DOE Bioenergy Technologies Office (BETO)
2023 Project Peer Review

Intensified Biogas Conversion to Value-added Fuels and Chemicals

WBS: 2.3.1.414

Friday, April 7, 2023

Catalytic Upgrading Session

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UNIVERSITY OF SOUTH FLORIDA
A PREEMINENT RESEARCH UNIVERSITY

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

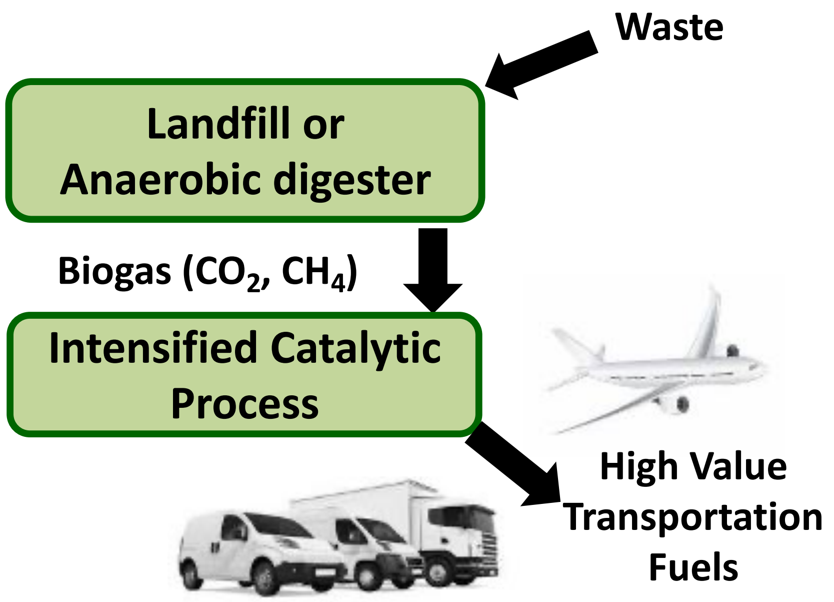
ChemCatBio
Chemical Catalysis for Bioenergy

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:

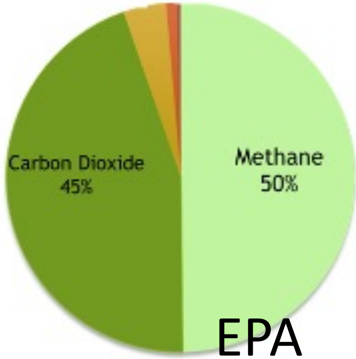
- **Intensified process** (catalyst and process)
- **Mild operating conditions** (moderate T, low P)
- **High value product** (high jet/diesel selectivity)
- **High carbon efficiency** to product
- **Demonstration** with industry partner, process gas

0. Overview
1. Approach
2. Progress and Outcomes
3. Impact

0. Overview

0. 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	$1.54 (~3 cents/kWh; retail to grid)	$2.88 (CNG) 3.63 (LNG)	$5.17 (diesel) 3.55 (propane)

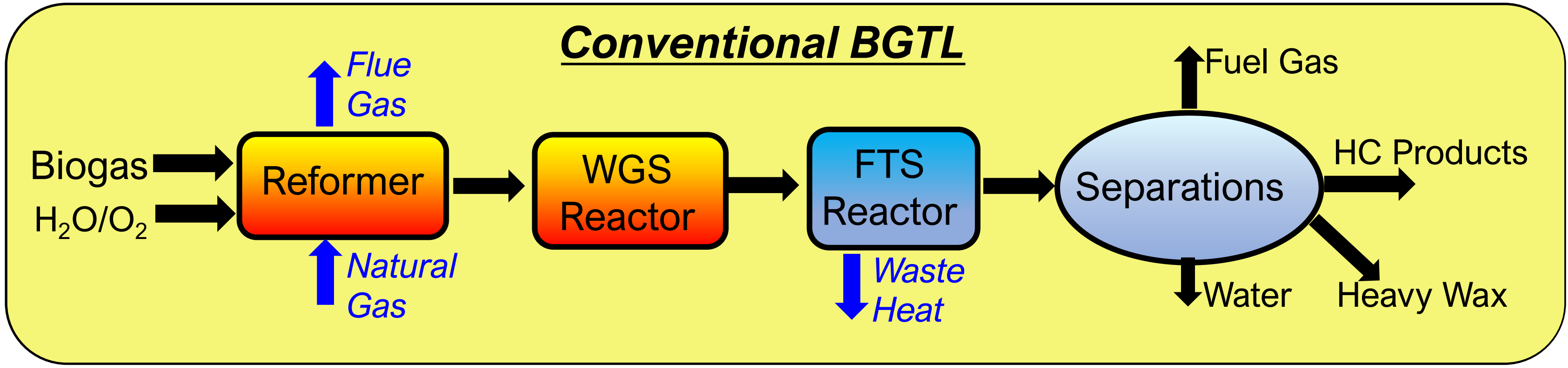
*Oct. 2022; https://afdc.energy.gov/fuels/prices.html

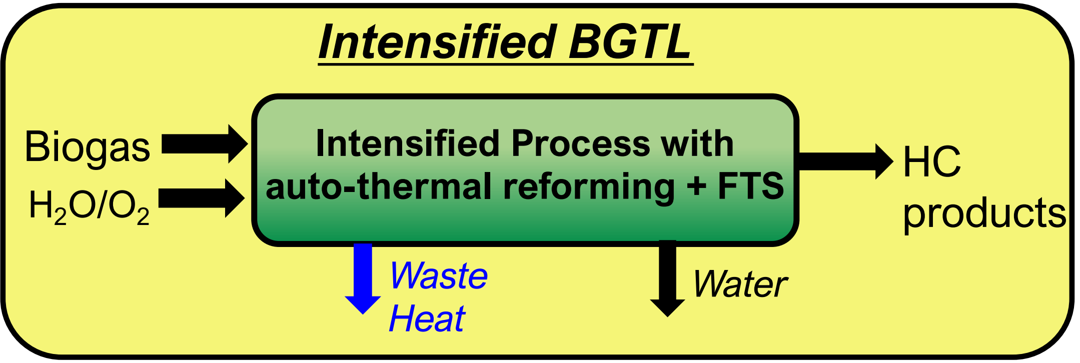
0. PROJECT OVERVIEW (2 OF 3)

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

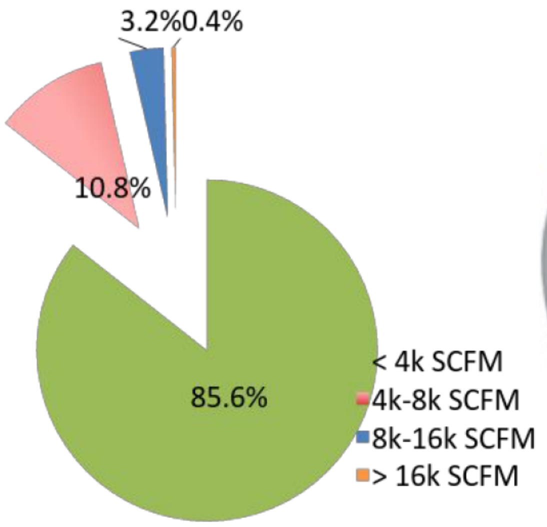
TriFTS™*:
- WGS removed via catalyst and process tuning
- Compressor and heat-exchanger are major costs

Intensified BGTL:
- Tune to small scale
- Mass and heat integration

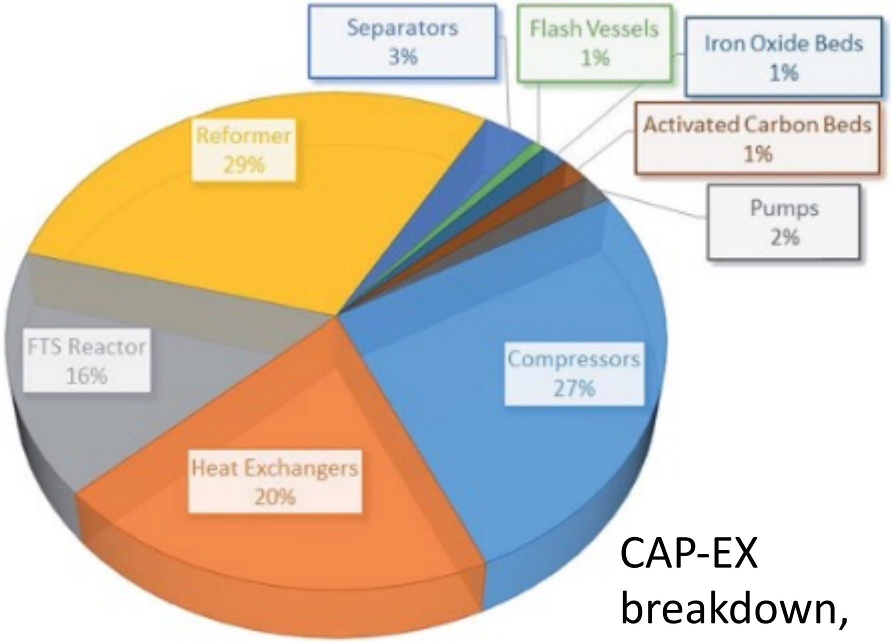




Landfill LFG Collection Rate



Often small scale



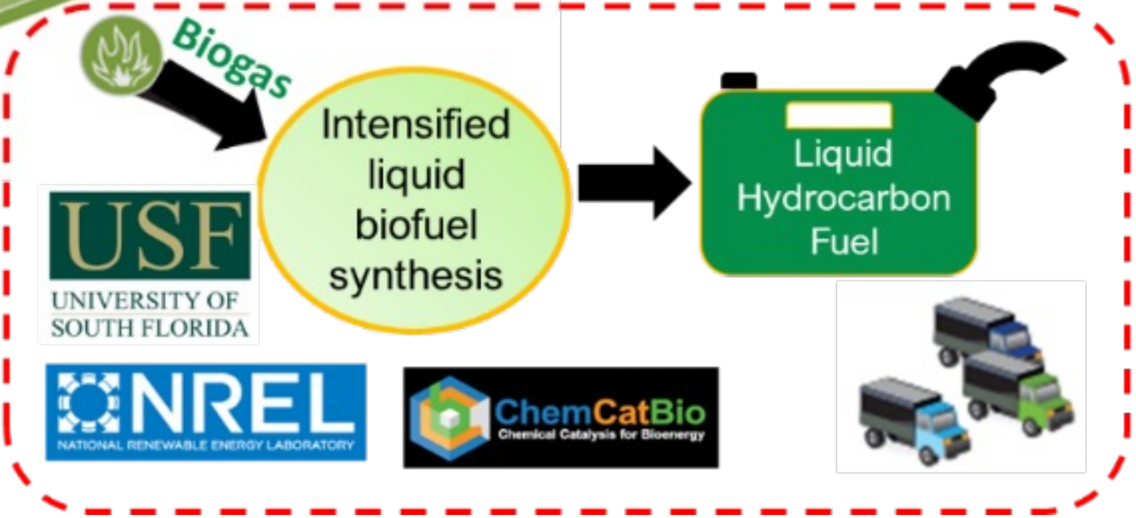
CAP-EX breakdown, TRiFTS™*

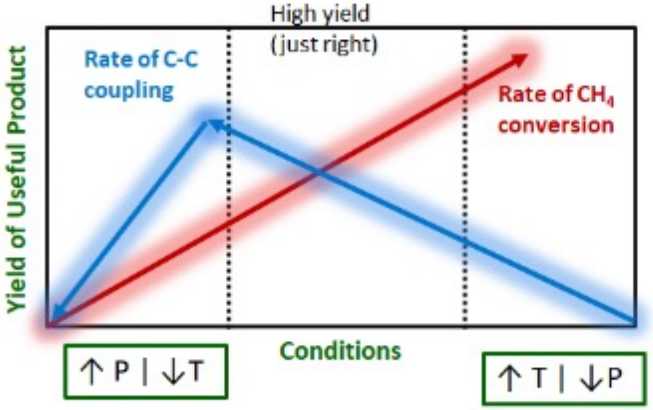
* T2CE led SDI project; USF COI, Zhao et al *Sust En Fuels* 2019

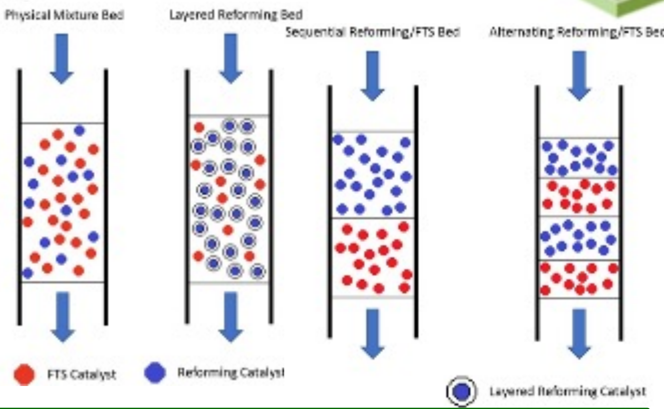
Biogas to liquid fuel via intensified catalytic synthesis

Landfill diversion of organic waste

Focus of proposed research







Catalyst system optimization and catalyst/bed configurations

0. Overview

1. Approach

2. Progress and Outcomes

3. Impact

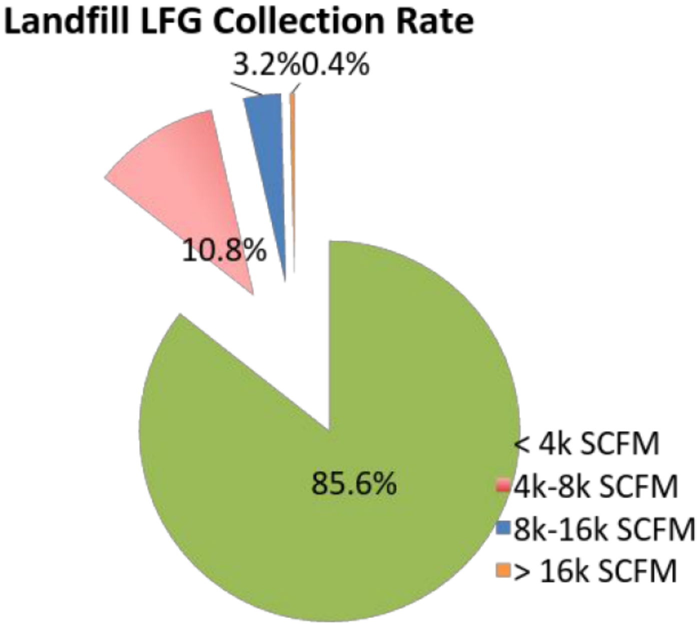
1. Approach

1. Approach (1 of 6)

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

1. Approach (2 of 6)

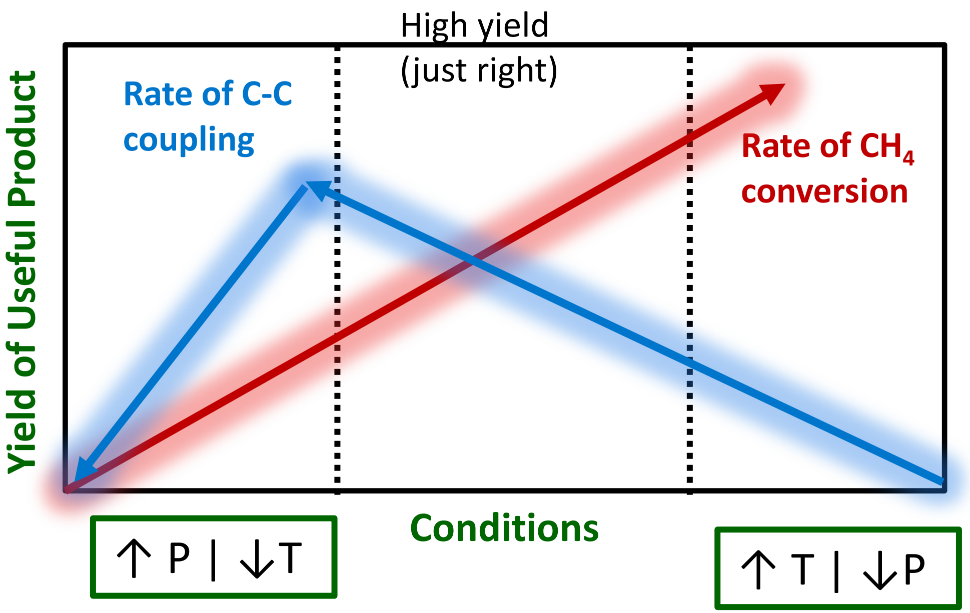
Tailor catalysts with varying functionality under similar conditions:

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

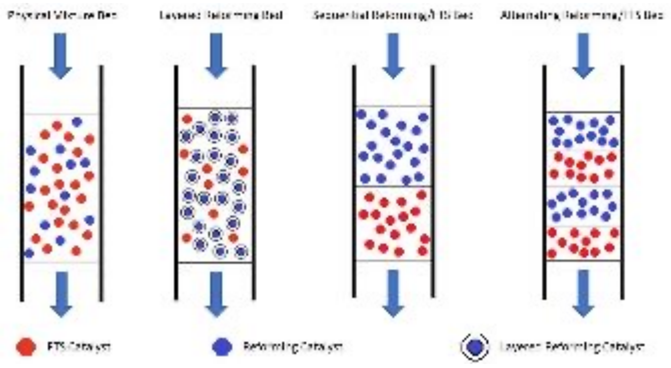
(2) In-situ separation

Important for upgrading to value-added chemical production

1. Catalytic activity

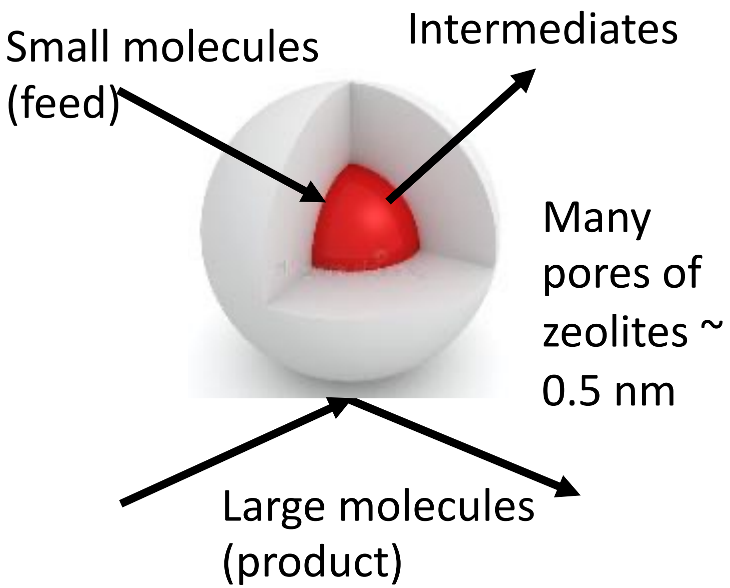


2. No separations/ Compression between beds



Novelty: Configuration arrangement predictions

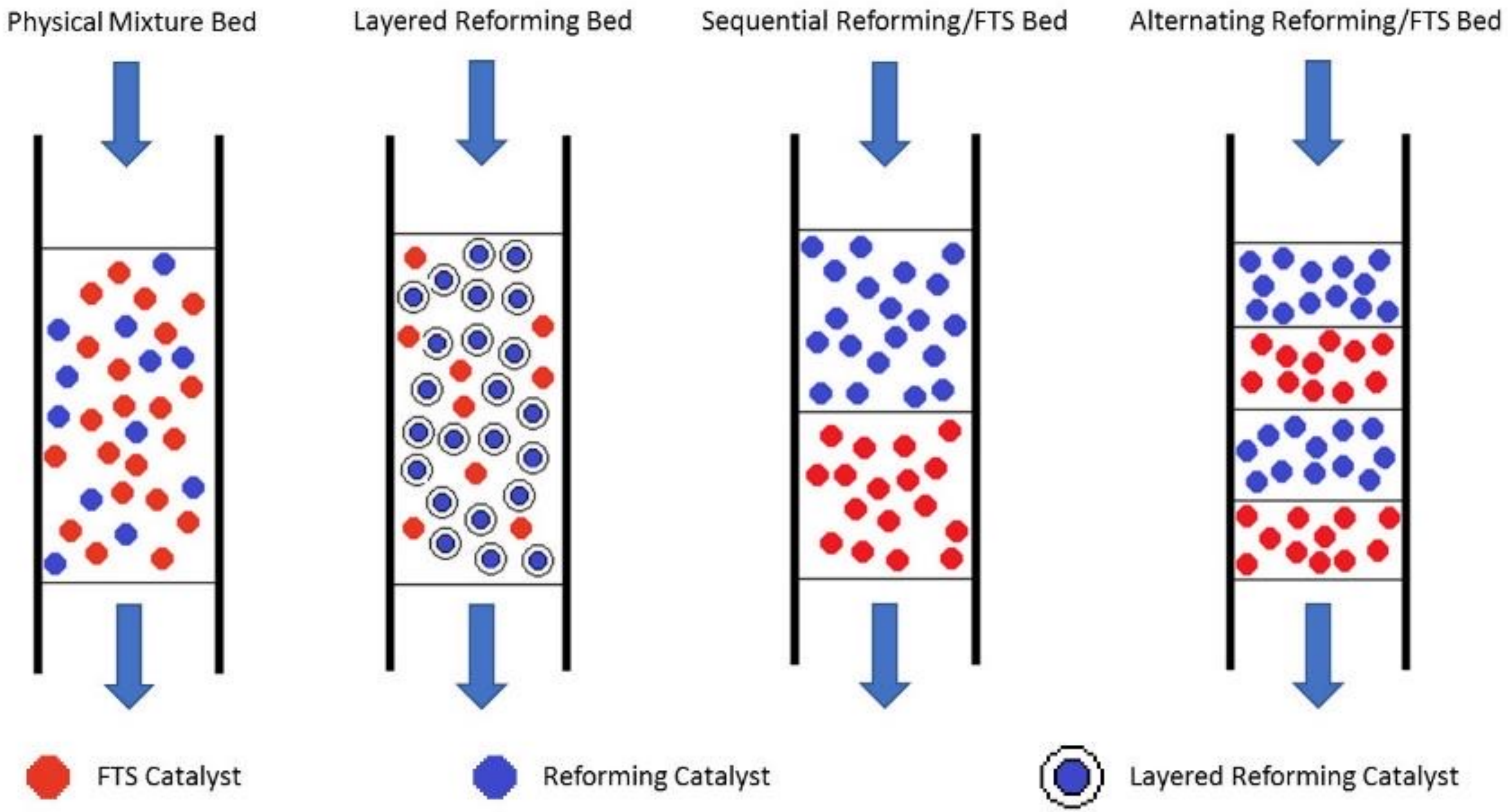
2. In-situ separation



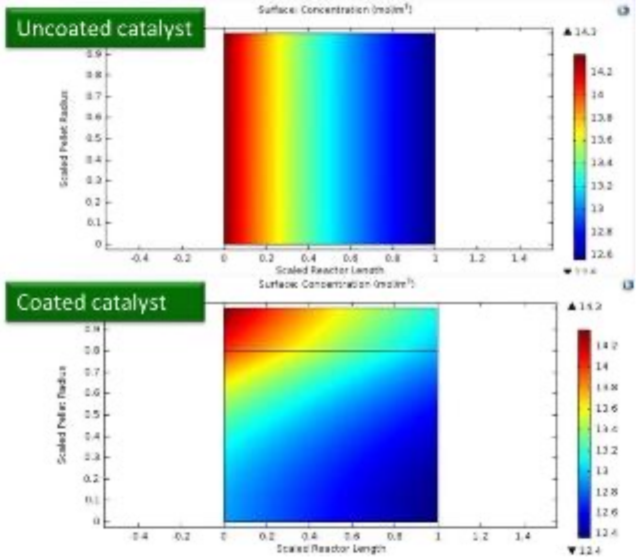
1. Approach (3 of 6)

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



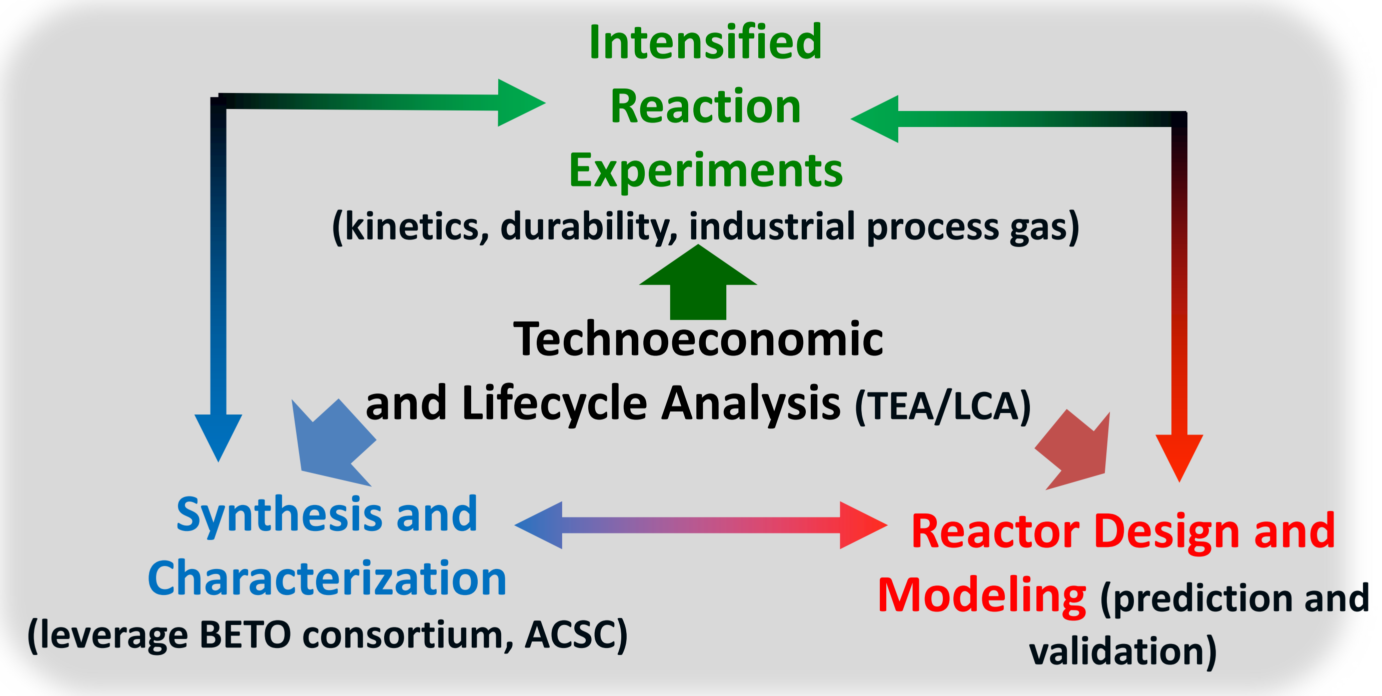
1. Approach (4 of 6)

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.

1. Approach (5 of 6)

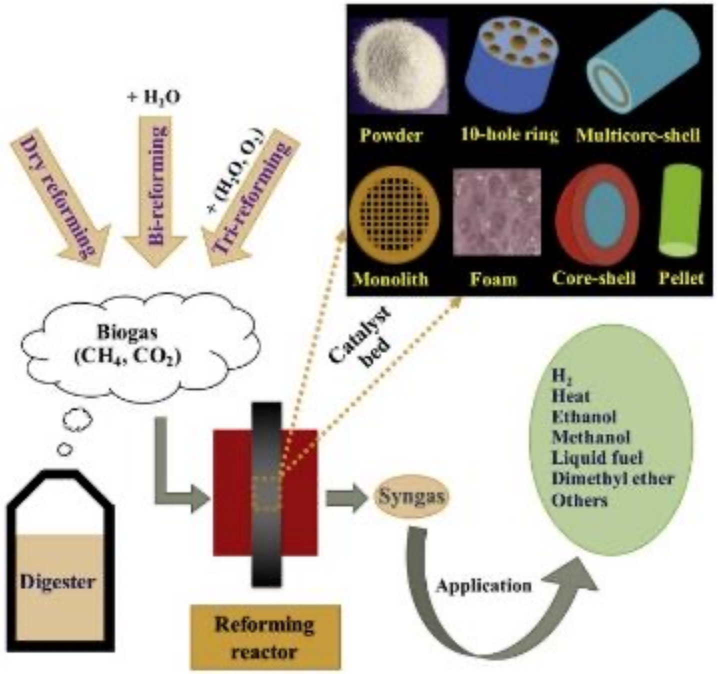
Go/No-Go – Focused on critical success factor – C2+ hydrocarbons :
"Demonstrate ≥10% yield of C2+ hydrocarbons on lab-scale…" in 2021
***(Already achieved 16% hydrocarbon yield on lab-scale with real biogas, up from 3%)**

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 DOE Investments–
Collaborate and leverage core competencies of NREL and BETO's ChemCatBio consortia for catalyst characterization (ACSC), and TEA/LCA, as well as other DOE facilities and expertise

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

1. APPROACH (6 OF 6)

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

- Catalyst selection for yield improvements
- Catalyst cost considerations (eliminate PMG metals and rare elements/precursors)
- Modeling predictions to justify experimental changes

Process Economics

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

Underlines and bullets indicate mitigation occurrences

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

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)

Biogas compression and filling unit (BRC FuelMaker).

Landfill gas cylinders at labs for reaction testing.

2. Progress and Outcomes

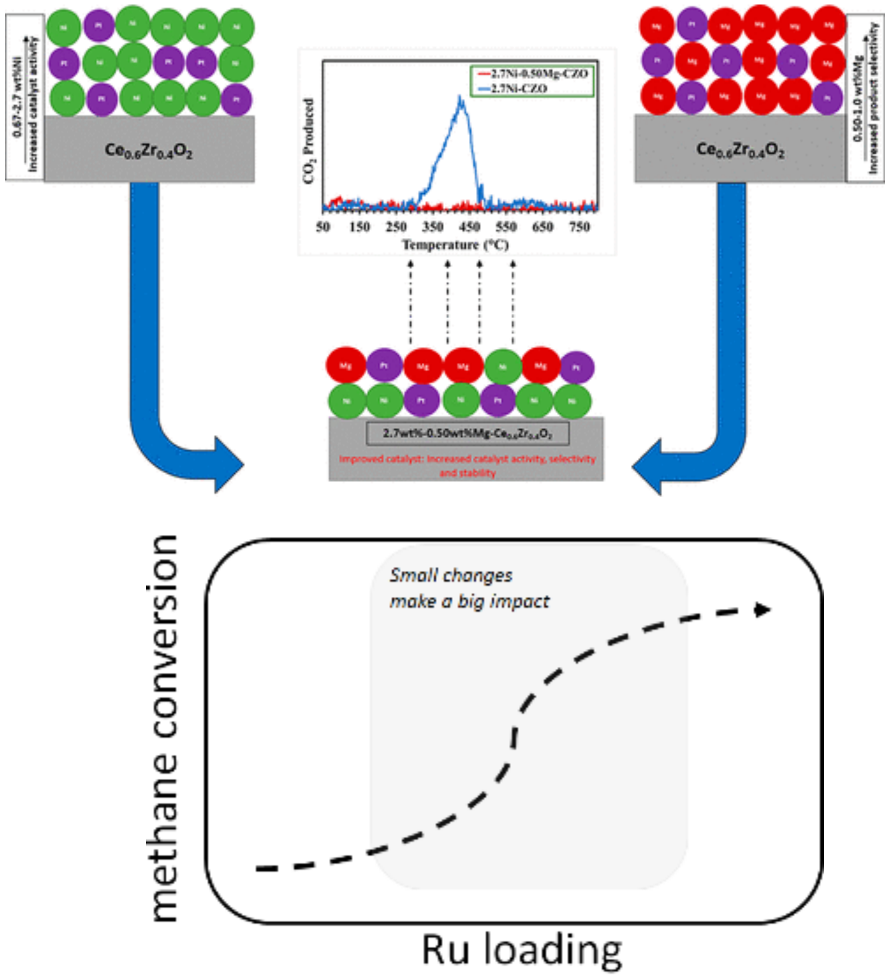
2. Progress and Outcomes: (1 of 14)

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

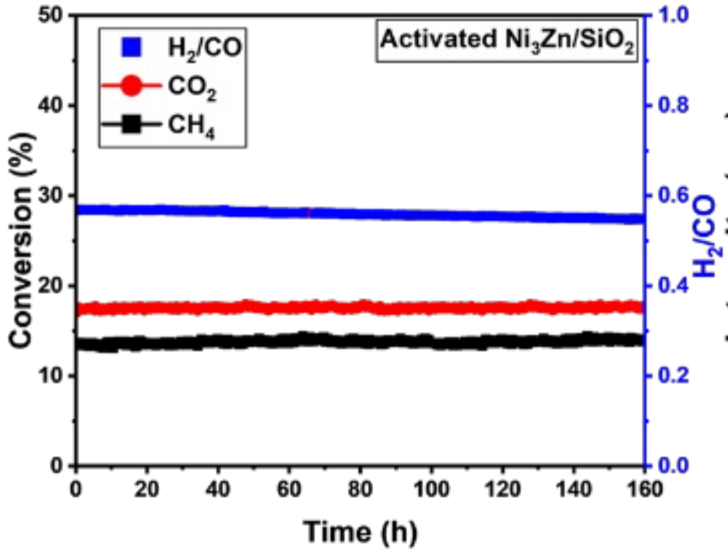
Selectivity:
- H_2: CO ratio tuned ~ 2 for optimal Fischer-Tropsch synthesis by feeding steam

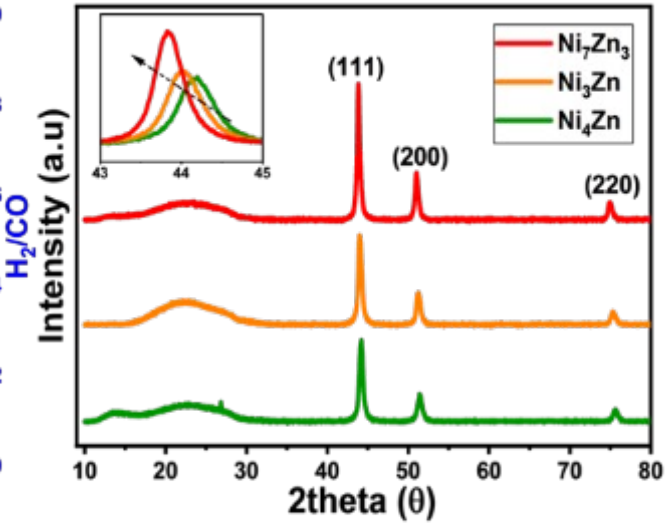
Stability:
- No CO_2 formed during TPO after ~ 100+ hr TOS (T = 450 °C)
- Coking rate < 4.4E-6 g-C/g-cat/h

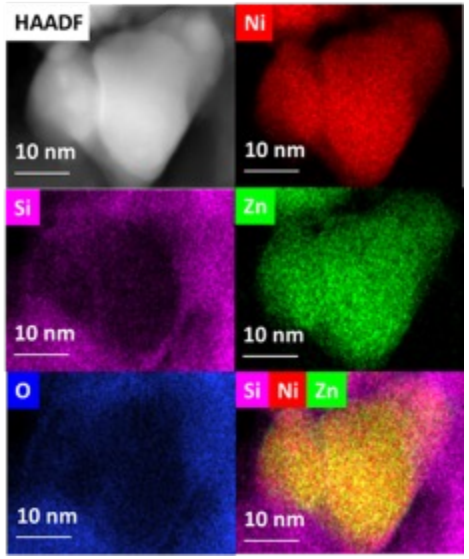
Elsayed, Kuhn et al.: *Cat Lett 2018; Top Cat 2017; Appl Cat B* 2015 – Sokefun, Kuhn at al: *IECR* 2019 , *Appl Cat A* 2021

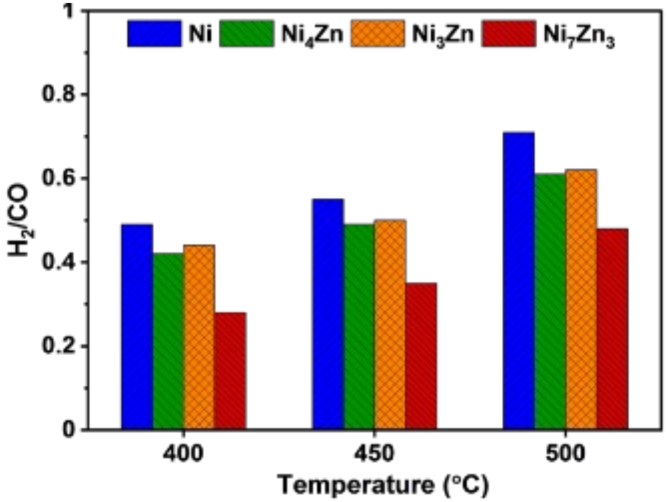
2. Progress and Outcomes (2 of 14)

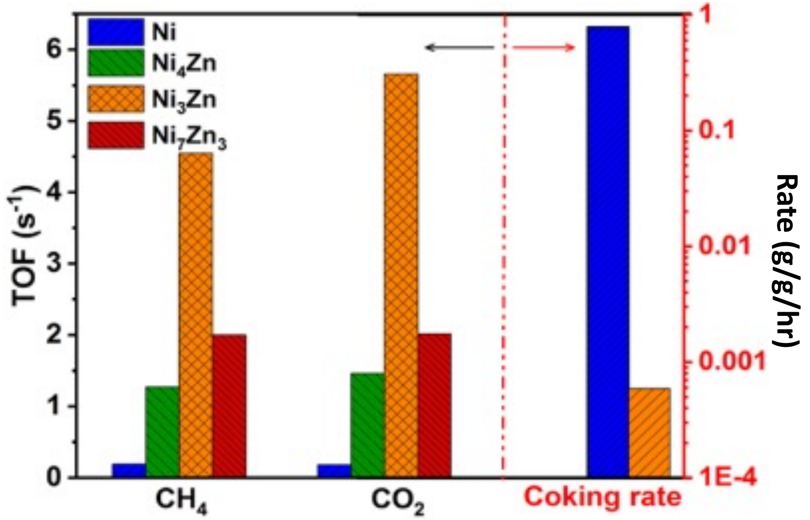
Precious metal free catalysts









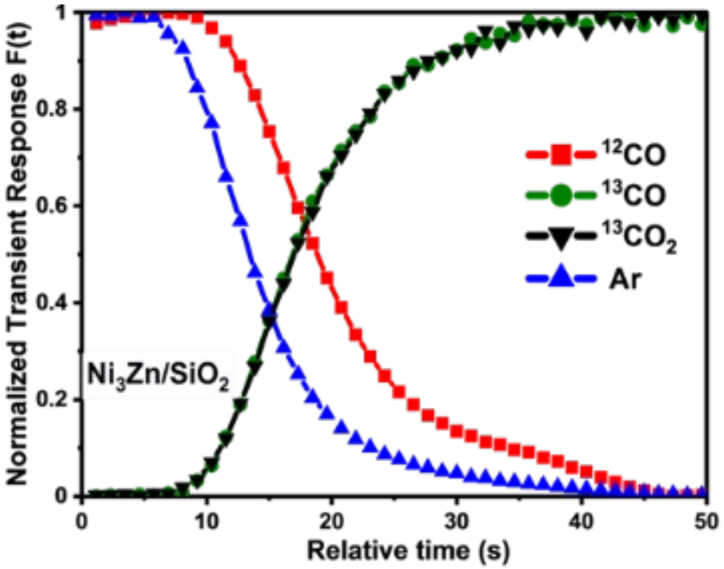


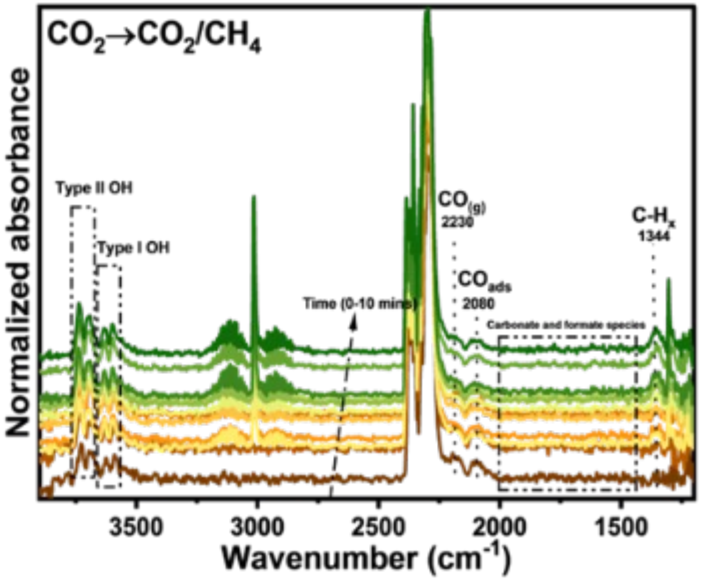
Catalyst advances:

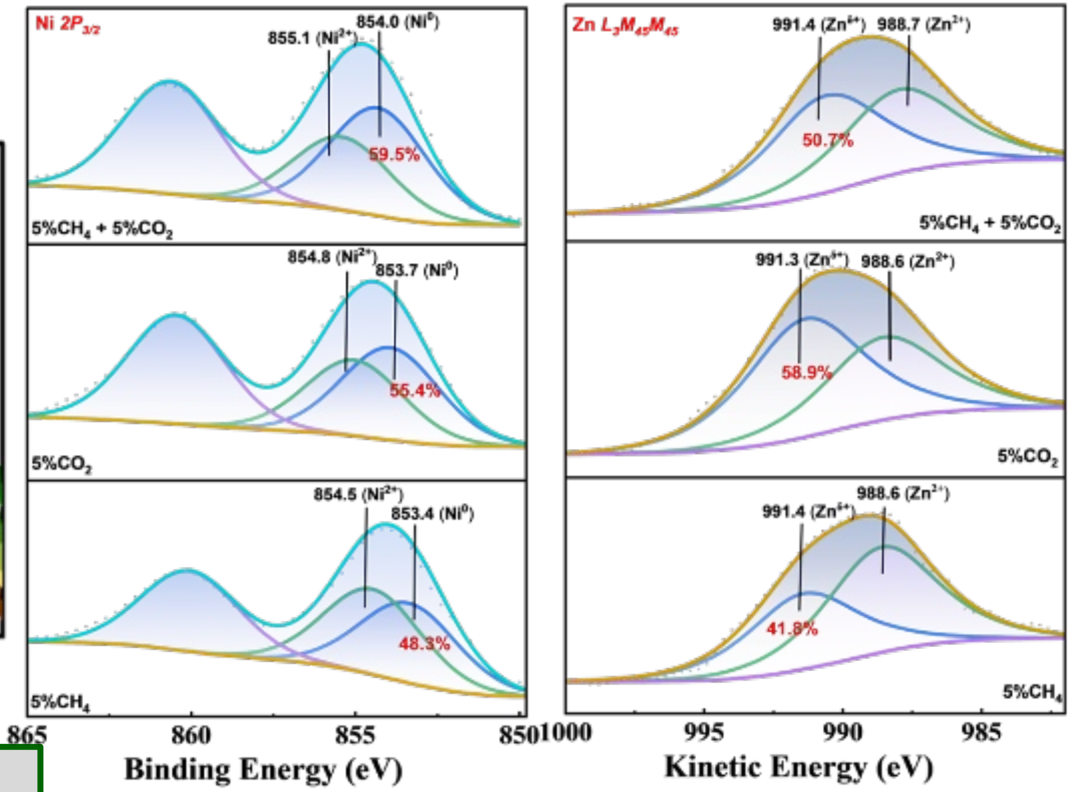
- Ni-Zn intermetallic compounds show high performance and stability for methane activation
- Dry reforming used as a harsh model reaction
- Results suggest Zn allows control of Ni reactivity at the surface
- Coking rate lowered by ~ 4 orders of magnitude compared to a Zn-free supported Ni catalysts

2. Progress and Outcomes (3 of 14)

Precious metal free catalysts

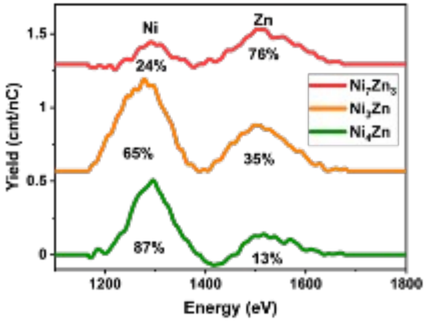




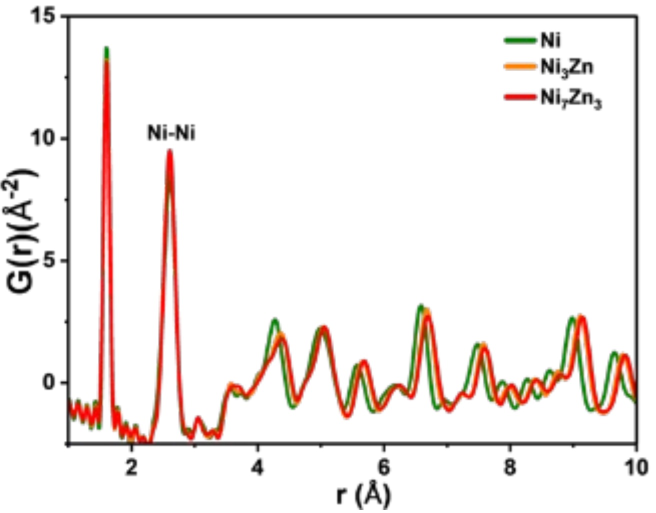


Mechanistic understanding:

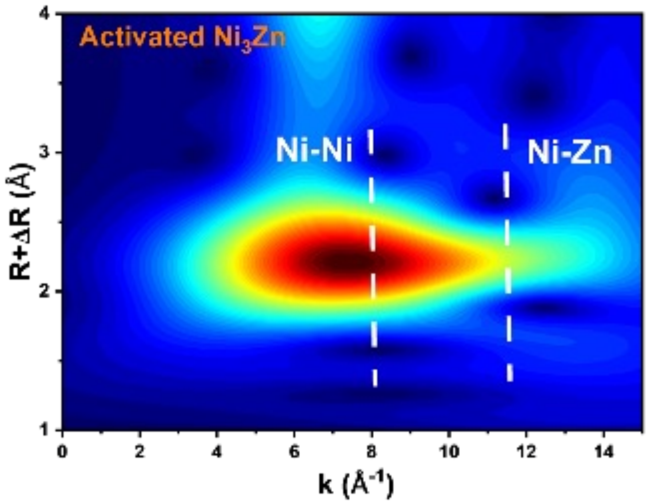
- Steady-state, isotopic transient kinetic analysis probes surface residence times
- IR (DRIFTS) and XPS used to correlate surface species to performance and environment
- Ion scattering used to determine top surface layer composition (LEIS)

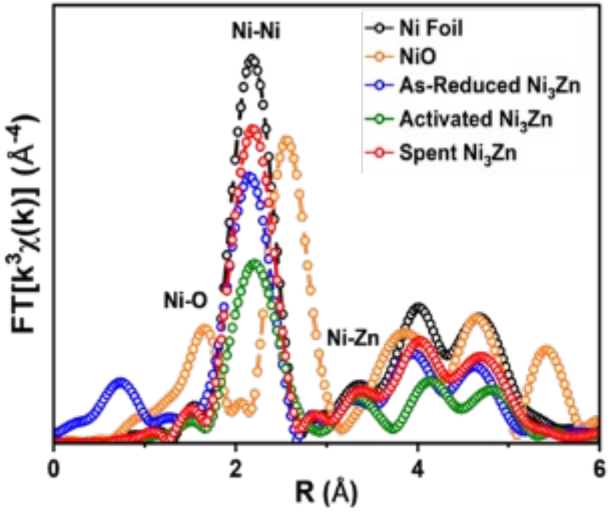


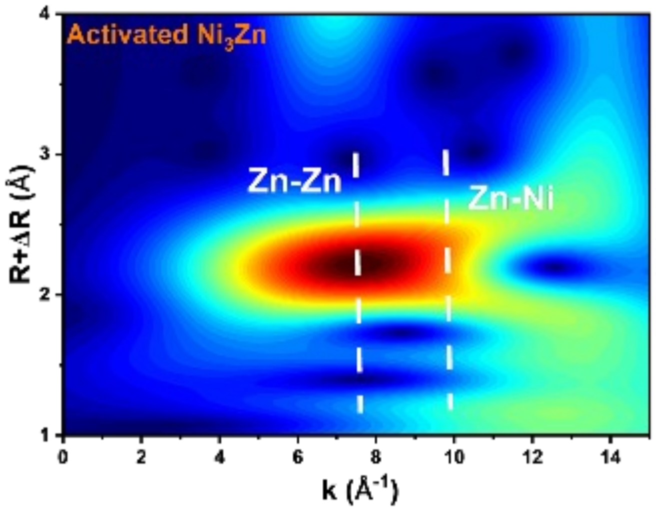
2. Progress and Outcomes (3 of 14)

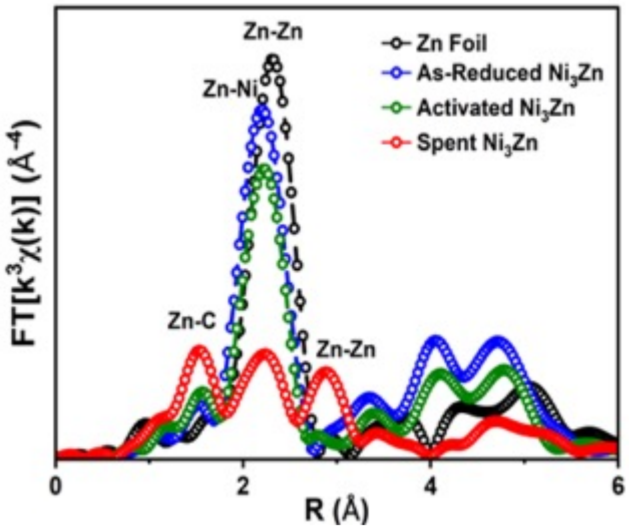


Sample	Ni^0 (%)	Ni^{2+} (%)
Reduced	88	12
Activated	91.6	8.4
Spent	92.2	7.8







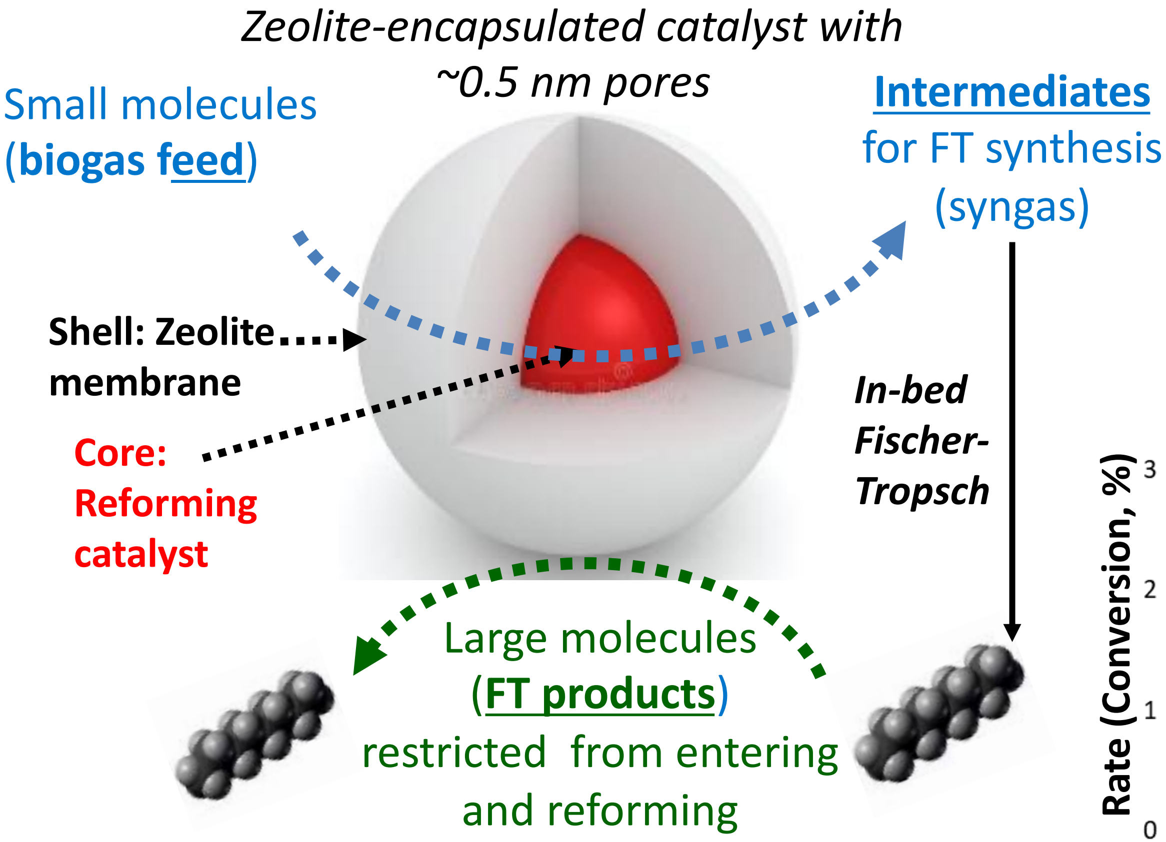


Mechanistic understanding:
(leverage unique DOE resources)

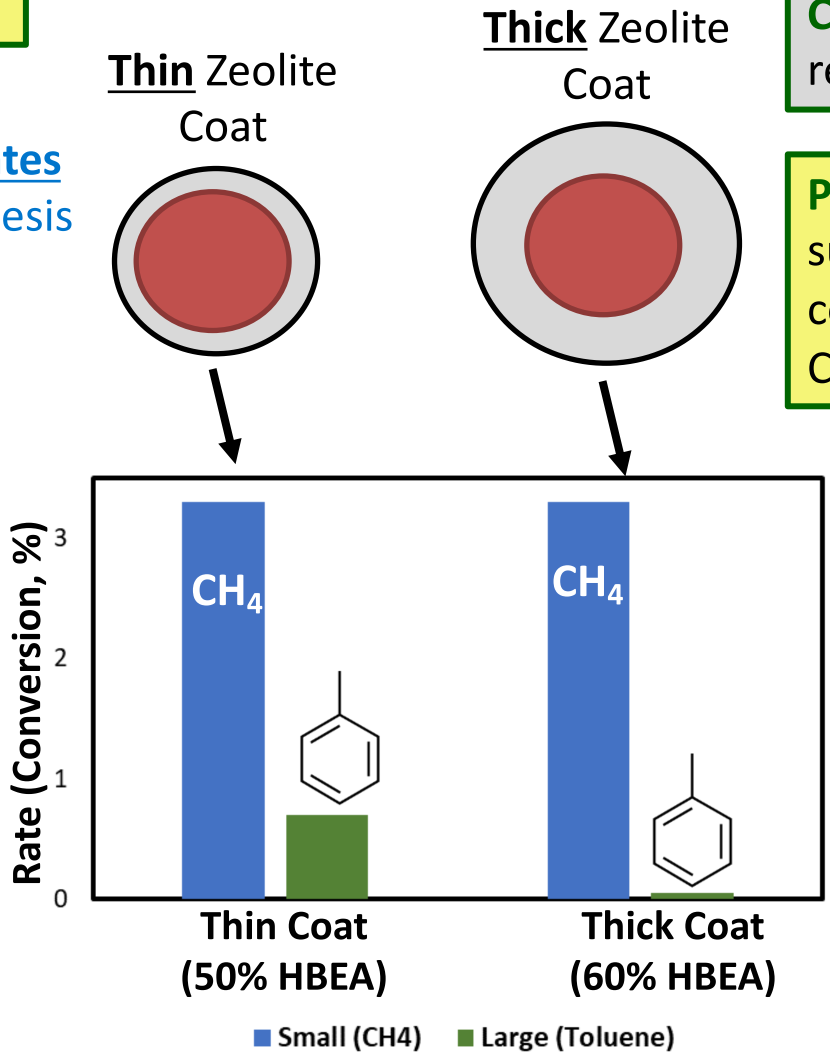
- EXAFS/XANES identifies unique local bonding
  - Ni-Zn, Zn-Ni, and Zn-C
  - Metallic Ni amount increased with use
- Neutron scattering detects long range order

2. Progress and Outcomes (4 of 14)

Reforming CH_4 without reforming fuel products

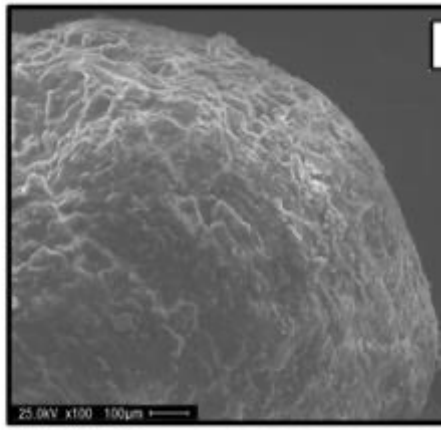


Demonstrated that intensified, single-reactor process with coated catalyst can be successful.



Challenge: FT products could react on reforming catalyst

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

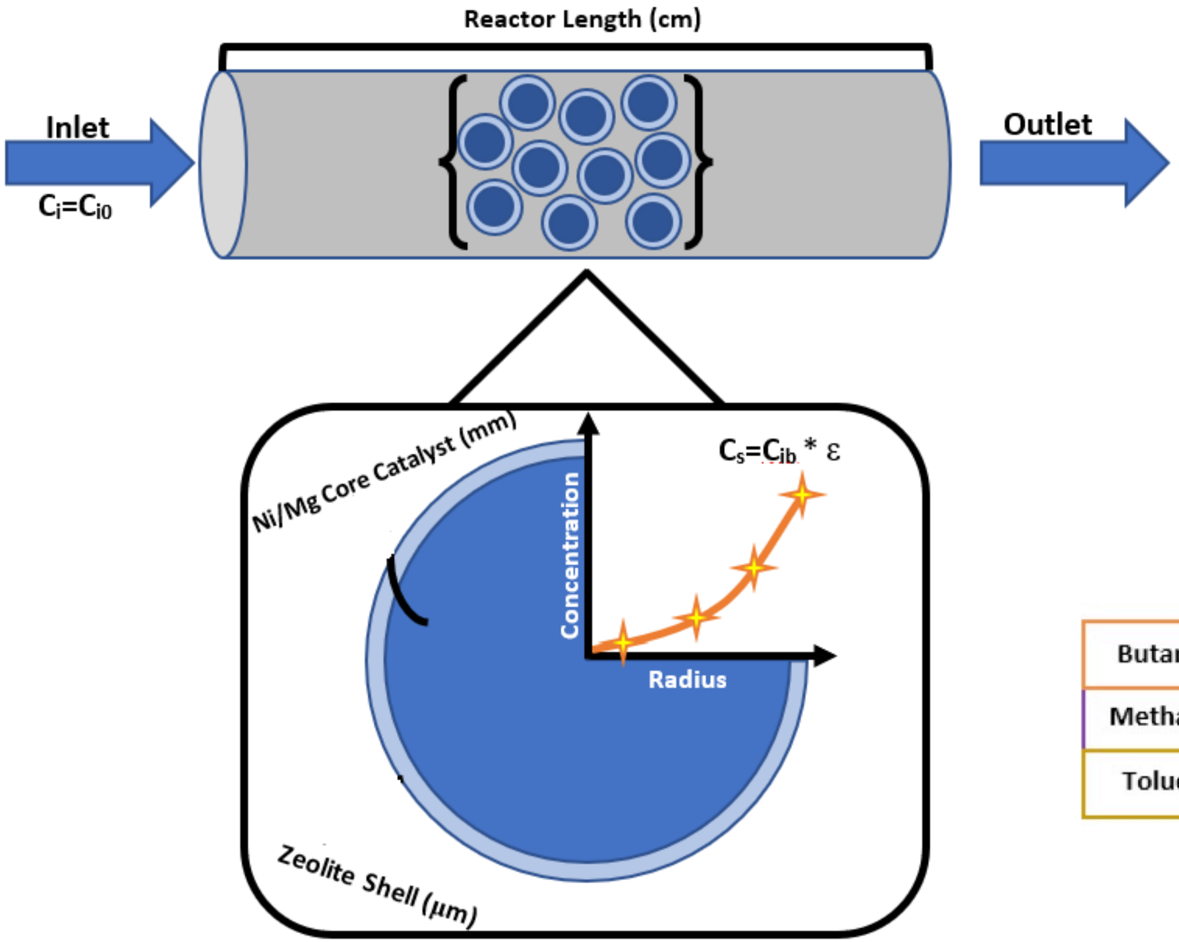


SEM image of zeolite-coated reforming catalyst

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

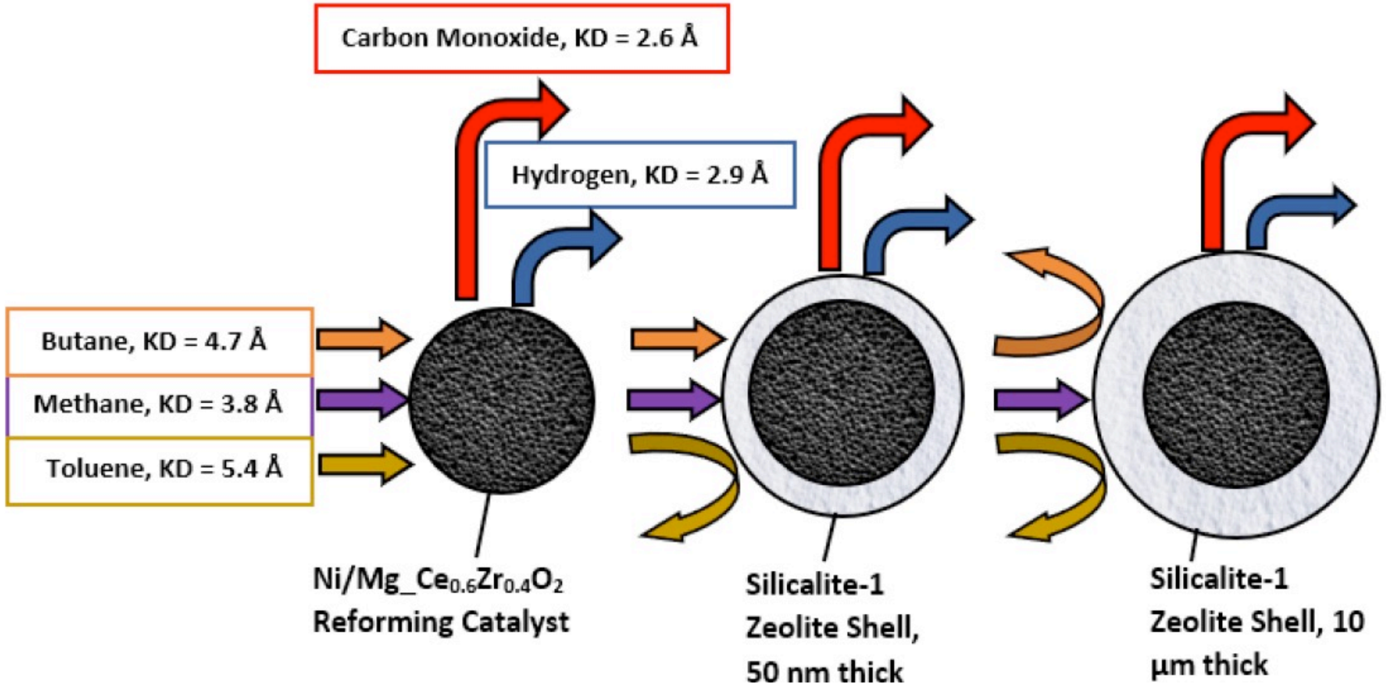
2. Progress and Outcomes (5 of 14)

Reforming CH_4 without reforming fuel products



Modeling and Simulations:

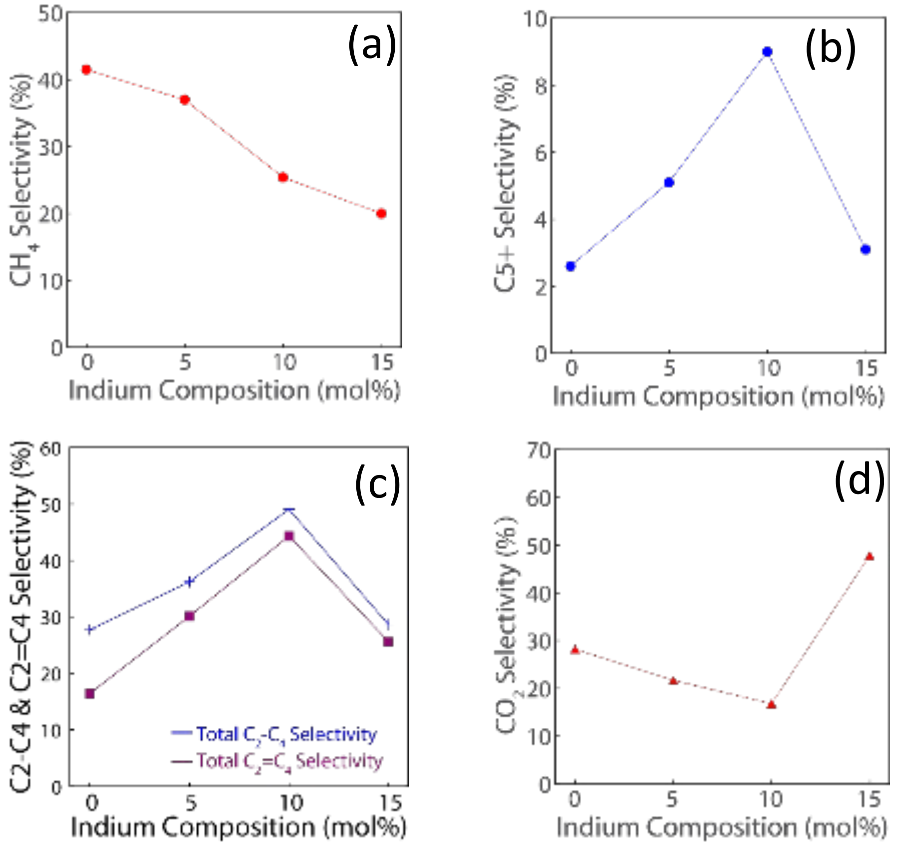
- Develop separate models for the reforming and FTS reactors using composite catalysts and examine variability
- Combine reforming and FTS catalysts in single reactor to optimize the intensified reactor in terms of bed packing and shell thickness



Gray, Kuhn et al, *Chemical Engineering Journal* 2022

High temperature C-C coupling: FTS

Selectivity study as a function of Fe:In loading



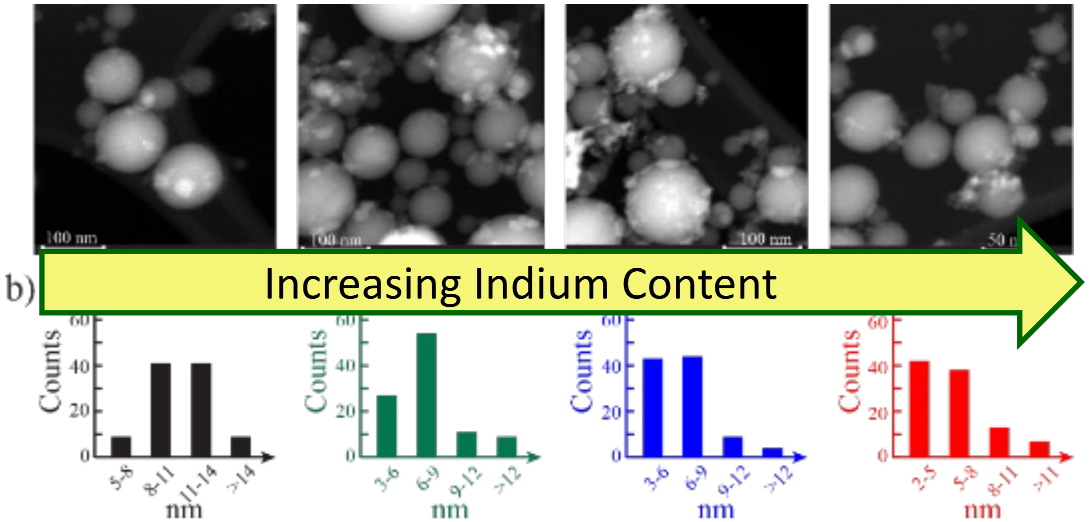
CO conversion was kept at ~10%

Challenge:

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

Progress:

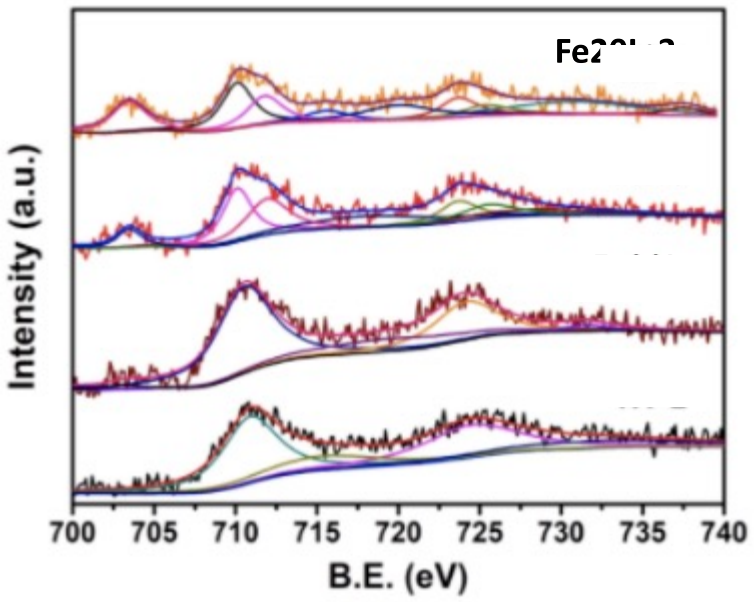
- Iterative reaction testing and characterization improved Fischer-Tropsch catalyst
- Indium promoting ↑Fe dispersion, and limits undesired CH_4 and CO_2 formation; optimal dopant ratio of 10:1 Fe:In of test matrix



Metal dispersion increases with increasing In (indium) content

2. PROGRESS AND OUTCOMES (7 OF 14)

XPS over the post-reaction catalysts

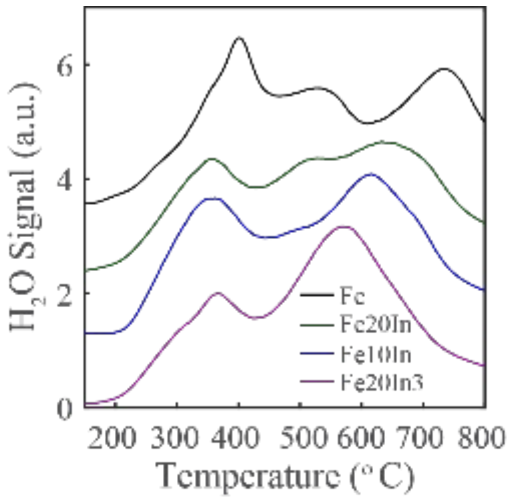


XPS analysis:

- 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

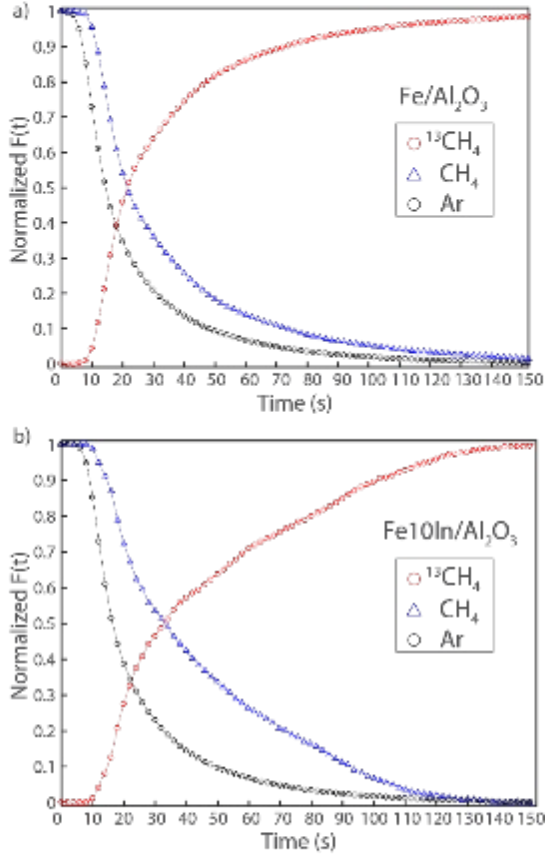
In promotes reducibility (TPR)

Isotopic Exchange Experiments

Surface residence time of CHx:

Fe/Al_2O_3: 7.0 s

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

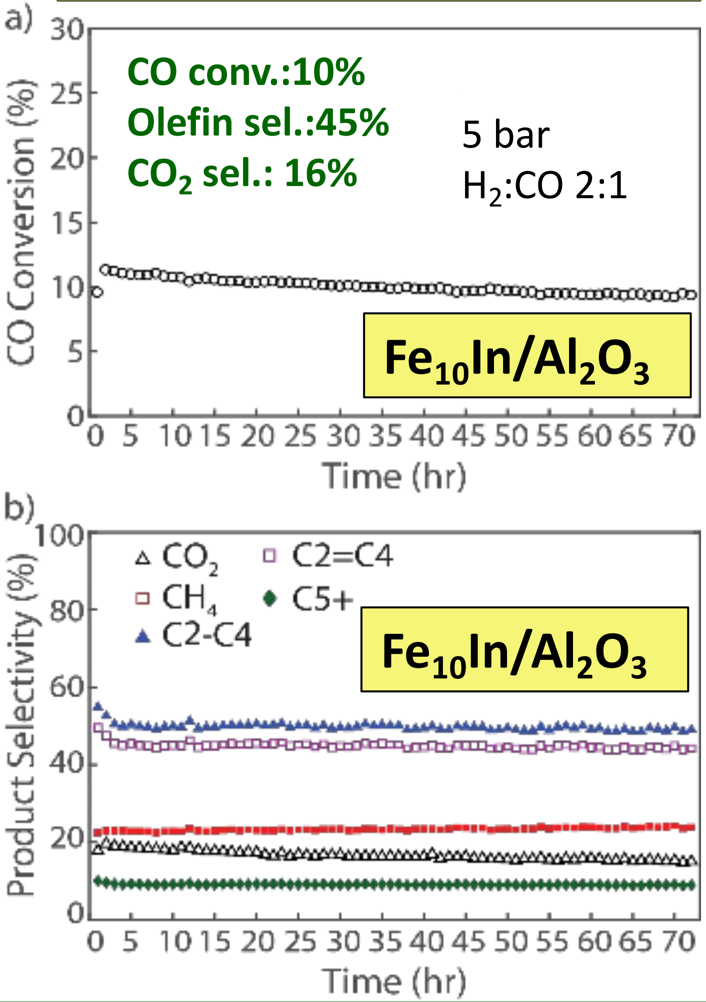


Challenge:

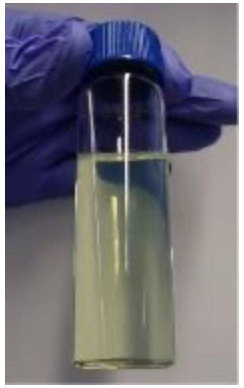
- Fischer-Tropsch synthesis (FTS) at high temp. limits molecule size (chain length)
- Stability can be challenging at high temperature (>400°C)

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



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

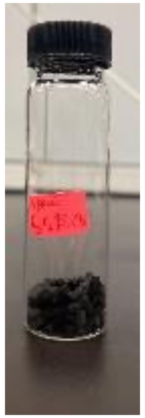
2. PROGRESS AND OUTCOMES (9 OF 14)

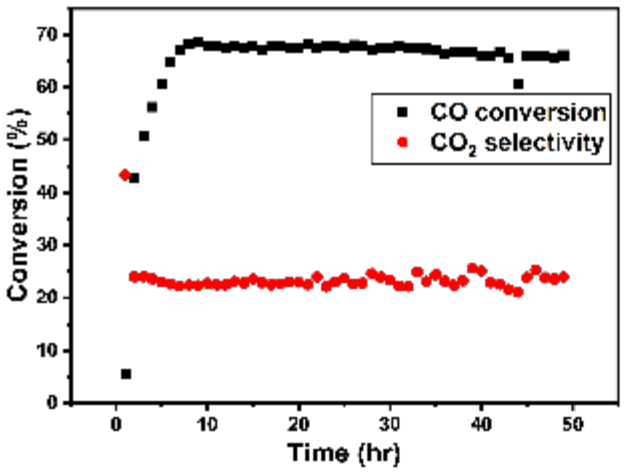
High temperature C-C coupling

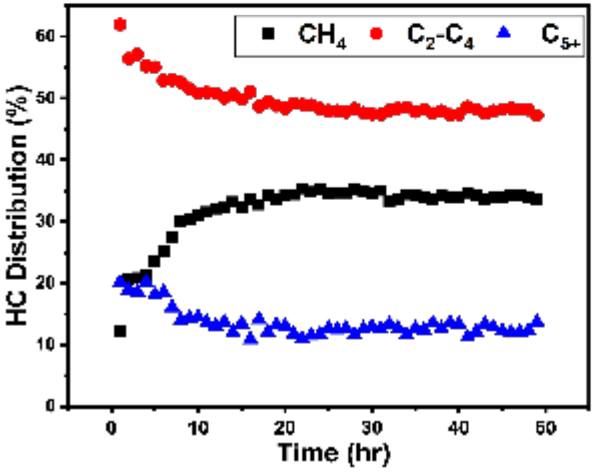
Catalyst	X_{CO} (%)	S_{CO2} (%)	HC Distribution			O/P	α
			S_{CH4} (%)	S_{C2-C4} (%)	S_{C5+} (%)		
Fe/SiO_2	11	21	48	50	2	1.8	0.48
$Fe_{20}K/SiO_2$	64	27	54	42	4	1.2	0.50
$Fe_{10}K/SiO_2$	73	25	56	41	3	1.2	0.49
Fe_5K/SiO_2	74	28	47	47	6	1.3	0.53
Fe_5K_2/SiO_2	72	30	39	50	11	2.3	0.56
" (T=350 °C)	50	30	29	51	20	5.9	0.57
" (T=300 °C)	24	31	25	54	21	9.1	0.57
" (H_2:CO = 1.5)	89	28	24	52	24	3.8	0.63

Progress:

- Selectivity and stability were acceptable for Fe-In catalysts, but activity was low
- Revisited literature and experimental screening to identify Fe-K among others
- K improved both CO conversion and C5+ selectivity

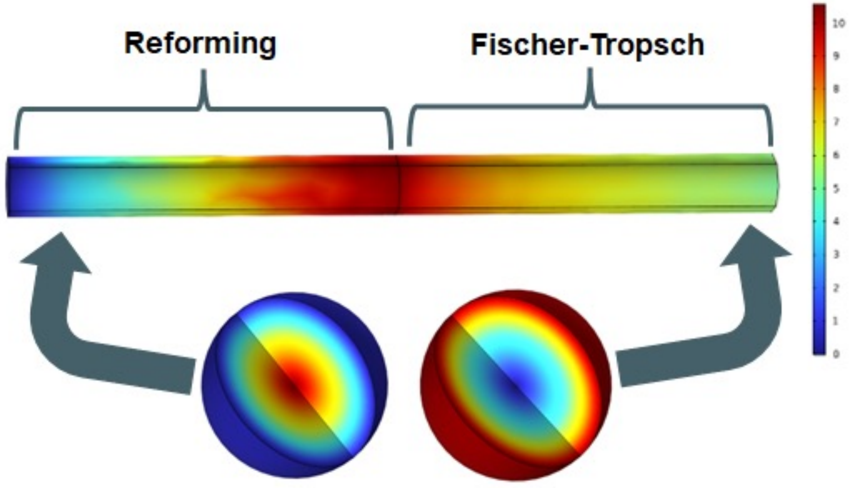






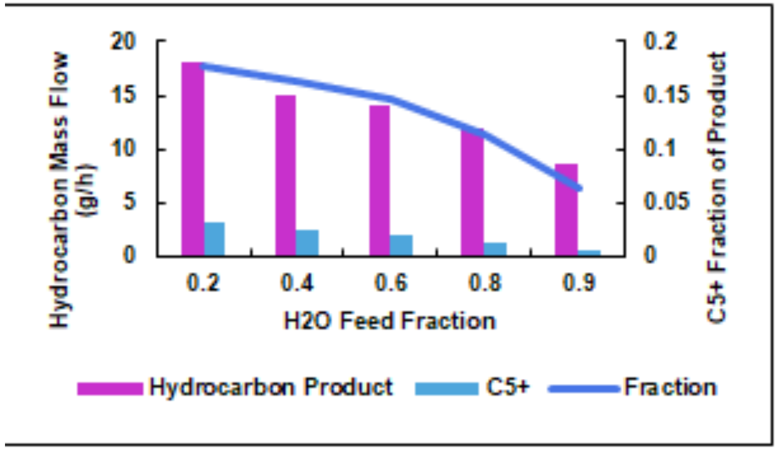
2. PROGRESS AND OUTCOMES (11 OF 14)

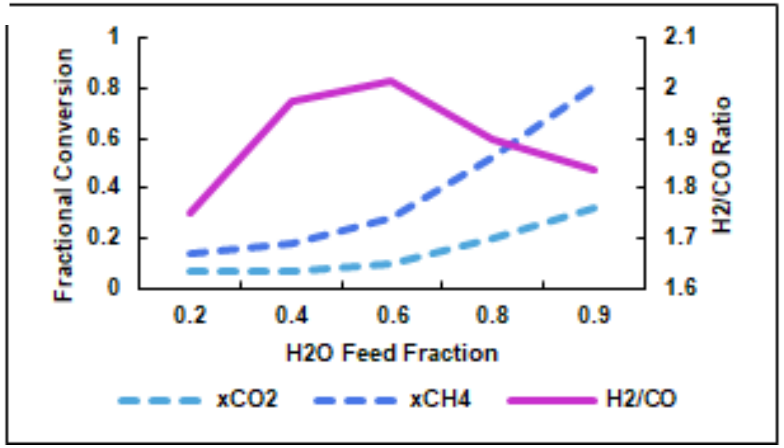
Simulation predictions – Analysis of Feed Composition



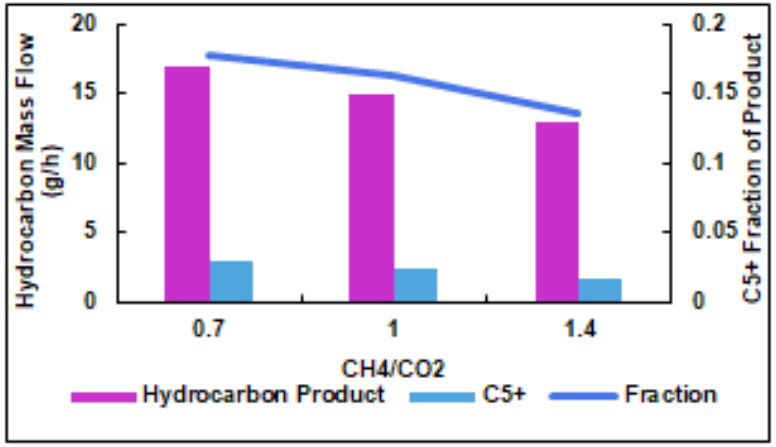
Concentration of carbon monoxide, bulk and pellet scale

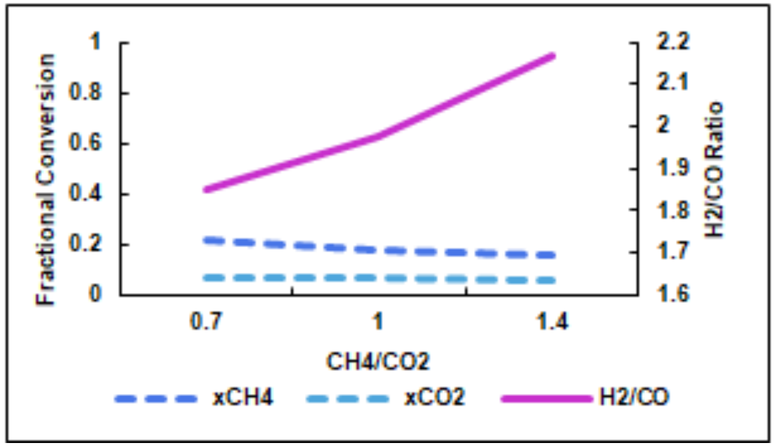
Fraction of H_2O – Impact on Product





$CH_4:CO_2$ Ratio – Impact on Product



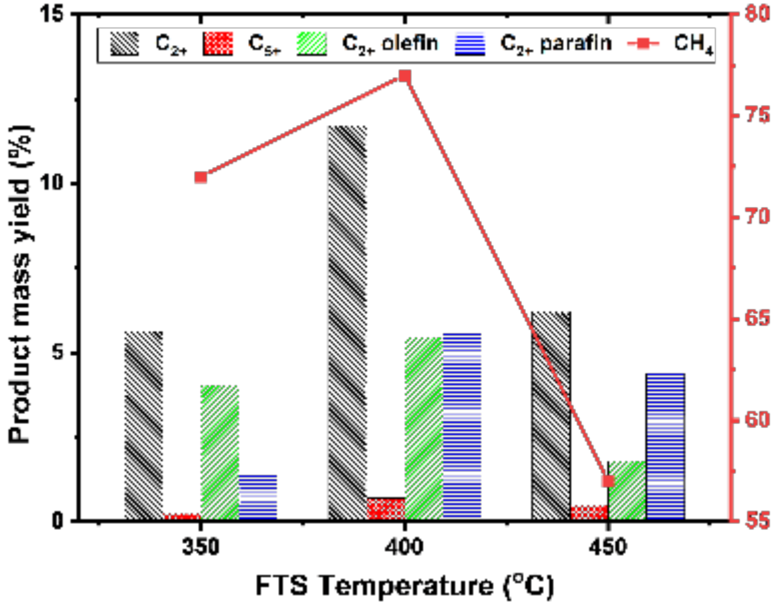


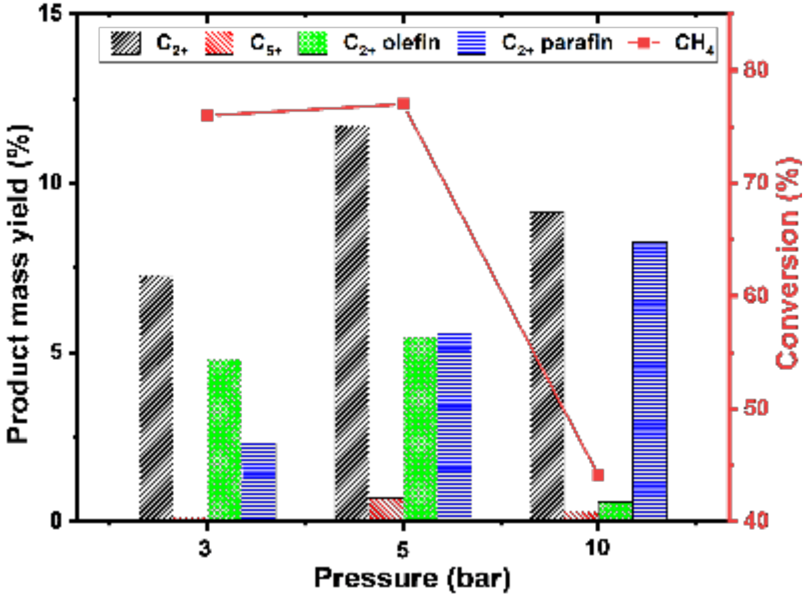
Stacked bed reactor modeling
(*left*) Steam enhances conversion but deters hydrocarbon formation
(*right*) CH_4:CO_2 ratio in biogas impacts performance. Real biogas samples ~ 1.4

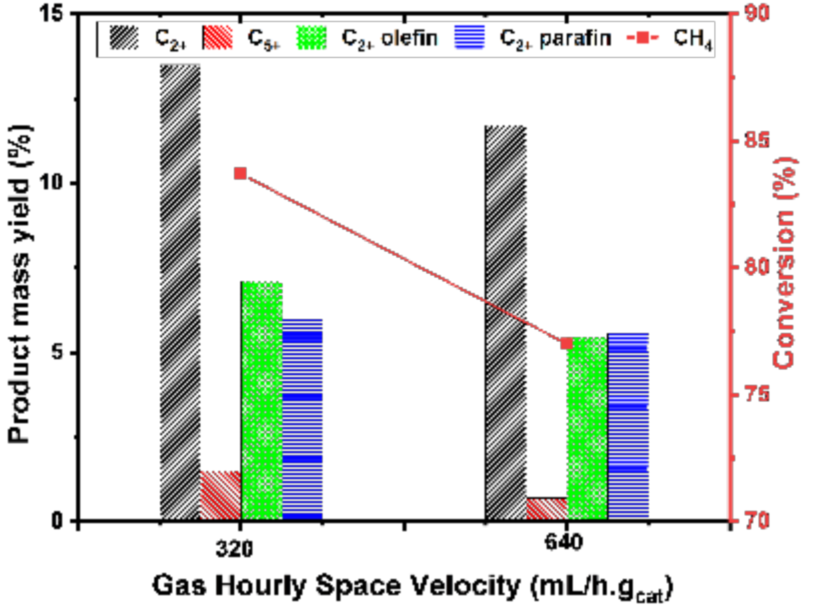
2. Progress and Outcomes (10 of 14)

Combined bed testing – model biogas

Precious metal free reforming catalyst + Fe-K based Fischer-Tropsch catalyst







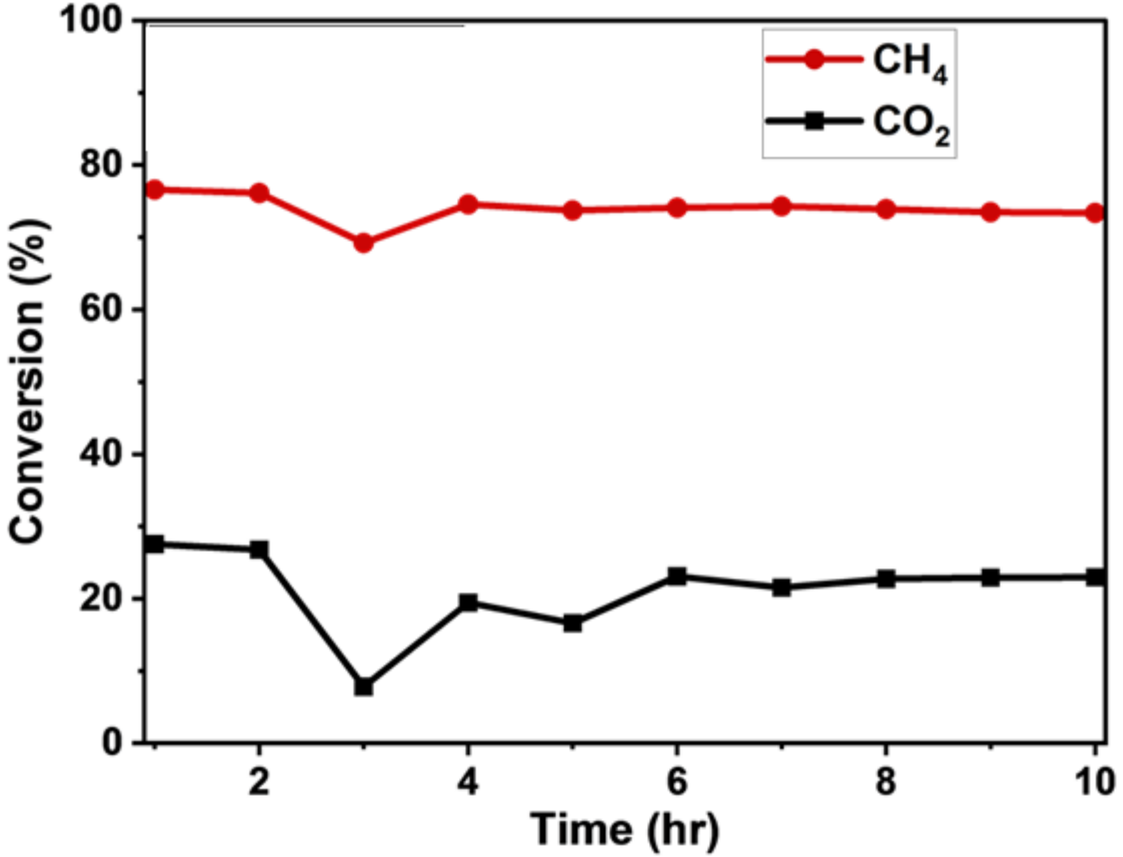
Progress:
- Successful demonstration of intensified process
- Conditions tuned to enhance C2+ and C5+ products
- High olefin selectivity allows for oligomerization to tune product molecular weight

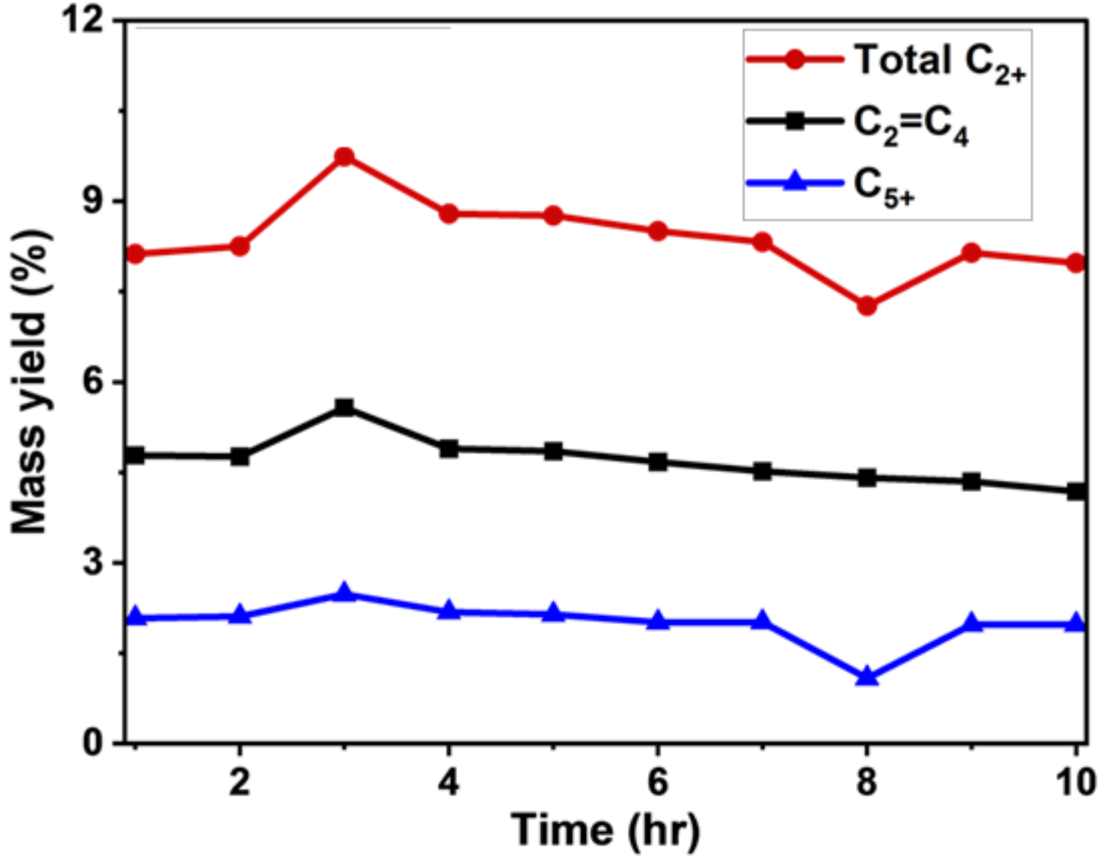
- Sequential catalyst beds in same reactor
- Temperature, pressure, and catalyst tuned products/rates
- Studies with minimizing inerts
- Recent focus on pellet catalysts

Values represent on-line gas-phase products only

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

Combined bed testing – model biogas – 2x scaleup



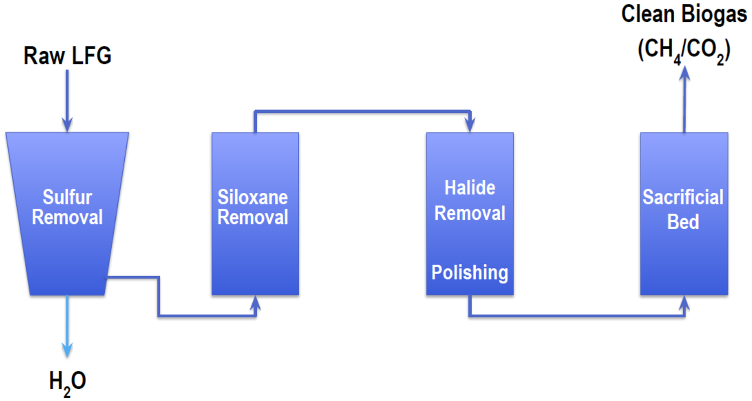


Similar results at 2x scaleup from BP2 GNG

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

2. PROGRESS AND OUTCOMES (12 OF 14)

Combined bed testing – real biogas

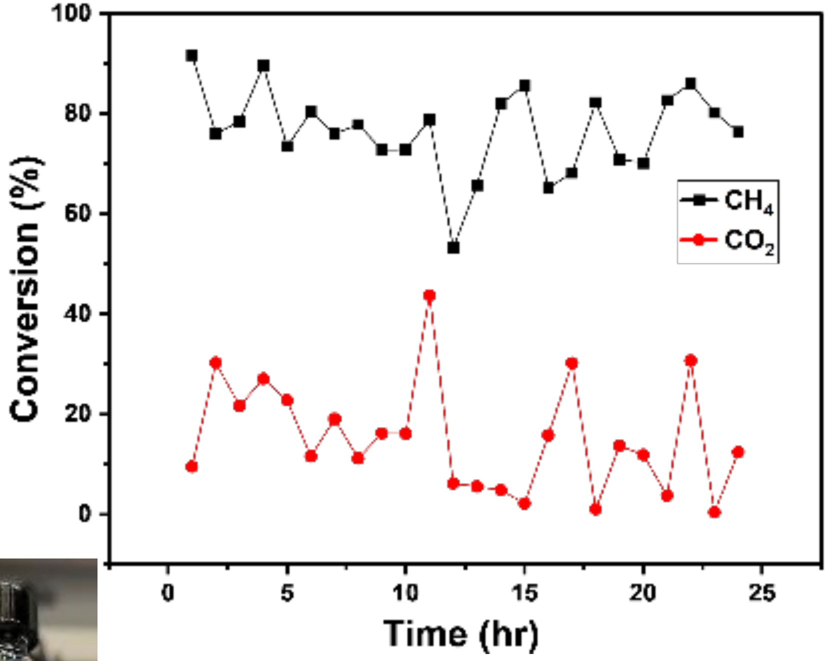


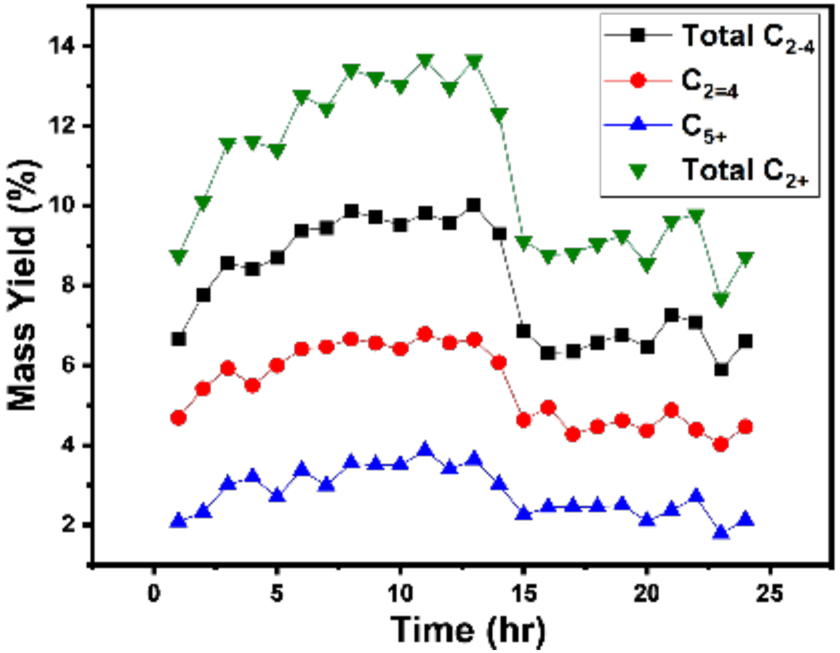
Vendor:
60% CH_4, 38% CO_2, 2% N_2
H_2S ~ 60 ppmv

cleaned gas @ USF:
57% CH_4, 41% CO_2, 2% N_2

(values on dry basis)

Values represent on-line gas-phase products only





Stacked bed testing of combined system with real biogas
(*left*) CH_4 and CO_2 conversion
(*right*) hydrocarbon mass yield from real biogas under a combined reforming and FTS study.

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

2. Progress and Outcomes (13 of 14)

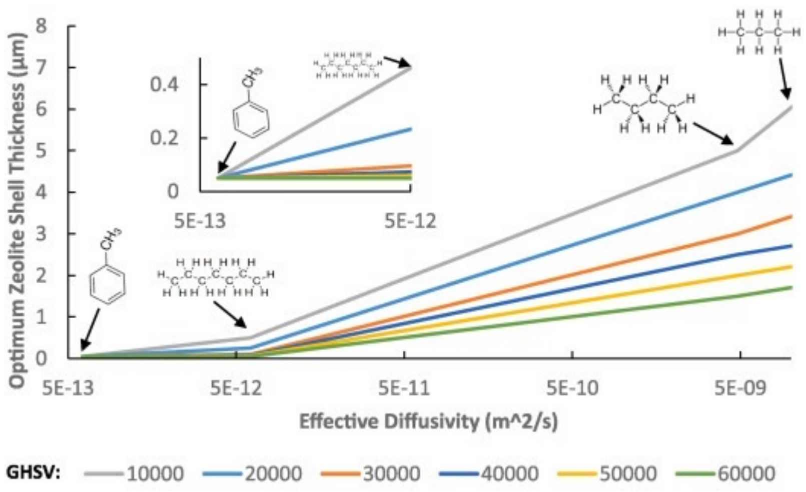
Simulation predictions – Bed Design

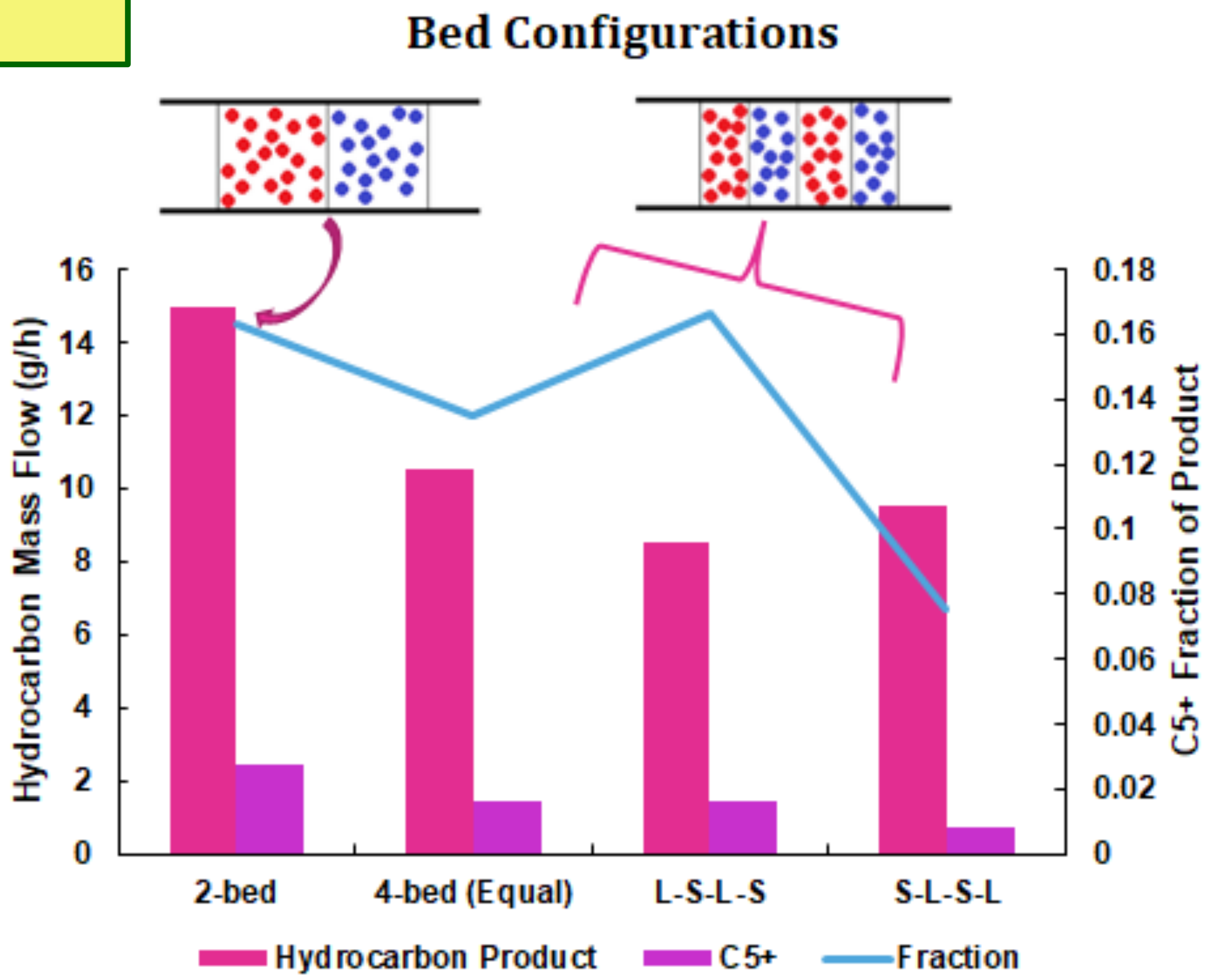
Current status

Prediction of bed performance for stacked bed configurations

To do:

- Refine model with new data
- Add in energy balance
- Refine enhancements with layered catalysts





S = Short L = Long

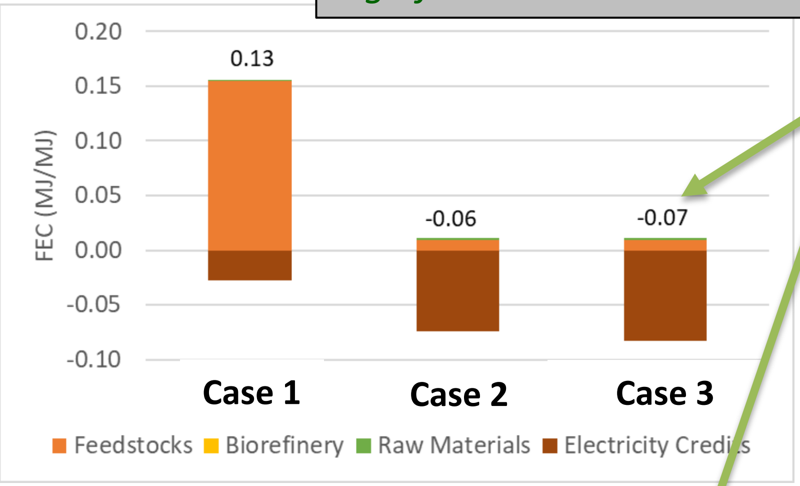
2. Progress and Outcomes (14 of 14)

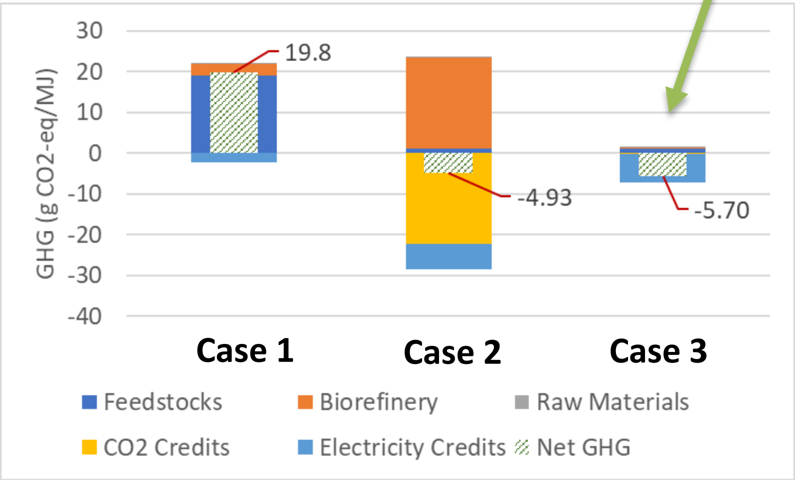
Environmental and Economic Assessment (TEA/LCA)

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

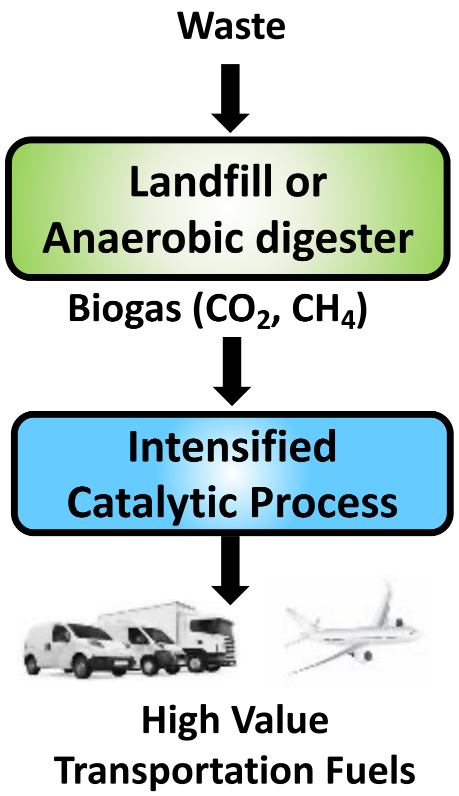
Progress:
- **CAP-EX** and **OP-EX** are lower than comparable techniques at this scale
- Yield of C5+ is a key parameter to lower the MFSP
  (Recycle currently under investigation)
- Co-products (i.e., LPG) is under study to aid in lowering MSFP
- Utilization of landfill gas results in **net-negative 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

3. Impact

3. 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

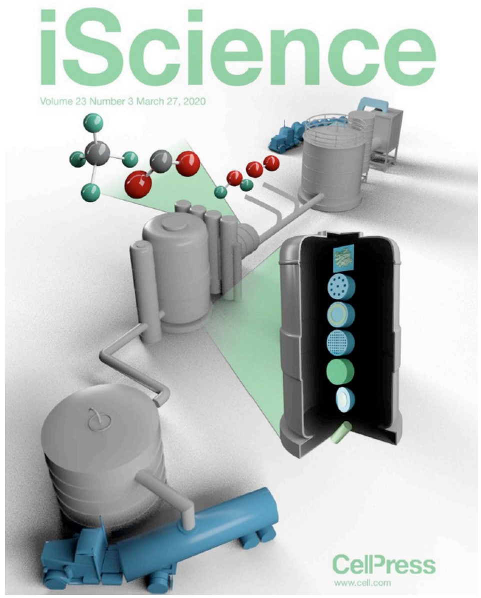
Increasing the Yield from Catalytic Processes
Decreasing the Time and Cost to Develop Novel Industrially Relevant Catalysts
Improving Catalyst Lifetime
Cost of Production

Relevant Criteria	Benchmark (FY18 SOT)	Status (FY21 SOT)	Long-Term Target
C2+ HC Yield (wt %) from biogas conversion (single-pass)	3%	16% (4% C5+)	>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***



3. 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, with potential for circular economy
  - Focus on products with large markets, high value, and potential for bio-adoption
  - ~2000 landfills in US plus many more ag waste & wastewater treatment facilities
- Creates a ***diversified revenue*** *stream* for biogas producers

Upstream

High value
Large markets

Downstream

3. Impact – Scientific Advancement (3 of 3)

Developing Foundational Science

Peer Reviewed Publications

External Presentations

Leverage unique DOE resources

Argonne NATIONAL LABORATORY

OAK RIDGE National Laboratory

SLAC NATIONAL ACCELERATOR LABORATORY

Generating Intellectual Property

Issued Patents

Pending Patent Applications

Building Industrial Partnerships

Multiple Industry/Municipality Collaborations

SWANA FLORIDA

Hinkley Center for Solid and Hazardous Waste Management

Manatee County FLORIDA

RENOVAREFUELS

Sarasota County

Training and Support for Next-Generation Engineers/Scientists

Ph.D. students supported
Post-doctoral researchers supported
Undergraduate internships
Collaborations and networking with DOE NLs

CCPC Consortium for Computational Physics and Chemistry U.S. DEPARTMENT OF ENERGY BIOENERGY TECHNOLOGIES OFFICE

INL Idaho National Laboratory

Argonne NATIONAL LABORATORY

OAK RIDGE National Laboratory

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: 16% 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 ~5x 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

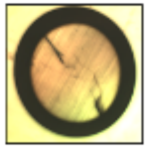
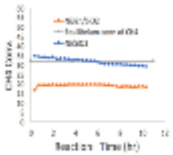
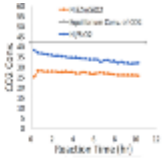
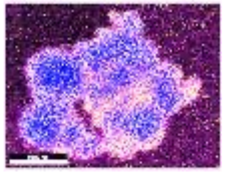
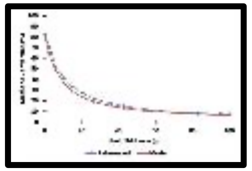
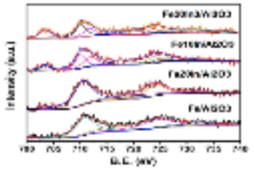
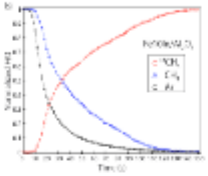
-Renewable, cost-competitive products are of interest to industrial partners (upstream and downstream)

4) Future work:

- Conduct tests for 100 hr end-of-project goal
- Predict
- **Scale-up** catalyst and biogas flow for bench-scale demonstration using real biogas 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, Bryce Finch, and the verification teams

USF students and NREL staff

USF (internal SIP grant)

Industry/Municipality partners

DOE Bioenergy Technologies Office (BETO)
2023 Project Peer Review

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

Friday, April 7, 2023

Catalytic Upgrading Session

PI: John N. Kuhn (USF)

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

QUAD CHART REVIEW

Timeline

- Project start date: 10/1/2018
- Project end date: 9/30/2023

Budget

	FY22 Budgeted*	Total Award
DOE Funding	$1,527,217	$1,836,459
Project Cost Share	$397,823	$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 (FY23)

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 FY22

2021 Peer Review

3 key comments from previous peer review

Small scale per site: This work aims to build a streamlined process with lower than conventional CAP-EX and OP-EX to facilitate small scale operations.

Recycle to increase yields: We have incorporated recycling into simulations and TEA to enhance yields.

Bridging conditions between differing reactions: A single optimized pressure has been achieved

HIGHLIGHTS OF GO/NOGO POINTS

Intermediate Verification Passed , June 2021 (report filing date 9/30/21)

- **SOPO Budget Period 2 Go/No-Go Decision Point:** Through catalyst development and/or process optimization, demonstrate a liquid hydrocarbon (C5+) yield of 4 wt% and net product yield (C2+) of 10 wt% at 0.0012 kg surrogate biogas/hr over 10 hours of operation.
- USF demonstrated a 10-hour run of surrogate biogas converted to liquid hydrocarbon yield (C5+) of approximately 4.3 +- 0.1 wt% and net product yield (C2+) of 16.2 wt% at a feed rate of 0.0012 kg surrogate biogas/hour. The facility was able to collect and analyze fuels with carbon number up to approximately carbon number 7. When following the Anderson-Schulz-Flory distribution model to consider less volatile components that may have stuck to the reactor, and which could have been capture more easily in a larger reactor setup, USF believes the actual yield of C5+ was 11 wt%. To test for reproducibility, the Verification run was compared to two prior runs under similar conditions, and results were generally reproducible.
- The criteria of the BP2 Go/No-Go decision point were reasonably approached or met by the project team and the targeted values as (C5+) yield of 4 wt% and net product yield (C2+) of 10 wt% at 0.0012 kg surrogate biogas/hr over 10 hours of operation were achieved.

Project Information			
Recipient:	University of South Florida		
Project Title:	Intensified Biogas Conversion to Value-added Fuels and Chemicals		
Key Individuals:	John Kuhn (USF), Babu Joseph (USF), Matt Young (NREL), Brian Gray (USF)		
Project Start:	10/1/2018		
Current Budget Period	BP2		
Project Cost (Federal):	$1,836,459		
Project Cost (Cost Share):	$460,297		
Technical Information			
Summary	The overall goal of this project is to establish an economically feasible pathway for producing liquid hydrocarbon fuels from residual biomass resources such as forest residues, municipal, and agricultural waste		
Project Highlights	USF demonstrated a 10-hour run of surrogate biogas converted to liquid hydrocarbon yield (C5+) of approximately 4.3 +- 0.1 wt% and net product yield (C2+) of 16.2 wt% at a feed rate of 0.0012 kg surrogate biogas/hour. The facility was able to collect and analyze fuels with carbon number up to approximately carbon number 7. When following the Anderson-Schulz-Flory distribution model to consider less volatile components that may have stuck to the reactor, and which could have been capture more easily in a larger reactor setup, USF believes the actual yield of C5+ was 11 wt%. To test for reproducibility, the Verification run was compared to two prior runs under similar conditions, and results were generally reproducible.		
Portfolio Information			
Award Number	EE0008488		
WBS	2.3.1.414		
TRL	3		
Program Area	Conversion		
Key Performance Parameters			
	Intermediate Verifications Results	Intermediate Targets	Final Targets
C5+ Yield	4.3 +- 0.1 wt%	4% wt	4% wt
C2+ Yield (Net Product)	16.2 wt%	10% wt	10% wt

Scientific Output

Publications

Zhao, X., Joseph, B., Kuhn, J.N., and Ozcan, 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)

He, Y., Shi, H., Johnson, O., Joseph, B., and Kuhn, J.N., "Selective and Stable In-promoted Fe Catalyst for Syngas Conversion to Light Olefins", *ACS Catalysis* 11 (2021) 15177-15186. (DOI: 10.1021/acscatal.1c04334)

Gray, B., Joseph, B., and Kuhn, J.N., "Enhancing Reactant Selectivity for Ni/Mg Reforming Catalysts Using Silicalite-1 Shells: A Modeling Study" *Chemical Engineering Journal* 437 (2022) 135353. (DOI: https://doi.org/10.1016/j.cej.2022.135353).

Sokefun, Y.O., Trottier, J., Yung, M., Joseph, B., and Kuhn, J.N., "Low temperature dry reforming of methane using Ru-Ni-Mg/Ceria-zirconia catalysts: Effect of Ru loading and reduction temperature" *Applied Catalysis A: General* 645 (2022) 118842. (https://doi.org/10.1016/j.apcata.2022.118842).

"Feasibility of intensified conversion of biogas to value added hydrocarbons" and several others in preparation.

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
Local presentations
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