

# CCB DFA: Catalytic Process Intensification of Bio-Renewable Surfactants Platform

2021 BETO Peer Review

Technology Session Area Review: Catalytic Upgrading

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LA-UR-21-21589

# ChemCatBio Project Structure

*Integrated and collaborative portfolio of catalytic technologies and enabling capabilities*

## *Catalytic Technologies*

**Catalytic Upgrading of Biochemical Intermediates**  
(NREL, PNNL, ORNL, LANL)

**Upgrading of C1 Building Blocks**  
(NREL)

**Upgrading of C2 Intermediates**  
(PNNL, ORNL)

**Catalytic Fast Pyrolysis**  
(NREL, PNNL)

**Electrocatalytic CO<sub>2</sub> Utilization**  
(NREL)

## *Enabling Capabilities*

**Advanced Catalyst Synthesis and Characterization**  
(NREL, ANL, ORNL)

**Consortium for Computational Physics and Chemistry**  
(ORNL, NREL, PNNL, ANL, NETL)

**Catalyst Deactivation Mitigation for Biomass Conversion**  
(PNNL)

## *Industry Partnerships (Phase II Directed Funding)*

**Opus12 (NREL)**

**Visolis (PNNL)**

**Sironix (LANL)**

## *Cross-Cutting Support*

**ChemCatBio Lead Team Support (NREL)**

**ChemCatBio DataHUB (NREL)**



# Project Overview

## Sironix company profile and technology



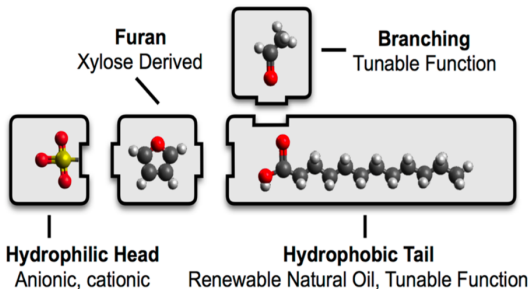
<https://sironixrenewables.com>

*"So your conscience can be as clean as your clothes."*

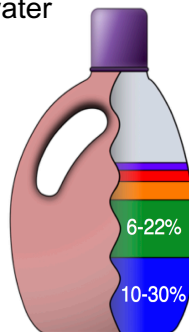
Company profile:

- Startup spun out of U. of Minnesota
- Named one of "50 Next Companies to Disrupt the World" by Biofuels Digest

Eosix® Surfactant technology based on oleo-furans:



Bifunctional oleo-furans eliminate the need for metal chelator additives; maintain function in hard and cold water



Consumer & Commercial Cleaning Products

6-22% Additive  
10-30% Active Chemical  
Oleo-Furan Surfactant

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ACS central science

Tunable Oleo-Furan Surfactants by Acylation of Renewable Furans

Daе Sung Park,<sup>1,4,8</sup> Kristeen E. Joseph,<sup>1,4,8</sup> Maara Koehle,<sup>1,4</sup> Christoph Krumm,<sup>1,4</sup> Lamin Ren,<sup>1,4</sup> Jonathan N. Damm,<sup>1</sup> Meera H. Shetty,<sup>1</sup> Han Seung Lee,<sup>1</sup> Xizhong Zuo,<sup>1</sup> Byeongghu Lee,<sup>1</sup> Wei Fan,<sup>1,4</sup> Dominik G. Vlachos,<sup>4</sup> Paul F. Lebo,<sup>4</sup> Michael Tsapras,<sup>1,2</sup> and Paul J. Dauenhauer<sup>1,4,8</sup>

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<sup>2</sup>Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716, United States  
<sup>3</sup>Department of Chemical Engineering, University of Massachusetts Lowell, Lowell, Massachusetts 01803, United States  
<sup>4</sup>Simon Renewable, Minneapolis, Minnesota 55455, United States  
<sup>5</sup>Catalysis Center for Energy Innovation, Energy Frontier Research Center, U.S. Department of Energy, Newark, Delaware 19716, United States  
<sup>6</sup>Casey Science Division, Argonne National Laboratory, Lemont, Illinois 60439, United States

Supporting Information

**ABSTRACT:** An important advance in field surface control was the amphiphilic surfactant composed of complex molecular structures (i.e., hydrophilic and hydrophobic) to reduce surface tension between two distinct fluid phases. However, implementation of complex surfactants has been hindered by the broad range of applications in water containing alkaline earth metals (i.e., hard water), which disrupt surfactant function and require extensive use of undesirable and expensive chelating additives. Here we show that sugar-derived furans can be linked with hydrophilic-derived fatty acid chains via Friedel-Crafts acylation within single layer (SP) zeolite catalysis. These bifunctional surfactants independently suppress the effect of hard water while simultaneously permitting broad tunability of size, structure, and function, which can be optimized for superior capability for forming micelles and stabilizing in water.

**INTRODUCTION**

The surface energy of droplets, bubbles, and foams determines the efficacy of applications in food, agriculture, cleaning, and drug delivery<sup>1</sup> and can be optimized for each use by chemical surfactants. Many approaches to surfactant design have utilized commodity chemicals to provide both hydrophilic (water engaging) and hydrophobic (oil engaging) functionality from low-cost feedstocks. The use of surfactants with eight to 18 saturated carbon atoms combined with a polar function has been particularly useful within aqueous systems,<sup>2</sup> as the carbon chains aggregate into micelles that trap oils or stabilize active ingredients within water. This approach has worked in soap and detergent technologies for over a century, but modern variations of green surfactants based on food feed precursors exhibit performance limitations inherent to their molecular structure.<sup>3</sup> In addition to modifying surfactant surface energy, surfactants are characterized by their ability to make hard and soft water, and to operate in aggressive conditions such as high temperatures or hard water. The breadth of performance targets is sufficiently large that modern surfactant structures cannot be independently optimized for all properties, requiring the use of substantial additives for effective application.<sup>4</sup> Here,

we report the use of heterogeneous catalysis for the efficient synthesis of surfactants from renewable furans and fatty acids with tunable structures that are optimized to form micelles in hard water (e.g., Ca<sup>2+</sup>) at low temperatures.

The largest volume surfactant for aqueous applications such as detergent remains linear alkyldiethanolamine (LAS). As depicted in Figure 1A, LAS chemicals are composed of a benzene ring connecting polar functionality (e.g., Na<sup>+</sup>SO<sub>3</sub><sup>-</sup>) with branched alkyl chains (up to 14 carbons). These surfactants are produced by alkylation of benzene with aliphatic olefins such as 1-halobutenes by the methoxy acid catalyzed process that leads to double bond migration and subsequent alkylation processes such as polymer to 1-olefin-dodecane.<sup>5,6</sup> The surfactant is then prepared by reacting alkylation processes with Na<sup>+</sup>SO<sub>3</sub><sup>-</sup> in sulfonic acid mixtures.<sup>7</sup>

The limited opportunity for tuning the LAS class of surfactants to further enhance its properties has necessitated incorporation of chemical agents such as metal chelates as depicted in Figure 1A. For example, LAS surfactants in hard water.

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ACS Cent. Sci. 2016, 2, 820 - 824

# Project Overview

## Project Goal:

- Develop low-cost hydrophobic tails for price parity with fatty acids and novel furan-tail coupling strategies, using TEA to assess cost of a range of tail options linked to surfactant performance

## Outcome:

- Accelerate the development of a technology transfer package for toll manufacture of surfactant products

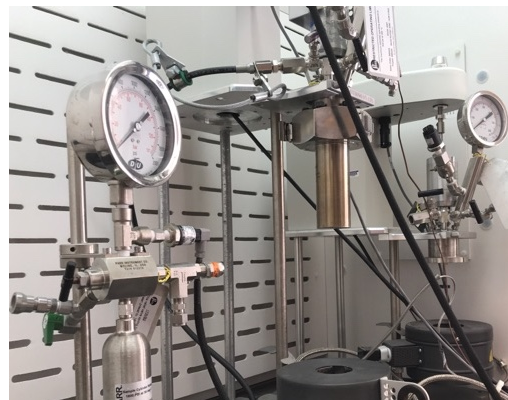
## Relevance:

- Aid in development and maturation of start-up company leveraging BETO-funded resources at national laboratories



# 1 – Management

## Leverage LANL/CCB capabilities to address challenges to OFS production



Monthly project meetings  
Regular coordination of  
production/testing  
Material transfer  
agreement to facilitate  
sample hand offs

**SIRONIX**  
RENEWABLES



Key tasks and responsibilities:

- Chemical conversion, catalyst synthesis and testing
- Scale up and techno-economic analysis (TEA)

Key tasks and responsibilities:

- Surfactant production, formulation
- Detergency and application testing



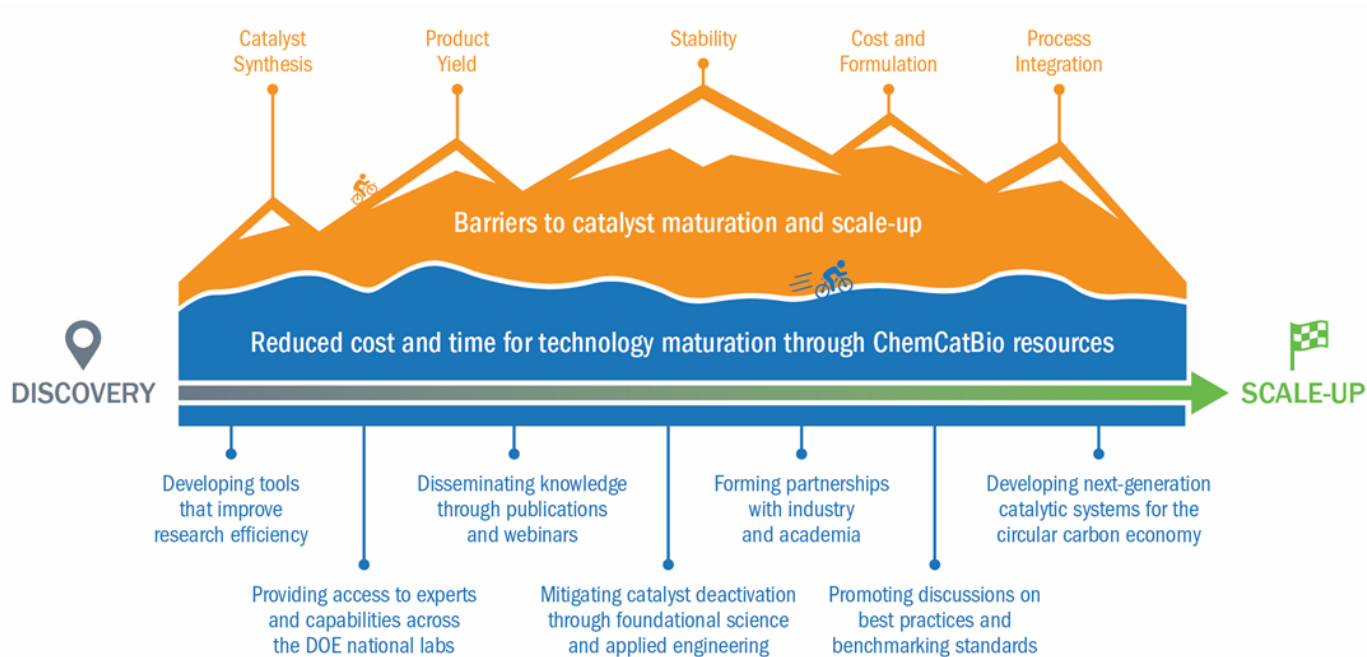
# 1 – Management

## Identified risks to technical challenges and mitigation paths

Identified Risk	Mitigation Approach
<b>Catalytic transformations do not meet Sironix needs and carbon yield is low</b>	Catalysis and system optimization will be performed and strategies to recycle unconverted products will be developed with engineering input in collaboration with Sironix
<b>Molecules exhibit poor surfactant performance</b>	Further structural iterations will be performed. However, preliminary results suggest that the proposed structural compositions will be effective surfactants.



## 2 – Approach

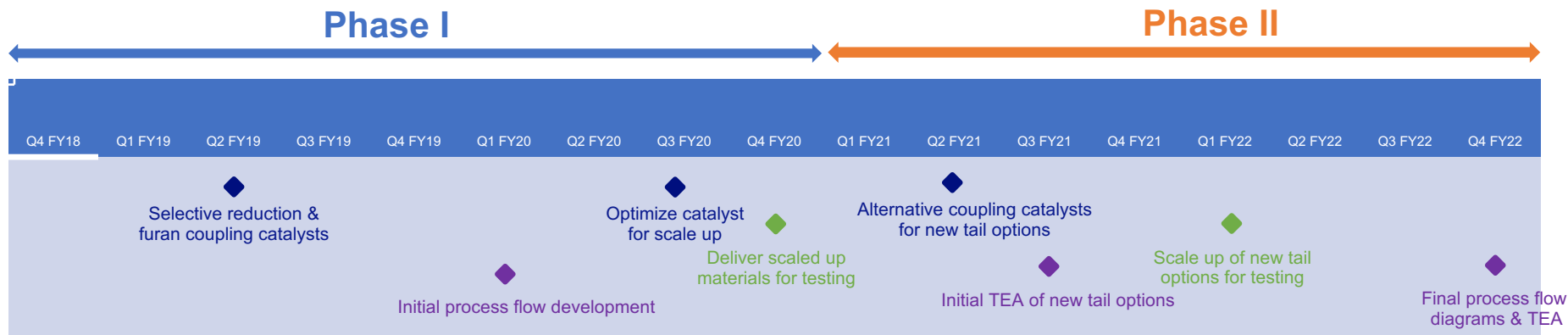


- Reducing barriers to scale up of Sironix technology
  - Addressing catalyst synthesis, yield, stability and process integration



# 2 – Approach

## Overall project timeline (Phases I and II)



- Project milestones tied to technical challenges:

*Catalyst development & testing*

*Material development & performance testing*

*Economic feasibility*





## 2 – Phase II Approach

### Iterative design cycle to meet project goals

- Select tail options and define chemistry based on molecular functionality
- Develop and test catalysts for furan-tail coupling approaches
- Characterize products for surfactant production and testing
- TEA evaluation to inform on all steps of development cycle



## 2 – Phase II Approach

### Upcoming Go/No-Go Decision Point and End-of-Project Milestone

#### Go/No-Go

**12/31/2021:** Economic feasibility assessment. Any possible barriers to commercialization will be identified. If any, the project will be re-evaluated in conjunction with BETO program managers.

#### End-of-project milestone

**9/30/2022:** Develop production pathways for price parity with fatty acids along with full process flow diagrams in concert with TEA to present design case to BETO and potential for market impact.




# 3 – Impact

## Two-for-one solution for industry enabling better function

- Technology addresses immediate market need for a higher performing bio-renewable detergent molecule
- Non-food carbon sources without negative environmental impact (e.g. palm)
- Development of new tail options, and associated chemistry, will greatly enhance the performance and economics of the process




 100% plant-based

“...worse than just plain water on wine stains”

*The Wirecutter (NYTimes), 2018*




 65% plant-based

**New York restricts 1,4-dioxane in cleaning and personal care products**  
State is first in US to limit level of this persistent pollutant in consumer goods

*American Chemical Society, Dec. 2019*



 100% plant-based

- ✓ Reduced cost
- ✓ Simpler formulation
- ✓ Better Performance
- ✓ Dioxane-free

*“Our collaboration with LANL is providing invaluable technical development, resources, and expertise to solve one of our biggest technical challenges toward commercialization”*

*– Christoph Krumm, Sironix CEO & Founder*



# 3 – Impact

## Dissemination of Phase I results

- Two patent applications filed
- R&D 100 Submission
  - Special Recognition Bronze Medal for Green Technology
- Federal Laboratory Consortium Notable Technology Award



2020 R&D 100 Special Recognition Medal for Green Technology  
Los Alamos National Laboratory & Sironix Renewables

# OLEO-FURAN SURFACTANTS

MADE FROM RENEWABLE BIOMASS

Changing the way the world cleans

- Higher cleaning performance, even in cold water
- 10X the hard water tolerance of current detergents
- Greener option from synthesis to consumer use
- Reduced energy use
- More concentrated
  - lower cost per unit dose



Los Alamos NATIONAL LABORATORY  
EST. 1943

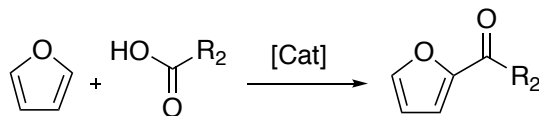
SIRONIX RENEWABLES  
sironixrenewables.com/about-us



# 4 – Progress and Outcomes

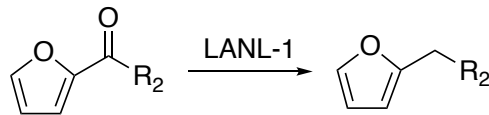
## Phase I Outcomes – overview

### 1. Newly synthesized surfactant precursor materials



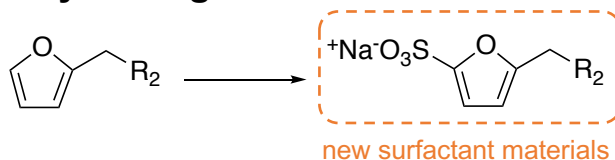
*Developed and screened catalysts for furan coupling reactions to carboxylic acids yielding new materials*

### 2. Development of selective hydrodeoxygenation methods



*Developed and screened new catalysts for hydrodeoxygenation (HDO) reactions of furans*

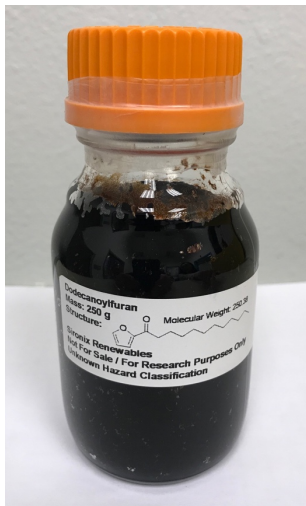
### 3. Sulfonation and property testing



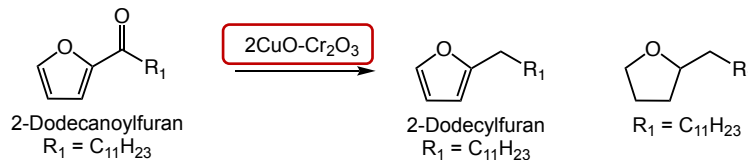
*LANL delivered over 50 g of 3 new materials for sulfonation and property testing by Sironix*

# 4 – Progress and Outcomes

## Phase I Outcomes – HDO catalyst screening and optimization in batch reactors



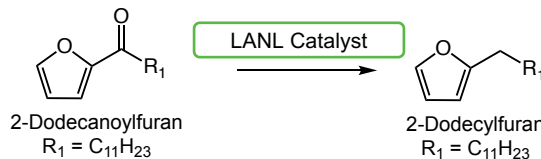
**SIRONIX**  
RENEWABLES



**70% selectivity** under the same reaction conditions  
**92% selectivity** under optimized reaction conditions

**Los Alamos**  
NATIONAL LABORATORY

screened over a dozen catalyst  
formulations



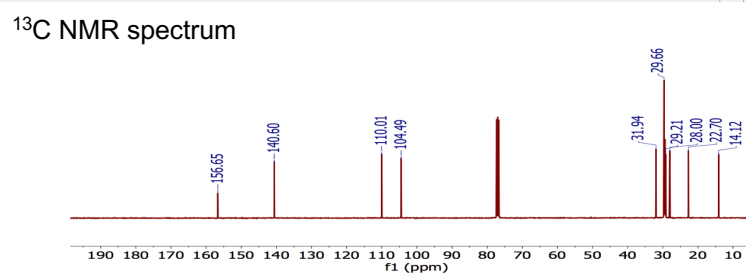
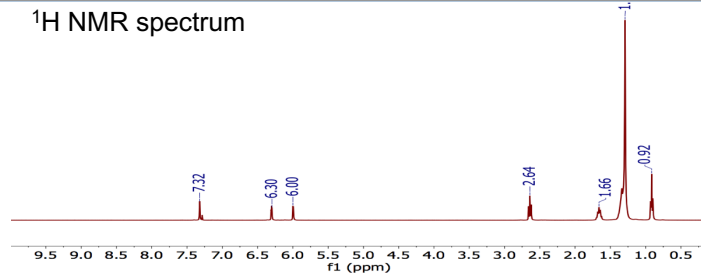
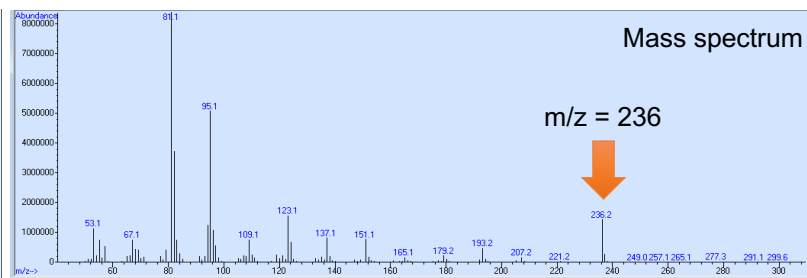
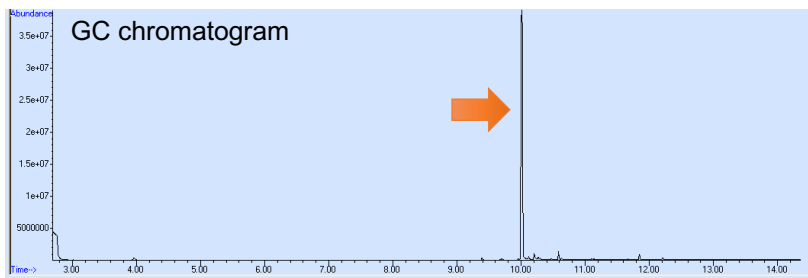
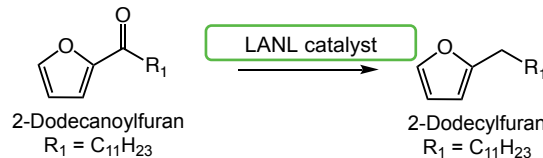
**~98% selectivity, >99% conversion**

Reaction conditions: 2-dodecanoylfuran 0.1 g, hexane 3 mL, catalyst 0.05 g,  $H_2$  150 psi, 220 °C, 5 hrs.



# 4 – Progress and Outcomes

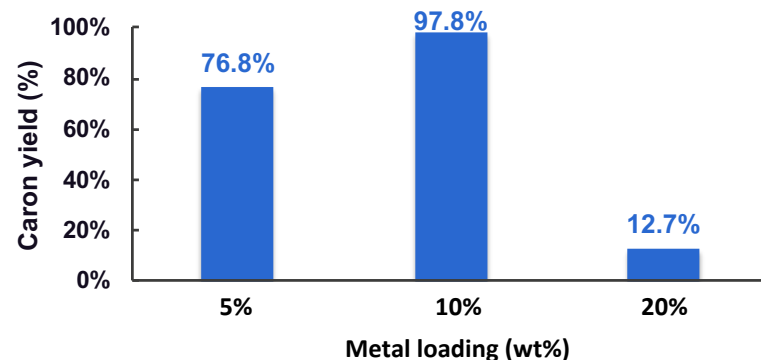
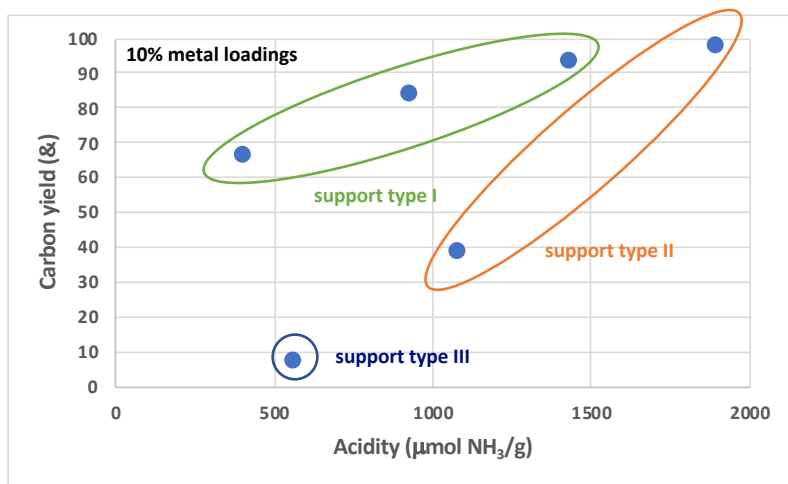
## Phase I Outcomes – product characterization from batch reactors



High purity product crucial for correlating performance to molecular structure

# 4 – Progress and Outcomes

## Phase I Outcomes – catalyst activity trends in flow reactors



Reaction conditions: 50 g/L 2-dodecanoylfuran in hexane, 1.0 g catalyst, 50% H<sub>2</sub>/Ar with 20 mL/min flow rate, 100 psi back pressure, 220 °C, 10 mins space time.

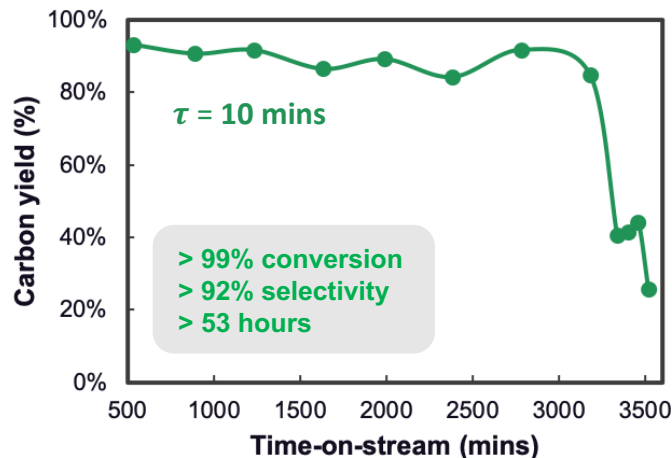
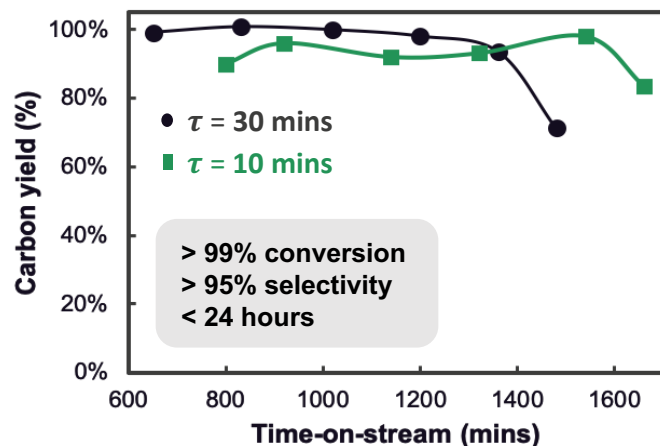
**High support acidity and 10% metal loading optimal for high carbon yields in HDO reaction**





# 4 – Progress and Outcomes

## Phase I Outcomes – catalyst lifetime in flow reactors



Reaction conditions: 50 g/L 2-dodecanoylfuran in hexane, 1.0 g catalyst, 50% H<sub>2</sub>/Ar with 20 mL/min flow rate, 100 psi back pressure, 220 °C, 10 or 30 mins space time.

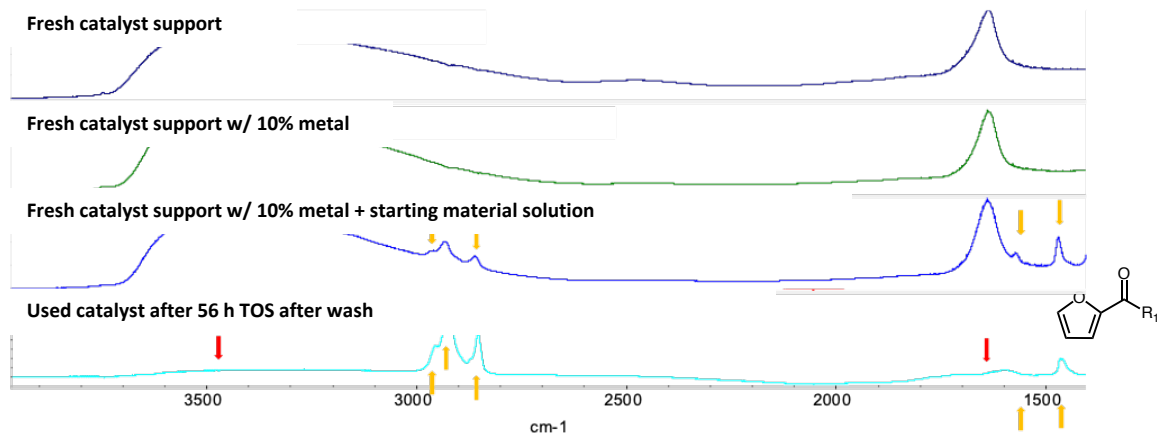
**Maintained activity/selectivity for over 50 hours time-on-stream**



# 4 – Progress and Outcomes

## Phase I Outcomes – deactivated catalyst characterization

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)



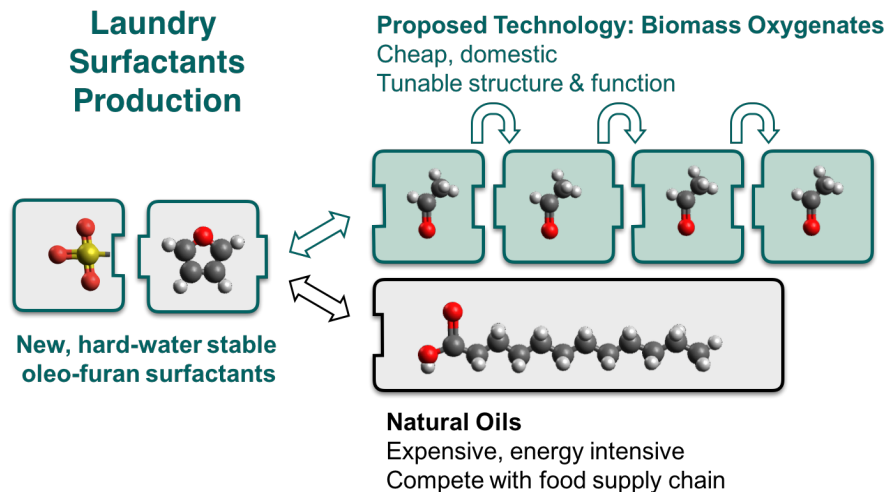
**Deactivated catalyst material contains starting furan material and characteristic peaks of zeolite frame change**

*Opportunity to leverage CCB enabling projects such as Catalyst Deactivation Mitigation (CDM) to further understand catalyst deactivation mechanisms*



# 4 – Progress and Outcomes

## Phase II Progress – new coupling chemistries with low-cost tails



- Developed new chemistry for coupling alcohols to furans
  - Alcohols readily available via biomass: fermentation or other catalytic pathways
- Delivered 10 g of new materials to Sironix



- Sulfonation and property testing underway



# Summary

## Accelerate the development of a technology transfer package for toll manufacture of surfactant products

### Management

- Leverage LANL and CCB capabilities to address challenges to OFS production
- Coordination through monthly meetings
- Early risk identification and mitigation strategies

### Approach

- Iterative development cycle
- Use TEA as a guide for all steps in development
- Go/no-go decision point tied to economic feasibility and barriers to commercialization

### Progress & Outcomes

- Increased yield and selectivity for HDO chemistry of OFS production
- New catalysts developed for furan-tail coupling
- 6 new materials delivered to Sironix for performance testing

### Impact

- De-risk process scale up for new product development
- Two new patents filed related to OFS production
- R&D 100 award for Green Tech



# Quad Chart Overview

## Timeline

- Project start date: 7/1/2018
- Project end date: 9/30/2022

	FY20	Active Project
<b>DOE Funding</b>	\$182k	\$1.03M (FY18 – FY22)

## Project Partners

- Sironix Renewables, LLC

## Barriers addressed

- Ct-F Increasing the Yield from Catalytic Processes
- Ct-J Identification and Evaluation of Potential Co-products
- Ct-K Developing methods for co-product production
- Ct-E Increasing Catalyst Lifetime

## Project Goal

Develop low-cost hydrophobic tails for price parity with fatty acids, use TEA to assess cost of a range of tail options linked to surfactant performance and develop novel furan-tail coupling strategies

## End of Project Milestone

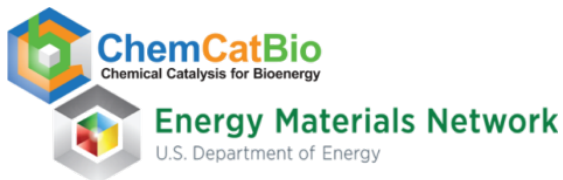
Develop production pathways for price parity with fatty acids along with full process flow diagrams in concert with TEA to present design case to BETO and potential for market impact.

## Funding Mechanism

DFO



# Acknowledgements



Andrew Sutton



Xiaokun Yang



Ruilian Wu



Sai Desai



Christoph Krumm



Shawn Eady



# Additional Slides



# Responses to Previous Reviewers' Comments

*“It appears that there are even more opportunities to reduce space time even more and go out further with time on stream (TOS) with an hydrodeoxygenation (HDO) catalyst operating at 99% conversion. Partial HDO seems like it will be tricky to scale even though lower pressures of 150 psi are used. Process safety hazard analysis should start early. Feed composition currently has 3 wt % of reactant in the feed, so increasing the concentration in future work to keep equipment sizing modest could be a near-term goal. The project team should continue to benchmark with commercial catalyst materials in parallel and develop a technology milestone chart to visually see progress. There has been good progress achieved in this work thus far.”*

- Response: We appreciate the comment on HDO parameter selection and process intensification. We have performed a large amount of optimization for conducting these reactions in flow reactors. Indeed, we have increased the feed concentration (now up to 7 wt%), while reducing the space time. There is undoubtedly a lot more optimization space to canvass. We have also been working to understand catalyst deactivation and how we can mitigate deactivation by appropriate selection of process conditions. We believe feed concentration could play a role in deactivation as the feed has low solubility and may adhere to the catalyst surface strongly, causing the catalyst pores to block. We are currently working to understand these effects more deeply.





# Responses to Previous Reviewers' Comments

*“This is a really interesting technology that may have a fairly short-term path to market, in that it specifically targets performance-advantaged bioproducts. This is perhaps due to the nature of the DFA program, but it is challenging for an external reviewer to comment on progress as technical details are relatively sparse. I had some concerns about the ways that stability and selectivity are being assessed. They may not be appropriately benchmarked, and it may give a false impression as to the origin of enhanced selectivity and/or stability.”*

- Response: We appreciate positive comments by the reviewer as well as their concerns on how to accurately benchmark our catalysts. We have used metrics common to the ChemCatBio consortium to measure catalyst stability, such as measuring the evolution of product selectivity as a function of catalyst time-on-stream. We have performed the same analysis on a variety of in-house prepared catalysts which provides a further understanding of the origins of selectivity. At present, the enhanced selectivity appears to be largely a function of support acid strength in conjunction with metal loading. We are still working to verify working hypotheses on the origins of catalyst stability.



# Responses to Previous Reviewers' Comments

***“The initial catalyst development for both the carbon-carbon coupling and HDO of the intermediate appear to be quite successful. Additional process intensification would be achieved if both reactions could be conducted simultaneously (though no explanation was given for why this might work), and if the process could be demonstrated to work in continuous mode.”***

- Response: We thank the reviewer for their positive review and agree that it would be ideal to combine coupling reactions and HDO into a single reactor. During Phase I work, we envisioned this would be an ideal scenario when utilizing carboxylic acid feedstocks and furan. However, initial work in Phase II has suggested that other feedstocks could be advantageous from an economic and sustainability standpoint. We have therefore pivoted our focus to look at small bio-derived oxygenates for coupling to furan to build the OFS materials. These reactions are likely not amenable to combining with HDO reactions in one reactor. However, we have not ruled out this possibility and will heed the reviewer's suggestion that this could be a path forward to further process intensification.



# Publications, Presentations, Patents, Awards

- Presentations
  - X. Yang; S. Eady; R. Wu; C. Beach; E. Judge; J. H. Leal; C. M. Moore; T. A. Semelsberger; C. Krumm; A. D. Sutton  
“From batch to continuous flow reaction: Selective hydrodeoxygenation (HDO) of bio-derived acyl furan to value-added renewable surfactant platform chemical” ACS Green Chemistry & Engineering Conference, (virtual) June 2020
- Patents
  - “Method for making substituted furan compound embodiments and derivatives thereof” U.S. Provisional Patent Application No. 63/130,506 filed December 24, 2020
  - “Processes for the Preparation of Alkyl Furans Using Bifunctional Copper Catalysts” U.S. Non-Provisional Patent Application No. 17/032,777, filed September 25, 2020
- Awards
  - Bronze Award – Special Recognition for Green Technology R&D 100
  - Federal Laboratory Consortium Mid-Continent Notable Technology Award

