Ammonium Looping with Membrane Absorber and Distributed Stripper for Enhanced Algae Growth (DE-FE0031921)

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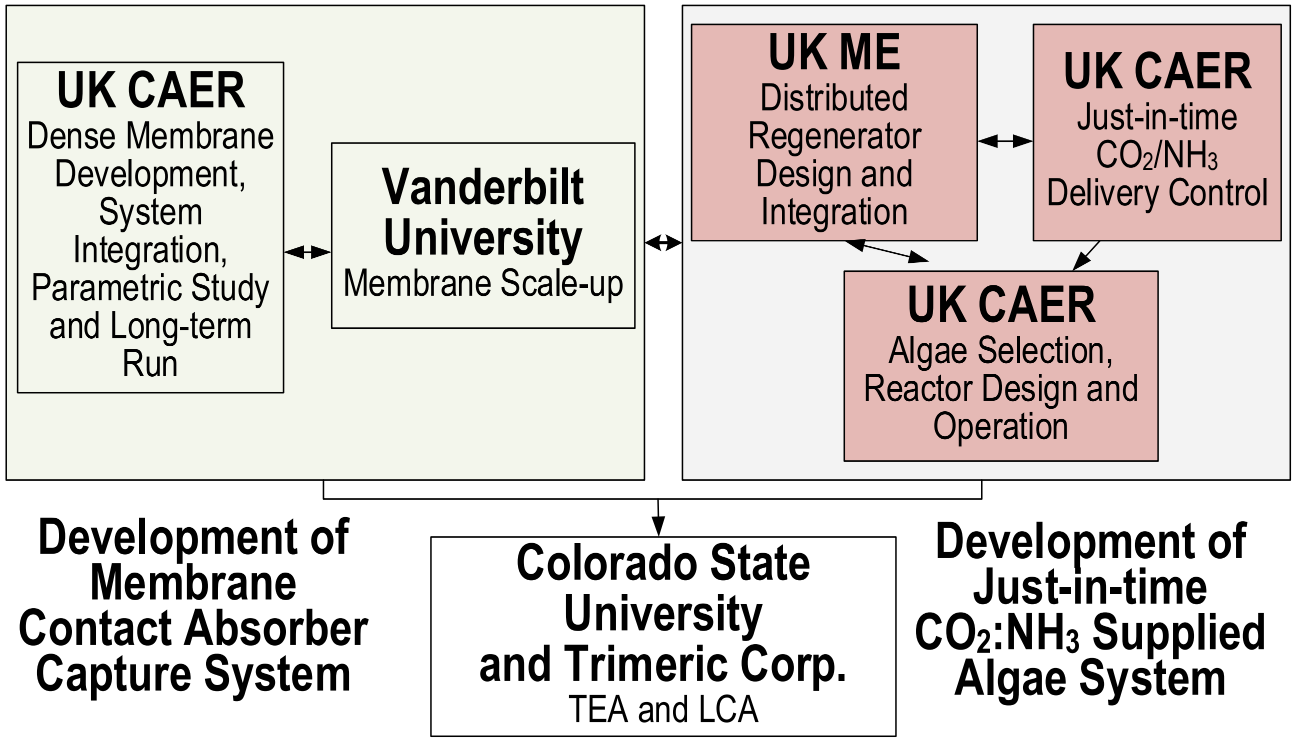
Carbon Management and Natural Gas & Oil Research Project Review Meeting
Virtual Meetings August 2 through August 31, 2021

Project Team and Funding

Project Manager
DOE/NETL
Isaac Aurelio



	DOE-NETL	Cost Share	Total
Total ($)	$2,999,564	$751,764	$3,751,328
Cost Share (%)	80%	20%	100%

Project Dates	BP1	BP2
Start	10/1/2020	4/1/2022
End	3/31/2022	9/30/2023

Project Objectives

Unique, integrated CO_2 capture and utilization technology that:

- **Reduces the cost of CO_2 capture**
- **Boots algae production**

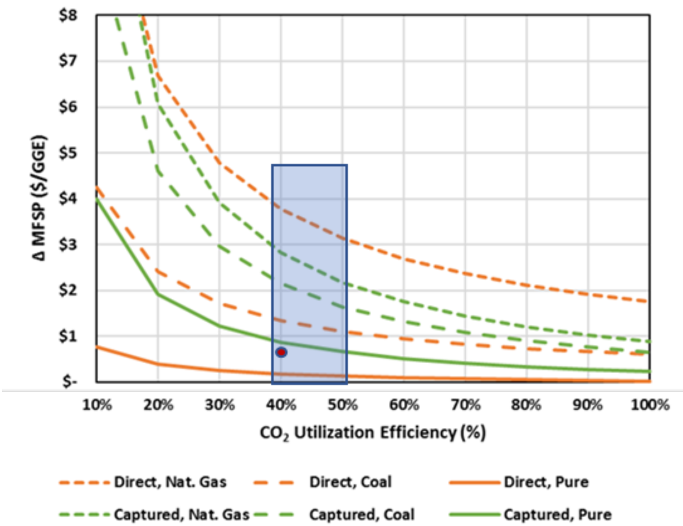
Developing a transformative method for CO_2 capture and biofixation for large-scale application through:

1) Use of 2 M ammonium solution with chemical additives as both capture reagent and algae nutrient
2) Membrane absorber with minimal NH_3 emissions coupled with distributed, solar-energy powered strippers located near to bioreactors
3) Integration of solvent regeneration and just-in-time CO_2 and NH_3 delivery to algae for productivity enhancement

Project Performance Dates

Task	Milestone Title & Description	Completion Date
1.0	Project Kickoff Meeting Held	12/7//2020
1.2	TMP Complete	1/17/2021
2.2	Membrane Absorber Integrated with Existing CCS	
5.0	Algae Production Evaluated	
6.1	Design Basis Report Completed	
6.2	Process Design Package Completed	
9.0	Integrated Process Installed	
10.0	Parametric Campaign Complete	
11.0	Long-term Campaign Complete	
12.4	TEA Complete	
13.0	TGA Complete	
14.0	LCA Complete	

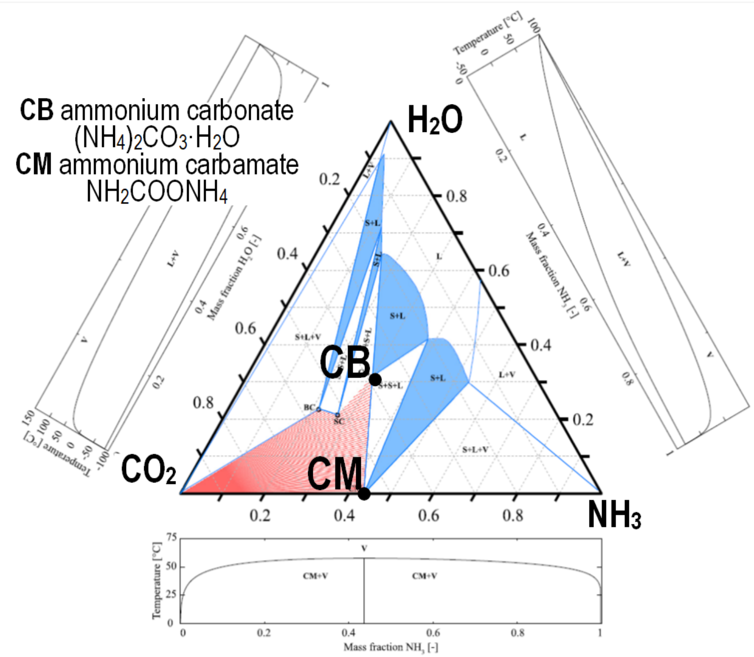
Background –
Favorable Economics and In-situ Antifouling



A 50% reduction of reselling price for CO_2 from coal-fired power plants is achievable, as indicated by the red dot (< $1/GGE).

Downflow Flue Gas Configuration

- Flue gas condensate continually washes membrane surface
- In-situ anti-fouling
- NH_3 slip recapture
- Flue gas condensate utilized as makeup water



Center for Applied Energy Research

Background – Enhanced Algae Growth

NH^{4+} consumption - excess CO_2 present (NH_4^+ limiting):

$$(NH_4)_2CO_3 \rightarrow H_2CO_3$$
$$NH_4HCO_3 \rightarrow H_2CO_3$$

CO_2 consumption - excess NH_4^+ present (CO_2 limiting):

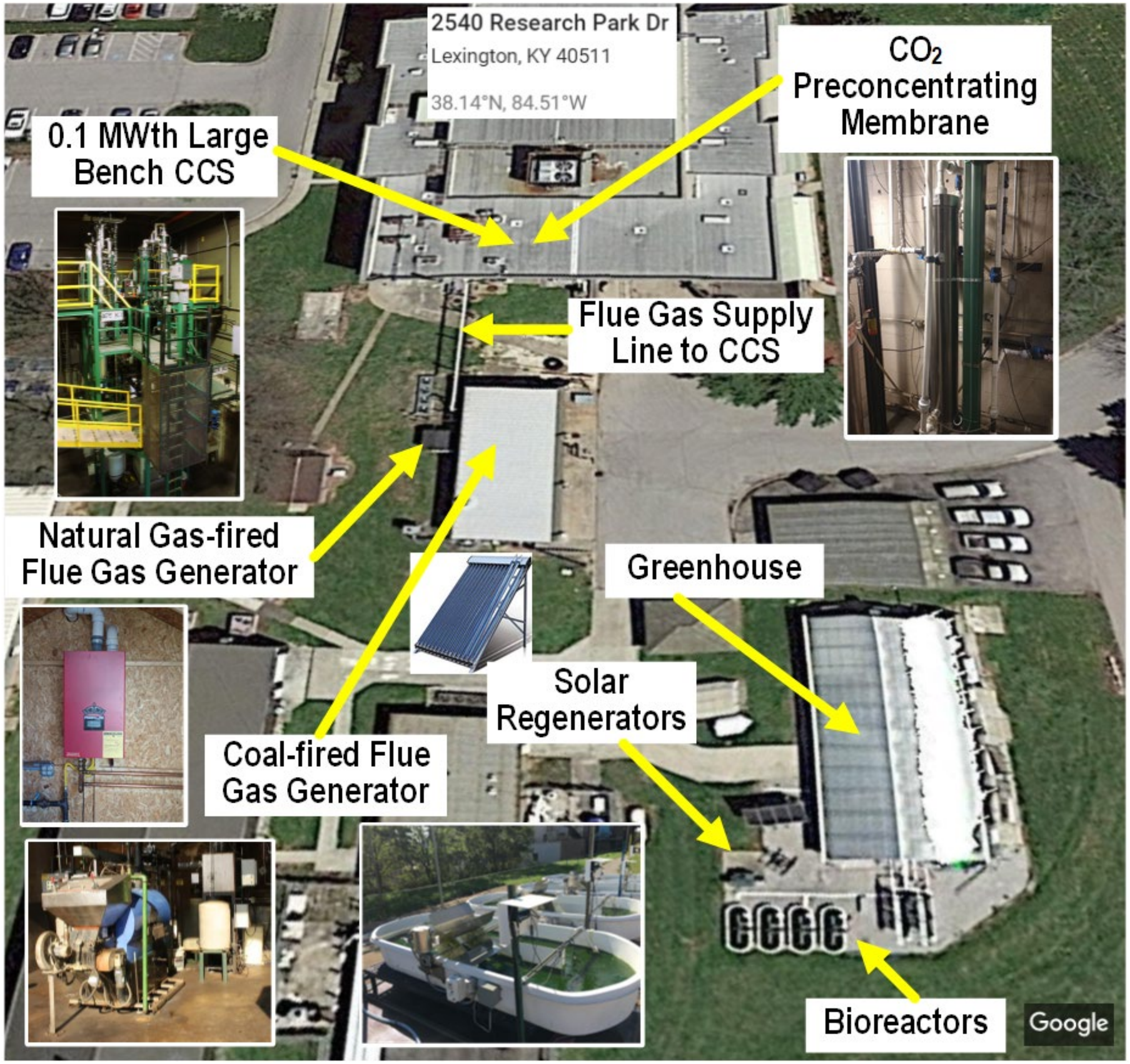
$$(NH_4)_2CO_3 + H_2O \rightarrow 2NH_4OH$$
$$NH_4HCO_3 \rightarrow NH_4OH$$

Left: 100,000 L cyclic flow PBR, Zhengzhou, China (2018). Center and Right: 1200 L cyclic flow PBR and 1100 L ORPs installed at Duke Energy's East Bend Station (2018).

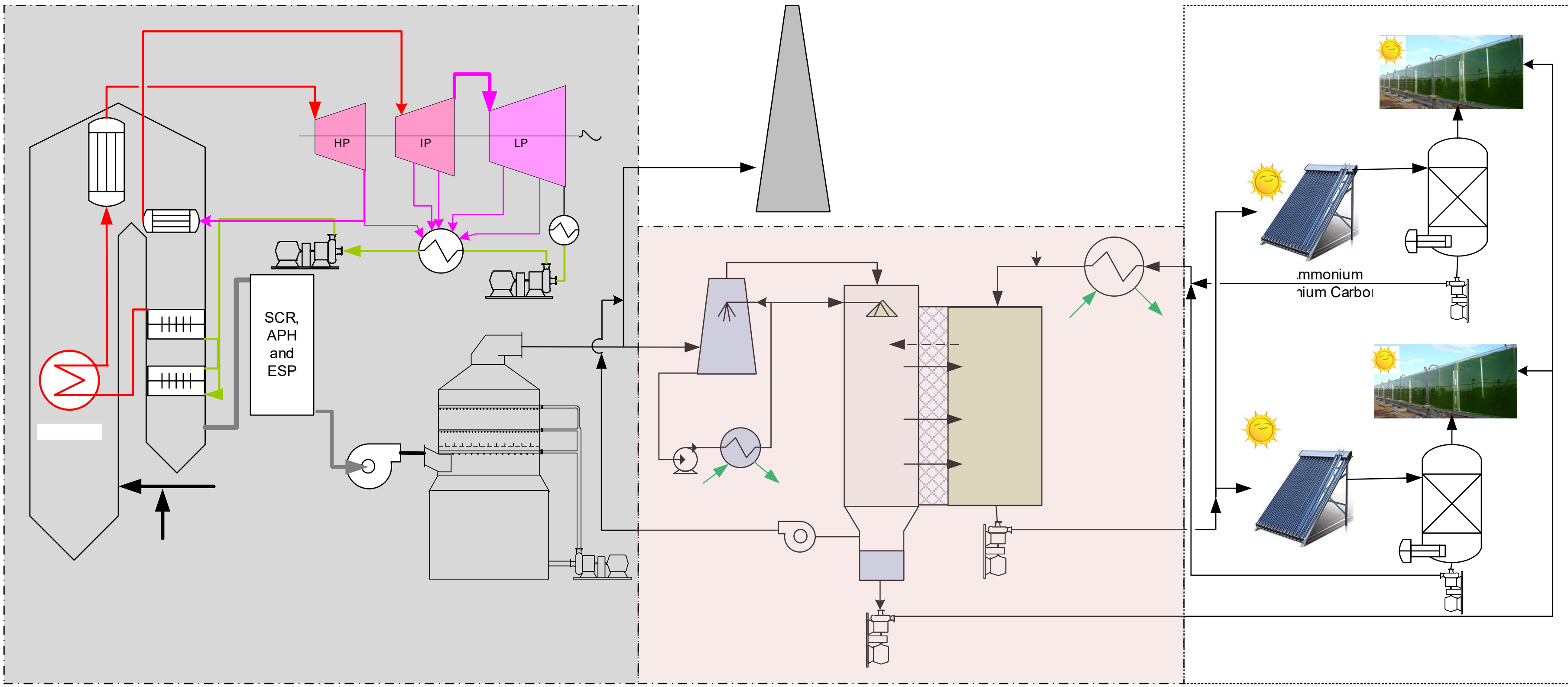
Just-in-time C:N Delivery at Appropriate Ratio

- Minimal stress on algae with continuous CO_2/NH_3 feed
- Direct connection between stripper and bioreactor
- Amount of CO_2 and NH_3 in product stream controlled with stripper pressure and temperature
- Thermally compressed CO_2/NH_3 product stream facilitated sparging into bioreactors for high utilization efficiency
- Product stream can continue to be generated for short periods even if flue gas source is disrupted

Background – UK CAER CO_2 Capture and Utilization Facilities



Technology Under Development



Approach and Task Summary

Reduce CO_2 Capture Costs and Boost Algae Production

- **Design, Fabricate and Research a Membrane CO_2 Absorber**
  - CO_2 Capture Efficiency
  - Continuous Operation
  - Ammonia Slip
- **Evaluate Algae Production**
  - CO_2:NH_3 ratio
  - pH
  - Productivity
- **Design, Fabricate and Research Integrated Process**
  - Parametric Campaign
  - Long Term Campaign
  - TEA
  - TGA
  - LCA
- **Develop**
  - TMP

BP1

- Task 2 – Membrane Absorber
- Task 3 – Absorber Performance Evaluation
- Task 4 – Advanced Membrane Development
- Task 5 – Algae Production Evaluation

BP2

- Task 6 – Integrated Process Design
- Task 7 – Integrated Process Test Plan
- Task 8 – Process Equipment Procurement
- Task 9 – Assembly
- Task 10 – Parametric Campaign
- Task 11 – Long-term Campaign
- Tasks 12, 13 & 14 – TEA, TGA and LCA

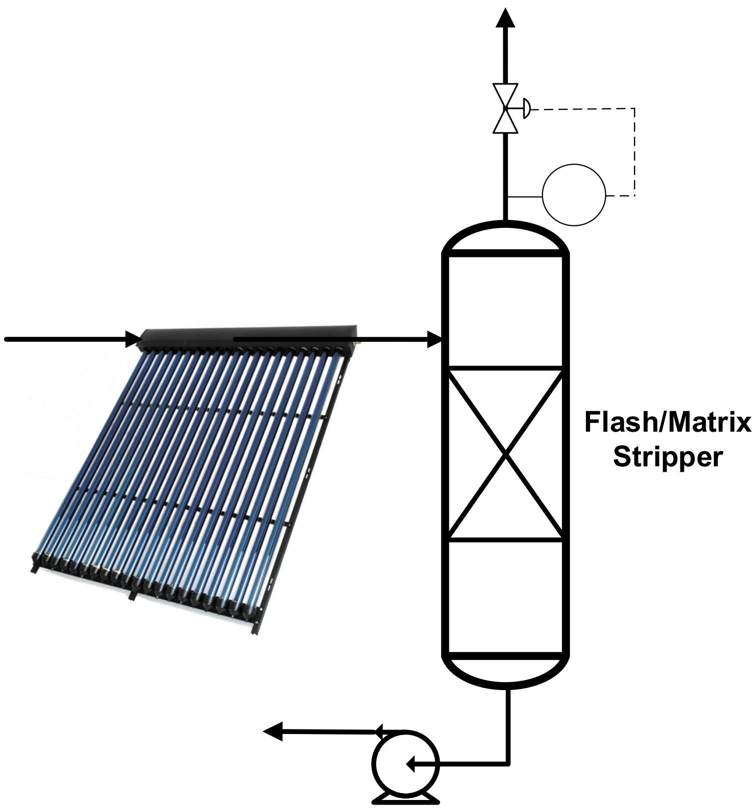
Technical Approach

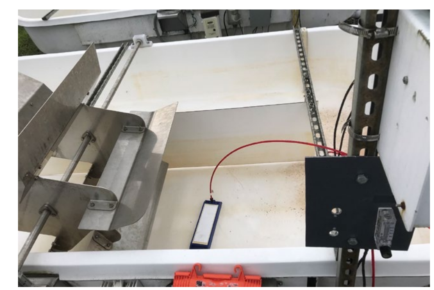
Nutrient Feed to Algae Directly from Solvent Regeneration Step

Thermal Compression for Nutrient Delivery

Constant and Controllable C:N for Constant pH

Steady, Sparging Feed to Algae

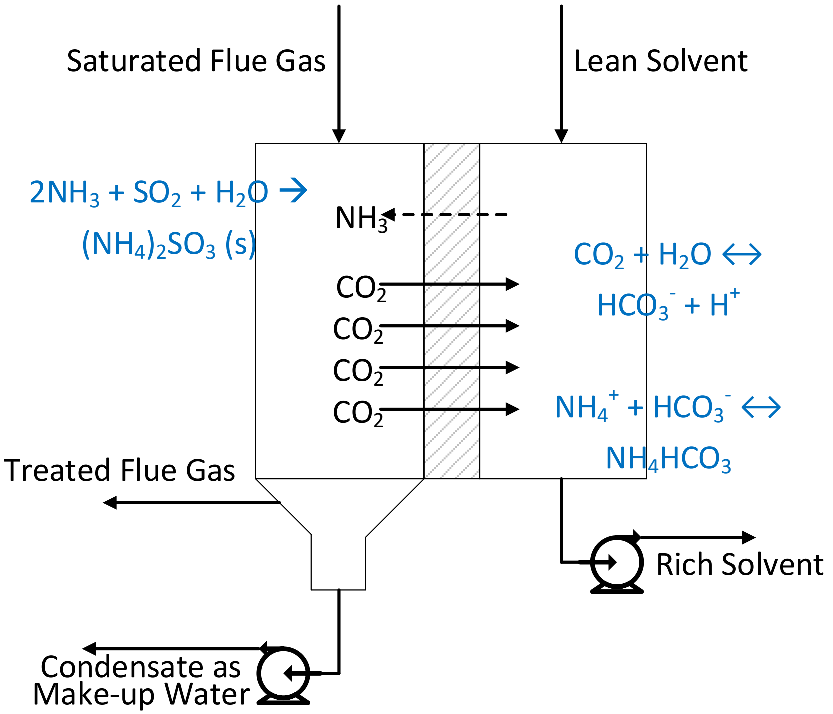




Technical Approach

Minimizing Ammonia Slip

Indirect Contact and Acid Washing using SO_2 in Flue Gas



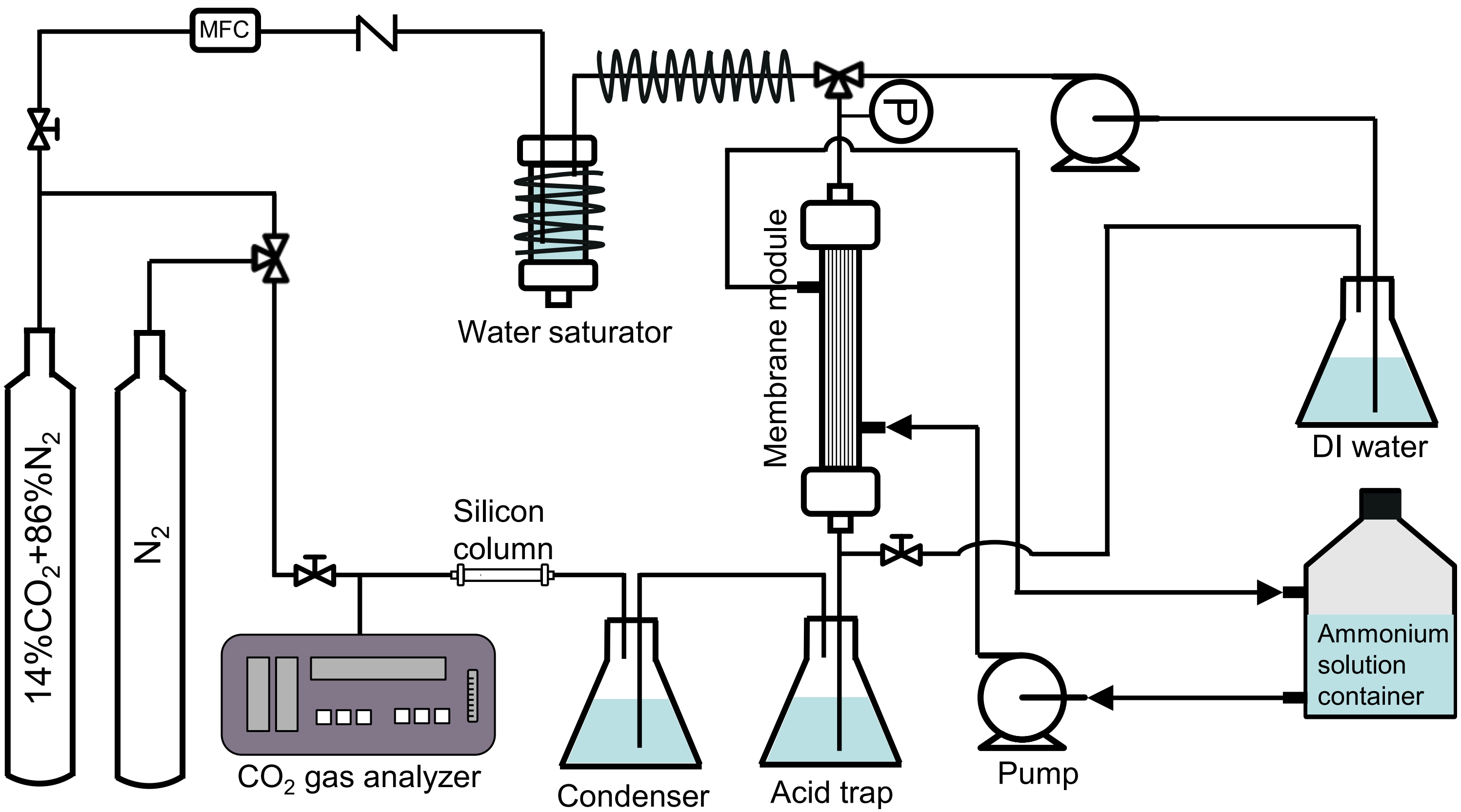
Solvent Formulation to Reduce the Gas Phase Partial Pressure

$$Zn^{2+} + 4NH_3 \leftrightarrow [Zn(NH_3)_4]^{2+}$$
$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$$
$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$
$$[Zn(NH_3)_4]^{2+} + HCO_3^- \leftrightarrow [Zn(NH_2COO)_2]_2 + 2NH_3 + 2H_2O$$
$$2NH_3 + CO_2 + H_2O \leftrightarrow (NH_4)_2CO_3$$

Project Success Criteria

Success Criterion	Percent Complete	Accomplishments
Demonstration of ppm levels of NH_3 slip	20%	The ammonia slip can be reduced by addition of chelating organic additives.
Demonstration that 100-hour stable operation via ammonium salts formed on gas side of membrane being washable by flue gas condensate	100%	400-hour stable operation has been finished on the lab-scale membrane testing system.
Demonstration that algae production is increased by 50% by continuous feed of CO_2:NH_3	25%	Best algae growth rate in initial experiments is ~25% higher than rate obtained using conventional N sources (e.g., $NaNO_3$).
Demonstration that capital and operating costs associated with CO_2 capture and delivery are reduced by 50%	0%	Scheduled for BP2.

Progress and Current Status – Lab-scale Testing Unit



Schematic Diagram of Lab-scale Testing Unit

Progress and Current Status – Ammonia Slip Rate Test

Ammonia slip rate test on CMS membrane

Established Ammonium Looping Test and Sampling Plan and sample testing SOP, repeatability verified by testing 3 batches of 1M NH_4OH+0.5M $(NH_4)_2CO_3$ solutions

Batch	Solvent	Testing time (hr)	NH_3 slip rate (ppm)
1	1M NH_4OH+0.5M $(NH_4)_2CO_3$	100	6345
2	1M NH_4OH+0.5M $(NH_4)_2CO_3$	100	5409
3	1M NH_4OH+0.5M $(NH_4)_2CO_3$	100	5795

Gas phase: 14% CO_2; Gas flow rate: 100 mL/min; Liquid flow rate: 80 mL/min; Pressure drop: 3-4 psi

Investigating the effect of organic additives on NH_3 slip rate

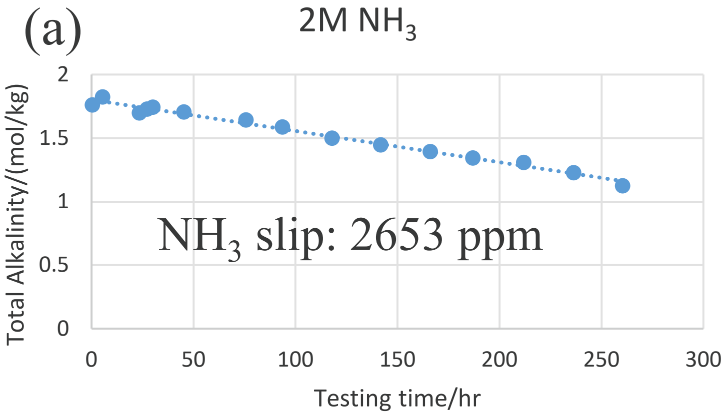
Try to reduce the NH_3 slip rate with addition of organic chelating agents like tetraethylene glycol dimethyl ether (TGDE) and 2-amino-2-methyl-1-propanol (AMP) in the feed solution

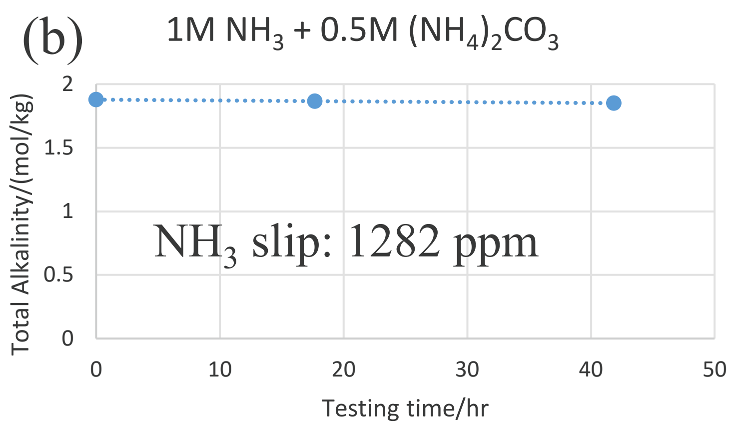
Batch	Solvent	Testing time (hr)	NH_3 slip rate (ppm)
4	1M NH_4OH+0.5M $(NH_4)_2CO_3$+1 wt% TGDE	50	5953
5	1M NH_4OH+0.5M $(NH_4)_2CO_3$+20 wt% TGDE	50	5049
6	1M NH_4OH+0.5M $(NH_4)_2CO_3$+10 wt% AMP	50	4826

Gas phase: 14% CO_2; Gas flow rate: 100 mL/min; Liquid flow rate: 80 mL/min; Pressure drop: 4 psi

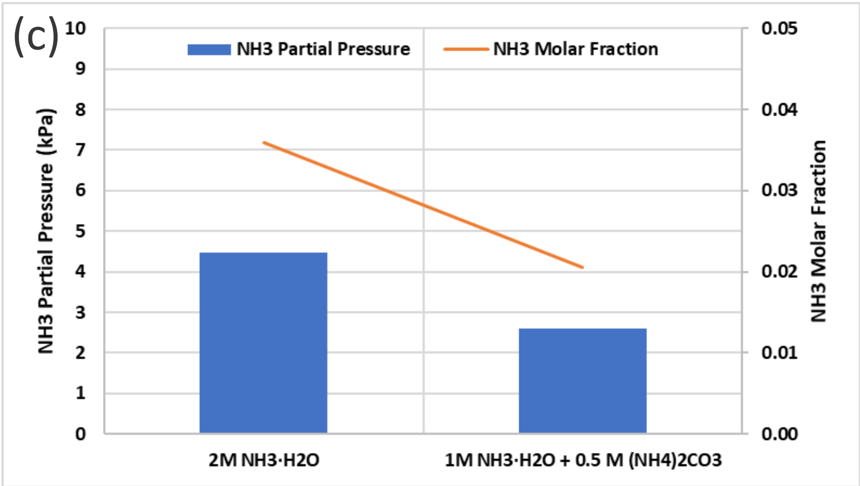
400-hour stable operation via ammonium salts formed on gas side of membrane being washable by flue gas condensate

Progress and Current Status: Composing of Ammonium Solution



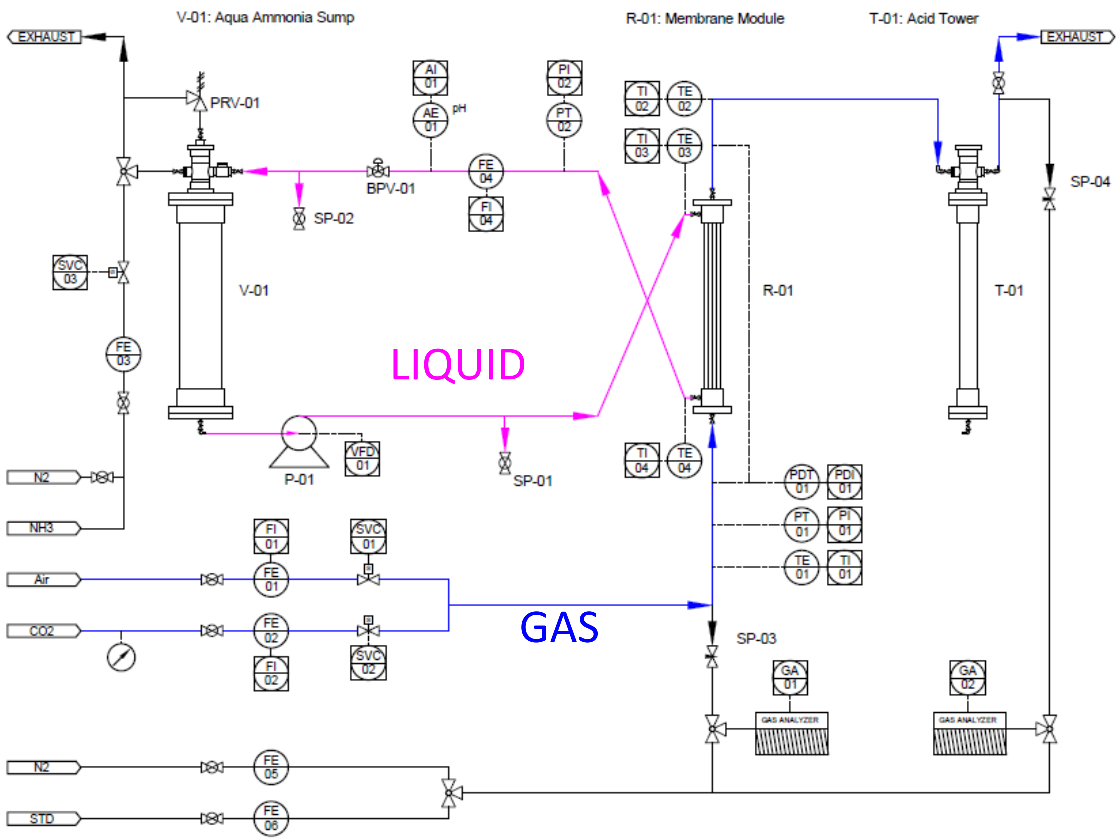


Gas phase: compressed air; Gas flow rate: 50 mL/min
Liquid phase: ammonium solution; Liquid flow rate: 50 mL/min



By replacing 50% of ammonium hydroxide with ammonium carbonate in the solvent, the NH_3 slip dropped from 2653 ppm to 1282 ppm due to the decline of NH_3 partial pressure.

Progress and Current Status: Bench Unit P&ID



Process Flow Diagram for Bench-Scale Absorption Unit

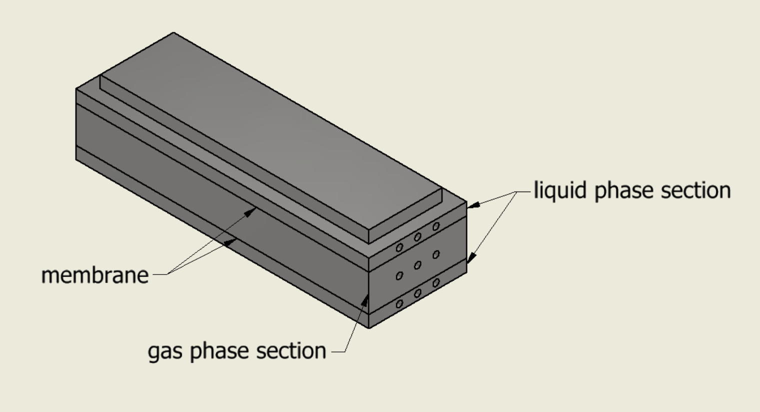
Purpose:

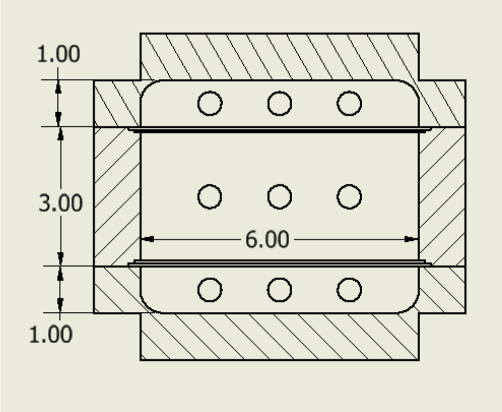
1. NH_3 slip rate at bench scale
2. Monitor and resolve possible membrane blockage

Analysis method:

- Off-line analysis of ammonia concentration
- On-line monitor of pH changes
- On-line analysis of gas concentration

Progress and Current Status – Design of Flat Sheet Membrane Absorber





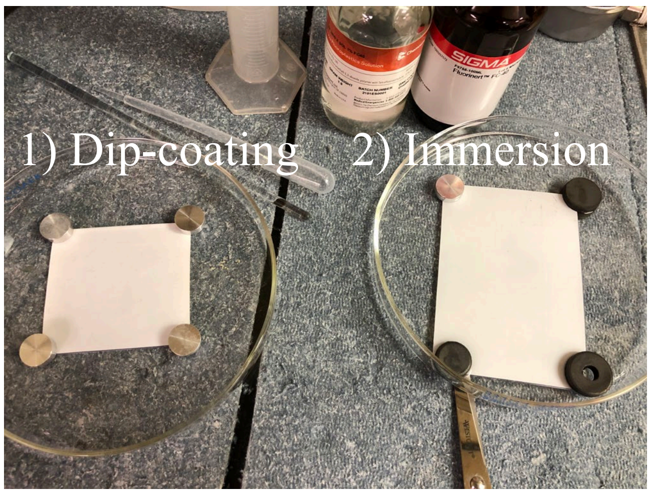
Bench Scale Membrane CO_2 Absorber

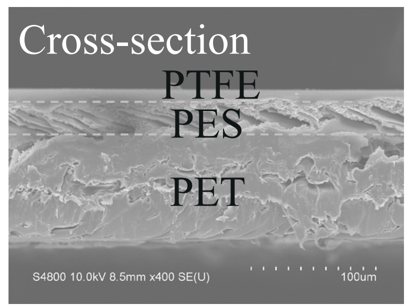
Machined Components of the Membrane CO_2 Absorber

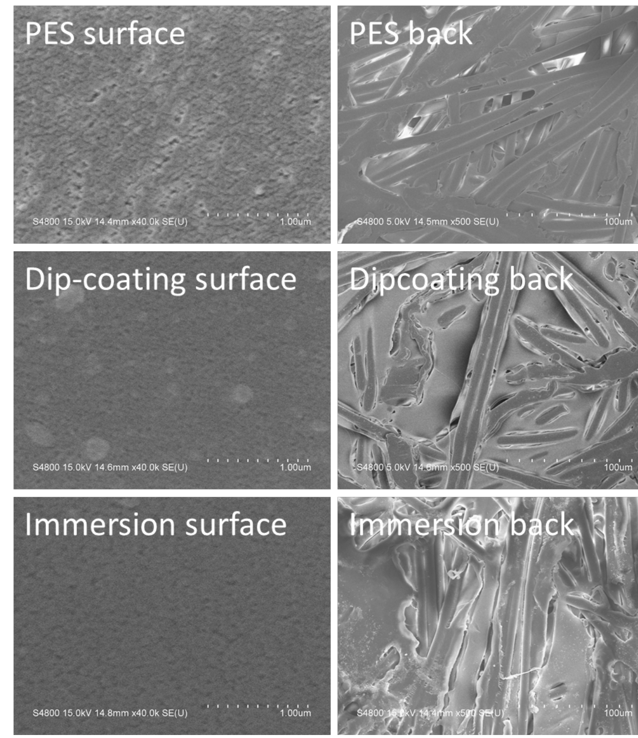
- Designed symmetric membrane CO_2 absorber for bench-scale testing to reduce gas-side pressure drop.
- Membrane absorber 6 inches wide x 24 inches deep, designed for 15 cfm and 2 second residence time.
- Liquid phase section part is shown partially machined.

Progress and Current Status: Development of Flat Sheet Membrane

Substrate: Polyethersulfone (PES) membrane supported by polyester (PET) nonwoven fabric
Modification material: 1 wt% Teflon AF2400 in FC-40
Solvent: Fluorinert™ FC-40





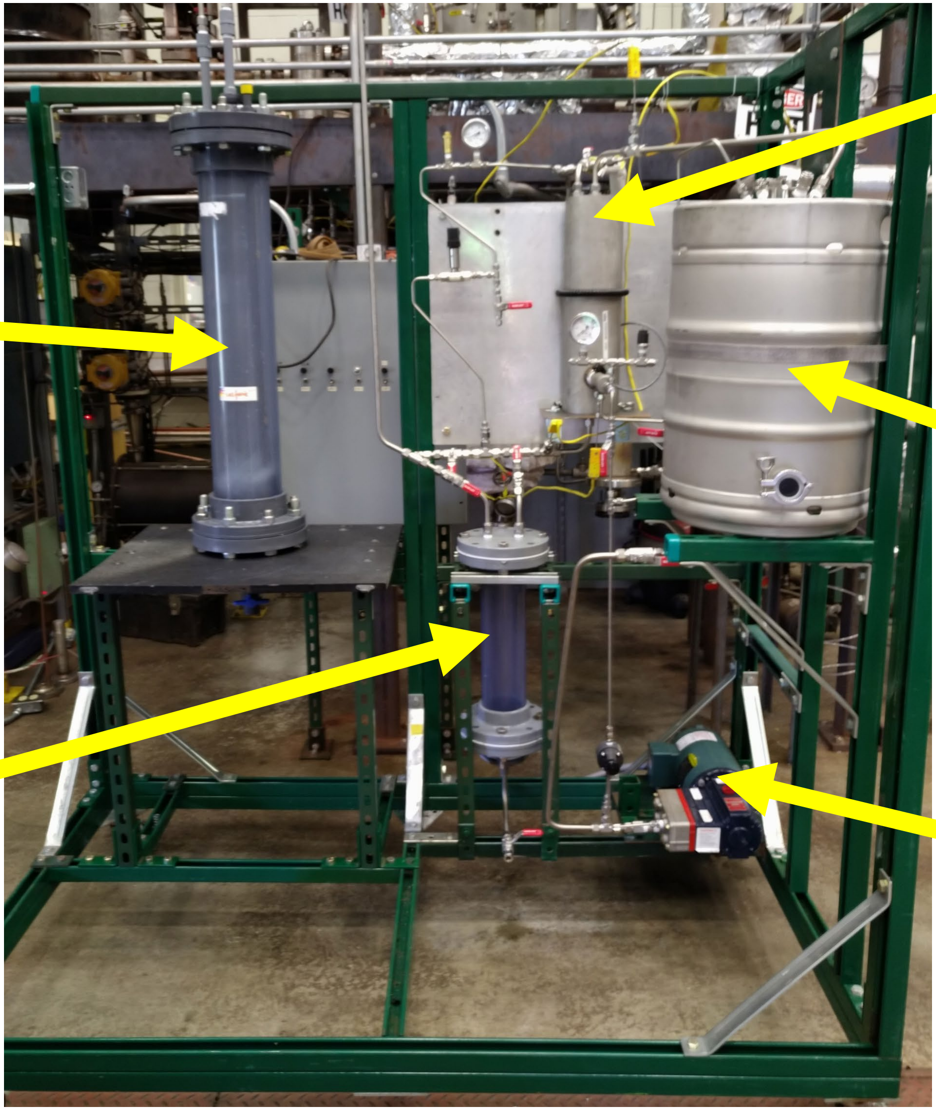


Teflon Hydrophobic Layer Obtained on Both Sides of PES Substrate

Contact Angle:

Position	1	2	3	4	5	Average
PES surface	74	88				**81**
PES back	81					**81**
Dip-coating surface	113	122	119	122	115	**118**
Dip-coating back	134	127				**131**
Immersion surface	112	125	129	119	124	**122**
Immersion back	143	147				**145**

Progress and Current Status – Bench Membrane Absorber



Hollow Fiber Membrane

Acid Trap

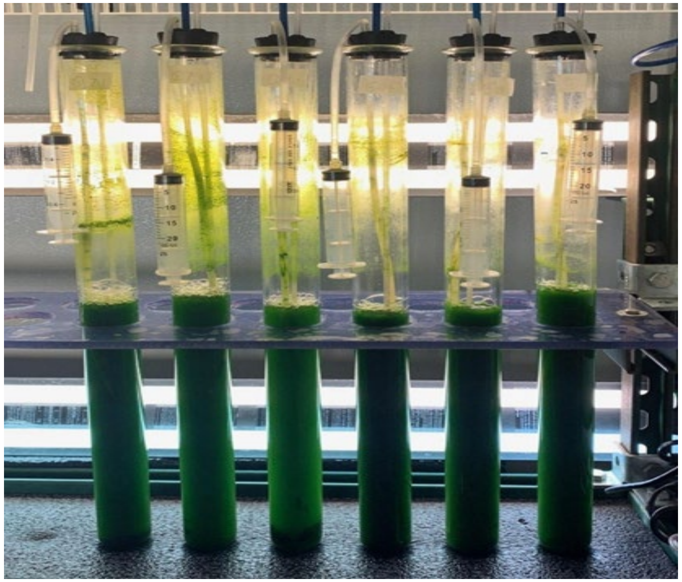
Solvent Tank

Condensate Trap

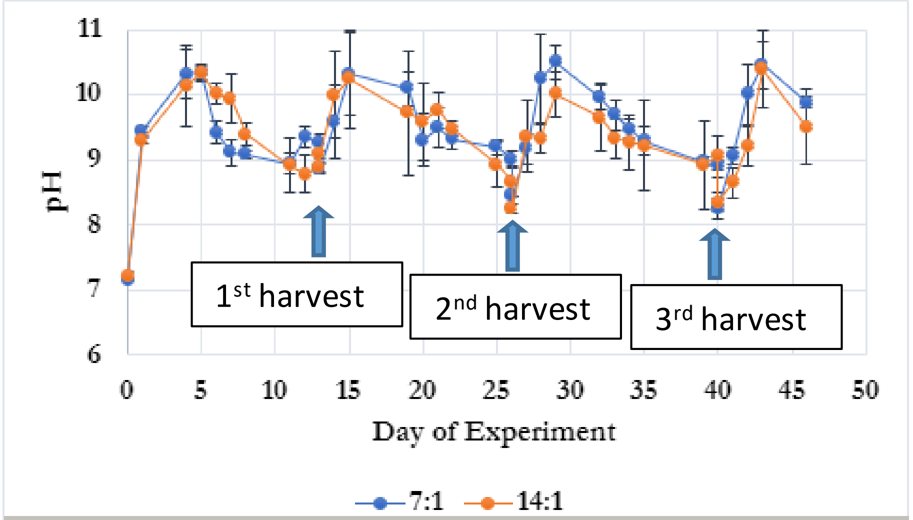
Solvent Circulation Pump

Progress and Current Status – Algae Production Evaluation

- Objective: to examine the effect of a range of CO_2:NH_3 mole ratios simulating the gas stream from the solar stripper on *Scenedesmus acutus* (UTEX B72) culture health and productivity
- Initial experiments performed in 800 mL bioreactors with constant gas sparging and four CO_2:NH_3 mole ratios, i.e., 7:1, 10:1, 14:1 and 18:1
- Initial pH increase attributed to superior NH_3 solubility (relative to CO_2)
- Irrespective of CO_2:NH_3 ratio, pH tends towards ~9 before each harvest



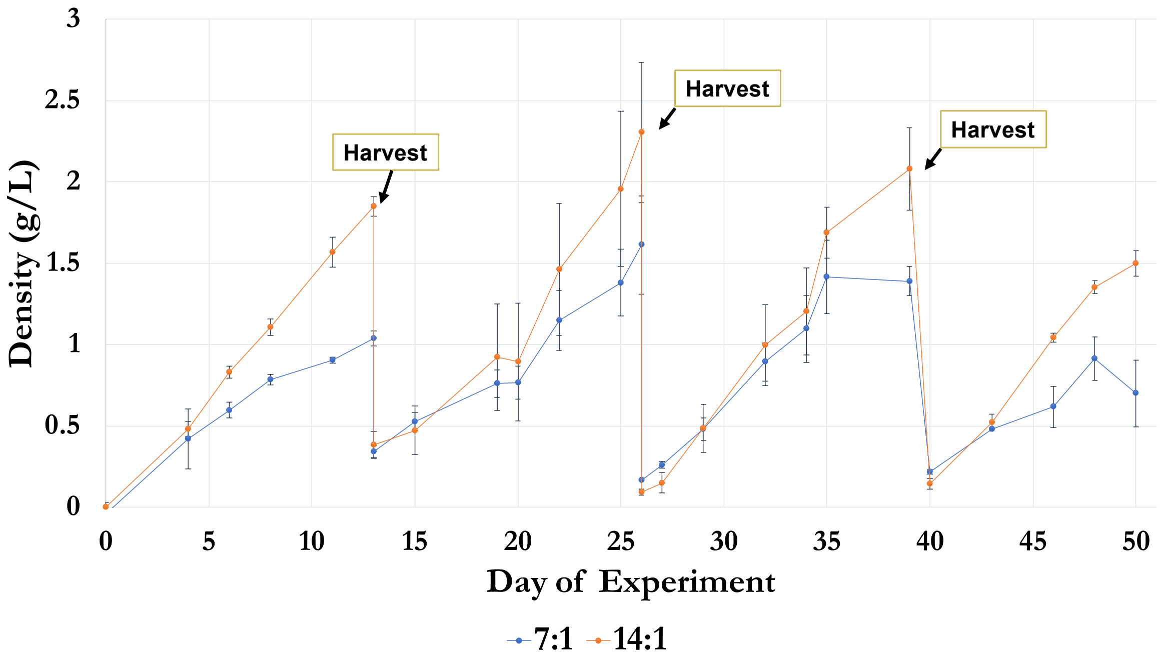
Appearance of cultures on 39th day of experiment (6/21/21)
7 CO_2:1 NH_3 (left triplicate) and 14 CO_2:1 NH_3 (right triplicate)



pH values during consecutive culturing cycles

Progress and Current Status: Algae Production Evaluation

- Growth rate obtained with 14:1 CO_2:NH_3 ratio is same as that previously obtained using ammonium carbonate and ammonium bicarbonate as N-source, typical values being ~0.16 g L^{-1} day^{-1}
- Fastest growth rate to date obtained using 10:1 CO_2:NH_3 ratio (~0.21 g L^{-1} day^{-1}; experiment still on-going)



Productivity (g L^{-1} day^{-1}):
7:1 : 0.114 ± 0.075
10:1 : 0.216 ± 0.119
14:1 : 0.164 ± 0.118
18:1 : 0.067 ± 0.065

Culturing experiments with gaseous CO_2 and NH_3.
Culture density vs. time. Error bars represent the st. dev. (n=3).

Plans for Future Testing

- Implement gas phase sampling and testing method
- Conduct membrane performance parametric campaign on bench unit
- Finish integrated process design
- Increase total CO_2 and NH_3 flow at fixed CO_2 : NH_3 ratio (10 : 1) to increase algae growth rate
- Outdoor algae culturing in 1100 L ponds

Summary

Task Name	Percent Complete	Accomplishments
1.0 Project Management and Planning	N/A	• Submitted TMP. • Submitted foreign national request and under review. • Quarterly planning meeting according to the PMP. • Conducted weekly project meetings with UK CAER team, discussing technical problems. • Monthly briefing with NETL PM.
2.0 Membrane Absorber	40%	• Established Test and Sampling Plan and standard operating procedure (SOP) for NH_3 slip measurements. • Complied piping and instrumentation diagrams (P&ID) for bench unit and integration unit. • NH_3 slip can be reduced by addition of organic additives.
4.0 Advanced Membrane Development	10%	• Finished design of customized flat-sheet membrane module.
5.0 Algae Production Evaluation	25%	• Consistent growth demonstrated for *Scenedesmus acutus* fed with gaseous CO_2/NH_3. • Growth rate for 10:1 $CO_2:NH_3$ exceeds that previously obtained using $(NH_4)_2CO_3$, nitrate or urea as N-source. • NH_3 utilization efficiency is >80% in culturing experiments using 10:1 and 14:1 $CO_2:NH_3$ (CO_2 utilization efficiency varies but can be as high as ~60% in experiments to date)

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Acknowledgements

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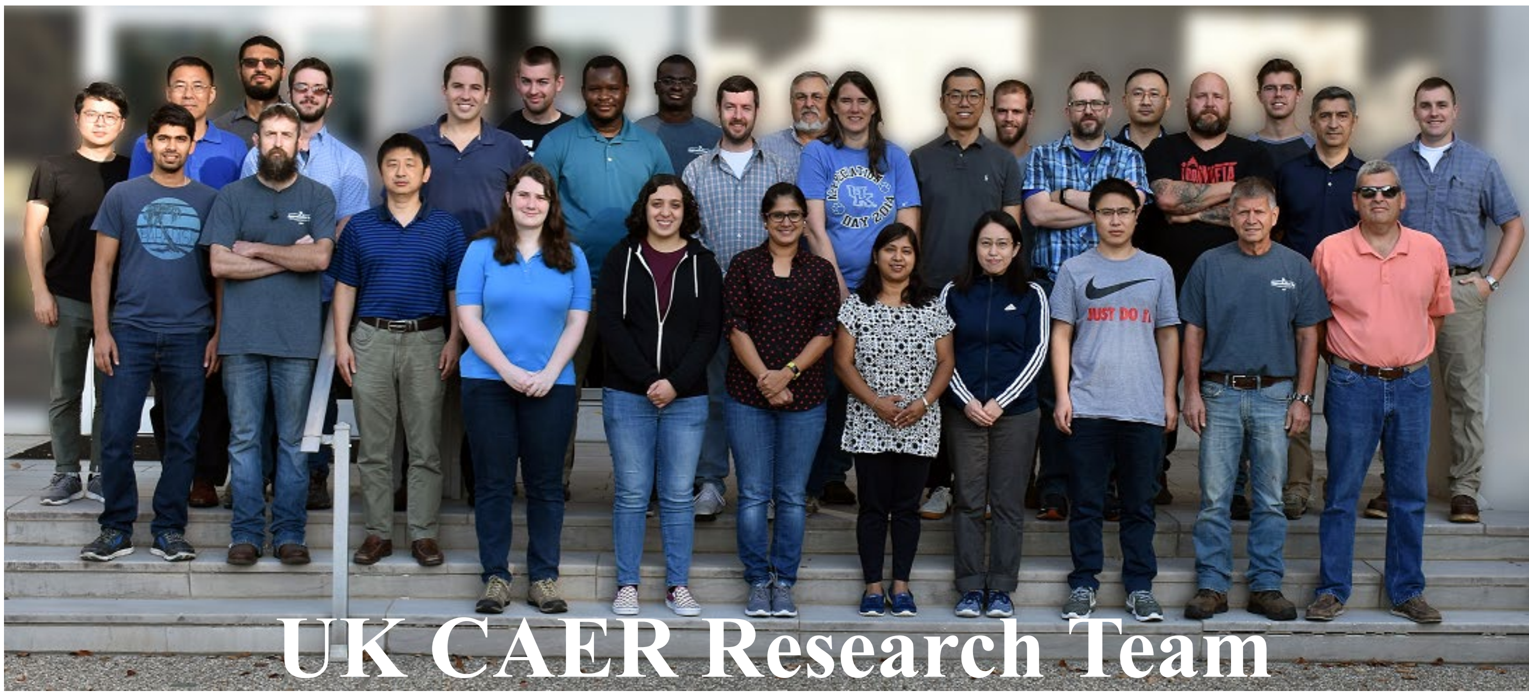
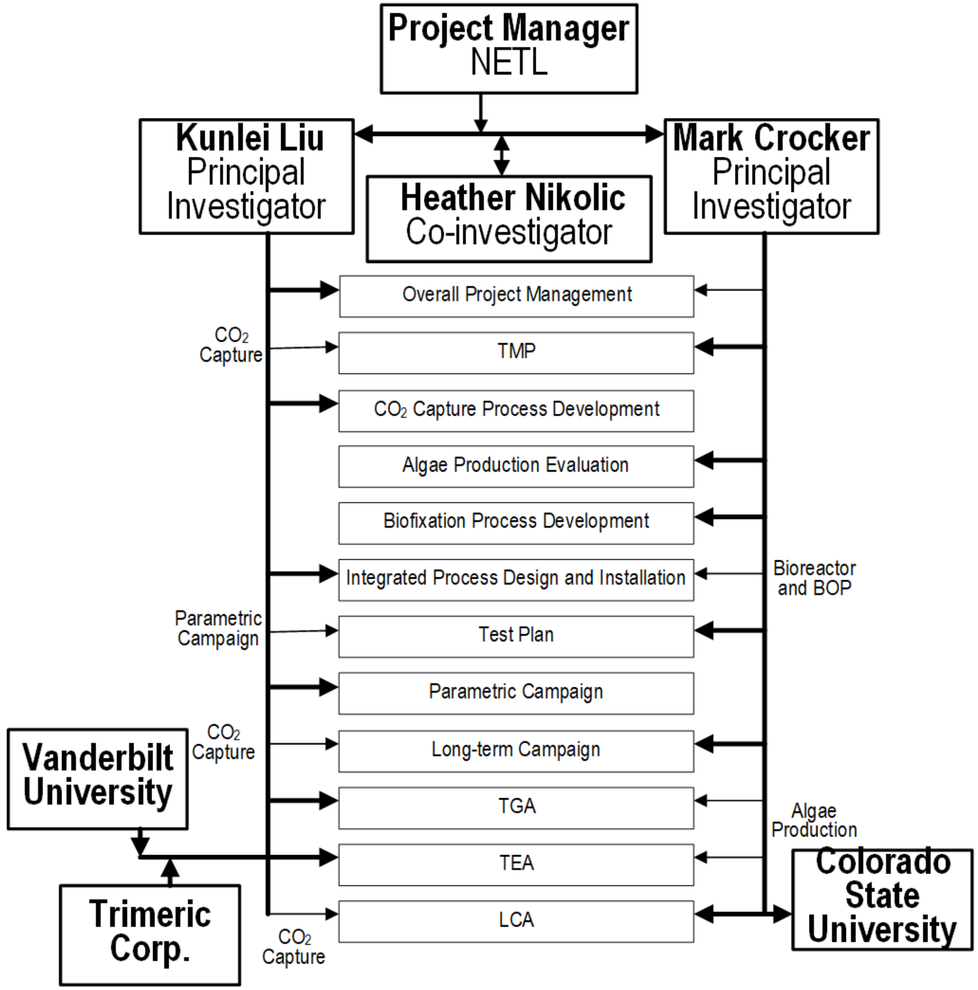


Organization Chart



Gantt Chart

ID	Task Name	Start	Finish	Task Cost
1	1.0 Project Management and Planning	10/1/20	9/30/23	$663,815
2	Budget Period 1	10/1/20	3/31/22	
3	1.1 PMP	10/1/20	10/31/20	
4	1.2 TMP	10/1/20	12/31/20	
5	2.0 Membrane Absorber	10/1/20	3/31/21	$260,644
6	2.1 Absorber Specificaiton and Purchase	10/1/20	12/31/20	
7	2.2 Absorber Installation and Integration	12/30/20	3/31/21	
8	3.0 Absorber Performance Evaluation	4/1/21	6/30/21	$246,582
9	4.0 Advanced Membrane Development	6/1/21	8/31/21	$ 79,418
10	5.0 Algae Production Evaluation	10/1/20	6/30/21	$270,207
11	6.0 Integrated Process Design	5/14/21	2/28/22	$258,228
12	6.1 Design Basis	5/14/21	8/31/21	
13	6.2 Design Package	8/30/21	2/28/22	
14	7.0 Integrated Process Test Plan	1/1/22	3/31/22	$ 60,763
15	Budget Period 2	4/1/22	9/30/23	
16	8.0 Process Equipment Procurement	4/1/22	6/30/22	$ 88,555
17	9.0 Assembly	7/1/22	9/30/22	$ 89,408
18	10.0 Integrated Process Parametric Campaign	9/1/22	10/31/22	$136,439
19	11.0 Long-term Campaign	12/1/22	8/31/23	$763,957
20	12.0 TEA	4/1/22	9/30/23	$540,932
21	12.1 Process Flow and Modeling	4/1/22	9/30/23	
22	12.2 Membrane Modeling	12/1/22	3/31/23	
23	12.3 Equipment Sizing and Cost Estimation	4/1/23	5/31/23	
24	12.4 TEA	6/1/23	9/30/23	
25	13.0 TGA	4/1/23	6/30/23	$ 75,702
26	14.0 LCA	11/1/22	7/31/23	$216,677