DOE Bioenergy Technologies Office (BETO)
2021 Project Peer Review

Intensified Biogas Conversion to Value-added Fuels and Chemicals
WBS: 2.3.1.414

Friday, March 12, 2021

Conversion

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UNIVERSITY OF SOUTH FLORIDA
A PREEMINENT RESEARCH UNIVERSITY

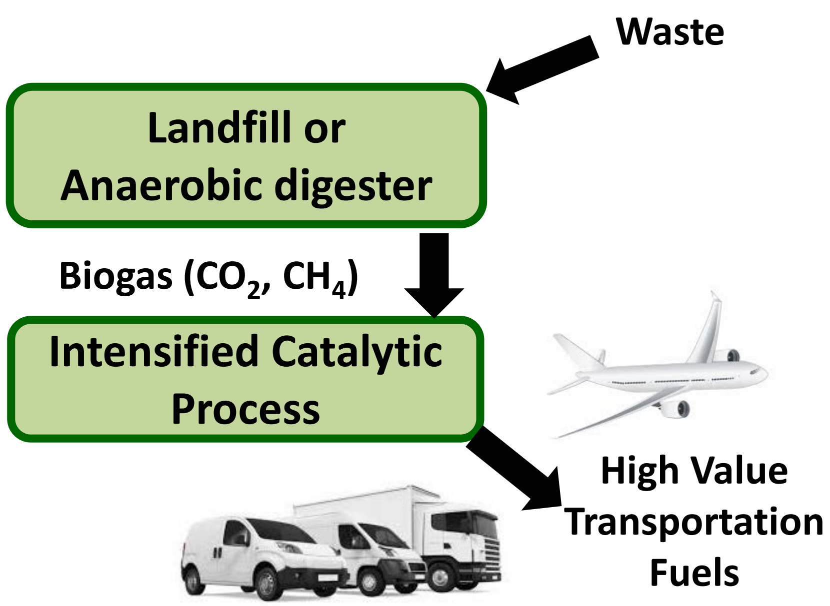
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

ChemCatBio
Chemical Catalysis for Bioenergy

Goal Statement

Goal: Convert **biogas** obtained from landfills or anaerobic digesters (AD) into **liquid hydrocarbon fuels (BGTL, biogas-to-liquids)**

- *Develop an intensified process to reduce CAPEX and enable a 15% reduction in MFSP (minimum fuel selling price) relative to SOT*



Outcome: A BGTL technology, **demonstrated on industrial process gas**, to convert biogas from distributed facilities (e.g., landfills, agricultural AD units, wastewater treatment plants) into cost-competitive fuels and to reduce fossil GHG emissions.

Relevance:

Drawbacks from current technology pathways:

- **High CAPEX** and **complex process** not suitable for distributed, small-scale productions
- Methane flaring or combustion for heat/power is a **low value product**

Advance biogas utilization technology by focusing on:

- **Intensified process** (catalyst and process)
- **Mild operating conditions** (moderate T, low P)
- **High value product** (high jet/diesel selectivity)
- **High carbon efficiency** to product
- **Demonstration** with industry partner, process gas

QUAD CHART REVIEW

Timeline

- Project start date: 10/1/2018
- Project end date: 9/30/2022

Budget

	FY20 Budgeted*	Total Award
DOE Funding	$1,174,021	$1,836,459
Project Cost Share	$292,539	$460,297

Partners/Collaborators

- **Industry/Community Partners:** T2C-Energy LLC, regional county landfills (Citrus, Manatee, Sarasota), Hinkley Center for Solid Waste Management
- **NREL /BETO Projects**: Advanced Catalyst Synthesis and Characterization (ACSC), Thermochemical Process Analysis

Project Goal

Develop a multi-functional catalyst to produce value-added fuels and chemicals from biogas via an intensified pathway

End of Project Milestone (FY22)

Achieve 100 hr operation using commercial biogas and ≥25% reduction in MFSP, as compared to the benchmark SOT

Funding Mechanism

FOA: DE-FOA-0001916

Topic area: BioEnergy Engineering for Products Synthesis (BEEPS)

Year: 2018

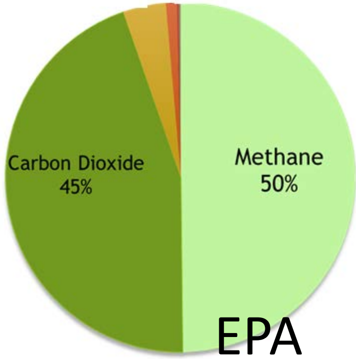
* Through end of FY20

1. Overview
2. Management
3. Approach
4. Impact
5. Progress and Outcomes

1. Overview

1. Project Overview (1 of 3)

Overarching Goal:
Upgrade biogas to value-added fuels and chemicals



EPA

Biogas (~500 BTU/SCF)

Potential:
Diversify to value-added products, circular economy, minimize flaring

Competing options to mitigate environmental impact of biogas/landfill gas:


FLARING


ELECTRICITY


CNG/LNG


FUEL/CHEMICAL

	FLARING	ELECTRICITY	CNG/LNG	FUEL/CHEMICAL
Retail prices* ($/GGE)	n/a	$1.00 (3 cents/kWh; retail to grid)	$2.18 (CNG) 2.42 (LNG)	$2.13 (diesel) 2.26 (methanol)

*Oct. 2020; https://afdc.energy.gov/fuels/prices.html

1. Project Overview (2 of 3)

Conventional process:

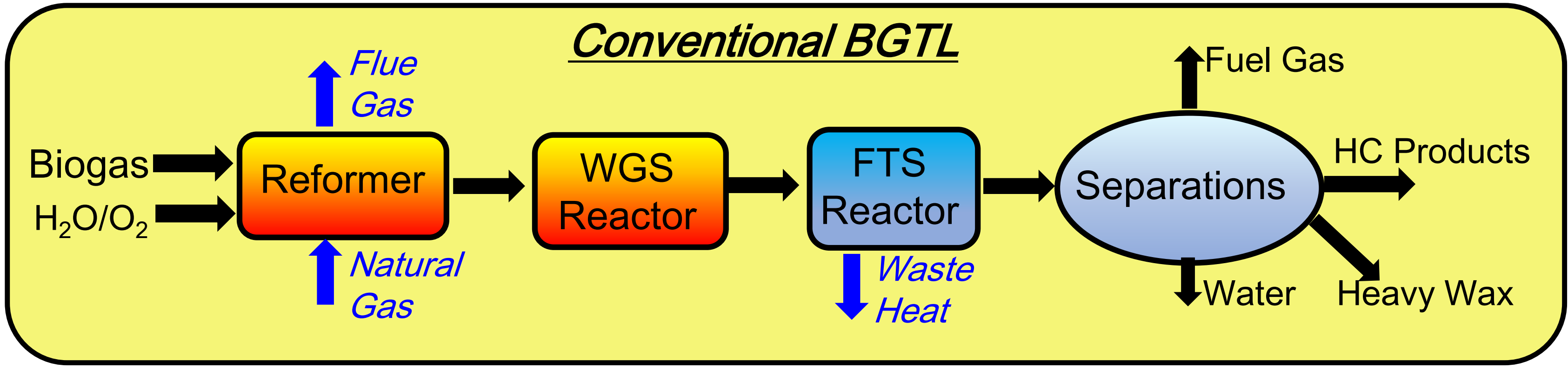
- 3 reactors
- >20% methane loss in reformer
- High pressure

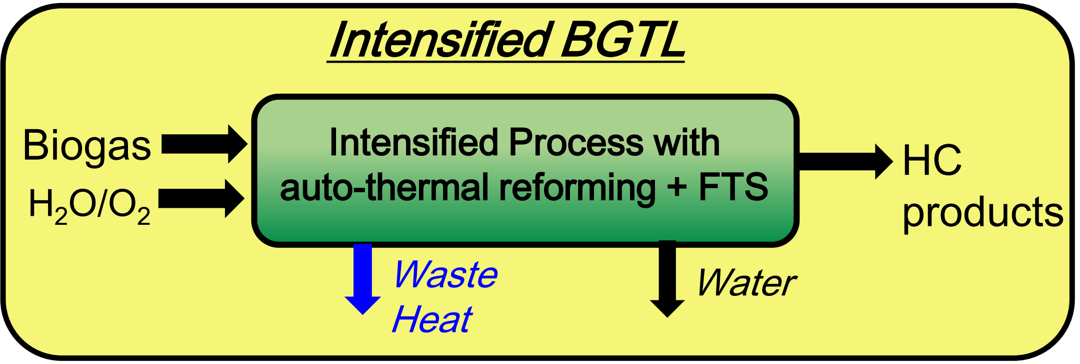
TriFTS™*:

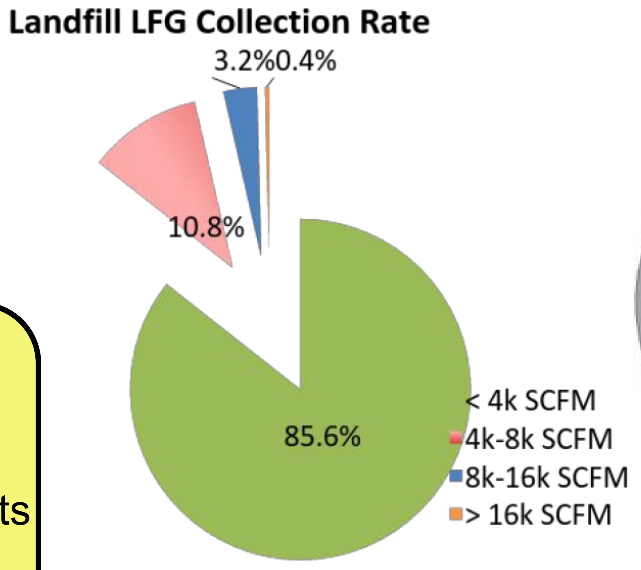
- WGS removed via catalyst and process tuning
- Compressor and heat-exchanger are major costs

Intensified BGTL:

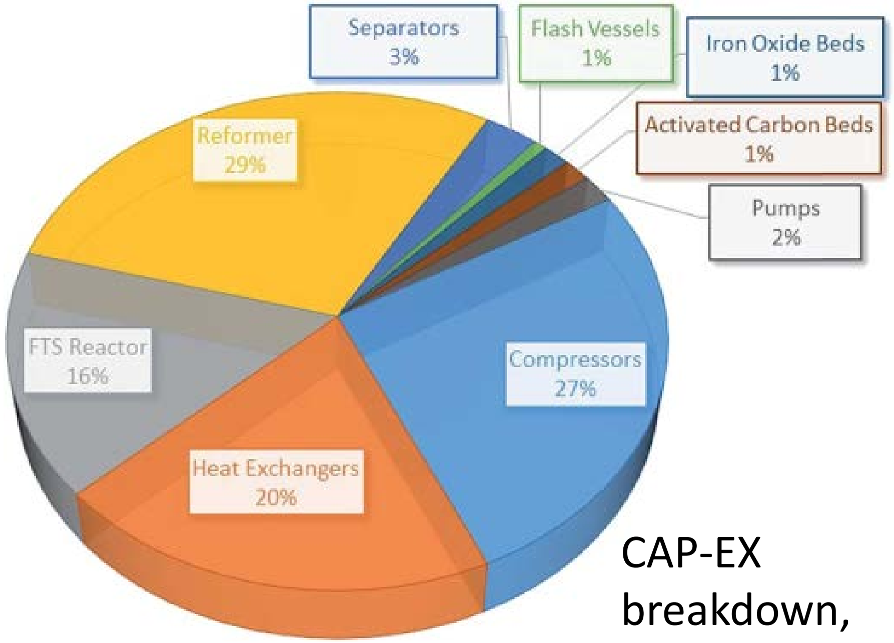
- Tune to small scale
- Mass and heat integration







Often small scale

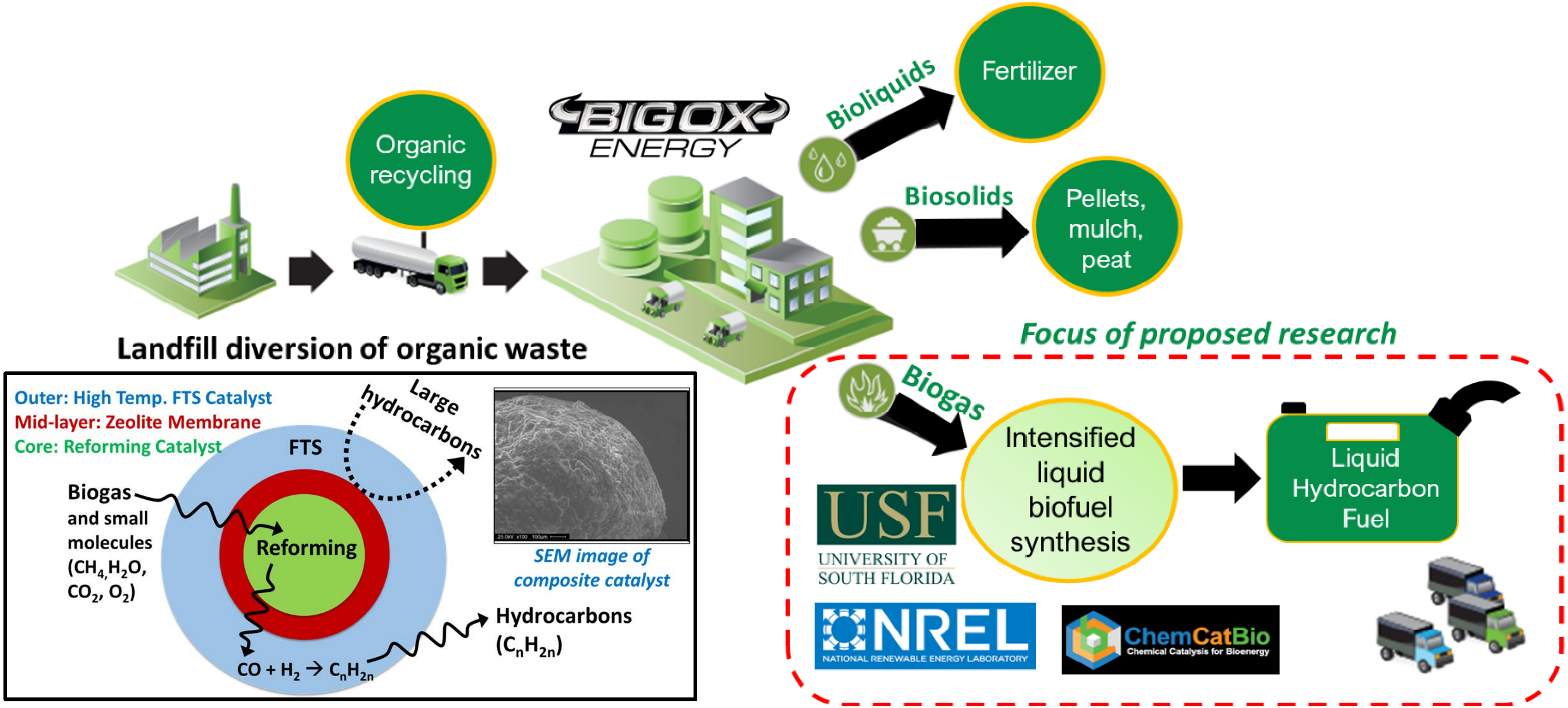


CAP-EX breakdown, TRiFTS™*

* T2CE led SDI project; USF COI, Zhao et al *Sust En Fuels* 2019

1. PROJECT OVERVIEW (ORIGINAL 3 OF 3)

Biogas to liquid fuel via intensified catalytic synthesis



2. Management

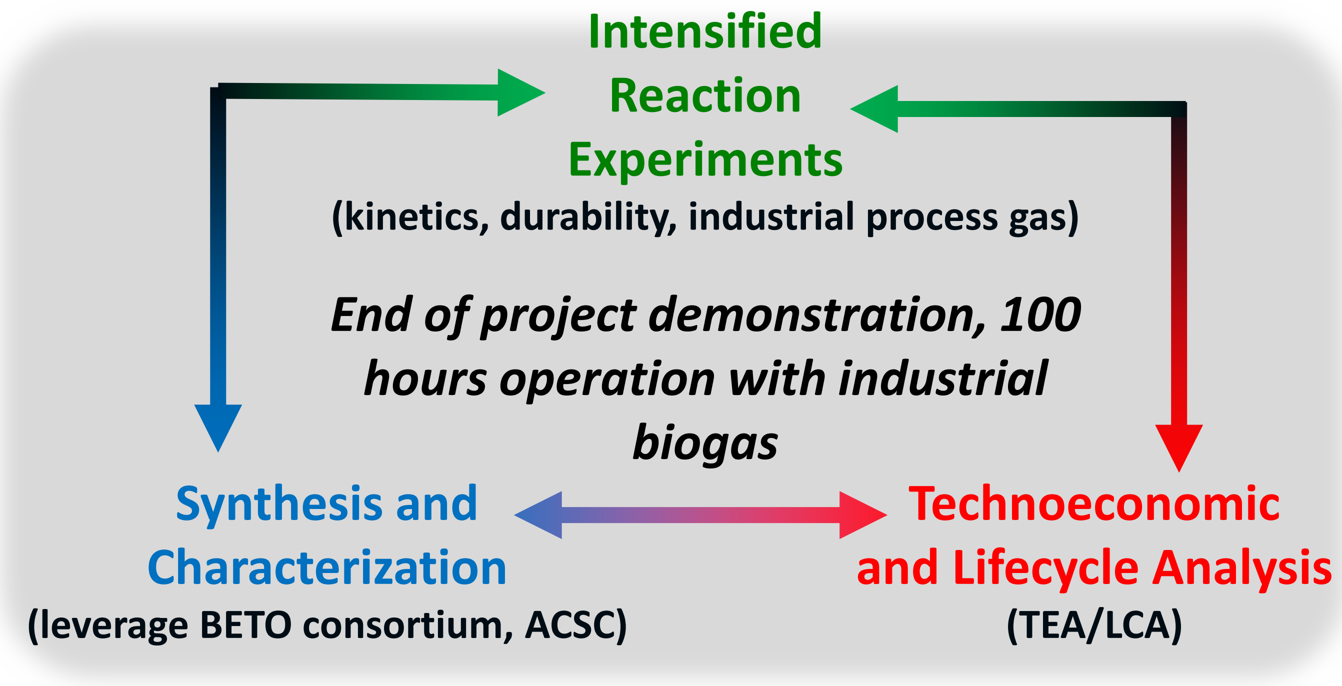
2. Management: Task Structure (1 of 3)

Task Structure

Task 1: Project Verification Lead: U. of South Florida
Task 2: Catalyst Synthesis, Validation and Reaction Testing Lead: U. of South Florida
Task 3: Advanced Materials Characterization and Design Lead: NREL
Task 4: Commercialization Readiness Lead: U. of South Florida with Industry Partners
Task 5: Technoeconomic and Lifecycle Analysis (TEA/LCA) Lead: NREL
Task 6: Project Management Lead: USF

Project Overview:

- **Develop intensified catalytic process for biogas-to-fuels and demonstrate technology on industrial biogas.**



The project management plan allows each organization to focus on its core capabilities to enable rapid catalyst and process development.

2. Management: Focus on Success Factors (2 of 3)

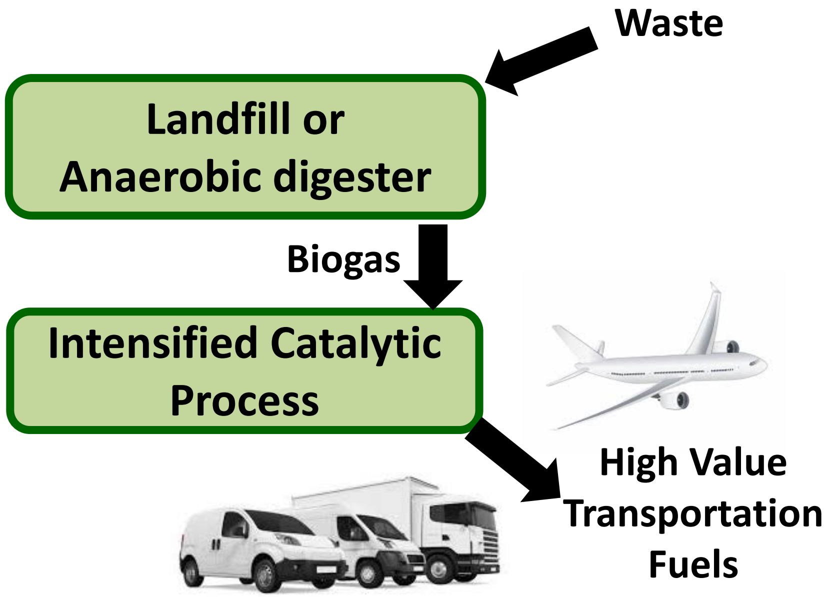
Go/No-Go – Focused on critical success factor – C2+ hydrocarbons :
"Demonstrate ≥10% yield of C2+ hydrocarbons on lab-scale…" in 2021
***(Already achieved 6% hydrocarbon yield on lab-scale, up from 3%)**

Activities focus on critical success factors by addressing the Go/No-Go criteria and reducing project risks.

Project Communication– Weekly meetings; quarterly DOE meetings; ongoing industrial input;

Interdisciplinary Team Members – Expertise in reaction engineering, characterization, synthesis,, TEA/LCA, scale-up, and industrial biogas production

Data Management – Secure data folders for all project files



Leverage BETO Investments– Collaborate and leverage core competencies of NREL and BETO's ChemCatBio consortia for catalyst characterization (ACSC) and TEA/LCA

Integrated Approach– Development is accelerated by an iterative, multifaceted approach to R&D challenges

2. Management: Risk Mitigation Plan (3 of 3)

Site visit to Citrus County landfill to procure biogas for testing.

Grabbing the "bull by the horns" during kick-off meeting in Tampa.

Project Risks and Mitigation Strategies

Carbon Efficiency
Concerted effort towards catalyst/process improvement to reduce uncertainty in yields to enable cost goals

Equipment failure and staffing disruption
Key capabilities and operations (e.g., reactor, analytical, characterization, industrial supply) have redundant capabilities to mitigate disruption to project progress

Process Economics
Establish performance targets and develop sensitivity analysis to identify largest cost reduction parameters

Contaminants Effects with Real Process Gas
Experience with gas clean-up (siloxanes, H_2S, NH_3) and working with real process gas reduces risk of unknown contaminant impacts (halides)

Suitability of Product Molecular Weight
Product molecular weight can be tuned by olefin oligomerization at reactor exit by adjusting C-C coupling (NiO/SiO_2-Al_2O_3)

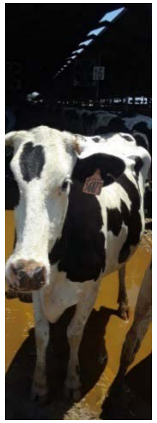
Biogas compression and filling unit (BRC FuelMaker).

Landfill gas cylinders at labs for reaction testing.

3. Approach

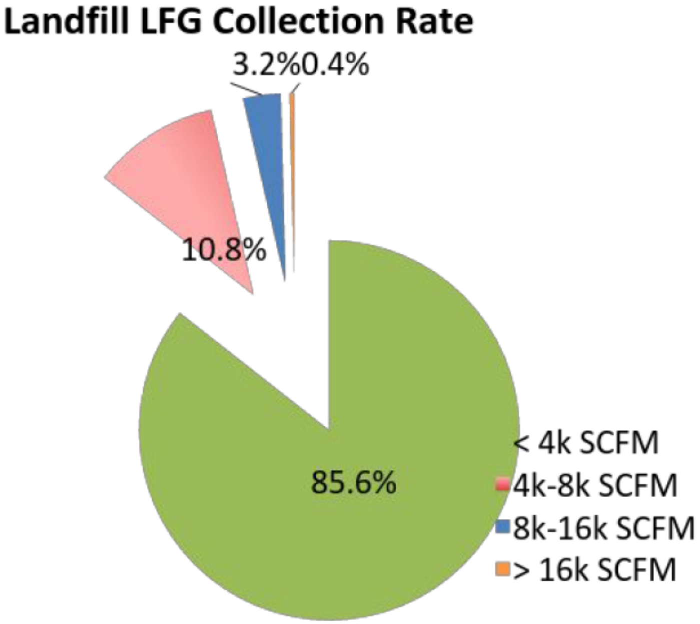
3. APPROACH (1 OF 4)

Convert biogas to valued added chemicals and fuels and avoid carbon loss to undesirable products.



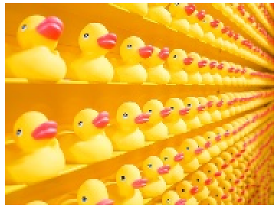
AD at dairy farm

Gas collection at landfill



Most biogas available at “small” scales

INCREASING PRODUCT VALUE

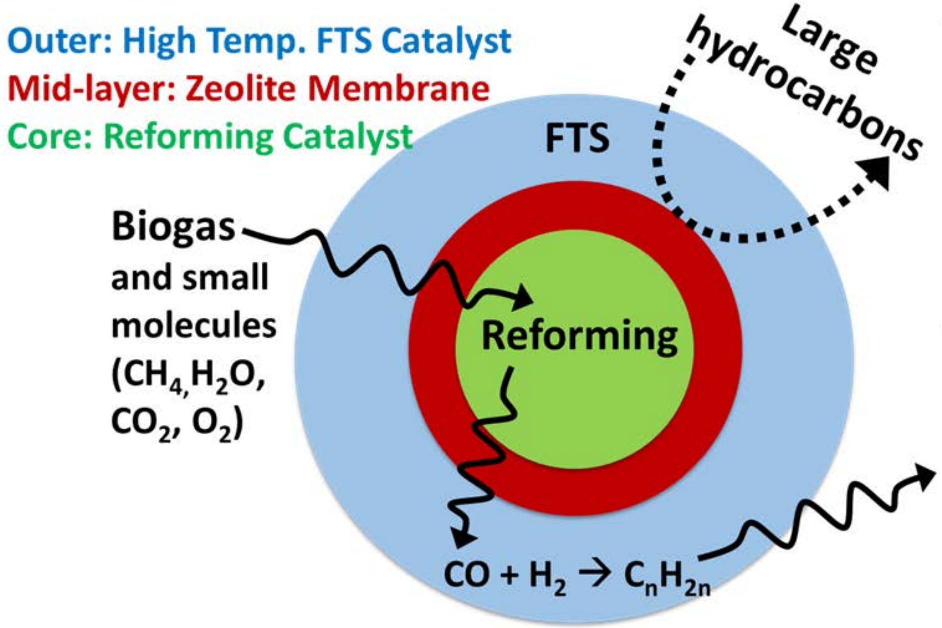


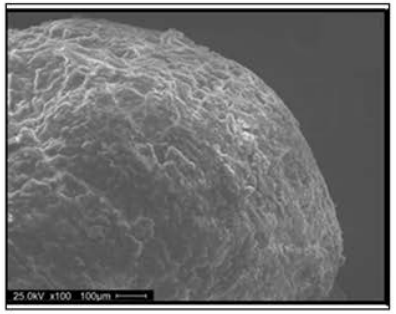
Challenges – Methane conversion, C2+ selectivity, catalyst stability, economies of scale

3. APPROACH (2 OF 4)

Catalyst design

Integrate catalysts for specific reactions separated by microporous (i.e., zeolite) shells





SEM image of composite catalyst

Novelty: Tandem catalysts for reforming and CO hydrogenation

- Single reactor strategy overcomes economy of scale (major C1 issue)
  - Lowering cap-ex
  - Lowering pump and compressor op-ex
- Mass and heat transfer inherently improved; achievable through composite bed catalyst approach
- Challenges: catalyst performance outside of typical operation ranges

3. Approach (3 of 4)

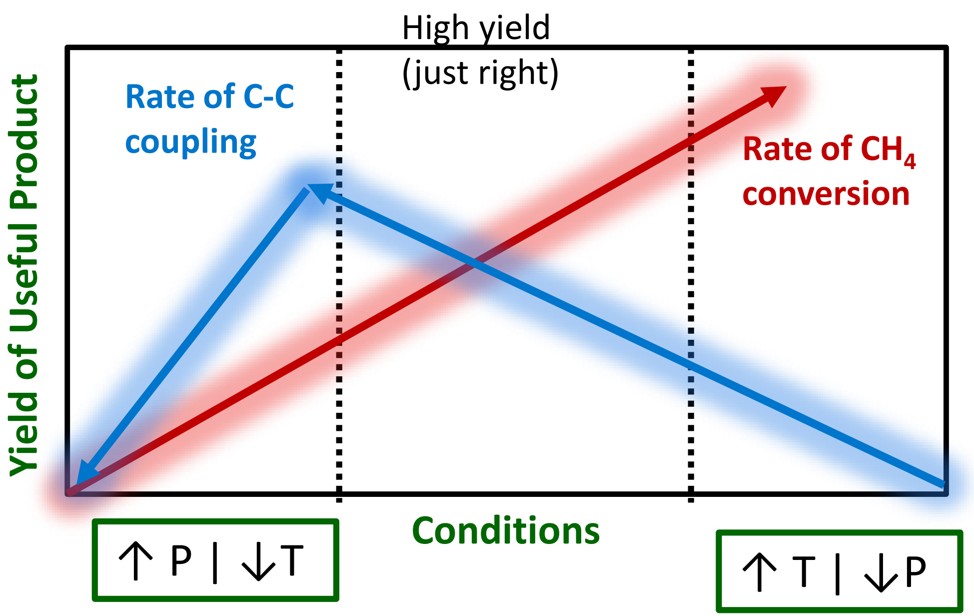
Tailor catalysts with varying functionality under similar conditions:

(1) Catalytic activity (methane activation and C-C bond forming)

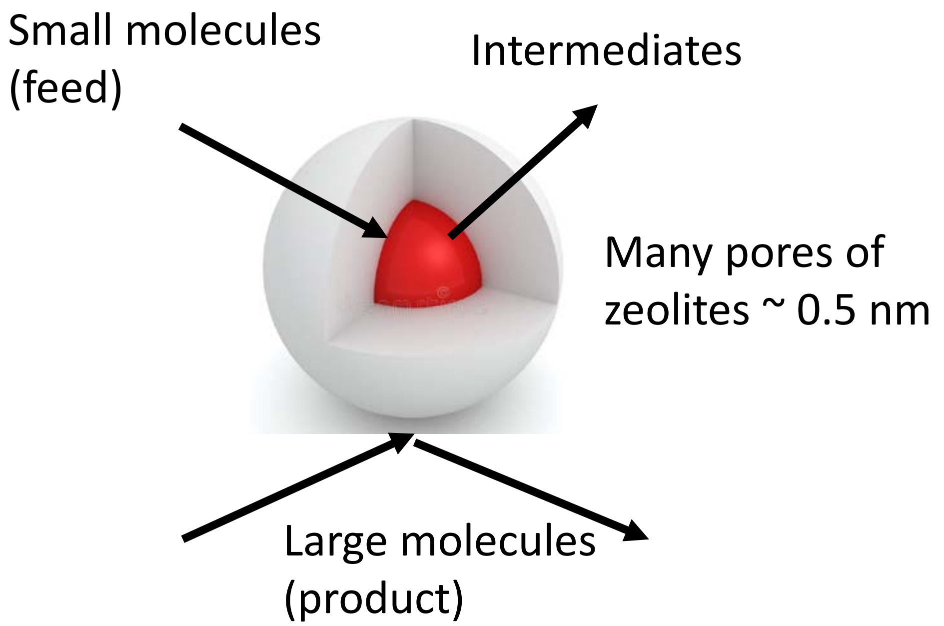
(2) In-situ separation

Important for upgrading to value-added chemical production

1. Catalytic activity



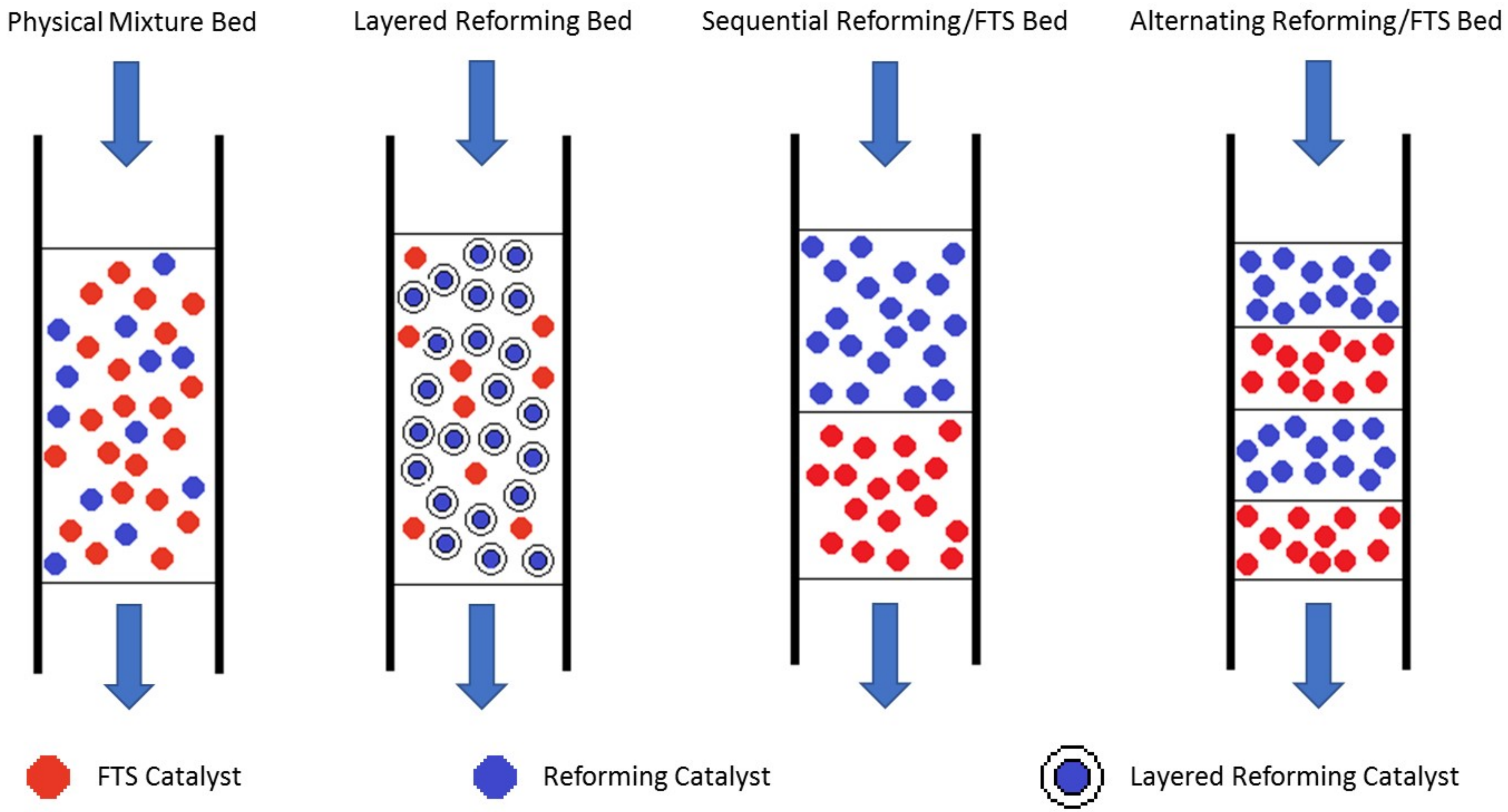
2. In-situ separation



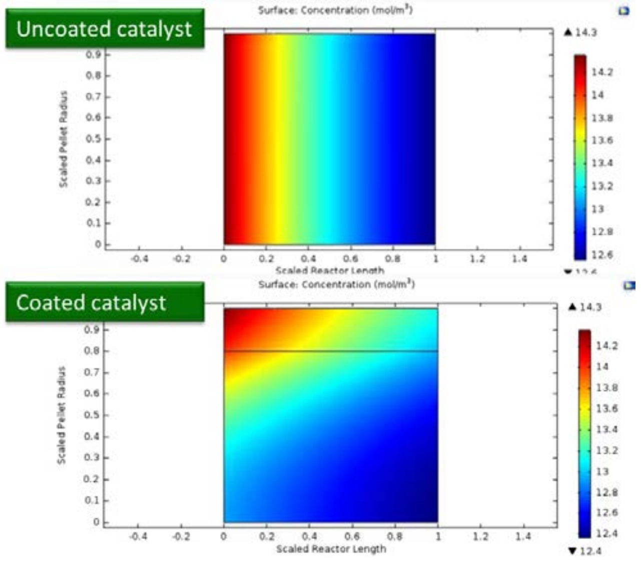
3. Approach (4 of 4)

Bed Configurations

Multiple process options to integrate components into a single catalyst bed:



- **Develop** reactor models for the *reforming* and *FTS* using composite catalysts and examine variability
- **Combine** in single reactor to optimize the intensified reactor in terms of bed packing and shell thickness



4. Impact

4. Impact – BETO Barriers & Goals (1 of 3)

Project Outcomes and Relevance – Demonstrate a new pathway to BETO for biofuel production

- Biogas underused as a feedstock
- Intensified strategy overcomes economy of scale challenges (major C1 issue)
- Novel approach provides portfolio diversification and low-cost route
- Collaborate across industry, academia, and ChemCatBio to accelerate catalyst development for bioenergy applications

BETO MYP Barriers

Ct-F. Increasing the Yield from Catalytic Processes
Ct-G. Decreasing the Time and Cost to Develop Novel Industrially Relevant Catalysts
Ct-E. Improving Catalyst Lifetime
Ot-B. Cost of Production

Relevant Criteria	Benchmark (FY18 SOT)	Status (FY21 SOT)	Long-Term Target
Biogas conversion (single-pass) to C2+ HCs	0.4%	6%	>10%

BETO Performance Goals:

By 2030, verify hydrocarbon biofuel technologies that achieve ≥50% reduction in emissions relative to petroleum-derived fuels at **$2.5/GGE MFSP**

- Providing ***early-stage R&D*** to enable verification reduce risk
- ***Identifying viable routes to $2.5/GGE***

4. Impact – Bioenergy Industry (2 of 3)

Industrially-relevant for both established and emerging companies, municipalities, and public-private ventures in providing routes to renewably-sourced products to penetrate existing markets and develop new markets.

- Interest from both ***upstream and downstream*** companies (landfills and agriculture to consumers)
- **Technology applies to a variety of processes and waste feedstocks**
- ***Market demand*** from existing companies to use renewably-sourced precursors and to minimize off-gas waste streams
  - Create a **cost-competitive** technology with an emphasis on the small scale
  - Focus on products with large markets, high value, and potential for bio-adoption
  - ~2000 landfills in US plus many more ag waste & waste wate treatment facilities
- Creates a ***diversified revenue*** *stream* for biogas producers

Upstream

High value
Large markets

Downstream

4. Impact – Scientific Advancement (3 of 3)

Developing Foundational Science

Peer Reviewed Publications

External Presentations

Building Industrial Partnerships

Multiple Industry/Municipality Collaborations

Generating Intellectual Property

Issued Patents

Pending Patent Applications

Training and Support for Next-Generation Engineers/Scientists

Ph.D. students supported
Post-doctoral researchers supported
Undergraduate internships

5. Progress and Outcomes

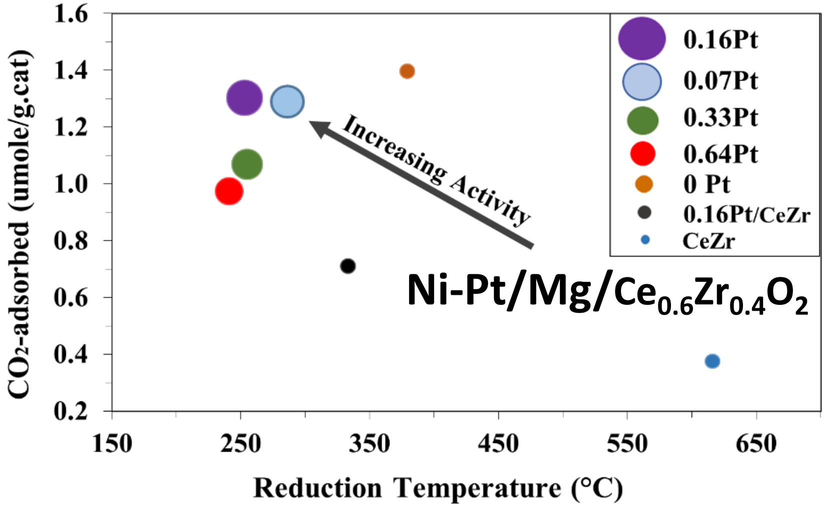
5. Progress and Outcomes: (1 of 7)

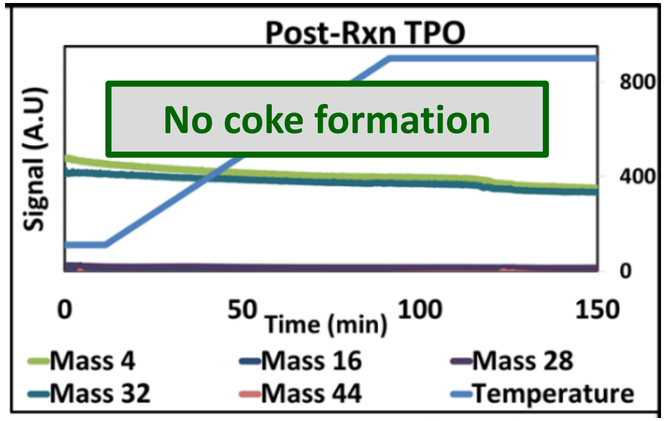
Low temperature CH_4 reforming

Challenge:
- Traditional CH_4 reforming requires high temp. on Ni catalyst for C-H activation
- High temp. not suitable for FTS

Progress:
- Increased activity (lowered C-H activation temp.) with Ni-Pt alloy
- Modified synthesis to improve dispersion, reduce Pt loading and cost, and increase activity
- New formulations (Ru, Zn) to eliminate Pt and further reduce catalyst cost (40% reduction, ~$12/kg)
- Durability testing for 100+ hours shows stable, robust process with minimal coke (high carbon efficiency)

Low temperature CH_4 activation for reforming (dry and bi-)





Improved reforming catalyst and reduced cost.
- **Catalyst cost reduced by 40%**
- **Low temp. (450°C) activity increased significantly**

Activity:
- Tuned via synthesis and enhance activity and reduce cost

Selectivity:
- H_2: CO ratio tuned ~ 2 for optimal Fischer-Tropsch synthesis by feeding steam

Stability:
- No CO_2 formed during TPO after ~ 100+ hr TOS (T = 450 °C)
- Coking rate < 4.4E-6 g-C/g-cat/h

Elsayed, Kuhn et al. i) *Catal Lett 2018* ii) *Topics in Catalysis 2017* iii) *Applied Catalysis B: Environmental* 2015

5. Progress and Outcomes (2 of 7)

Reforming CH_4 without reforming fuel products

Zeolite-encapsulated catalyst with ~0.5 nm pores

Small molecules (**biogas feed**)

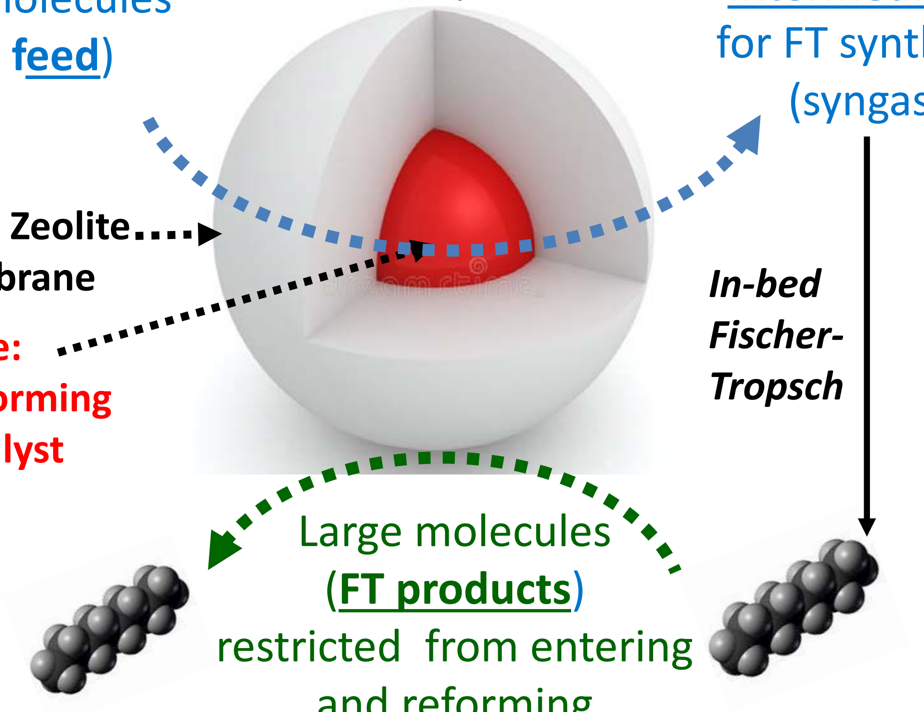
Intermediates for FT synthesis (syngas)

Shell: Zeolite membrane

Core: Reforming catalyst

In-bed Fischer-Tropsch

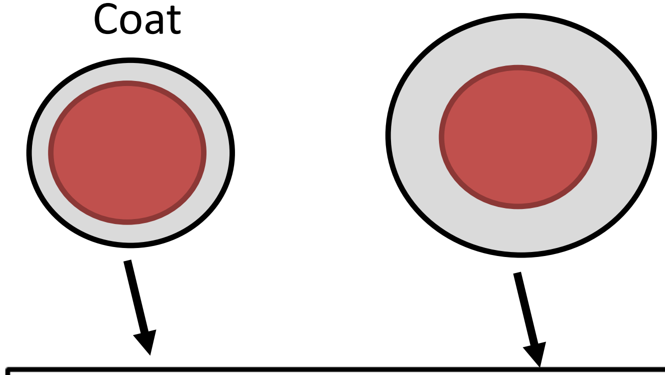
Large molecules (**FT products**) restricted from entering and reforming

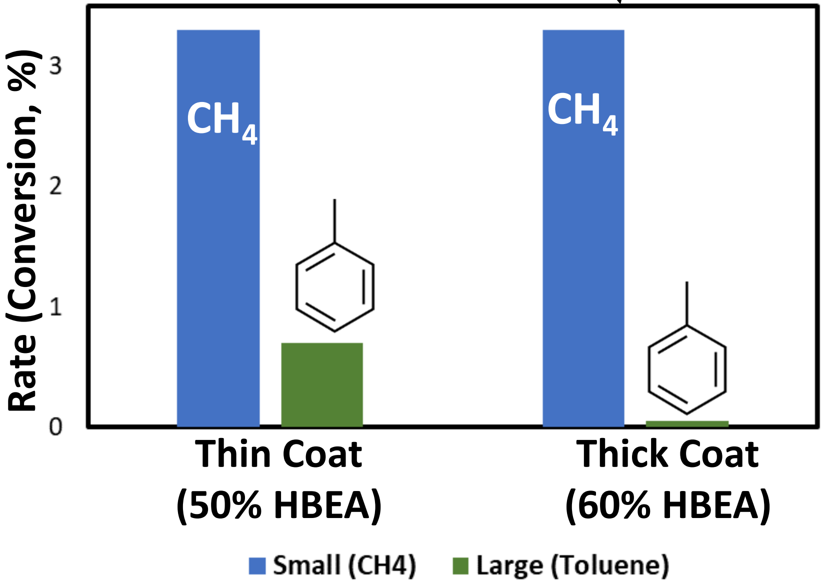


Demonstrated that intensified, single-reactor process with coated catalyst can be successful.

Thin Zeolite Coat

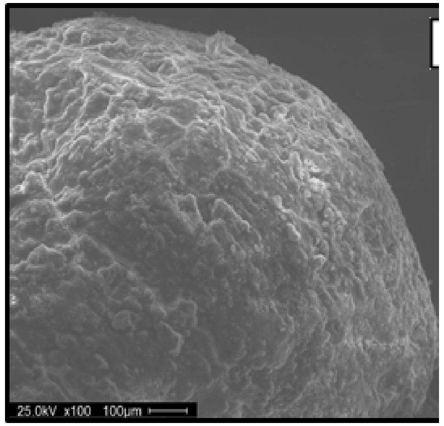
Thick Zeolite Coat





Challenge: FT products could react on reforming catalyst

Progress: Coating successfully suppressed large molecule conversion without affecting CH_4 reforming activity



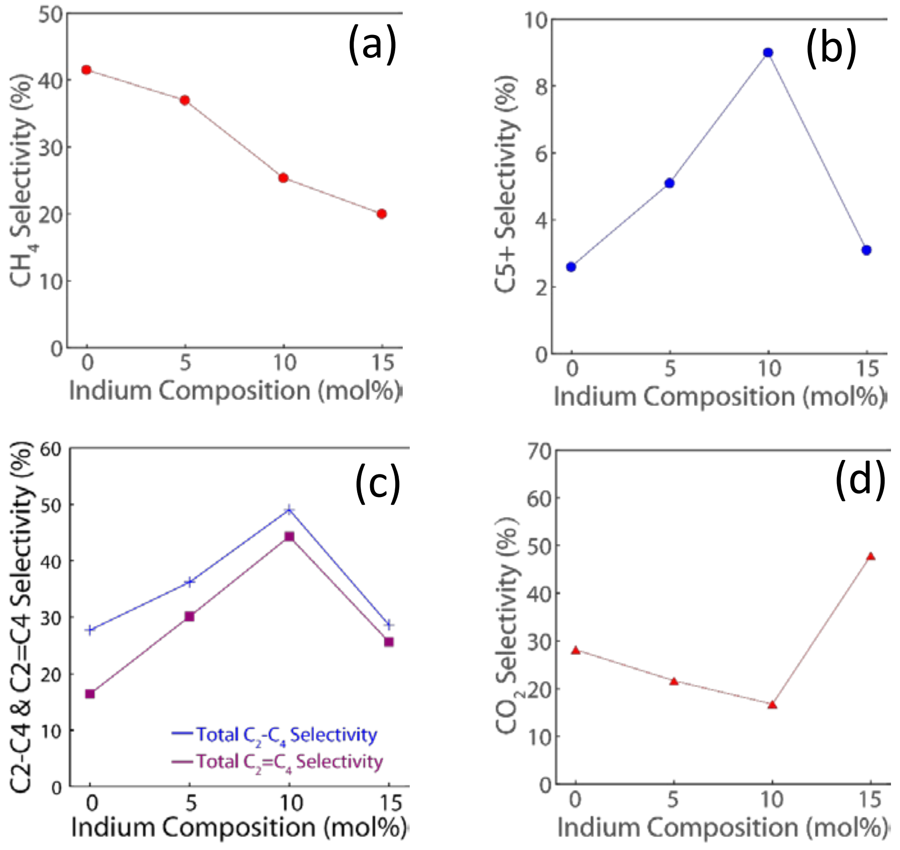
SEM image of zeolite-coated reforming catalyst

Cimenler, Kuhn et al. i) *Topics in Catalysis* 2018 ii) *AICHE Journal* 2017 iii) *Energy & Fuels* 2016 iv) *Applied Catalysis A: General* 2015

5. Progress and Outcomes (3 of 7)

High temperature C-C coupling: FTS

Selectivity study as a function of Fe:In loading

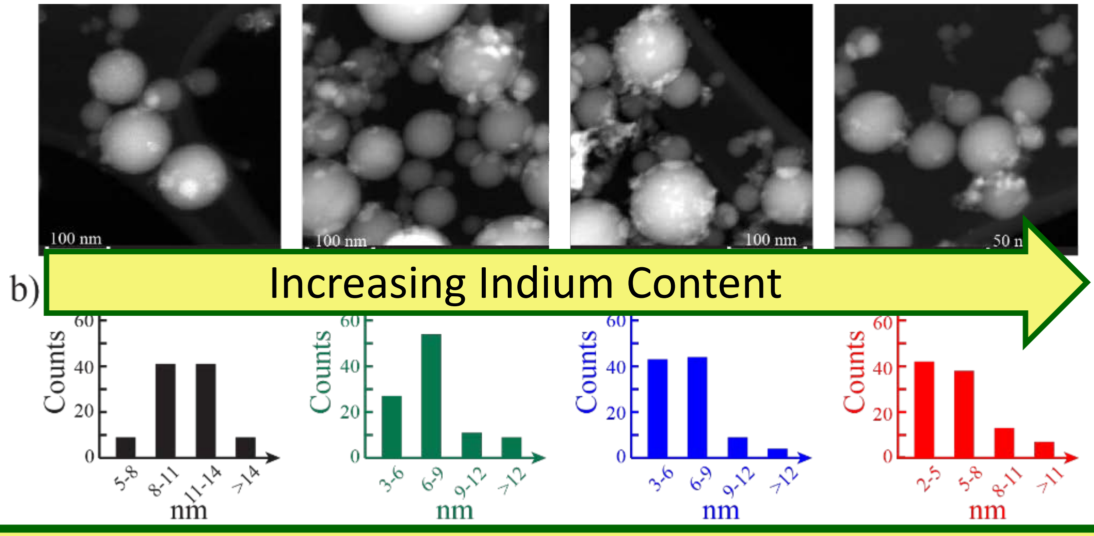


Challenge:

- Fischer-Tropsch synthesis (FTS) at high temp. limits molecule size (chain length)
- Stability can be challenging at high temperature (>400°C)

Progress:

- Iterative reaction testing and characterization improved Fischer-Tropsch catalyst
- Indium promoting ↑Fe dispersion, and limits undesired CH_4 and CO_2 formation; optimal dopant ratio of 10:1 Fe:In of test matrix



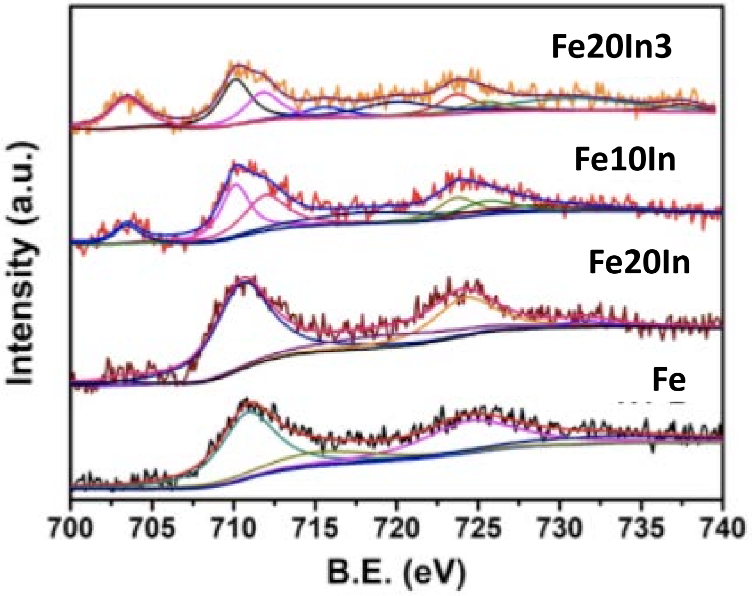
Metal dispersion increases with increasing In (indium) content

CO conversion was kept at ~10%

5. Progress and Outcomes (4 of 7)

High temperature C-C coupling

XPS over the post-reaction catalysts

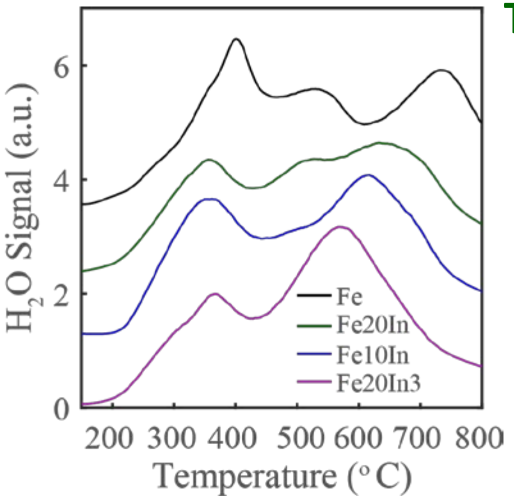


XPS analysis:

- suggested Fe-In interaction
- more In present near the surface layers when In loading increased

Progress:

- Indium increases surface reactant (CH_x) residence time by 3-fold (↓ methane formation and ↑ selectivity for C-C coupled products)
- Mechanistic insight
  - **Isotopic studies** in methanation regime and **characterization** (e.g., XPS, TPR) revealed insight to effect of indium promotion
  - $Fe_{10}In/Al_2O_3$ has stronger surface intermediates than Fe/Al_2O_3



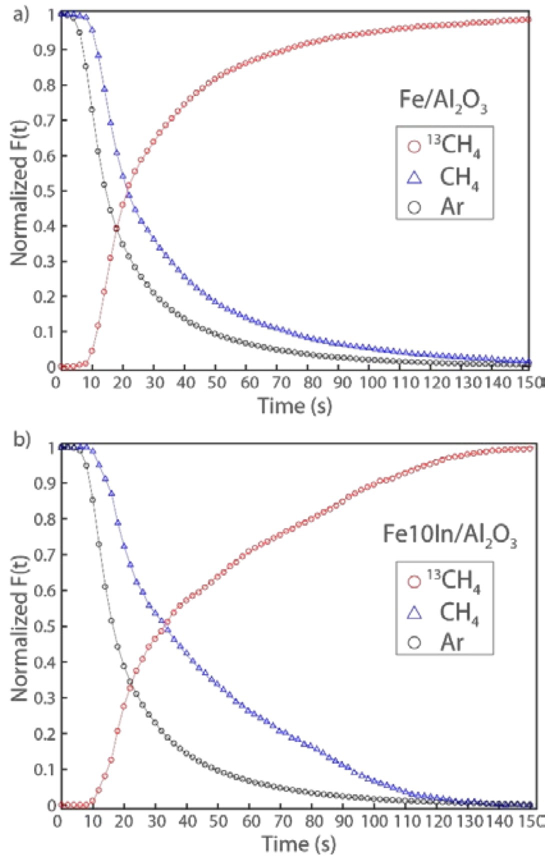
TPR

In promotes reducibility (TPR)

Isotopic Exchange Experiments

Surface residence time of CHx:

Fe/Al_2O_3:	7.0 s
$Fe_{10}In/Al_2O_3$:	20.1 s



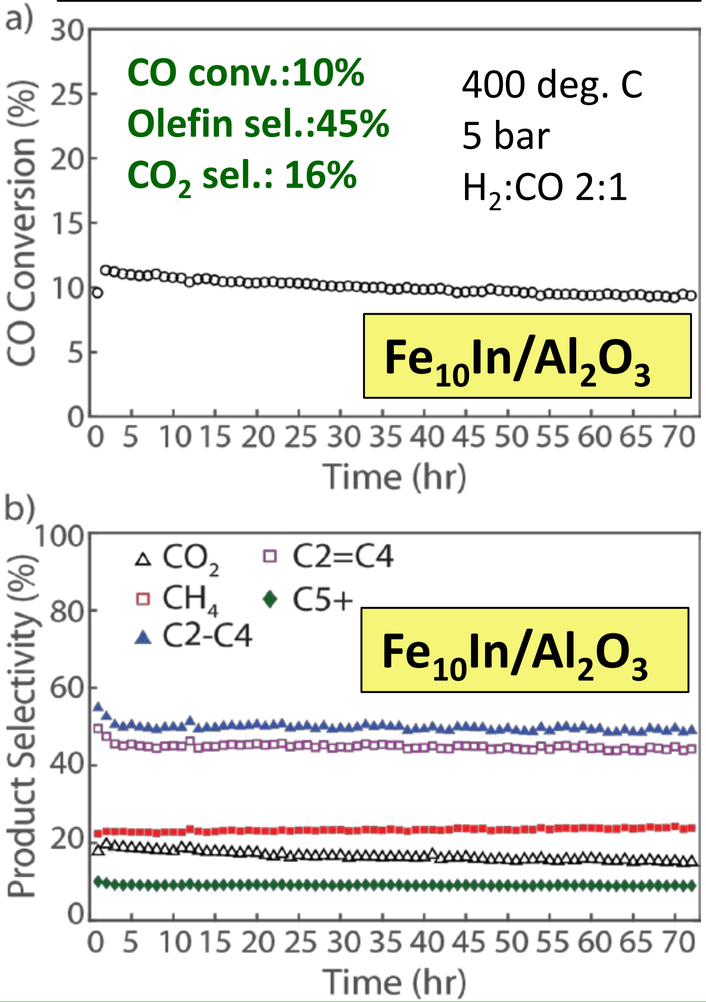
5. Progress and Outcomes (5 of 7)

Fischer-Tropsch Synthesis
High temperature (400°C) C-C coupling

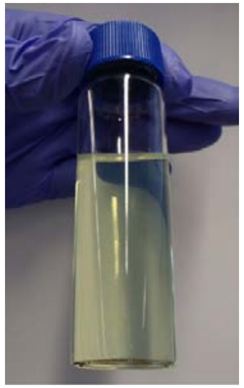
Challenge:
- Fischer-Tropsch synthesis (FTS) at high temp. limits molecule size (chain length)
- Stability can be challenging at high temperature (>400°C)

Progress:
- Synthesized **high stability** $Fe_{10}In/Al_2O_3$ catalyst
- Demonstrated >70 hours of stable Fischer-Tropsch activity
- **High olefin selectivity** allows facile m.w. tunings via oligomerization (demonstrated with Ni/SiO_2-Al_2O_3)
- **Lower CO_2 production** and **benign reaction conditions** (lower T, P) compared to literature/SOT

Stability study
>70 h of stable Fischer-Tropsch reaction



Partners have history of successful lab-to-pilot demonstration.

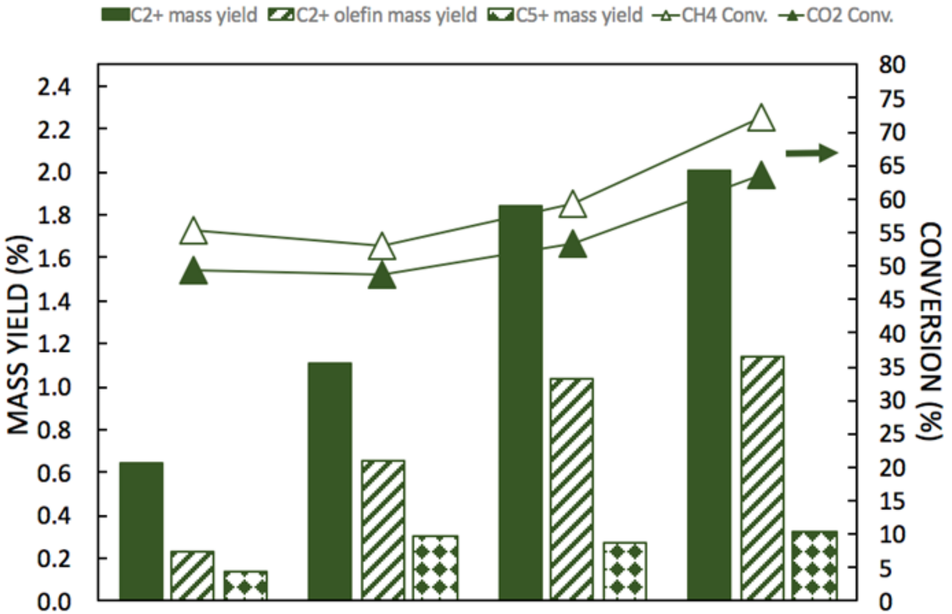


Industrial partners T2C Energy and Citrus County Landfill photographed with skid pilot plant for producing 75 gal/day of fuel from landfill gas using two-reactor (reforming + FT) process and resulting diesel product

5. Progress and Outcomes (6 of 7)

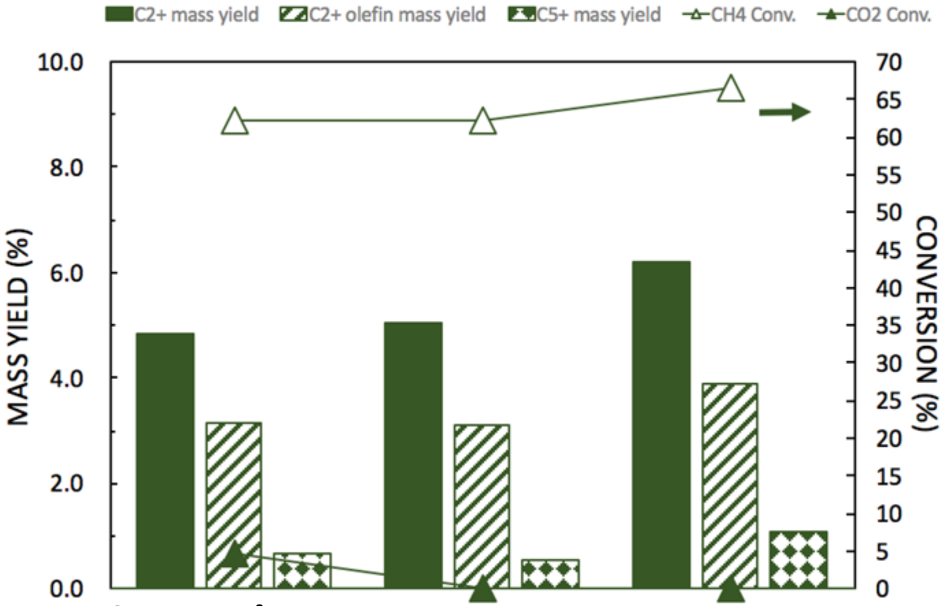
Combined bed testing

$CH_4 + CO_2$



Various temperature and pressure combinations

$CH_4 + CO_2 + H_2O$



Increasing steam

Pt-free reforming catalyst +
Fe-based Fischer-Tropsch catalyst

Challenge:

- High-single pass CH_4 conversion at T<500°C

Progress:

- Successful demonstration of intensified process
- Steam improves the mass yields of C2+ hydrocarbons significantly (utilize moisture in biogas)
- High olefin selectivity allows for oligomerization to tune product molecular weight

- Sequential catalyst beds in same reactor
- Temperature, pressure, and catalyst tuned products/rates
- Space velocity not a major factor
- Evaluated CO and H_2 co-feed to simulate recycle

**Precise catalyst compositions and reaction conditions confidential for IP/patent protections.*

5. Progress and Outcomes (7 of 7)

Environmental and Economic Assessment (TEA/LCA)

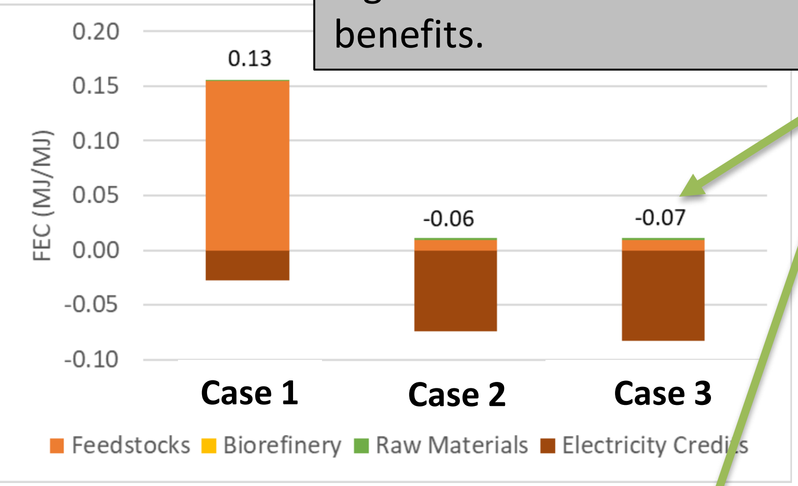
Challenge:

- Cost-competitive technology is needed to attract industrial interest
- Environmental benefits must be shown for "green premium," RINs, etc.

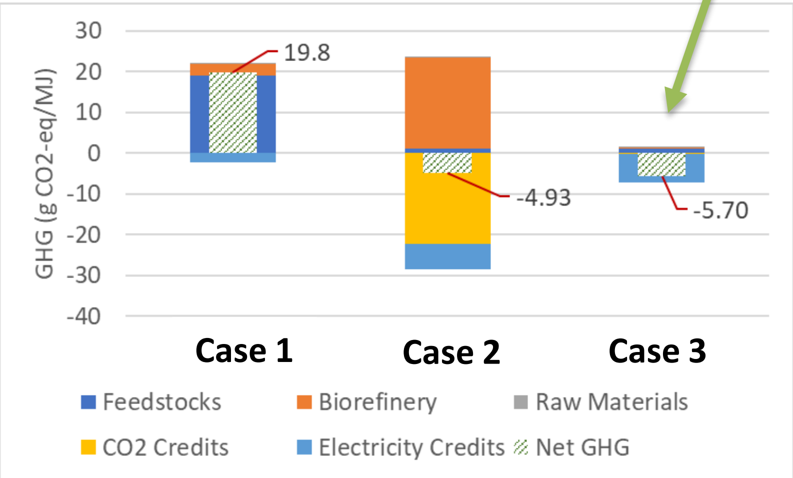
Progress:

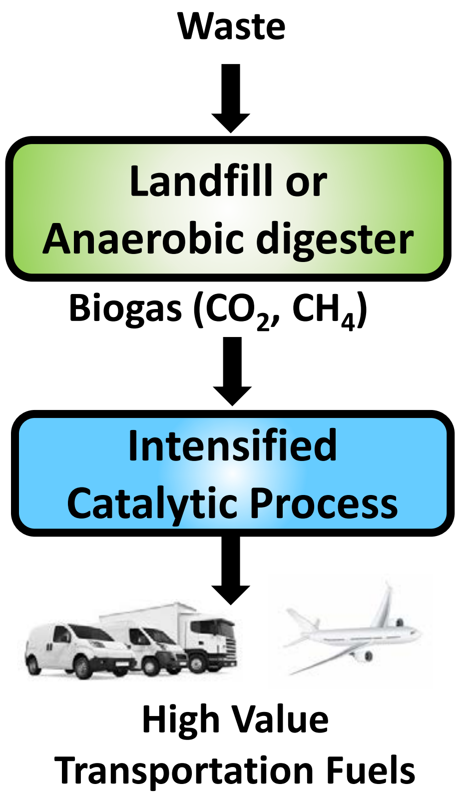
- Detailed TEA/LCA models developed
  - 700+ process and heat and work streams with ~400 process units (reactors, separators, etc.
  - Compare intensified landfill gas process to traditional process using natural gas or landfill gas
- ~10-20% **reduction in MFSP** ($3/GGE) using landfill gas in intensified vs. conventional process
- Utilization of landfill gas results in **net-negative greenhouse gas emissions** (GHGs) and **negative fossil energy consumption** (FEC)

Significant environmental benefits.



Negative fossil energy consumption and GHG emissions





Case 1: Conventional, natural gas; Case 2: Conventional, landfill gas; Case 3: Intensified, landfill gas

Summary

Goal: Develop catalysts and process to convert biogas into value-added fuels and chemicals, adding a diversified revenue stream to enable economic biofuels

-Target: 10% yield to C2+ by 2022 on bench-scale

-Status: 6% yield to C2+ on lab-scale using real biogas

1) Approach:

- Integrated, collaborative approach to multicomponent catalyst design for biogas upgrading to achieve value-added and diversified product distributions
- Develop catalytic materials by enhancing core function in spatially separated components

2) Technical accomplishments:

- Developed multicomponent catalysts with 2x improvement in C2+ yield over SOT
- Demonstrated 70+ hours of stable catalyst performance

3) Relevance to Bioenergy Industry

-Address critical challenges (adding value to biogas upgrading and improve yield of catalytic processes)

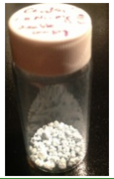
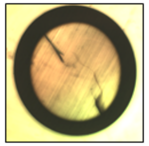
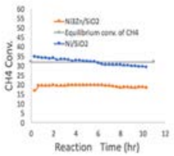
-Focus on BETO barriers and performance targets

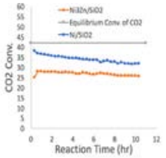
-Renewable, cost-competitive products are of interest to industrial partners (upstream and downstream) – diversify revenue streams

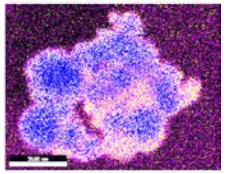
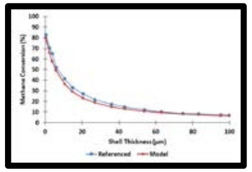
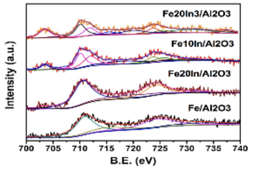
4) Future work:

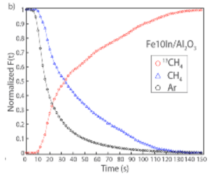
- Improve **C2+ yields** and determine **catalyst stability**
- **Scale-up** catalyst and biogas flow for bench-scale demonstration using LFG and **link data to TEA/LCA**

Biogas upgrading ⟷ Catalyst design to achieve high C2+ yields and $$$





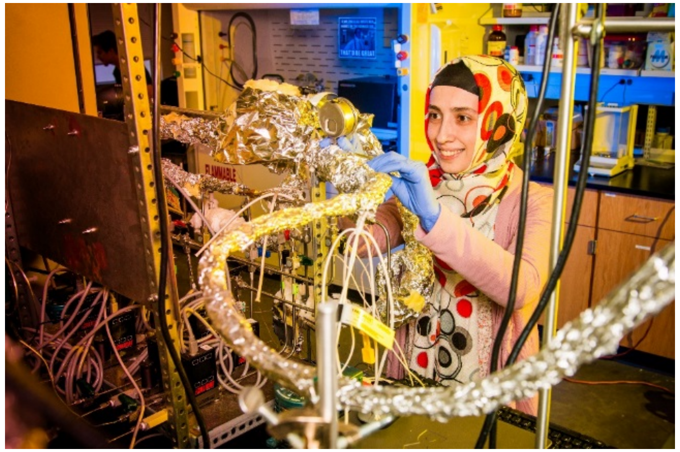
ACKNOWLEDGEMENTS

DOE BETO program
Trevor Smith, Nicole Fitzgerald, Seth Menter and the verification team

USF students and NREL staff

USF (internal SIP grant)

Industry/Municipality partners



DOE Bioenergy Technologies Office (BETO)
2021 Project Peer Review

Intensified Biogas Conversion to Value-added Fuels and Chemicals
WBS: 2.3.1.414

Friday, March 12, 2021

Conversion

PI: John N. Kuhn (USF)

co-PIs: Babu Joseph (USF) and Matt Yung (NREL)

UNIVERSITY OF SOUTH FLORIDA
A PREEMINENT RESEARCH UNIVERSITY

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

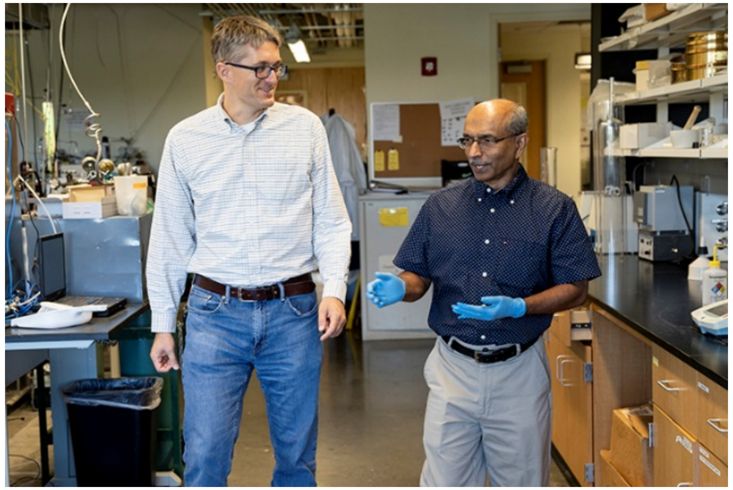
ChemCatBio
Chemical Catalysis for Bioenergy

2019 Peer Review

A poster was presented at the 2019 peer review. Comments were not received as this project had just started.

HIGHLIGHTS OF GO/NOGO POINTS

Verification passed , summer 2019



Scientific Output

Publications

Zhao, X., Joseph, B., Kuhn, J.N., and Ozkan, S., "Biogas reforming to syngas: a review" iScience 23 (2020) 101082. (DOI: 10.1016/j.isci.2020.101082)

Sokefun, Y.O., Joseph, B., and Kuhn, J.N., "Impact of Ni and Mg loadings on dry reforming performance of Pt/ceria-zirconia catalysts" Industrial & Engineering Chemistry Research 58 (2019) 9322-9330. (DOI: 10.1021/acs.iecr.9b01170)

Impact of structural changes from metal deposition method on the catalytic performance of Pt/ceria zirconia-based catalysts, in prep.

Tuning of the performance of Ru-Ni-Mg/Ceria-zirconia dry reforming catalysts through strategic reduction conditions and Ru loading, in prep.

Selective In-promoted Fe Catalyst for Syngas Conversion to Light Olefins, in prep.

Experimental and Modeling Study of Zeolite Encapsulated Ni/Mg Catalysts: Optimization of Shell Thickness for Reactant Selectivity in Hydrocarbon Steam Reforming, in prep.

Feasibility of intensified conversion of biogas to value added hydrocarbons, in prep.

Patents, Presentations, and Commercialization

Hinkley Center Solid Waste Research Colloquium Webinar Series
(https://swanafl.org/events/hinkley-center-solid-waste-research-colloquium-webinar-series/)

Frequent conference presentations /contributions
AICHE, ACS, ICC, NASCRE, NACS/NAM, NOBCChE, etc

Department Seminars
Various institutions
Also guest class lectures

IP
U.S. patent number 9,328,035
Record of Invention: ROI 20-141 at NREL

BFD of Intensified BTL Process