ChemCatBio
Chemical Catalysis for Bioenergy

Direct Catalytic Conversion of Cellulosics (DC3)

DOE Bioenergy Technologies Office
2019 Peer Review

Derek Vardon, NREL

March 7, 2019

U.S. DEPARTMENT OF ENERGY | *Office of* ENERGY EFFICIENCY & RENEWABLE ENERGY
BIOENERGY TECHNOLOGIES OFFICE

Direct Catalytic Conversion of Cellulosics (DC3)

Background, Goal, and Outcome

ChemCatBio Goal: Accelerate the development of catalysts and related technologies for the commercialization of biomass-derived fuels and chemicals

❖ DC3 Background

Conversion processes are needed to valorize both the cellulosic and lignin fractions of biomass. Lignin monomers can be selectively removed by "Lignin First" solvolysis for upgrading. However, compatible processes are still needed for the residual cellulosics.

❖ DC3 Goal

The goal of DC3 is (i) develop a semi-continuous solvolysis + catalysis process to upgrade residual cellulosics from delignified biomass, and (ii) demonstrate the resulting oxygenates are suitable as a biofuel.

❖ DC3 Outcome

This project will advance a new conversion process within the BETO portfolio that is (i) fully compatible with "Lignin First" upgrading, and (ii) expands the slate of fuels and chemicals derived from cellulosics.

Quad Chart

Timeline

- **Project start date:** Oct 1, 2018
- **Project end date:** Sept 30, 2020
- **Percent complete:** 25%

	Total Costs Pre FY17*	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19- End)
DOE Funded	$0k	$0k	$134k	$402k

BETO Projects: Lignin First, Lignin Utilization, Co-Optima, Catalytic Upgrading of Biochemical Intermediates
Universities: University of Wisconsin (George Huber)

Barriers Addressed

Ot-B. Cost of Production
Ct-F. Increasing Yield from Catalytic Processes

Objectives

Aim 1. Deploy a semi-continuous solvolysis + catalysis process for converting delignified woody biomass to mixed aliphatic alcohols

Aim 2. Evaluate multi-functional catalysts for tailoring the alcohol production distribution

Aim 3. Produce DC3 biofuel to validate the fuel properties and target >15% MFSP savings compared to state-of-the-art

End of Project Goal

Establish a semi-continuous solvolysis + catalysis approach to (i) generate oxygenated fuels with suitable properties from delignified woody biomass, and (ii) determine metrics necessary to meet a <$3.00/GGE based on integrated TEA with “Lignin First” valorization

1 - Project Overview

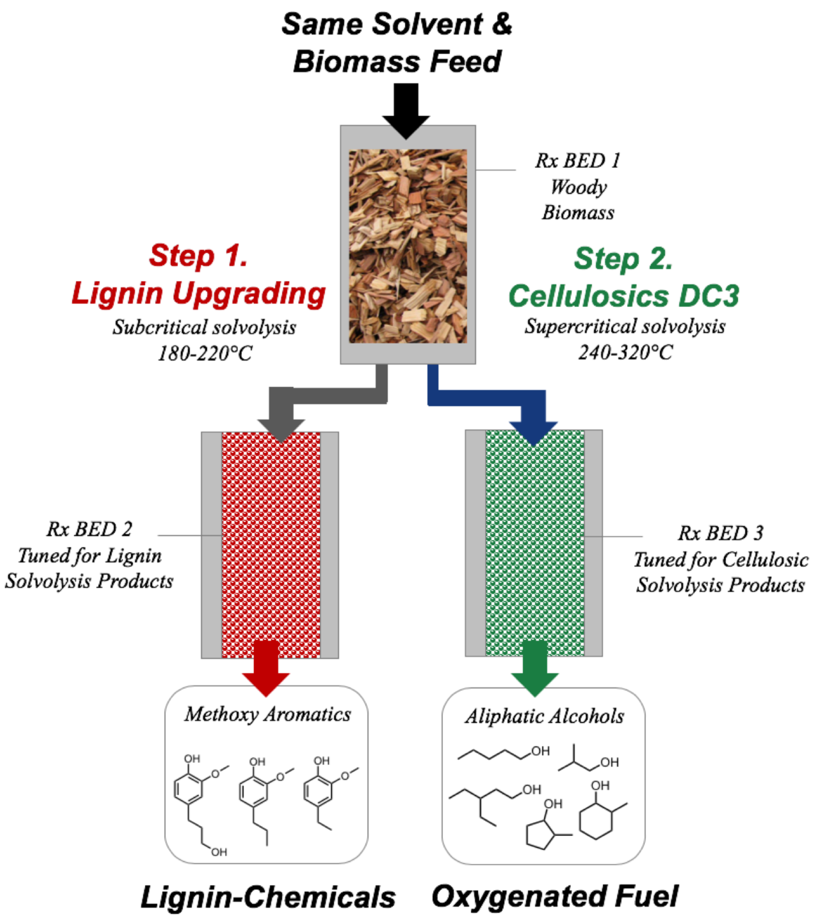
Enable an integrated approach for "Lignin First" upgrading

Background on "Lignin First"

- ✓ Lignin monomers initially removed by subcritical solvolysis with methanol
- ✓ After solvolysis, lignin monomers processed with downstream catalysis for making fuels and/or chemicals

Integration with DC3

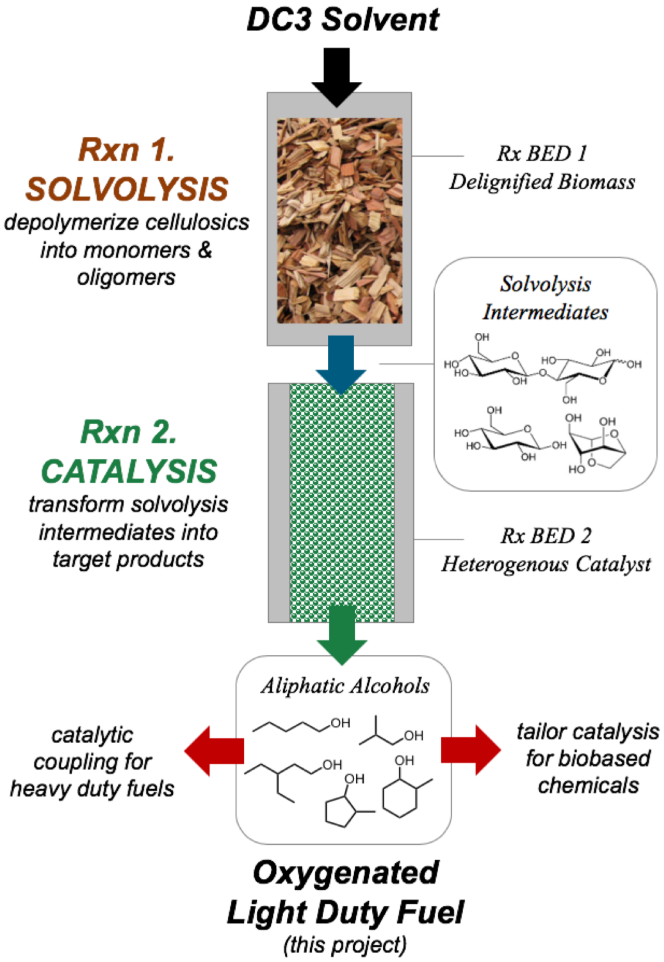
- ✓ Residual cellulosics can be fully solubilized using same solvent under supercritical conditions
- ✓ Cellulosic monomers can be processed over their own tailored catalyst bed for making fuels and/or chemicals



DC3 integrates with "Lignin First" upgrading via solvolysis + catalysis

1 - Project Overview

Motivation and key questions remaining for DC3



Motivation for DC3

- ✓ DC3 can convert delignified woody biomass, as well as waste cellulosics, into energy dense liquid oxygenates
- ✓ Provides opportunity to target gasoline, precursors for diesel, and/or chemicals

Key Questions for DC3

- ✓ Need to better understand feedstock and interface with "Lignin First"
- ✓ Need to assess (i) DC3 oxygenate fuel properties, (ii) ability to steer product distribution, and (iii) overall economics

DC3 utilizes solvolysis + catalysis to upgrade cellulosics

1 - Project Overview

Prior history and proposed processing approach to advance DC3

History of DC3 Batch Rxn

Batch Rxn combines

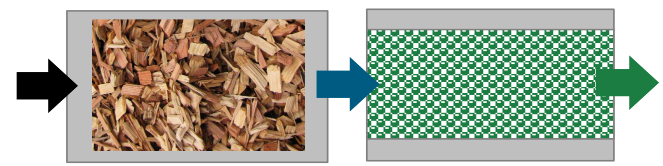
SOLVOLYSIS
& CATALYSIS

- ✓ Challenge to scale low-cost, high-volume batch processes
- ✓ Relies on contacting solid biomass w/solid catalyst initially
- ✓ Cannot decouple solvolysis and catalysis reaction steps

Move to Semi-Continuous

Semi-continuous decouples rxn

Step 1. SOLVOLYSIS ***Step 2. CATALYSIS***



- ✓ Potential for simplified flow through solvent processing
- ✓ Only react soluble monomers & oligomers over solid catalyst
- ✓ Independently tune solvolysis and catalysis reaction steps

DC3 project will extend prior batch studies to semi-continuous

2 - Approach (Management)

How DC3 fits within CCB and interfaces with the BETO portfolio

ChemCatBio
Chemical Catalysis for Bioenergy

DC3 Seed

Catalytic Technologies	*Enabling Capabilities*	*Industry Partnerships (Directed Funding)*
Catalytic Upgrading of Biochemical Intermediates (NREL, PNNL, ORNL, LANL, NREL*)	**Advanced Catalyst Synthesis and Characterization** (NREL, ANL, ORNL, SNL)	**Gevo** (NREL)
Catalytic Upgrading of Indirect Liquefaction Intermediates (NREL, PNNL, ORNL)	**Catalyst Cost Model Development** (NREL, PNNL)	**ALD Nano/JM** (NREL)
Catalytic Fast Pyrolysis (NREL, PNNL)	**Consortium for Computational Physics and Chemistry** (ORNL, NREL, PNNL, ANL, NETL)	**Vertimass** (ORNL)
Electrocatalytic and Thermocatalytic CO_2 Utilization (NREL, ORNL*)	**Catalyst Deactivation Mitigation for Biomass Conversion** (PNNL)	**Opus12**(NREL)
		Visolis (PNNL)
		Lanzatech (PNNL) - Fuel
		Gevo (LANL)
		Lanzatech (PNNL) - TPA
		Sironix (LANL)

*FY19 Seed Project

Cross-Cutting Support

ChemCatBio Lead Team Support (NREL)

ChemCatBio DataHUB (NREL)

'Lignin First'

Biorefinery Development

Co-Optimization of Fuels & Engines

- *Work with ChemCatBio on catalyst cost modeling (CCM) and advanced characterization (ACSC)*
- *Coordinate with 'Lignin First' on delignified biomass and solvent selection*
- *Collaborate with Co-Optima on leveraging latest fuel property tools*

DC3 is a new start seed project within ChemCatBio

2 - Approach (Management)

Project team with management best practices

Project Team Roles and Current Collaborations

Derek Vardon, PI

NREL DC3 Team: *Hannah Nguyen, Nick Cleveland*

NREL Collaborators:

- ***Lignin First*** - *Gregg Beckham*
- ***Economic Analysis*** - *Mary Biddy*
- ***CatCostModel***- *Fred Baddour*
- ***ACSC*** - *Susan Habas*

External Collaborators:

- ***Catalysis + Solvolysis*** - *George Huber, University of Wisc.*

DC3 Project Communication & Coordination

1) Biweekly technical planning meetings with core team

- Recap accomplishments, assign action items, review objectives

2) Quarterly planning meetings with DC3 collaborators

- Discuss alignment, review progress, coordinate next steps

Utilize best management practices and build collaborations

2 - Approach (Technical)

Major project goals and research approach

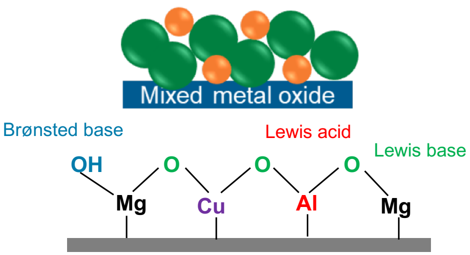
DC3 for Upgrading Residual Cellulosics

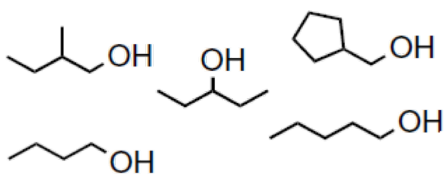
Process Development

Deploy a semi-continuous DC3 process for converting delignified woody biomass to mixed aliphatic alcohols

Catalyst Design

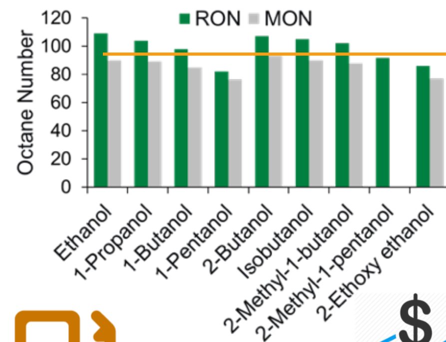
Evaluate multi-functional catalysts for aliphatic alcohol production and solvent reforming





Biofuel Evaluation

Produce DC3 biofuel to validate the fuel properties and >15% MFSP savings compared to state-of-the-art



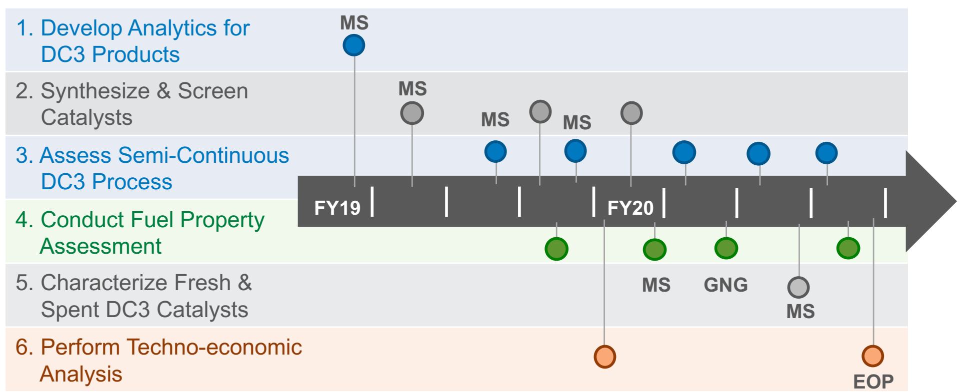
Span process development, catalyst design, and biofuel R&D

2 - Approach (Technical)

Well-defined milestones and strategies to address risk

Potential Risk	Mitigation Strategy
✓ Rapid catalyst deactivation during DC3 biomass processing	✓ Evaluate regeneration schemes, as well as biomass pre-wash
✓ Poor oxygenate recovery following conversion	✓ Assess separation techniques (distillation, extraction)
✓ In-sufficient information on fuel properties of oxygenate blendstock	✓ Collaborate with Co-Optima for latest fuel property prediction tools

Project Milestones (MS) with Go-No/Go (GNG)



Progress measurable with risk mitigation in place

2 - Approach (Technical)

Critical success factors, challenges, and key activities

Critical Success Factor	Challenge to Overcome	Activity to Address
Transition from batch to semi-continuous operation	• Lack of published data • Differing performance	Deploy semi-continuous DC3 reactor as major focus in FY19
Achieve high yields of oxygenates with minimum solvent loss	• Excess MeOH reforming • Low yield of fuel target	Evaluate tunable catalyst suite with pre/post characterization
Deliver lower cost higher performing oxygenated biofuel	• Unknown fuel properties • Low TRL for process	Conduct mid and final TEA with fuel property assessment

Project activities designed to address barriers to success

3 - Relevance

How DC3 contributes to BETO goals and objectives

Contribute to BETO Goals

Ot-B. Cost of Production

- Assess new “solvolysis + catalysis” that allows for parallel lignin valorization
- Conduct TEA to inform production costs and identify major cost drivers for follow-on R&D

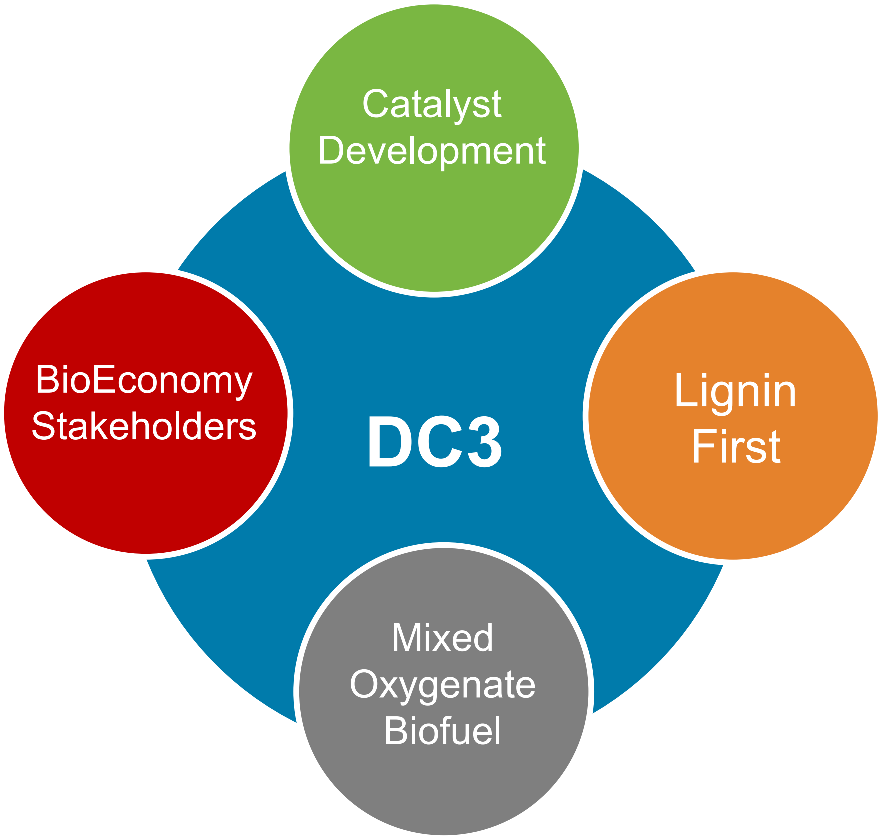
Ct-F. Increase Yield from Catalytic Processes

- Benchmark against commercial and literature catalysts
- Leverage fuel property tools to define targets
- Test suite of catalysts to improve target product yields

ChemCatBio Goal: Accelerate the development of catalysts & related technologies for the commercialization of biomass-derived fuels & chemicals

3 - Relevance

Potential applications, advancement in SOT, impact to viability



Impact Viability of Bioenergy

- Develop strategy with "Lignin First"
- Leverage solvolysis + catalysis to simplify unit operations for upgrading
- Demonstrate value of fuel that retains oxygen inherent to biomass

Potential DC3 Applications

- Target industries that have waste cellulosic feedstocks (pulp and paper)
- Develop tunable process to target oxygenated fuels *and* chemicals

Advancement in SOT

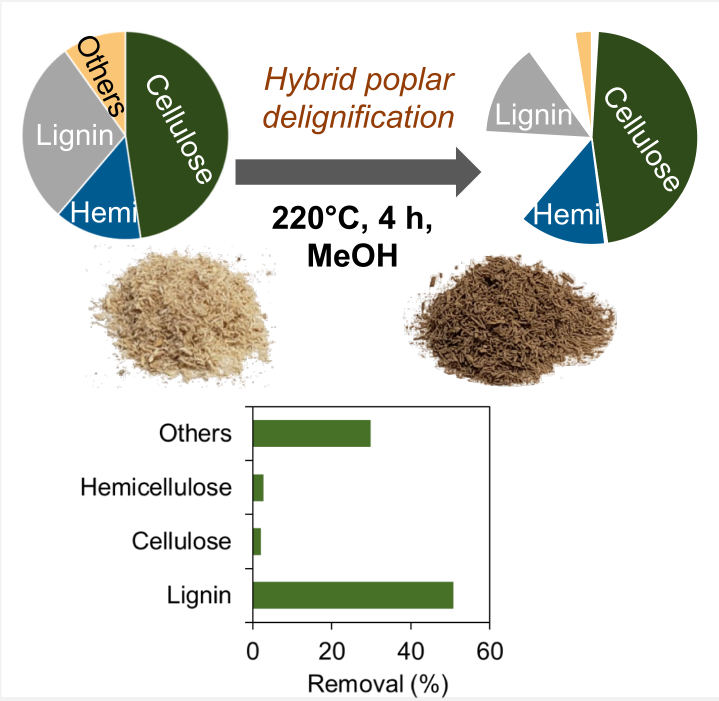
- Further derisk catalytic solvolysis strategies from batch to flow
- Assess catalyst tailorability and stability and resulting economics

Ensure DC3 project is of high impact to biomass community

4 - Future Work

Produce and characterize delignified DC3 biomass feedstock

Research Goal: Generate delignified biomass and retain (hemi)cellulose



Planned Activities:

- Generate delignified hybrid poplar using subcritical MeOH solvolysis
- Assess feedstock composition using NREL expertise in biomass compositional analysis
- Collaborate with "Lignin First" team on lignin removal technology

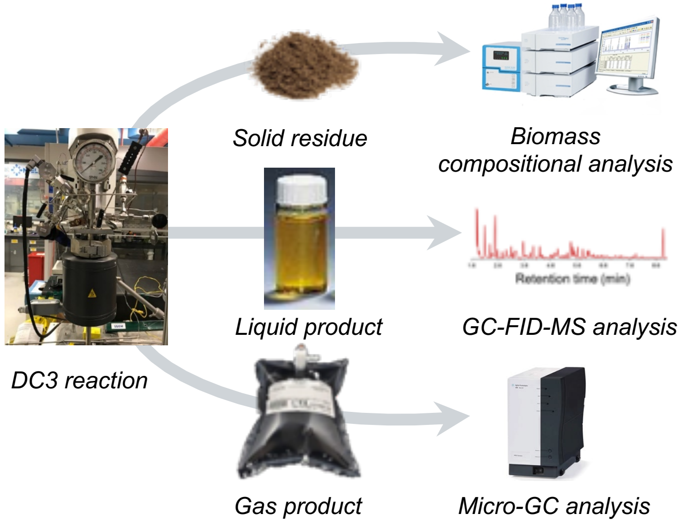
Target: Produce and analyze DC3 feedstock at the >10-gram scale

4 - Future Work

Develop analytical methods for DC3 processing

Research Goal: Quantify biomass conversion, products, and solvent

Leverage suite of analytical methods for mass and carbon balance



Planned Activities:

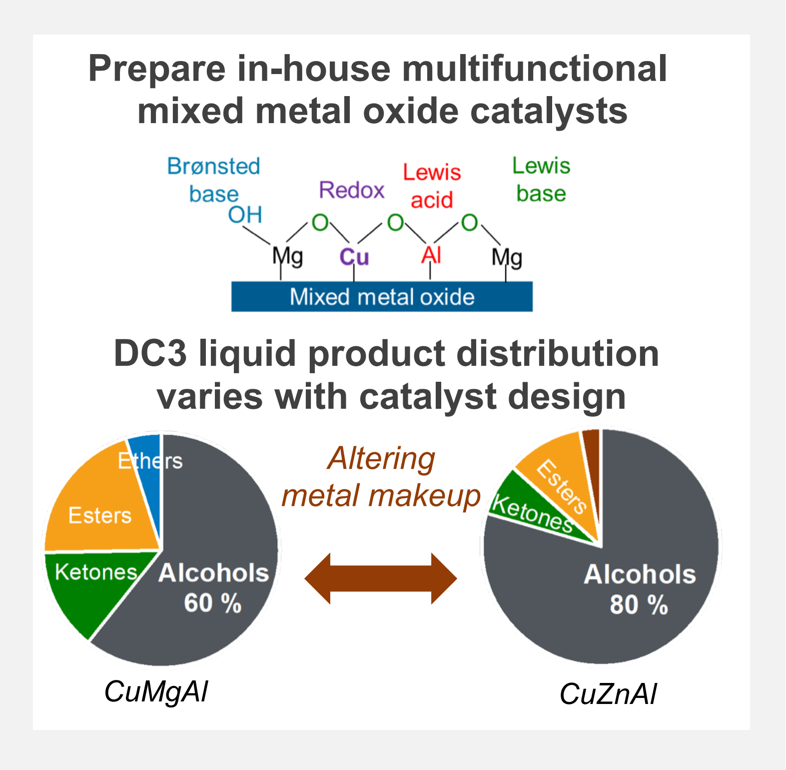
- Develop GC/LC methods to analyze composition of gas/solid/liquid products
- Quantify conversion, yield, selectivity and solvent loss
- Develop collaborations for complex product analysis via NMR and FT-ICR-MS

Target: Achieve gas/liquid/solid mass & C-balance with 90% closure

4 - Future Work

Tune catalyst composition for desired products and solvent retention

Research Goal: Develop tunable mixed metal oxide catalysts for DC3



Planned Activities:

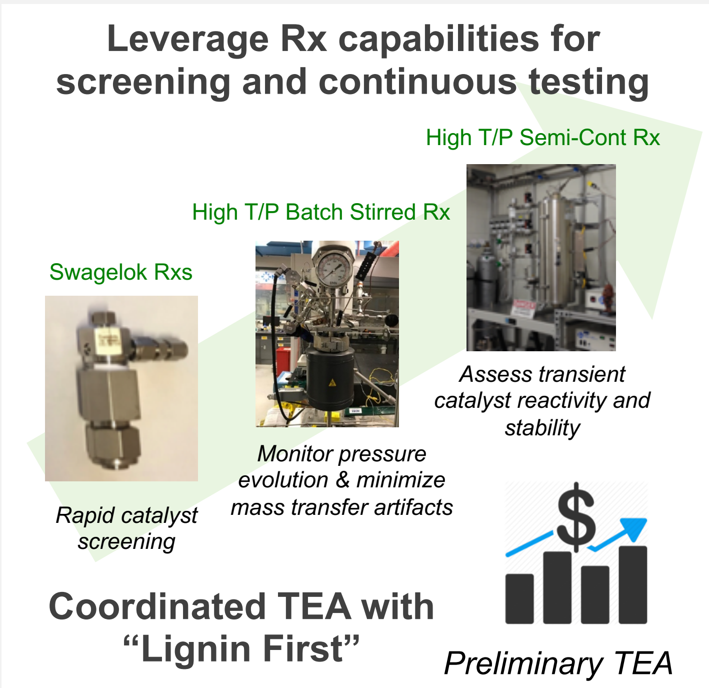
- Benchmark against commercial and literature
- Evaluate tailored suite of mixed metal oxides
- Leverage ChemCatBio ACSC and Catalyst Cost Model
- Link product distribution to favorable fuel properties and/or chemical applications

Target: Baseline against commercial and screen >8 tuned catalysts

4 - Future Work

Deploy semi-continuous DC3 process with informed TEA feedback

Research Goal: Deploy semi-continuous DC3 at 5-g biomass scale



Planned Activities:

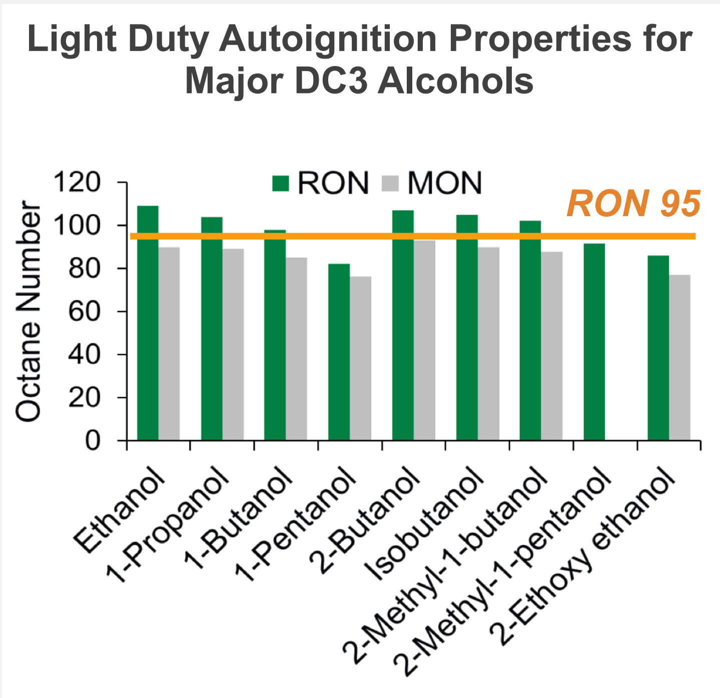
- Investigate DC3 performance in batch and flow
- Utilize a high T/P flow reactor for semi-continuous DC3
- Investigate sustained activity for down-selected catalysts
- Leverage early-stage TEA to inform process parameters

Target: Achieve semi-continuous >50% C-yield to aliphatic alcohols

4 - Future Work

Evaluate fuel properties of DC3 aliphatic alcohols

Research Goal: Set DC3 conversion targets based on fuel properties



Planned Activities:

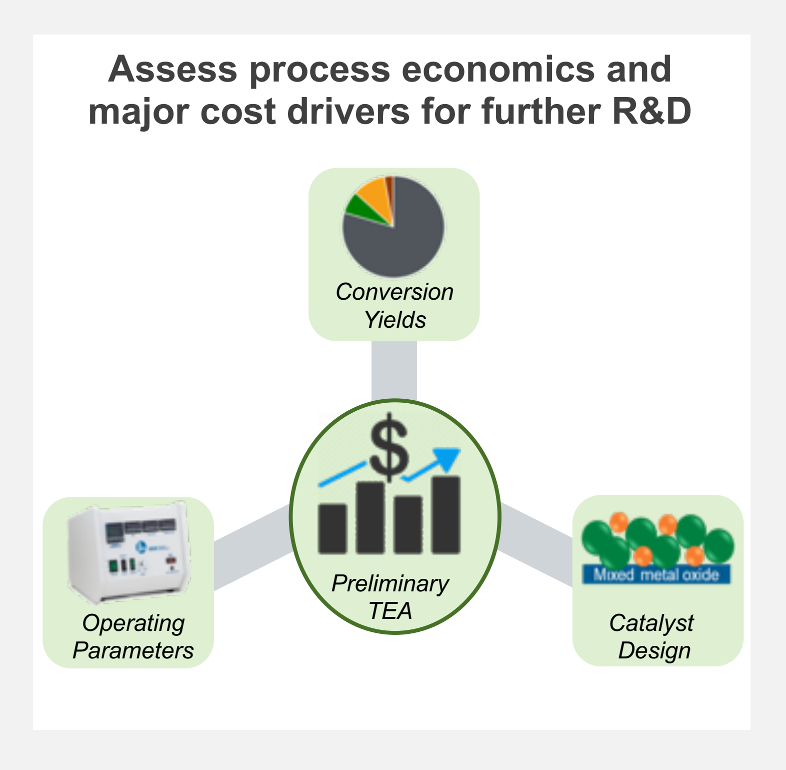
- Leverage Co-Optima fuel property tools to set conversion targets
- Tune catalyst & process conditions to generate desirable oxygenate fuel
- Generate >20 mL of DC3 oxygenates and measure fuel properties as 20% blend

Target: Demonstrate suitable DC3 fuel properties at 20% blend level

4 - Future Work

Perform integrated TEA analysis to inform process development

Research Goal: Understand major process cost drivers for DC3



Planned Activities:

- Provide process parameters for TEA and plan R&D to address major cost drivers
- Utilize Catalyst Cost Model to inform catalyst down-selection
- Update cost models at end of project with “Lignin First” to show pathway to <$3/GGE

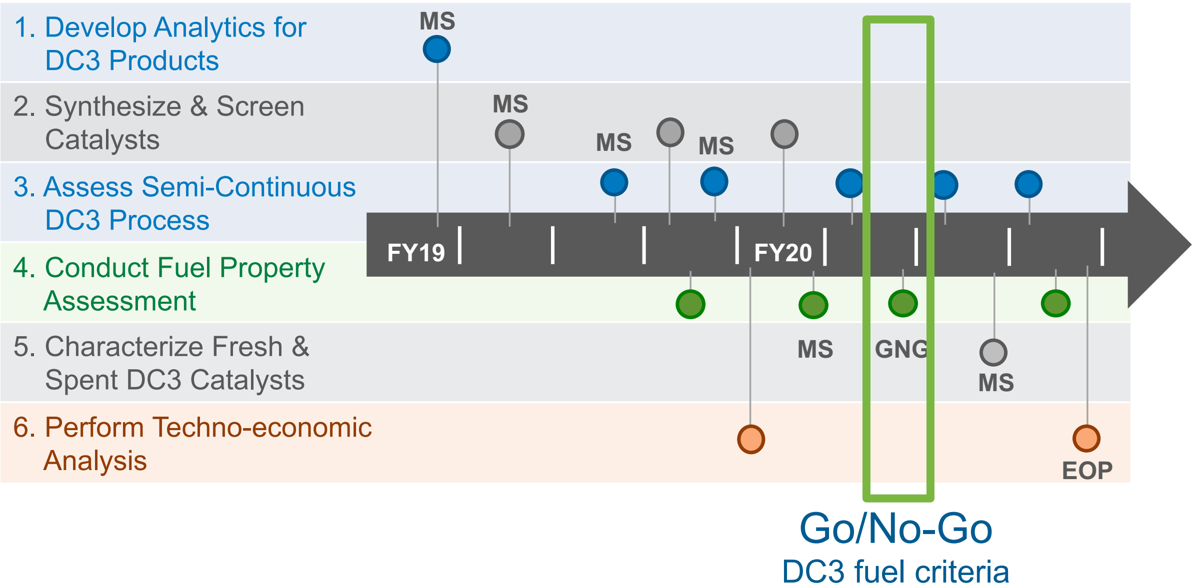
Target: Show pathway to <$3.00/GGE fuel with DC3 & Lignin First

4 - Future Work

FY20 Deliverables will integrate lessons learned

Biofuel Yield & Quality

FY20 Q2 GNG: Validate ≥50% of carbon from delignified hybrid pine can be converted to aliphatic alcohols. Establish that major products are suitable as blendstock at the ≥20% level.



Future milestones will address conversion and fuel success criteria

Summary for DC3 Project

Overview	**Goal to develop a semi-continuous process for the direct catalytic conversion of cellulosics (DC3) to upgrade delignified biomass and evaluate the resulting oxygenates for light and/or heavy duty fuel.**
Approach	• Develop semi-continuous process for residual cellulosics conversion • Design catalyst to target desirable product composition based on fuel properties • Leverage ChemCatBio enabling capabilities, Co-Optima fuel properties knowledge, and Lignin First expertise
Technical Progress	• Reproduce current state-of-the art batch DC3 process • Demonstrate influence of catalyst formulation on liquid product distribution • Evaluate preliminarily fuel properties of major DC3 alcohol products
Relevance	**The DC3 project seeks to upgrade delignified woody biomass to advantaged fuels and provide alternative to enzymatic hydrolysis**
Future Work	• Deploy semi-continuous DC3 reactor for with delignified biomass at 5-g scale • Tailor catalyst and process design for desired fuel targets • Generate DC3 fuel samples for biofuel validation and inform integrated TEA

Thank you for listening…
Let’s discuss!

ChemCatBio
Chemical Catalysis for Bioenergy

U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY
BIOENERGY TECHNOLOGIES OFFICE