

**U.S. Department of Energy (DOE)
Bioenergy Technologies Office (BETO)
2017 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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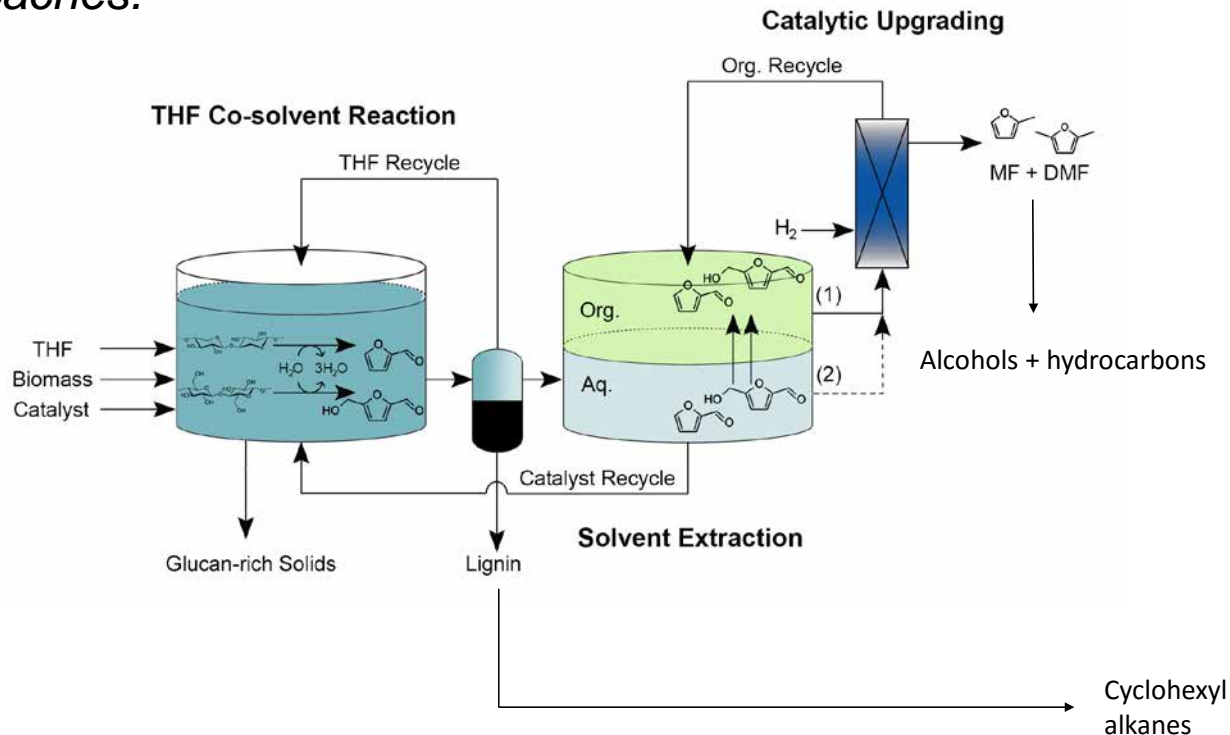
Goal Statement

Advancing transformative Co-Solvent Enhanced Lignocellulosic Fractionation (CELf) to achieve high yield production of “drop-in” oxygenated liquid fuels from poplar wood.

- High yield co-conversion of C5 and C6 sugars directly to MF and DMF fuels in only two reaction steps directly from biomass.
- High yield solubilization, depolymerization, and conversion of biomass lignin to liquid fuels in only two reaction steps.
- Develop extraction, separation, and recovery techniques 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: 2/31/2018 (6M NCTE)
Percent complete: 50%

Budget

	Total Costs FY 16 –FY 18 (\$M)	FY 16 Costs (\$M)	FY 17 Costs (\$M)	Total Planned Funding FY17- (\$M)
DOE Funded	0.400	0.400	-	1.060
Project Cost Share (MG Fuels)	0.112	0.112	-	0.265

Barriers

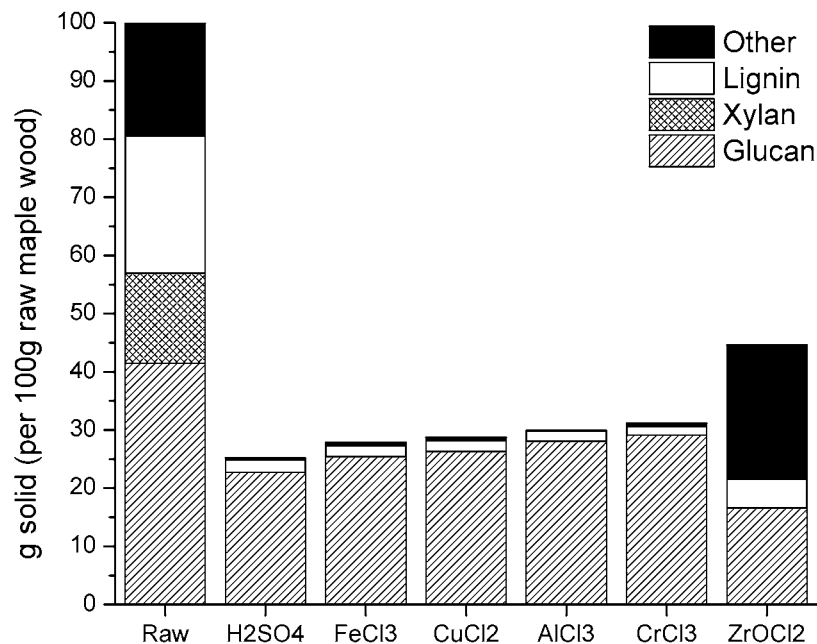
- Achieving high co-production of precursors from biomass.
- Achieving high co-production of fuels from precursors.
- Any additional barriers?

Partners

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

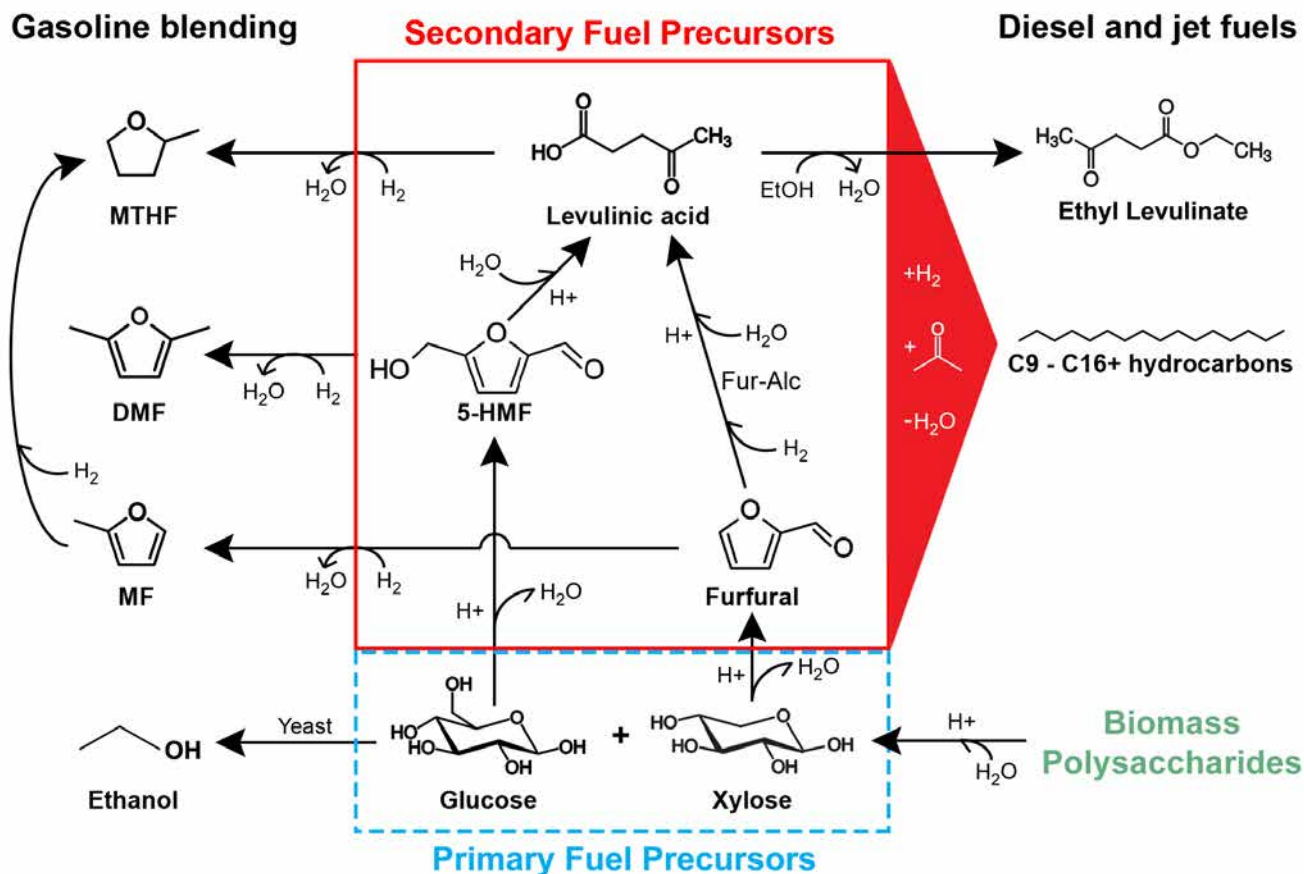
1 - Project Overview

- *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 tackle the processing of 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.*



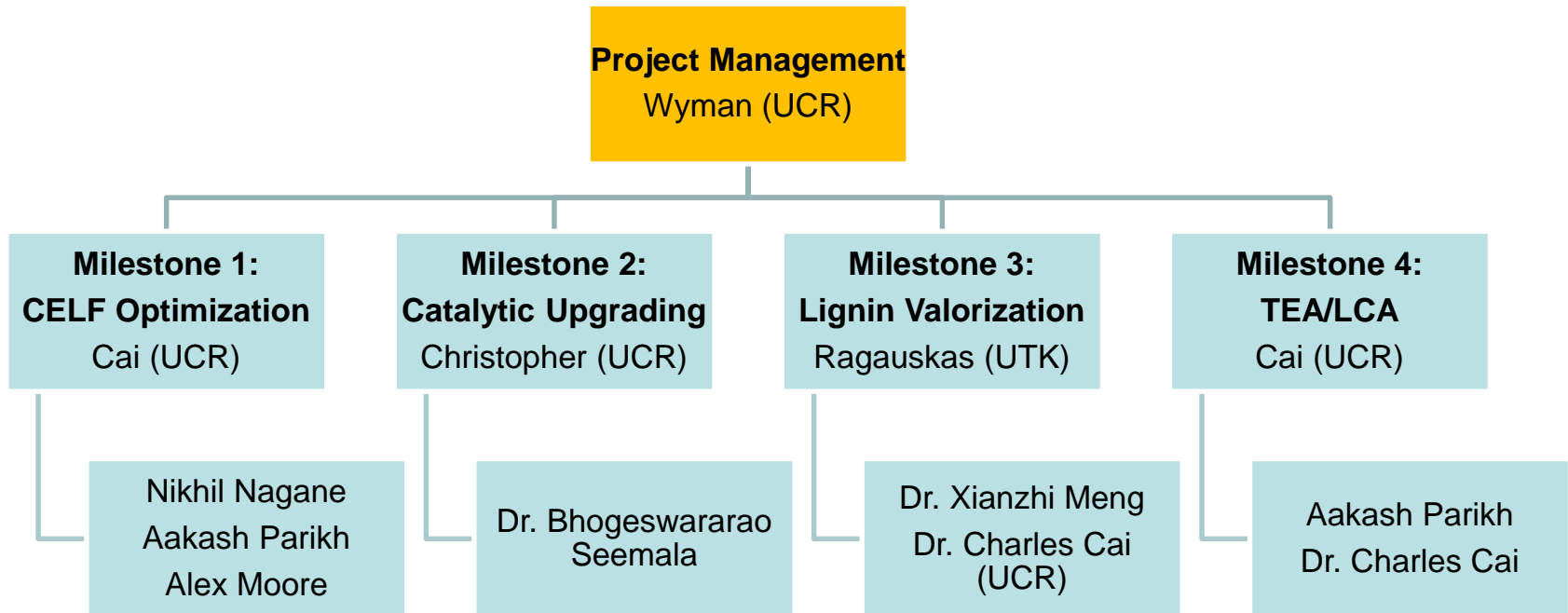
1 - Project Overview

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 higher product selectivities (>60%) while eliminating significant char/tar formation.



2 – Approach (Management)

- *UC Riverside (UCR) is the lead organization with subcontractor UT Knoxville (UTK).*
- *The project is managed by milestones as outlined below:*



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 plant techno-economics** 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 will 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** to final fuels MF and DMF. Economically feasible extraction process.*
- 3. **Improved fractionation of CELF lignin** into useful fractions by molecular weight will allow more targeted conversion of lignin to 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 (Month 9)

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 (Month 9)

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 (Month 9)	60%	60%
Result (Month 9)	81.5%	74%

Three solid catalysts were synthesized, all rare metal free.

- 1. Cu-Ni/TiO₂***
- 2. Cu-Ni/Al₂O₃***
- 3. Cu₂O-PMO***

High substrate:catalyst loading = 5:2 (w/w) minimizes catalyst demand and maximizes FP loading.

3 – Technical Accomplishments/ Progress/Results

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

Catalytic Upgrading of CELF Lignin	Bio-oil (% theoretical)	Cyclohexyl derivatives
Target (By Month 18)	50%	50%
Result (Currently at Month 12)	43.4%	TBD

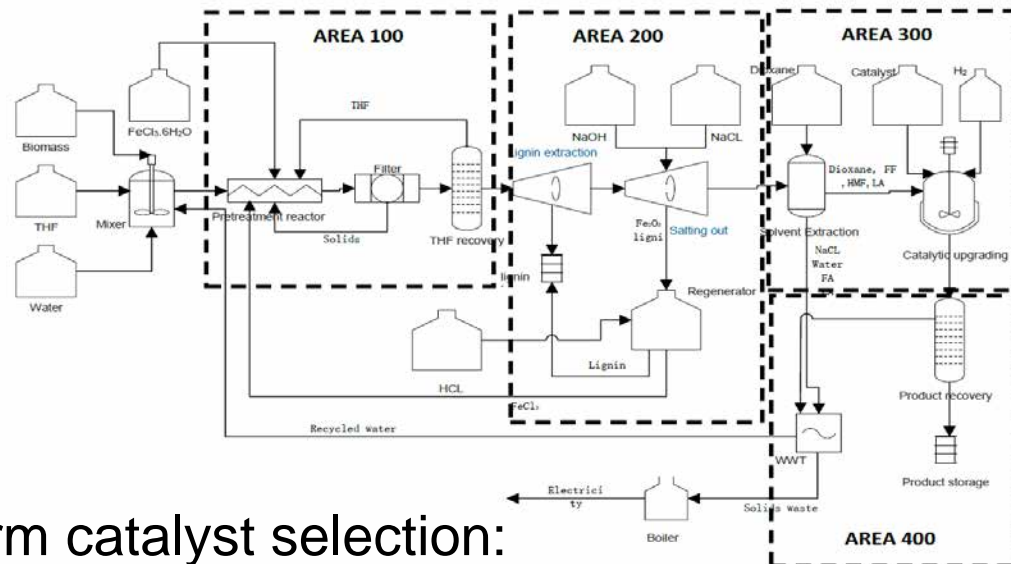
Developed a simple solvent fractionation method to separate CELF lignin fractions based on molecular weight:

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

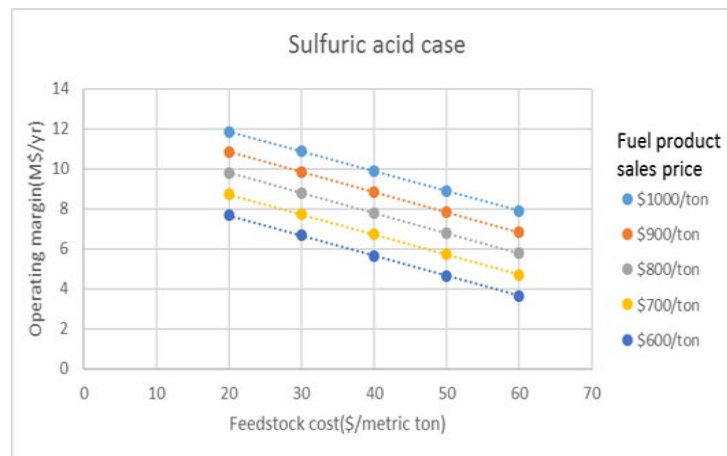
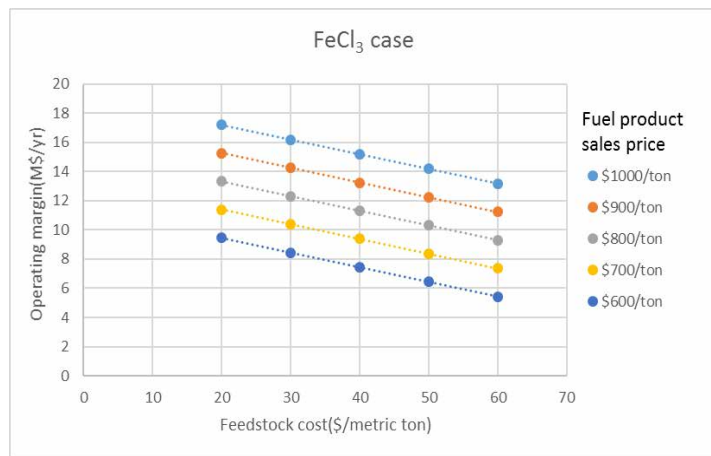
3 – Technical Accomplishments/ Progress/Results

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 enough to replace petroleum for the 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 costs.

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 hazardous waste.

4 – Relevance

Specific BETO objectives addressed/achieved:

- **Ct-C Efficient Processing:** Complete fractionation of biomass in one step using the low temperatures and pressures; suitable for catalysis.
- **Ct-D Efficient Pretreatment:** Single phase, high solids, and high yield. Nearly 100% utilization of carbon from biomass to intermediates.
- **Ct-E Efficient Low-T Deconstruction:** 99% conversion to glucose at 3FPU.
- **Ct-F Efficient High-T Deconstruction:** Little char/tar formation. ~75% conversion biomass sugars to furfural and HMF at <200C.
- **Ct-G Efficient Cleanup:** Novel solvent extraction methods increase lignin recovery, high yields reduces waste, solvent recycle achieved through low-T distillation (b.p. 66C). All sugars utilized.
- **Ct-H Efficient Catalytic Upgrading:** High yields to final fungible fuels. Integrated co-processing of C5 and C6 sugar intermediates. Non-nobel metal catalyst. Yields achieved at high substrate-to-catalyst loadings. Stable catalyst.
- **Ct-I Product Finishing:** High purity of final product stream due to highly selective catalytic pathway from two starting intermediates (FF and HMF) to final fuels (MF and DMF). Lignin-based fuels will require further finishing steps.
- **Ct-J Process Integration:** Pretreatment, fractionation, catalytic dehydration integrated to a single step. Catalytic co-upgrading of intermediates to final fuels in one step. Single solvent recovery step simultaneously recovers lignin/ash.

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 by drastic viscosity reductions to biomass slurry to improve high solids operations.
- No carbon loss.
- 100% biogenic fuels resulting in drastic GHG reductions.
- Efficient fractionation 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

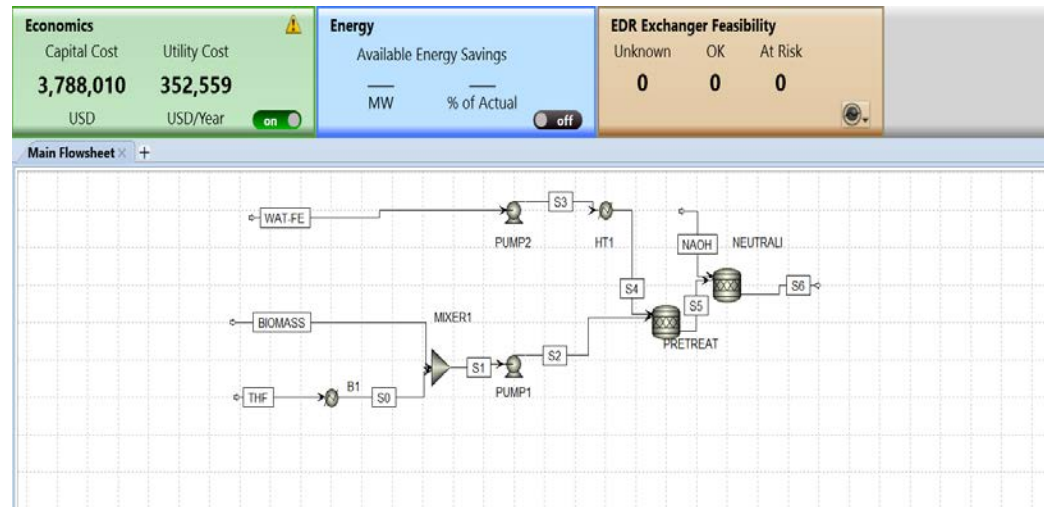
Tasks/Subtasks	Period 1 (Months from start)				Period 2 (Months from start)			
	1-3	4-6	7-9	10-12	13-15	16-18	19-21	22-24
1. Go/No Go decision on CELF acid catalyst (sulfuric acid vs. metal halide)	G/NG							
1.1 Tune CELF to produce FF and HMF at high yields using sulfuric/mineral acid	-----x							
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

5 – Future Work

Anticipated budget remaining for FY17 (Red)

	Total Costs FY 16 –FY 18 (\$M)	FY 16 Costs (\$M)	FY 17 Costs (\$M)	Total Planned Funding FY17- (\$M)
DOE Funded	0.400	0.400	0.66	1.060
Project Cost Share (MG Fuels)	0.112	0.112	0.153	0.265

Plant model on AspenOne software



Summary

The overall project goal is to evaluate different catalysts, reaction conditions, and process strategies to optimize the design of an integrated biorefinery based on CELF technology for the 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