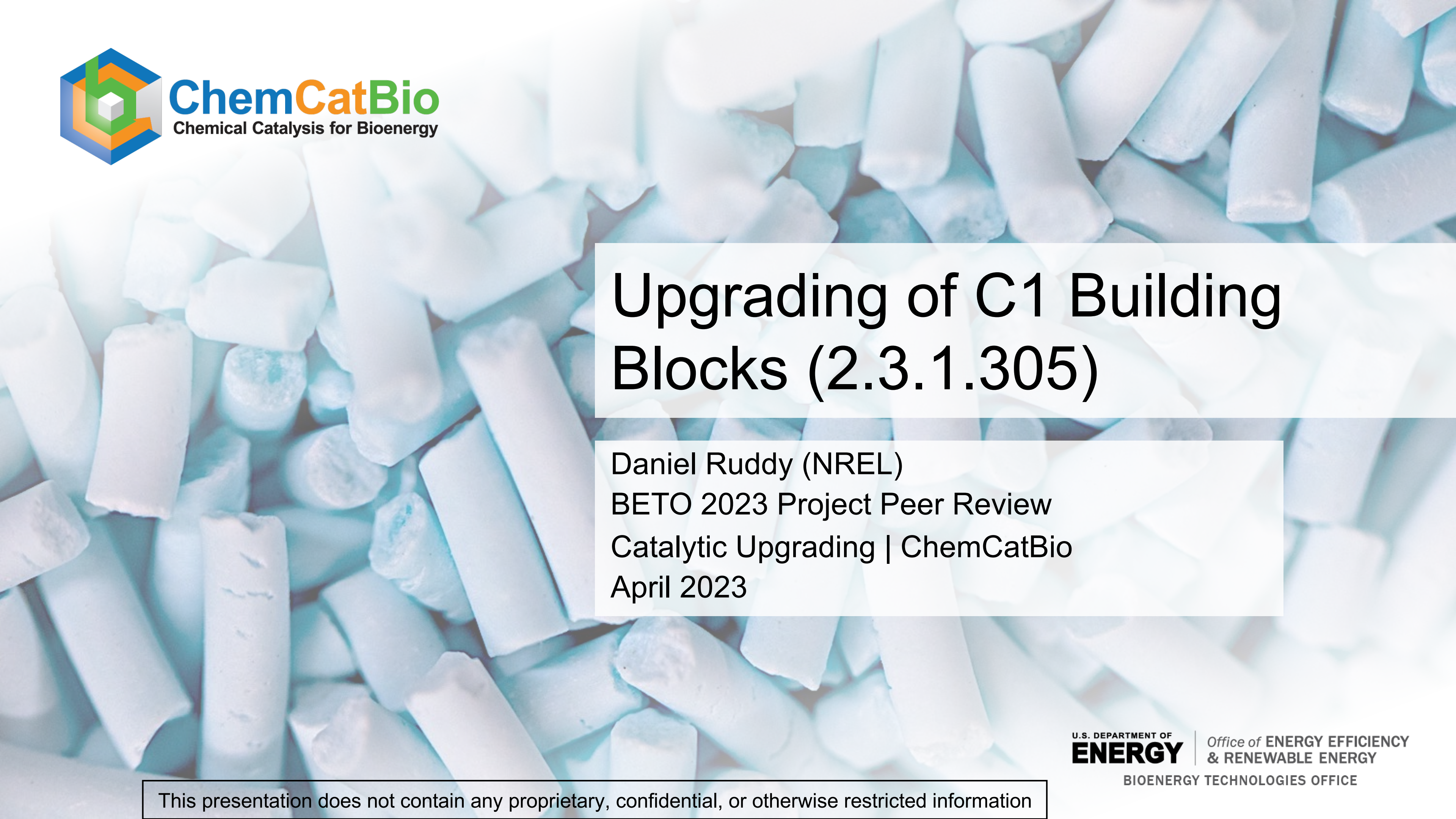
ChemCatBio
Chemical Catalysis for Bioenergy



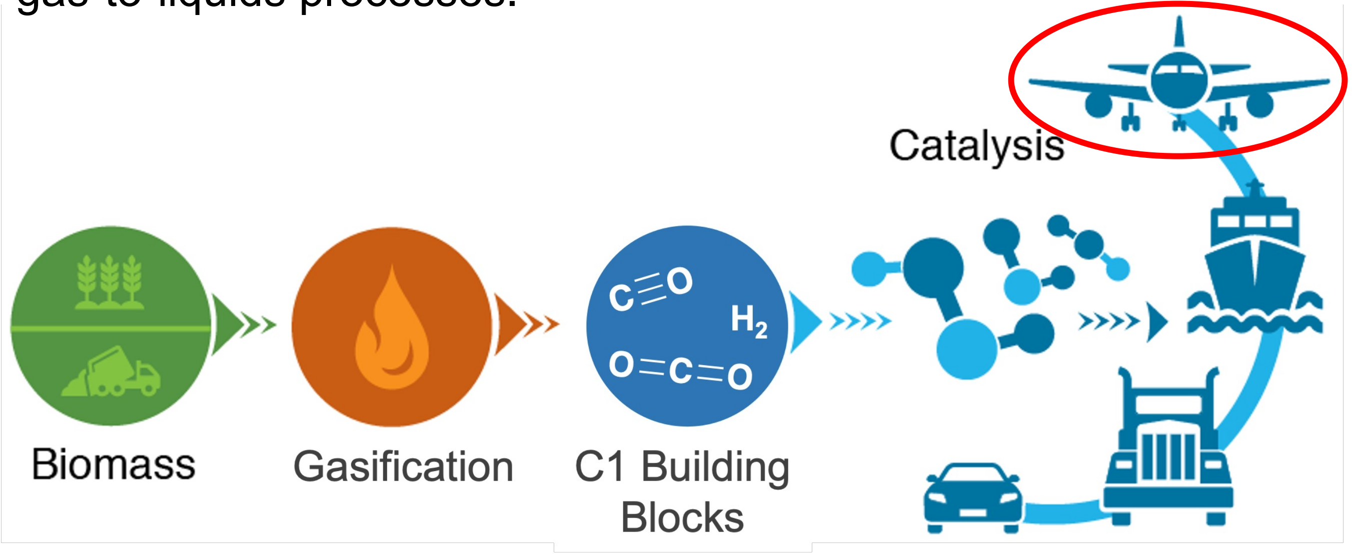
Upgrading of C1 Building Blocks (2.3.1.305)

Daniel Ruddy (NREL)
BETO 2023 Project Peer Review
Catalytic Upgrading | ChemCatBio
April 2023

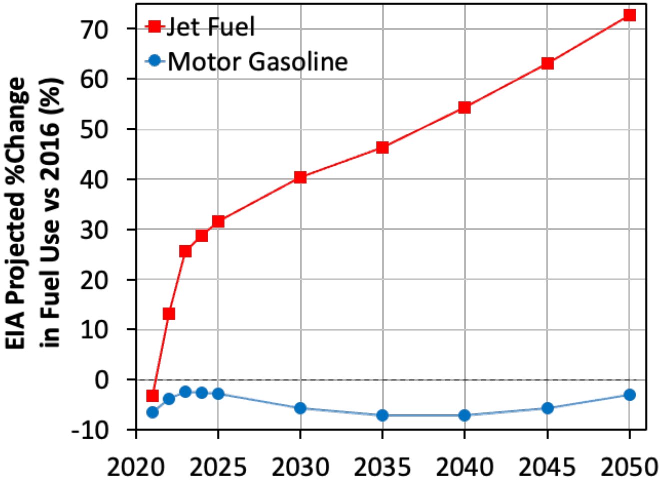
U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY
BIOENERGY TECHNOLOGIES OFFICE

Project Overview

Develop the centerpiece technology for an integrated biorefinery concept based on the **conversion of renewable and waste sources of C1 intermediates** (e.g., syngas, CO_2, methanol) to produce sustainable aviation fuel (SAF) with **improved carbon efficiency and reduced capital and operating expenses** compared to traditional gas-to-liquids processes.



Project Overview – Fuel Market Trends



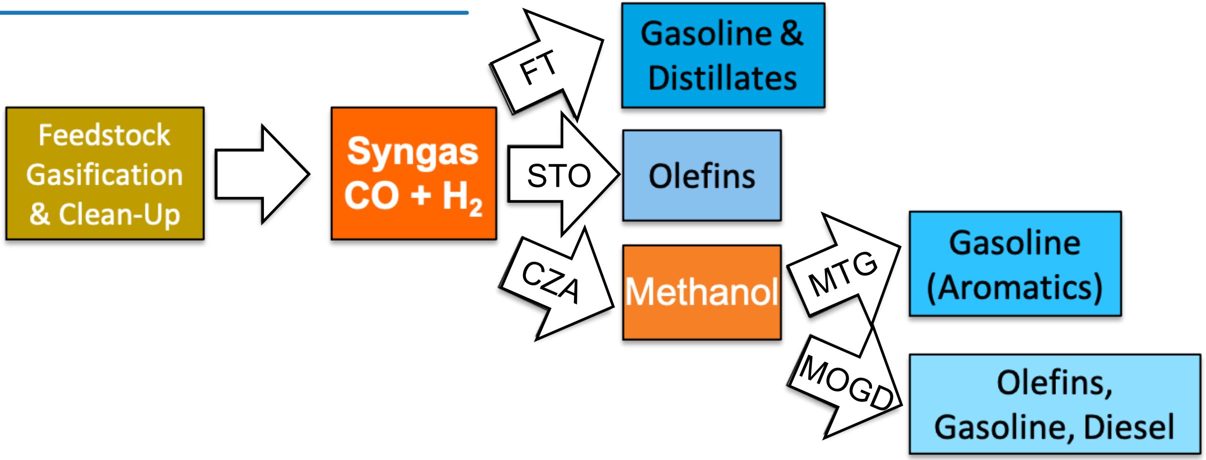
Project Outcome

Develop catalysts and processes that enable the **direct conversion of CO_2-rich syngas** (15-20% CO_2 in syngas) to hydrocarbons (STH) in a single reactor **and** the subsequent **conversion of this hydrocarbon stream to SAF with >70% reduction in GHG emissions** versus petroleum jet fuel.

Key Differentiators

Address **known drawbacks for traditional syngas-to-fuels** processes at smaller production scales – high capital cost, limited product quality – by focusing on **process intensification, high carbon efficiency, high-quality ("on-spec") fuel products**

Overview - Traditional Syngas-to-Fuels Processes



Traditional syngas to hydrocarbon fuels have known drawbacks

- *Fischer-Tropsch (FT)*: Costly catalytic upgrading to produce quality fuels
- *Syngas-to-Olefins (non-bio "STO")*: Lower TRL, designed for polymer precursors
- *Methanol-to-Gasoline (MTG)*: Capital intensive, high aromatics content, *not SAF*
- *Mobil Olefins-to-Gasoline-and-Distillate (MOGD)*: Capital intensive, high number of process steps to SAF

Advanced upgrading technologies can reduce SAF cost and GHG emissions through reduced process complexity, reduced separations duty, higher quality fuel products

Overview – An Alternative Pathway: HOG

NREL developed the High-Octane Gasoline (HOG) Pathway through biomass-derived methanol/dimethyl ether (DME)

Key Differentiators of HOG versus MTG

- HOG pathway yields **branched alkanes, not aromatics**
- Higher octane (102 vs 87), higher value fuel product
    - **Alkylate versus regular-grade gasoline**
- Lower severity conditions for HOG vs MTG
    - **Higher yield (18% relative), higher C-efficiency**
- Modeled costs for MeOH-to-HOG of \$0.40/GGE in FY21 compare favorably against other alcohol conv tech.
    - EtOH-to-Jet \$0.89–1.19/GGE (L. Tao *et al*., *Green Chem.* 2017, *19*, 1082)
- **HOG pathway also provides a high carbon-efficiency route to a SAF product**

Peer-reviewed publications: *ACS Catal.* 2015; *Biofpr* 2016; *ACS Catal.* 2017; *Nat. Catal.* 2019; *Appl. Energy* 2019; *Appl. Catal. B Environ.* 2021; *Appl. Catal. B Environ.* 2022; *Biofpr* 2022; *Appl. Catal. A* 2022.

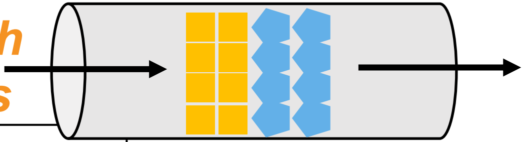
Overview – An Alternative Pathway: STH (FY20)

Process intensification enables a direct Syngas-to-Hydrocarbons (STH) pathway

Stacked bed "CZA+A|Cu/BEA"

CuZnO/Al_2O_3 + γ-Al_2O_3 (DME synthesis) 🟨

⬟ ***Cu/BEA*** (HC synthesis)



CO_2-rich Syngas

Branched Hydrocarbons

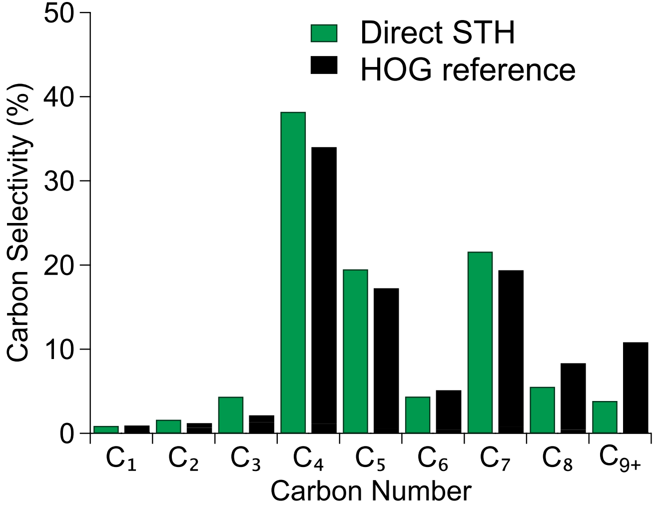
CO_2-rich syngas
1 CO + 0.8 CO_2 + 2 H_2

US Patent Appl. 63/065,648, Aug 14, 2020;
ACS Catalysis **2022**, *12*, 9270;
J. CO_2 Utilization **2022**, *66*, 102261.

- **Product selectivity similar to DME-to-HOG**
  - Stacked-bed outperformed mixed-bed
  - NREL's Cu/BEA outperformed commercial BEA
- **Co-conversion of CO_2 with syngas**

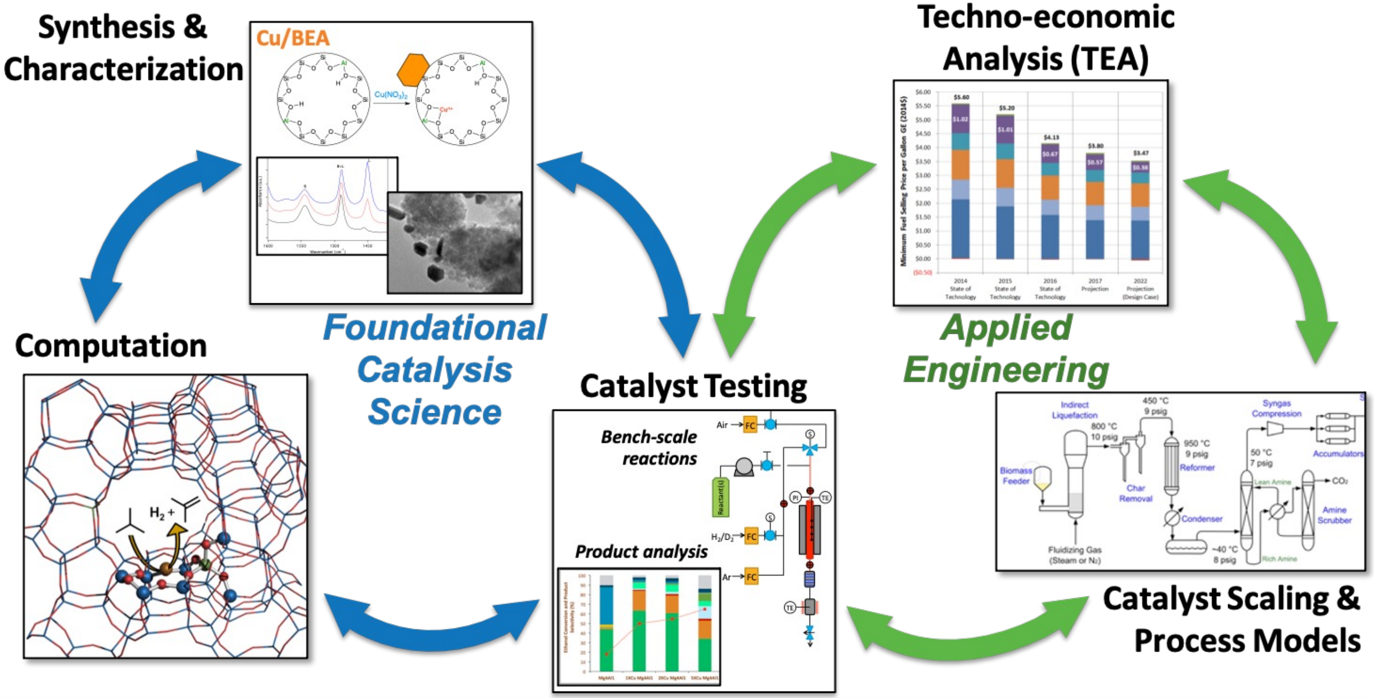
Differentiators versus STO

- **Catalysts**
  - CuZnO/Al_2O_3 vs $ZnCrO_x$
  - BEA vs AEL zeolite
- **Intermediate**
  - MeOH vs Ketene
- **Product composition**
  - Alkylate vs Light Olefins



1. Approach: Dual R&D Cycles

- **Hypothesis-driven catalyst and process development** coupled with:
  - Sophisticated catalyst characterization (*with Adv. Cat. Synthesis. & Characterization*)
  - Reactor design for cascade chemistry (*with Cons. Comp. Physics & Chemistry*)
- **TEA-informed research targets**, experimental data informs process models and TEA



Synthesis & Characterization

Techno-economic Analysis (TEA)

Computation

Foundational Catalysis Science

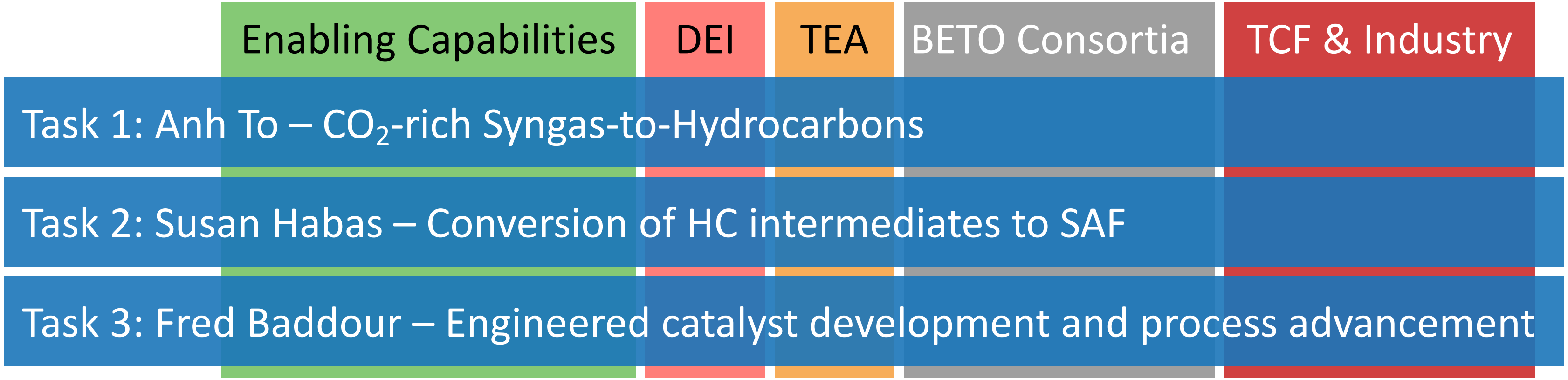
Applied Engineering

Catalyst Testing

Catalyst Scaling & Process Models

1. Approach: Management and DEI

Task management integrated with CCB enabling capabilities, CCB DEI team, BETO analysis and consortia, and technology advancement opportunities



Enabling Capabilities | DEI | TEA | BETO Consortia | TCF & Industry

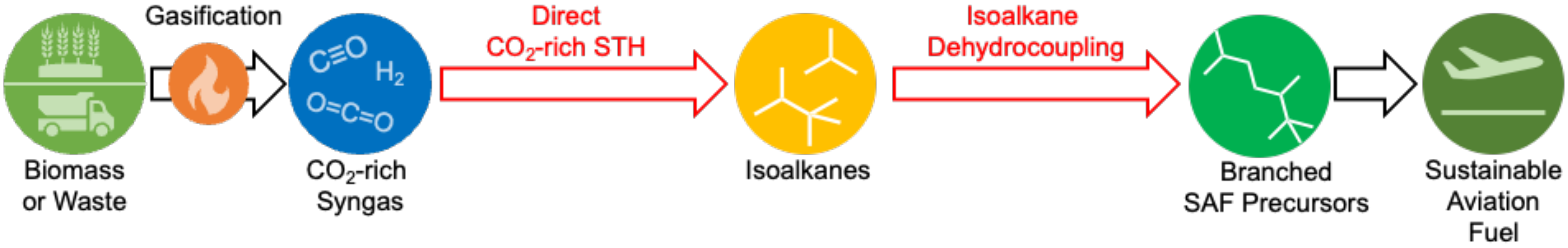
Task 1: Anh To – CO_2-rich Syngas-to-Hydrocarbons

Task 2: Susan Habas – Conversion of HC intermediates to SAF

Task 3: Fred Baddour – Engineered catalyst development and process advancement

- Project-specific DEI milestones to be determined in FY24 and FY25 with ChemCatBio DEI Lead Team

1. Approach: Pathways Explored in this Project



Pathway Objectives

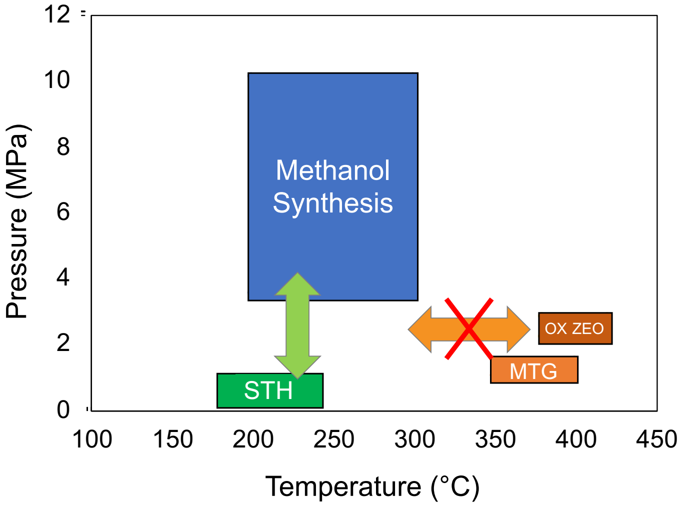
Direct CO_2-rich STH with NREL's Cu/BEA catalyst

- Catalyst and process development for **improved carbon efficiency and GHG emissions reductions** informed by process models and TEA/LCA
- Establish **multi-component catalyst lifetime and regeneration**
- Translate performance from powdered catalysts to **engineered catalysts**

Isoalkane Dehydrocoupling (DHC)

- Catalyst and process development to establish the state-of-the-art for this ***new*** **process intensification approach to SAF**
- Compare to **benchmark 2-step process** – dehydrogenation + olefin oligomerization

1. Approach: Opportunities and Challenges



Similar process conditions offer the opportunity for process intensification **in a single reactor**

- Utilize commercial, inexpensive Cu-based MeOH synthesis catalyst “CZA” and NREL’s Cu/BEA
- Co-convert CO_2 with CO during STH
- **Go/No-Go Decision in FY21** outlined a clear path for STH to approach $2.50/GGE with >30% C-efficiency
  - 5% reduction in both CapEx and OpEx

Research Challenges/Risks and Critical Success Factors for STH and DHC

- **Decrease CO_2 selectivity** in STH to increase C-efficiency
- **Regenerate** multi-component catalyst mixtures
- **Operate** for extended times-on-stream with **biomass-derived syngas feed compositions**
- **Maximize yield and carbon efficiency** with multi-functional catalyst systems
- **Advance technology** with bioenergy industry partners, TCF funding

2. Progress & Outcomes: Baseline in FY21

	MOGD Benchmark	**"3-step" DME-to-HOG**	**Direct STH**	**Isoalkane Dehydrocoupling**
Catalyst	ZSM-5	Cu/BEA	CZA|Cu/BEA	–
Severity of Process Conditions	350–400 °C 20 atm *Frequent regen.*	230 °C, 3.5 atm *Stable >100h, Multiple regens demonstrated*	220 °C, 7-20 atm *Stable >50 h* ***No regen protocol established***	*New Effort in FY22*
FY21 Metrics	–	44% DME conv. 0.094 $g/g_{cat}/h$	>50% CO conv. 0.08 $g/g_{Cu/BEA}/h$	*New Effort in FY22*
C-Efficiency and MFSP	approx. 30% $4.23/GGE	26.2% $3.38/GGE	**18.8%** **$4.72/GGE**	–

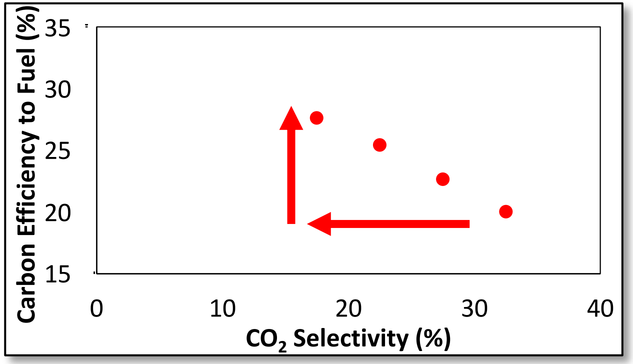
FY21 data **set the stage for catalyst and process development**

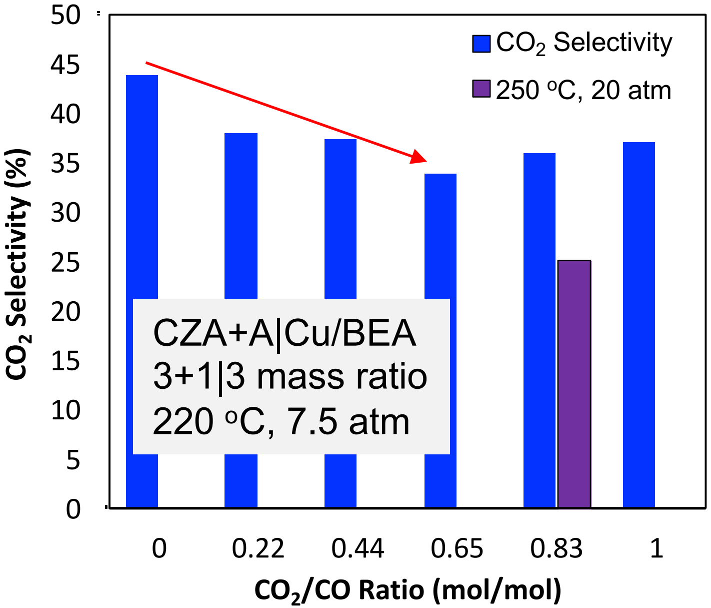
- TEA-directed research goals to increase C-efficiency and reduce cost
- Compare Direct STH against 3-step DME-to-HOG and benchmark MOGD process

2. Progress & Outcomes: Increased C-efficiency in STH

Conceptual process models correlated **decreasing CO_2 product selectivity through CO_2 recycle** with **increasing C-efficiency**

- **Goal:** Determine the effect of CO_2/CO simulated recycle ratio on CO_2 and C_{4+} product selectivity, carbon efficiency in STH





CZA+A|Cu/BEA
3+1|3 mass ratio
220 °C, 7.5 atm

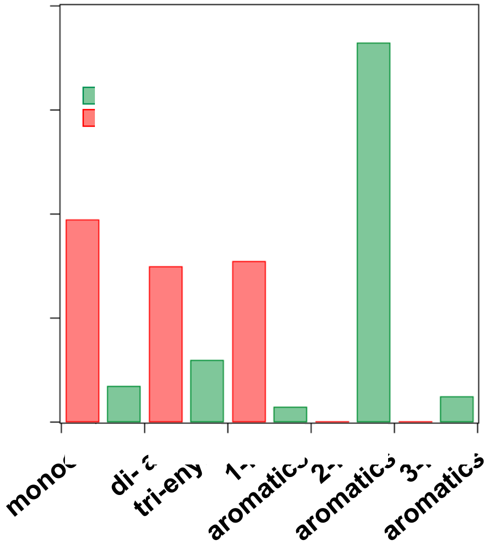
- Systematic study across a range of CO_2/CO ratios indicated **recycle decreases overall CO_2 selectivity and molar production rate**
- **No change** to typical HC product selectivity
- At 250 °C, 20 atm, CO_2 selectivity further reduced to 25% giving a **modeled C-efficiency to C_{4+} HCs of 32.2%**

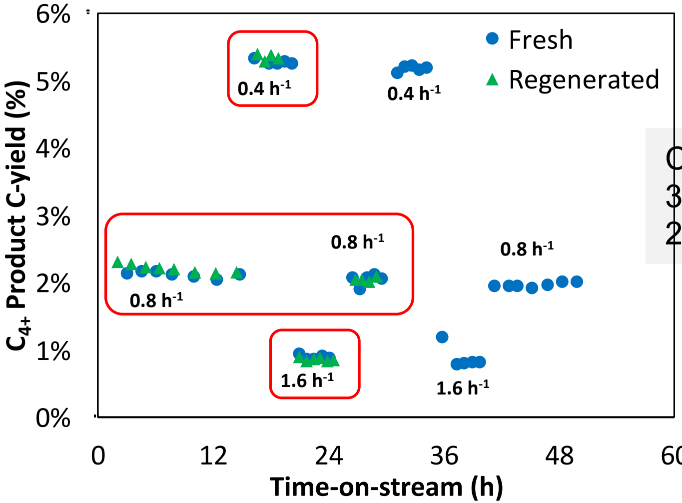
2. Progress & Outcomes: STH Catalyst Regeneration

- **Goal:** Compare deposited carbon species on Cu/BEA from syngas versus DME feeds, **develop Cu/BEA regeneration protocol** compatible with CZA temperature limit (ca. 300 ^oC)
  - with Advanced Catalyst Synthesis and Characterization Project

DRUV-vis analysis of post-reaction Cu/BEA catalysts

Appl. Catal. B Environ. **2021**, 287, 119925



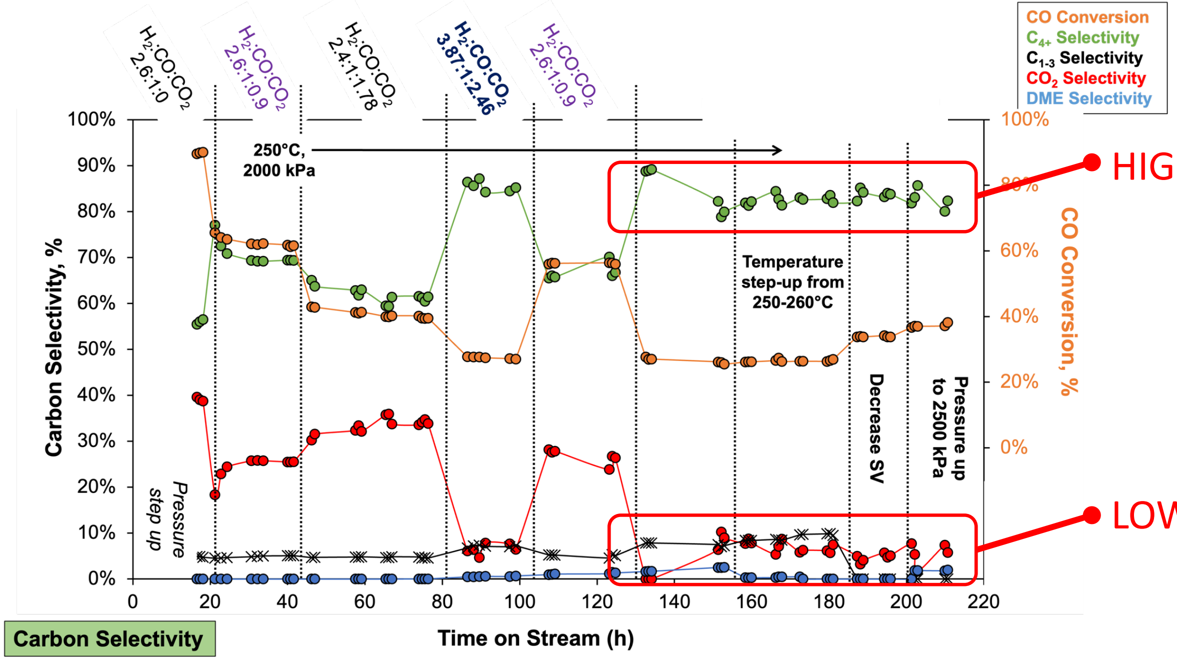


CZA+A|Cu/BEA
3+1|1 mass ratio
220 ^oC, 7.5 atm

- More multi-ring aromatics observed with syngas feed compared to DME feed
- Developed a 250 ^oC oxidative regeneration protocol that **enabled full recovery of the multi-component catalyst** after 50 h TOS across a range of space velocities

2. Progress & Outcomes: STH Extended TOS

- **Goal:** Operate the STH reaction for **at least 200 h time-on-stream** with analysis-informed syngas compositions representing process gas recycle
  - with Thermochemical Platform Analysis Project



HIGH C_{4+} Selectivity

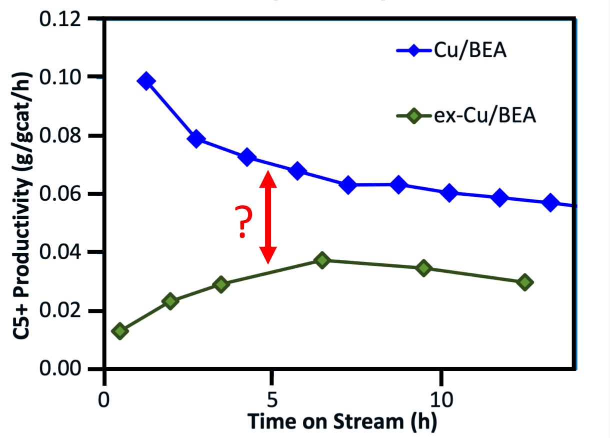
LOW CO_2 Selectivity

- No significant deactivation observed, no regeneration needed over 200 h

2. Progress & Outcomes: Engineered Cu/BEA Catalyst

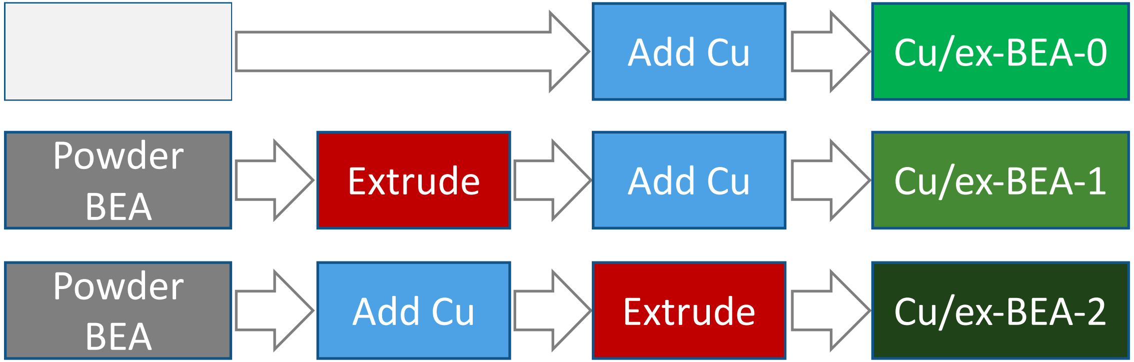
- **Goal:** Identify the initial **structure-property-performance relationships** that reduce the risk to transition from powder to engineered forms of Cu/BEA

Initial extrudate prepared in 2017 for pilot operation



Initial **promising results with "Cu-first" material** set the baseline for this effort through FY25

Seeking to understand **how and when addition of Cu affects speciation** and resulting catalytic performance (with ACSC, CDM)

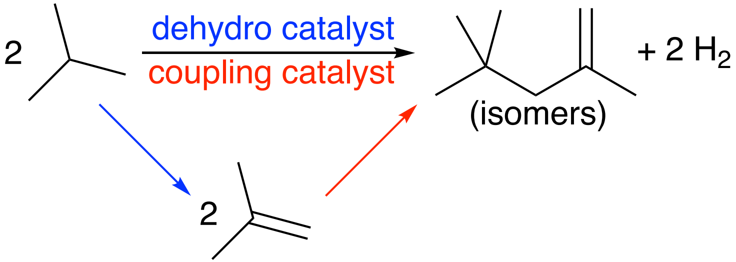


250 °C, 20 atm H_2:CO:CO_2 = 2.6 : 1 : 0.9	CO Conv. (%)	CO_2 Sel. (%)	C_{4+} Sel. (%)	DME Sel. (%)
Powder Cu/BEA	68	18	70	8.4
Cu/ex-BEA-2 "Cu-first"	70	17	**61**	**17**

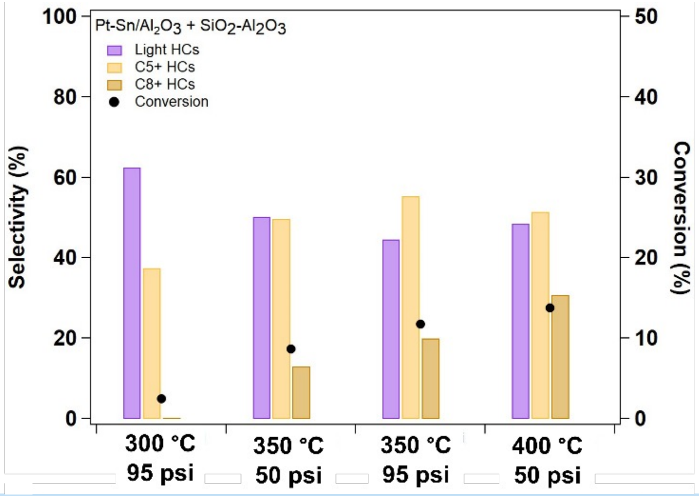
2. Progress & Outcomes: Isoalkane Dehydrocoupling

- Goal (FY22): Establish **proof-of-concept for a process intensification approach** to isoalkane dehydrocoupling using a mixed-bed of catalysts

Desired cascade chemistry



ACS Catal. **2017**, 7, 3662
Appl. Catal. B **2022**, 301, 120801
J. Catal. **2022**, *413*, 264



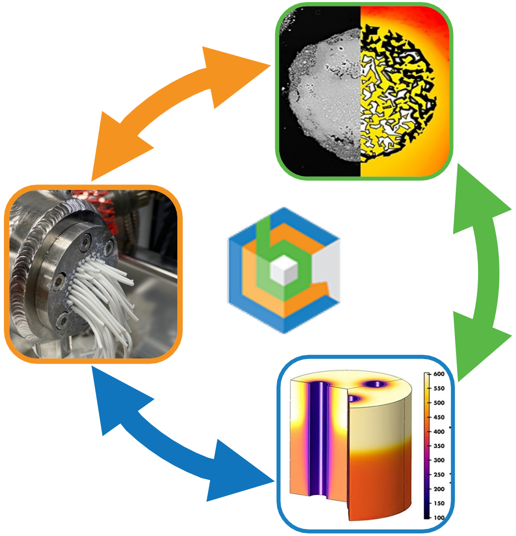
- Tested 7 catalyst combinations inspired by literature and patents
- Commercial Pt-Sn/Al_2O_3 with an acid coupling catalyst (2:1 mass ratio) **provided proof-of-concept data** to build upon in FY23-25
- **R&D focus on reducing hydrocarbon cracking chemistry** at higher temperatures and **favor C_{8+} products for SAF**

2. Progress & Outcomes: Summary through FY23-Q1

	MOGD Benchmark	**“3-step” DME-to-HOG**	**Direct STH**	**Isoalkane Dehydrocoupling**
Catalyst	ZSM-5	Cu/BEA	CZA|Cu/BEA	Pt-Sn/Al_2O_3+$SiAlO_x$
Severity of Process Conditions	350–400 °C 20 atm *Frequent regen.*	230 °C, 3.5 atm *Stable >100h, Multiple regens demonstrated*	250 °C, 20 atm *Stable >200 h* ***Regen protocol established***	300-400 °C 1-7 atm *Proof-of-concept established*
FY23-Q1 Metrics	–	44% DME conv. 0.094 $g/g_{cat}/h$	62% CO conv. 0.125 $g/g_{Cu/BEA}/h$	*Baseline to be set at FY24 G/NG*
C-Efficiency and MFSP	approx. 30% $4.23/GGE	26.2% $3.38/GGE	**32.2%** **$2.61/GGE for C_{4+} hydrocarbons**	To be determined in FY24-25

- Direct STH offers **advantages in activity, C-efficiency, cost** compared to 3-step DME-to-HOG and MOGD
- Isoalkane dehydrocoupling to be assessed in **FY24 Go/No-Go Decision**

2. Progress & Outcomes: Future R&D



- **FY23-Q4:** Determine the impact of engineered catalyst formulation on Cu speciation and catalyst deactivation mechanisms (*with Enabling Capabilities*)
  - Correlate **Cu speciation** with differences in STH catalytic performance and deactivation profile
  - Reduces the risk associated with assumptions for engineered catalyst performance
- **FY24-Q4:** Establish coke characteristics for at least two catalyst systems from different ChemCatBio catalytic technologies
  - **Multi-project effort** to experimentally and computationally understand the deactivation and regeneration of engineered catalysts
- **FY24 Go/No-go:** Feasibility of one-step dehydrogenative coupling versus two-step alkane dehydrogenation and coupling
  - **Metric for comparison**: at least a 10% relative cost reduction in the CapEx and OpEx for the 1-step process compared to the 2-step process.
- **End of Project Goal (FY25):** Integrate process steps to generate SAF from syngas
  - Use **real biomass syngas** to generate 150 mL SAF for Tier α and β testing

3. Impact: High-Octane Gasoline (HOG) Product

HOG product targets ***growing premium gasoline fuel demand and value***

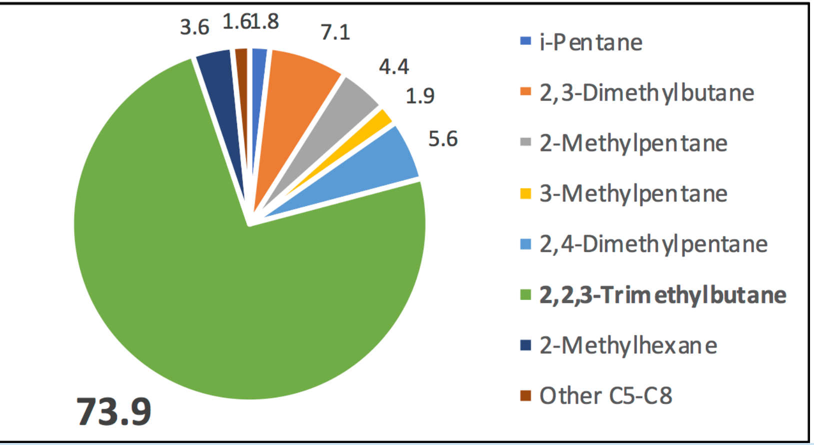
- Unlike ethanol, **gasoline product has no blend limit**

HOG technology awarded a ***Technology Commercialization Fund***

$740k investment by DOE + $750k cost-share from Enerkem in 2018-2019

- HOG production at the **pilot scale** (20-kg$_{\text{cat}}$) with ***MSW-derived methanol for 500 h time-on-stream***
- Produced **20 L of high-octane gasoline**
- Sent to **refinery industry partners**

Composition
73.9% Triptane
(2,2,3-trimethylbutane)
RON = 108 MON = 97

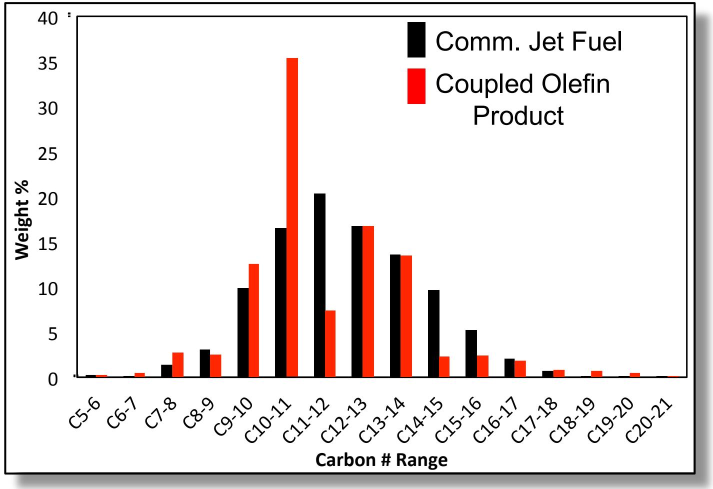


- This TCF project was critical to generate liquid product for industry analysis
- Research license to commercialize NREL's HOG technology with large energy company executed Phase 1 in 2020, Phase 2 in 2022

3. Impact: SAF Product

Developed a mild-condition route for olefin coupling to jet-range hydrocarbons

C_4-C_8 Branched OLEFINS → **C_8-C_{20} Branched JET**



Product meets 5 key ASTM Int'l jet fuel property specifications

Fuel Property	ASTM D1655	Coupled Olefins
Density (kg/m³)	775–840	783
Freeze point (°C)	–40 max	–81
Viscosity (mm²/s)	8.0 max	7.6
Net Heat of Combustion (MJ/kg)	42.8 min	43.8
T10 (°C)	205 max	178
T50	Report	188
T90	Report	239
FBP	300 max	281

- Process model and TEA indicated only a minor fuel synthesis cost increase to generate this additional SAF product from HOG Pathway
- Sets baseline comparison for Isoalkane DHC approach

Ruddy *et al.*, *Nature Catalysis* **2019**, 2, 638.

Summary

Project Goal

Develop new catalytic upgrading technologies for renewable C1 building blocks to **SAF with lower CapEx and OpEx, higher C-efficiency** than traditional approaches.

Approach

- **Process intensification** with **multi-functional catalysts** to perform selective cascade reactions, leading to **low operating costs, high C-yields, and high C-efficiency**
- Interdisciplinary, **collaborative approach** within ChemCatBio leveraging enabling technologies, process models, techno-economic and life-cycle analyses

Impact

- Demonstrated **technology transfer with the bioenergy industry** (e.g., TCF with Enerkem, research license) **to reduce risk of commercialization**
- **Patented** intellectual property, and published results in **top-tier peer-reviewed journals**

Research Progress & Outcomes

- **CO_2 recycle** enables C-efficiency of 32% and C_{4+} cost of $2.61/GGE for STH
- **Regeneration** protocol established, STH catalyst operates >200 h without regeneration
- Initial results with **engineered catalysts** highlight importance for continued R&D
- **Proof-of-concept** established for isoalkane DHC

Quad Chart Overview

Timeline

- *10/01/2022*
- *09/30/2025*

	FY22 Costed	Total Award
DOE Funding	*$1600k*	*$1600k for FY23* *$4800k for FY23-25*

TRL at Project Start: *2*
TRL at Project End: *4*

Project Goal

Develop new catalytic upgrading technologies for renewable C1 building blocks to SAF with lower CapEx and OpEx, higher C-efficiency than traditional approaches

End of Project Milestone

Integrate process steps to generate SAF from syngas: Generate at least 150 mL of finished SAF from syngas via STH and dehydrogenative coupling reactions using engineered catalysts developed in this project and perform Tier a and b fuel property analysis.

Funding Mechanism

AOP LabCall 2023 - ChemCatBio

Project Partners*

- Prof. Aditya Bhan, Univ. of Minnesota ($100k)

Acknowledgements

Task Leaders in this Project

Anh To
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Q&A: 10 minutes

chemcatbio.org

This work was performed in collaboration with the Chemical Catalysis for Bioenergy Consortium (ChemCatBio, CCB), a member of the Energy Materials Network (EMN)

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BIOENERGY TECHNOLOGIES OFFICE

ChemCatBio
Chemical Catalysis for Bioenergy

Energy Materials Network
U.S. Department of Energy

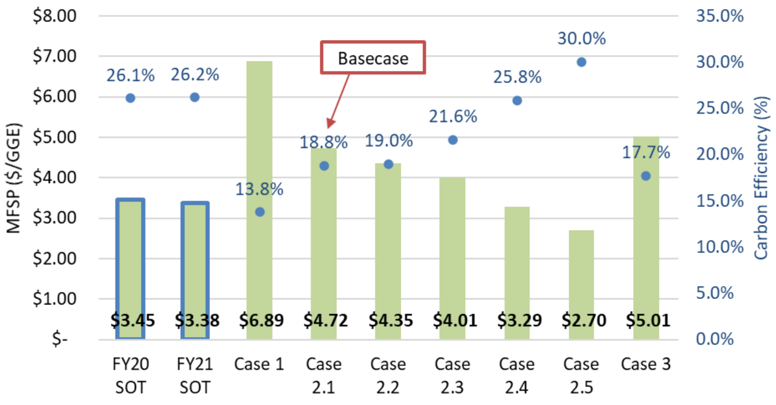
Responses to Previous Reviewers' Comments

- **Comment: A critical result was the C13 results proving that CO2 activation occurred over CZA:Cu/BEA… One of the challenges in the work is working at such low conversions and not providing a clear reaction pathway insight.**
  - Response: Work through FY23 focused on higher conversion to increase per-pass yield
- **Comment: Cu/Zn is a good shift catalyst. Does that present a limit ?**
  - Responses: We are working with the CCPC to computationally identify how the series of reactions work together and to gain insight into the pathway.
  - The reviewer is correct to note that WGS is critical in this system. We're exploring the limit of this both experimentally with CO2 co-feeds at varying CO:CO2 ratios and computationally with a reactor model that can identify limitations related to each catalyst's performance
- **Comment: It could be beneficial if the team could collaborate with CCPC and other enabling groups to investigate the confinement effect for their Cu/BEA catalysts and the nanoscale effect of their nanoparticle catalysts**
  - Response: Confinement effects in BEA zeolite that affect this chemistry have been explored and reported in a series of papers by Iglesia. This knowledge enables us to investigate reactor-scale effects for the system with the CCPC.
  - There is on-going work with the CCPC to identify new carbide compositions that we will seek to build upon with the nanomaterials.

Highlights from FY21 Go/No-Go

- Go/No-Go Description: Evaluate the STH process model for FY21 and future SOT reports.
- Go/No-Go Criteria: Using TEA models and experimental data, the direct STH process model will be chosen for SOT updates based on the modeled MFSP determined in FY21-Q3.
- Outcome: We demonstrated a modeled baseline MFSP value for the direct STH pathway of $4.72/GGE, and have **identified sensitivity cases that outline a clear path forward** to achieve continued cost reductions approaching the BETO goal of $2.50/GGE with associated C-efficiency improvements. Our recommendation is to proceed with the tasks as they are laid in the FY22 AOP that address the critical path forward.

Case 2.5 identifies low CO_2 selectivity and high C_{4+} selectivity as the target case for R&D to meet high yields and low costs



Publications, Patents, Presentations, Awards, and Commercialization

- Publications since Peer Review in 2021
  1. "Spectroscopic insight into carbon speciation and removal on a Cu/BEA catalyst during renewable high-octane hydrocarbon synthesis" *Applied Catalysis B: Environmental*, **2021**, *287*, 119925.
  2. "Throughput Optimization of Molybdenum Carbide Nanoparticle Catalysts in a Continuous Flow Reactor Using Design of Experiments" *ACS Applied Nano Materials*, **2022**, *5*, 1966.
  3. "Catalyst design to direct high-octane gasoline fuel properties for improved engine efficiency" *Applied Catalysis B: Environmental*, **2022**, *301*, 120801.
  4. "Connecting cation site location to alkane dehydrogenation activity in Ni/BEA catalysts" *Journal of Catalysis*, **2022**, *413*, 264.
  5. "Direct conversion of renewable CO_2-rich syngas to high-octane hydrocarbons in a single reactor" *ACS Catalysis*, **2022**, *12*, 9270.
  6. "A separations and purification process for improving yields and meeting fuel contaminant specifications for high-octane gasoline produced from dimethyl-ether over a Cu/BEA catalyst" *Biofuels, Bioproducts and Biorefining*, **2022**, *16*, 1469.
  7. "Benchmarking Cu/BEA and HBEA catalysts for high-octane gasoline synthesis" *Applied Catalysis A: General*, **2022**, *643*, 118799.
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  9. "Revealing the Reaction Behavior of $Co_{0.86}Mn_{0.14}O$ under H_2 using in situ Closed-Cell Gas Reaction S/TEM" *Microscopy and Microanalysis*, **2022**, *28*, 1884.
  10. "Direct synthesis of branched hydrocarbons from CO_2 over composite catalysts in a single reactor" *Journal of CO2 Utilization*, **2022**, *66*, 102261.
- Patents since Peer Review in 2021 (9 total since 2017)
  - "Methods, systems, and catalysts for the direct conversion of syngas to high-octane hydrocarbons" US Patent Application 17/401,778, August 13, 2021

Publications, Patents, Presentations, Awards, and Commercialization

- Presentations since Peer Review in 2021
  1. "Developing new processes for the conversion of methanol to advantaged biofuels within a market-responsive biorefinery concept enabled by catalysis" presented virtually at Pacifichem Conference, Dec 19, 2021.
  2. "Process intensification for direct conversion of biomass-based syngas to high octane gasoline" presented virtually at 2021 AIChE Annual Meeting, Nov. 16, 2021.
  3. "Developing new processes for the conversion of methanol to advantaged biofuels within a market-responsive biorefinery concept enabled by catalysis" Presented at the ACS National Meeting, San Diego, CA. March 20, 2022.
  4. "Catalyst design to direct high-octane gasoline fuel properties for improved engine efficiency" Presented at the ACS National Meeting, San Diego, CA. March 22, 2022.
  5. "Direct synthesis of branched hydrocarbons from CO2 hydrogenation over composite catalysts in a single reactor" Presented at the 27th North American Catalysis Society Meeting, New York, NY. May 22-27, 2022
  6. "New processes for the conversion of renewable methanol to advantaged biofuels within a market-responsive biorefinery concept enabled by catalysis" Presented at the Green Chemistry and Engineering Conference, Reston, VA. June 8, 2022.
  7. "Roles of Cu in coke oxidation during regeneration of spent Cu/BEA catalyst from renewable high octane hydrocarbon synthesis" Presented at the 96th ACS Colloid & Surface Science Symposium, Golden, CO. July 11-13, 2022
  8. "Using Chemistry and Engineering to Accelerate Technology Development for Sustainable Transportation Fuels" invited seminar at Lafayette College, Easton, PA, Nov 18, 2022.
  9. "Direct Conversion of Renewable CO2-Rich Syngas to High-Octane Hydrocarbons in a Single Reactor" 2022 American Institute of Chemical Engineers Annual Meeting, Phoenix, AZ, Nov 17, 2022.
- Commercialization update
  - Phase 2 R&D project initiated in 2022 to assess high-octane gasoline technology for commercialization at the small pilot scale (200-250 g_{cat})