U.S. Department of Energy (DOE) Bioenergy Technologies Office (BETO) 2019 Project Peer Review

THF Co-Solvent Biomass Fractionation to Catalytic Fuel Precursors with High Yields

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Biomass Conversion

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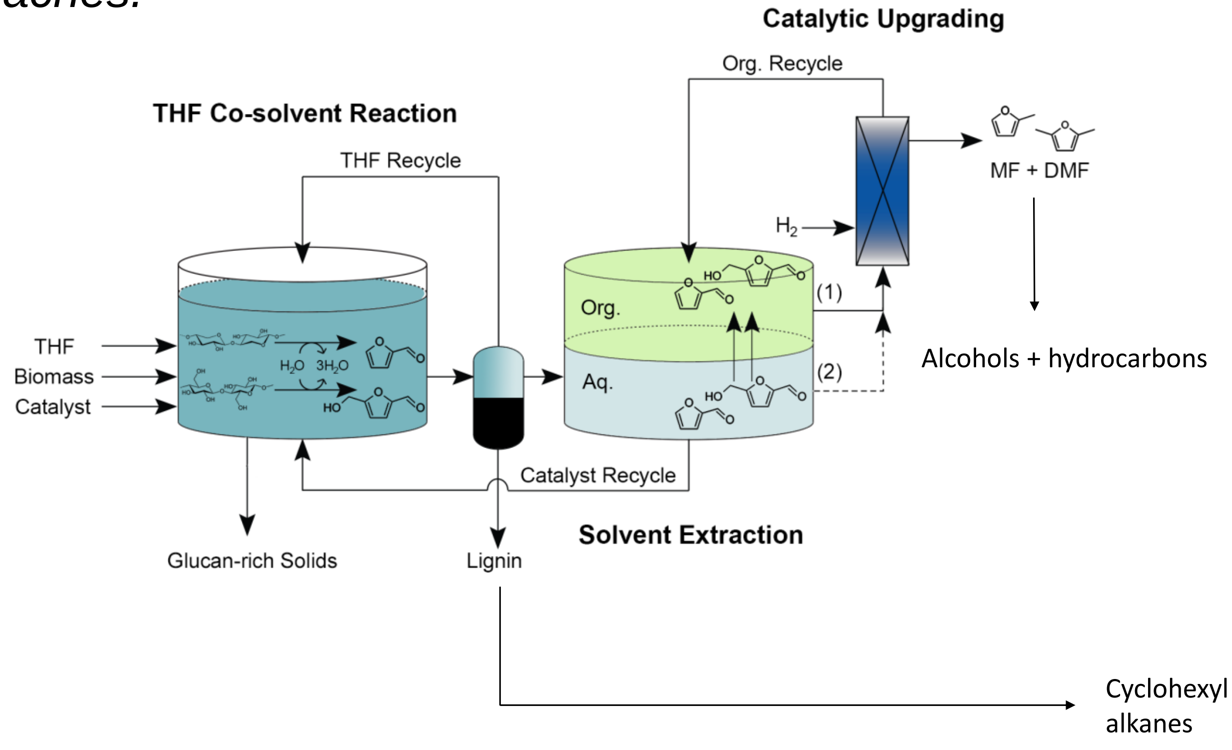
Goal Statement

Advance transformative Co-Solvent Enhanced Lignocellulosic Fractionation (CELF) to achieve high yield production of "drop-in" oxygenated liquid fuels from poplar wood.

- Achieve high yield co-conversion of C5 and C6 sugars directly to MF and DMF fuels in only two reaction steps directly from biomass.
- Achieve high yield solubilization, depolymerization, and conversion of biomass lignin to liquid fuels in only two reaction steps.
- Develop extraction, separation, and recovery operations to enable integration of the three critical processes for a CELF-based biorefinery.
- Screen for optimal catalyst type using computer plant model based on experimental results (TEA/LCA).

Goal Statement

- CELF technology is the newest generation of biomass processing techniques that integrates pretreatment, fractionation, and catalytic conversion in a one-pot single phase process enabling higher yields, lower process complexity, and the deconvolution of biomass conversion to fungible fuels.
- *Our project attempts to overcome the low product yields, high tar formation, and difficult processability typically suffered by other thermochemical approaches.*



Quad Chart Overview

Timeline

Project start date: 9/1/2015 (Effective)
Project end date: 9/1/2018 (Final)
Percent complete: 100% Completed

Budget

	Total Costs FY 16 – FY 18 ($M)	FY 16 Costs ($M)	FY 17 Costs ($M)	FY 18 Costs ($M)	Total Planned Funding FY17- ($M)
DOE Funded	1.06	0.400	0.400	0.26	1.06
Project Cost Share (MG Fuels)	0.265	0.112	0.0754	0.0776	0.265

Barriers

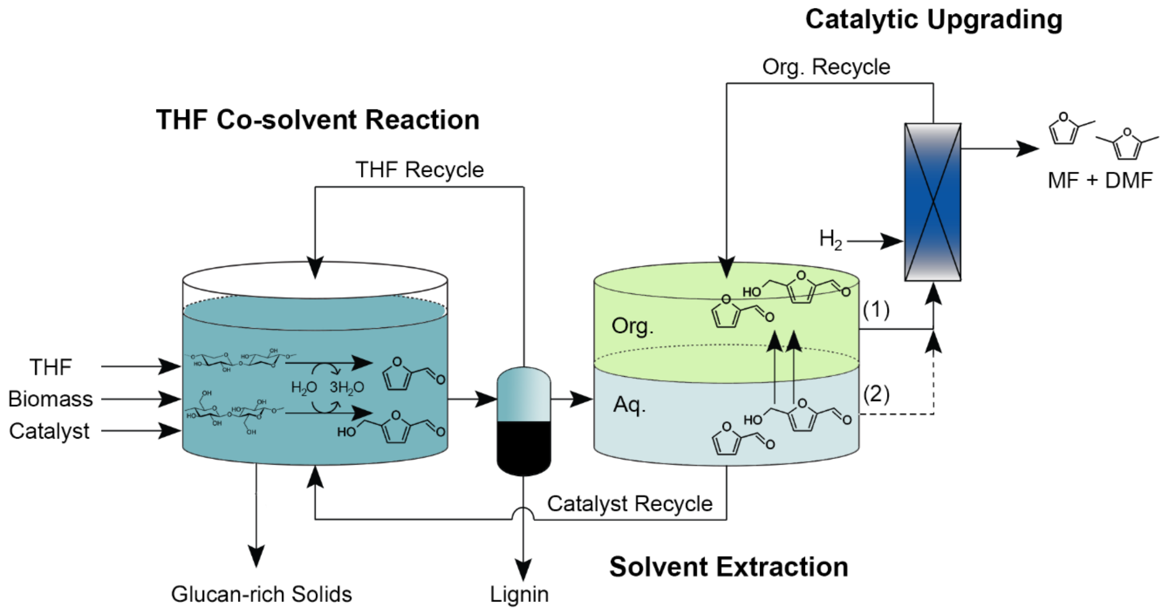
- Ct-B. Efficient Preprocessing and Pretreatment
- Ct-C. Process Development for Conversion of Lignin
- Ct-F. Increasing the Yield from Catalytic Processes

Partners

- FY16-FY18: UCR 68%, UTK 32%
- Cost Share: 20% MG Fuels, LLC

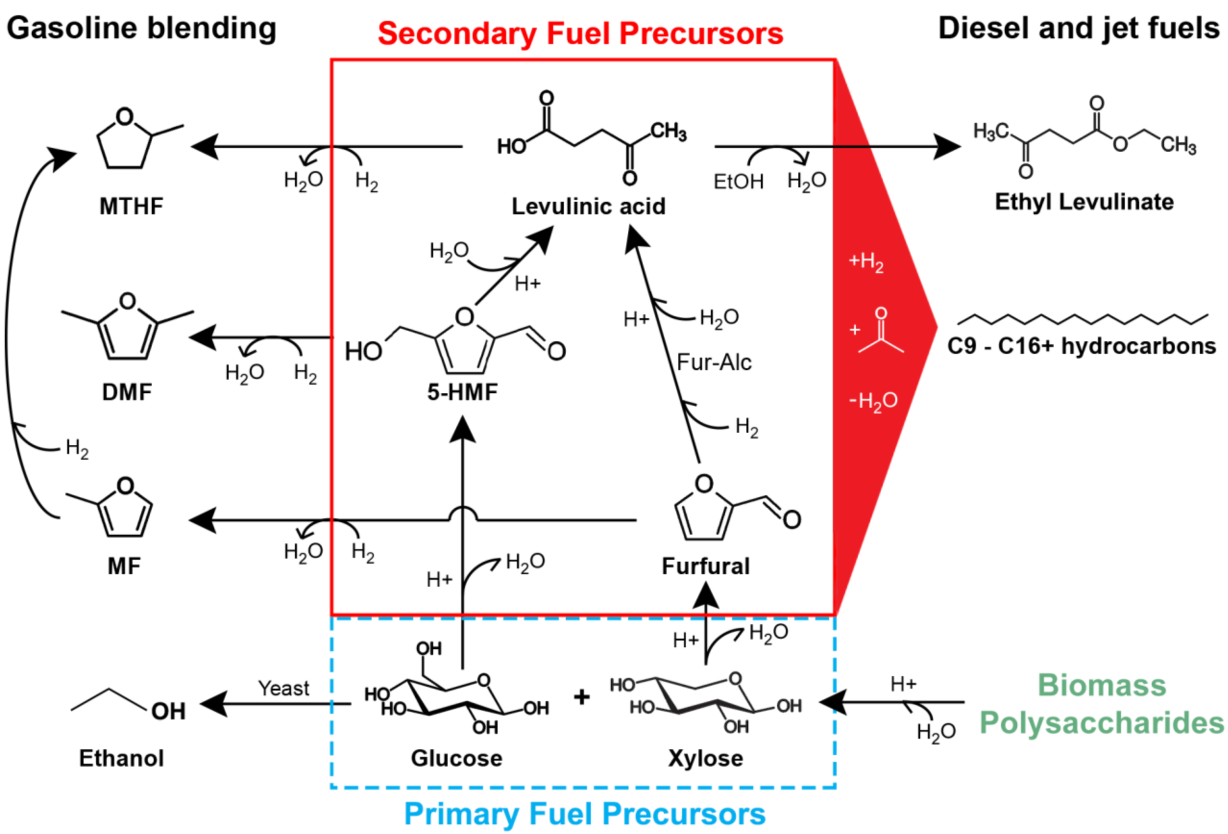
1 - Project Overview

- *Conventional pretreatment methods have solely focused on improving the processing of sugar fractions in biomass, neglecting lignin as a low-value byproduct. They also make very limited improvements to biomass handling.*
- *CELF pretreatment was developed to process all major biomass components and improve their conversion into useful intermediate fuel precursors. CELF also enables high solids handling by significantly reducing the viscosity of biomass slurries.*



1 - Project Overview

Catalytic dehydration of biomass sugars has been highlighted as a promising route to fungible fuels that requires lower reaction temperatures (<200C) than pyrolysis or gasification and can potentially achieve selective production of fungible biofuels while eliminating significant char/tar formation.



2 – Approach (Management)

- *UC Riverside (UCR) is the lead organization with subcontractor UT Knoxville (UTK). PI and Co-PI's in blue.*
- *The project is managed by milestones as outlined below:*

Project Management
Cai (UCR)

- **Milestone 1: CELF Optimization** – Wyman (UCR)
  - Nikhil Nagane
  - Aakash Parikh
  - Alex Moore
- **Milestone 2: Catalytic Upgrading** – Christopher (UCR)
  - Dr. Bhogeswararao Seemala
- **Milestone 3: Lignin Valorization** – Ragauskas (UTK)
  - Dr. Xianzhi Meng
- **Milestone 4: TEA/LCA** – Cai (UCR)
  - Aakash Parikh

2 – Approach (Technical)

*The broad **scope** of the project is divided into four milestones:*

1. *Achieve simultaneous co-production of fuel precursors HMF and furfural from biomass sugars with yields exceeding 50% and 85% of theoretical from poplar wood, respectively.*
2. *Achieve simultaneous co-production of “drop-in” fuels dimethylfuran (DMF) and methylfuran (MF) from HMF and furfural with yields exceeding 60% theoretical for each.*
3. *Characterize CELF lignin and develop a fractionation method to enable valorization. Achieve over 50% conversion of extracted lignin from poplar into liquid hydrocarbon fuels.*
4. *Develop a computer model to evaluate process technoeconomics to inform decisions on catalyst selection, processing strategy, and separations to achieve highest overall profitability.*

2 – Approach (Technical)

The broad ***challenges*** *for this project are outlined by the milestones:*

1. *Inherently different reaction kinetics between conversion of C5 and C6 sugar to fuel precursors will limit co-production yields. The simultaneous optimization of FP yields and lignin solvation would rely heavily on catalyst selection.*
2. *Analogous reaction mechanism for the hydrodeoxygenation of furfural and HMF lend these FPs to co-catalysis. However, factors such as product yields, catalyst loading, catalyst composition, and robustness greatly impact overall plant economics.*
3. *Conversion of lignin to fuels has been challenged by extensive processing requirements, high resource demands, limited product yields, and low value end products.*
4. *Dynamic assembly of computer models to inform experimental design is risky due to complexity of the overall process. Useful for sanity checks on experimental work "as you go".*

2 – Approach (Technical)

*Critical **success factors** to enable technical and commercial viability based on each milestone:*

1. *High utilization of all biomass components will require simultaneous optimization of product yields from hemicellulose, cellulose, and lignin fractions. Reduce waste products.*
2. *High yield co-catalysis of FPs (FF and HMF) to final fuels MF and DMF. Economical extraction process.*
3. *Improved fractionation of CELF lignin into useful fractions by molecular weight to achieve more targeted lignin conversion into fuel products. Lignin liquefaction.*
4. *Design of an efficient solvent recovery system to achieve greater than 97% THF recovery. Mass closure of all component streams to evaluate economics.*

3 – Technical Accomplishments/ Progress/Results

Milestone 1: CELF conversion of poplar to HMF and FF + catalyst selection and enzymatic conversion of residues.

Target

Co-production of Fuel Precursors	FF (% theoretical)	HMF	LA
Baseline (No CELF)	55%	<5%	60-70% (separate rxn)
Sulfuric Acid (CELF)	85%	20%	75% (separate rxn)
Metal Halide (CELF)	85%	50%	<8% (single rxn)

Result

Co-production of Fuel Precursors	FF (% theoretical)	HMF	LA
Baseline (No CELF)	52%	<5%	71% (separate rxn)
Sulfuric Acid (CELF)	86%	22%	73% (separate rxn)
⇨ **Metal Halide (CELF)**	**93.5%**	**66%**	**8% (single rxn)**

>98% conversion of remaining solid residue to glucose at ~3FPU enzyme loading.

3 – Technical Accomplishments/ Progress/Results

Milestone 2: Catalytic co-conversion of HMF and FF to DMF and FF (respectively) + Catalyst Synthesis

Catalytic Upgrading of Fuel Precursors	MF (% theoretical)	DMF
Target	60%	60%
Result	**87.5%**	**88.5%**

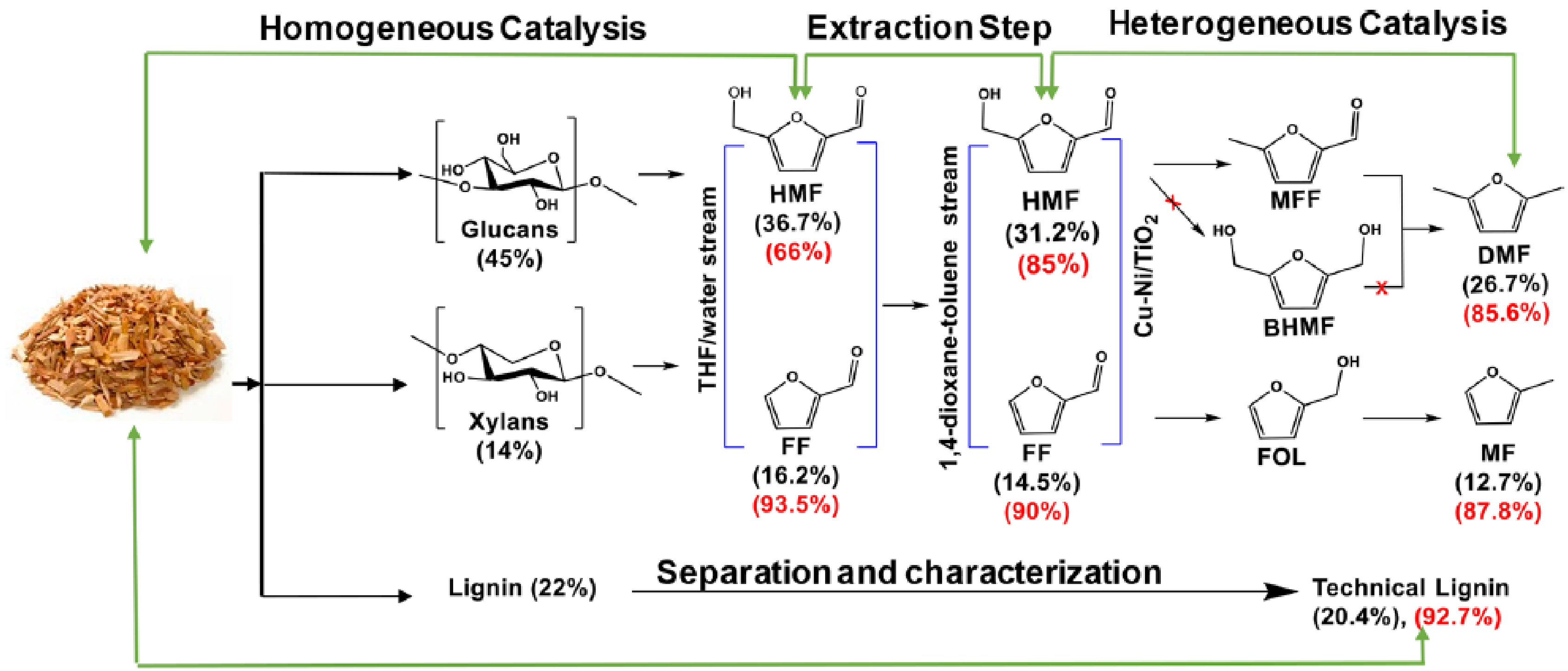
Single step hydrodeoxygenation (HDO) of furfural and HMF to MF and DMF over Cu-Ni/Al2O3 catalyst

Catalytic Upgrading of Fuel Precursors	Furfural (Extracted)	Pentanol
Target	85%	60%
Result	**90%**	**71.1%**

Single step hydrodeoxygenation (HDO) of furfural to pentanol over Cu-Co/Al2O3 catalyst

3 – Technical Accomplishments/ Progress/Results

Process Flow Diagram and Yields of Integrated Hybrid Catalytic Conversion of Lignocellulosic Biomass to Methylated Furans and Technical Lignins:



Hybrid Catalytic Biorefining Process

3 – Technical Accomplishments/ Progress/Results

Milestone 3: Characterization of CELF lignin and valorization to liquid fuels.

Catalytic Upgrading of CELF Lignin	Pyrolysis to Bio-oil (% theoretical)	HT-HDO* to Cyclohexyl derivatives
Target	50%	50%
Result	70%	80%

Developed a simple solvent fractionation method to separate CELF lignin fractions based on molecular weight:

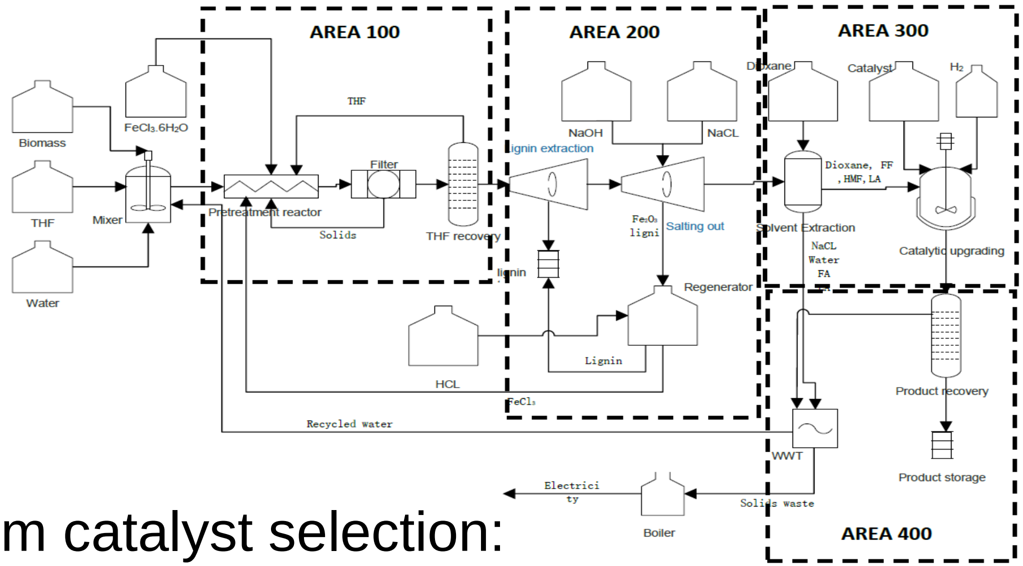
Sample	M_w	M_n	PDI
F40	1353	976	1.39
F35	1047	849	1.23
F30	928	771	1.2
F25	819	708	1.16
F20	774	686	1.13
F<20	493	394	1.25
H2O soluble	245	113	2.17

*HT-HDO: Hydrogen transfer hydrodeoxygenation

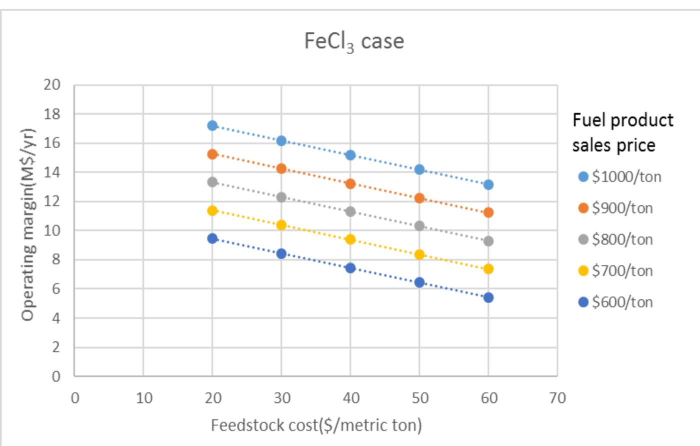
3 – Technical Accomplishments/ Progress/Results

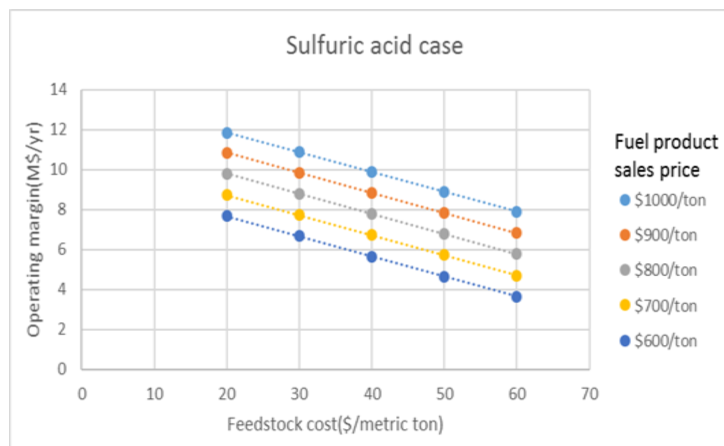
Milestone 4: Dynamic construction of computer TEA to inform process design and project outcomes.

Computer Plant Model:



Sensitivity analysis to inform catalyst selection:





4 – Relevance

Project goal: Increasing economic competitiveness of biofuels by maximizing carbon utilization of biomass through integrated catalytic processing.

Background: Lignocellulosic biomass in the form of forestry and agricultural residues is the only sustainable natural resource that is abundant and inexpensive enough to significantly displace petroleum for production of liquid fuels and chemicals.

Market Objective: Our project seeks to de-risk new CELF technology for commercial deployment in an integrated biorefinery that converts wood to liquid fuels at high yields with low fuel costs (<$3/GGE target).

Target Products: "Drop-in" fungible oxygenate fuels that can be blended into existing petroleum-based fuels on top of existing bioethanol infrastructure.

Process design: focuses on carbon efficiency and high yields that inherently generate less waste.

4 – Relevance

Specific BETO objectives addressed/achieved:

- **Ct-B Efficient Pretreatment:** Single phase, high solids, and high yield: Nearly 100% utilization of carbon from biomass to intermediates after pretreatment.
- **Ct-C Lignin Valorization:** Integrated processing of both lignin and sugars from to hydrocarbon fuels. Lignin processing achieved via 1) lignin pyrolysis and 2) lignin hydrogen transfer hydrodeoxygenation (HT-HDO)
- **Ct-F Increasing yields of Catalytic Process:** Achieved total 60% carbon utilization of biomass into final fuel products by catalytic-only process.

4 – Relevance

How our project is aligned with BETO objectives:

- Improving yields of target intermediates HMF and FF from biomass.
- Simplifying plant design by integrating multiple process steps while maintaining high yields of final fuel products DMF and MF.
- Improving feedstock handling of multiple by drastic viscosity reductions to biomass slurry to improve high solids operations.
- Minimal carbon loss.
- 100% biogenic fuels resulting in overall GHG reductions.
- Efficient fractionationation and depolymerization of lignin to low MW components suitable for targeted valorization to fuels and chemicals.
- Low temperature, low pressure operation.
- Project metrics and performance driven by dynamic TEA development.

5 – Future Work (Completed)

	Period 1 (Months from start)				Period 2 (Months from start)			
Tasks/Subtasks	1-3	4-6	7-9	10-12	13-15	16-18	19-21	**22-24**
1. Go/No Go decision on CELF acid catalyst (sulfuric acid vs. metal halide)				**G/NG**				
1.1 Tune CELF to produce FF and HMF at high yields using sulfuric/mineral acid	**--------------------x**							
1.2 Tune CELF to produce FF and HMF at high yields using metal halide acids		**----------------------x**						
1.3 Develop system for THF recovery and recycle					**--------------------x**			
2.1 Develop catalyst system to maximize yields of methylated furans from FF and 5-HMF	**----------------------------------x**							
2.2 Develop catalyst system to maximize yields of alcohols and hydrocarbons from FPs			**----------------------------------x**					
2.3 Develop catalyst system to achieve coupling of alcohols						**-----------------x**		
3. Define most suitable CELF lignin valorization strategy: bio-oil or cyclohexyl alkanes							**G/NG**	
3.1 Characterize CELF lignin and recommendations	**---------------------x**							
3.2 Oxidative fragmentation of CELF lignin into bio-oil			**---------------------------------x**					
3.3 Catalytic hydrodeoxygenation of CELF lignin into cyclohexyl alkanes				**---------------------------------x**				
4.1 Design plant computer model and track cost progress	**----------------------x-------------------x-----------------x**							
4.2 Develop high pressure wood chip pump system to support continuous feeding for CELF				**--------------------------------x**				
5. Regular and final project reporting	**R**	**R**	**R**	**R**	**R**	**R**	**R**	**F**

Publications

1. XM, AP, BS, RK, YP, CEW, CMC, AR. 2019. “Characterization of fractional cuts of co-solvent enhanced lignocellulosic fractionation lignin isolated by sequential precipitation”. *Bioresource Technology*. 272, 202-208.
2. BS, RK, CMC, CEW, PC. 2019. “Single-step catalytic conversion of furfural to 2-pentanol over bimetallic Co–Cu catalysts”. *Reaction Chemistry & Engineering*. 4, 261-267
3. BS, XM, AP, NN, RK, CEW, AR, PC, CMC. 2018. “Hybrid Catalytic Biorefining of Hardwood Biomass to Methylated Furans and Depolymerized Technical Lignin”. *ACS Sustainable Chemistry & Engineering.* 6 (8), 10587–10594
4. MDS, CMC, XC, LP, JS. 2018. “Temperature-dependent phase behaviour of tetrahydrofuran–water alters solubilization of xylan to improve co-production of furfurals from lignocellulosic biomass”. *Green Chemistry*. 20, 1612-1620.
5. XZM, AP, BS, RK, YP, CEW, CMC, AR. 2018. “Chemical transformations of poplar lignin during co-solvent enhanced lignocellulosic fractionation process”. *ACS Sustainable Chemistry & Engineering.* 6 (7), 8711–8718
6. BS, CM Cai, RK, CEW, PC. 2017. “Effects of Cu-Ni bimetallic catalyst composition and support on activity, selectivity and stability for furfural conversion to 2-methyfuran”. *ACS Sustainable Chemistry & Engineering*. 6, 2152-2161
7. BS, CM Cai, CEW, PC. 2017. “Support Induced Control of Surface Composition in Cu-Ni/TiO2 Catalysts Enables High Yield Co-Conversion of HMF and Furfural to Methylated Furans”. *ACS Catalysis*. 7, 4070-4082.

Summary

The overall project goal is to define catalysts, reaction conditions, and process strategies to optimize an integrated biorefinery based on CELF technology for economic conversion of biomass/wood to liquid fuels.

The four main thrusts/milestones are:

1. *Catalytic delignification of biomass and dehydration of biomass sugars to intermediate fuel precursors. (Yield targets)*
2. *Catalytic hydrodeoxygenation of fuel precursors to fungible liquid fuels. (Yield targets)*
3. *Depolymerization and fractionation of lignin for targeted conversion to liquid fuels and chemicals. (Yield targets)*
4. *Process design optimization and computer modeling to inform experimental work and evaluate plant economics. (Cost targets)*

Additional Slides