ChemCatBio
Chemical Catalysis for Bioenergy

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

04/07/2023

Technology Area Session: Catalytic Upgrading

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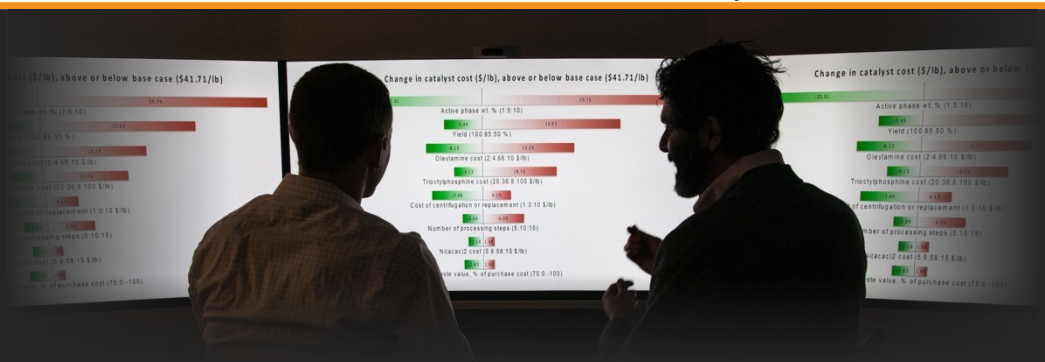
Los Alamos National Laboratory



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BIOENERGY TECHNOLOGIES OFFICE

Project Overview

Aid in development and maturation of Sironix's technology

by leveraging LANL/CCB capabilities to address challenges to OFS production

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- Materials synthesis
- TEA guided
- Process development

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SIRONIX RENEWABLES

https://sironixrenewables.com

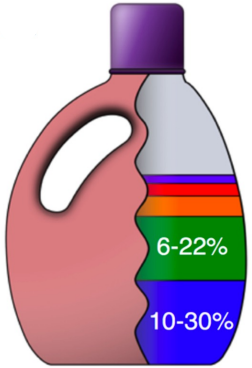
"So your conscience can be as clean as your clothes."

CRADA
COOPERATIVE RESEARCH AND DEVELOPMENT AGREEMENT

Project Overview

Aligns with BETO's goal of supporting bio-advantaged products

by developing performance-advantaged biobased surfactants



Consumer & Commercial Cleaning Products

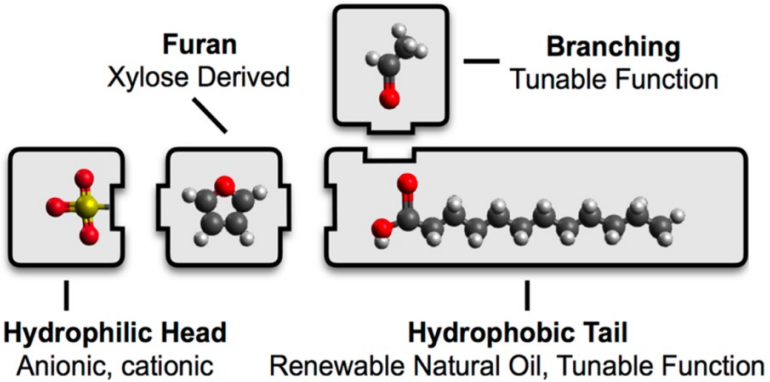
Additive

Active Chemical

Oleo-Furan Surfactant

Christoph Krumm and Paul Dauenhauer et. al.
ACS Cent. Sci. 2016, 2, 820 - 824

Eosix® Surfactant:



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

Project Overview

Project Goal: Reducing barriers to scaling up Sironix technology by addressing catalytic upgrading and process intensification challenges

*Develop new **catalysts** to achieve higher yields, longer lifetime, lower cost, and environmentally friendly*

*Intensify **reaction processes** to easier reaction process scaling up*

*Produce new **OFS products** to increase product diversity*

*Explore new **biomass feedstock** to achieve a greener pathway and less production cost*

1 – Approach

Advance the state-of-art OFS with capabilities in both LANL and Sironix

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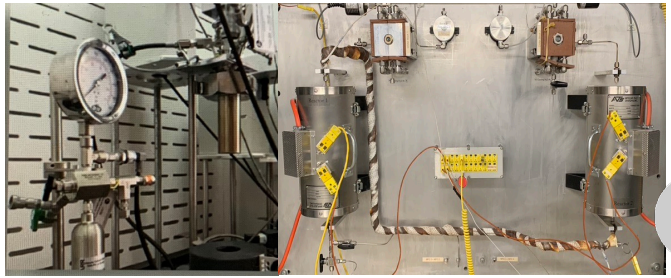


Batch reactors Continuous flow reactors

Increasing reaction scales and TRL

Monthly Updates
Material Transfer
Sample Testing
On-site Visit

SIRONIX RENEWABLES

Key tasks and responsibilities:

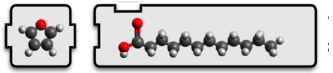
- *Catalyst synthesis and testing*
- *Chemical conversions*
- *Scale up and techno-economic analysis (TEA)*

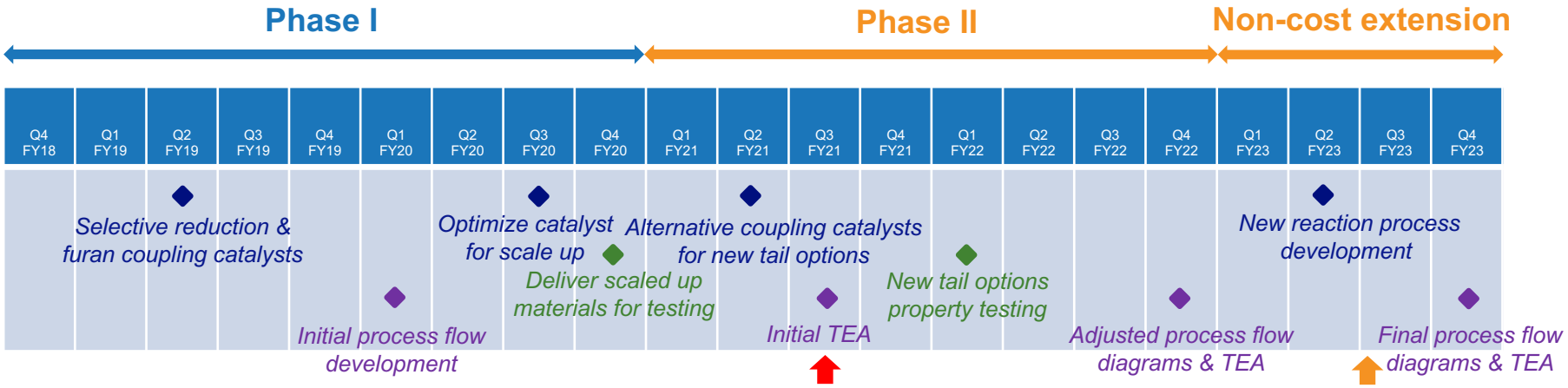
Key tasks and responsibilities:

- *Surfactant production, formulation*
- *Detergency and application testing*

1 – Approach

Overall project timeline management





Project milestones tied to technical challenges:

- ***Catalyst development & reaction process development***
- ***Material development & performance testing***
- ***Economic feasibility***

1 – Approach

Iterative design cycle to meet project goals

Risk mitigated

Go/No-Go

Q1 FY22: Economic feasibility assessment. The possible **barriers** to commercialization **were identified**. **Alternative pathways were investigated** that align with Sironix company's goals.

End-of-project milestone

Q4 FY23: Develop production pathways with an **improved process** that will positively impact capital and operating costs in concert with TEA to **present a design case to BETO and potential for market impact**.

2 – Progress and Outcomes

Phase I accomplishments

Developed new catalysts for selective HDO of furanic ketones and intensified reaction process to continuous flow system

Catalyst

Optimized selective hydrodeoxygenation (HDO) of OFS platform intermediates

- Patent 1 catalyst vs $Cu_2Cr_2O_5$
- 98 % vs 76 % of selectivity

Process

Intensified reaction process from batch to flow reactor

- > 99 % conversion
- 6-fold shortened reaction time
- ½ reduced reaction pressure
- > 50 hours time-on-stream with > 92% selectivity

Product

Developed new OFS platform chemicals

- Synthesized and delivered > 50 g of 3 new materials

Surfactant production and property testing

- Sulfonation and property testing
- Excellent hard water tolerance, foaming, and cleaning properties

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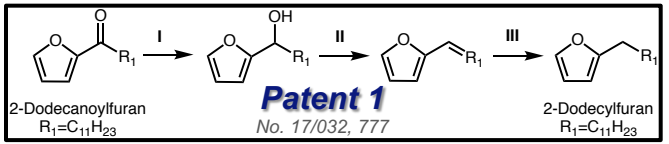
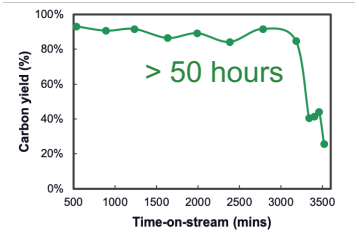
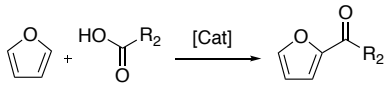
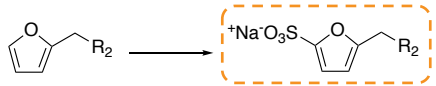








SIRONIX RENEWABLES

new OFS materials

2 – Progress and Outcomes

Phase II outcomes

Developed new approaches for furan-tail coupling, with low-cost hydrophobic tails based on techno-economic assessment (TEA)

Developed new chemistry for coupling alcohols to furans

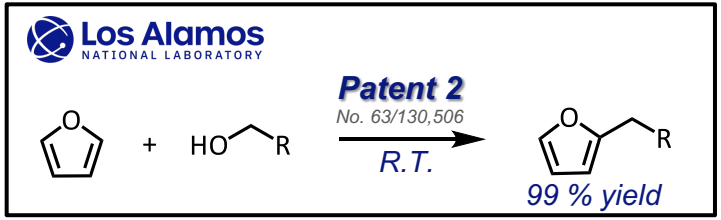
Catalyst
- Patent 2 catalyst vs trifluoroacetic acid (TFAA)
- H_2O vs acetic acid as the only side product

Process
- Room temperature reaction conditions

Product
- New potential OFS platform chemicals

Feedstock
- Fatty alcohols vs fatty acids

- Delivered 10 g of new materials to Sironix



2022 Market price	USD/MT
Fatty alcohols	~1780
Fatty acids	~1900

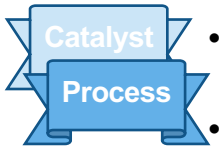
Calculated average price based on 2022 price
Particularly for the carbon chain lengths for OFS

2 – Progress and Outcomes

Phase II outcomes

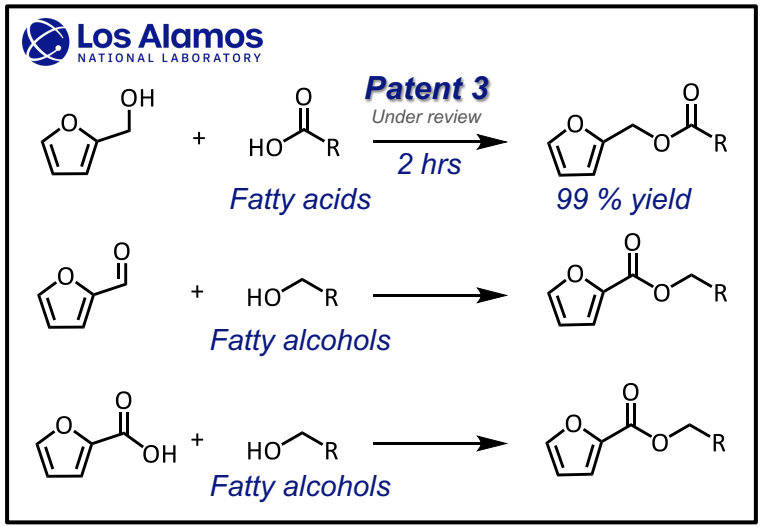
Developed new approaches for furan-tail coupling, with low-cost hydrophobic tails based on techno-economic assessment (TEA)

Developed new chemistry with furan derivatives



- Patent 3 catalyst vs mineral acids
- Stable & recyclable catalyst vs catalyst fouling

- Low-cost furfural, furfural alcohol, and furoic acid were investigated as new feedstock without self-condensation and/or polymerization during reaction
- New intermediates delivered to Sironix for surfactant production and product formulation



2 – Progress and Outcomes

Phase II outcomes (Q1 FY22 Milestone)

Product property testing results feed into the iterative design cycle and defined chemistry strategies

Formulated product

Excellent surfactant properties

in personal care product formulations

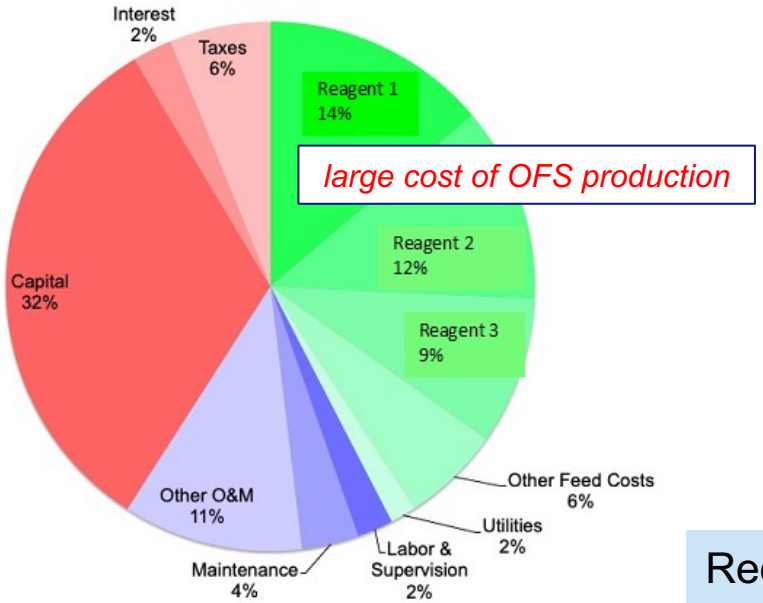
- ✓ Moderate to high foam
- ✓ Good foam stability and foam feel
- ✓ Good viscosity building
- ✓ Excellent fabric wetting kinetic
- ✓ Good shelf life over multiple weeks (with 6+ months long term stability testing ongoing)

High Shear Foam Test

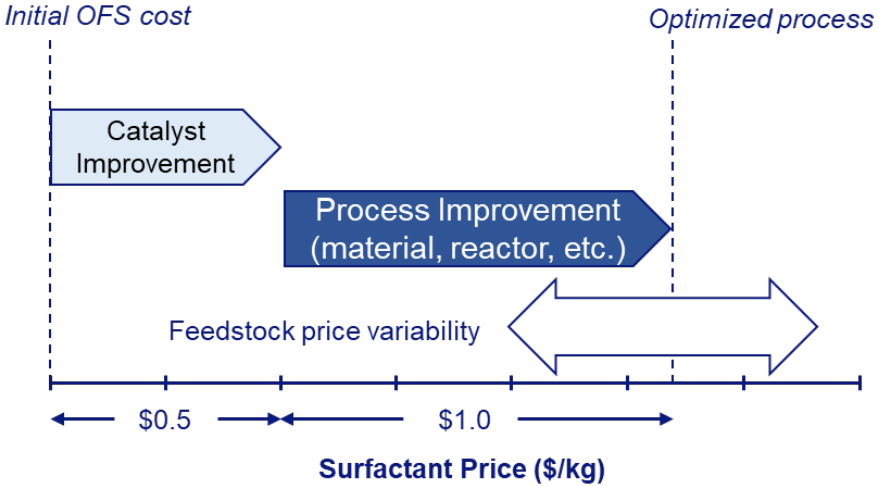
2 – Progress and Outcomes

Phase II outcomes (Q4 FY22 Milestone)

Evaluated the sensitivity of economics, and identified two areas for improvements



Product cost breakdown



Reduced materials cost, capital cost, and operational cost with catalyst and process improvements

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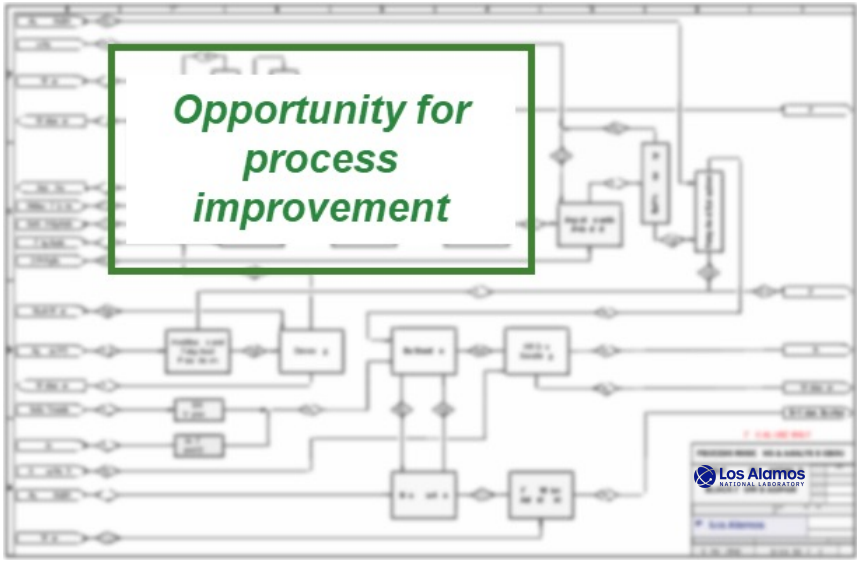
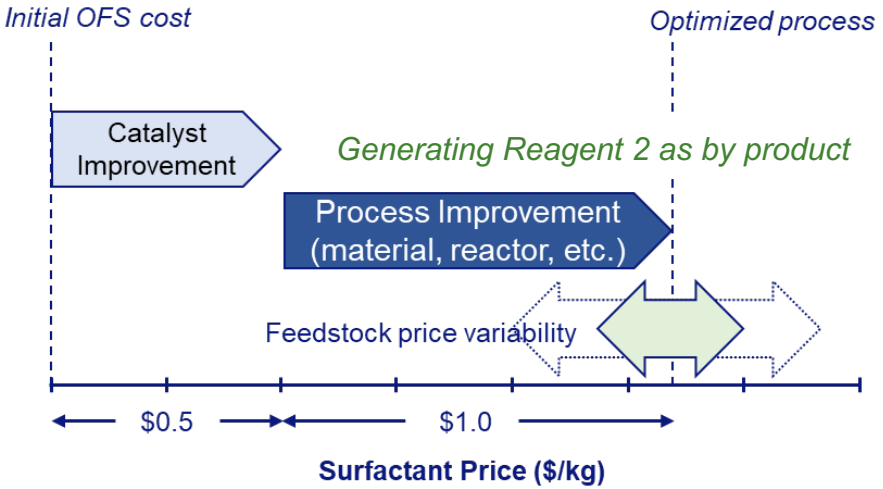
2 – Progress and Outcomes

Phase II outcomes

Identified technical challenge to associated mitigation path





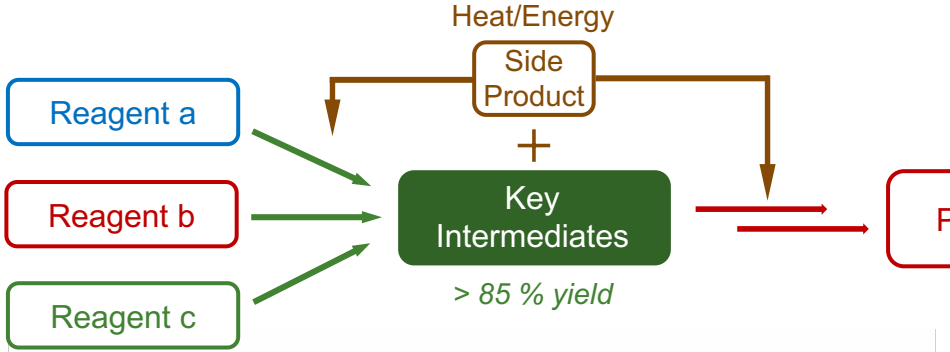
Reducing price variability and gaining profit by producing previously high cost reagent with further process improvement

2 – Progress and Outcomes

Phase II (non-cost extension) outcomes (Q2 FY23 Milestone)

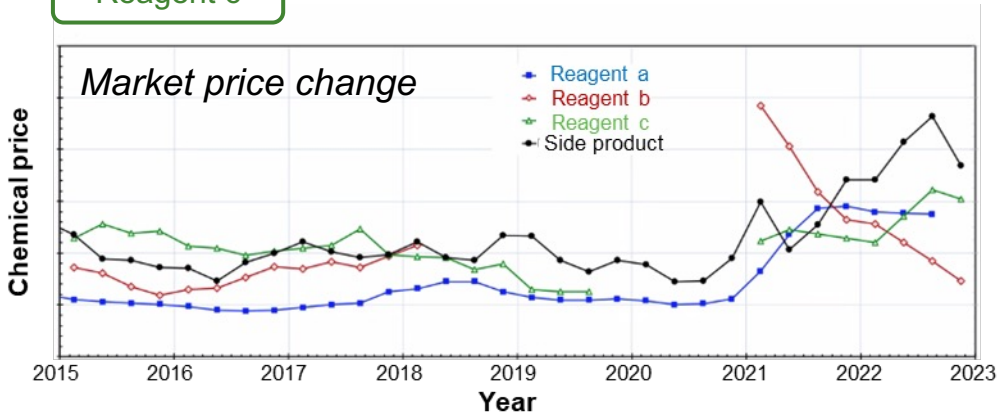
Process
Feedstock

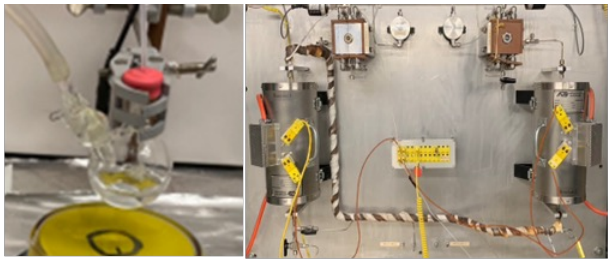
De-risking OFS production by designing a universal reaction process



- ✓ Smart market response
- ✓ Reaction scale-up and TRL increase

Switch high-cost reagent to product ***sale for profit!***





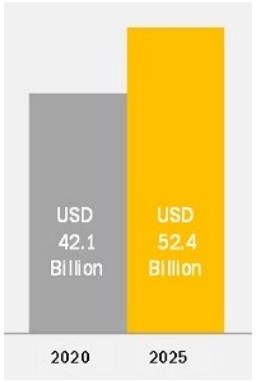
Batch reactor *Continuous flow reactor*

Increasing reaction scales and TRL

3 – Impact

Two-for-one solution for industry enabling better function

Surfactants Market,
reported on Jun 2020



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

American Chemical Society, Dec. 2019

100% plant-based

- ✓ Reduced cost
- ✓ Simpler formulation
- ✓ Better performance
- ✓ Free of toxic chemicals

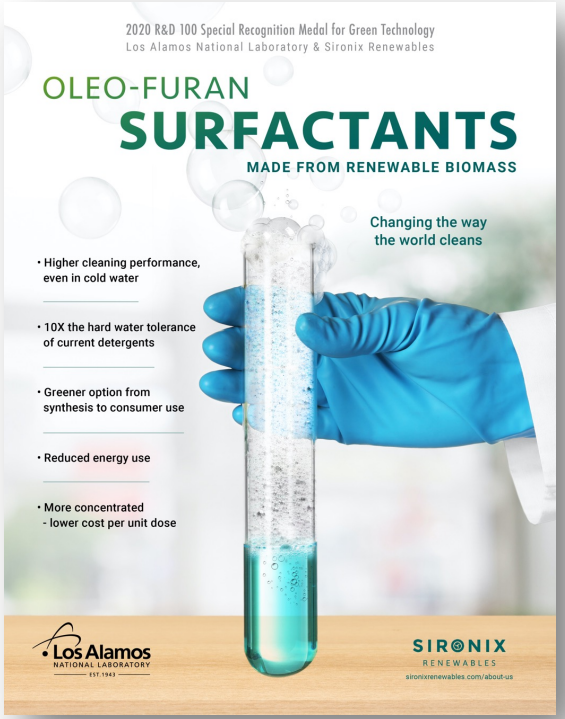
- The success of this work will enable the company to advance its technology and move towards entering the $12 billion U.S. cleaning products market
- Development of detergent formulations is currently underway, including a laundry product partnership with leading laundry enzyme producer

3 – Impact

- ✓ **3 patent** applications
- ✓ **R&D 100** Submission
  - Special Recognition Bronze Medal for **Green Technology**
- ✓ Federal Laboratory Consortium **Notable Technology** Award
- ✓ **2 ongoing scale-up partnerships** with U.S. and European chemical manufacturers
- ✓ Joint development agreement with **top-10 worldwide personal care consumer packaged goods (CPG)**
- ✓ Non-cost extension for **further collaboration**

2020 R&D 100 FINALIST

SPECIAL RECOGNITION 2020 R&D 100 BRONZE



"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

FLC Federal Laboratory Consortium for Technology Transfer

Summary

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

1-Approach

- Leverage LANL and CCB capabilities to address challenges to OFS production
- Iterative development cycle
- Go/no-go decision point tied to economic feasibility and barriers to commercialization
- Early risk identification and mitigation strategies

2-Progress & Outcomes

- New catalysts and chemistry strategies developed for furan-tail coupling
- Excellent surfactant properties tested
- De-risk OFS production with new process development based on TEA
- Increased reaction scales and TRL

3-Impact

- De-risk process scale-up for OFS production
- 3 new patents filed related to surfactant production
- R&D 100 award for Green Tech
- Ongoing scale-up partnership
- CPG development
- Future collaborations

Quad Chart Overview

Timeline

- *Project start date 7/01/2020*
- *Project end date 9/30/2023*

	FY22 Costed	Total Award (FY21-FY23)
DOE Funding	*$203,649*	*$464K*
Project Cost Share*	*$75,132*	*$171.4K (in-kind)*

Project Goal

Reducing barriers to scaling up Sironix technology by addressing catalytic upgrading and process intensification challenges

End of Project Milestone

Develop production pathways with an improved process that will positively impact capital and operating costs in concert with TEA to present a design case to BETO and potential for market impact.

Funding Mechanism

DFO

TRL at Project Start: 1
TRL at Project End: 4

Project Partners*

Sironix Renewables, LLC

*Only fill out if applicable.

Acknowledgement

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Ricardo Navar
Postdoc (from MSI)
LANL (Material Science)

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U.S. Department of Energy

Additional Slides

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Additional Slides

SLES: Sodium laureth sulfate
LAS: Linear Alkylbenzene Sulfonate
SLS: Sodium Lauryl Sulfate

Property comparison: OFS with commercial surfactants

	Detergency Efficiency	Detergency Strength	Hard Water Tolerance	Cold Water Performance	Fabric Wetting	Transport Form	Renewable	Sulfate Free	Dioxane Free
	Critical Micelle Concentration (CMC, ppm) *Lower is Better*	Surface Tension (mN/m) *Lower is Better*	Ca^{2+} Stability (ppm) *Higher is Better*	Krafft Point (ºC) *Lower is Better*	Draves Wetting (sec) *<45 sec is best*	*More concentrated = cheaper transport*	(% carbon from plants) *More = eco-friendly*		
OFS	300	33	>50,000	0 ºC	25	100%	100%	✓	✓
SLES	449	32	>50,000	0 ºC	14	30%	65%	X	X
LAS	460	35	230	20 ºC	5	100%	0%	✓	✓
SLS	2,010	31	33	15 ºC	6	30%	100%	X	✓

Green: Optimal
Yellow: Acceptable
Red: Problematic

Performance in nearly every field is as good or improved compared to commercial anionic surfactants

Response to reviewer's comments

"Replacement of Linear Alkyl Benzene Sulfonate (LAS) surfactants in the detergents market in my opinion is too big a challenge but would have high impact if successful. Numerous technologies have been developed in the past to try and replace LAS such as Methyl Ester Sulfonates and even higher performing biodegradable branched LAS. There is insufficient information to comment on the statement that this new surfactant can replace both existing surfactants and chelants in one formulation, however chelants do more than sequester calcium to avoid precipitation of surfactant as stated by team. A suggestion to the team is to try and find some higher cost niche markets for faster entry into the market at lower volumes once sound technical result is achieved. Beauty care surfactants may be a better target for replacement."

- Response: We appreciate the reviewer's insight into the difficulties replacing LAS in the detergents market, and we recognize the additional contributions chelants provide in detergent formulations that complicate removal. To this end, Sironix is investigating detergent formulations using biorenewable soy-based chelants in collaboration with the Indiana Soybean Association to provide fully-biorenewable, functional products without removing chelants.

  Recent efforts guided by Sironix's board of advisors follow your advice to target personal care products as a higher cost niche market for faster initial market entry at lower volumes. The formulation testing results provided for the surfactants ingredients produced in collaboration with LANL (shown here on slide 11) are for body wash formulations developed with guidance from contracted formulations experts.

Response to reviewer's comments

"The quality of the final products and the reliable supply could play a key role. It would be beneficial if the team could use TEA to assess the economic output of their products. It could also be beneficial if the team could estimate a proper scale-up size for their products considering the market, the availability of the feedstock, and investment."

Response: A complete economic analysis for Sironix's surfactant technology is still in development. Sironix request a TEA analysis for commercial scale plant with a production volume of 50,000 tonnes/yr of surfactant. Sironix based this base-line capacity on on international surfactant distribution with product applications across multiple consumer packaged goods industries including personal care, cleaning products, and detergents. Producing 50,000 tonnes/yr of surfactant will consume approximately 29,000 tonnes of fatty acids derived from natural oils and 12,000 tonnes of furans derived from agricultural. Fatty acid consumption is less than 3% of current C12-C14 domestic fatty acid consumption, so an adequate supply should be available. Furan consumption represents about 25% of current domestic furan consumption, so the supply of furan is a concern. We have investigated corn bran from corn ethanol plants as a potentially inexpensive domestic source of furans.

We also considered strategies for breaking into the surfactant market. Initial surfactant production and product distribution (estimated FY25) will focus on domestic personal care and green cleaning markets and will leverage funding from chemical manufacturers to achieve pilot scale production and assist with technology commercialization. We evaluated modular construction as a method of reducing the initial investment and allowing for a gradual penetration of the market. Tolling parts of the process, such as sulfonation, was considered another method of reducing the initial capital investment.

Response to reviewer's comments

"The project concern about the cost of natural oils may be misplaced. Many companies are investigating these for the production of renewable diesel, certainly a less valuable material (without incentives) than the surfactants that Sironix is pursuing."

Response: We agree with the reviewer's point and believe with the strategy to target higher cost markets, such as beauty and personal care, product margins will be more than adequate despite increasing natural oil costs. In addition, Sironix is currently investigating new process steps to diversify natural oil feedstock selection, which is expected to provide greater feedstock availability and versatility while lowering surfactant production costs.

Patents, Presentations, Awards, and Commercialization

- **Patents**
  - "Fast synthesis of furfuryl esters and alkyl furoate with enzymatic method" Internal LANL disclosure application submitted No.4690, 2023
  - "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
- **Publication**
  - X. Yang; S. Eady; R. Wu; C. M. Moore; C. C. Krumm; A. D. Sutton; "Selective hydrodeoxygenation (HDO) of bio-derived acyl furan to surfactant platform molecule from batch to continuous flow reaction" *under review*
- **Presentations**
  - X. Yang; S. Eady; R. Wu; C. C. Krumm; A. D. Sutton; C. M. Moore "Catalyst Development for Renewable Surfactant and its Reaction Process Intensification" AIChE Annual Meeting, Nov. 2021
  - 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, June 2020
- **Awards**
  - Bronze Award – Special Recognition for Green Technology R&D 100, 2020
  - Federal Laboratory Consortium Mid-Continent Notable Technology Award, 2020
- **Commercialization Efforts**
  - Initiated product development agreement with a top-10 worldwide personal care CPG
  - Continued surfactant production process development with U.S. and European chemical manufacturers