CO_2 Reduction and Upgrading for e-Fuels Consortium

U.S. DEPARTMENT OF ENERGY

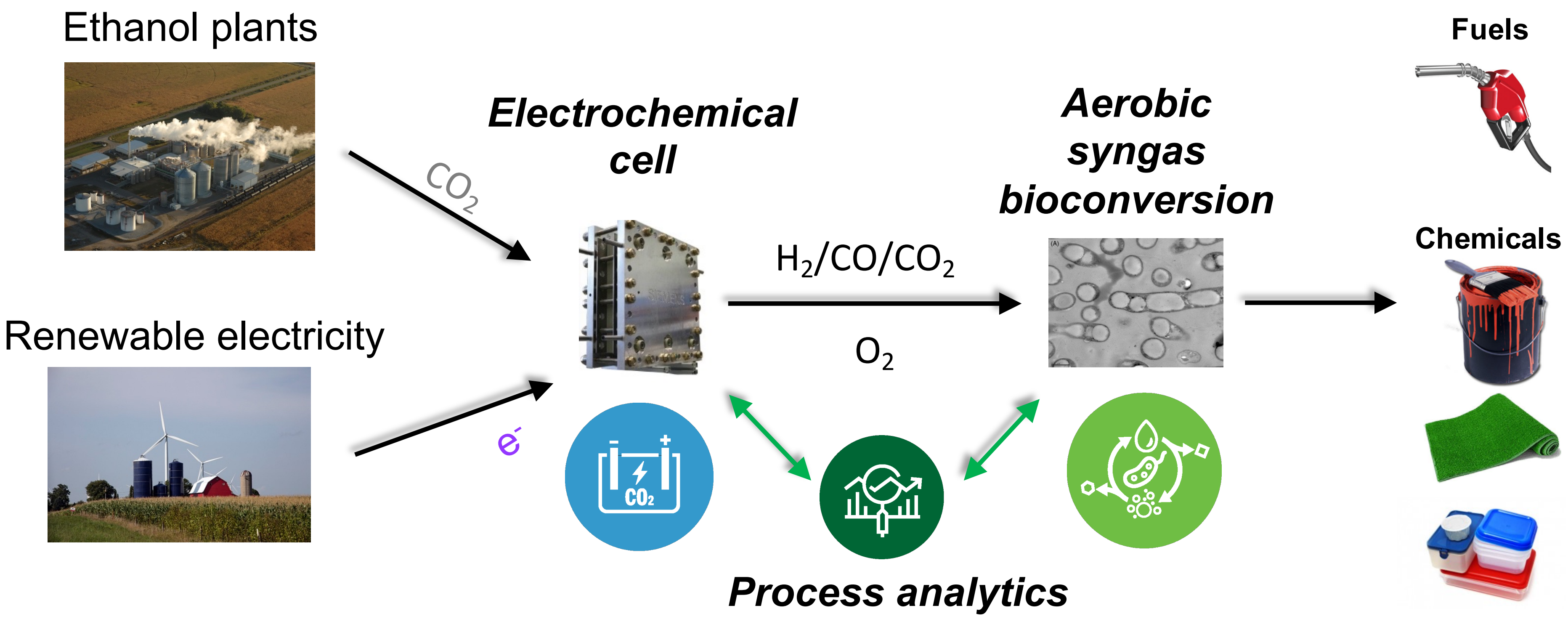
Bioconversion of Syngas from Electrochemical CO_2 Reduction to Sustainable Aviation Fuels

Eric Sundstrom, Lawrence Berkeley National Laboratory
Chris Hahn, Lawrence Livermore National Laboratory

BETO Peer Review
April 5, 2023

Project Overview: Objectives

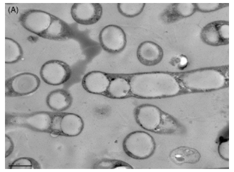
- Develop controlled and predictable electrochemical conversion of CO_2 and H_2O to defined mixtures of syngas ($H_2/CO/CO_2$)
- Combine metabolic engineering and bioprocess improvements to convert biologically syngas mixtures to precursors for sustainable aviation fuel
- Generate technical data to inform TEA / LCA and develop performance targets



Project Overview: Team

Biochemical Development

- Genetic tool development
- Bioprocess improvement
- Terpene biosynthesis



BERKELEY LAB
Lawrence Berkeley National Laboratory

OAK RIDGE
National Laboratory


Eric
Sundstrom (PI)


Justin
Panich


Adam
Guss


Sara Tejedor
Sanz


Neha
Bansal


Melissa Tumen-
Velasquez

Electrochemical Development

- Modeling
- Design optimization
- Control of microenvironments

BERKELEY LAB
Lawrence Berkeley National Laboratory


Adam
Weber


Eric
Lees


Chris
Hahn (co-PI)


Tiras
Lin


Nick
Brady


Peter
Agbo


Tobias
Kistler


Victoria
Ehlinger

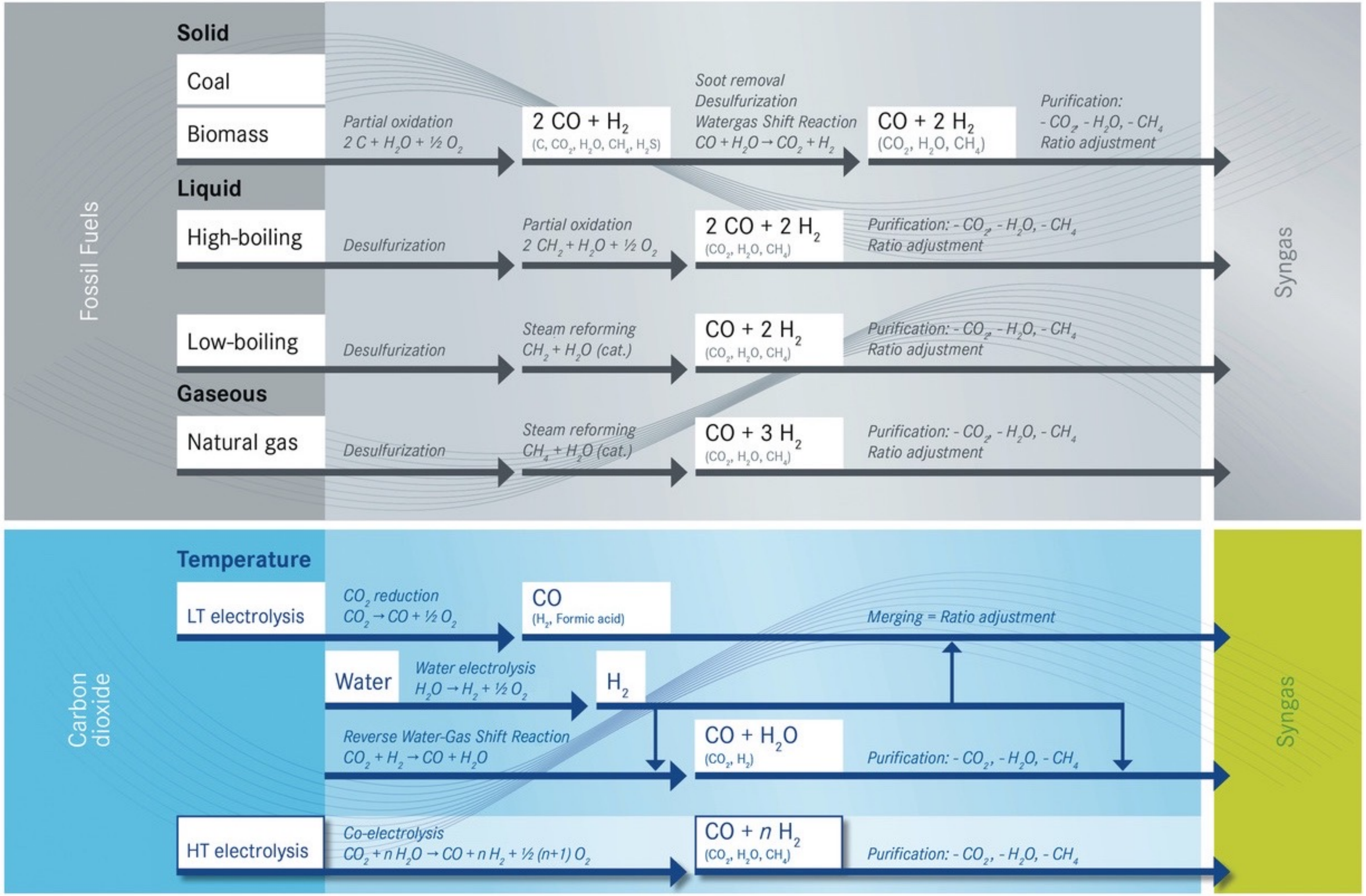

Max
Goldman

1 – Approach: Syngas from CO_2 electrolysis

Advantages of our approach

- Decarbonization of syngas (CO + H_2) manufacturing through electrification and utilization of CO_2, which will have significant impacts on industrial sectors such as chemicals, traffic/transportation, and energy storage

- 1-stage low temperature (LT) electrolysis to syngas has the potential to lower costs when compared to 2-stage electrolysis



R.A. Eichel *et al.*, *Angew. Chemie*, 2016, 56, 5401-5411

1 – Approach: Electrolyzer gaps

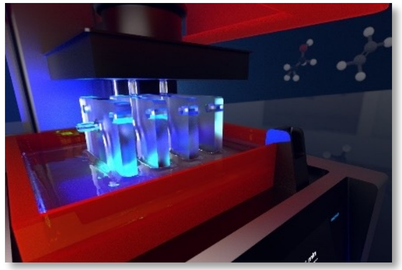
- Efficient and durable low temperature CO_2 electrolyzers with precise control over the full range of syngas (H_2/CO) compositions
- Catalysts and ionomers that are tailored for energy efficient CO and H_2 co-production
- Predictive models that provide guidance on optimizing electrolyzer operating parameters
- Inverse approaches to component (e.g., flow field) design

1 – Approach: Electrolyzer development and target outcomes

Strengths in our approach:

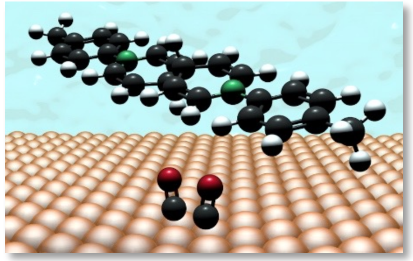
- Tight integration between simulations and experiment
- Proximity of LBNL-LLNL for cross-project exchange

Manufacturing

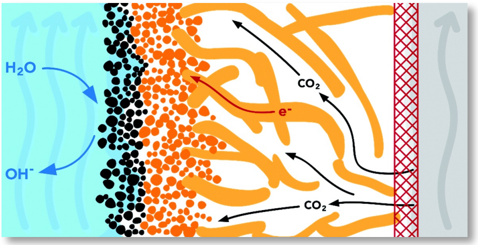


Electrolyzer Integration and Optimization

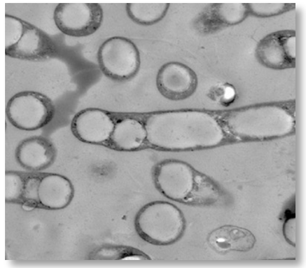
Microenvironments



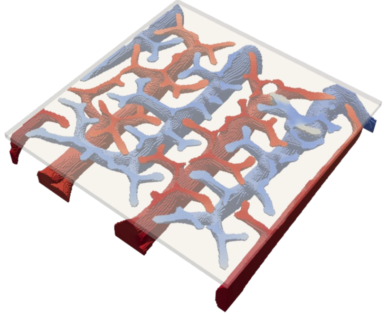
Modeling



Bioprocess Informs Electrolyzer Outputs



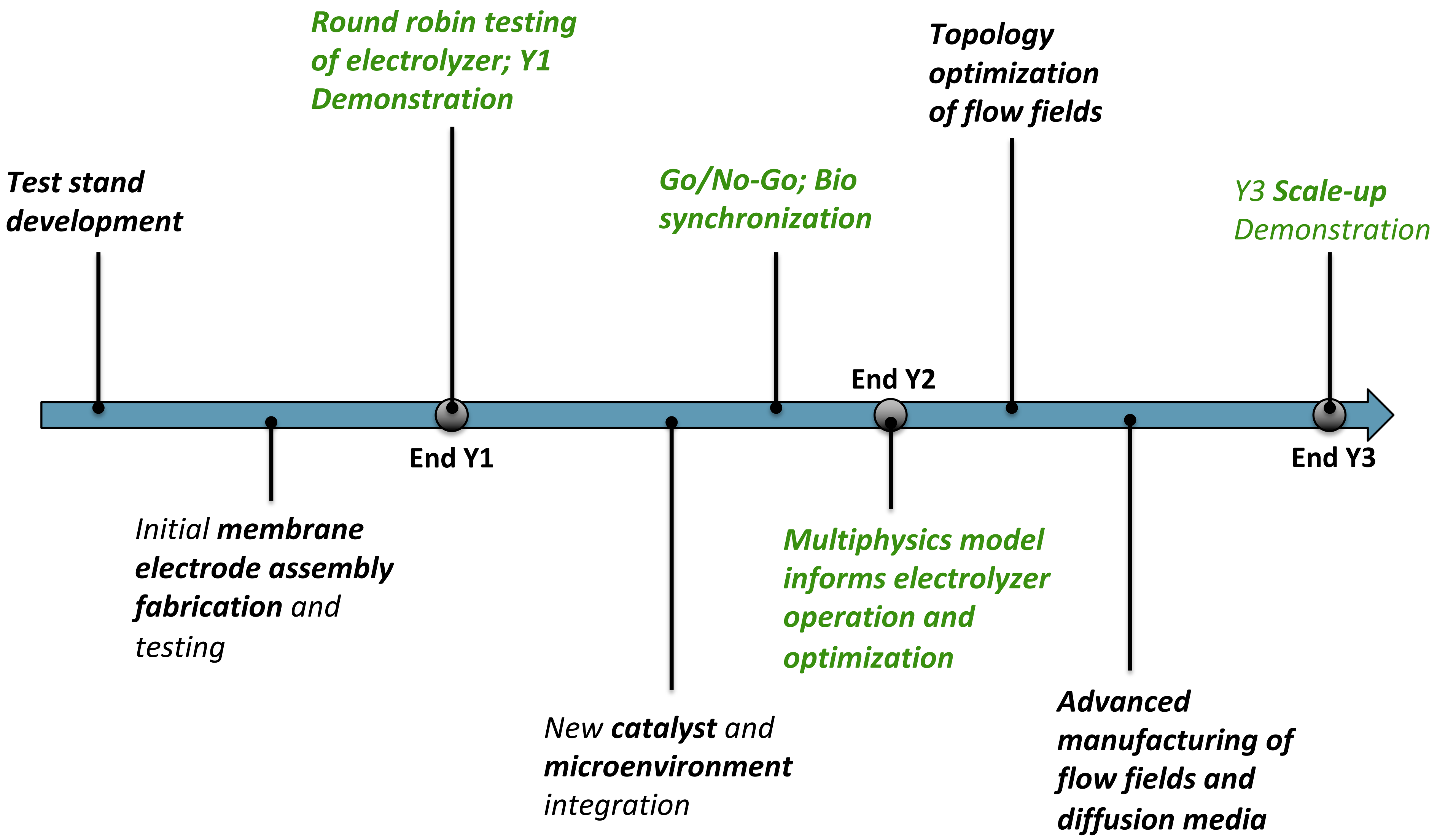
Design Optimization



Key Outcomes:

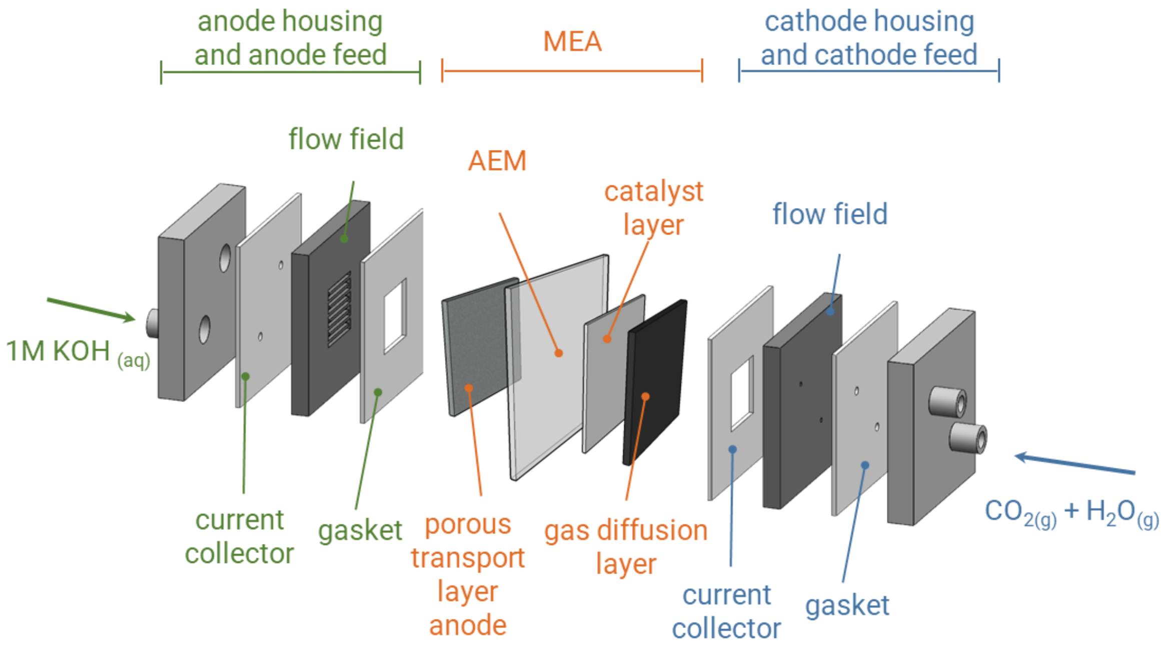
- Efficient, durable, and scalable electrolyzer that generates tunable syngas ratios
- Identification of translatable component designs through scale-up
- Predictive models that enable inverse design of electrolyzers

1 – Approach: Electrolyzer project plan and timeline



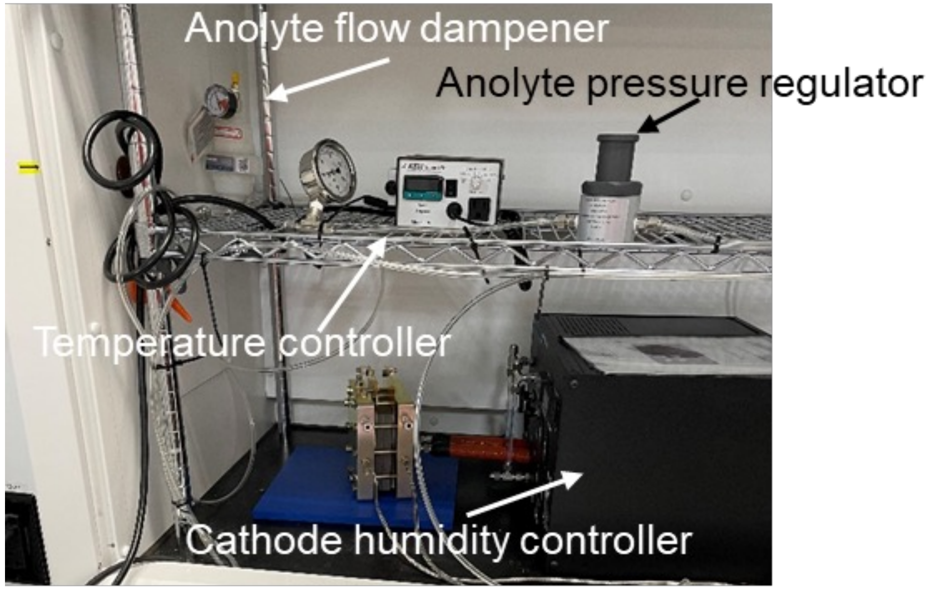
1 – Approach: Electrolyzer system development

Electrolyzer optimization



- 5, 25, and 100 cm^2 zero-gap cells
- Catalyst (Fe modification of Au, Ag, Au)
- Ionomer (custom formulations)
- Cathode ionomer/catalyst ratios
- Gas diffusion layer
- Alkaline and neutral anolyte

Operating condition optimization



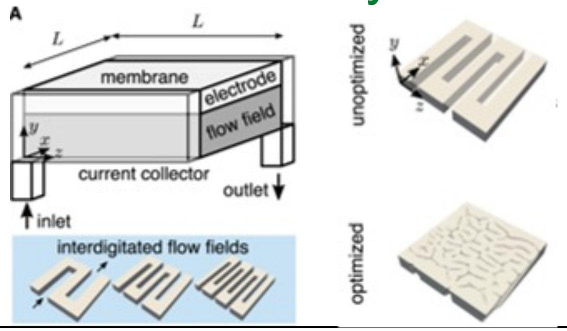
- CO_2 flow rate and backpressure
- Temperature
- Humidity
- Pulsed current

1 – Approach: Electrolyzer modeling

Optimization Model (LLNL)

Simplified Physics

Detailed Geometry

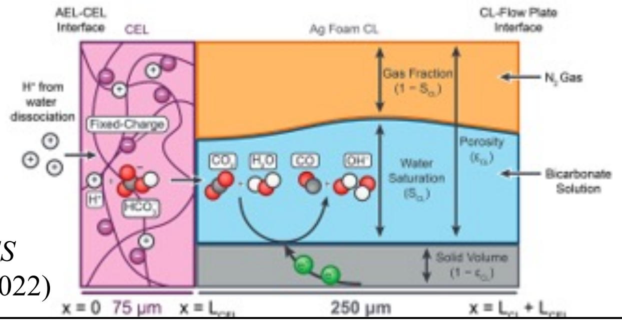


Lin, et al. *JES* (2022)

System Model (LBNL)

Detailed Physics

Simplified Geometry



Lees, et al. *ACS Energy Lett.* (2022)

Optimal Flow Field Reactor Outputs

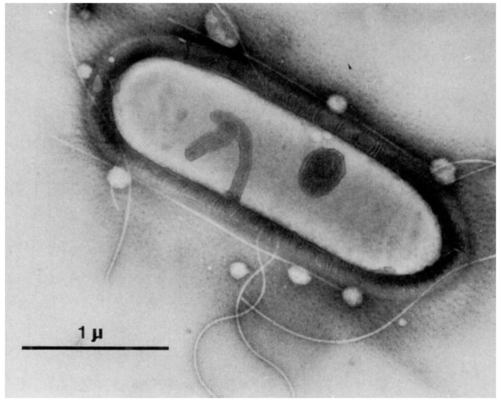
Inform Physics

- Reaction Kinetics
- Boundary Conditions
- Simplifying Assumptions

Experiments

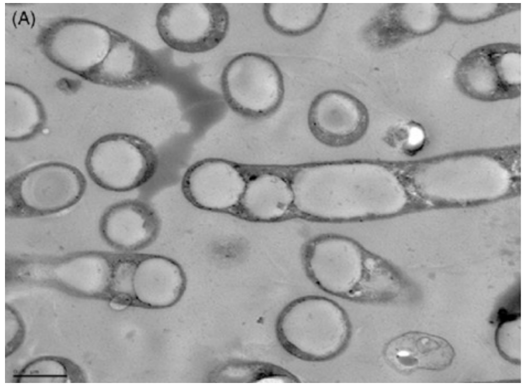
1 – Approach: Aerobic syngas conversion

Anaerobic CO-oxidizers



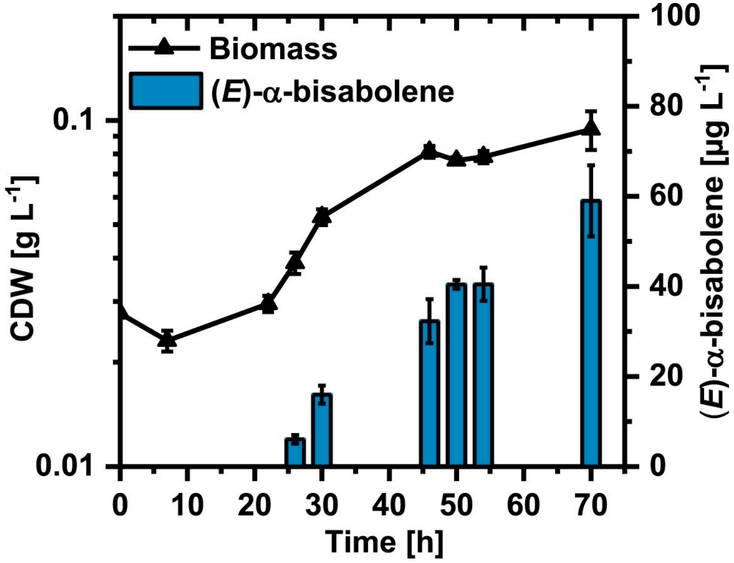
- Low biomass
- **Limited products (C_2-C_4)**
- Genetics challenging
- Efficient substrate use
- Commercial scale for EtOH

Aerobic CO-oxidizers



- High biomass and productivity
- **Diverse products (C_5-C_{20})**
- Genetics tractable
- *Inefficient substrate conversion*
- *Lab scale*

Hydrogenophaga pseudoflava



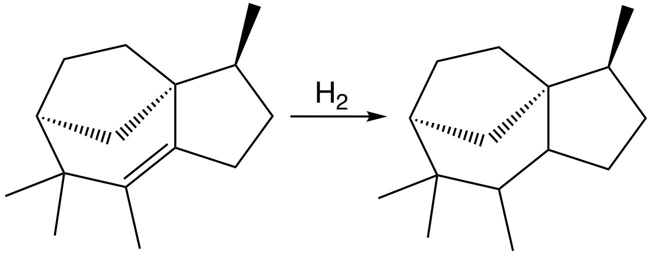
- Aerobic CO utilization
- Flexible metabolism (CO/CO2/H2)
- CO tolerance **at >40% concentration**
- Engineered for isoprenoid production [1]

- **Can we achieve high titer terpene production?**
- **Can we find conditions to support robust growth?**

1. Grenz et al. Metabolic Engineering, **2019**, *55*, 220

1 – Approach: High energy density fuels and precursors

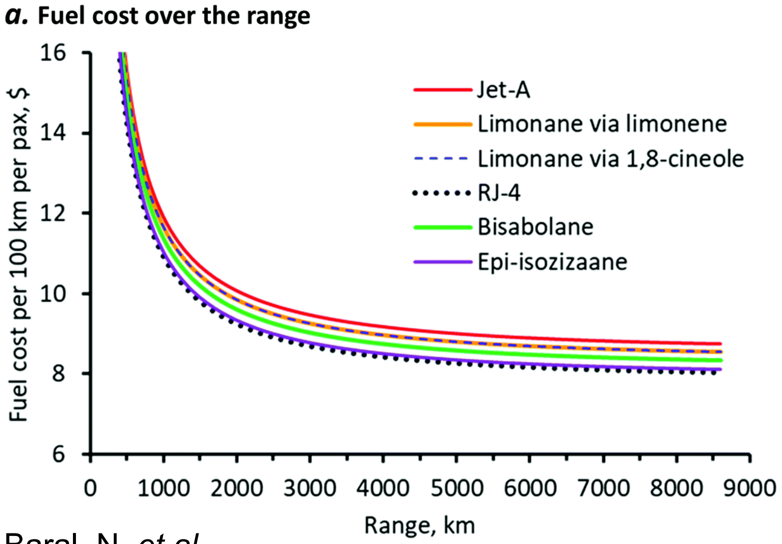
Target 1: *epi*-isozizaene

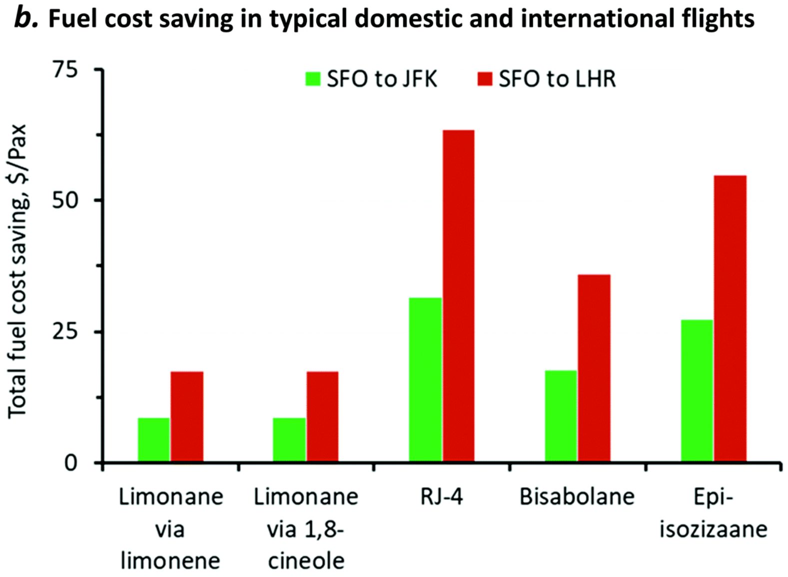


epi-isozizaene
(~ 1 g/L in *E.coli*)

epi-isozizane

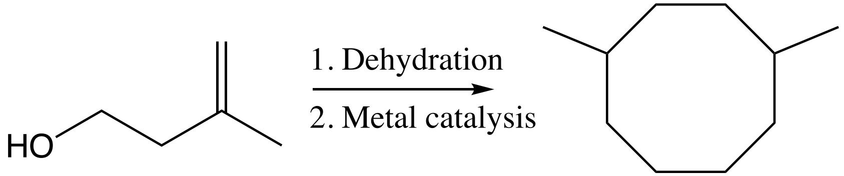
C15 sesquiterpene: higher energy density thanJet-A





Baral, N. *et al.*
Energy and Environmental Science, **2018**, *12*, 807-824

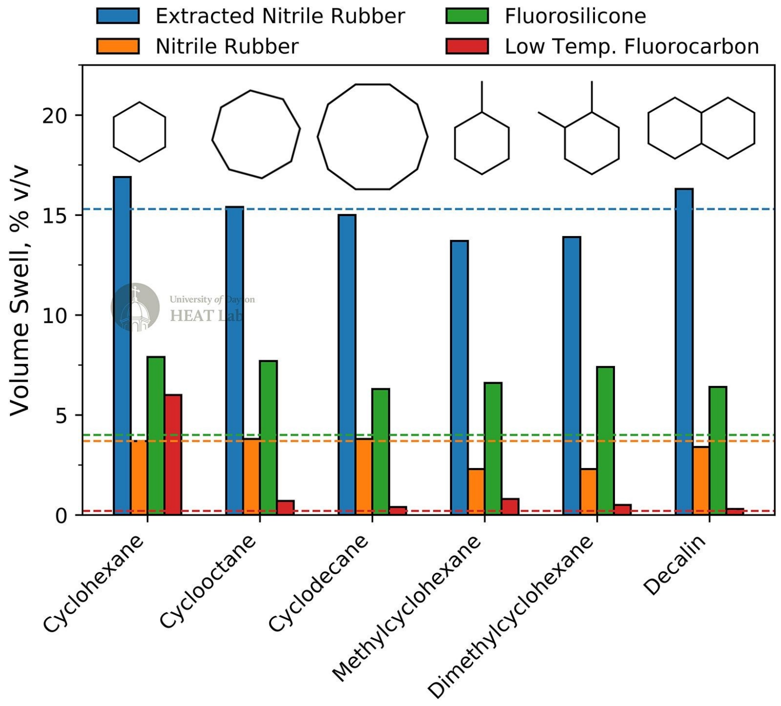
Target 2: isoprenol



isoprenol
(~ 11 g/L in *E.coli*)

DMCO

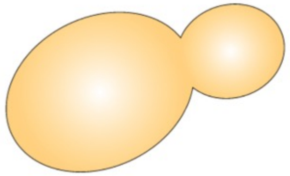
Replaces aromatics for O-ring swelling



Kosir, S.. *et al.* *Fuel*, **2020**, *274*, 117832

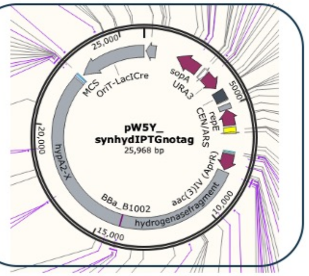
1 – Approach: Design-build-test-learn cycle for isoprenoid production

PCR fragments +
240 bp linkers



Chemical transformation
Yeast recombination

Plasmid recovery



Whole plasmid sequencing

Build

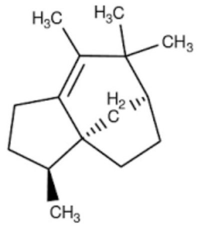
Design ← *Learn* ← *Test*

SnapGene®
Software for molecular biology

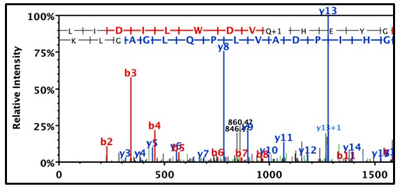
Design next build

PubMed

Consult literature
Discuss results



GC-MS



Proteomics

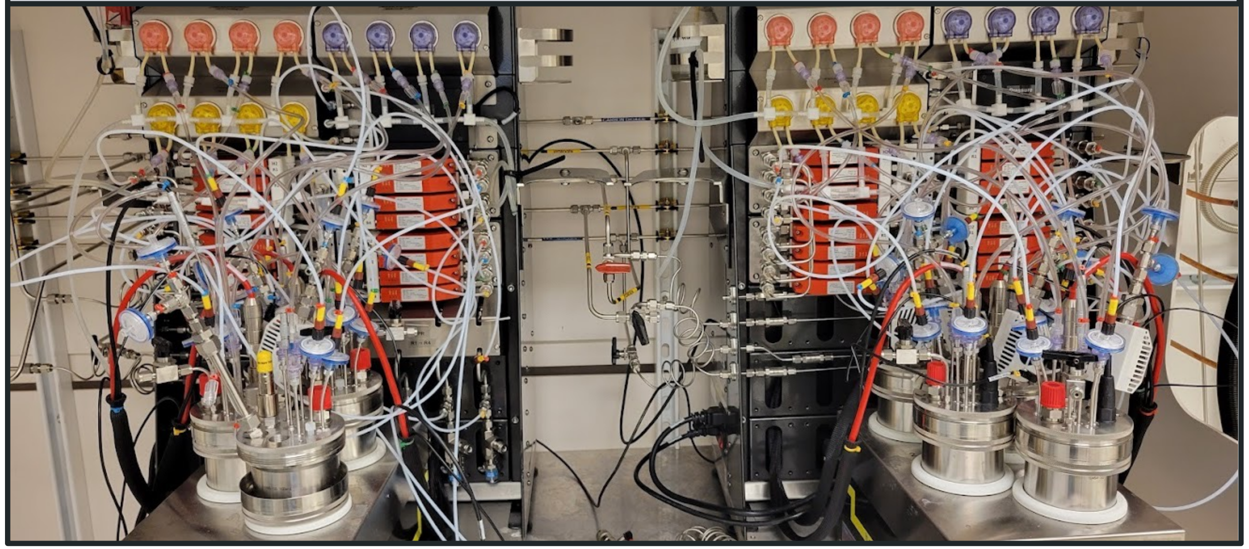
Measure pathway expression
Measure metabolite concentration

Electroporate
Move to *H. pseudoflava*

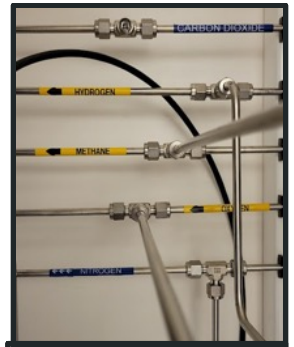
1 – Approach: Bioprocess development and intensification

- Flexible gas supply: ($CO/CO_2/H_2/O_2$)
- Feedback-based process controls
- High cell density cultivation
- Significant investment in safety:
  - Separated spargers
  - Fully enclosed operation
  - Gas monitoring
  - High strength stainless steel vessels
  - Protocol development and operator training

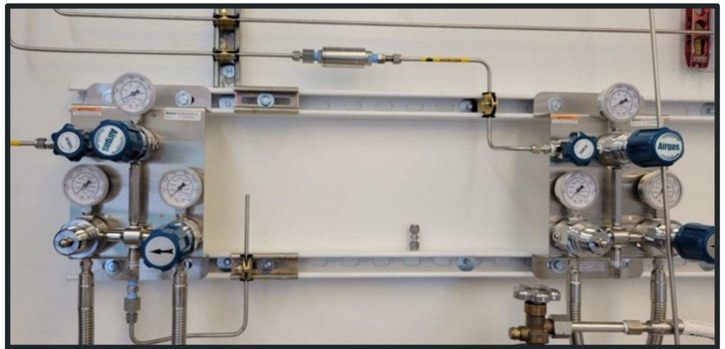
8 x 500 mL bioreactor setup – 5 bar pressurization



20 L reactor



Five-gas manifold

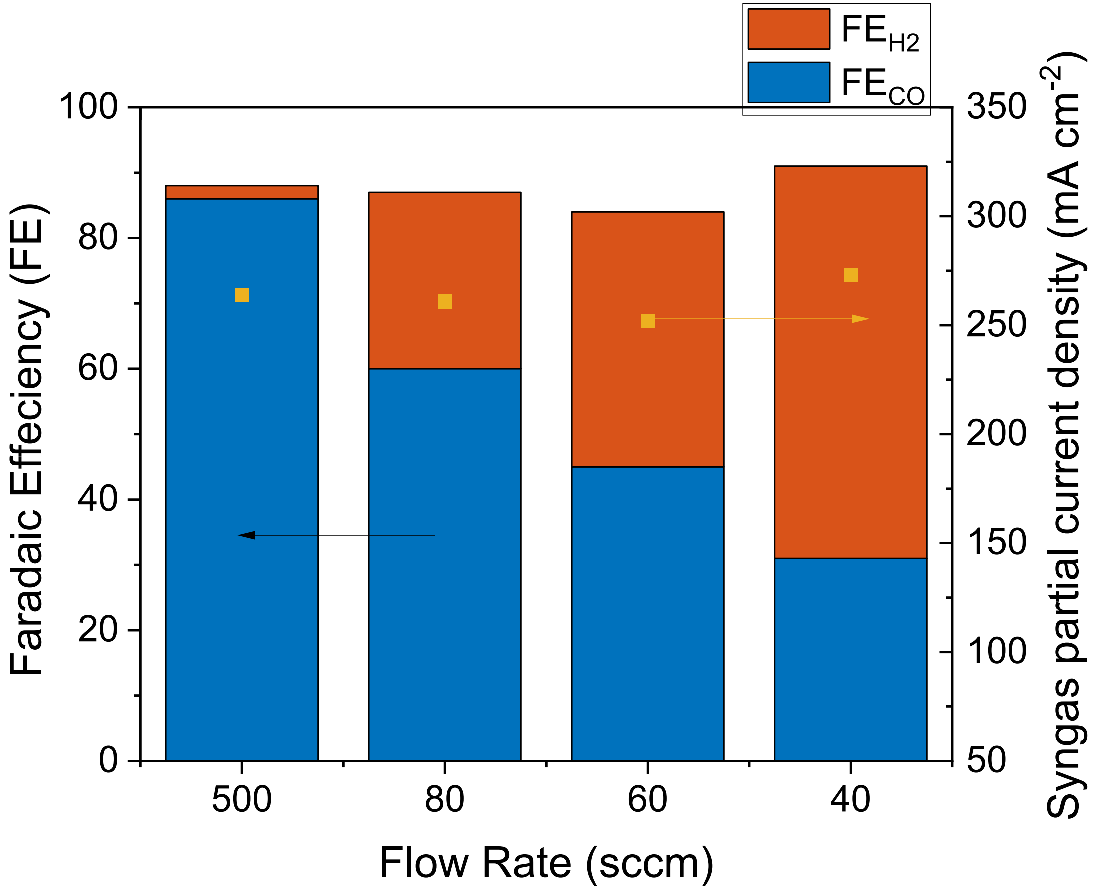


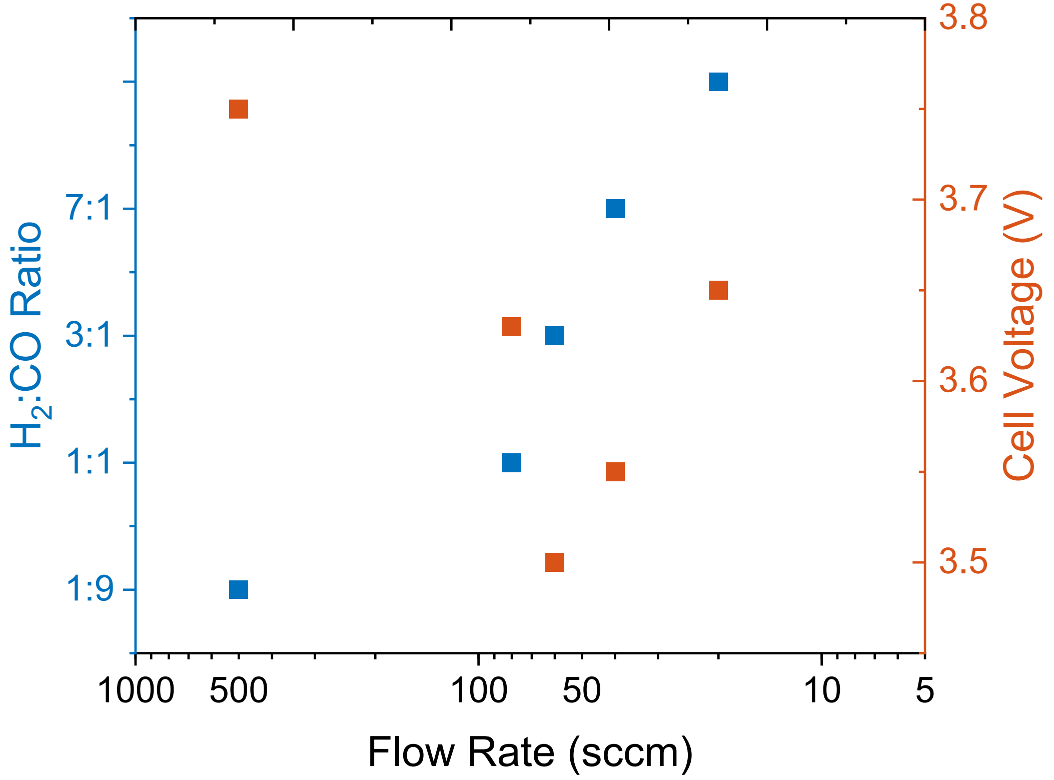
Automated changeover valves

1 – Approach: Project milestones and status

- Q2 FY22: Report on outcomes of kickoff meeting with partner labs to program sponsors: **100% complete**
- Q3 FY22: Perform methylome analysis and design expression cassettes for expression of the corresponding methyltransferase(s) in *E. coli*: **100% complete**
- Q4 FY22: Achieve 3 different H_2/CO ratios (7:1, 3:1, and 1:1) at near-ambient temperatures and pressures, syngas partial current density (> 300 mA/cm2), > 90% syngas FE, < 3 V total cell potential, and electrode geometric area (5 cm2): **100% complete**
- Q1 FY23: Growth of one *Hydrogenphaga pseudoflava* strain ($t_d \leq 4$ h; cell weight >1 g/L) with $CO/CO_2/H_2$ in 500 mL reactors; CO concentration in gas mixture >5%. (LBNL): **80% complete**
- Q2 FY23: A chromosomally-encoded T7 polymerase-based regulated gene expression system in *Hydrogenophaga pseudoflava* that is induced in the absence of an essential nutrient such as nitrogen
- Q3 FY23: Generation of a defined $CO/H_2/CO_2$ ratio at total syngas current density of > 300 mA/cm2 and 90% syngas FE; conversion of gas mixture at that ratio by H. pseudoflava to SAF terpene at >100 mg/L after 24 h. **(Go/no-go milestone)**
- Q4 FY23: Establish a multiphysics model that informs experiments on CO_2 electrolyzer operating conditions to control the ratios of $CO/CO_2/H_2$ in the exit stream
- Q4 FY24: Generate tunable syngas ratios and pressures and rates from CO_2 electrolysis using membrane-electrode assemblies at > 90% FE, 100 ml/min CO, < 3 V total cell potential at a size of >25 cm2; demonstrate production of SAF terpene precursor at > 1 g/L at 500 mL in 24 h **(End of project milestone)**

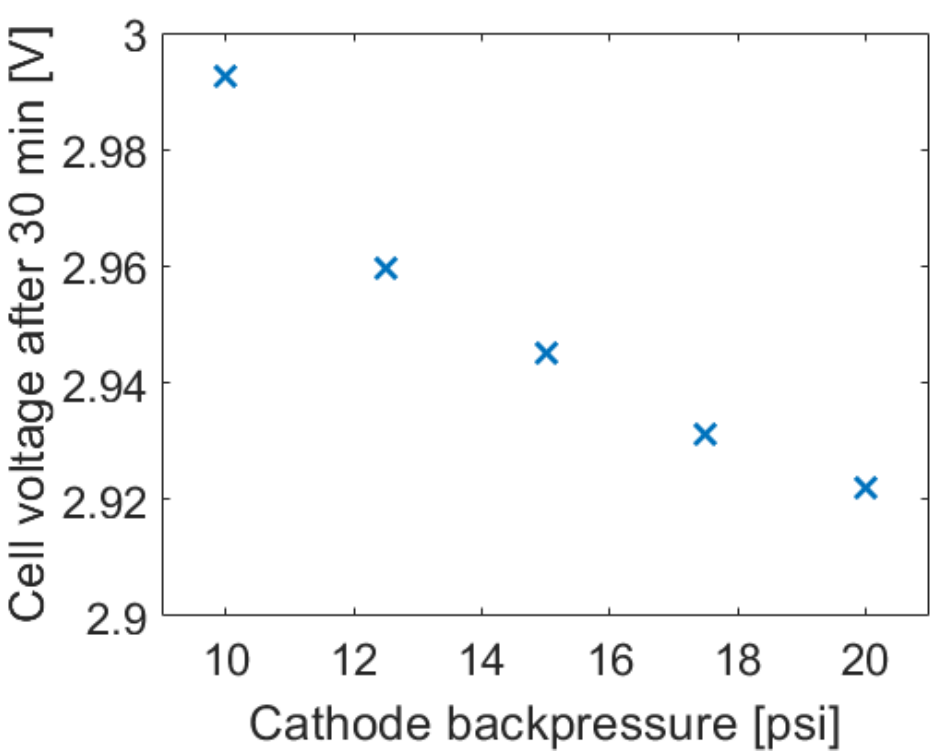
2 – Progress and Outcomes: Electrolyzer development [H_2:CO Ratios]

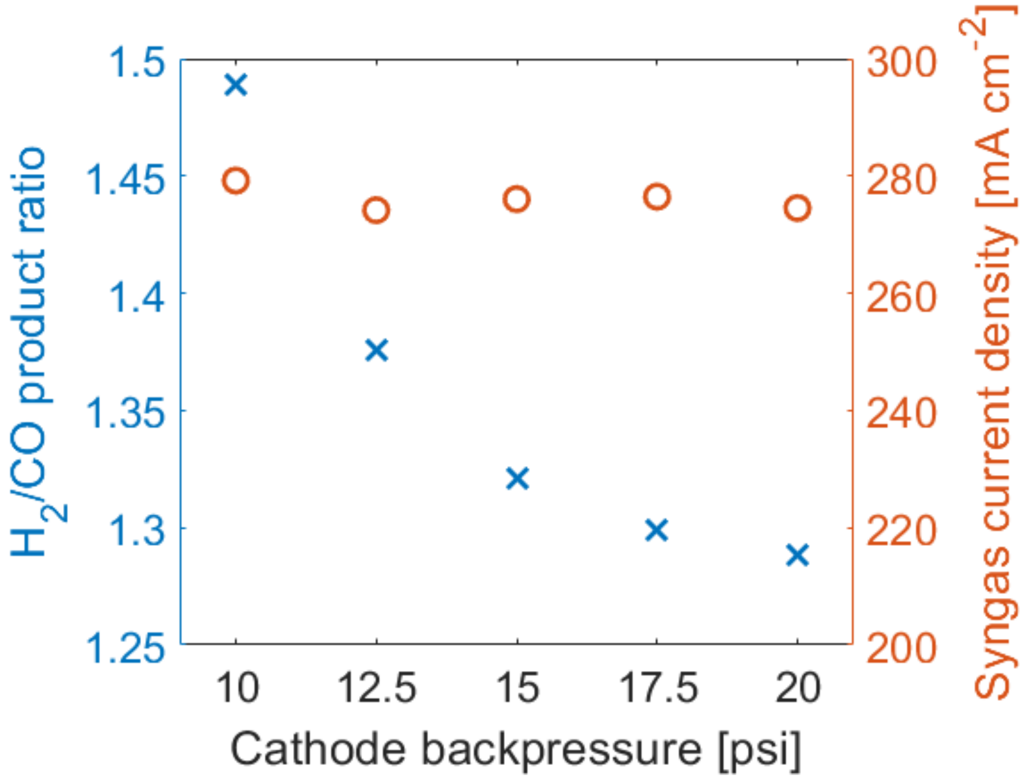




We have identified strategies to tune CO:H_2 ratios through controlling operating conditions such as the CO_2 flow rate. We are on schedule to achieve our end of project scale-up goals.

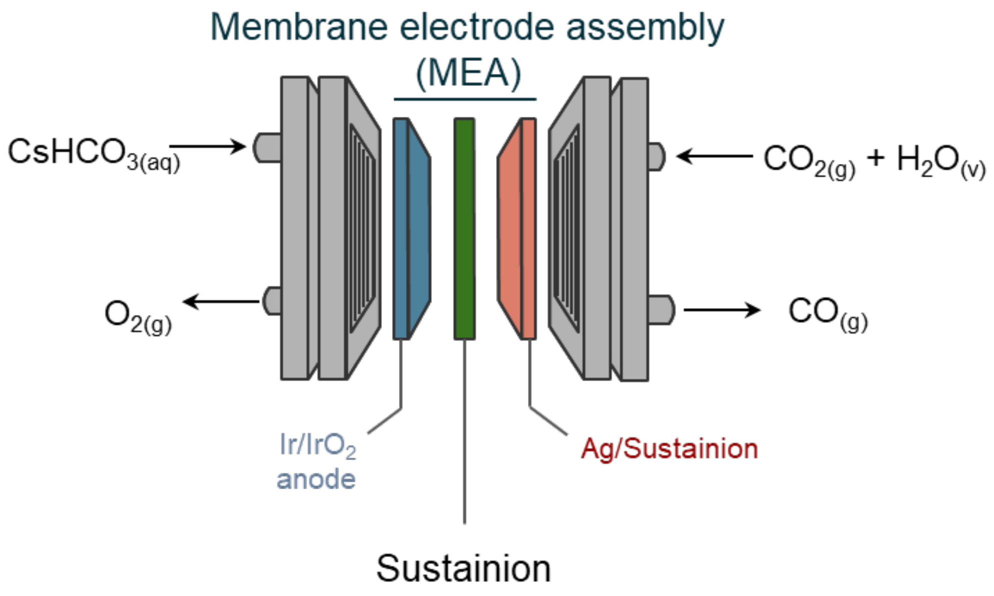
2 – Progress and Outcomes: Electrolyzer development [H_2:CO Ratios]

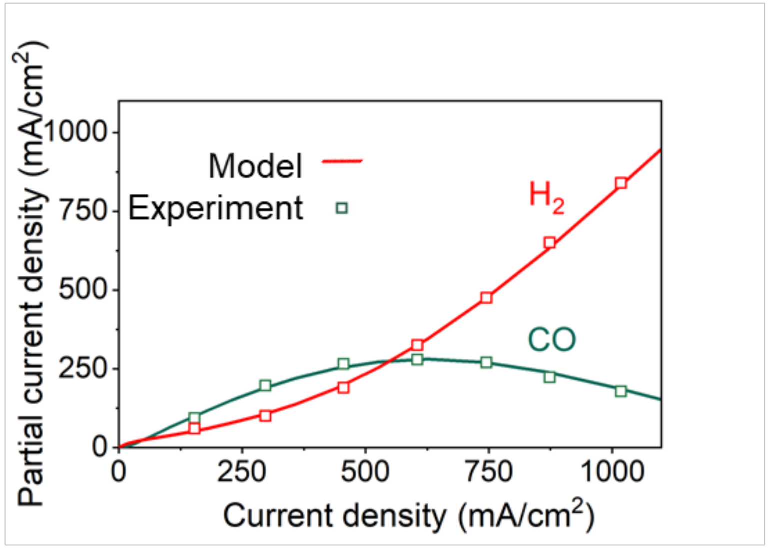


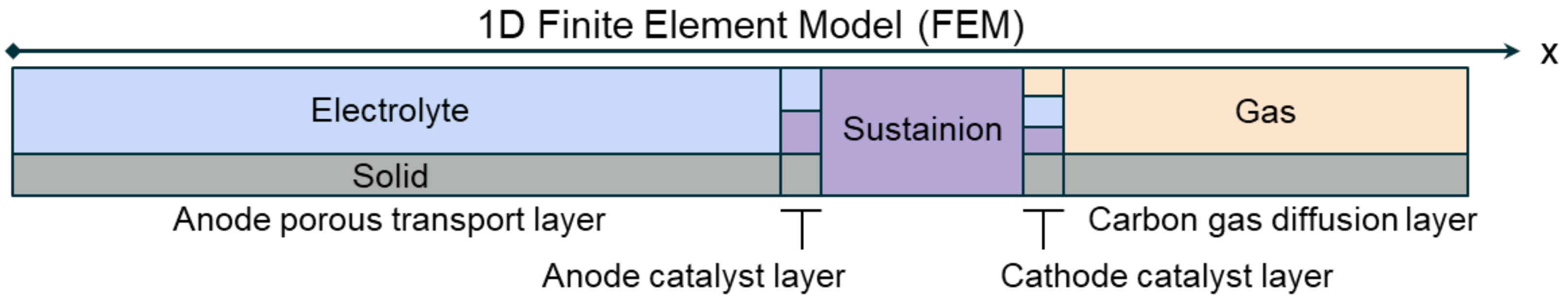


We have further evaluated different operating conditions resulting in stable operation time of ~10 h.

2 – Progress and Outcomes: Electrolyzer modeling

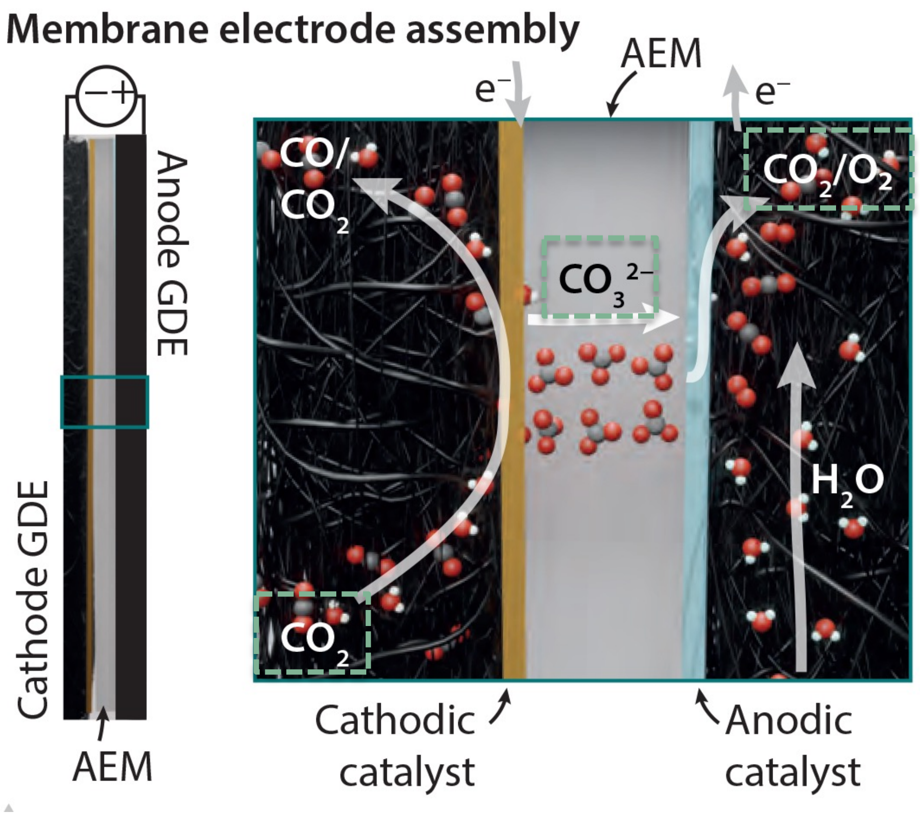


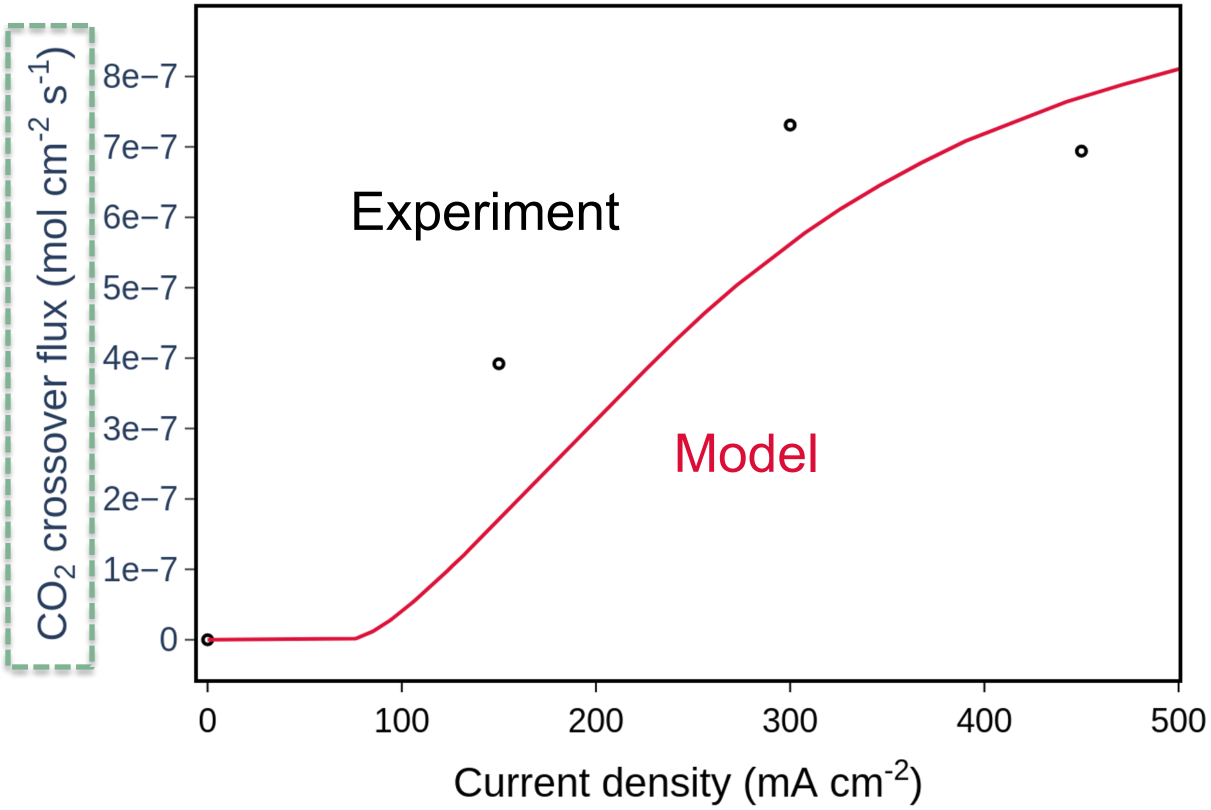




We have developed a model that simulates local transport profiles and informs optimization of electrolyzer operating conditions for syngas composition.

2 – Progress and Outcomes: Electrolyzer modeling

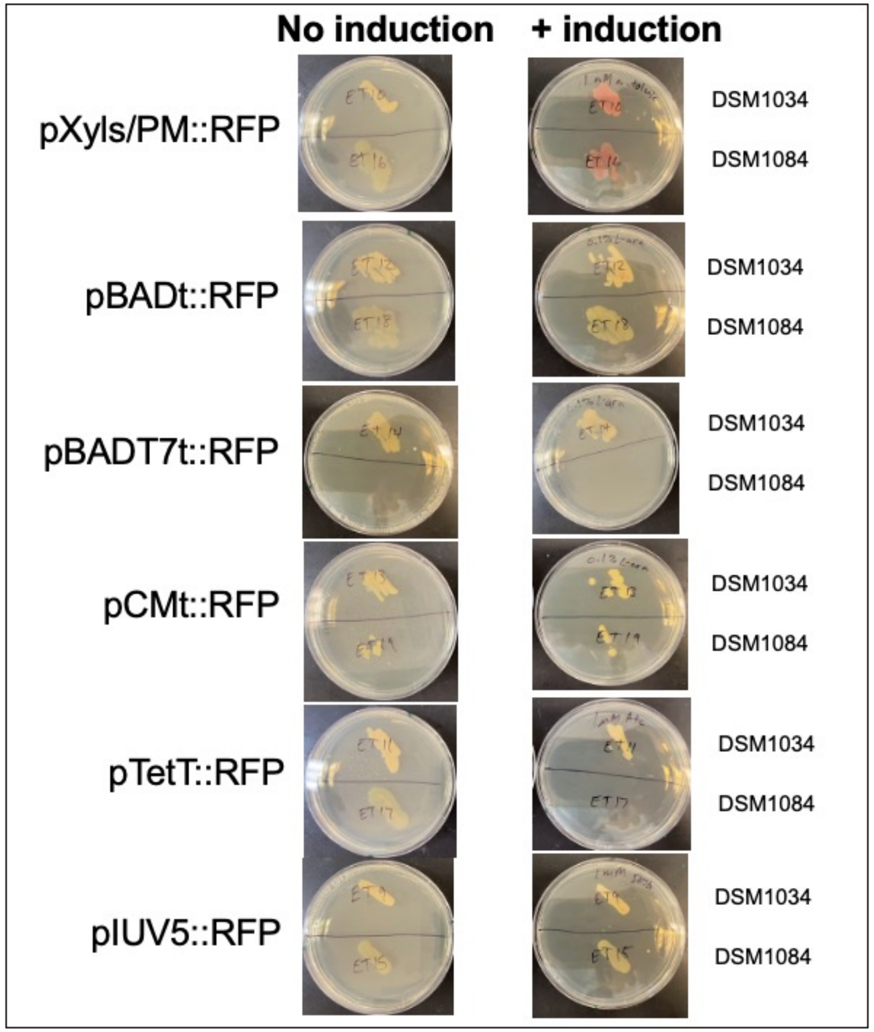




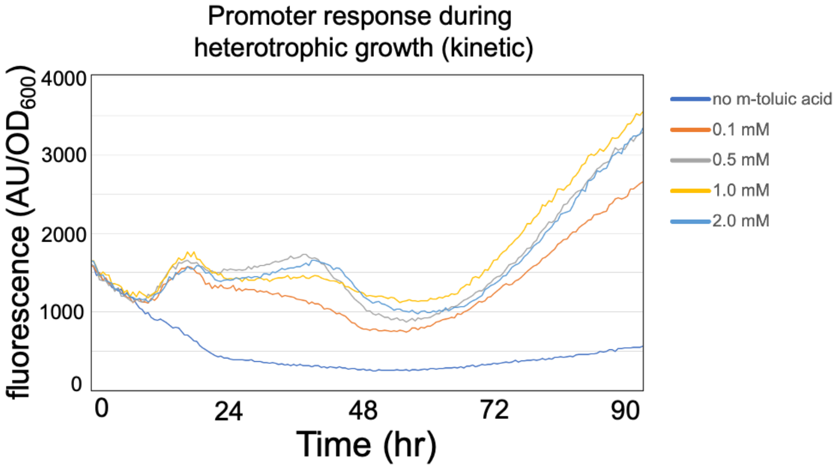
We have simulated CO_2 crossover to inform operating conditions for optimizing carbon utilization.

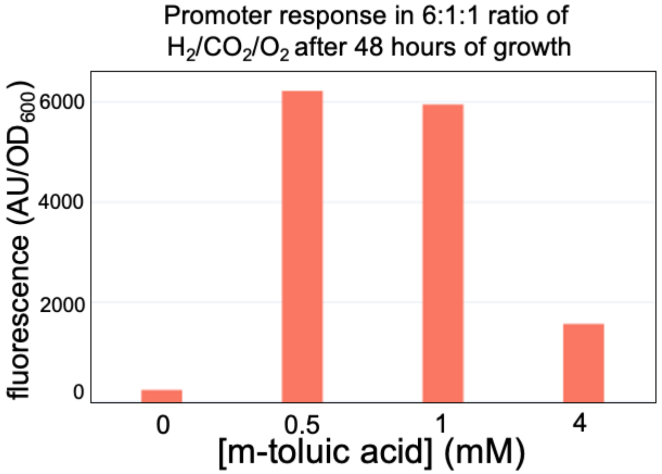
2 – Progress and Outcomes: Inducible promoters

Inducible promoter screen (plasmid)



pXyls/PM::RFP induction (m-toluic acid)

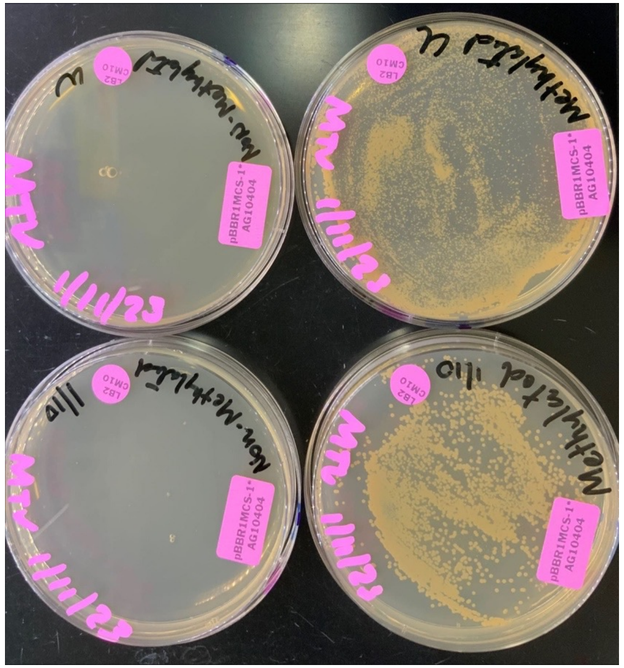




2 – Progress and Outcomes: Improving transformation

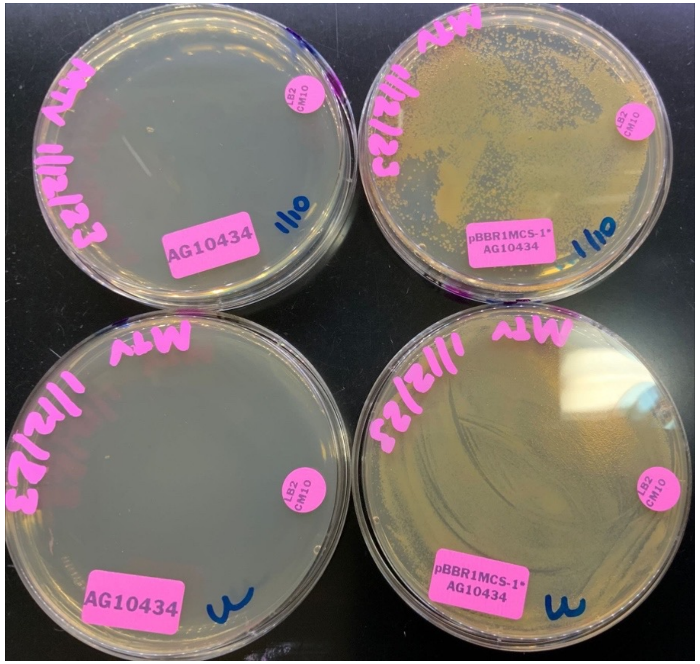
DSM1034

Unmethylated Methylated



DSM1084

Unmethylated Methylated

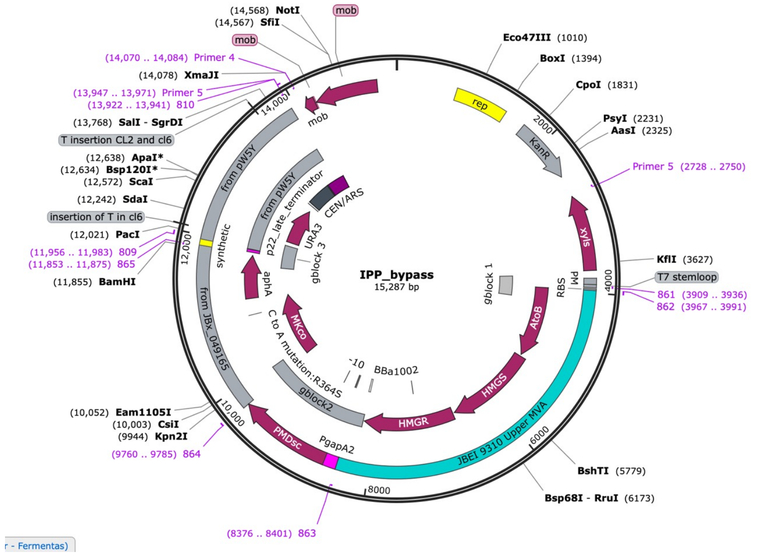


- Performed methylome analysis on *H. pseudoflava* DSM1034 and 1084
- Constructed E. coli strains that express corresponding DNA methyltransferases
- Demonstrated transformation with replicating plasmids

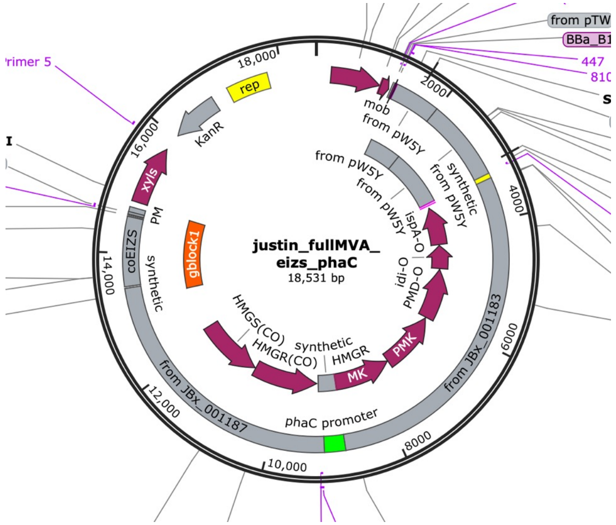
2 – Progress and Outcomes: Construction of isoprenoid pathways

Plasmids constructed and sequenced for isoprenol and epi-isozizaene production, functional analysis underway.

Isopentenyl diphosphate (IPP) bypass mevalonate (MVA) pathway: Isoprenol production



Full MVA pathway + epi-isozaene synthase (EIZS): Epi-isozizaene production



Toxic IPP accumulation avoided by promiscuous activity of PMD

- Upper MVA pathway under Pxyls/PM
- Lower MVA pathway under PgapA2

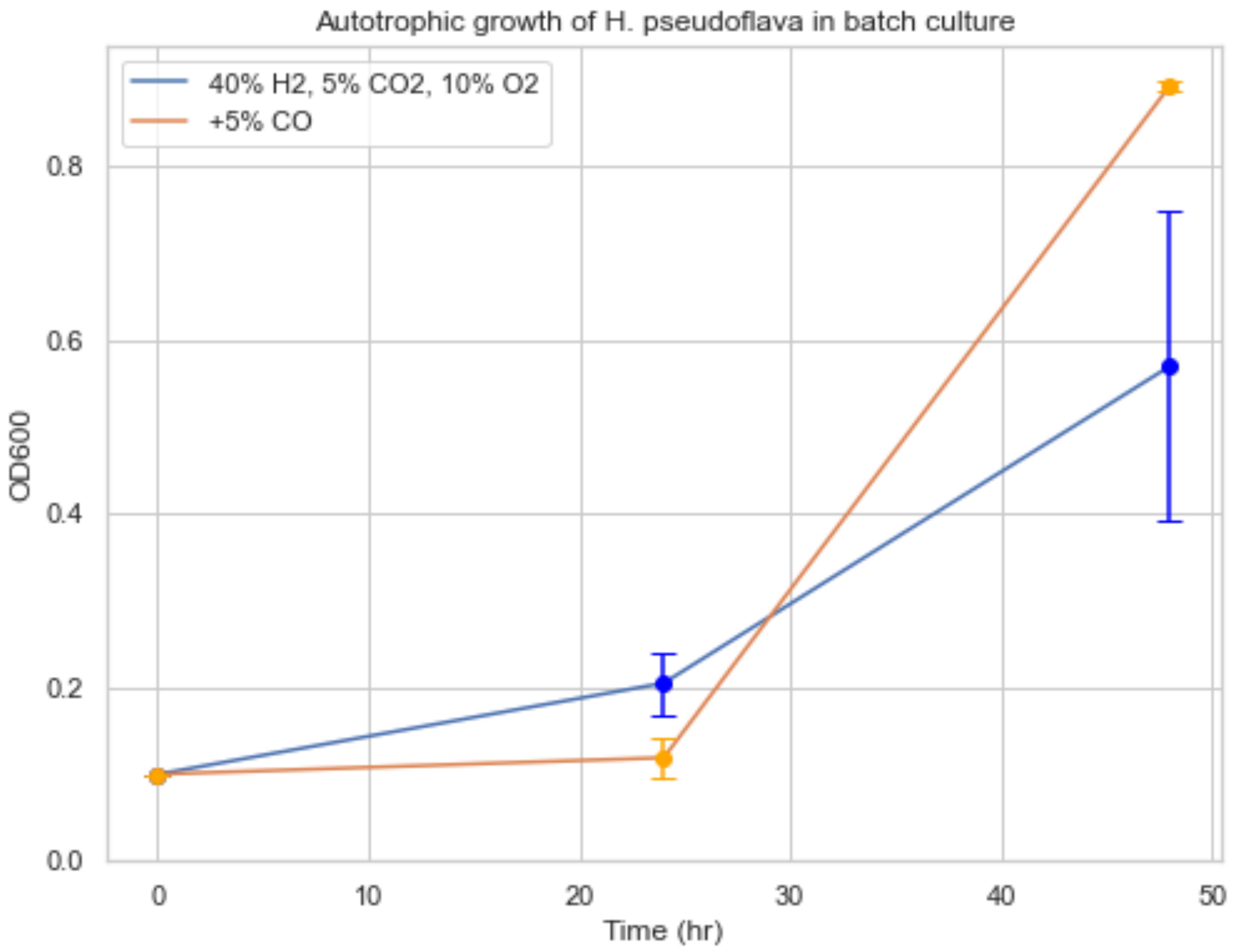
FPP overproduction for

- Upper MVA pathway + EIZS under Pxyls/PM
- Lower MVA pathway under PgapA2 promoter

2 – Progress and Outcomes: Growth with CO

H. pseudoflava growth on CO:

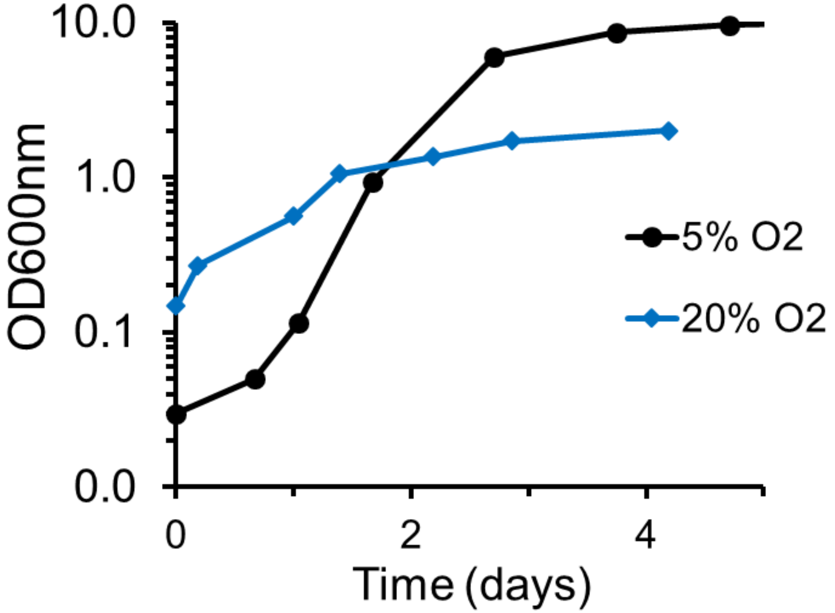
- Batch cultivation underway – confirming tolerance to CO at 5% concentration
- Growth enhancement effect observed after initial growth inhibition
- Bioreactor experimentation will initiate pending final EH&S approval



2 – Progress and Outcomes: Bioprocess development

- Bioreactor commissioning at 5% O_2: **O_2 limitation**
- Bioreactor operation at 20% O_2: **O_2 inhibition**

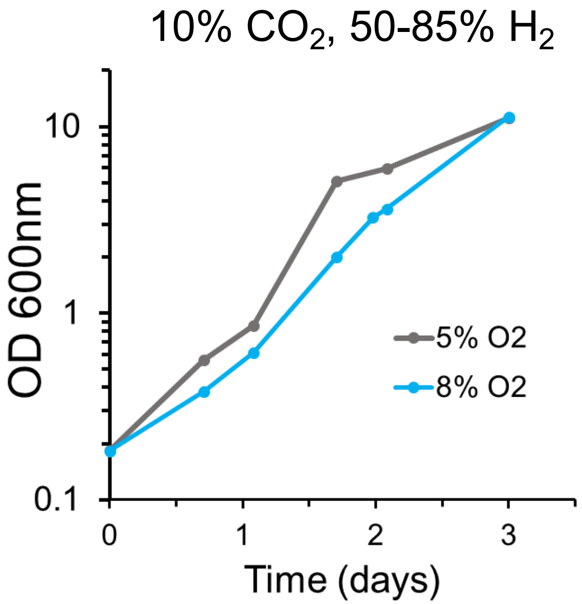
Autotrophic growth with constant O_2

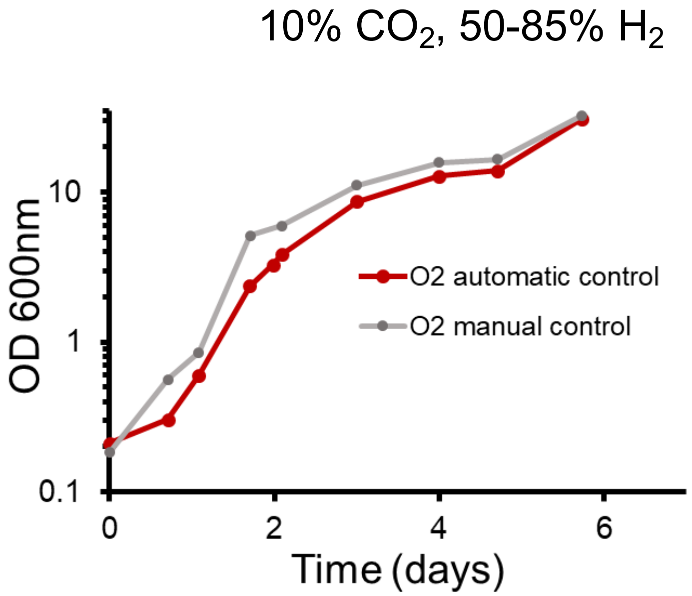


- Max t_d =5.4 ±0.3 h
- Max dry weight=4.7±0.18 g/L

- Growth with adaptive oxygen supply: **resolves DO limitation and oxygen toxicity**
- Validated across DO cascade conditions

Autotrophic growth with dynamic O_2 control





- Max dry weight = 14 ±1 g/L vs 0.1 g/L current SOT[1]
- Media optimization ongoing

1. Grenz et al. Metabolic Engineering, **2019**, *55*, 220

3 – Impacts

Technology development: Creation of an efficient and flexible pathway from CO_2 to reduced long-chain products, including high energy density SAF.

Scientific impact: Development of *H. pseudoflava* as a new platform host for aerobic syngas conversion, demonstration of robust electrochemical syngas generation.

Technical collaboration: Creation of synergies within the BETO portfolio including ABF host onboarding, Separations Consortium volatile product capture, and ABPDU gas fermentation efforts. Establishes electrochemical – biochemical collaboration between LBNL, LLNL, and ANL.

Technology transfer: New upstream platform ties into ongoing SAF commercialization efforts including the Praj Matrix BETO TCF project, ongoing US Navy collaborations, and JBEI isoprenol commercialization efforts, and ongoing electrolyzer development and deployment efforts with TotalEnergies and SiemensEnergy.

Summary

Mission relevance: Development of a high-efficiency platform to generate high energy density SAF and SAF-precursors from CO_2 and renewable electrons in alignment with BETO program goals

Approach: Coupled electrochemical syngas production with aerobic syngas bioconversion

Electrochemical Progress: Demonstration of syngas generation with high faradaic efficiency, tunable $CO:H_2$ ratios, and 10+ hour longevity

Biochemical Progress: Inducible promoter and methylation systems developed, isoprenoid pathways constructed, growth with CO confirmed, bioreactors commissioned achieving 14.1 g/L dry cell weight,

Next Steps:

- Integration of biocatalyst development and bioprocess development targeting bioreactor isoprenoid titers > 1g/L over 24 hours
- Integration of modeling and electrochemical system design to achieve 100+ hour longevity, >90% faradaic efficiency, <3 V cell potential, and CO flow >100ml/min

Quad Chart

Timeline

- Project start data: 1/1/2022
- Project end date: 9/30/2024

	FY22 Costed	Total Award
DOE Funding	$1M / yr	$3M
Project Cost Share *	N/A	N/A

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

Project Goal

Convert CO_2 by electrochemistry to syngas mixtures ($CO/CO_2/H_2$) and upgrade these syngas mixtures to biofuels and bioproducts, focusing on sustainable aviation fuel (SAF). These SAFs will have higher energy density and swelling properties superior to current SAFs.

End of Project Milestone

Generate tunable syngas ratios and pressures and rates from CO_2 electrolysis using membrane-electrode assemblies at > 90% FE, 100 ml/min CO, < 3 V total cell potential at a size of >25 cm2; demonstrate production of SAF terpene precursor, at > 1 g/L at 500 mL in 24 h.

Funding Mechanism

AOP project (Direct-Funded Lab Project)

Project Partners

- LBNL, Eric Sundstrom (PI), esundstrom@lbl.gov
- LLNL, Chris Hahn (co-PI), hahn31@llnl.gov
- ORNL, Adam Guss, gussam@ornl.gov