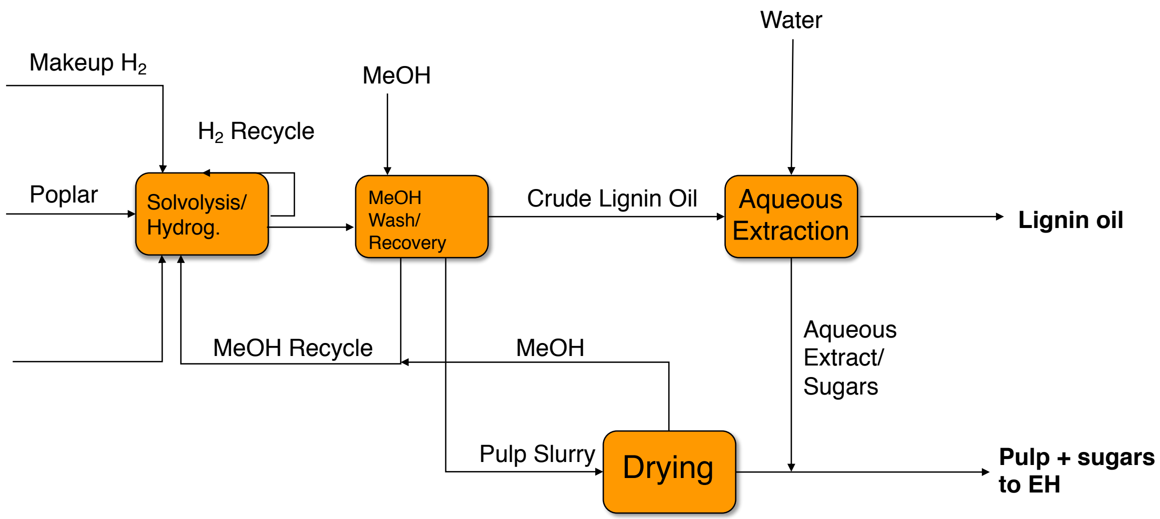




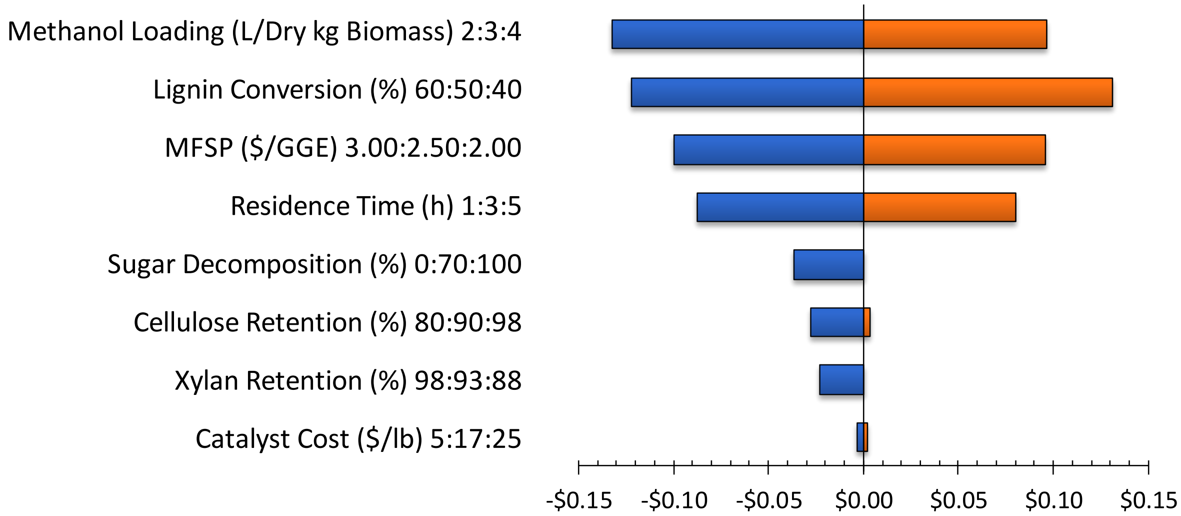
- State-of-the-art oil separation is LLE with hexane
- Aimed to compare distillation to LLE
- ~80% of monomers recovered via distillation
- Cuts 2 and 3 show >75% monomer selectivity
- >90% mass closure
- **Outcome: demonstrated that distillation is more selective than hexane-based LLE for monomer recovery and purification**

Kruger, Thornburg *et al.*, in preparation

Aim 2: Preliminary TEA of RCF process



Sensitivity Analysis – Change to Lignin Oil Selling Price ($/lb)



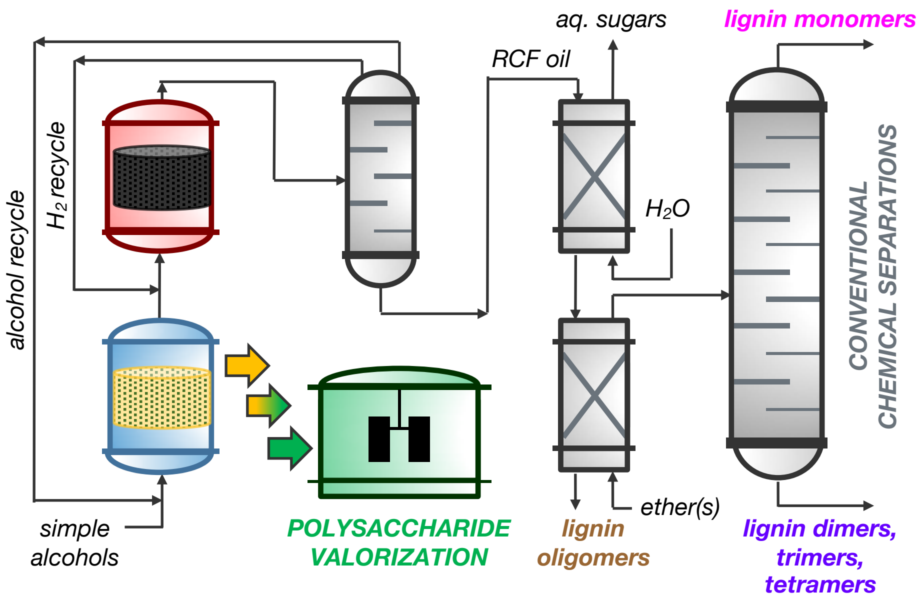
- Modeled as a recirculating reactor
- **Outcome: Energy is the major cost driver:**
  - MeOH loading/recovery
  - Lignin conversion
  - Reactor residence time (CapEx)
- Could feasibly achieve >50% cost reduction for lignin oil selling price
- Outcome led directly to new separations and R&D strategies
- Sugar retention is surprisingly a minor driver
- Catalyst cost is not a major driver

Relevance

Goal: Develop lignin-first biorefining to achieve $2-3/gge modeled cost for integrated lignin and polysaccharide conversion

Why is this project important and what is the relevance to BETO/bioenergy goals?

- Lignin is highly underutilized
- RCF offers alternative to sugar-centric pretreatments for lignin upgrading
- RCF produces **stable** lignin co-products
- May enable $2-3/gge BETO cost targets



How does this project advance the State of Technology and contribute to biofuels commercialization?

- New approach to effective biomass fractionation
- **Industrially-relevant RCF** in an integrated process
- Lignin co-products will be essential to commercialize biofuels and bioeconomy

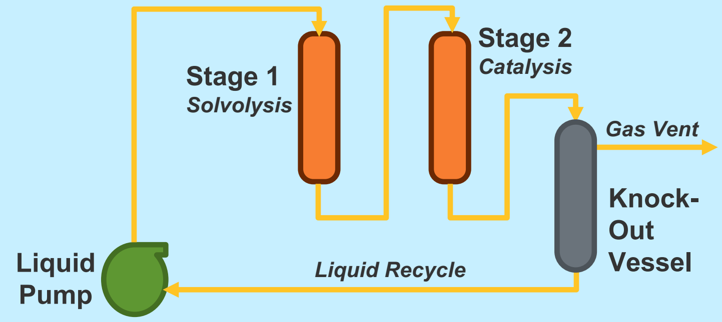
Technology transfer activities:

- Patent applications for catalyst formulations
- Establishing best practices for analytics, mass balances of RCF
- Deploying to existing lignocellulosic waste streams (e.g., almond hulls)

Future work: process engineering towards cost-effective RCF

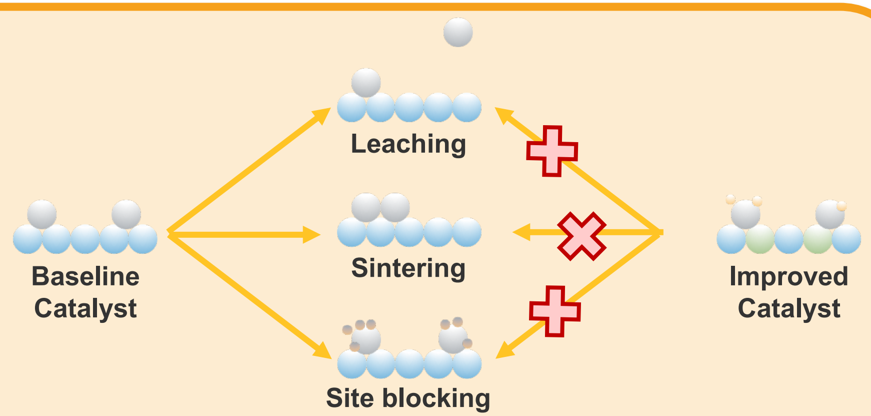
Reduce Solvent Usage

- **Challenge:** Flow-through RCF uses 10x solvent to achieve same monomer yield as batch
- **Strategy:** Re-configure semi-continuous reactor to explore solvent recycle or recirculating product loops



Improve Catalyst Stability

- **Challenge:** RCF catalysts deactivate with extended time-on-stream
- **Strategy:** Characterize post-reaction catalysts to understand deactivation and inform new designs (**Q7 Milestone**)



Reduce Process Severity and Capital

- **Challenge:** MeOH and H_2 pressure require capital-intensive reactors to handle high *T*, *P*
- **Strategy:** Explore alternative solvents and H sources to mitigate pressure requirements.

Solvents	H-Donors
MeOH	H_2
H_2O	*in-situ* formic acid
Glycols	Solubilized sugars
Binary mixtures	Alcohols

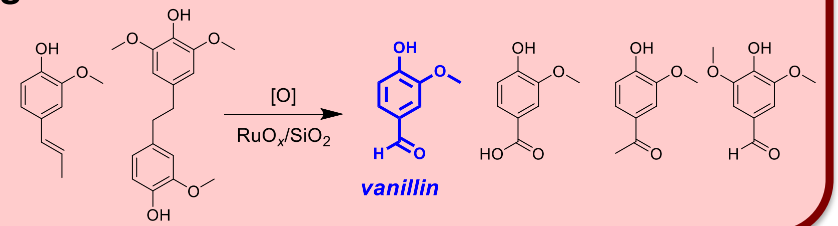
Future work: product engineering leveraging project interactions

All below related to 1.5-year target 50% lignin val., 3-year target 60% lignin val.

Lignin Utilization

Transform RCF Streams to Value-Added Monomers

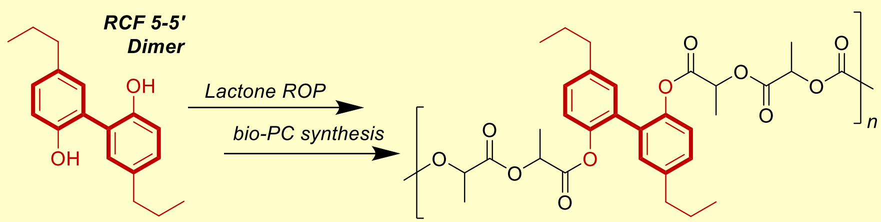
- **Challenge:** Dimers exhibit recalcitrant C–C bonds
- **Strategy:** Optimize oxidation catalysts for C–C cleavage by molecular O_2



Performance-Advantaged Bioproducts

Upgrade Dimers to Value-Added Polymers

- **Challenge:** Dimers do not resemble traditional petrogenic building blocks
- **Strategy:** Develop new polymers utilizing lignin dimers for high-value, recyclable materials



Accelerating Inventions to Market (AIM) Award
(NREL Technology Transfer Office)

Valorize Dimer & Oligomer Streams As Mixtures

- **Challenge:** Dimers/oligomers have limited reactivity and near-zero commercial value
- **Strategy:** Formulate dimers+ into functional replacements for valuable chemical mixtures

Process Fluids

Surfactants

Pesticides

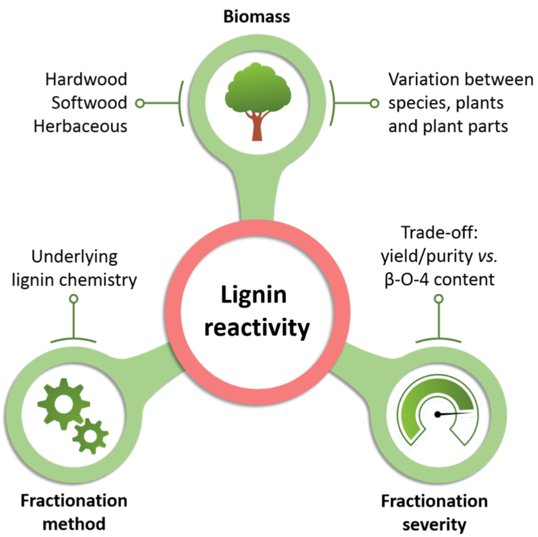
Summary

Overview

- Replace standard pretreatment with selective lignin/polysaccharide fractionation technology
- Equally weights lignin and sugar valorization for integrated biorefinery

Approach

- Co-develop RCF reactor/catalyst to produce high monomer yields
- Develop RCF process with scale-up in mind
- Process integration and scaling informed by TEA
- Collaborate with BETO projects for separations, sugars/lignin products



Schutyser *et al. Chem. Soc. Rev.* 2018

Technical accomplishments

- Initial flow-through RCF demonstrated
- Enabled independent study of solvolysis and catalysis
- Biomass particle modeling initiated for solvolysis reactions
- Distillation successfully applied to RCF oil separations

Relevance

- Lignin-first biorefining may enable a new integrated approach to valorize lignin and sugars
- Lignin valorization is essential for lignocellulosic carbon economy

Future work

- **Develop a process for a lignin-first biorefinery that achieves >60% lignin valorization. Report TEA that shows potential to meet a <$3/gge cost target**

Acknowledgements

BETO: Jay Fitzgerald

NREL contributors

- Brenna Black
- David Brandner
- Rick Elander
- Rui Katahira
- Jacob Kruger
- William Michener
- Joel Miscal
- Ashutosh Mittal
- Darren Peterson
- Kelsey Ramirez
- Michelle Reed
- Nicholas Thornburg

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

BIOENERGY TECHNOLOGIES OFFICE

Collaborators

- **Yuriy Román**, Eric Anderson, Mickey Stone, MIT
- International RCF group for improving standards and analytics: Joseph Samec (U Stockholm), Mahdi Abu-Omar (UCSB), Katalin Barta (U Groningen), Jeremy Luterbacher (EPFL), Roberto Rinaldi (Imperial College London), Bert Sels (KU Leuven), Feng Wang (DICP)

Collaborators on BETO projects:

- Steve Decker, Mike Himmel, Enzyme Engineering and Optimization
- Derek Vardon, Direct Catalytic Conversion of Cellulosics
- Allison Robinson, Lignin Utilization
- Eric Karp, Separations Consortium
- Nicholas Rorrer, Caroline Hoyt, Performance-Advantaged Bioproducts
- Peter Ciesielski, Consortium for Computational Physics and Chemistry

Milestones

FY18		
Q1	QPM	Demonstrate enzymatic digestibility of RCF polysaccharides from batch processing including both fungal cellulases and cellulosome systems. [Base case]
Q2	QPM	Develop analytical methods and identify a minimum of five dimer aromatic compounds from the RCF process; provide recommendations on a generalizable, rapid method for identification and quantification of lignin dimers and oligomers. [Base case]
Q3	QPM	Design, construct, and commission a staged flow reactor capable of semi-continuous RCF of whole biomass and residual lignin streams. [Base case]
Q4	Annual	Evaluate separation of monomers from a hardwood RCF lignin oil using at least two techniques, such as distillation and liquid-liquid extraction. Determine monomer recoveries and selectivities for each technique. Demonstrate selective separation of a monomer stream from at least one type of RCF oil (e.g., from a hardwood feedstock). Target 75% monomer recovery and 75% monomer selectivity in separated fraction, at greater than 90% overall mass closure.

Milestones

FY19		
Q1	Annual	Evaluate separation of monomers from a hardwood RCF lignin oil using at least two techniques, such as distillation and liquid-liquid extraction. Determine monomer recoveries and selectivities for each technique. Demonstrate selective separation of a monomer stream from at least one type of RCF oil (e.g., from a hardwood feedstock). Target 75% monomer recovery and 75% monomer selectivity in separated fraction, at greater than 90% overall mass closure
Q2	G/NG	Demonstrate the valorization potential of at least 50% of the overall lignin stream based on monomers, dimers, and oligomers through further separations and downstream catalytic processing
Q3	QPM	Produce a comprehensive analytical method that fully details dimeric species from RCF oil, encompassing 15 species or greater, and is transferrable for relative abundance of dimers between RCF samples produced between two systems.
Q4	QPM	Evaluate catalyst stability during semi-continuous RCF operation throughout at least 6 hours of time-on-stream. If necessary, explore possible regeneration strategies to improve catalyst lifetime.

Publications

1. Eric M. Anderson, Michael L. Stone, Rui Katahira, Michelle Reed, Wellington Muchero, Gregg T. Beckham*, Yuriy Román-Leshkov*, "Differences in S/G ratio in natural poplar variants do not predict catalytic depolymerization monomer yields: Implications for lignin biosynthesis", in revision at ***Nature Comm***.
2. Michael L. Stone, Eric M. Anderson, Kelly M. Meek, Michelle Reed, Rui Katahira, Fang Chen, Richard A. Dixon, Gregg T. Beckham*, Yuriy Román-Leshkov*, "Reductive catalytic fractionation of C-lignin", in press at ***ACS Sus. Chem. Eng.***
3. Eric M. Anderson, Michael L. Stone, Max Hülsey, Gregg T. Beckham*, Yuriy Román-Leshkov*, "Kinetic studies of lignin solvolysis and reduction by reductive catalytic fractionation decoupled in flow-through reactors", ***ACS Sust. Chem. Eng***. (2018) 6, 7951-7959.
4. Eric M. Anderson, Michael L. Stone, Rui Katahira, Michelle Reed, Gregg T. Beckham*, Yuriy Román-Leshkov*, "Flowthrough reductive catalytic fractionation of biomass", ***Joule***. (2017) 1, pp. 613-622.

Presentations

1. Catalytic valorization of lignin in the biorefinery, 4th Ibero-American Congress on Biorefineries, **Plenary** Invited Lecture, October 24, 2018
2. Lignin depolymerization and fractionation in flow-through systems, 14th International Conference on Renewable Resources and Biorefineries, May 31st, 2018
3. Developing new processes to valorize lignin and sugars to building-block chemicals and materials, RWTH Aachen University, May 28th, 2018
4. Recent adventures in the deconstruction of cellulose and lignin, LBNet3 Meeting (UK), May 16th, 2018
5. Lignin conversion by biological funneling and chemical catalysis, COST FP1306 Workshop, **Plenary** Invited Lecture, March 12th, 2018
6. Hybrid biological and catalytic processes to produce chemicals and materials from biomass, University of Delaware, October 5, 2017