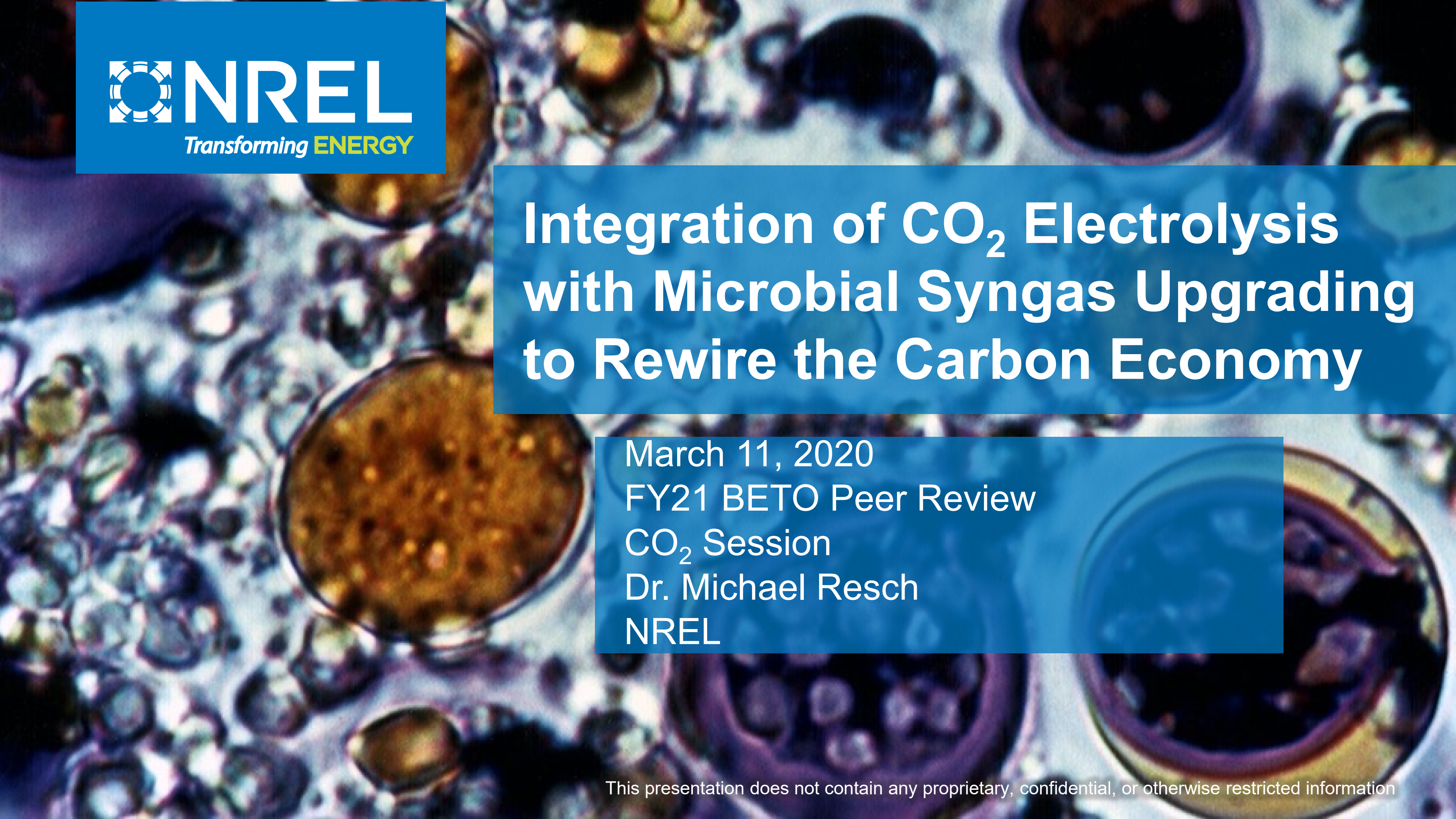
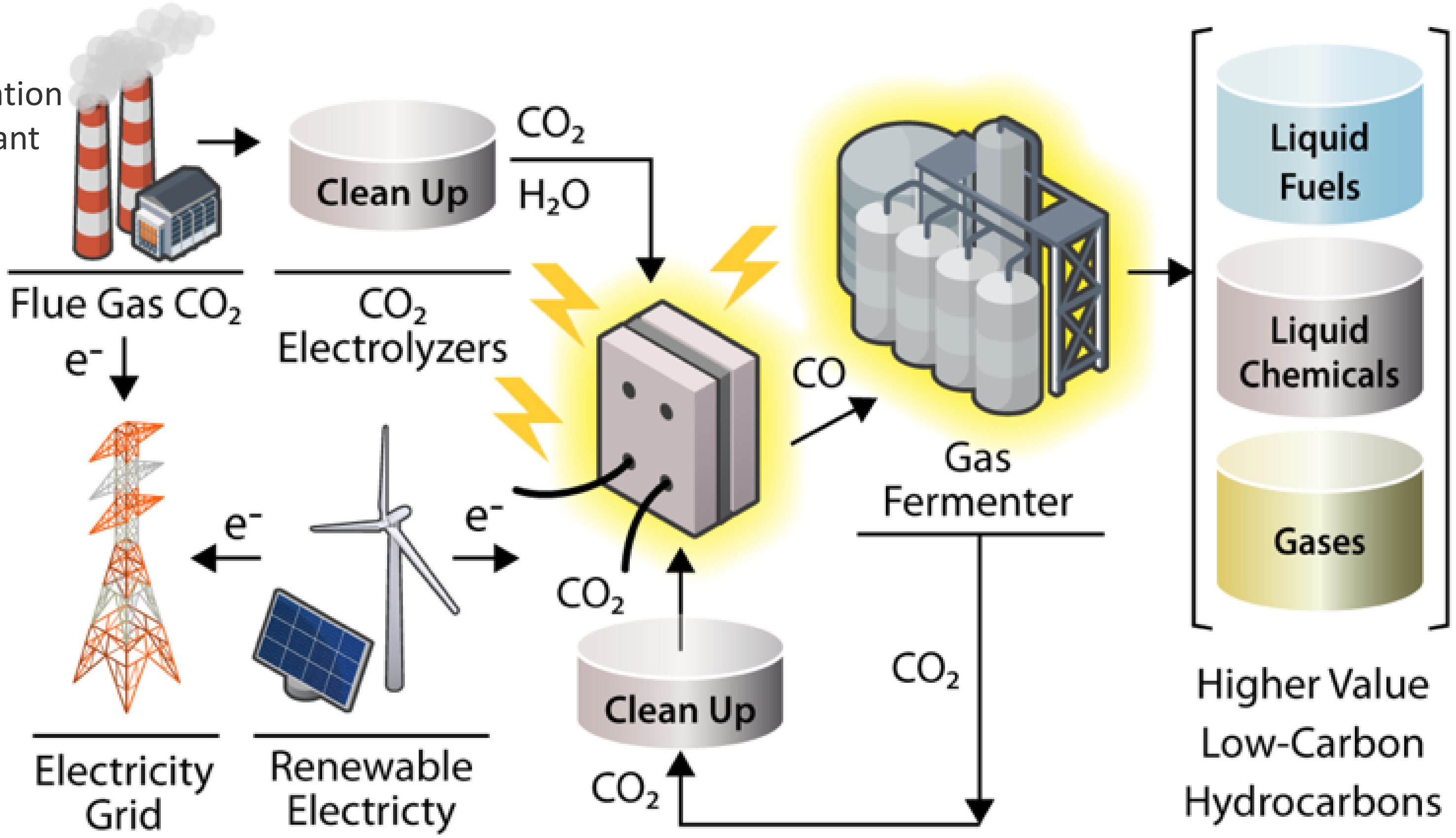


Integration of CO_2 Electrolysis with Microbial Syngas Upgrading to Rewire the Carbon Economy

March 11, 2020
FY21 BETO Peer Review
CO_2 Session
Dr. Michael Resch
NREL

Project Overview

Fermentation
Power plant
Cement
DAC



Higher Value
Low-Carbon
Hydrocarbons

Project Goals

Goal

- Demonstrate the conversion of CO_2 flue gas mixtures by electrolysis and syngas fermentation with high electron and carbon efficiency

Outcome

- Determine the impact of typical flue gas contaminates on electrolyzer efficiency, lifetime, and specificity
- Understand biocatalytic conversion performance as a result of varying syngas compositions, and identify targets for improvement
- Identify key TEA and LCA drivers
  - electricity cost and source impacts
  - carbon intensity
  - feedstock inventory requirements

Market Trends

Category	Trend
Product	Gasoline/ethanol demand decreasing, diesel demand steady
	Increasing demand for aviation and marine fuel
	Demand for higher-performance products
	Increasing demand for renewable/recyclable materials
Feedstock	Sustained low oil prices
	Decreasing cost of renewable electricity
	Sustainable waste management
	Expanding availability of green H_2
	Closing the carbon cycle
Capital	Risk of greenfield investments
	Challenges and costs of biorefinery start-up
	Availability of depreciated and underutilized capital equipment
Social Responsibility	**Carbon intensity reduction**
	Access to clean air and water
	Environmental equity

NREL's Bioenergy Program Is Enabling a Sustainable Energy Future by Responding to Key Market Needs

Value Proposition

- By producing valuable products out of CO_2 this project will incentivize CCU to realize carbon circular economy opportunities

Key Differentiators

- Utilization of inexpensive feedstocks to produce products with low carbon intensity
- Process integration to link concepts
- Core national lab capability
- Market drive to low carbon fuels and chemicals
- Industrial partners
- Best in class technology

1. Management

Task 1 - Liu (DM)

CO_2 Electrolyzer performance optimization

Design, fabricate and scale carbon- and energy-efficient CO_2 electrolyzer with optimized functionality on biopower-derived effluent gas streams.

Task 2 - Guarnieri

Gas fermentation process development and strain optimization

Define microbial and gas fermentation requirements to maximize the carbon uptake and conversion efficiencies.

Task 3 - Resch

Analysis and Integration of combined CO_2 electrolysis with gas fermentation

Integrate technologies to increase industrial carbon efficiencies by creating value-added products from waste carbon.

1. Investigating Industrial Feedstocks

ICM

POET
HUMAN + NATURE

2. Approach

Year 1

Start Q1 FY19

✓Electrolyzer fabrication and evaluation on CO_2
✓Determine flue gas composition from two industrial sources
✓Electrolyzer performance on CO_2
✓Biocatalyst performance on syngas feeds
✓Baseline TEA and LCA (partner AOP)

Year 2

✓Electrolyzer evaluation on mixed typical flue gas components
✓Biocatalyst performance on syngas from electrolyzer run on flue gas mixtures
✓Biocatalyst strategies to increase carbon efficiency
✓Integrate system with GC for real time gas monitoring
✓Match scale of electrolyzer with bioreactor needs
✓Update TEA SOT and R&D targets

Year 3

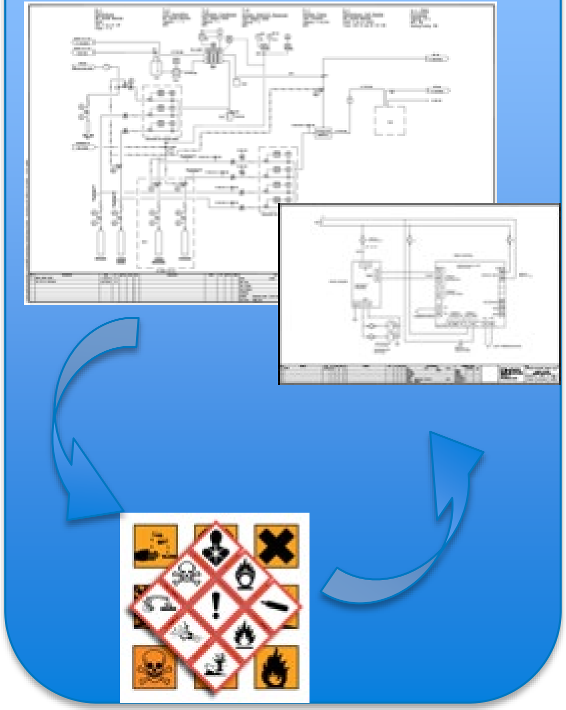
End Q4 FY21

✓Determine the impact electricity costs have on economic viability
✓Identify key cost drivers for future R&D commercial deployment
✓Determine economic and environmental benifits by integration of this process with Industrial CO2 flue gas streams

- Run electrolyzer and bioreactor on representative industrial flue gas contaminates
- Determine purity of flue gas needed to maintain electrolyzer performance

2. NREL apparatus design and assembly – Establishing core capabilities at NREL

Design and hazard analysis



Build

Readiness verification and commissioning

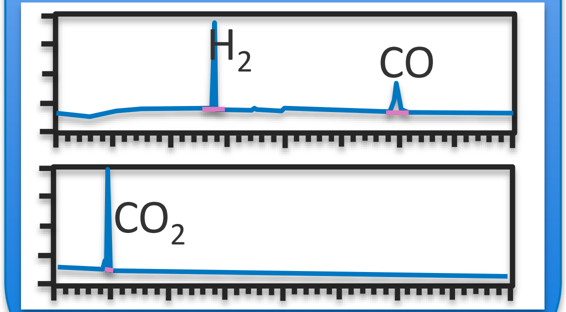
National Renewable Energy Laboratory

READINESS VERIFICATION – AUTHORIZATION TO OPERATE

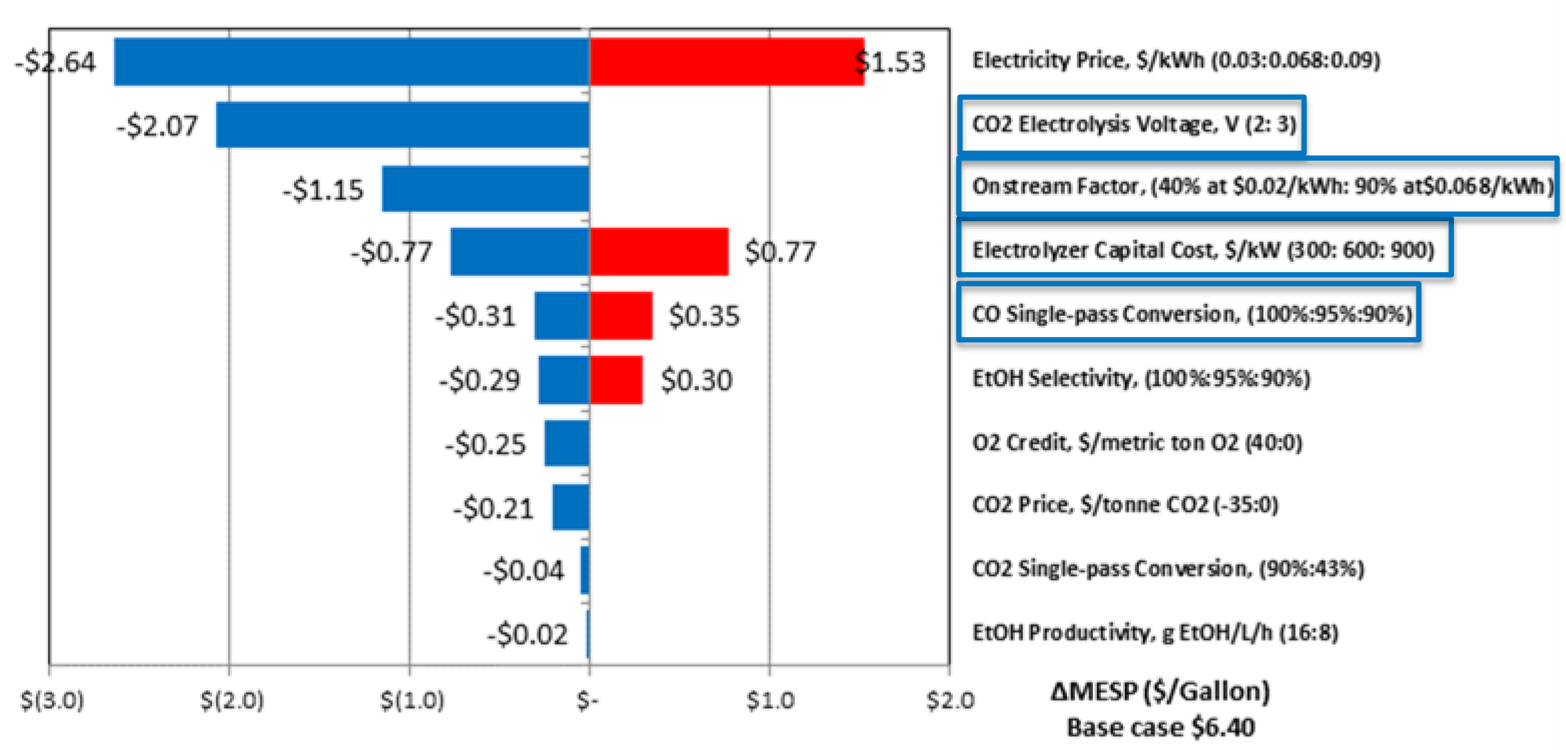
RESEARCH ACTIVITY – FACILITY INFORMATION	
Activity/Facility Description	**Organization Number** 5100 & 2700
Location BRF 290	**Environment, Safety, and Health (ESH) Point of Contact (POC)**
Date / **Updated**	**Operating Restrictions**
Authorization to Operate (Granted or Conditional)	

INTRODUCTION

INSTRUCTIONS



2. Key Cost Drivers



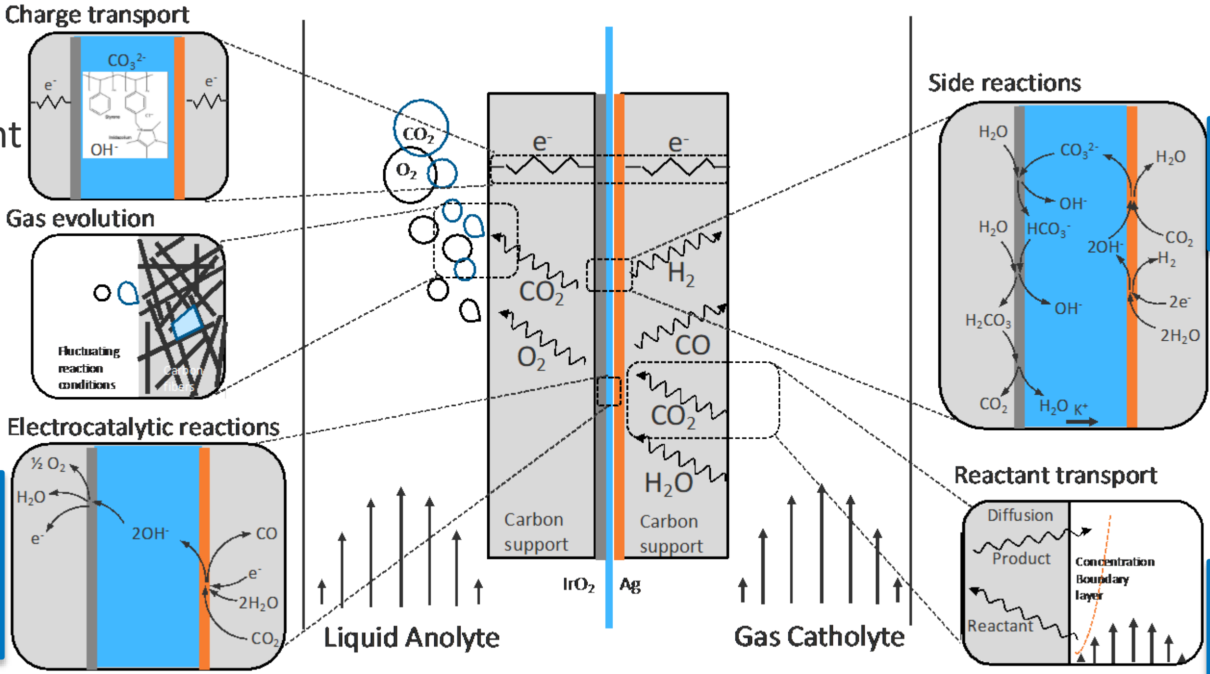
2. Electrochemical CO_2 Reduction Gaps

Technology gaps

- Carbon support stability
- Heat management

- Carbon support chemistry
- Channel design

- Catalyst stability
- Contaminant tolerance



Technology gaps

- Mechanisms
- pH effects

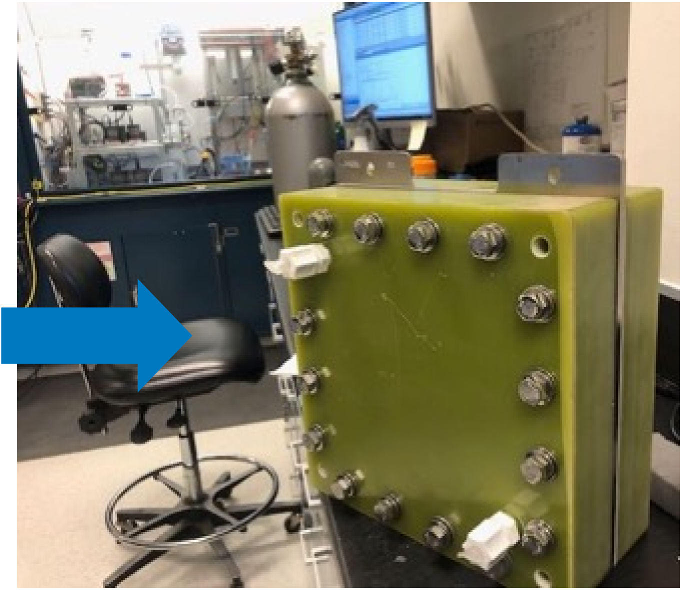
- Channel design
- Humidification requirement

2. Building larger electrolyzers to meet fermenter needs

- Fermenter requires 0.1-2 LPM influent gas stream with at least 50% CO from CO_2 electrolyzer
  - Require a total current of 150A with ≥95% CO Faradaic Efficiency
  - Scale up from 5cm^2 cell to 500cm^2 CO_2 electrolyzer stack

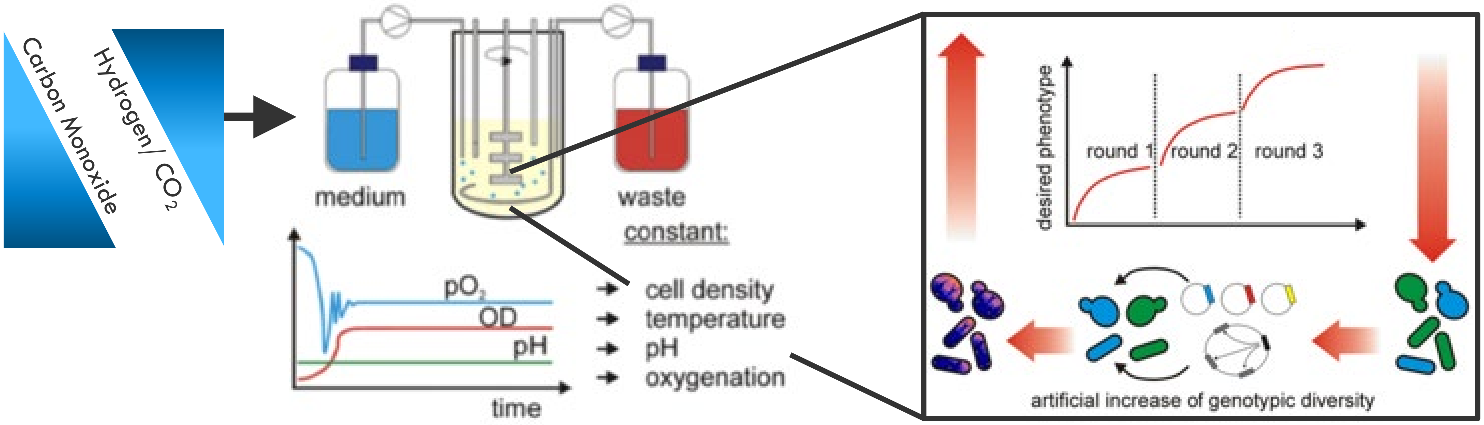
5cm^2 CO_2 electrolyzer

250cm^2 CO_2 electrolyzer



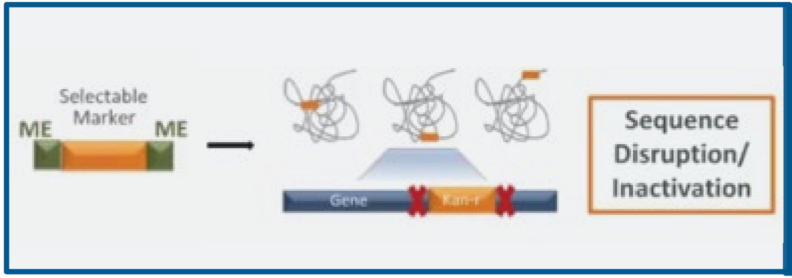
2-cell CO_2 electrolyzer stack
500cm^2 total surface area

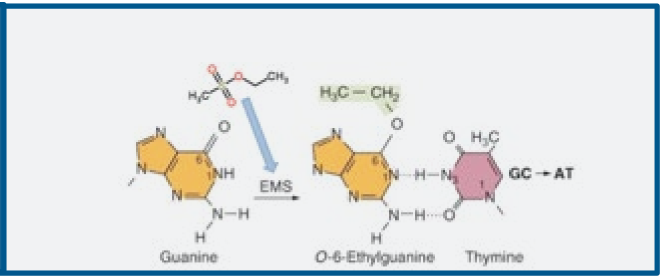
2. Adaptive Laboratory Evolution



- **ALE:** evolutionary engineering of microorganisms by combining genetic variation with the selection of beneficial mutations.

2. Generating Genetic Diversity





☑ **FY19Q4: Successfully generated >4,000 library mutants via transposon mutagenesis (>1X genome coverage)**

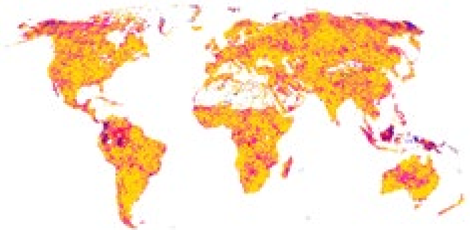
☑ **FY20Q4:Successfully generated >10,000 library mutants via chemical mutagenesis (>3X genome coverage)**

- Variable CO:H_2 concentrations affects gene pathway and product selectivity
- Genome-wide mutagenesis will enable:
  - Direct selection – identify novel genes essential for CO:H_2 cultivation
  - Adaptive evolution – run in parallel with chemostat under representative electrolytic gas stream
  - Genome minimization – conduct Tn5-seq to identify frequency of insertion: essential vs. non-essential genes and remove for enhanced energetics.

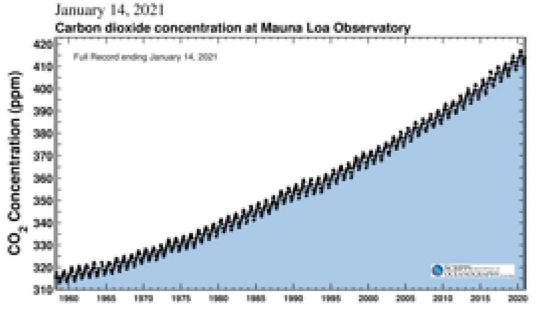
3. Impact

Fires raging from Australia to California

Drought recovery time. The longest recovery times are blue and pink,



NASA Woods Hole Research Center



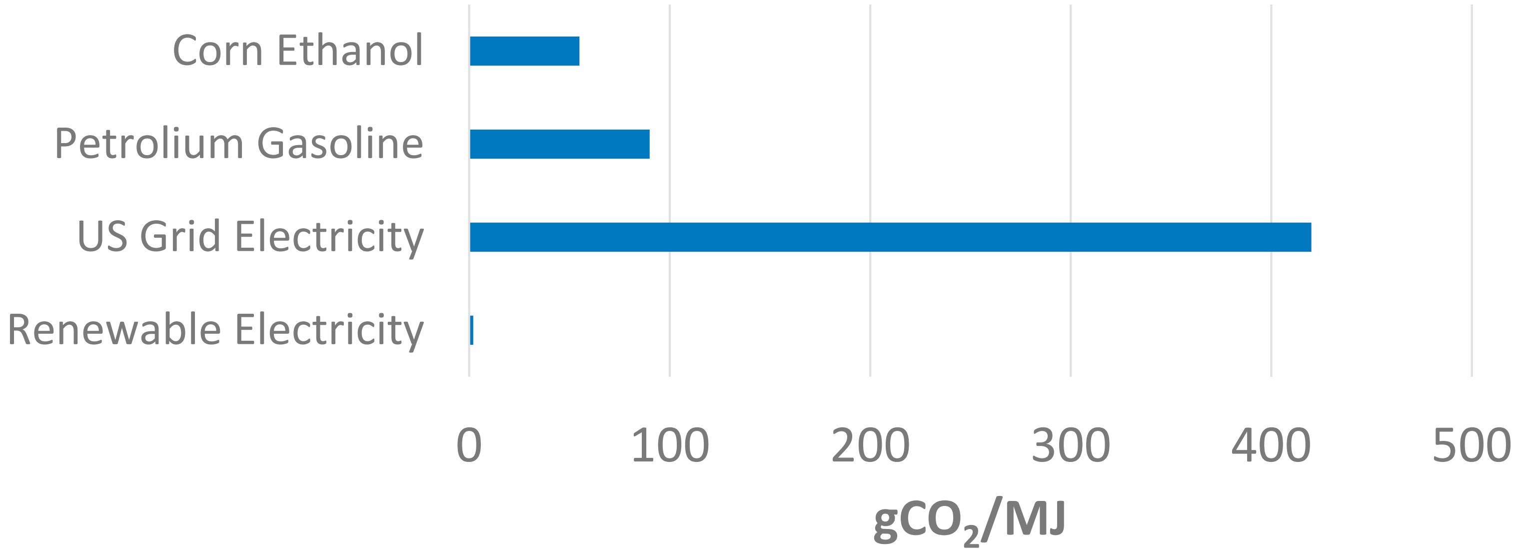
January 14, 2021

Carbon dioxide concentration at Mauna Loa Observatory

Floods ranging from Miami to Jakarta

Slide Credit: Zia Abdullah (NREL)

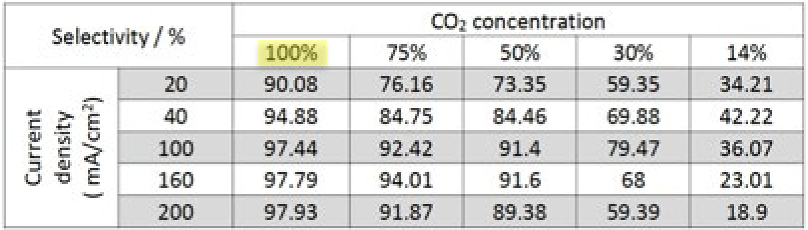
3. Carbon Intensity
Renewable vs. Typical Grid Electricity



- CI of ethanol using renewable electricity is magnitudes lower than when using U.S. average grid electricity

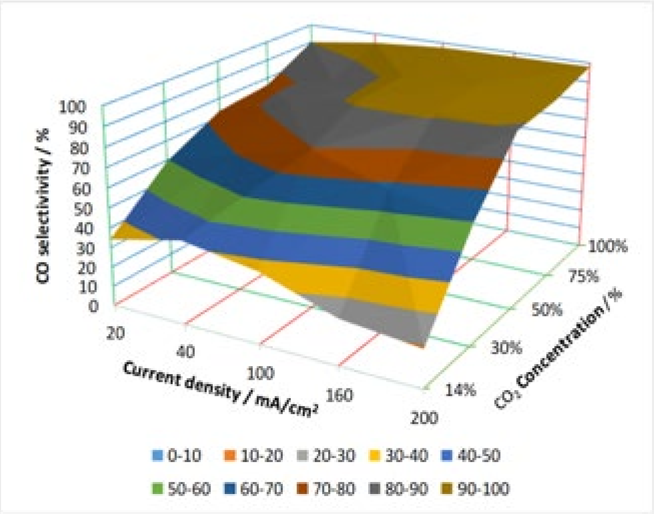
Data adopted from Lee *et. Al. Biofpr (2020)*

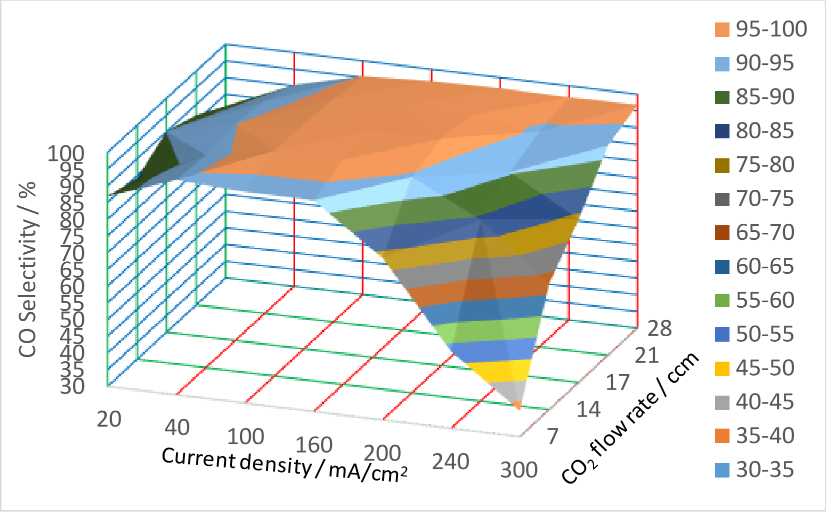
4. Performance on Dilute Streams of CO_2



Selectivity / %		CO_2 concentration				
		100%	75%	50%	30%	14%
Current density (mA/cm^2)	20	90.08	76.16	73.35	59.35	34.21
	40	94.88	84.75	84.46	69.88	42.22
	100	97.44	92.42	91.4	79.47	36.07
	160	97.79	94.01	91.6	68	23.01
	200	97.93	91.87	89.38	59.39	18.9

CO selectivity (%)		CO_2flow rate (ccm)				
		7	14	17	21	28
current density (mA/cm_2)	20	86.9	84.21	90.08	86.87	77.01
	40	94.28	93.59	94.88	93.55	90.33
	100	93.24	97.39	97.44	96.56	95.4
	160	93.18	97.25	97.79	97.04	96.45
	200	78.51	94.61	97.93	96.78	96.79
	240	53.01	84.29	90.42	94.49	96.6
	300	37.79	67.76	78.82	92.82	96.87

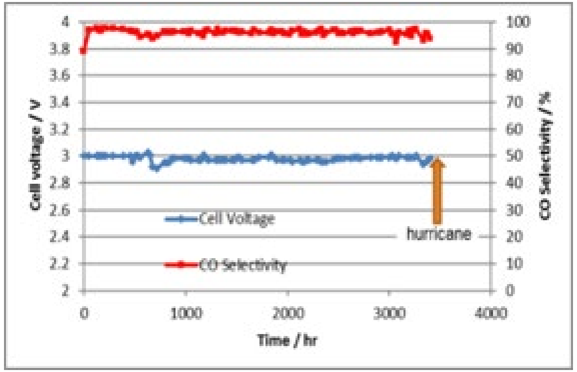




4. Flue Gas Components Tested

Components	Testing Conditions	Results	Dilute CO_2 Flue gas	[High] CO_2 Flue gas
CO_2	14-100%		14-17%	99%+
VOC			15 – 30 ppm	< 1000 ppm (combined)
Acetic Acid	100+ hrs.	OK up to 500 ppm		N.D.
Acetone	100+ hrs.	OK up to 500 ppm		0.6
VSC			N.D.	< 10 ppm (combined)
Hydrogen Sulfide	0-50 ppm	Decrease @ 3 ppm		2.3
Methyl mercaptan	0-10 ppm	Decrease @ 2 ppm		0.1

4. Progress and Outcomes

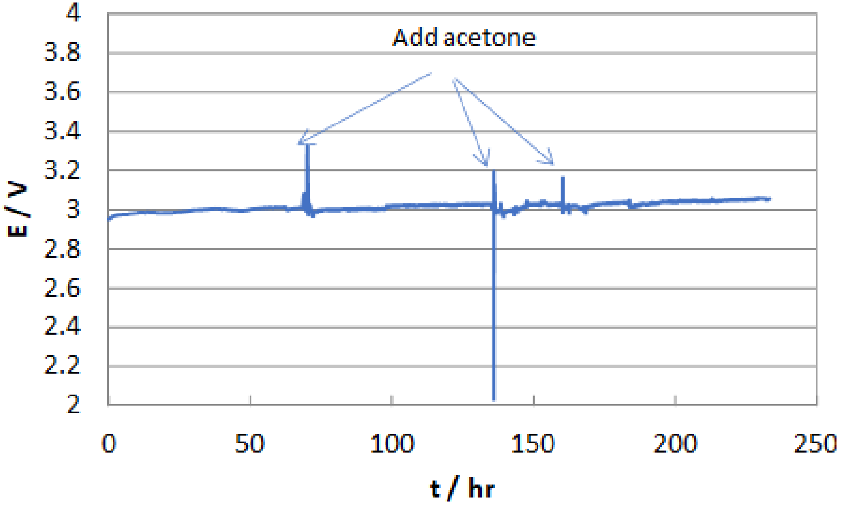


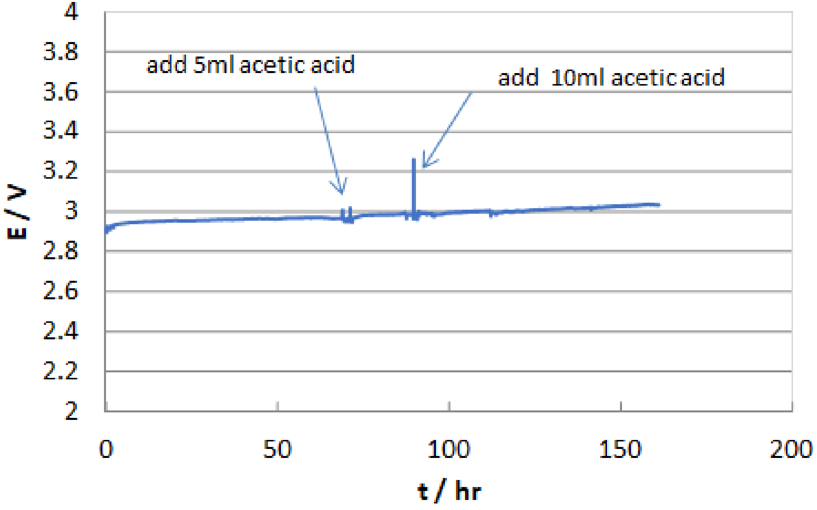
5cm2 cell performance and impurity effect

- DM 5cm2 cell demonstrated over 3800hr stable performance
  - CO selectivity >95%

Tolerant to acetone and acetic acid up to 500ppm

- No effect on CO selectivity

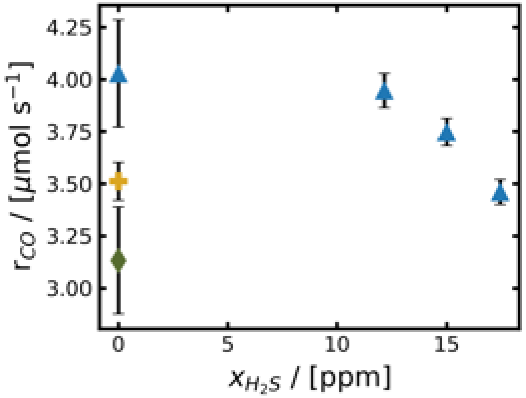




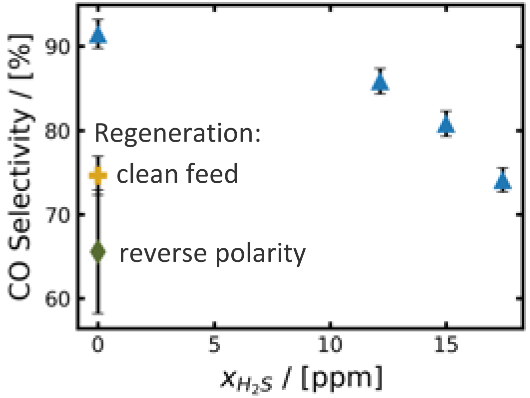
Electrolyzer flue gas contaminant tolerance

H_2S

CO Production rate

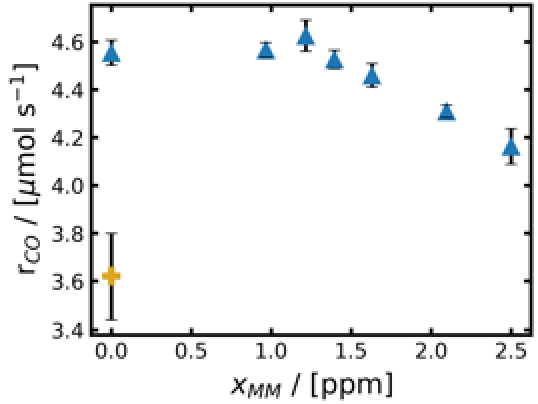


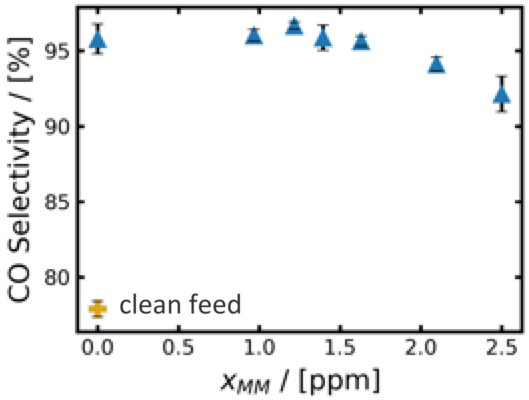
CO Selectivity



- H_2S tolerant up to 13 ppm
- 10% performance loss over 17 ppm

Methyl mercaptan

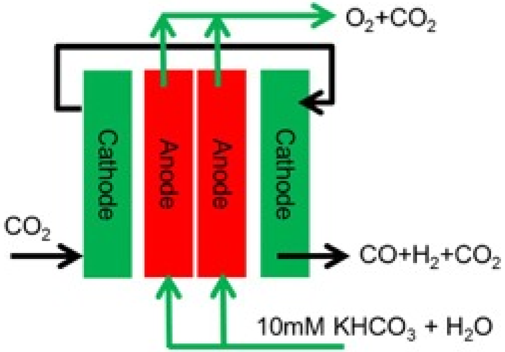


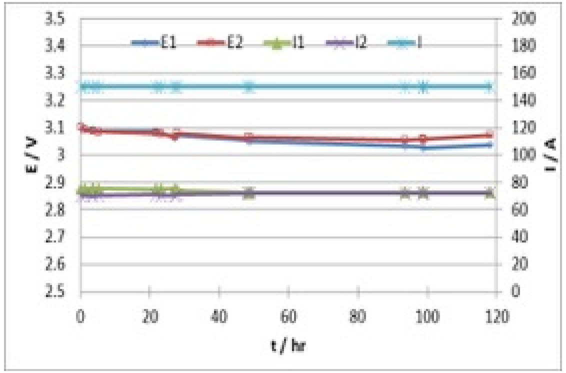


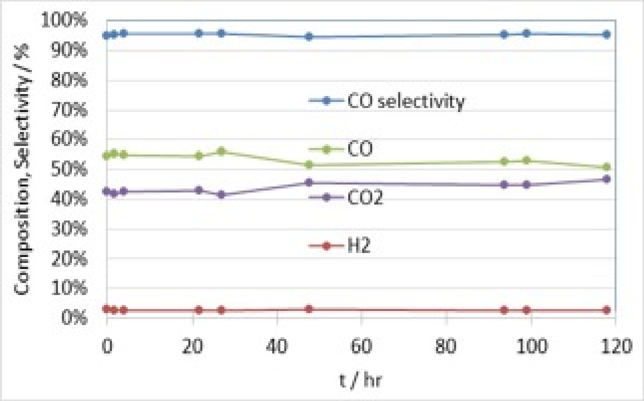
- Methyl mercaptan tolerant up to 1.25 ppm
- 10% performance loss over 2 ppm
- Selectivity was minimally impacted

4. Developing gas delivery to stacks

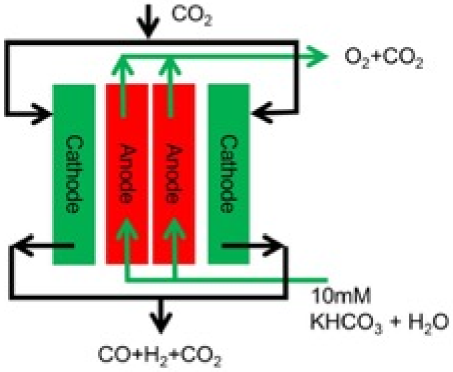
- CO_2 fed to cathode in series

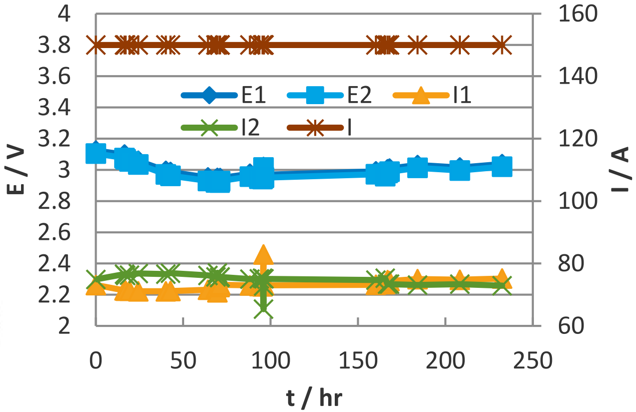


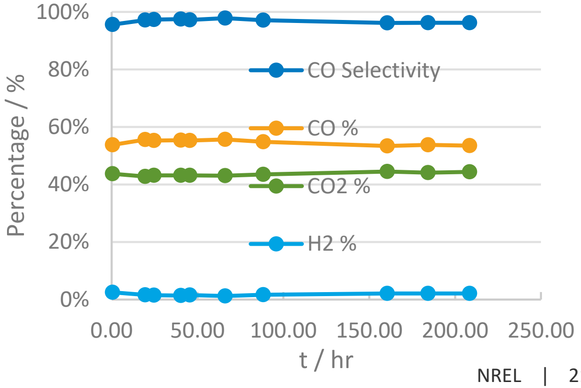




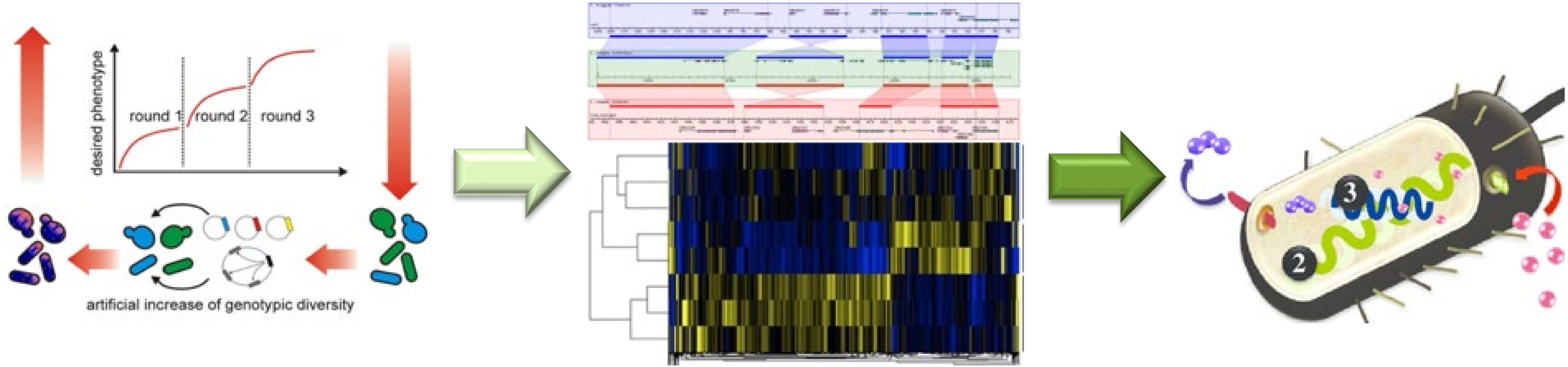
- CO_2 fed to cathode in parallel





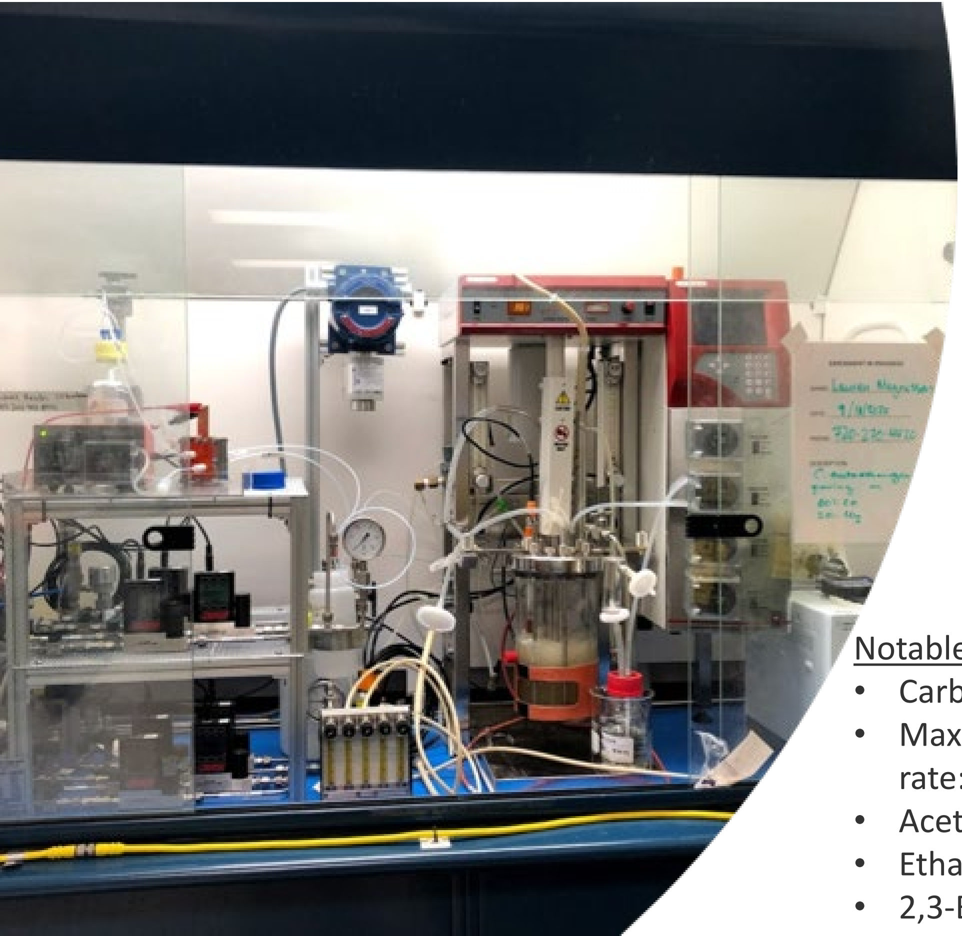


4. Mutagenesis progress

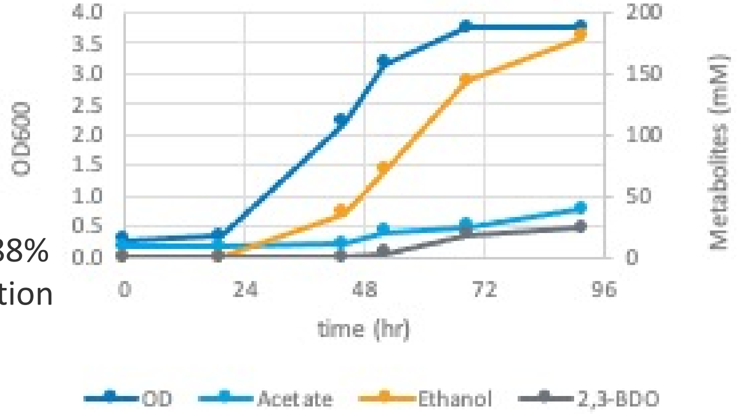


- **Comparative omic analyses:** Conduct comparative analysis of evolved biocatalysts versus wild-type organism and deliver a report detailing rational strain engineering for enhanced CO uptake under variable electrolyzer conditions based upon resultant data.
- **Targeted Metabolic Engineering:** Implement omic-informed strain engineering strategies to generate biocatalysts with enhanced CO uptake and flux.

4. Fermentation



- We are successfully running batch fermentations with minimal lag. Improvements to the system included:
  - Adding baffles for higher CO consumption
  - Reducing solution added to drop the redox before inoculation
- We have generated repeatable data, and moving forward will focus on continuous fermentation for ALE



Notable data

- Carbon Balance: 88%
- Max CO consumption rate: 22.3 g/L/d
- Acetate: 2.3 g/L
- Ethanol: 8.25 g/L
- 2,3-BDO: 2.4 g/L

Future Directions

- Evaluate Biopower flue gas contaminant deactivation mechanisms
- Strain Engineering and assimilation improvements
- Biological co-product evaluation
- Electrolysis and gas fermentation scaling integration
- Identification of key technical and economic hurdles for industrial applications
- Industrial partnership projects and demonstrations

Team Members:

NREL: Michael Guarnieri
Leah Ford
Lauren Magnusson
Erick White

Dioxide Materials:
Rich Masel
Zengcai Liu

3M: Laura Nereng
Chris Thomas

Lanzatech: Christophe Mihalcea
Sean Simpson
Michael Koepka

Q & A

www.nrel.gov

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CO_2 Fuel Dioxide Materials™

3M

LanzaTech

NREL Transforming ENERGY

Quad Chart Overview

Timeline

- Project start date: 10/1/2018
- Project end date: 9/30/21

	FY20	Active Project
DOE Funding	$490,000	$1.4M DOE funds $800k Cost Share

Project Partners

- Dioxide Materials
- 3M
- Lanzatech (no-cost partner)

Barriers addressed

Ct-A. Defining Metrics around Feedstock Quality

Ct-D. Advanced Bioprocess Development

ADO-D. Technology Uncertainty of Integration and Scaling:

Project Goal

Incentivize BioEnergy with CO_2 Capture and Sequestration (BECCS) via integration of downstream electrolytic and biocatalytic upgrading of flue gases into fuels and chemical intermediates.

End of Project Milestone

Run the CO_2 electrolyzer integrated to a bioreactor to determine the feedstock inventory needed to maintain continuous operation. Determine the effects flue gas composition has on electrolysis and biocatalysis.

- Determine the minimum electricity cost for process viability.
- Determine the carbon intensity of the process.

Funding Mechanism

FY18 CO_2 Lab Call

Additional Slides

Electrons to Molecules

Concept

- Use of excess renewable electrons to convert waste CO_2 into value added fuels and chemicals

Benefit

- Upgrade low-cost and abundant carbon feedstocks to value-added chemicals, materials, and fuels
- Improve carbon conversion efficiency at biorefineries

Efficiency Challenges

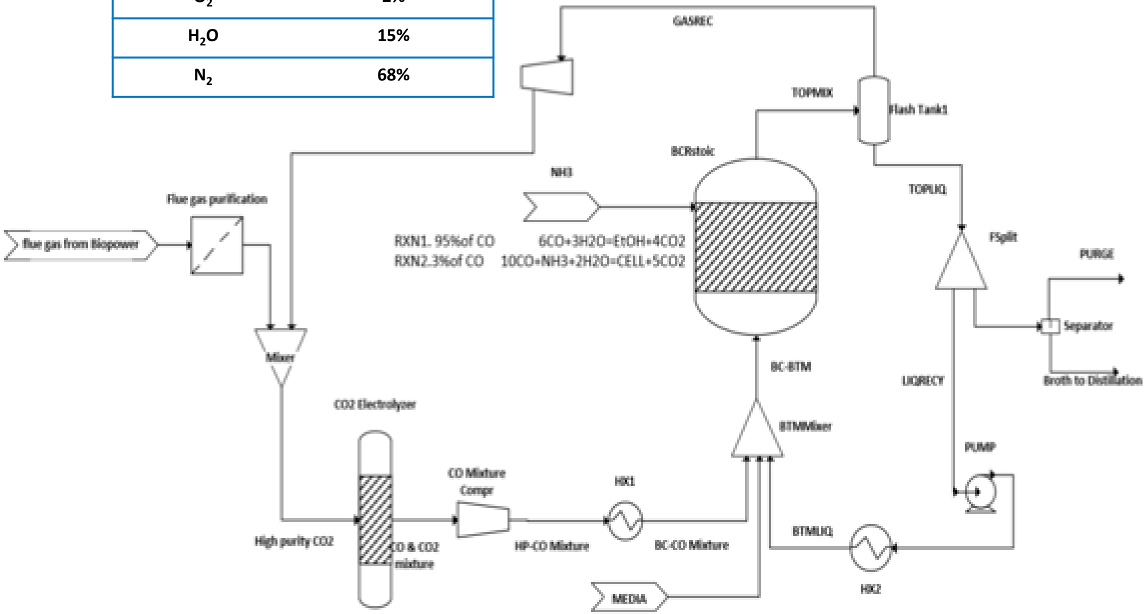
- Use of electrons via improved electrocatalysis and bio-catalysis.
- Integration of hybrid electrochemistry with biology
- Siting to identify dependable carbon incentives and low-cost feedstocks.

Preliminary Process Flow Diagram of Baseline Case

Scale: 50MW Biopower Plant

Component	Volume Percentage
CO_2	14%
O_2	2%
H_2O	15%
N_2	68%

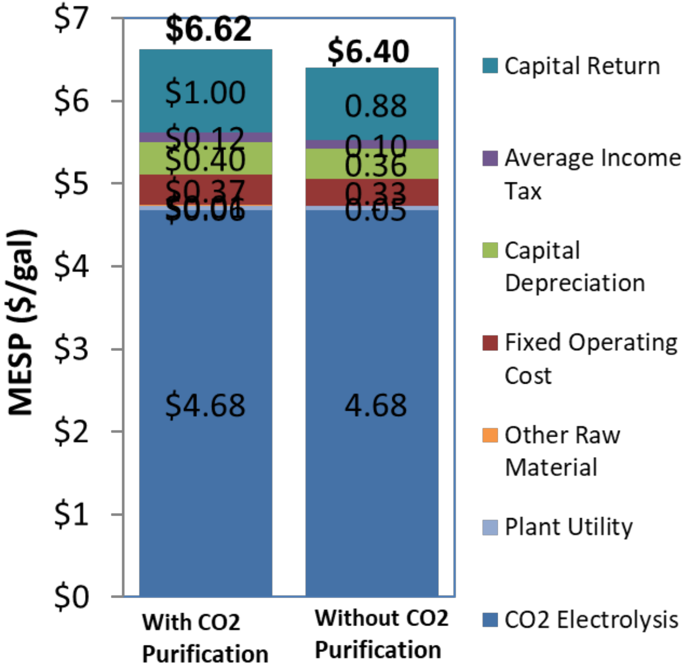
For CO_2 Electrolyzer	Values	Data Source
CO_2 Electrolyzer Operation Pressure (atm)	1.5	R&D team
CO_2 Electrolyzer Operation Temperature (C)	60	R&D team
CO_2 Electrolyzer Current Density (mA/cm2)	200	R&D team
CO_2 Electrolyzer Faradaic Efficiency to CO (%)	98	R&D team
CO_2 Electrolyzer Applied Voltage (V)	3	R&D team
CO_2 Single-pass Conversion (%)	43	R&D team

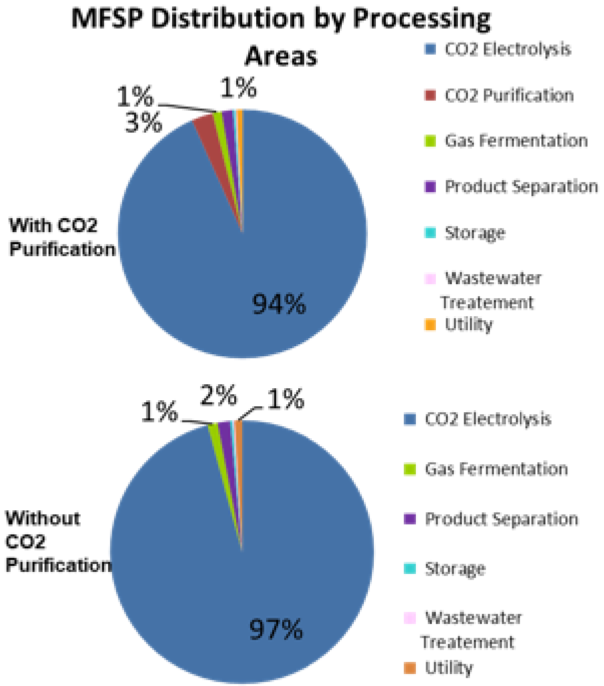


For Bioreactor	Values	Data Source
Governing equation	$6CO+3H_2O$=Ethanol+$4CO_2$	R&D team
Product Productivity (g Ethanol/L/h)	8	Literature
Ethanol Selectivity (%)	95	Literature
CO Single-pass Conversion (%)	95	Literature
Product Titer (g Ethanol/L)	60	Literature
Bioreactor Operation Temperature (C)	32	Literature
Bioreactor Operation Pressure (atm)	1.7	Literature
Media recycle process (%)	50	Literature

Preliminary TEA Results – MESP (Minimum Ethanol Selling Price)

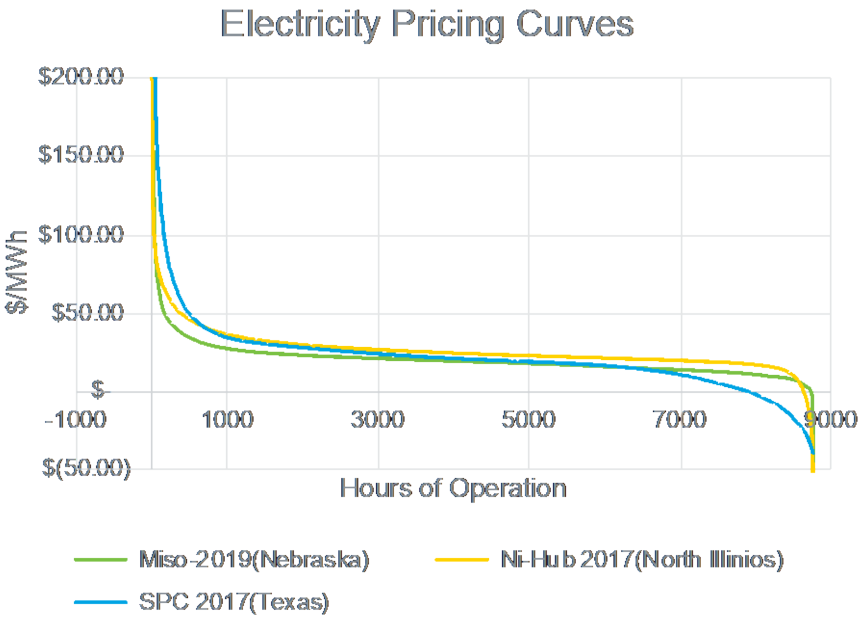
MESP	**With CO2 Purification**	**Without CO2 Purification**
$/Gallon	6.62	6.40
$/GGE	10.06	9.73



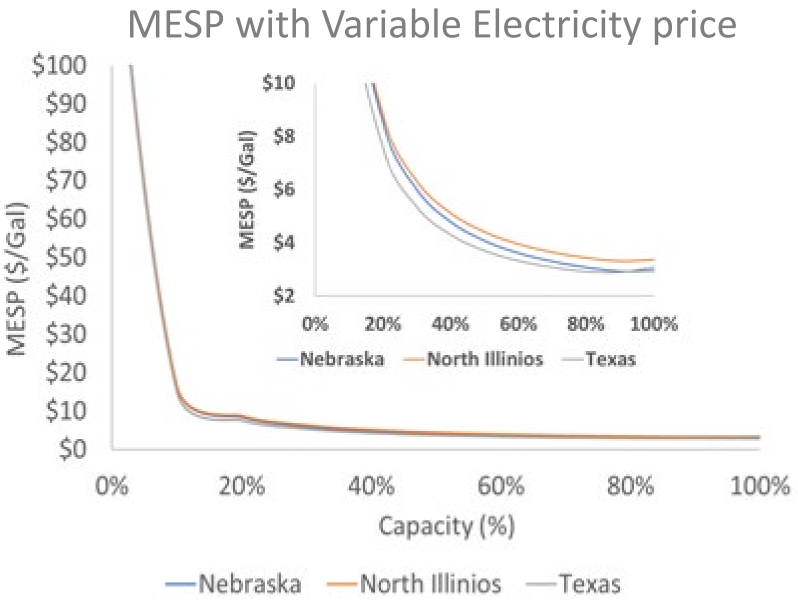


- CO_2 electrolysis process dominates
- Note that electricity prices is $0.0682/kWh with 90% onstream factor, contributing $4.68/gal or $7.11/GGE

3. Variable electricity pricing



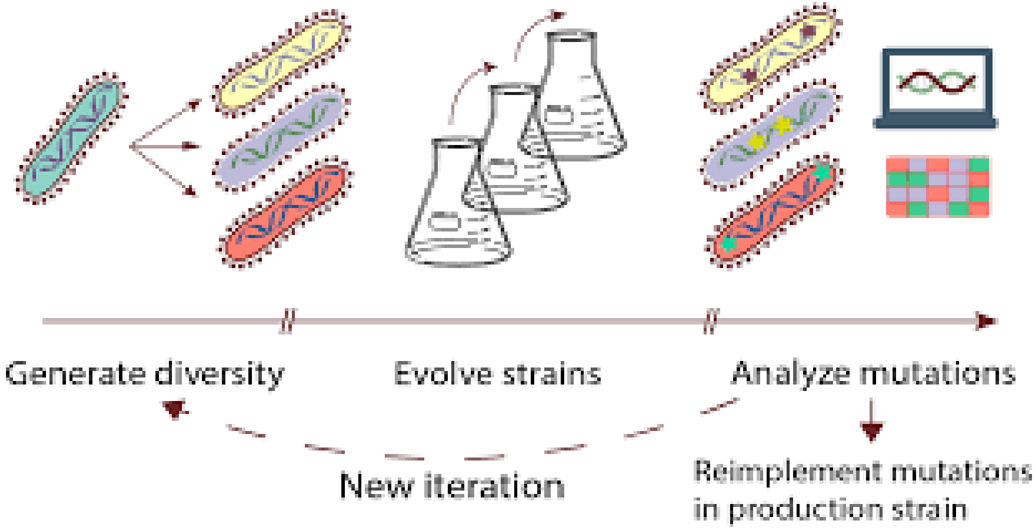
Electricity Pricing Curves



MESP with Variable Electricity price

Approach: Adaptive Laboratory Evolution

- **Problem:** Variable CO_2 gas streams present process integration hurdles to couple electrolyzers and bioreactors.
- **Goals**
  - Generate biocatalysts with optimal cultivation capacity on high-, medium-, and low CO concentrations.
- **Approach:**
  - Establish transposon and chemical mutagenesis capabilities in *Clostridia autoethanogenum*.
  - Conduct comparative genomics and metabolomics on top-candidate strain(s) to generate systems biology knowledgebase for rational strain engineering strategies.
- **Challenges**
  - SOP related to anaerobic mutagenesis and scale-up
  - Low transformation efficiency



Responses to Previous Reviewers' Comments

Review Comment: The project demonstrates clear goals and technical approaches to integrate CO2 electrolysis with microbial syngas upgrading to ethanol. It contributes to BETO objectives, and the partnership with industry improves the potential of applicability. The project can be improved with more quantitative milestone measures, such as product yields, rates, and conversion efficiencies. The low value products can be better justified. TEA and LCA should be done very carefully to justify what this approach is advantageous compared to mature alteratives such as fermentation. The novelty of the approach is not clear as the industry partners have already demonstrated similar systems and published results.	We appreciate the Reviewers' supportive comments on how this meets BETO objectives and industrial partnership. We agree that the milestones could be more quantitate. We are using the native product(s) as a proxy for diverse microbial syngas conversion product suites. A variety of biocatalysts from our industrial partner, LanzaTech, can be substituted and produce a variety of fuels and high value chemicals. However, the primary goal of this project is to evaluate the potential impact of flue toxins to the electrocatlysts and the biocatalysts. Notably, previous work by our partners has exclusively evaluated pure CO2. We will determine how the flue gas components effect selectivity when low concentrations of impure CO2 are utilized, and how do these varied gas streams propogate downstream to effect fermentation. There is a need for catalysts that are more tolerant of lower quality feedstocks. Ultimatlyu, what methods might be used for mitigation (filtration or other), this project will lead to understanding of what is tolerable and not, and costs associated with cleaning gases can be determined. This should have been made more clear in the presentation. We have worked with our industrial partners on building the detailed (although preliminary) TEA models, as some of their data came from vendors' quotations or pervious demonstrations. We agree that TEA and LCA should be done very carefully as this is process is much different from terrestrial lignocellulose conversion or water splitting H2 electrolysis. We have a Q3 FY19 to update the TEA metrics needed for TEA under varying electricity availability and potential CO storage and gas clean-up.
Weakness: It is not clear what would be the main advancements to be made by this project beyond the process integration. For example, among the range of feedstocks for gas fermentation, they will focus on CO which has already been demonstrated at scale. The investigation of a wide range of feedstock to the gas fermentation unit would be more interesting and greater impact. This will give a flexibility to the electrolyzer as well. It is not clear how two units with different capacity factors will work in series without requiring a very large storage system for CO and recycled CO2.	The progression of our experimental plan will incrementally add to the complexity of the system. First, we will work to achieve electrolyzer and biocatalyst performance similar to published results by our industrial partners under controlled conditions on clean gas. This is also an opportunity to establish this core capability at the National Renewable Energy Laboratory. In parallel, we will evaluate the potential electrolyzer toxicity of known flue gas components such as thiophene, hydrogen sulfide, methyl mercaptan, hydrogen cyanide, acetaldehyde, and ethyl acetate. Previous work using DM electrolyzers has only evaluated pure CO2 and these proposed experiments will be necessary to identify catalyst robustness or known limits of the components, and what gas clean-up strategies will be required. If some of these flue gas components are acceptable and evolve through the system along with CO then we will determine the effects and compatibility with the downstrewam biological catalyst.

Publications, Patents, Presentations, Awards, and Commercialization

Publications

- Grim, et al. Transforming the carbon economy: challenges and opportunities in the convergence of low-cost electricity and reductive CO2 utilization. *Energy Environ. Sci*., 13, 472-494. (2020)
- Huang, et al. Using waste CO_2 to increase ethanol production from corn ethanol biorefineries: Techno-economic analysis, *Applied Energy*., v. 280, (2020)
- *Kaczur, J. J.; Yang, H.; Liu, Z.; Sajjad, S. D.; Masel, R. I., A Review of the Use of Immobilized Ionic Liquids in the Electrochemical Conversion of CO_2. *(*2020), *6*, (2), 33.
- *Masel, R. I.; Liu, Z.; Yang, H.; Kaczur, J. J.; Carrillo, D.; Ren, S.; Salvatore, D.; Berlinguette, C. P., An industrial perspective on catalysts for low-temperature CO_2 electrolysis. *Nature Nanotechnology (*2021).

Presentation

- White E., Liu Z., Resch M., Catalyst deactivation and regeneration for alkaline CO2 electrolysis processes. ACS National Virtual Meeting. (2021)
- Liu, Zengcai, et al. Effect of CO_2 concentration on the electrolytic conversion of CO_2 to CO. ACS National Meeting (2019)

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