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

Technology Session Area Review: Catalytic Upgrading

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Quad chart overview

Timeline

- Project Start date: July 2018
- Project End date: June 2020
- Percent complete: 38 %

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**

	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded	$333,333	$666,666
Project Cost Share	$100,000	$200,000

•Partners: Sironix Renewables

Objective

Improve process to achieve efficient scale-up of existing Oleo-Furan Surfactants (OFS) and the development of a new class of furan-based structures to address an emerging market need for non-ionic surfactants.

End of Project Goal

Optimize catalyst choice and reaction conditions for furan C-C coupling reactions and furan selective reduction reactions; synthesis and characterization of new non-ionic surfactant structures derived from bio-derived furanics.

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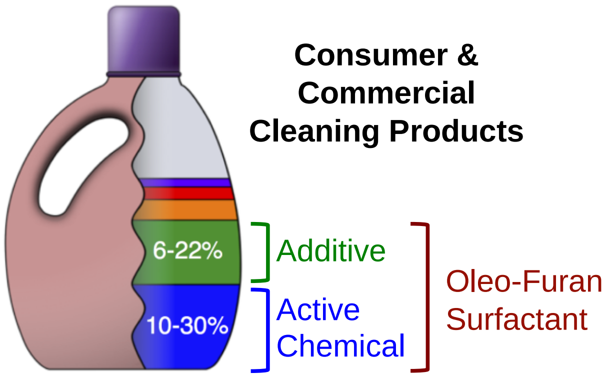
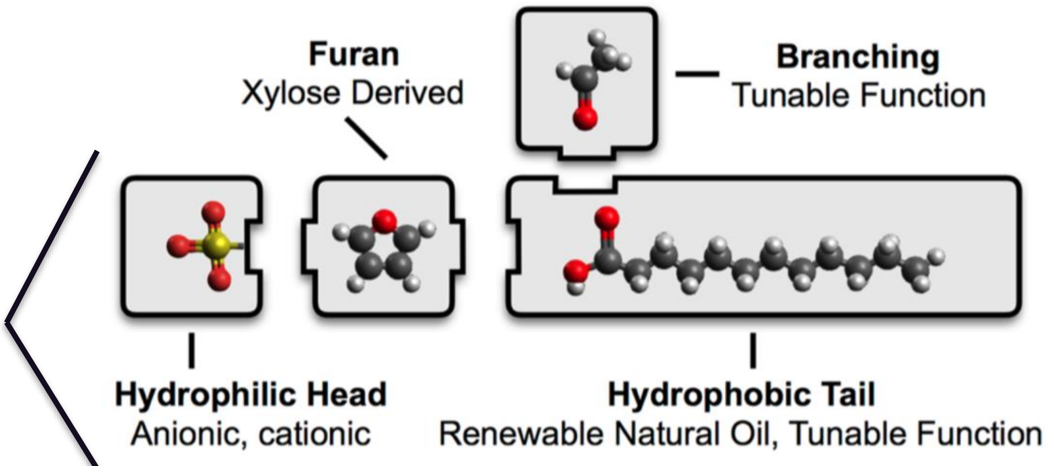
Oleo-furan Surfactant (OFS)

Consumer & Commercial Cleaning Products





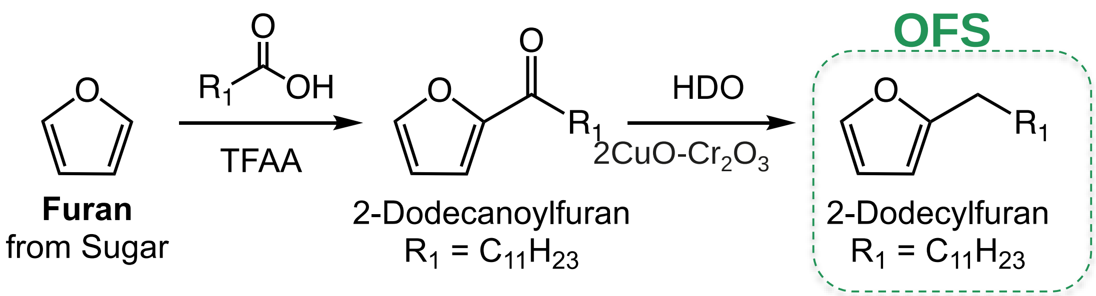
ACS Cent. Sci. *2016*, *2*, 820−824.

The oleo-furan surfactant replaces the need for two detergent components with one multi-functional molecule.

- ✓ No need of additional environmental harmful builder ingredients
- ✓ Lower product cost
- ✓ Lower product volume
- ✓ **Bio-degradable and eco-friendly**

Challenges Addressed

Current synthesis routes

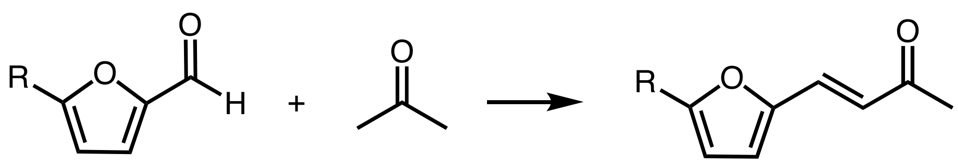


- X Scale-up
- X Catalyst toxicity

ACS Cent. Sci. *2016*, *2*, 820−824.

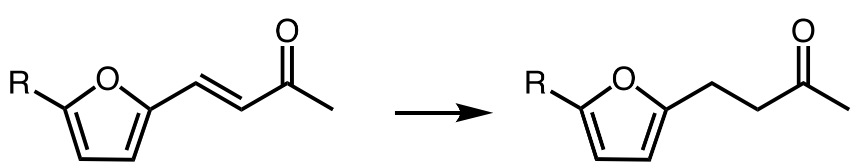
LANL expertise in furans

Furfurals chain extension



A R = H
B R = OH

Exocyclic unsaturation removal



Sutton et al., *Nature Chemistry,* **2013**, 5, 428.

Gordon, Silks, Sutton, Wu, et.al. "Compounds and methods for the production of long chain hydrocarbons from biological sources." U.S. Patent 9,422,207

Technical Approach

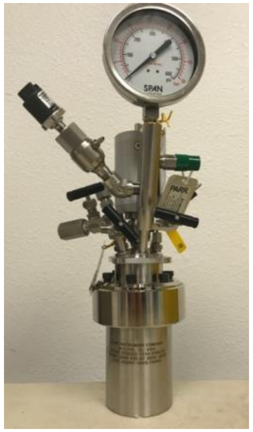
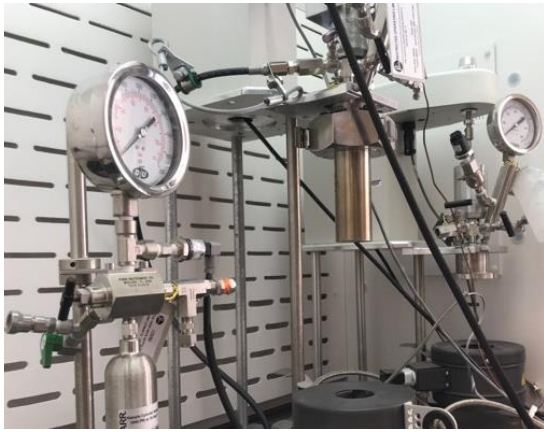
- Develop eco-friendly efficient catalysts
- Catalytic C-C coupling of furanics
- Selective reduction of furanics
- Property test and computational modeling
- Design new non-ionic surfactants

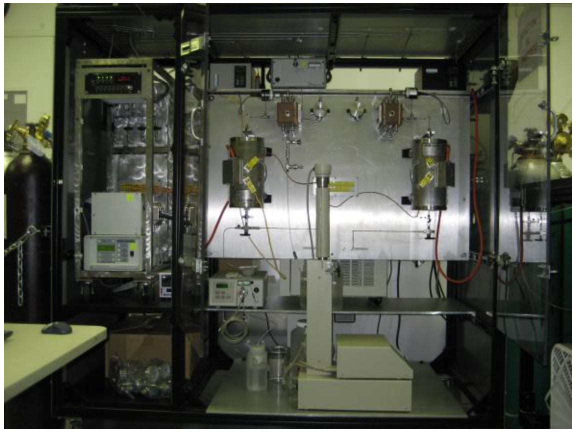
Relevance

- Produce new type of low cost, eco-friendly bio-based surfactant to get rid of environmental harmful builder ingredients
- Develop a efficient OFS synthesis process to achieve a large market impact.
- Accelerate the development of a technology transfer package for toll manufacture of surfactant products

"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*

Laboratory for Biomass Catalytic Conversion


- Capabilities to rapidly catalysts screening
- Initial scale-up test in continuous reaction system
- New catalyst development, synthesis and characterization
- New surfactant synthesis and characterization

Outline of Technical Accomplishments

Q1 & Q3

Selective catalytic reduction of furan-based surfactants.

- Characterize Starting Materials from Company
- Design & Synthesize Bi-functional Catalysts
- Screening Catalysts in Batch Reactor
- Apply New Catalysts for Selective HDO

Q2

Catalytic C-C coupling reactions to produce surfactant precursors.

- Produce New Surfactants via C-C Coupling
- Send Purified Product for Property Test

More Progress

Translate promising catalyst to continuous flow reactor

- Selective HDO in Continuous Reactor
- Time-on-stream test in Continuous Reactor
- Apply Reaction Process to New Surfactant

Catalysts Screening in Batch Reactor

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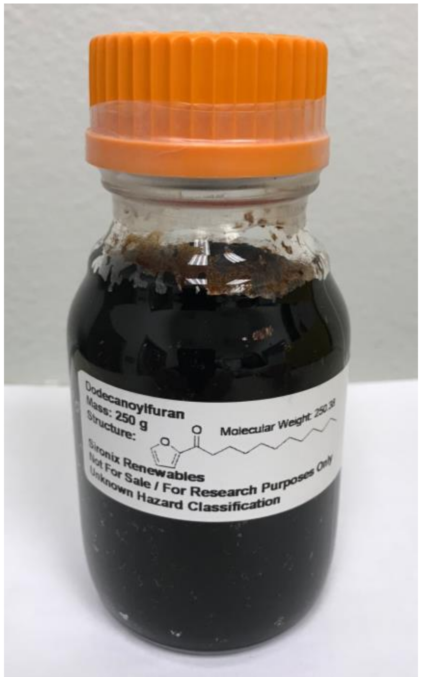
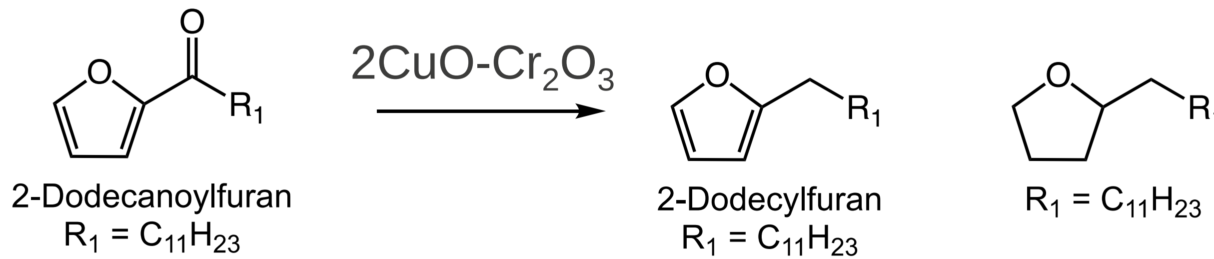


2-Dodecanoylfuran sample (1 kg) from *Sironix Renewable LLC.*



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

LANL-1 catalyst performs best among 12 catalysts

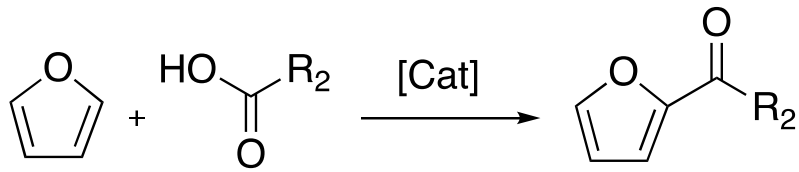
Los Alamos NATIONAL LABORATORY EST. 1943

~ 98% selectivity
> 99% conversion

Reaction conditions: 2-dodecanoylfuran 0.1 g, hexane 3 mL, LANL-1 catalyst 0.05 g, H_2 150 psi, 220 °C, 5 hrs.

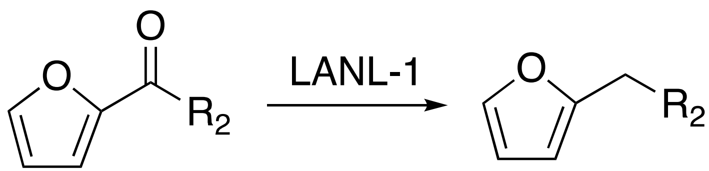
New Surfactant Development

1. Newly synthesized surfactant precursor



1) Catalyst LANL-4, 0-rt, 86% yield
2) Catalyst LANL-5, 0-rt, 86% yield
3) Catalyst LANL-6, 0-rt, 93% yield
4) Catalyst LANL-7, 0-rt, **95% yield**

2. Selective HDO in batch reactor



75% isolated yield
Two samples sent to Sironix

HDO Reaction conditions: Feedstock 0.1 g, hexane 3 mL, LANL-1 catalyst 0.05 g, H_2 50 psi, 220 °C,15 hrs.

3. Sulfonation & property test

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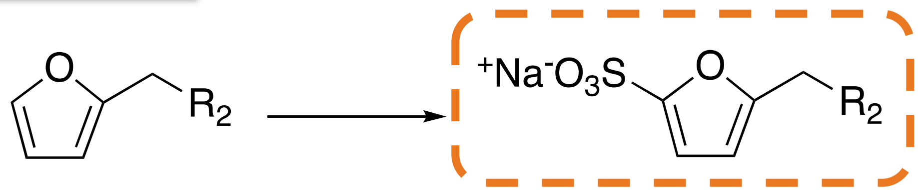
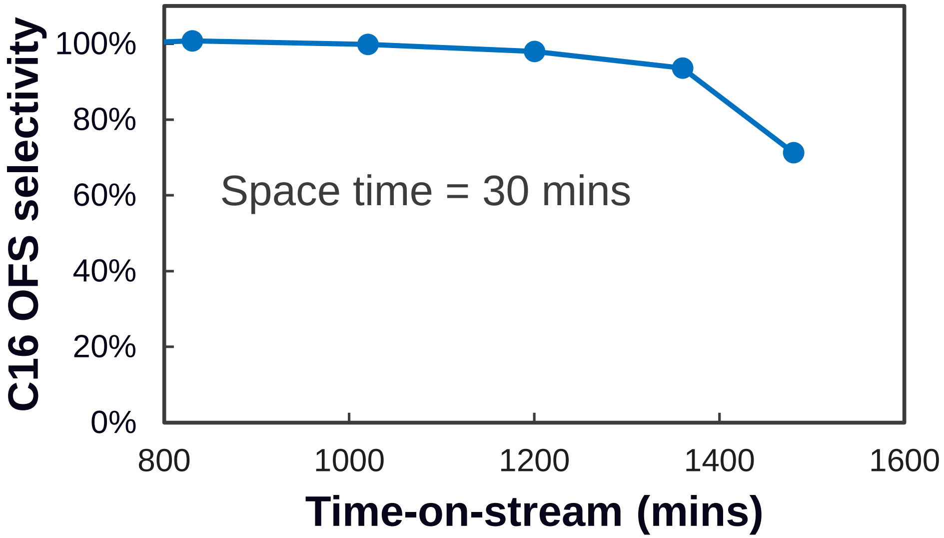


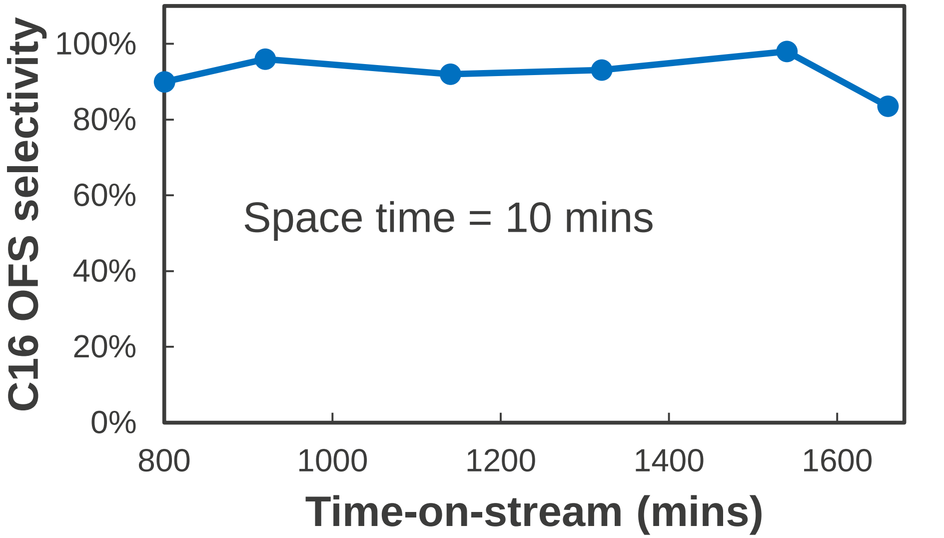
New surfactant

Preliminary surfactant property test shows promising results!

Selective HDO in Continuous Reactor



- > 95% mass balance
- > 99% conversion
- > 95% crude yield
- > 80% isolated and purified yield



- > 95% mass balance
- > 99% conversion
- ~ 92% crude yield
- Longer time-on-stream performance

Reaction conditions: 50 g/L 2-dodecanoylfuran in hexane, LANL-3 catalyst 1.0 g, 50% H_2/Ar atmosphere, 220 °C.

Future Works

Q3 continue

Characterize catalysts and improve catalysts performance for extending lifetime and robustness.

Q4

Combine C-C coupling and selective reduction steps in batch reactors

Q6 & Q8

Develop a process flow diagram in concert with initial TEA to identify the economic feasibility of the overall process

Q10

Engage computational models to identify potential structural improvements and develop new non-ionic surfactant molecules

Q12

Translate most promising catalyst and molecules to continuous flow reactor, achieve > 24 hours continuous operation and produce > 5 liters of surfactants for testing

Summary

Technical accomplishments

- Designed and synthesized bi-functional heterogeneous catalysts for selective HDO
- Screened out promising catalysts for selective reduction furanic ketones in batch reactions
- Synthesized new potential OFS precursor with high isolated yield (~ 95%)
- Translated catalytic conversions of OFS precursors to continuous flow reactor with > 20 hours time-on-stream
- Increased time-on-stream by decreasing space time

Future work

- Combine C-C coupling and selective reduction steps in batch reactors
- Develop a process flow diagram in concert with initial TEA
- Engage computational models to identify potential structural improvements
- Develop new non-ionic surfactant molecules
- Translate batch reactions to continuous flow reactor

Acknowledgements

BETO

Andrea Bailey

Nichole Fitzgerald

Contributors (LANL)

Cameron Moore

Xiaokun Yang

Juan Leal

Troy Semelsberger

Sironix Collaborators

Christoph Krumm

Shawn C. Eady

Connor A. Beach

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Additional Slides

Presentation & Commercialization

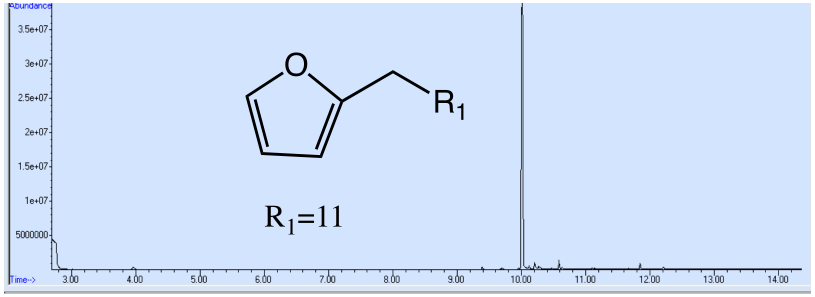
Poster Presentation:

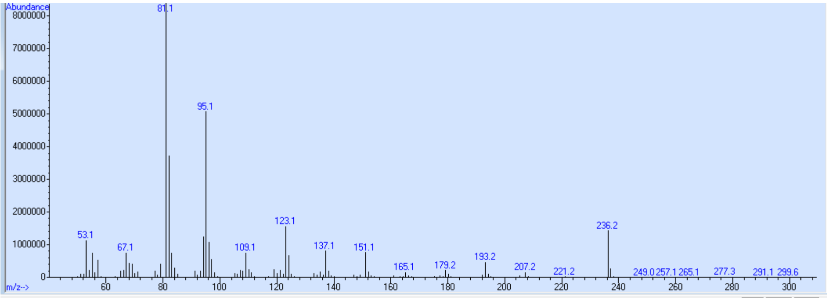
- **Xiaokun Yang** (*Los Alamos National Laboratory*) Hydrodeoxygenation of bio-derived ketones with heterogeneous catalysts for fuel and chemical production – Frontiers in Biorefining Conference, Nov 5th - 8th 2018, St Simmons Island, GA.

- IP disclosure:
  - Internal LANL disclosure S133720 “Improved Defunctionalization Catalysts”
  - Sent to Outside Council for Provisional Patent submission

Selective HDO Product

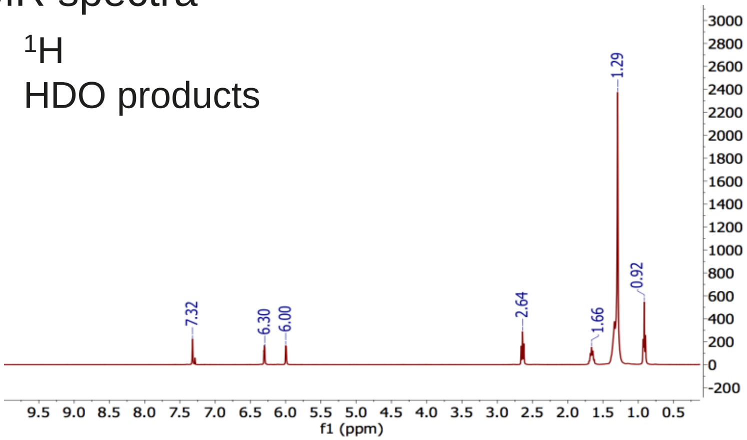
GC/MS spectra



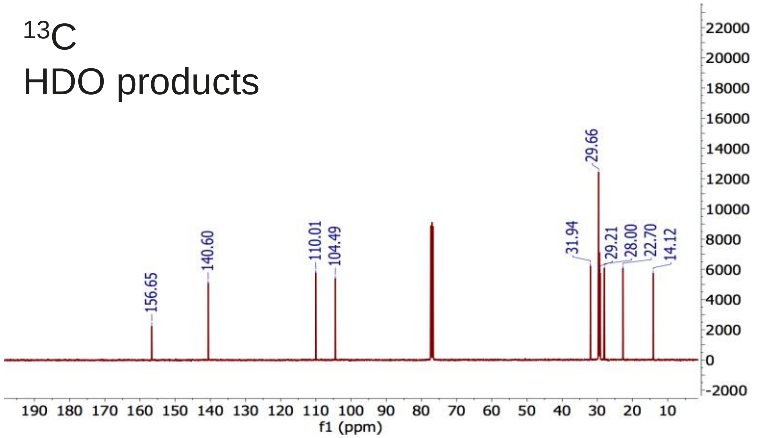


NMR spectra

^{1}H
HDO products



^{13}C
HDO products



Reaction conditions: 2-dodecanoylfuran 0.1 g, LANL-3 0.05 g, 220 °C, hexane 3 mL, H_2 initial pressure 150 psi, 5 hours.