



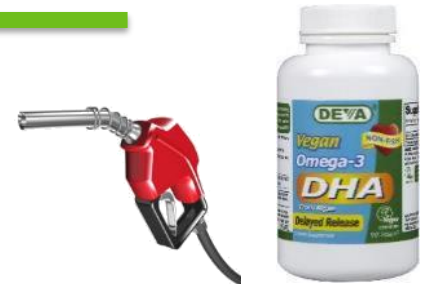
DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review Atmospheric CO₂ Capture and Membrane Delivery (ACED)



CO₂



Large-scale algae cultivation (courtesy of Joule®)



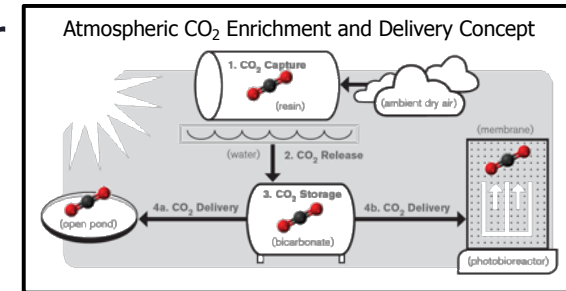
Bruce Rittmann, Ph.D.

Principal Investigator, Arizona State University

**March 4, 2019
Technology Session
Area Review**

ACED Goal Statement

- **Goal:** Design, build, and demonstrate a system for capturing and concentrating CO₂ from ambient air and delivering the CO₂ to microalgae.
- **Outcomes:**
 - Capture and concentrate CO₂ from ambient air
 - Store CO₂ in a carbonate brine
 - Extract, concentrate, and pressurize CO₂
 - Efficiently deliver CO₂ to grow microalgae
 - Outdoor algal cultivation for 1 month 1500-L pond with CO₂ captured from ambient air.
- **Relevance:** Provide a renewable, clean, and concentrated CO₂ stream to microalgae grown in any sunny location.



Quad Chart Overview

Timeline

- **Start:** 10/1/15 (Validation), 3/1/16 (Research)
- **Official End:** 8/1/18
- **Status:** 100% complete, Final Report submitted in December

Budget

| | Total Costs Pre FY 19 | FY 19 Costs (Project ended 9/30/18) |
|-----------------------------|-----------------------|-------------------------------------|
| DOE Funded | \$1,000,000 | \$0 |
| Project Cost Share (Comp.)* | \$251,991 | \$0 |

Barriers

- **Technical Barriers**
 - Atmospheric **CO₂ Capture** and Concentration
 - Efficient **CO₂ delivery** and utilization
- **MYP Technical Targets**
 - **CO₂ Utilization:** 90%
 - **CO₂ + Nutrient Cost:** \$120 / ton AFDW (2022)

Objective

Develop a system for concentrating CO₂ from ambient air and delivering the CO₂ to microalgae.

End of Project Goal

CO₂ delivery: >90% into media, >70% into biomass

1 – Project Overview

History

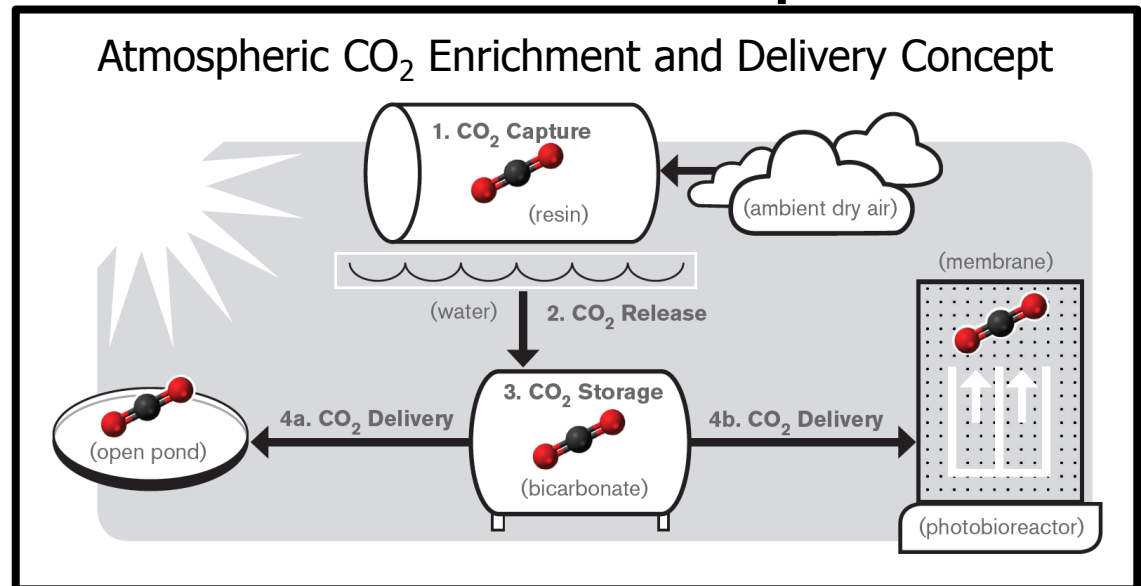
- Bruce Rittmann patented technology using membranes to deliver H₂ to treat wastewater and adapted it for microalgae carbonation in 2011.
- Klaus Lackner joined ASU in Fall 2014, bringing technology to capture and concentrate CO₂ from ambient air.

Objective --

Build a system that:

1. Captures and concentrate atmospheric CO₂
2. Stores CO₂ in a buffer to ensure adequate supply at any time and further concentrate CO₂ for delivery
3. Uses bubble-less CO₂ delivery: >90% into media, >70% into biomass

ACED Concept

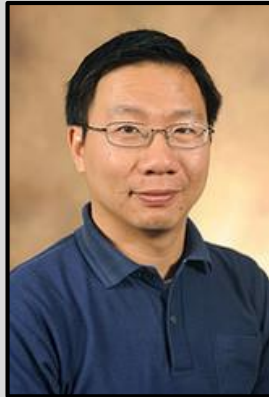


2 – Approach (Management)

Membrane Carbonation (MC)



Bruce Rittmann
Principal Investigator



Yen-jung Lai
Research Scientist



Everett Eustance
Research Scientist



Justin Flory
Technical Project
Manager



Robert Stirling
Techno-Economic
Analyst

Moisture Swing Sorption (MSS)



Klaus Lackner
Co-Principal
Investigator



Allen Wright
Lead Engineer



Jason Kmon
Engineer



William Barr
Postdoc

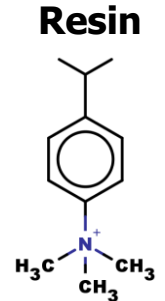


Zara L'Heureux
Research Technologist

2 – Approach (Technical)

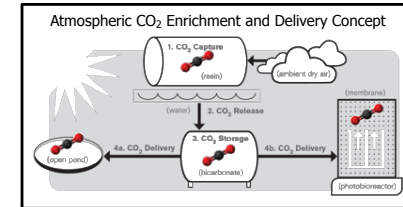
• Technical Approach

- Anionic exchange resin sheets capture CO₂ when dry and release when wet
- CO₂ is transferred to sodium carbonate/bicarbonate brines to buffer capture and demand rates; thermally extracted and pressurized
- ~100% CO₂ is delivered on demand to microalgae using membrane fibers
- System is tested ≥1 months outdoors in a 1500-L pond



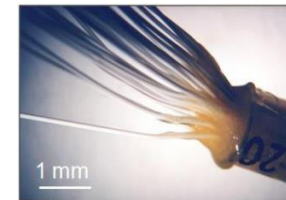
• Challenges

- CO₂ Capture: Support structure cost, resin density, and dead space
- CO₂ Storage: CO₂ transfer rate and efficiency into and out of brine
- CO₂ Delivery: Accumulation of non-CO₂ gases in fibers



• Success Factors

- Capture: kg CO₂ / kg resin; kg structure / kg resin
- Storage: transfer rates; heat recovery; storage cost / kg CO₂
- Delivery: CO₂ transfer efficiency and flux stability over time



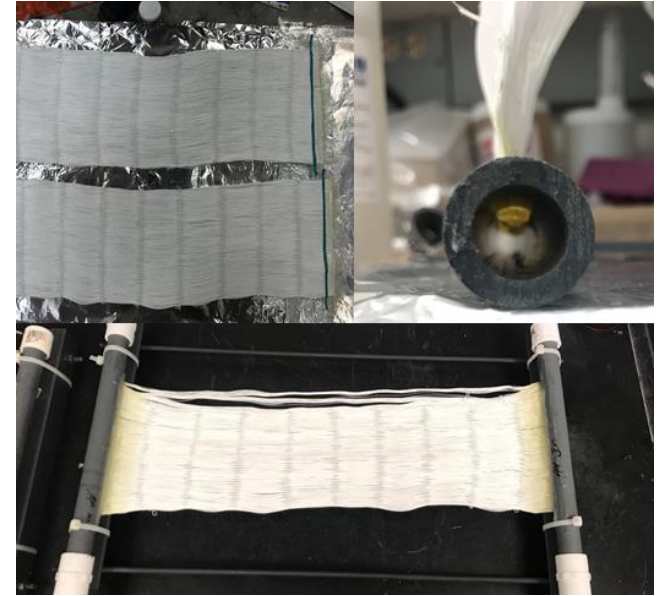
Hollow Fiber Membranes

1500-L pond

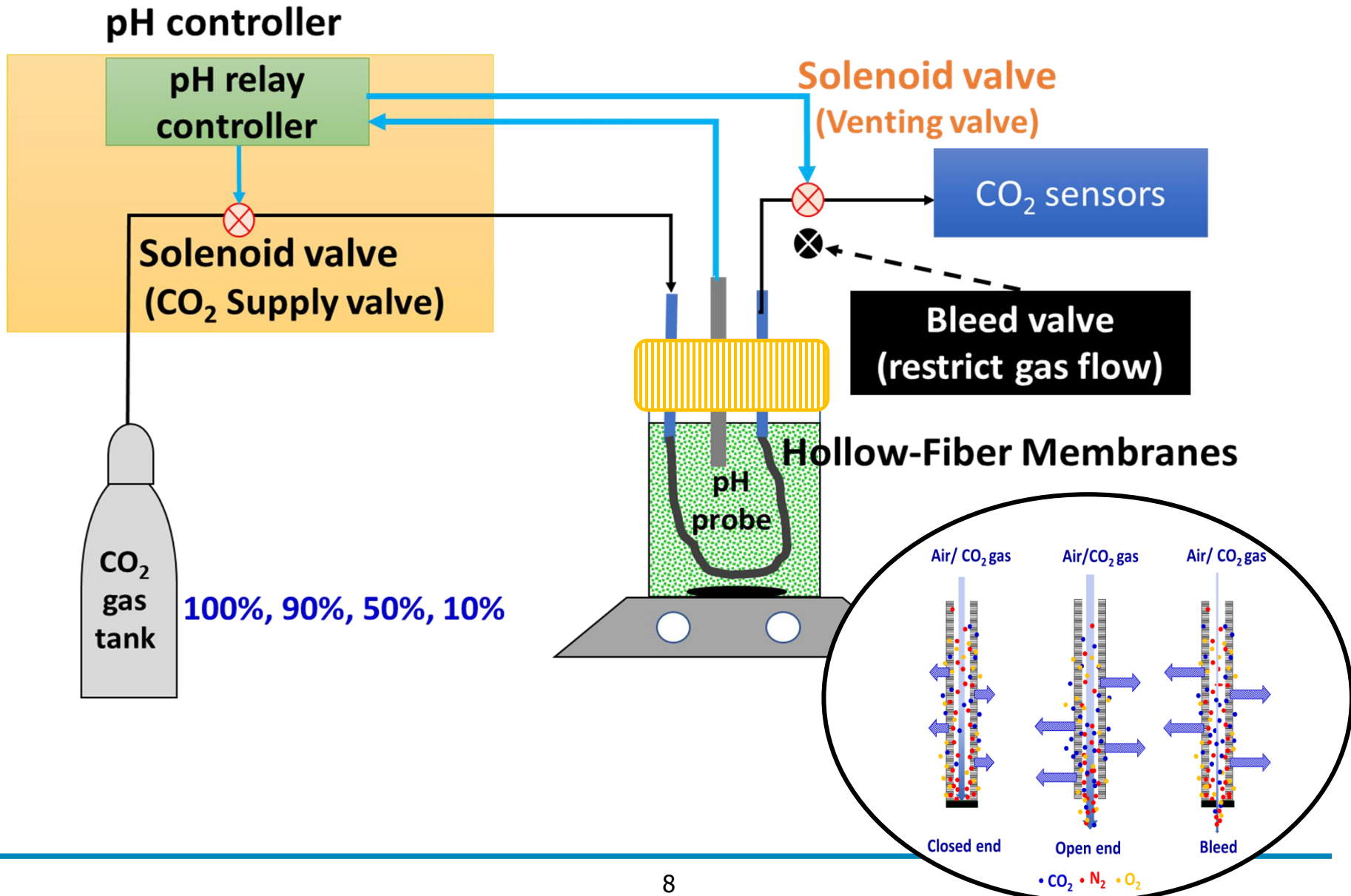


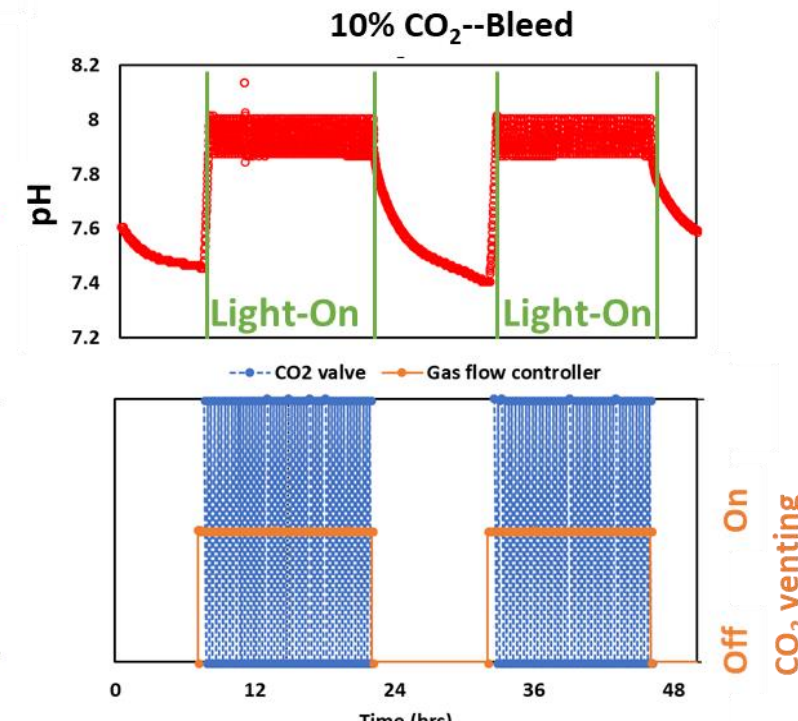
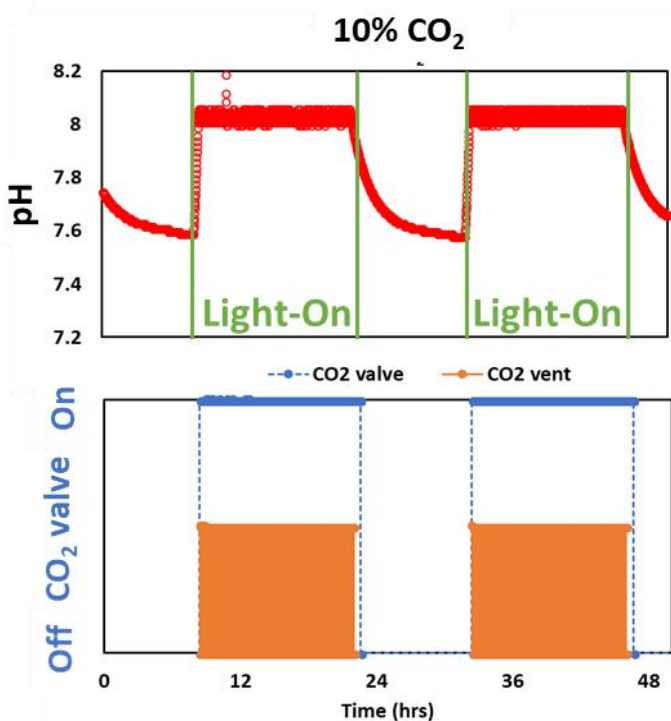
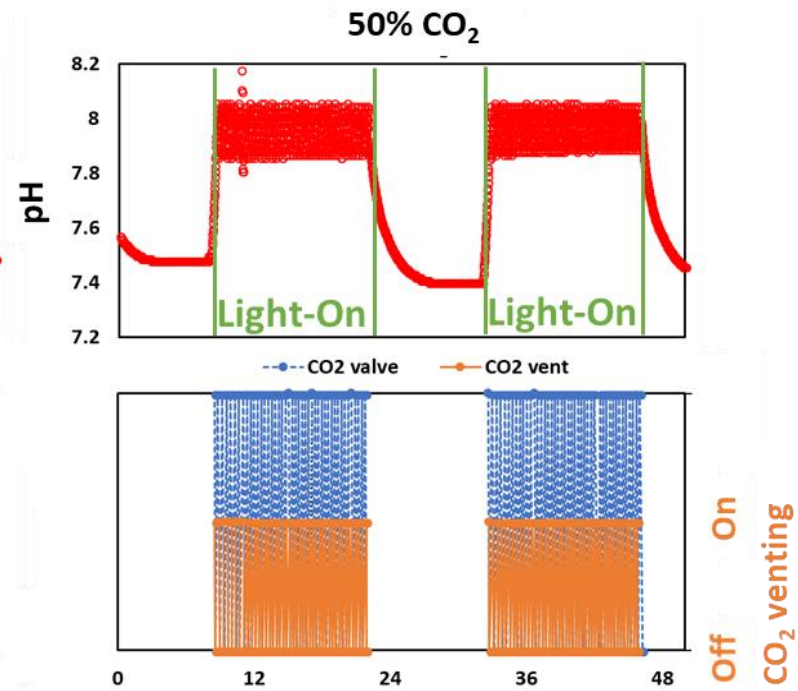
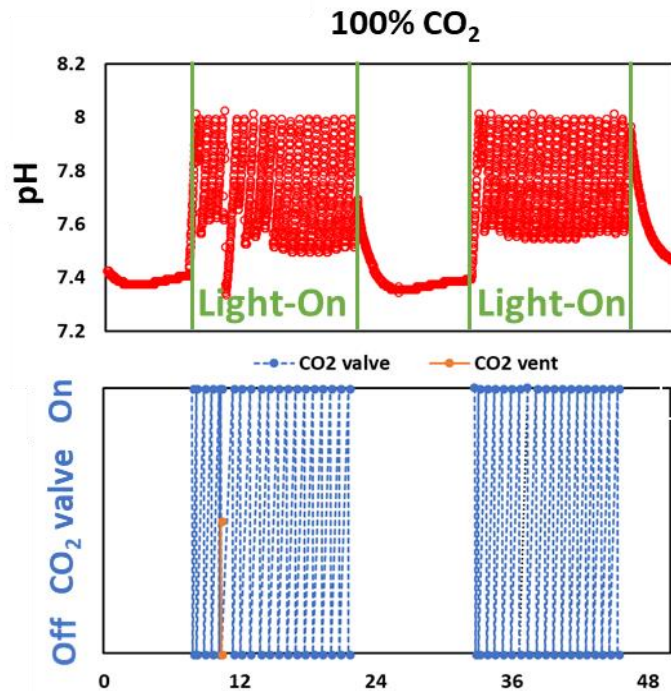
3 – Technical Results (CO₂ Delivery)

1. Biomass productivities were equal and pH control was superior with MC, compared to sparging.
2. ~100% delivery efficiency and 3-fold higher Carbon Utilization Efficiency (CUE) versus sparging.
3. CO₂ delivery rates were not adversely affected by months of operation outdoors.
4. Effective strategies were developed to relieve inert gas accumulation when delivering < 100% CO₂.

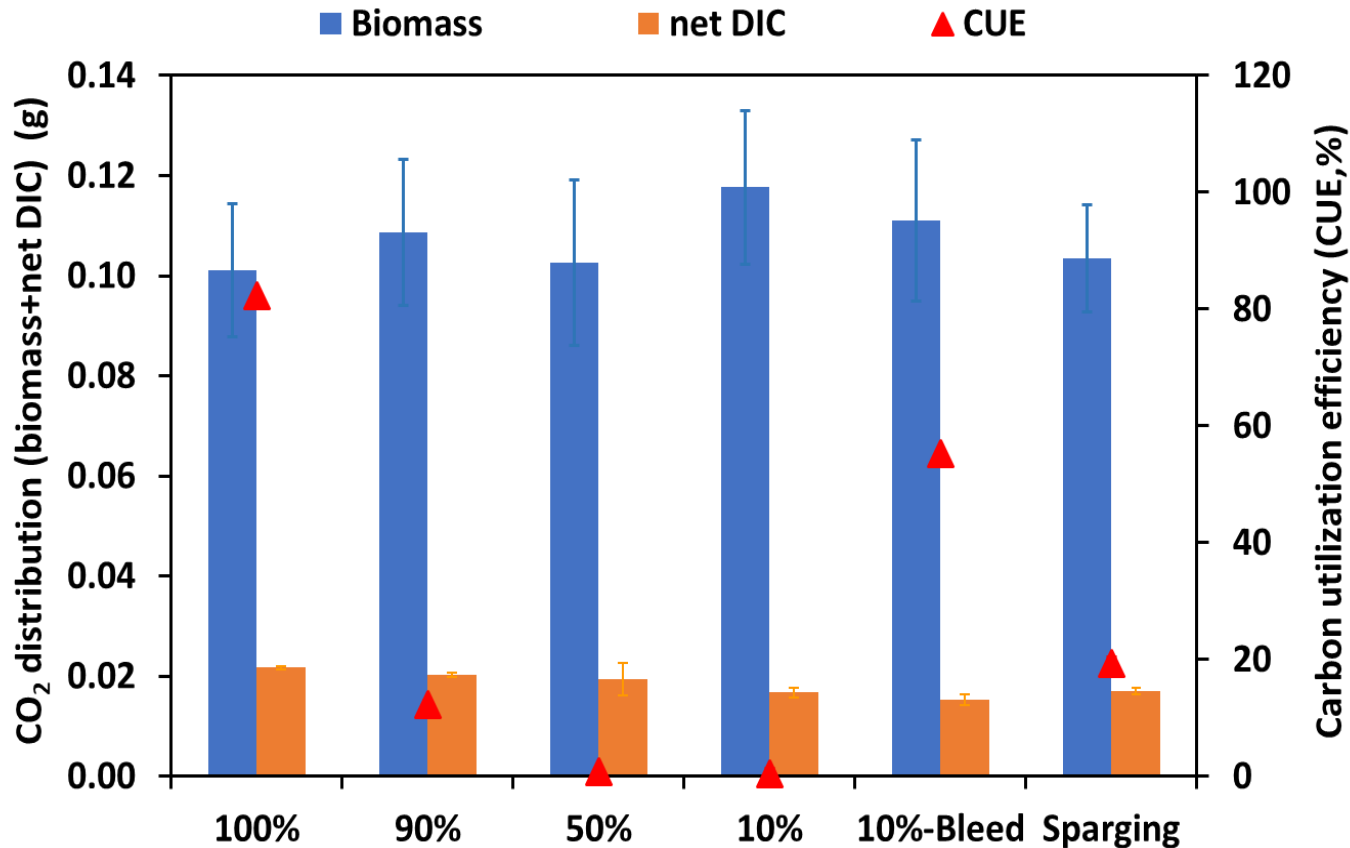


Venting-Bleed MC strategy





Indoor Carbon-Utilization Efficiency



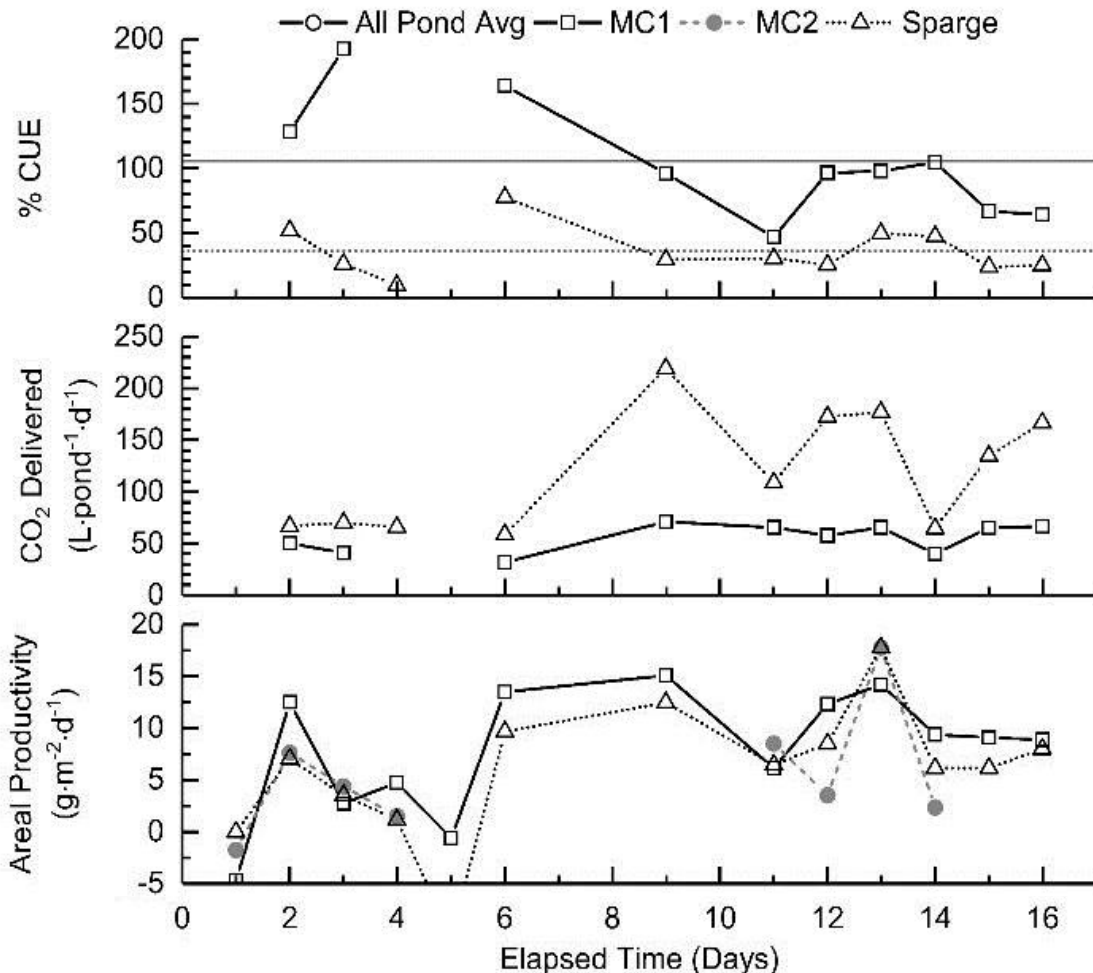
In 100% CO₂: 80% CUE

In 90% CO₂: Low CUE related to small scale of reactors, where we could not cut back the gas flow through the fibers.

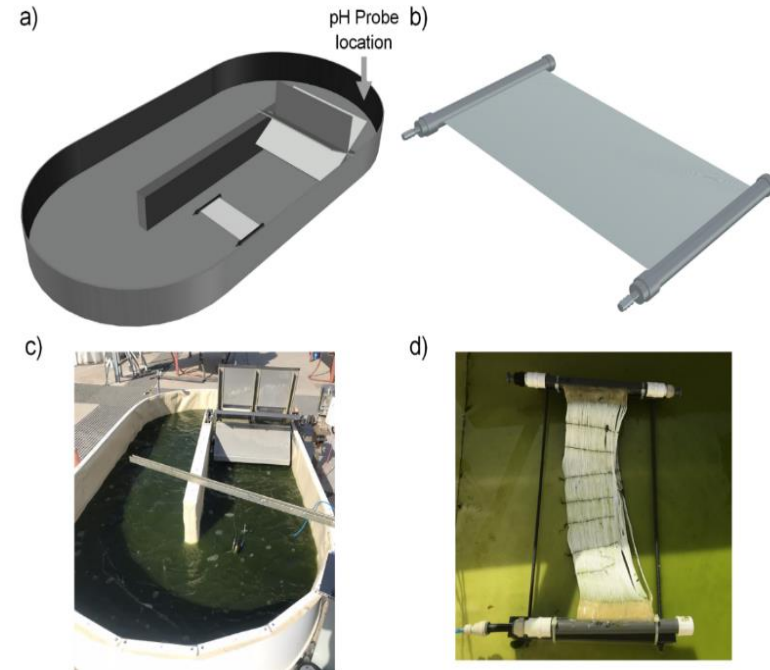
In 10% CO₂ with Bleed: Up to 60% CUE in unoptimized operation (due to small scale)

Outdoor Carbon Capture

- Achieved $>100\%$ CUE with pure CO_2 with similar areal productivity as sparging (CUE $\sim 40\%$)
 - 100% delivery + capturing additional CO_2 from atmosphere



Experiment: April 18 to
May 4, 2018



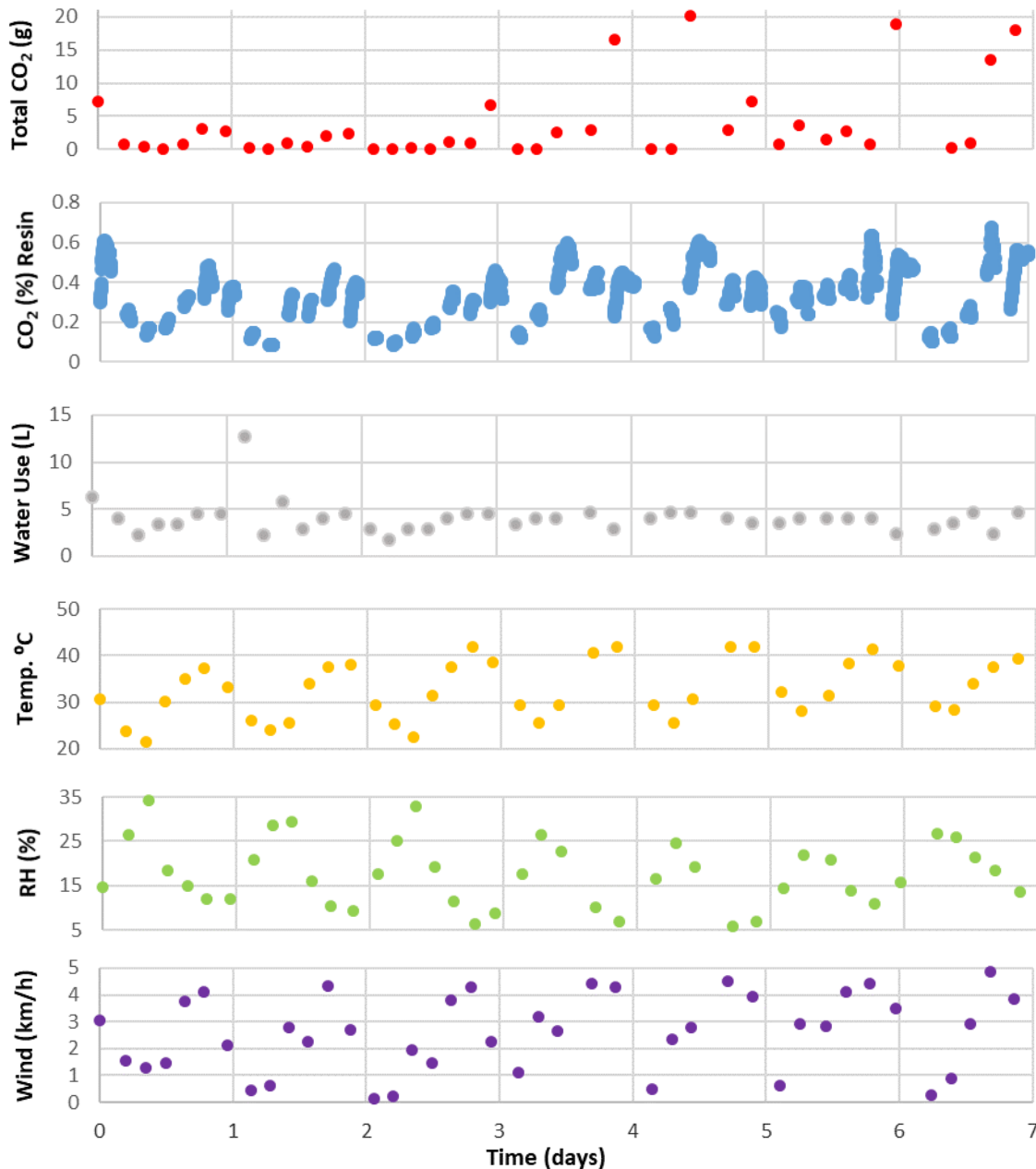
| | Experiment 2 | Experiment 3 | Experiment 4 |
|--|---------------------|-------------------------|-------------------------|
| Dates | 3/16 to 4/11/18 | 4/18 to 5/4/18 | 5/18 to 6/5/18 |
| pH Setpoint | 8.5 | 8.5 | 8.0 |
| Average temp (°C) | 17.6 ± 4.3 | 20.3 ± 4.8 | 23.1 ± 5.1 |
| Average Light (kWh·m⁻²·d⁻¹) | 6.2 ± 0.7 | 7.2 ± 0.8 | 8.3 ± 0.3 |
| Nitrogen source | Nitrate | Ammonium bicarbonate | Ammonium bicarbonate |
| Biomass Productivity (g·m⁻²·d⁻¹) | 10.2 ± 3.6 | 6.7 ± 6.0 | 11.8 ± 6.9 |
| Average fiber flux (g-CO₂·m⁻²·d⁻¹) | 1360 ± 860 | 2220 ± 750 | 2290 ± 610 |
| CUE MC1 | 67 ± 35% | 106 ± 45% | 51 ± 27% |
| CUE Sparging | 25 ± 18% | 36 ± 19% | 17 ± 10% |
| CUE Ratio MC/Sparging | 2.65 | 2.94 | 3.0 |

3 – Technical Results (CO₂ Capture)

1. Over 10% of CO₂ in air was captured by dry resin in lab wind tunnel tests at 1 m/s.
2. A prototype was constructed and captured CO₂ outdoors.
3. Performance data were collected periodically over 6 months and for up to 11 consecutive days; limited by hardware, software, and weather issues.
4. System, and sorbent, survived ~9 months in outdoor conditions, and remained intact.



7 day CO₂ Capture during June, 2018



- Outdoor performance was best when: temperature >25 °C, wind speed >2 km/h, and < 25% relative humidity.
- Wetting resin to release CO₂ by flooding made resin too wet, slowing drying, reducing performance and wasting water.

3 – Technical Results (CO₂ Capture)

- Adding sodium bicarbonate to supply water mitigated performance reduction from anions in tap water.

| Date | Days in Field (approx.) | Performance (ppm) / % of new | After 1 M Na ₂ CO ₃ wash / % of new | Tapwater [Cl ⁻] | Tote Water [Cl ⁻] | Na ₂ CO ₃ in Tote Water? |
|-----------------------|-------------------------|------------------------------|---|-----------------------------|-------------------------------|--|
| Feb 2018 | 60 | 20 ppm / 11% | 100 ppm / 57% (1 x wash) | 144 ppm | 240 ppm | No |
| Mar 6, 2018 | 90 | | | | 345 ppm | Yes |
| April 24, 2018 | 150 | 55 ppm / 31% | 90 ppm / 51% (1 x wash) | 259 ppm | 369 ppm | Yes |
| Aug 2-4, 2018 | 240 | 60 ppm / 34% | 170 ppm / 97% (3 x wash) | 173 ppm | 637 ppm | Yes |
| Aug 3, 2018 | 0 (new) | 175 ppm / 100% | | | | |

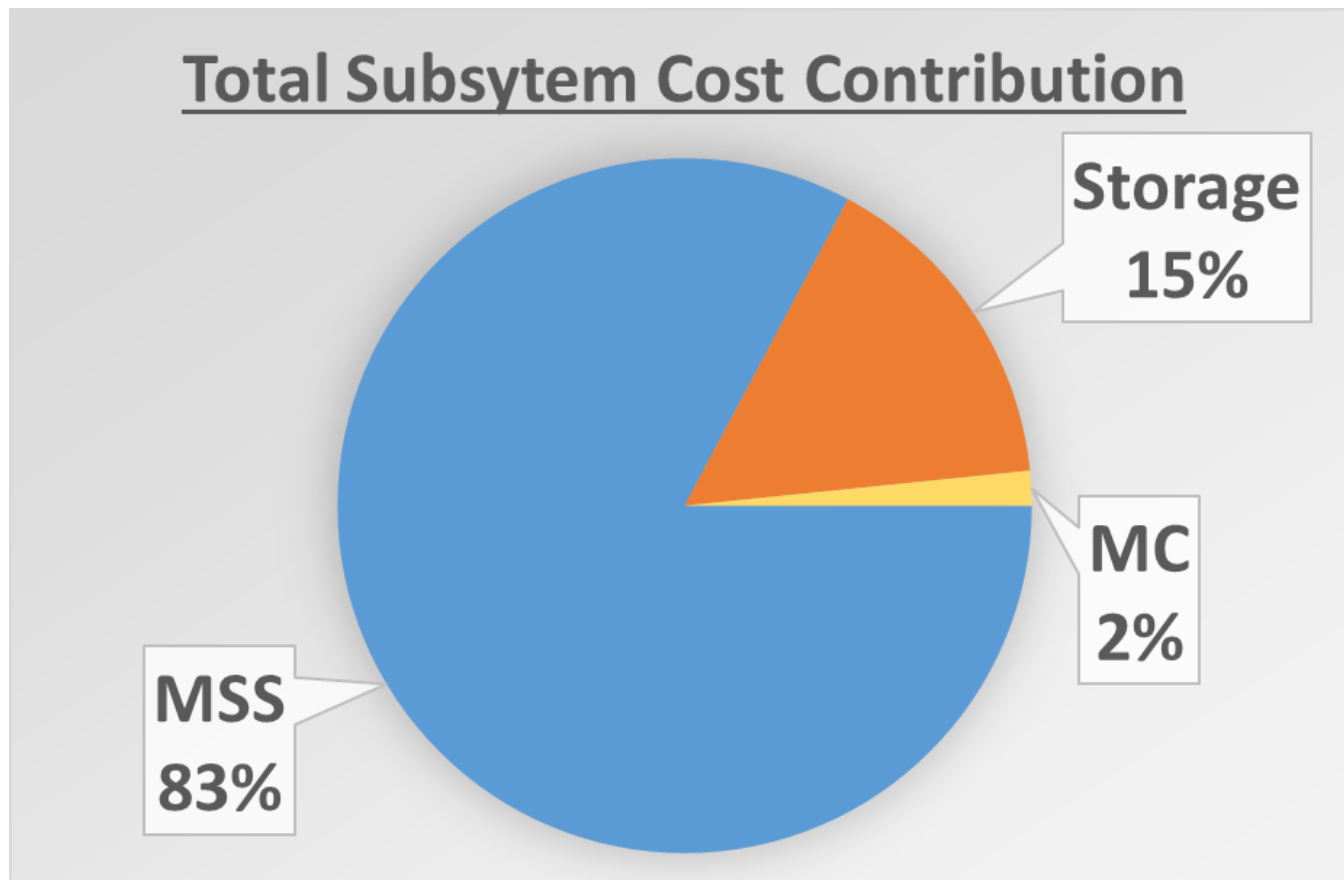
3 – Technical Results (CO₂ Storage)

1. A low-energy system for storage of CO₂ in carbonate/bicarbonate brines was demonstrated.
2. Heating the storage brine to near 100°C releases gas with >90% CO₂ on lab scale and >70% outdoors.
3. A transfer mechanism using wetted fabrics was demonstrated for dissolving captured CO₂ into storage brine.
4. The concept to capture CO₂ was demonstrated over a range of concentrations into multiple brine tanks.
5. Software emerged as a major bottleneck in technology development. Software frequently terminated CO₂ delivery into storage prematurely, reducing production.
6. CO₂ flux into storage is highly dependent on the air flow rate and brine composition.



Techno-Economic Analysis

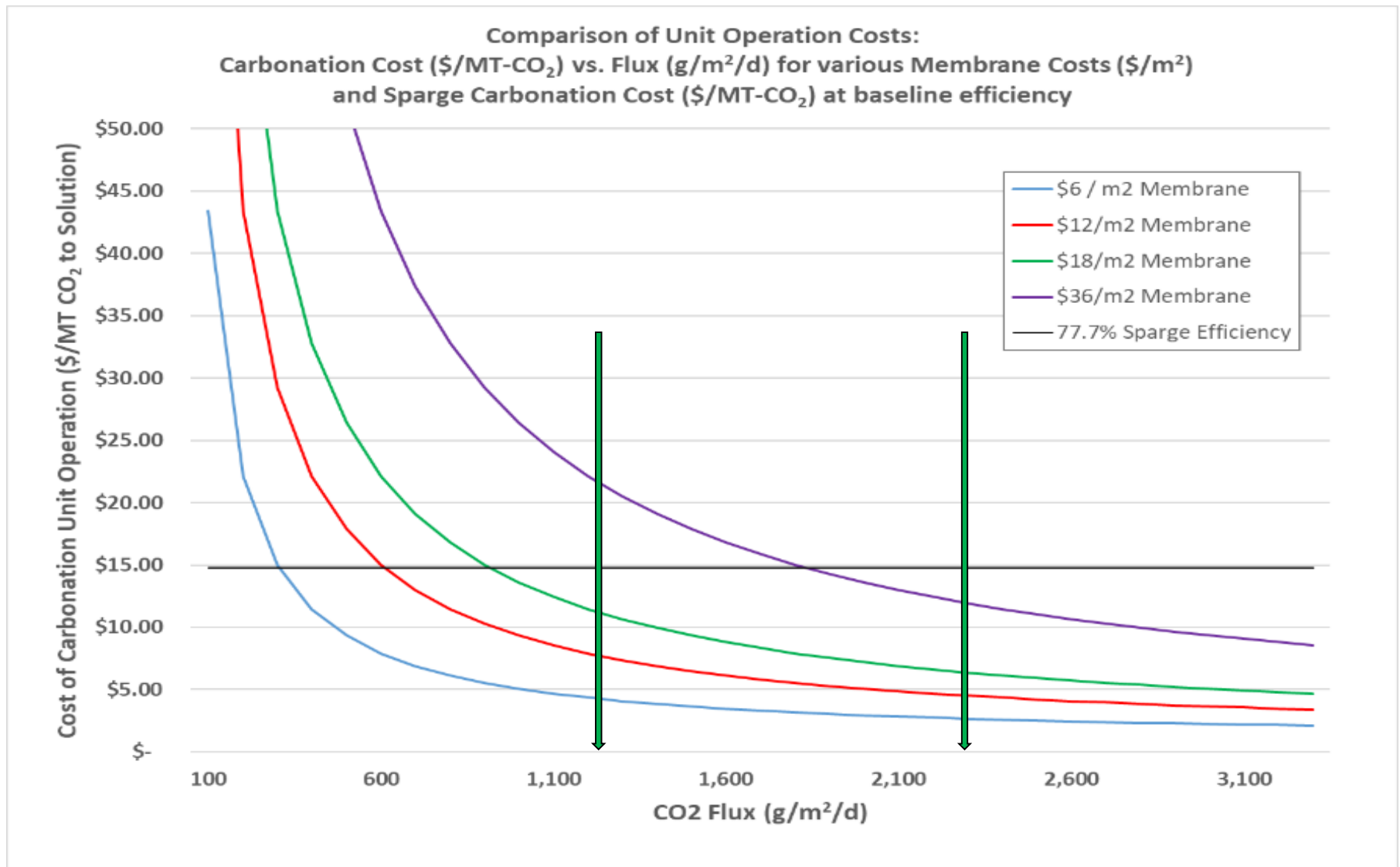
- MC contributed a small amount in comparison with prototype CO₂ capture and storage device



Techno-Economic Analysis - MC

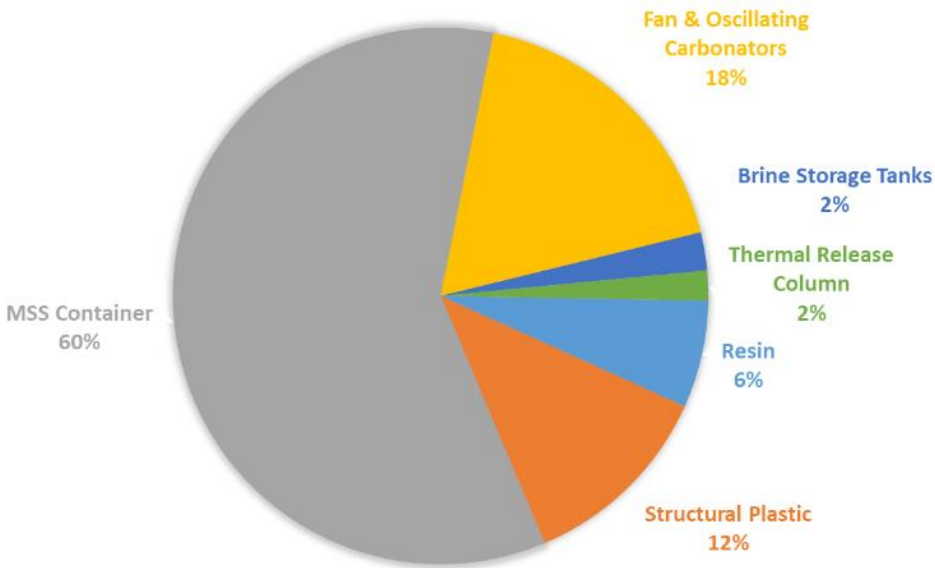
- MC reduces the cost of supplying CO₂ by at least 40–50% for current operators who pay \$120–500 / tonne for CO₂.
- MC should reduce total CO₂ costs by 15–20% at the large scales envisioned by BETO.
- Cost of operating MC is less than sump sparging at 80% efficiency. MC fluxes greater than 1800 g-CO₂/m²-d has an install cost of ~ \$3/MT CO₂ delivered.

Install Cost for MC VS Sparging

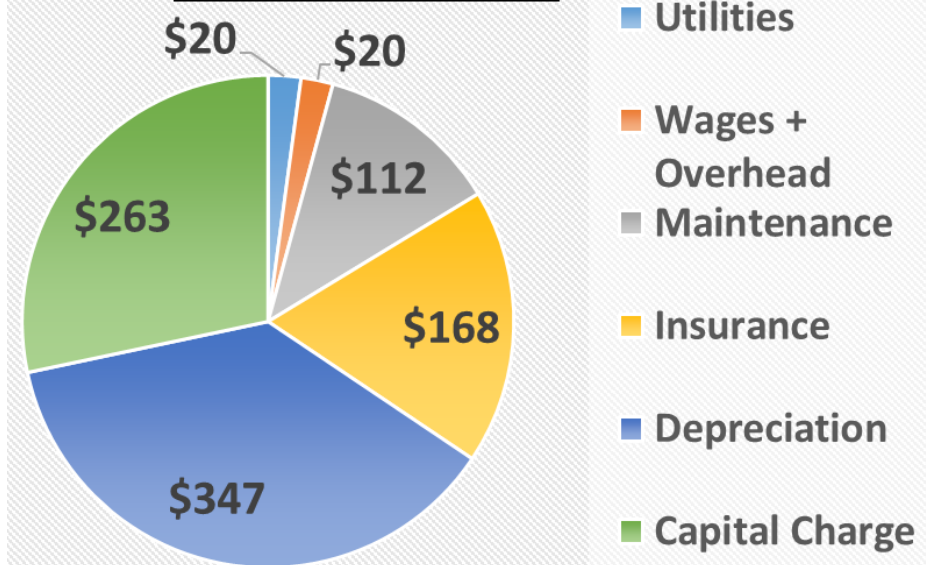


Techno-Economic Analysis MSS

CAPITAL EXPENSE CONTRIBUTION (TOTAL INSTALLED COST)

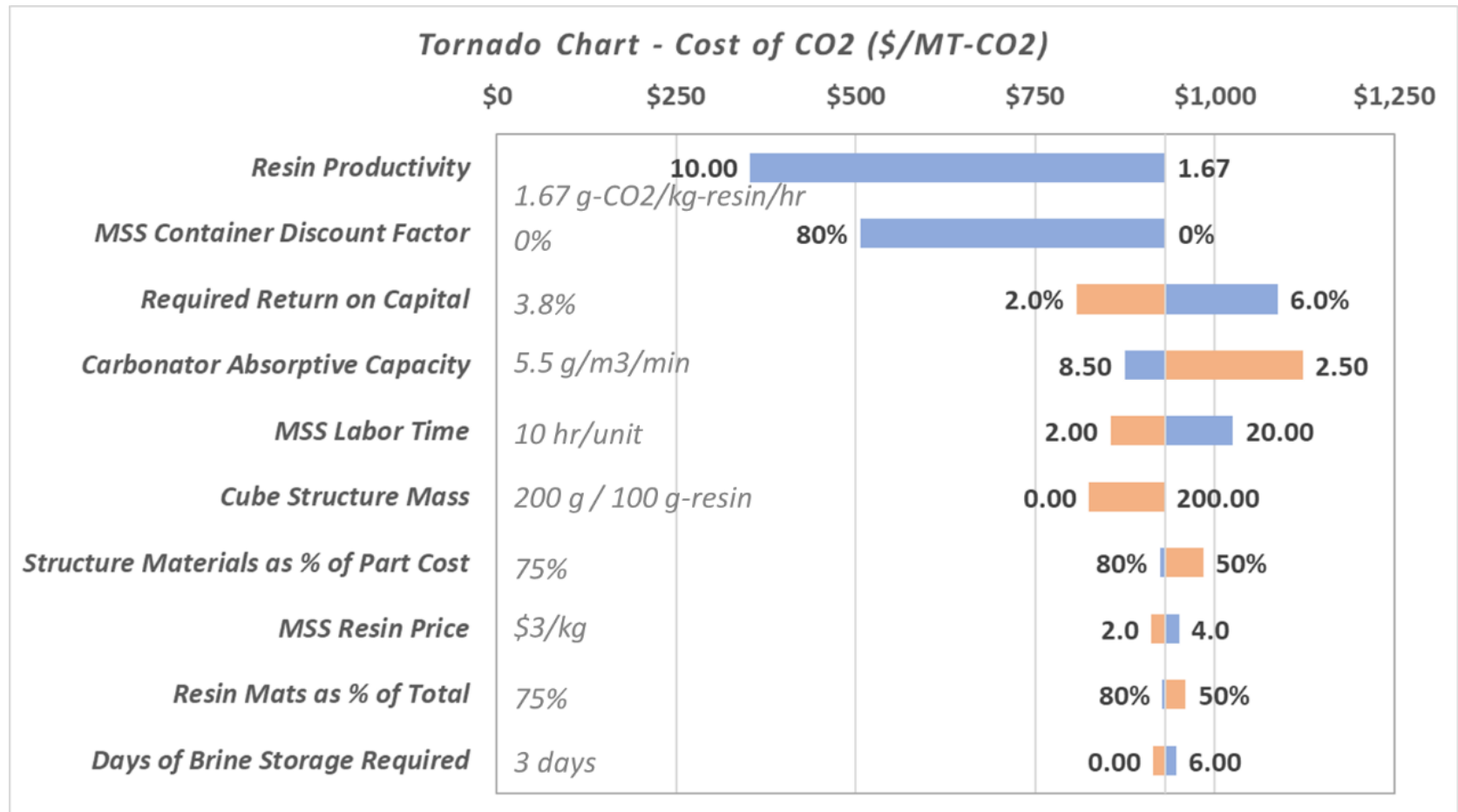


Cost / Tonne (\$/MT)



- Extrapolating the Prototype housing design to large scale leads to an estimated cost of dissolved, bioavailable CO₂ of ~\$900 per metric ton.
- The majority of the cost comes from the CapEx required to enclose, wet, and dry the functional resin.

TEA: Tornado Chart for MSS



Observations & Recommendations:

1. Maximize resin productivity
2. Minimize MSS container cost

Blue = Assumption Increases
Orange = Assumption Decreases

Relevance

- **Goal:** Design, build, and demonstrate outdoors a system for capturing and concentrating CO₂ from ambient air and delivering the CO₂ to microalgae.
 - Each component worked on its own.
 - Integration was not achieved due to hardware and software failures in MSS.
- **Demonstrated $\geq 100\%$ CO₂ delivery using MC outside**
- **Industry Relevance**
 - We definitely can deliver concentrated CO₂ into PBR with $\sim 100\%$ efficiency
 - This provides a major cost saving for delivering concentrated CO₂
- **Project Impact**
 - Efficient CO₂ delivery enables high productivities
- **Marketability**
 - **MC:** Besides pairing with MSS, MC can work with flue gas, digester gas, fermenter off-gas, landfill gas, and more.



Summary

- **Overview**

- Provide concentrated CO₂ in sunny locales far from concentrated sources and delivered into PBRs with ~100% efficiency.

- **Approach**

- Moisture swing sorption CO₂ capture + carbonate brine storage + membrane carbonation for CO₂ delivery.

- **Technical Accomplishments / Results**

- All subsystems were validated: CO₂ was captured, stored in brine, extracted from brine, and delivered to microalgae.
- We achieved outdoor demonstration of the MC part of ACED.
- MSS components worked, but could not be integrated due to failures.

- **Relevance**

- Efficient CO₂ delivery enables high productivities
- In addition to MSS, MC can work with flue gas, digester gas, fermenter off-gas, landfill gas, and more.



Questions?

Bruce Rittmann, Ph.D.

ACED Principal Investigator

Director, Swette Center for Environmental Biotechnology

Regents' Professor of Environmental Engineering

The Biodesign Institute

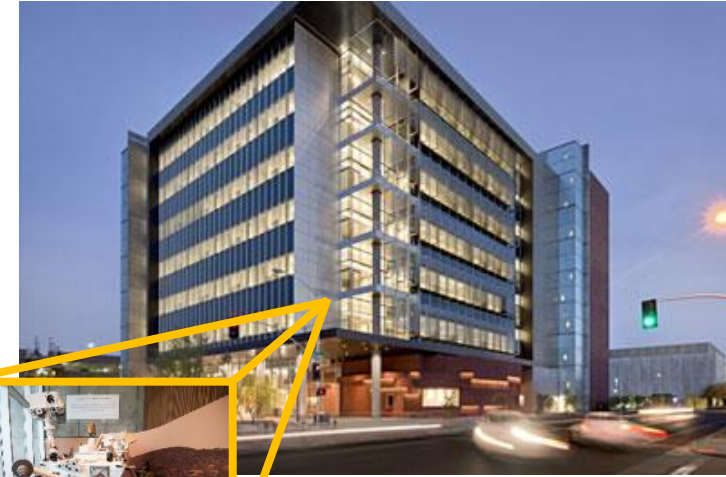
Arizona State University



Arizona State University

Biodesign Institute

ISTB-4



Arizona Center for Algae Technology and Innovation (AzCATI)





Supporting Slides

Publications, Patents, Presentations, Awards, and Commercialization

- **Publications**

- Characterization of CO₂ Flux Through Hollow-Fiber Membranes Using pH Modeling (Submitted-2018). Journal of Membrane Science. Tarun Shesh, Everett Eustance, Yen-Jung Lai, Bruce Rittmann
- Shi, X., Xiao, H., Liao, X., Armstrong, M., Chen, X. and Lackner, K.S., 2018. Humidity effect on ion behaviors of moisture-driven CO₂ sorbents. The Journal of Chemical Physics, 149(16), p.164708.

- **Awards:**

- DOE grant DE-EE0008517: "Membrane Carbonation for 100% Efficient Delivery of CO₂ from Industrial Gases"
- DOE grant DE-FOA-0001858: "Mining Air for Fuels and Fine Chemicals"
- Bruce Rittmann, 2018 Stockholm Water Prize

- **Patents:**

- Use of Hydrophobic Coatings on Direct Air Capture Sorbents Used for Carbon Dioxide Removal from Air. 62/752,725. Wright and Lackner
- Microalgae-driven CO₂ removal from mixed gases using hollow fiber membranes. Internal ASU disclosure M19-138L. Everett Eustance, Bruce Rittmann, Yen-Jung Lai, Tarun Shesh, Justin Flory

- **Commercialization: Nothing to report yet**

Publications, Patents, Presentations, Awards, and Commercialization

• Presentations

- Klaus Lackner, *CO₂ Removal Steering Group Meeting, La Jolla, CA*. Feb. 22-23, 2018
- Klaus Lackner, "Research and development for CO₂ Removal" *The 4th Science & Energy workshop, École de Physique des Houches, Les Houches, France*. Mar. 4-9, 2018
- Klaus Lackner, "Cleaning up Climate Change; A Business Opportunity" *American Gas Association's Sustainable Growth Committee, Scottsdale, AZ*. Mar. 15, 2018
- Klaus Lackner, "45Q-The new carbon economy" *Earth Day (EarthX 2018), Dallas, TX*. April 21, 2018
- Klaus Lackner, "Direct Air Capture" *REVERSAPALOOZA- A summit to jumpstart a new carbon removal marketplace, Seattle, WA*. April 26, 2018
- Klaus Lackner, "The New carbon economy" *AREDAY Summit, American Renewable Energy Day, Aspen, CO*. June 21, 2018
- Klaus Lackner, "Recovering from the overshoot in Carbon Dioxide Emissions" *The University of Edinburgh, Germany*. July 5, 2018
- Klaus Lackner, "CCS and Direct Air Capture" *Circular Carbon Economy, Golden CO*. July 24, 2018
- Klaus Lackner, "Strategies for lowering the cost of direct air capture" *Google X, Menlo Park CA*. August 21, 2018
- Klaus Lackner, "Cleaning up our carbon dioxide waste: Technologies to achieve global climate targets" *Elizabeth and Frederick White Conference on Gas-Solid Reactions, Australia*. September 6, 2018
- Klaus Lackner, "Introduction to Center for Negative Emissions at ASU" *Negative Emissions Technologies in the Energy Sector Workshop, Houston TX*. September 14, 2018

Publications, Patents, Presentations, Awards, and Commercialization

- **Presentations (cont)**

- Klaus Lackner, "Reflections on IPCC Perspectives and CO₂ Capture from the Air" 2018 CCUS STUDENT WEEK, Golden CO. October 15, 2018
- Everett Eustance, "Membrane Carbonation for Improved Carbon Capture Efficiency in Algal Cultivation", Algae Biomass Summit. The Woodlands, TX. October 15, 2018

Responses to Previous Reviewers' Comments

- This project is attempting two innovative developments. One is for capturing atmospheric CO₂ using a “filter unit,” and the other is a new method for delivering CO₂ to PBRs using membranes. I would rather these were separate projects so the focus would be strengthened. The approach for releasing CO₂ from a carbonate mixture and delivering gaseous CO₂ to the media using membranes has several processing steps, equipment, and requires energy input. It is not clear to me the cost-benefit of this approach, as we could much more directly feed the carbonate solution to the media. The cost of the filter unit is prohibitive. I understand that the project is exploring cost-reduction ideas for the filter unit. If the team is not able to significantly reduce the cost of the filter unit, maybe they will be able to recommend where additional research is needed to potentially make this approach feasible in the future.
- In principal, the carbonate/bicarbonate storage solution could be fed directly to the PBR in lieu of extracting and compressing the CO₂ gas for delivery via MC. However, this approach presents several problems: (1) photosynthesis normally drives up the pH by consuming inorganic carbon and reducing nitrate, so delivering the acidic form avoids the need for adding acid to regulate the pH; (2) delivering bicarbonate requires a balancing cation, usually Na⁺, which increases the salt concentration; and (3) the storage tank contains a mixture of carbonate and bicarbonate at high pH such that it can more efficiently take up CO₂ delivered from the capture system, whereas PBRs are typically operated at a pH near 8.5. Thus, adding bicarbonate from storage will tend to increase the pH of the bioreactor, requiring compensating forms of acidity. Put another way, extracting accumulating alkalinity from the algae pond would be expensive. The storage system, as designed, retains the alkalinity in the storage tank and only transfers CO₂ to the microalgae.
- Another more direct approach might be to deliver captured CO₂ directly to the PBR using a fabric contactor and bypassing the storage subsystem. As part of the final report, the team will suggest future lines of research to address commercial feasibility.
- These are responses to the 2017 peer review.