Scalable and Highly-Efficient Microbial Electrochemical Reactor for Hydrogen Generation from Lignocellulosic Biomass and Waste

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Award # EE0008844

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DOE Hydrogen Program
2024 Annual Merit Review and Peer Evaluation Meeting

Project ID P184

Project Goal

Project Goal: Develop a scalable hybrid microbial electrochemical reactor (combining fermentation and MEC) for hydrogen production from waste streams at a production cost close to or less than \$2/kg H_2.

This goal will be achieved by:

- Developing scalable and low-cost electrodes to reduce the capital cost of the reactor
- Developing a scalable reactor design to reduce the capital and operating costs
- Optimizing operating conditions using robust microbial communities to reduce the operating cost

Overview

Timeline

- Project Start Date: 10/1/2019
- Project End Date: 6/30/24#

no-cost extension is granted

Barriers

- High electrode cost (AAA)
- Low hydrogen production rate (AAB)

Budget

- Total Project Budget: $1,277,145
  - Total Recipient Share: $277,239
  - Total Federal Share: $999,906
  - Total DOE Funds Spent*: $996,208

* As of 1/31/24

Partners

- **US DOE**: project sponsor and funding
- **OSU**: project lead; cost-share funding
- **TAM:** co-project lead; cost-share funding
- **PNNL**: co-project lead

Relevance/Potential Impact

Specific Objectives for this Budget Period:

1. **Objective**: Build and operate a larger-scale MEC reactor with synthetic medium.
    - **Impact**: Verify the effectiveness of cost-effective electrodes and the microbial consortium in an expanded MEC setup. Assess MEC system capacity, establishing a hydrogen production benchmark.
2. **Objective**: Optimize operational conditions to maximize hydrogen production from a brewery wastewater in the upscaled MEC.
    - **Impact**: Address operational challenges and evaluate MEC system performance with specified waste streams.
3. **Objective**: Execute a cost evaluation employing H2A models, utilizing performance data.
    - **Impact**: Develop an economic model to reduce hydrogen production costs, guiding subsequent R&D for improved system performance and cost-efficiency.

Approach

- **Construct a 10-L MEC reactor with:**
  - Anode: N-doped carbon nanotube (CNT) coated stainless steel mesh, boasting high corrosion resistance and electrical conductivity, developed at TAM.
  - Cathode: Economical, high-efficiency Ni alloy mesh, evaluated at PNNL.
  - Designed with 28 electrode assemblies to simplify operation and maintenance.

- **Monitor the fluctuations in a local brewery's waste stream over time.**

- **Develop and test new pretreatment strategies enhancing MEC performance, utilizing yeast and Acetobacter to optimize the waste stream as a feedstock.**

- **Assess the MEC's effectiveness using both a standard synthetic medium for baseline comparison and the tailored waste stream to determine the system's specific functionality.**

- **Perform a cost-efficiency analysis of the MEC for this particular waste stream using the H2A model.**

Approach/Milestone

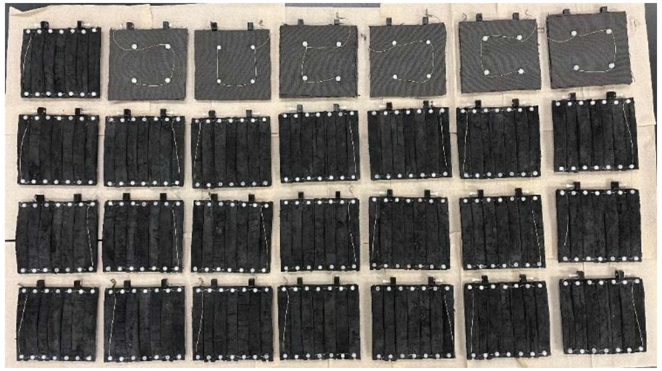
Phase I Electrode material development and evaluation (FY 20-22)	Original planed date	Revised planed date	Percent complete
Milestone 1.1: Synthesize low-cost CNT electrodes capable of producing an anodic current density > 20 A/m^2 in MECs and fabricate roll-to-roll setup	3/31/20		100%
Milestone 1.2: Optimize the synthesis conditions and fabricate low-cost CNT sponge electrodes capable of producing an anodic current density > 30 A/m^2 in MECs	6/30/20		100%
Milestone 1.3: Fabricate functionalized CNT sponge electrodes capable of producing an anodic current density of 40 A/m^2 in MECs	9/30/20	12/30/20	100%
Milestone 2.1: Synthesize HER catalyst that can deliver > 40 A/m^2 in MECs	12/31/20	6/30/21	100%
Milestone 3.1: Design and fabricate small MECs (~0.5L) using the developed electrodes and HER catalyst with an electrode area with reactor volume ratio ranging from 20-100.	3/31/21	12/30/21	100%
Go/NoGo: Demonstration of continuous production of 30 L-H_2/L/day for 48 hours using wastewater in ~0.5 L reactors.	6/20/21	3/30/22	100%
Phase II Scaled-up reactor fabrication and evaluation (FY 22-24)			
Milestone 1.4: Fabricate CNT anode material for the large reactor	9/30/21	6/30/23	100%
Milestone 2.2: Develop cathode material for the large reactor	12/31/21	12/30/22	100%
Milestone 4.1: Fabricate a 10-L large reactor with the total anode and cathode areas of at least 1 m^2 and the liquid volume of at least 6 liters.	3/31/22	9/30/23	95%
Milestone 6.1: Develop cost performance model	6/30/22	3/30/24	95%
Milestone 5.1: Demonstrate the large reactor is capable of 35 L H_2/L/day continuous production for 72 hours with wastewater.	9/30/22	6/30/24	65%
Final deliverable: Demonstrate the techno-economic feasibility of the proposed system based on the cost performance modeling, and define a pathway for this system to achieve the FCTO cost goal of <$2/gge.	12/31/22	6/30/24	75%

Approach: Safety Planning and Culture

- **This project was required to submit a safety plan for review by the HSP**
  - Review comments were addressed and an updated safety plan is on file
- **Prioritizing safety and analyzing hazards**
  - Primary safety concerns in operating our hydrogen-producing reactors include the risks of flammability and explosion, particularly related to gas storage.
  - Laboratory researchers are required to undertake practical training prior to commencing any experiments to prevent errors that could result in reactor leaks or other safety incidents.
  - Laboratory researchers are certified through OSU EHS lab safety course.
  - Designated team members are responsible for managing changes, conducting assessments, and performing inspections.
- **Incorporating best safety practices and lessons learned:**
  - Mitigation measures are taken to lower the probabilities of the occurrence of the key safety concerns
    - Reactor operations are conducted beneath a canopy hood that channels the generated gases outside to a vent stack
    - No open flame or spark is allowed in the lab
    - The reactors and hood are checked daily by researchers including weekends
    - A new hydrogen detection system was installed.

Accomplishments and Progress

10 L Reactor Assembling



Anodes (left) electrode cassette assemblies (right) in the reactor

Completed 10L MEC reactor with wiring system

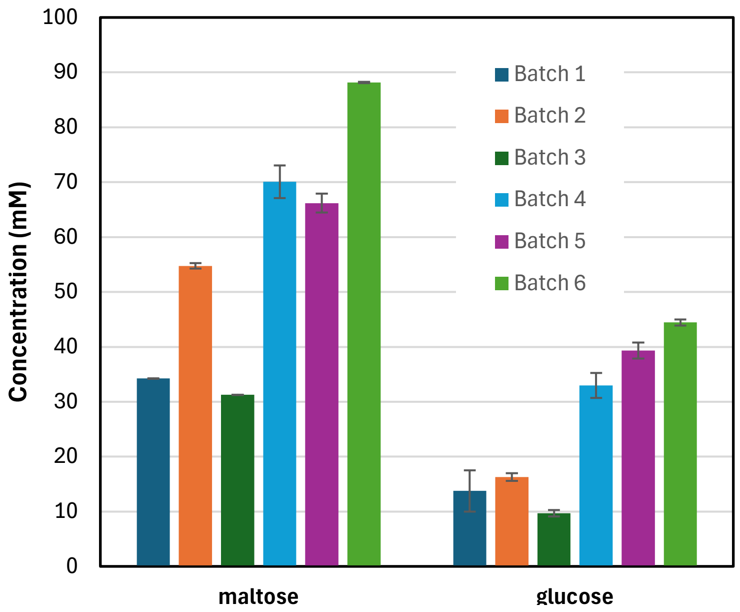
- Dense electrode structure enhances surface area-to-volume ratio for higher hydrogen production rate.
- Elimination of cloth separator to avert gas entrapment and lower resistance.
- Designed for simple extraction of cassettes with shorts from the reactor

Accomplishments and Progress (con.)

Characterization of a brewery wastewater (discarded Sweetwater)

Schematic of the brewing process and wastewater (discarded sweetwater) generation

(Craftbeerclub.com)

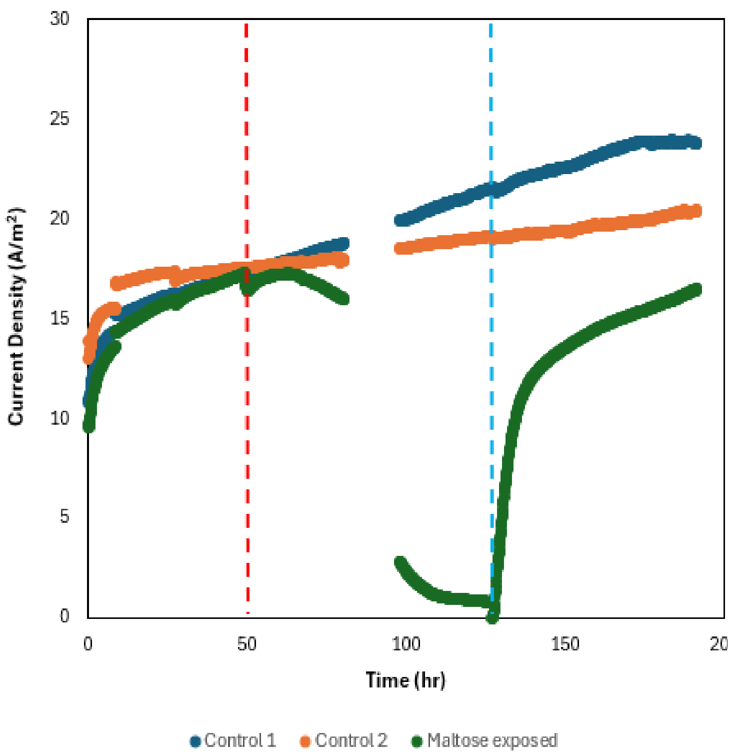


Variability of primary organic compounds in the collected brewery wastewater across various batches.

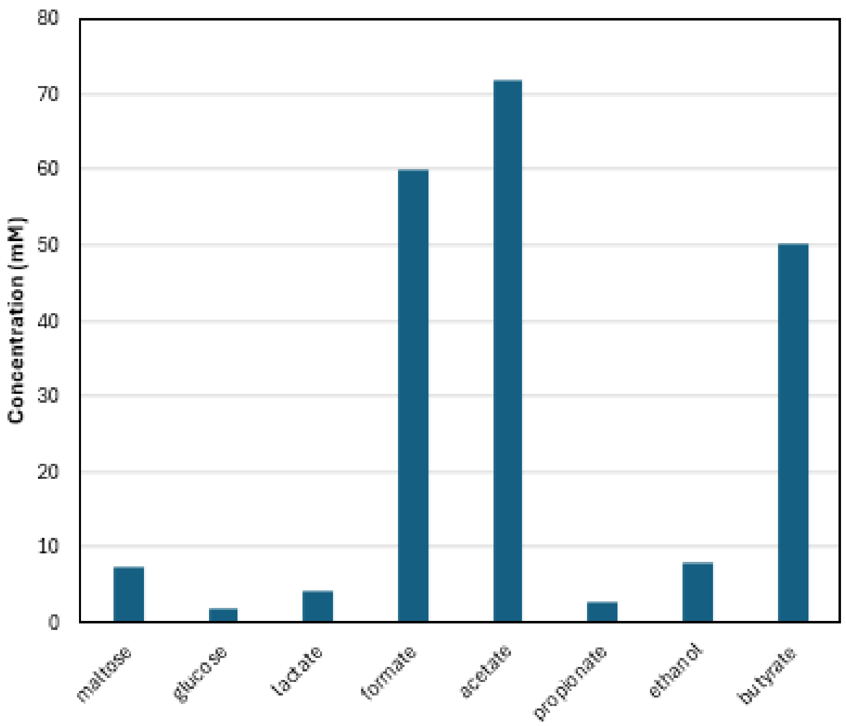
- Produced during wort creation.
- Sweetwater waste: 0.2L per 1L of beer.
- Maltose and glucose, key components, show variable concentrations batch-to-batch, reflecting inconsistency.
- Nutrient-rich, low in contaminants.
- BOD: 30-80 g/L; Conductivity: 1.2-1.9 ms/cm; pH: 4-5.
- Primarily sent to WWTP.
- Wastewater surcharge: ~$0.6/lb BOD (19-city average)

Accomplishments and Progress (con.)

Impact of sugars in wastewater on MEC performance



MEC performance influenced by maltose present in wastewater: red dashed line indicates 50 mM maltose addition; blue dashed line represents acetate replacement

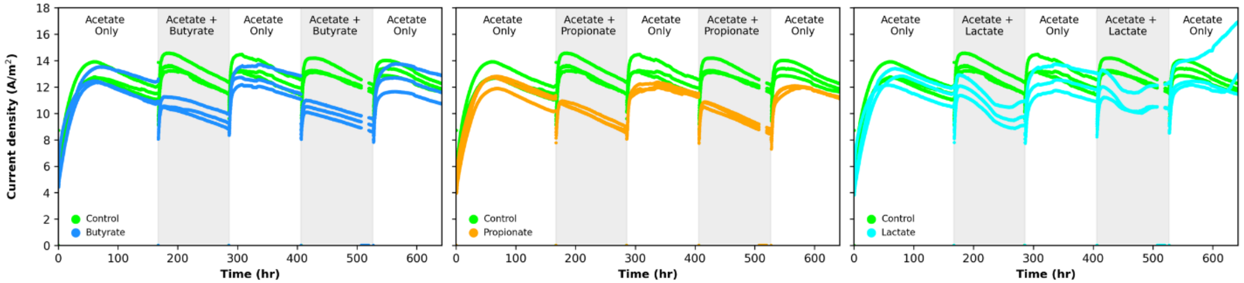


Composition of MEC effluent following maltose feed

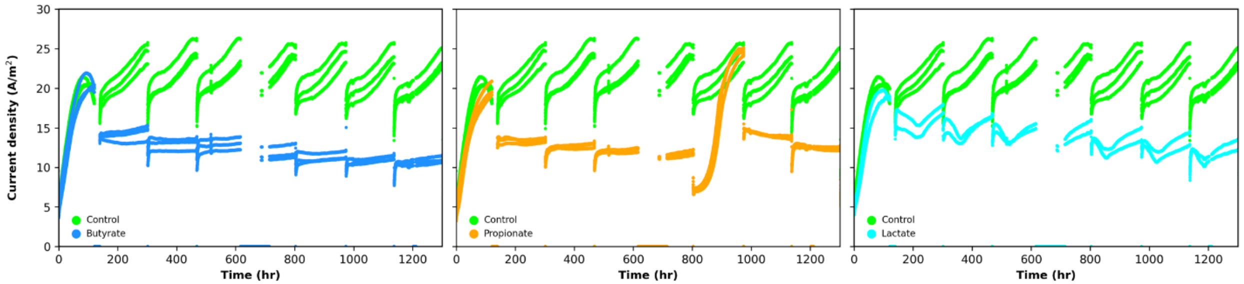
- Enriched mixed-culture MEC microbial communities can convert waste carbohydrates to various short-chain fatty acids.
- Potential synergy from acetate uptake by exoelectrogens for hydrogen production is offset by the inhibitory effects of certain fatty acids like butyrate.
- Managing fermentative carbohydrate products to favor MEC-friendly fatty acids (e.g. acetate) presents a challenge.
- Pretreatment of the sugar rich waste stream in a separate reactor is essential for optimal MEC processing

Accomplishments and Progress (con.)

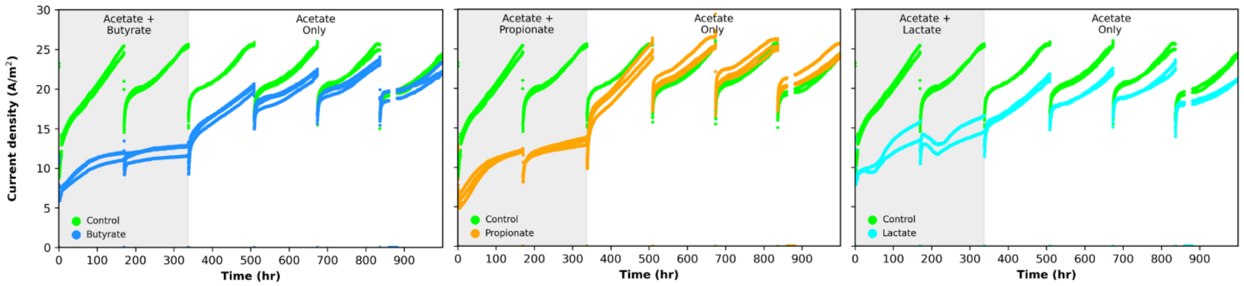
Impact of short chain fatty acids on MEC performance



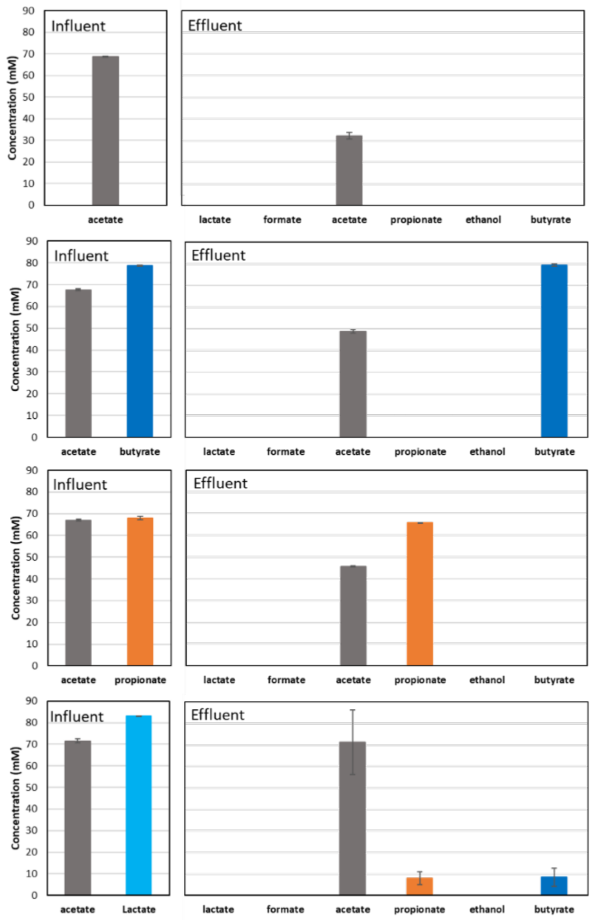
Current density for each alternating VFA treatment



Current density for each VFA treatment during long term VFA exposure



Current density for recovery phase of VFA treated cell

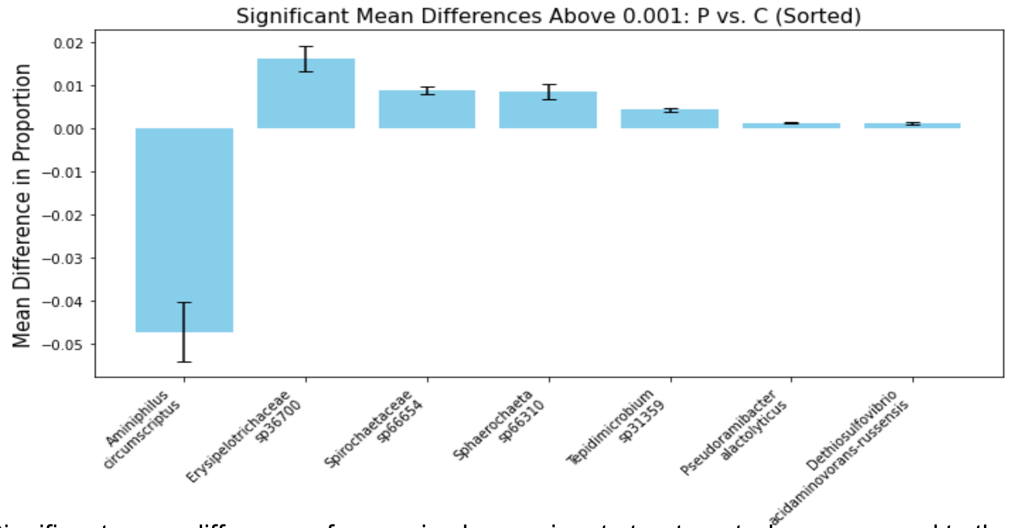


Influent and effluent VFA concentrations for the last batch of the long-term exposure phase

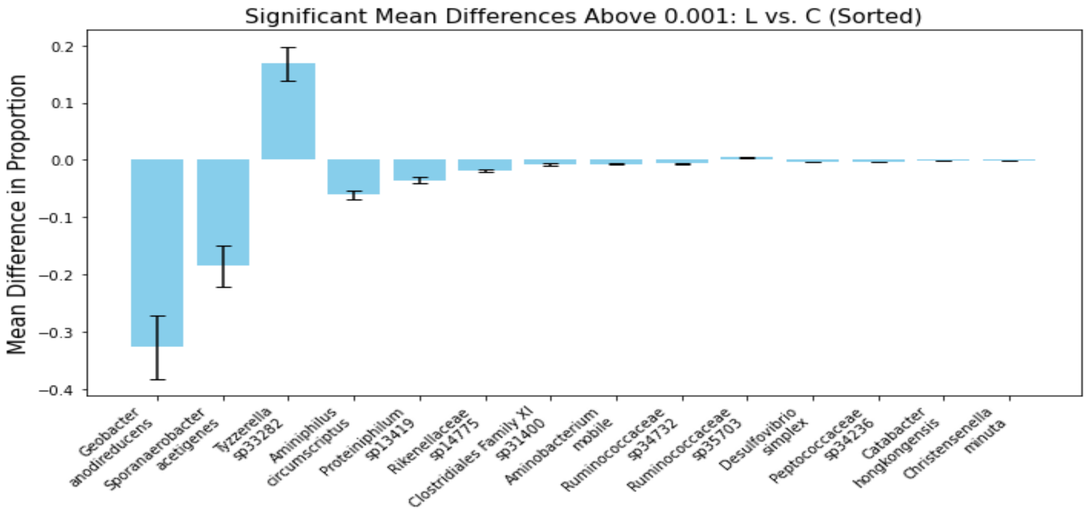
- Butyrate, propionate, and lactate presence detrimentally impacts MEC performance, particularly over long-term exposure.
- Upon the removal of butyrate and propionate, current density swiftly returns to baseline, indicating the microbial community's resilience to the effects of these fatty acids.
- Recovery from long-term lactate exposure may take a more extended period.
- Despite prolonged exposure, the microbial community in the MEC does not utilize propionate or butyrate. Conversely, lactate can be broken down by the MEC community.

Accomplishments and Progress (con.)

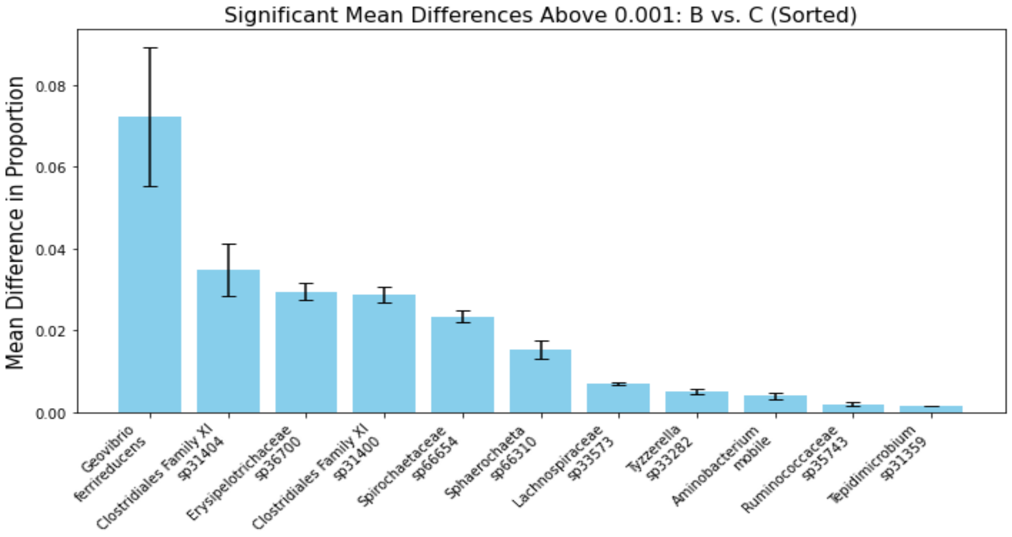
Impact of short-chain fatty acids on MEC microbial community dynamics



Significant mean differences for species by propionate treatment when compared to the control



Significant mean differences for species by lactate treatment when compared to the control



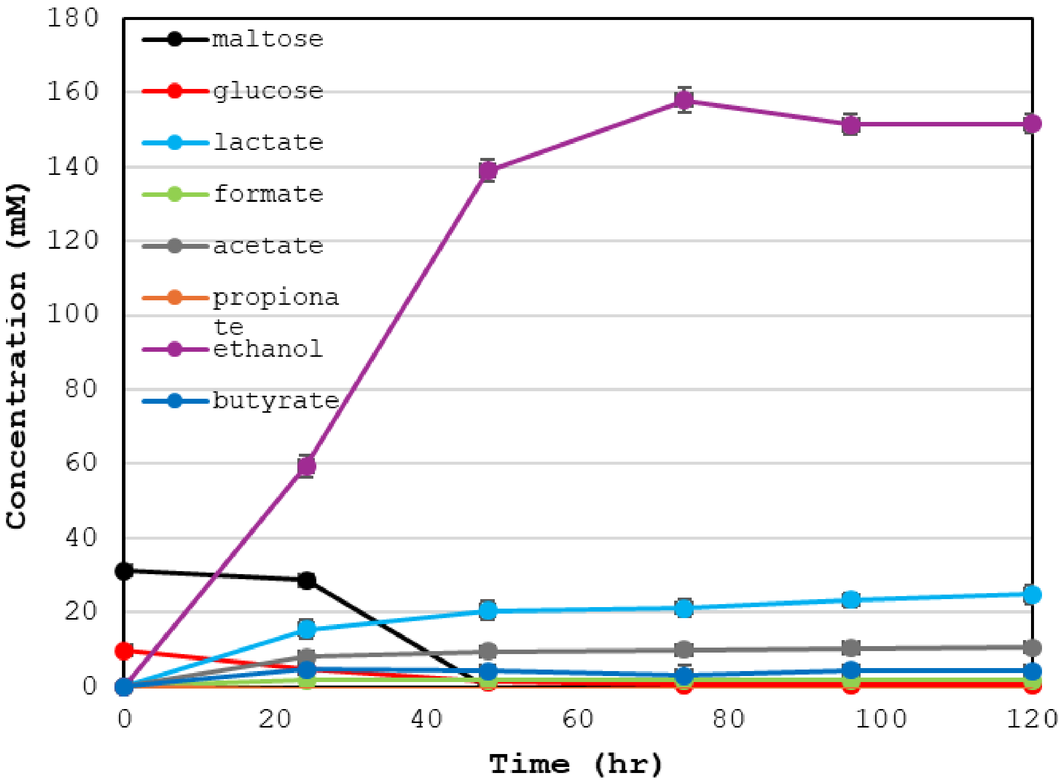
Significant mean differences for species by butyrate treatment when compared to the control

- **Community shifts were noted in all fatty acid treatments, with mean proportion differences observed.**
- **Propionate and butyrate treatments resulted in less than a 6% difference in species proportions, correlating with their poor utilization.**
- **In contrast, lactate treatments led to over a 30% difference in the proportion of Geobacter species, crucial for MEC processes, correlating with the prompt utilization of lactate and the delayed recovery from prolonged exposure.**

Accomplishments and Progress (con.)

Pretreatment of wastewater using yeast

Bioreactor (60 L) for the wastewater pretreatment

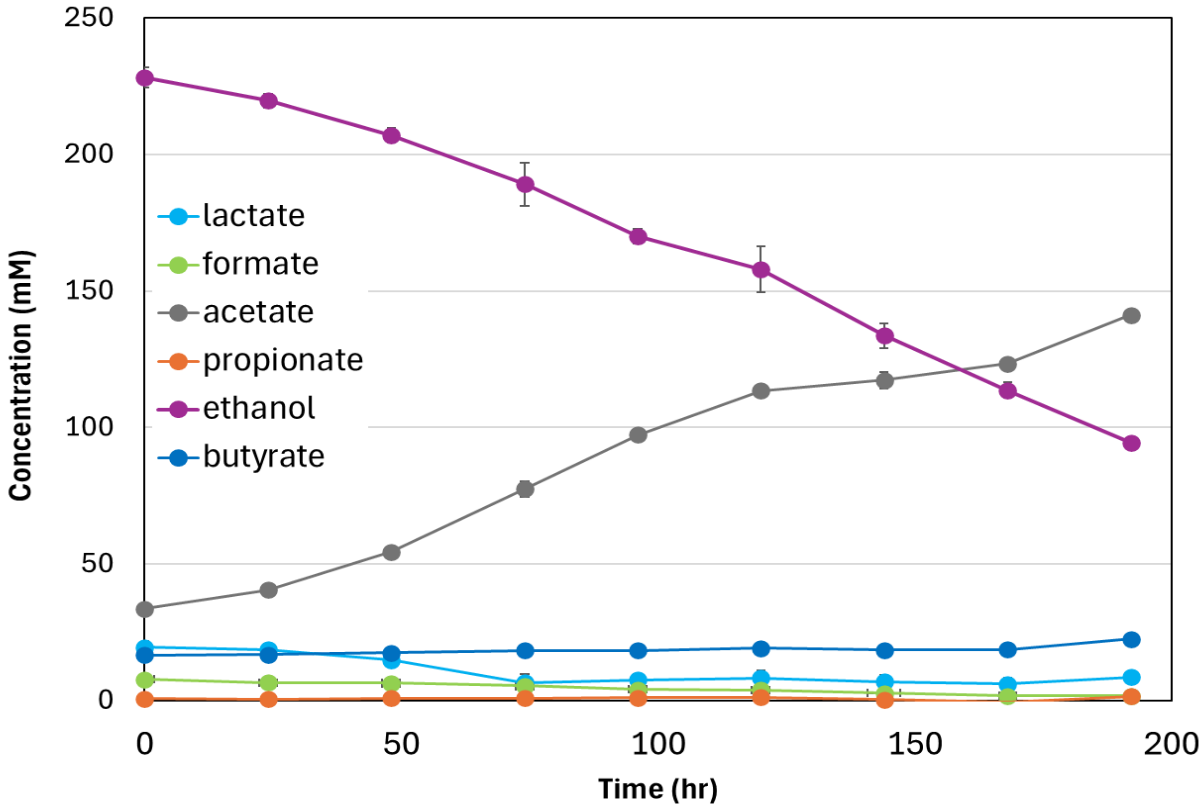


Product profile of pretreated fermentation using residual yeast over three batch cycles

- Ethanol predominates in anaerobic yeast pretreatment.
- Reusing yeast from previous batches for inoculation maintains ethanol dominance without extra yeast, nutrients, or pH adjustments, indicating a low-maintenance process using this specific waste stream.
- The pretreatment process remains stable despite variations in the collected wastewater composition.

Accomplishments and Progress (con.)

Pretreatment of wastewater using yeast and acetobacter

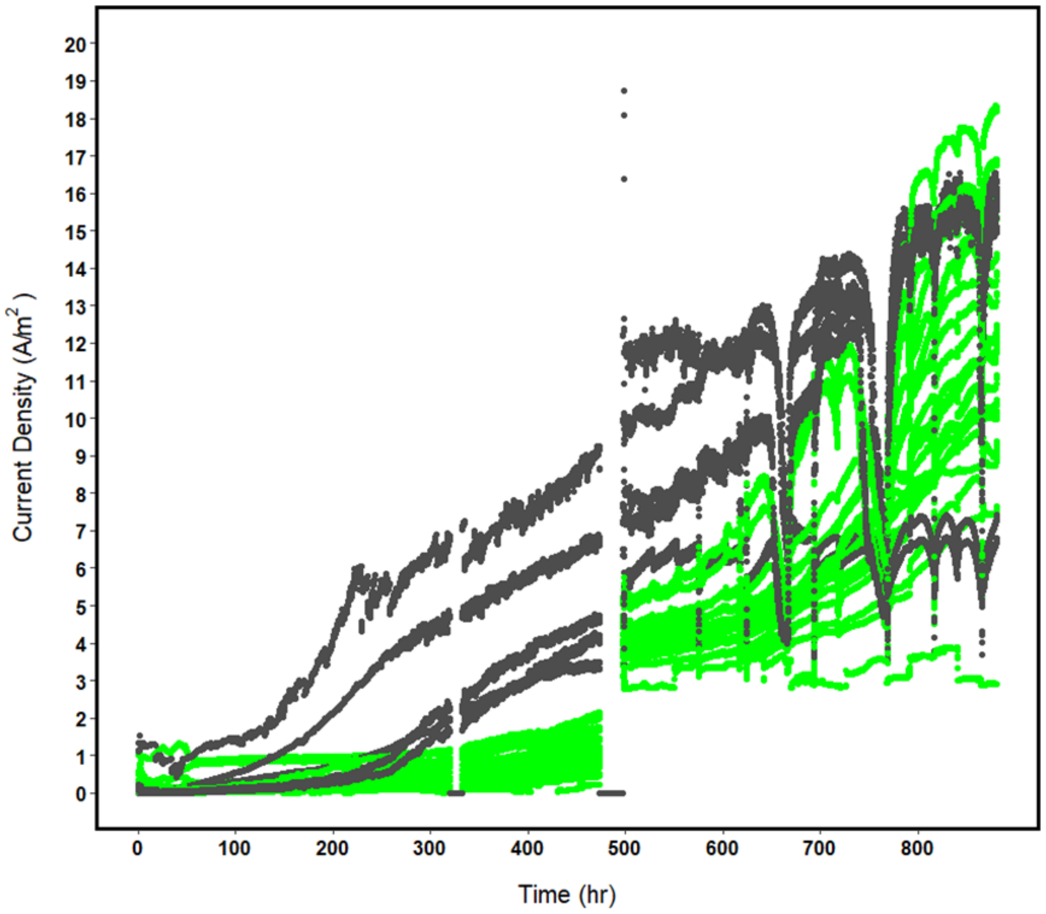


Product profile from combined yeast and acetobacter pretreatment

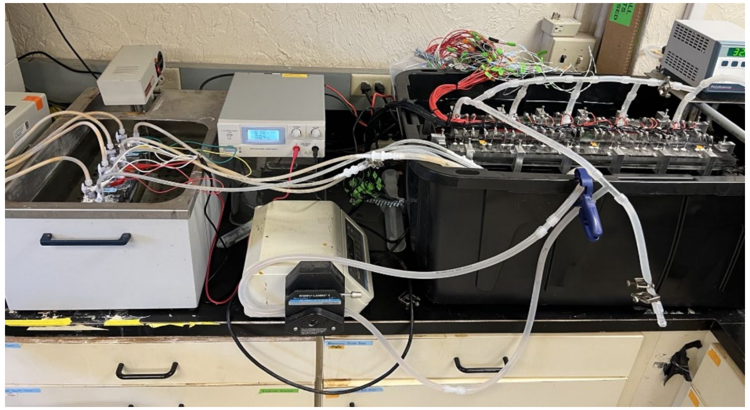
- To mitigate potential inhibition from high ethanol levels post-yeast pretreatment, Acetobacter, well-known for vinegar creation, was investigated to further convert ethanol into acetate.
- Acetate production is sustained by inoculating with reused Acetobacter cultures, eliminating the need for additional bacteria or nutrients, indicating a potential low-maintenance process.
- Minor pH adjustments are necessary.

Accomplishments and Progress (con.)

Startup of the 10 L MEC



Current densities of the MEC during startup

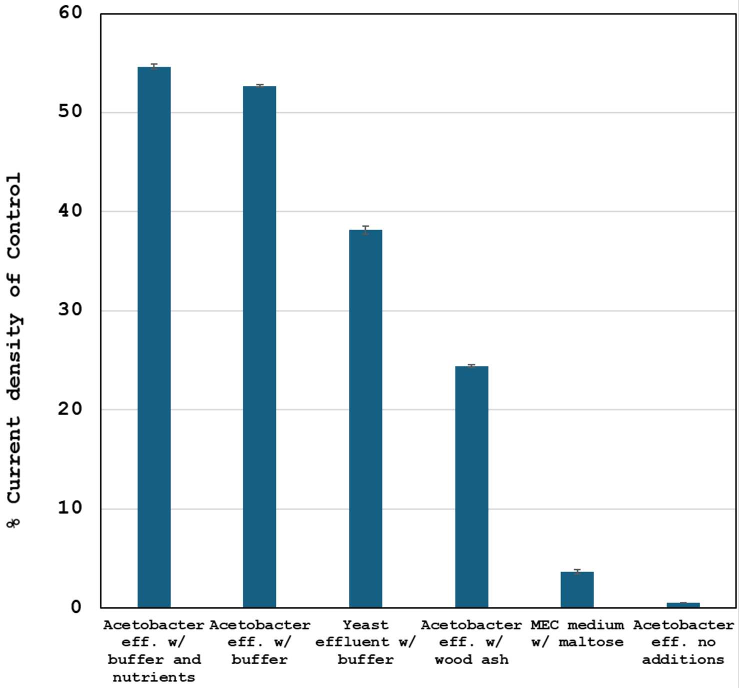


MEC reactor set up

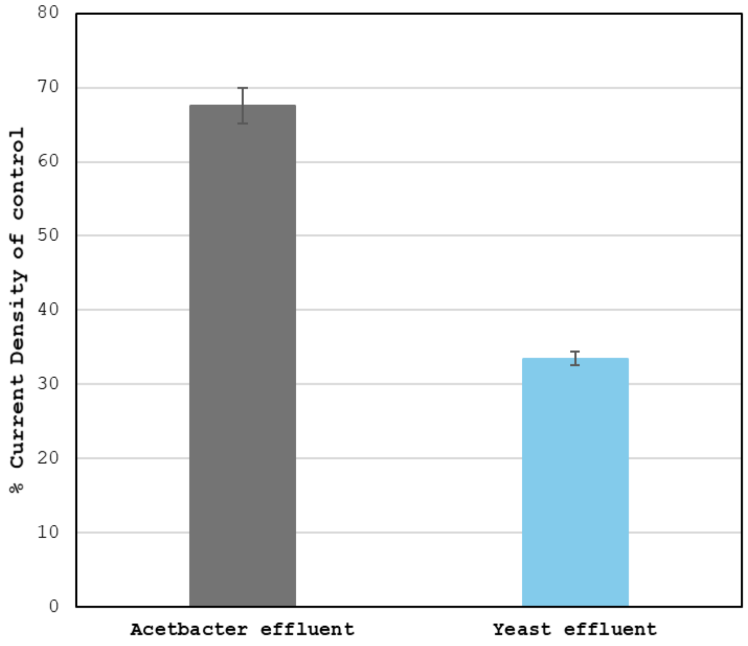
- Reactor inoculation employed three methods:
  - Added MEC effluent to the reactor at startup.
  - Inserted small piece of mature biofilm-laden carbon cloth between each of the 28 anodes and current collectors.
  - Directed effluent from a continuous flow reactor into the large reactor's inlet.
- A short circuit was detected in one of the 28 asseblies during the setup process.
- The large reactor's startup was slower than the small-scale 0.5 L MEC (reached 40 A/m² within two weeks).

Accomplishments and Progress (con.)

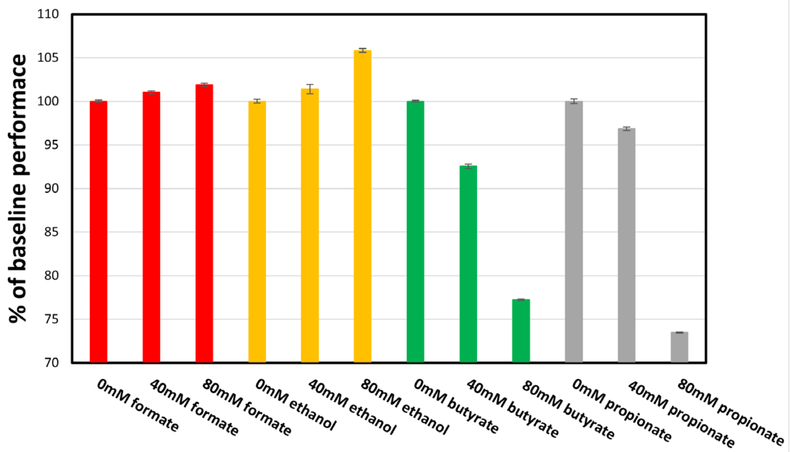
MEC performance of the pretreatment waste stream



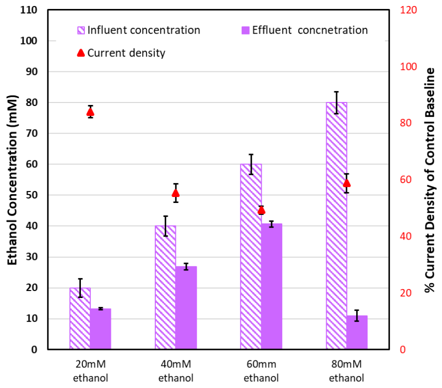
Current density changes using pretreated wastewater in batch mode



Current density changes using pretreated wastewater in continuous flow mode



Impact of VFA and ethanol on current under batch mode

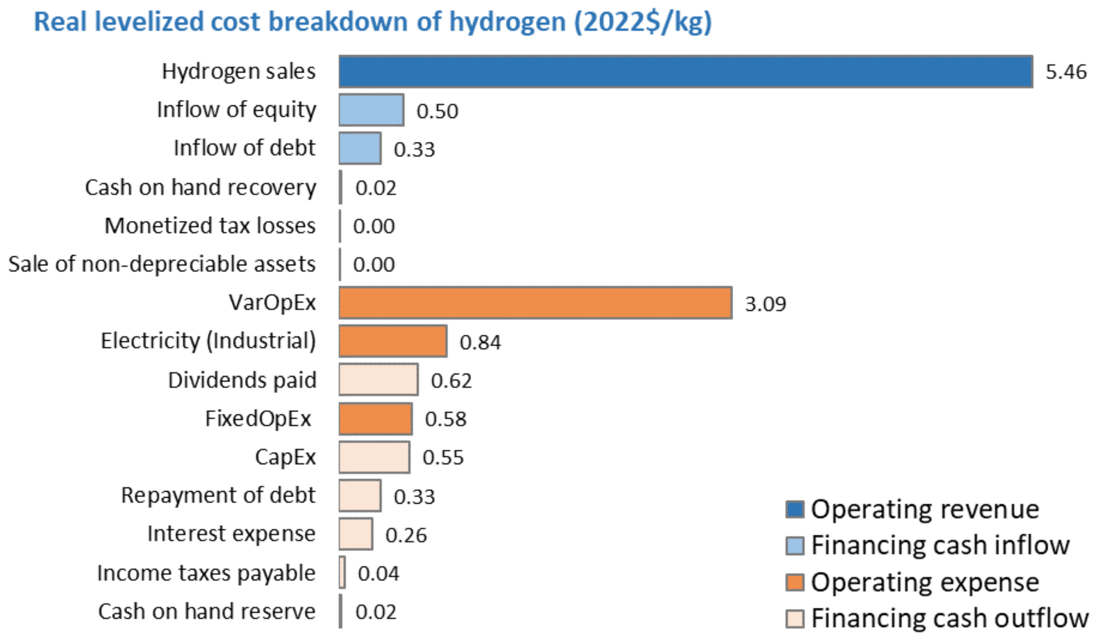


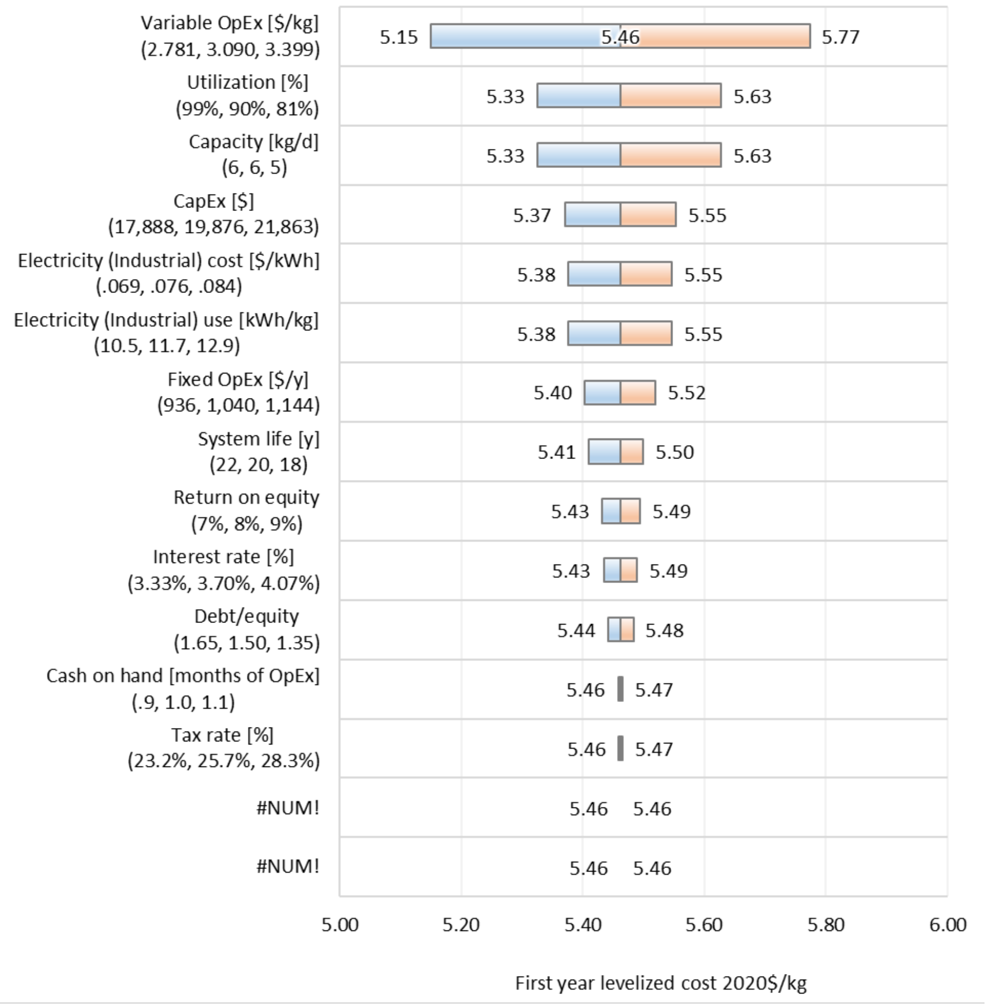
Impact of ethanol on current under continuous flow mode

- Decreased current density suggests the presence of other inhibitors, even when acetate is the primary product after the pretreatment.
- Variations in MEC performance between batch and continuous flow operations highlight the system's complexity.
- The waste stream provides adequate nutrients for the MEC's microbial processes.
- Effective pH management is crucial for MEC efficiency, particularly due to the low initial pH of this specific waste stream.

Accomplishments and Progress (con.)

Preliminary H2A model





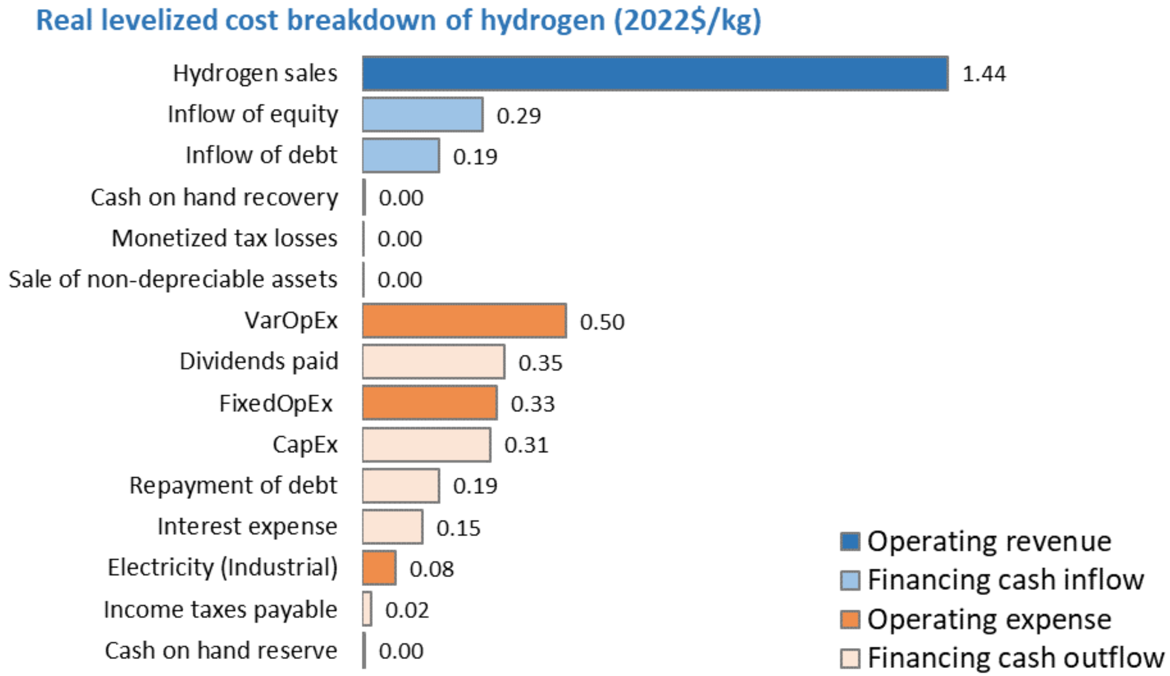
Key assumptions:

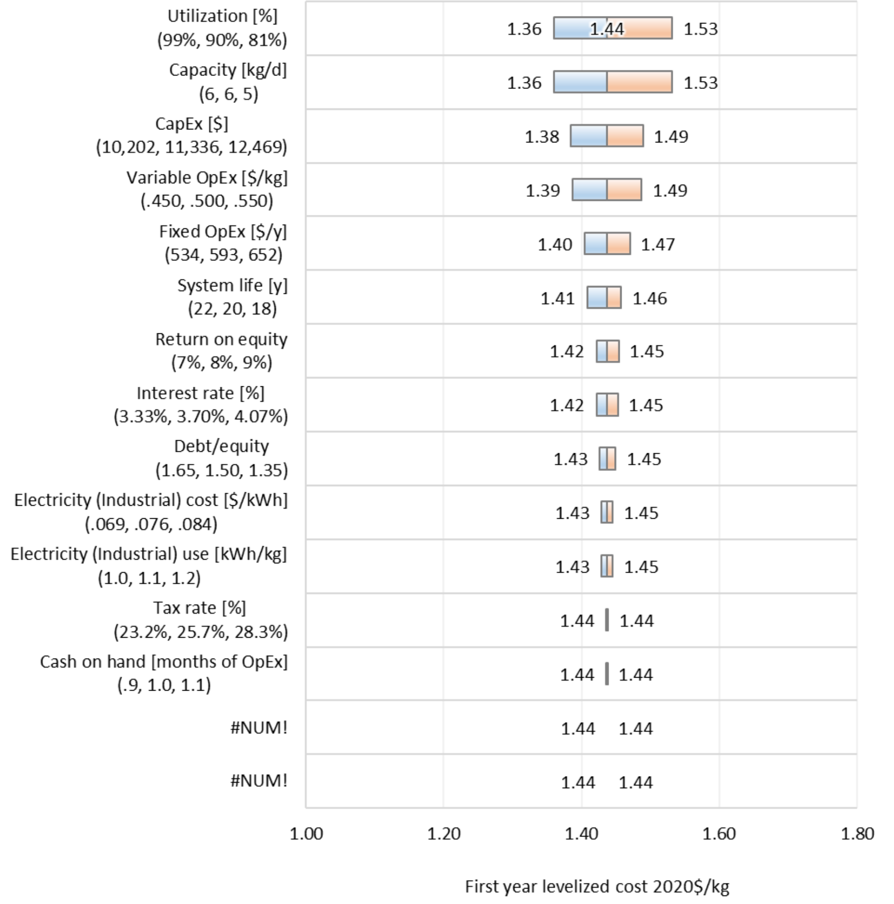
- Anode Replacement: 20% annually
- Cathode Replacement: 10% annually
- Reactor Vessel Lifespan: 20 years
- Maintenance Cost: 2% of initial capital, annually
- Production Goal: 2,000 kg H_2/year for a beverage facility
- Heating Source: Electricity
- pH Control: Caustic soda and bicarbonate (VarOpEx)
- Production Rate: 19 L/L/day (current value)
- **Wastewater Treatment Credit of $10/kg H2 is not included**

Chemical expenses, particularly for pH control, are significant in the economic feasibility of biohydrogen production.

Accomplishments and Progress (con.)

Preliminary H2A model





Key assumptions:

- Anode Replacement: 20% annually
- Cathode Replacement: 10% annually
- Reactor Vessel Lifespan: 20 years
- Maintenance Cost: 2% of initial capital, annually
- Production Goal: 2,000 kg H_2/year for a beverage facility
- Heating Source: waste head from beverage production
- pH Control: Caustic soda is used in conjunction with a waste material, as determined through our laboratory tests (VarOpEx)
- Production Rate: 35L/L/day (expected at the end of the project)
- Wastewater Treatment Credit of $10/kg H2 is not included

Lower production costs to under $2/kg through:

- Employ NaCO3-rich waste for pH control
- Utilize facility's waste heat for reactor heating
- Increase hydrogen production

Responses to Previous Year (2023) Reviewers' Comments

- *Most of the initial work was focused on synthetic media, overlooking the complex composition of real media. The impact of the wastewater composition on performance can limit impact of the proposed work.*

Response: We acknowledge the reviewer's concern regarding the influence of wastewater composition on MEC performance, as waste streams can indeed vary significantly between industries. Some may have high acetate concentrations, which are favorable for MECs, while others may be rich in sugars, volatile fatty acids, or might require nutrient supplementation for optimal microbial activity. SInce it is impractical to tailor a MEC system for peak performance with every possible waste stream, the primary goals of this project are to 1) develop cost-effective electrode materials, a major cost barrier (AAA), previously identified by the DOE, and 2) demonstrate the feasibility of achieving high hydrogen production rates, addressing another DOE-identified challenge (AAB). Our initial work with synthetic media is designed to evaluate our developed electrodes and reactor design under standardized conditions and to establish a hydrogen production benchmark. Further testing with diverse real-world wastewater streams—one for this project and more for potential future studies—will be crucial to confirm our results and tailor the technology for practical use.

- *The project needs to clarify which electrode approach is better and how robust these developments will prove to be when put into a working device.*

Response: Our selected electrodes, N-doped CNT-SS anode and Ni alloy cathode, after being evaluated in a 0.5L MEC for performance and cost-effectiveness, have shown comparable results to those achieved on the milliliter scale. These electrodes are now undergoing trials in our 10L MEC, with early results indicating a positive outcome. This step-wise scaling is critical to determining the electrode efficacy and resilience in operational systems, addressing the project's goal to establish which electrode configuration offers the best performance for practical application.

- *The project indicates that pre-fermentation of the wastewater would be required to sustain high-current-density operation. The cost of this additional pre-treatment step needs to be estimated.*

Response: Additional research has been conducted on pretreatment processes designed for the specific waste stream, which is detailed in our presentation. The costs of these pretreatment steps, including both capital and operational expenses, have now been accounted for in our updated H2A model, ensuring a thorough economic evaluation. Particularly, the expenses for pH adjustment and maintenance after the pretreatment, previously not elaborated upon, have emerged as significant in the revised economic model.

- *It appears solid work has been done, but the project has not yet pulled together to demonstrate overall improvement in cost or productivity.*

Response: Our updated H2A model reflects a substantial reduction in capital costs, primarily due to the cost-effective electrodes we developed—addressing a key concern identified by the DOE. Additionally, these electrodes, together with optimized waste stream pretreatment, have led to higher hydrogen production rates, thus improving the MEC system's productivity.

- *The project is still in a very low technology readiness level, and it is not clear how much commercial interest there would be for technology application*

Response: Our updated H2A model has delineated the primary cost factors, steering future steps and informing the selection of waste streams that capitalize on available resources, such as waste heat and materials with intrinsic caustic properties.

Collaborations

Partner	Project Roles
Oregon State University Prof. Liu's Lab	Project lead, management and coordination; Identification of key properties required for electrodes and catalyst in MECs; Evaluation of electrodes in MECs; Bioreactor design, fabrication, and evaluation
Texas A&M University Prof. Yu's lab	Scalable CNT electrode synthesis method development; CNT material modification and characterization, CNT electrode fabrication for large MEC reactor
Pacific Northwest National Laboratory Dr. Shao's group	Cathode evaluation and characterization
Block 15, Corvallis, Oregon	Industry collaborator, brewery wastewater provider

Remaining Challenges and Future Work

Remaining challenge:

- Our former collaborator, Mazama Brewing, ceased operations unexpectedly. We have since partnered with Block 15, although variability in their production schedule and fermentations could influence our reactor's performance. To mitigate this, we're implementing refrigerated storage for wastewater and will conduct regular wastewater quality assessments to adapt to any changes.

Future work in the remaining budget period of 2024:

- Finish the evaluation of the 10-L reactor using wastewater
- Update the cost performance modeling

*Any proposed future work is subject to change based on funding levels

Summary - progress and accomplishment

- Assembled a 10-liter MEC reactor featuring a dense electrode structure for enhanced performance, with removable electrode pairs to facilitate testing and maintenance.
- Analysis of local brewery waste streams reveals significant fluctuation in organic compound concentrations between batches.
- A dedicated pretreatment reactor is crucial for managing the composition of sugar-rich waste streams for effective MEC operation.
- Major fermentation by-products, such as butyrate, propionate, and lactate, have been shown to adversely affect MEC performance, even at 20 mM.
- Ethanol, when present in concentrations below 80 mM, exhibits low impact on MEC functionality.
- Employing yeast and Acetobacter could result in an effluent rich in ethanol or acetate, suggesting a potentially simplified pretreatment method for the waste stream evaluated.
- A drop in current density indicates potential inhibitors within the waste stream, even when acetate is the primary product after the pretreatment.
- Chemical costs, especially those related to pH management, play a critical role in the economic viability of biohydrogen production from low pH, sugar-rich waste streams.