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

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https://caer.uky.edu/co2capture/

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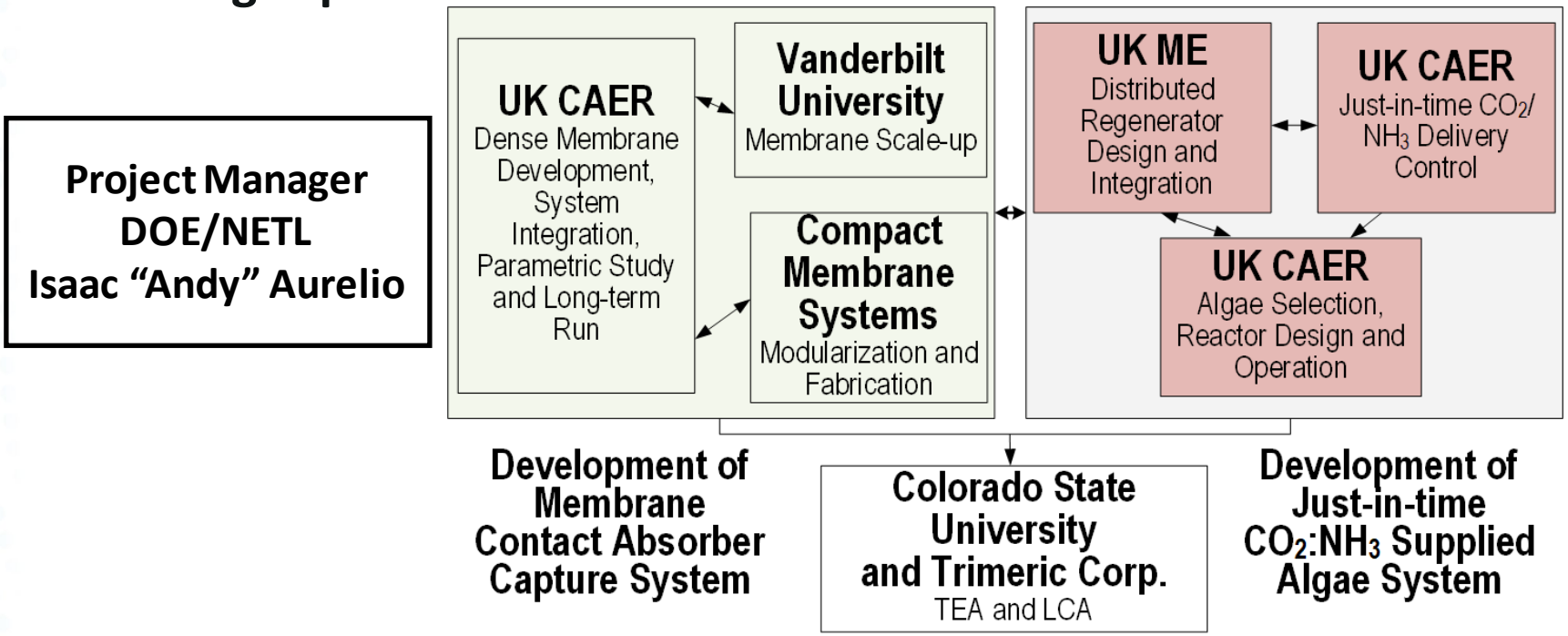
Project Objectives, Team and Funding

Unique, integrated CO_2 capture and utilization technology that:

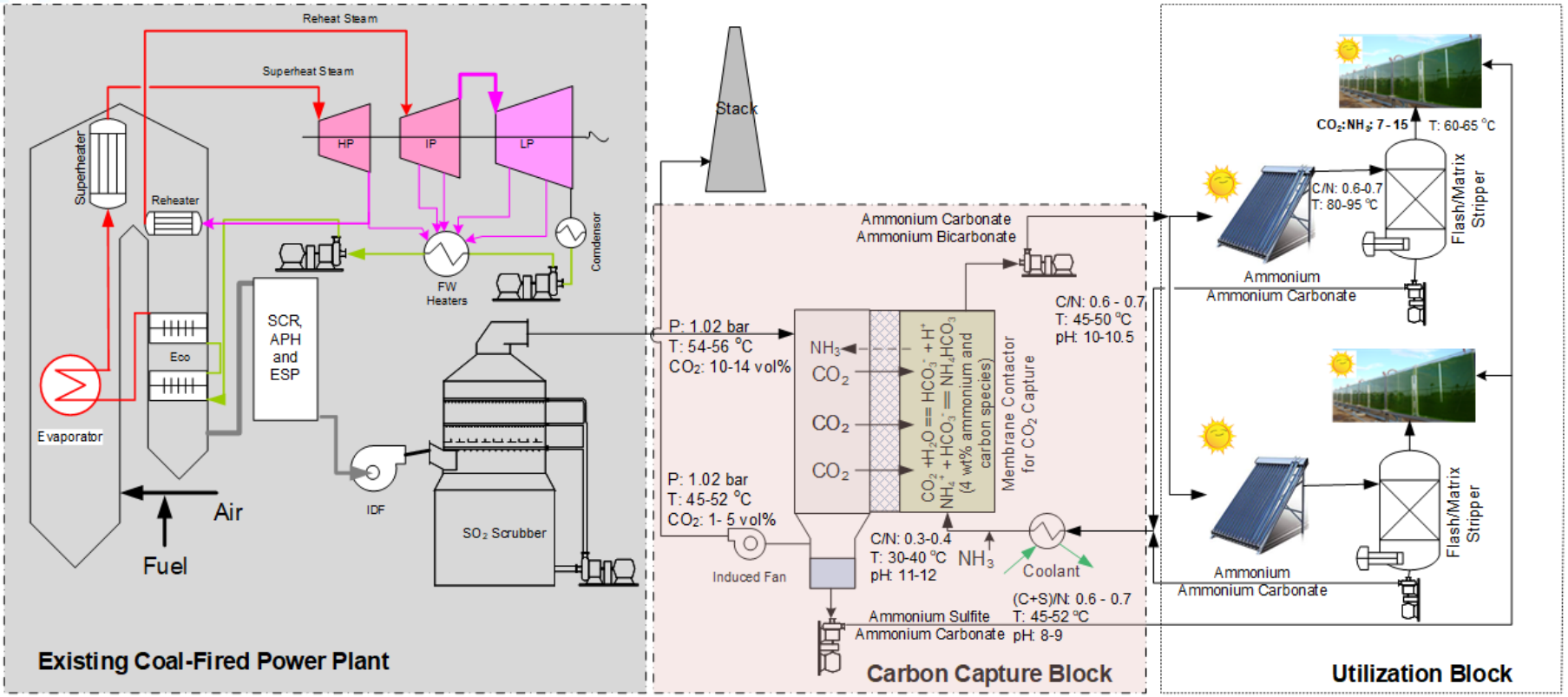
- **Reduces the cost of CO_2 capture**
- **Boosts algae production**



	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	7/1/2022
End:	6/30/2022	9/30/2023

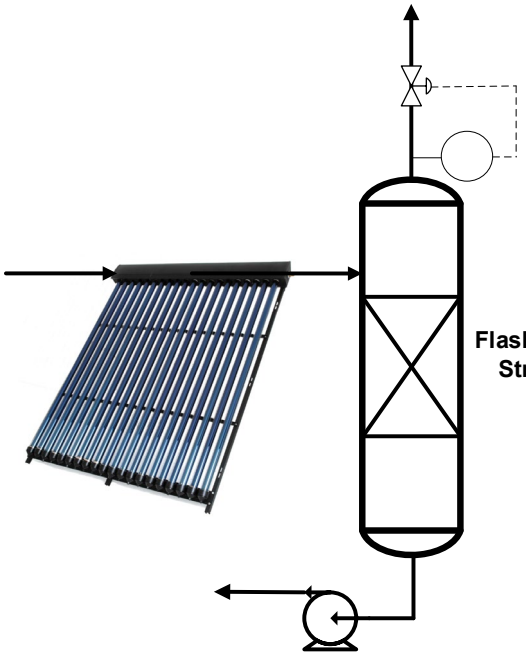
UK CO_2 Capture and Utilization Technology

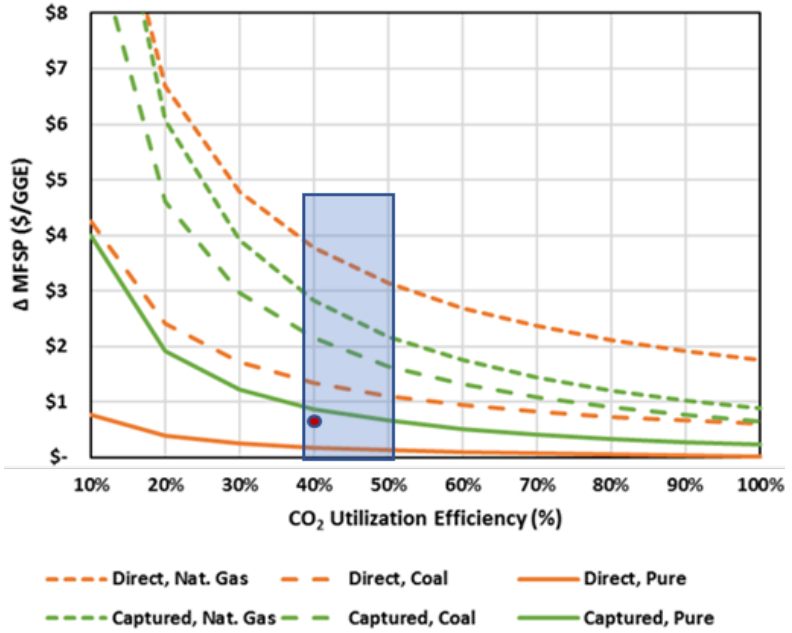


- **Capture:** Membrane CO_2 absorber with ammonium solvent
- **Regenerate:** Distributed, solar-energy powered strippers

Enhanced Algae Growth and Cost Reduction

Nutrient feed to algae directly from Solvent Regeneration Step



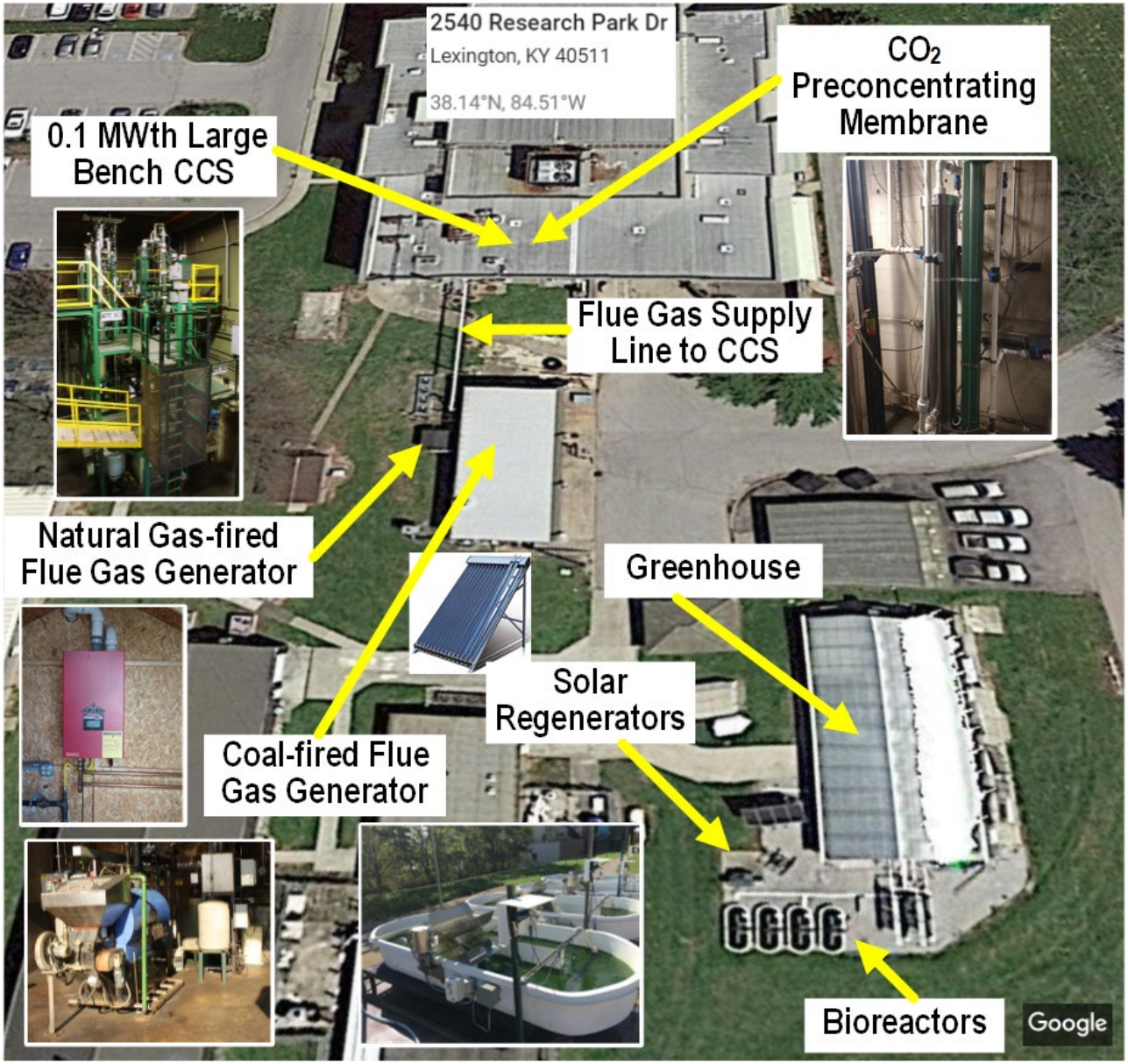


A 50% reduction of reselling price for CO_2 from coal-fired power plants is achievable, as indicated by the red dot (< $1/GGE).

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

- **Minimal chemical stress** on algae with continuous CO_2/NH_3 feed
- **Thermally compressed CO_2/NH_3** product stream facilitates sparging into bioreactors for high CO_2 utilization efficiency

UK CO_2 Capture and Utilization Facilities



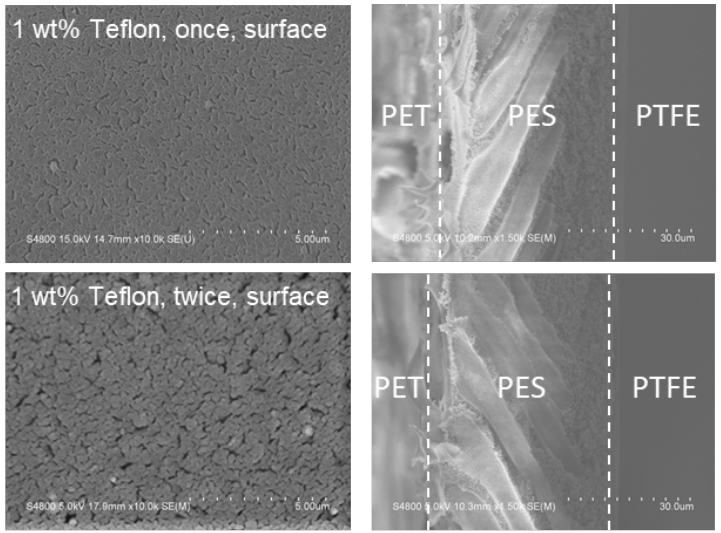
Project Performance and Achievements

Task	Milestone Title & Description	Verification Method	Planned Completion Date	Actual Completion Date
1.0	Project Kickoff Meeting Held	Quarterly Report	10/31/2020	12/07/2020
1.2	TMP Complete	TMP Submitted	12/31/2020	01/17/2021
2.2	Membrane Absorber Integrated with Existing CCS	Quarterly Report	03/31/2022	02/18/2022
5.0	Algae Production Evaluated	Quarterly Report	03/31/2022	01/31/2022
6.1	Design Basis Report Completed	Topical Report	12/19/2021	12/19/2021
6.2	Process Design Package Completed	Topical Report	06/30/2022	06/30/2022

Success Criterion	Percent Complete	Accomplishments
1. Demonstration of ppm levels of NH_3 slip	100%	Lab-scale testing of NH_3 slip on flat sheet membranes achieved below 100 ppm.
2. Demonstration that 100 hour stable operation via ammonium salts formed on gas side of membrane being washable by flue gas condensate	100%	Accomplished 500-hour stable operation on both lab scale and bench scale membrane testing systems.
3. Demonstration that algae production is increased by 50% by continuous feed of CO_2:NH_3	100%	Under lab culturing conditions, algae growth rate using 10:1 CO_2:NH_3 is 0.17 g/L/day, versus 0.13 g/L/day and 0.11 g/L/day, respectively, using the standard N-sources $NaNO_3$ and urea.

Advanced Membrane Development for Low NH_3 Slip

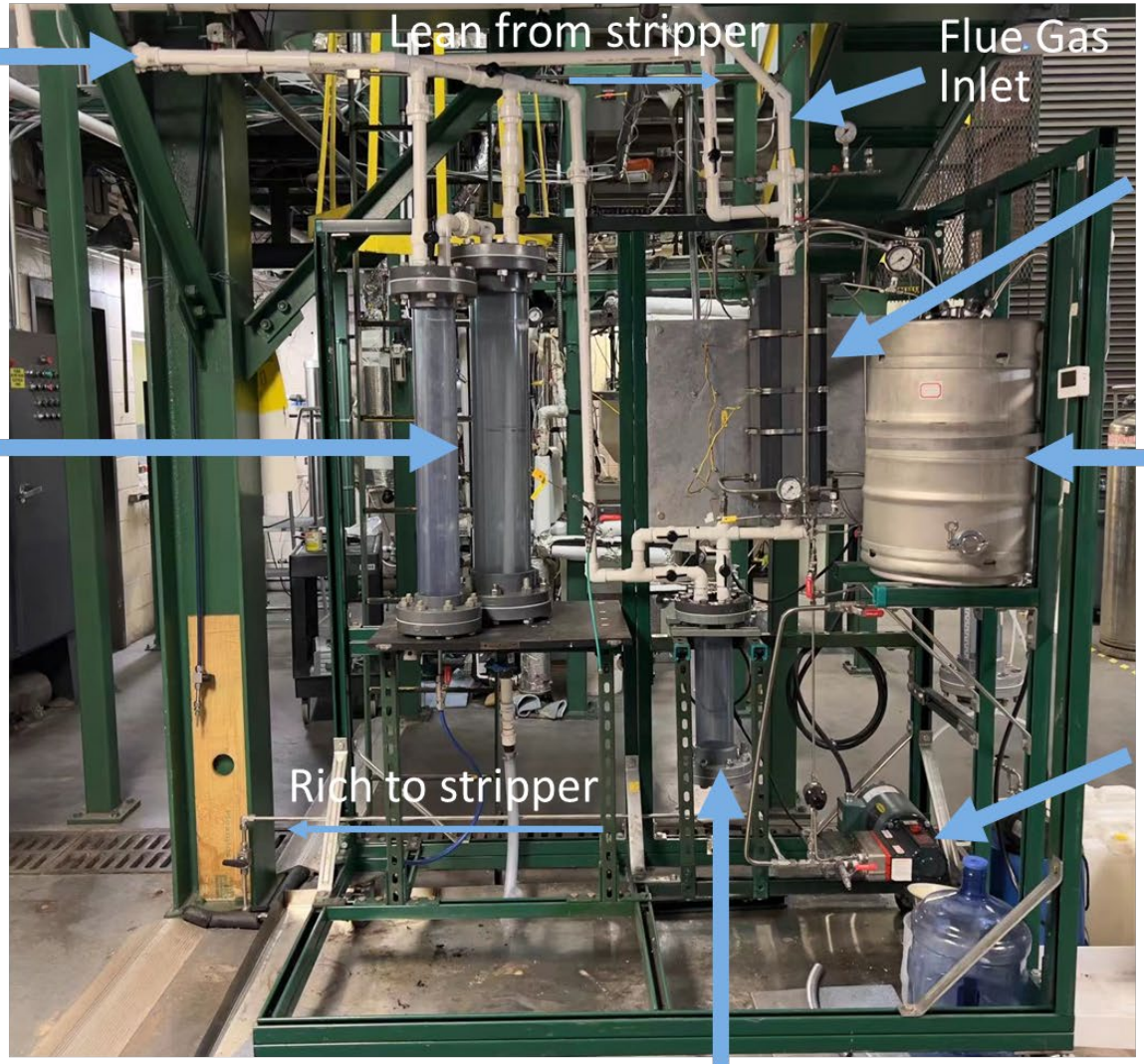
Lab-scale testing of NH_3 slip on flat sheet membranes achieved below 100 ppm.



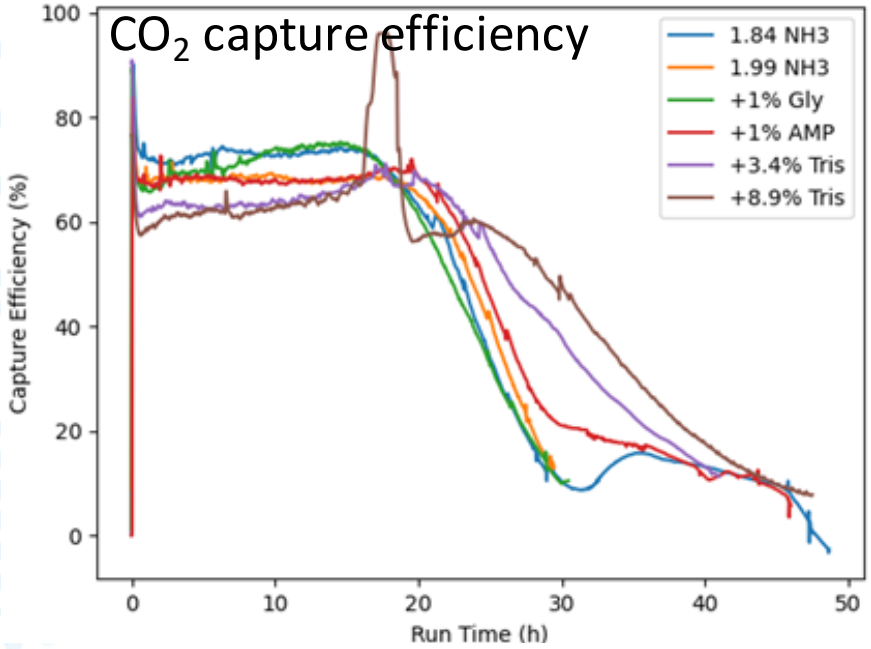
Substrate: Polyethersulfone (PES) membrane supported by polyester (PET) nonwoven fabric
Modification solvent: Teflon AF2400 in Fluorinert™ FC-40

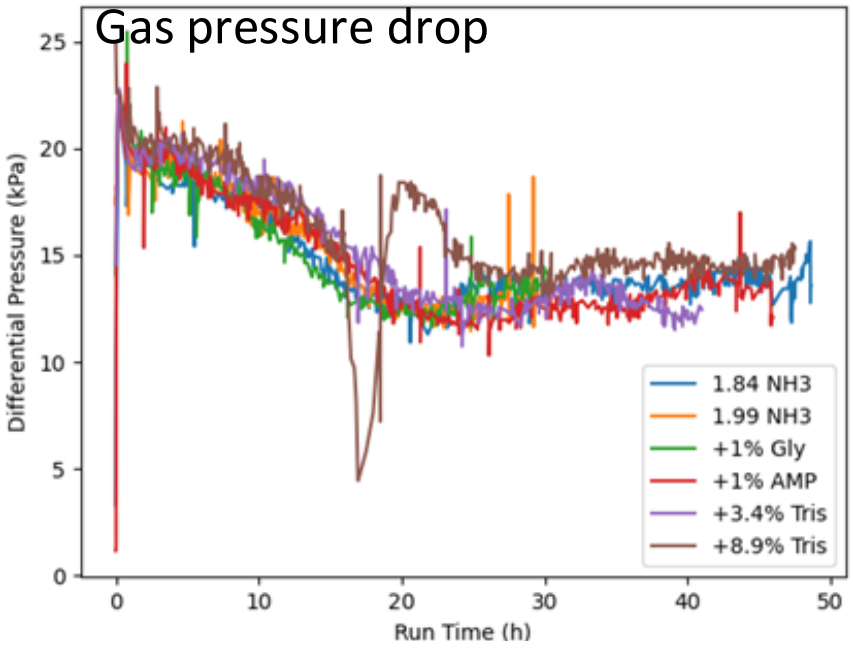
Membrane	Contact Angle/°	NH_3 Slip (ppm)
PES substrate	81	559
PES coated with 0.1 wt% Teflon AF2400 for 10 min	118	65
PES coated with 1 wt% Teflon AF2400 for 1 min	125	40
Sterlitech PTFE 0.1 µm laminated	134	80
Sterlitech PTFE 0.2 µm laminated	130	734

Membrane Contactor Construction, Installation and Tested



Performance at Bench Scale





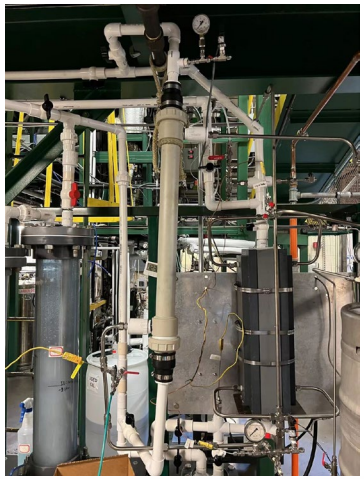
Solvent	Total alkalinity (mol/kg)	Carbon loading (mol/kg)	Carbon loading (mol C / mol N)	Outlet CO_2 (%)	NH_3 slip (ppm)
2M NH_4OH	1.718-1.706	1.26-1.36	0.733-0.797	6.77-8.39	1001
2M NH_4OH+8.9 wt% Tris	2.295-2.281	1.36-1.39	0.592-0.609	6.94-7.76	1050

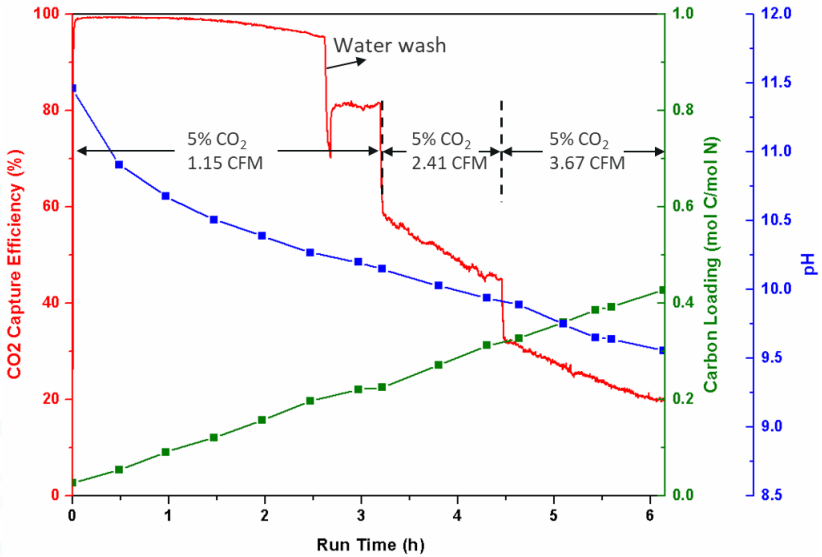
With the hollow fiber membrane, 1000 ppm NH_3 slip can be achieved at a carbon loading 0.6 C/N (higher free amine concentration) with addition of instead of 0.8 C/N (lower free amine concentration) in 2 M NH_4OH.

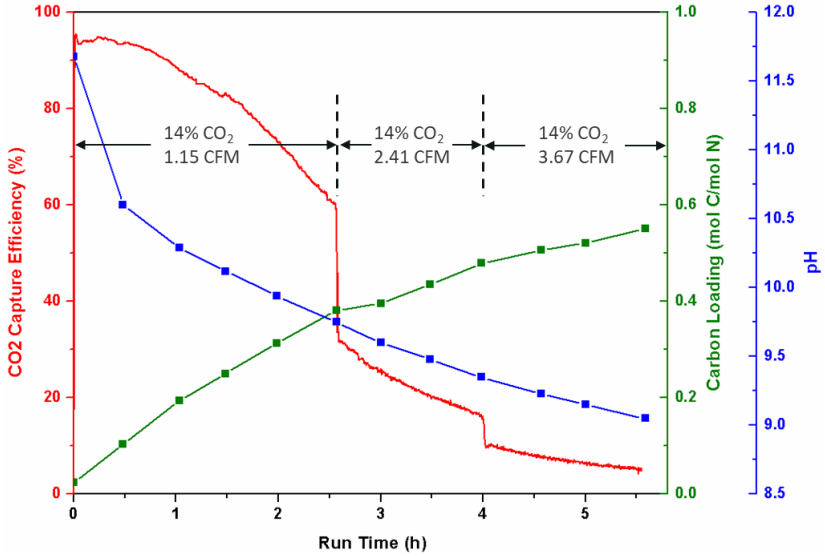
Parametric Campaign – CO_2 Capture

MICRODYN hollow fiber membrane

- Membrane inner diameter: 1.8 mm
- Membrane area: 0.75 m^2
- Free flow area: 5 cm^2
- Inlet CO_2 concentration: 5%, 14%
- Gas feed flow rate: 1.15 CFM, 2.41 CFM, 3.67 CFM
- Liquid inlet pressure: 1 psig
- Gas inlet pressure: ~0.5 psig





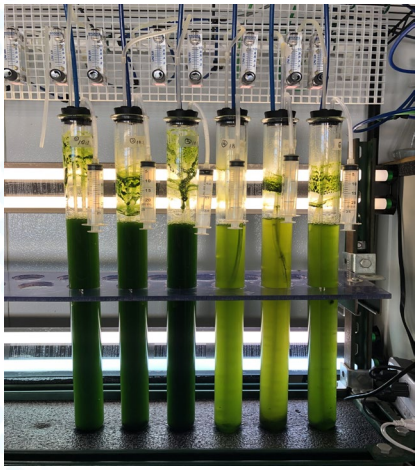


- The increase if membrane inner diameter dramatically decreased the pressure drop
- Residence time is main impact on CO_2 capture efficiency

Algae Production Demonstration

Effect of CO_2:NH_3 Mole Ratio

Objective: to examine the effect of CO_2:NH_3 mole ratios - simulating the gas stream from the solar stripper - on *Scenedesmus acutus* culture health and productivity



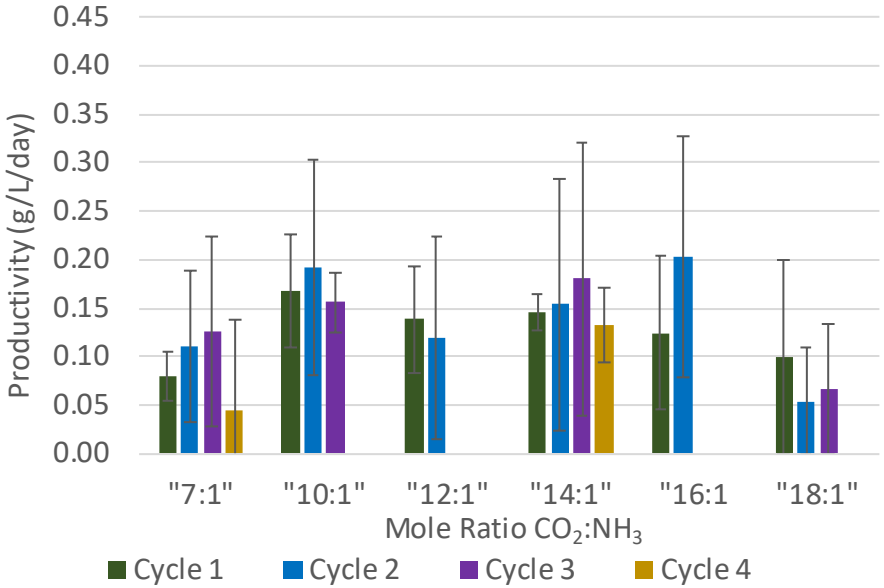
Experiments conducted in 800 mL bioreactors with constant gas sparging and different CO_2:NH_3 mole ratios (ranging from 7:1 up to 18:1)

Average productivity in g L^{-1} day^{-1} of *Scenedesmus acutus* grown using different N-sources*,**

Urea	$NaNO_3$	CO_2/NH_3 (10:1)
0.11 ± 0.04	0.13 ± 0.05	0.17 ± 0.05

*Other nutrients supplied according to BG-11 recipe
**Growth rates represent averages of daily growth rates

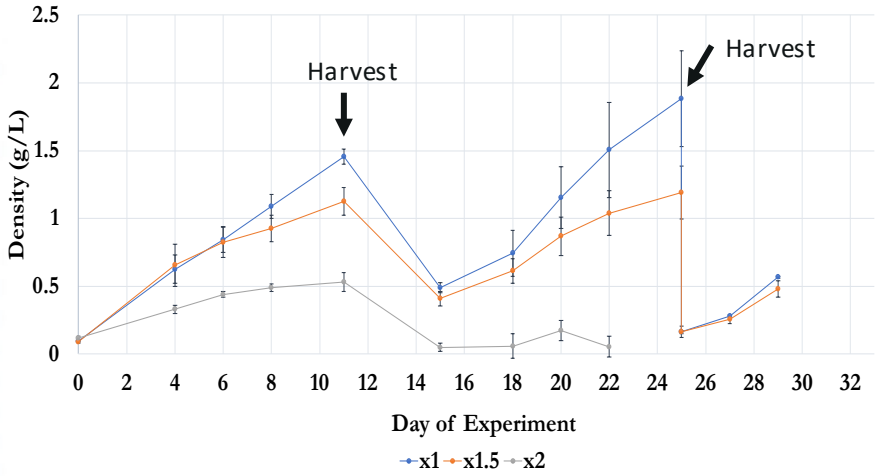
- Optimal CO_2:NH_3 mole ratio lies in the range 10:1 – 16:1
- Growth rate for 10:1 CO_2:NH_3 ratio is higher than obtained using traditional N-sources such as $NaNO_3$
- For 10:1 CO_2:NH_3, NH_3 utilization ≈ 100%, CO_2 utilization ≈ 70%

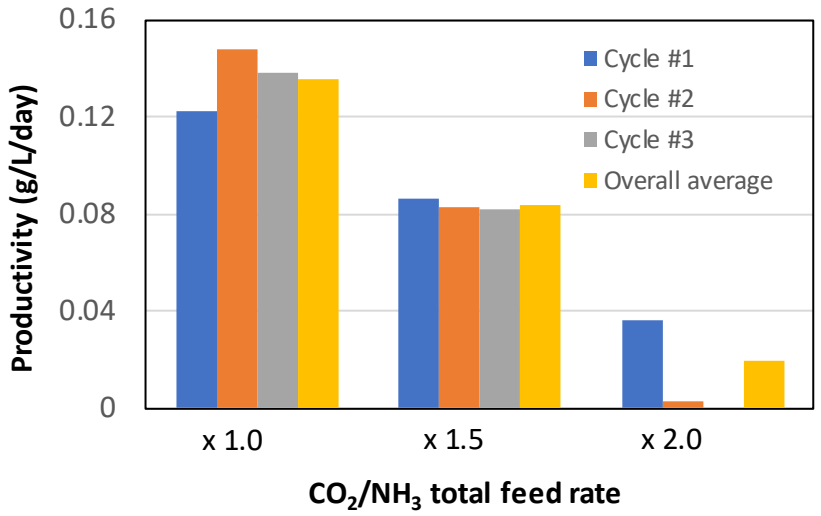


Average culture growth rate as a function of molar CO_2:NH_3 ratio.

Algae Production Demonstration

Effect of CO_2/NH_3 Feed Rate (x1, x1.5, x2.0); CO_2/NH_3 fixed at 10:1





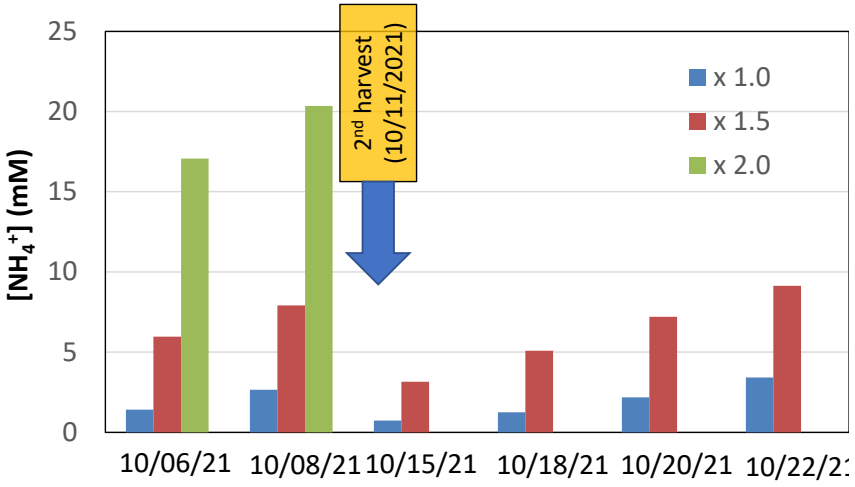
- Dry mass measurements show that increasing the gas feed rate is detrimental to algae growth
- Accumulation of NH_4^+/free NH_3 at higher NH_3 feed rates creates toxic environment for algae cells: according to one study, NH_3 is toxic at concentrations of >3 mM (>50 ppm)*
- Note: NH_4^+/free NH_3 equilibrium dependent on pH and temperature:

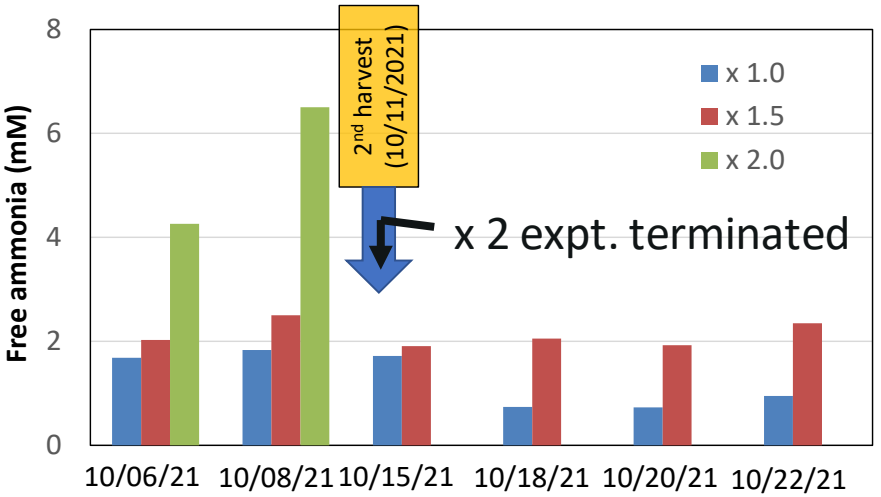
  mole fractn. $NH_3 = 1/(10^{pKa-pH} + 1)$, where $pK_a = 0.0902 + 2729.92/T_k$

*A. Abeliovich, Y. Azov, *Appl. Environ. Microbiol.*, 1976, 31(6), 801-806.

Algae Production Demonstration

Results of ammonium ion analysis (ion chromatography) during indoor culture experiment performed at different CO_2/NH_3 gas feed rates (standard feed rate x 1, x 1.5, x 2); CO_2/NH_3 = 10

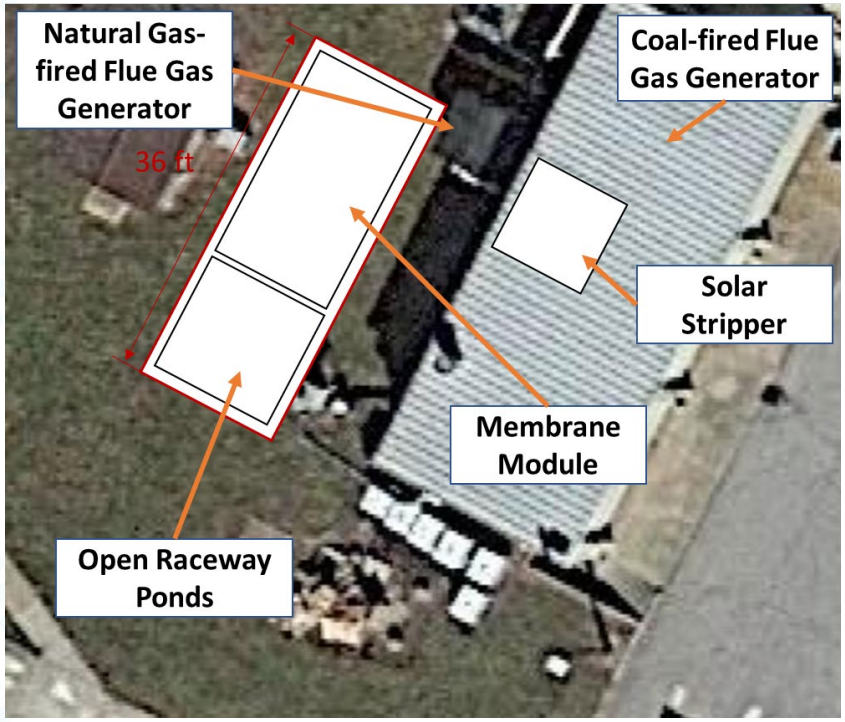


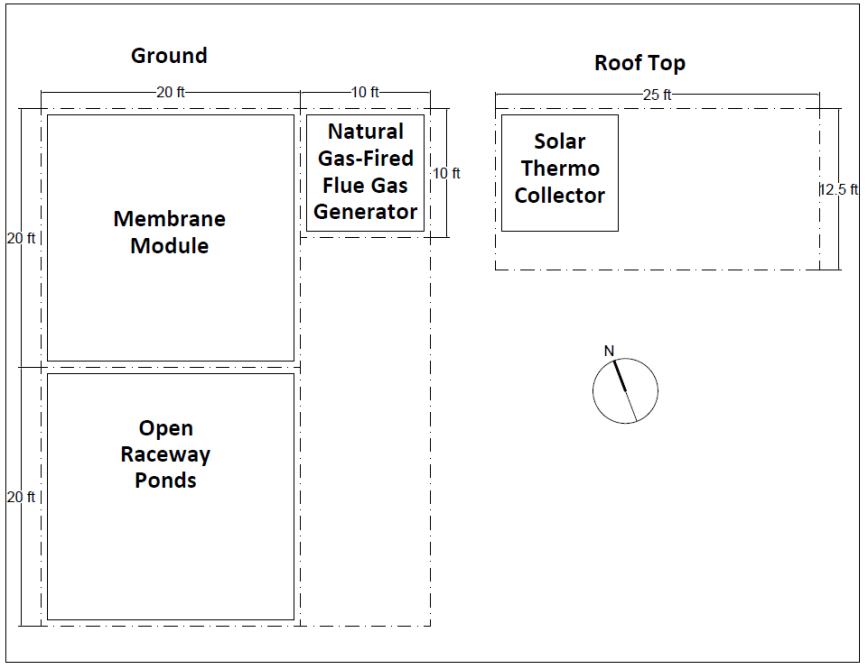


- Gradual accumulation of NH_4^+ and free NH_3 in solution as culture cycle progresses, i.e., not all the NH_3 is consumed
- Free NH_3 stays within safe limit (~2 mM) for x 1 feed rate; slightly over limit for x 1.5 feed rate and significantly over limit for x 2; results consistent with observed growth rates

Future Testing

Integrated Process: General Layout





- The solar thermal stripper will be located on top of the roof.
- One of the existing Open Raceway Ponds will be moved to this area to ensure just-in-time CO_2 and NH_3 delivery.

Algae System Performance Data

	Units	Measured/Current Performance	Projected/Target Performance
Algae Characteristics			
Proposed Algae Strain	-	*Scenedesmus acutus* (UTEX B72)	
Lower Heating Value @ 25°C	kJ/kg (dry)	18,000 – 19,500	
Lipid Content[1]	wt%	1 – 15	
Protein Content	wt%	35 – 55	
Carbohydrate Content	wt%	20 – 25	
Algae Cultivation			
Method of Cultivation	-	Pond and PBR	
Water Source		Municipal	Municipal
Pond or PBR Surface Area	m^2	4.2 (pond)	4.2 (pond)
Pond Depth or PBR Width	cm	25 (pond)	25 (pond)
PBR Type[2]	-	Open raceway	Open raceway
Pond or PBR Volume	L	1100 L (pond)	1100 L (pond)
Nutrient Source - N	-	NH_3	NH_3
Nutrient Source - P	-	Triple super phosphate	Triple super phosphate
Scale of Operation – CO_2 delivered[3]	kg/hr	0.02	0.02
CO_2 Utilization			
CO_2 Source[4]	-	Bottled	Coal-derived flue gas
CO_2 Content of Source Gas	mol%	10%	4 - 12%
Impurity or contaminant processing requirements[5]	-	None (impurities removed during CO_2 capture)	None (impurities removed during CO_2 capture)
CO_2 Processing Requirements[6]	-	Gaseous CO_2 from decomposition of ammonium (bi)carbonate solution in solar regenerator	Gaseous CO_2 from decomposition of ammonium (bi)carbonate solution in solar regenerator
CO_2 Concentration after Processing[7]	mol %	10 vol%	90-93% with balance of NH_3
Delivery Method to Pond/PBR[8]	-	Gas sparger	Gas sparger
CO_2 Pond/PBR Retention[9]	%	10-14% (pond); 60-70% (PBR)	50-70% (pond); 60-70% (PBR)
***Algae* Productivity[10]**			
Peak Productivity	$g/m^2/day$	8.7	>12 (Kentucky)
Annual Average Productivity	$g/m^2/day$	~6	~8 (Kentucky)
Projected Finished Products[11]		(*Market Value*)	(*Market Size*)
Bioplastic feedstock (e.g., for EVA composite, etc.)	-	$1000 – 5000/ton	2 x 10^6 ton/yr (all bioplastics)

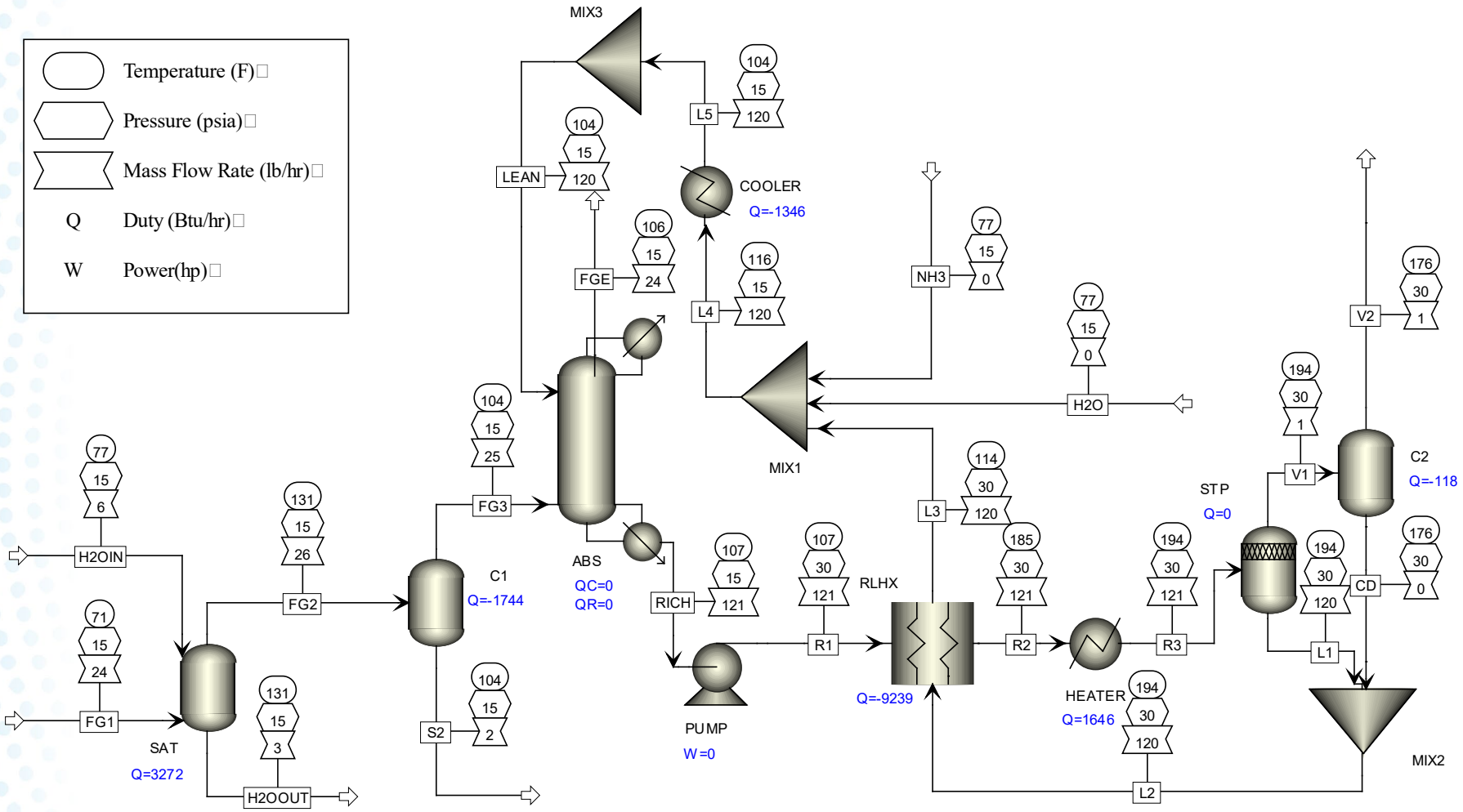
Summary

Task Name	Percent Complete	Accomplishment
1.0 Project Management and Planning	N/A	• The project kickoff meeting was held on 12/07/2020. • The TMP was submitted on 01/17/2021. • The revised PMP was submitted on 01/12/2022.
2.0 Membrane Absorber	100%	• Bench scale membrane unit integrated with existing CO_2 Capture System for real fossil fuel generated flue gas supply and continuous operation with solvent regeneration.
3.0 Absorber Performance Evaluation	90%	• Validated inhibition effect of chelating additives on ammonia slip. Evaluated absorber performance applying the hollow fiber membrane and flat sheet membrane modules. • Parametric campaign is underway, following the test plan, to establish solvent regeneration conditions producing the target product stream CO_2:NH_3 composition using real fossil fuel derived flue gas.
4.0 Advanced Membrane Development	100%	• Coated hydrophobic layer on PES substrate with Teflon AF2400 on the customized flat sheet membrane. Lab-scale testing of ammonia slip achieved below 100 ppm.
5.0 Algae Production Evaluation	100%	• Outdoor cultivation experiments in 1100 L ORPs confirmed superior productivity of cultures fed with 10:1 CO_2/NH_3 compared with CO_2/$NaNO_3$. • Outdoor cultivation with 10:1 CO_2/NH_3 feeds was found to be ~25% and ~43% during daylight hours The corresponding productivity was 0.025 g/L/day. • Algae biomass produced using the 10:1 feed possessed a remarkably high protein content (55%) and low ash content (<6%), making it well-suited for use as a bioplastic feedstock.
6.0 Integrated Process Design	100%	• Completed and submitted design basis report on 12/19/2021. • Completed and submitted process design package on 6/30/2022.
7.0 Integrated Process Test Plan	100%	• Completed integrated system test.

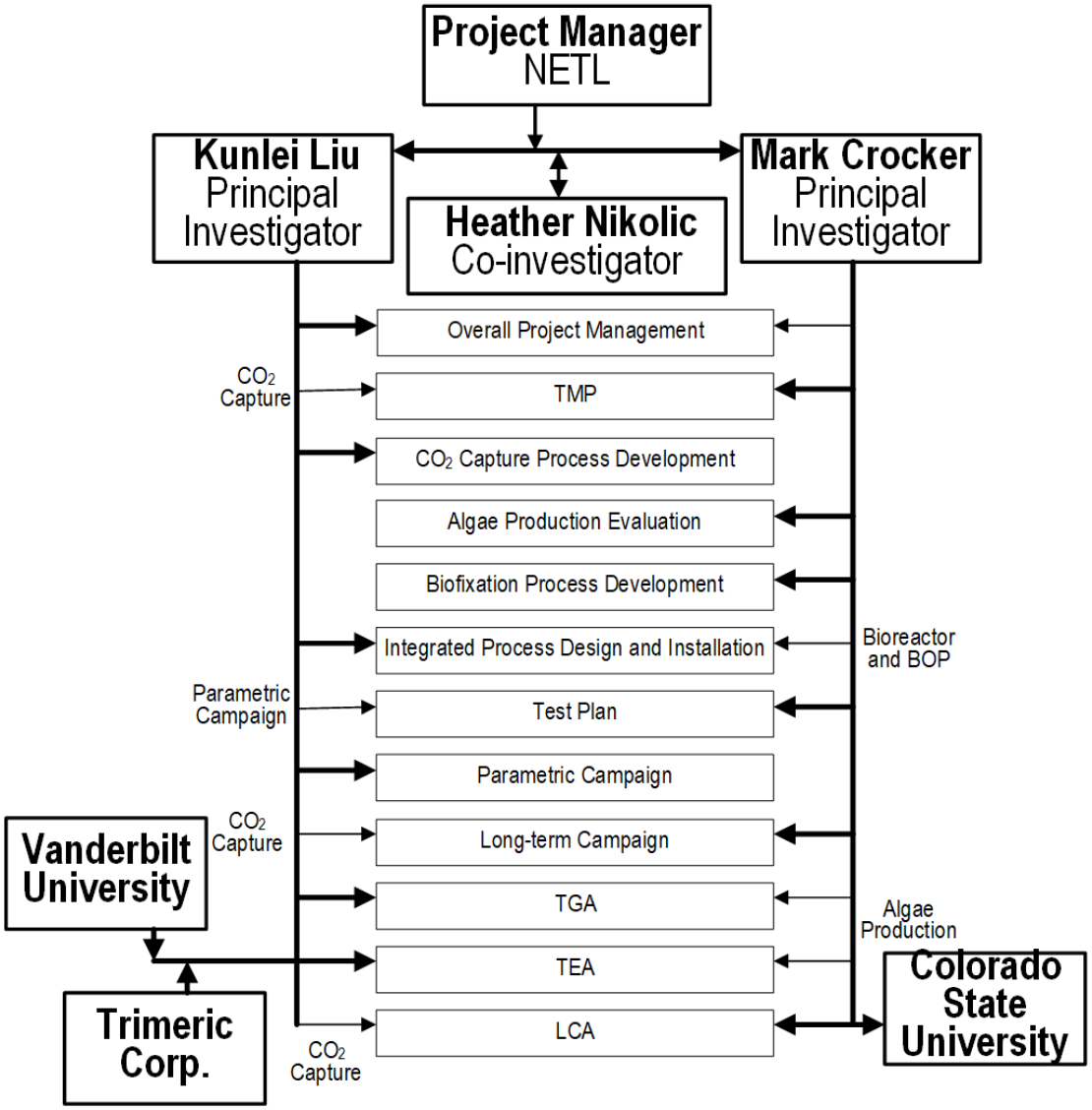
Acknowledgements

- **DOE-NETL**: Isaac Aurelio, Patricia Rawls, Joseph Stoffa
- **DOE-HQ**: Amishi Kumar
- **UKy**: Lisa Richburg, Feng Zhu, Xiaoshuai Yuan, John Adams, Fritz Vorisek, Yaying Ji, Steve Summers, and Reynolds Frimpong
- **Colorado State University**: Jason Quinn
- **Vanderbilt University**: Shihong Lin
- **Trimeric Corporation:** Andrew Sexton

Appendix Model of Integrated System



Appendix: Organizational Chart



Appendix: Gantt Chart

Task Name	Start	Finish
1.0 Project Management and Planning	Thu 10/1/20	Sat 9/30/23
Budget Period 1	Thu 10/1/20	Thu 6/30/22
1.1 PMP	Thu 10/1/20	Sat 10/31/20
1.2 TMP	Thu 10/1/20	Thu 12/31/20
2.0 Membrane Absorber	Thu 10/1/20	Wed 3/31/21
2.1 Absorber Specificaiton and Purchase	Thu 10/1/20	Thu 12/31/20
2.2 Absorber Installation and Integration	Wed 12/30/20	Thu 3/31/22
3.0 Absorber Performance Evaluation	Thu 4/1/21	Wed 6/30/21
4.0 Advanced Membrane Development	Tue 6/1/21	Tue 8/31/21
5.0 Algae Production Evaluation	Thu 10/1/20	Thu 3/31/22
6.0 Integrated Process Design	Fri 5/14/21	Thu 6/30/22
6.1 Design Basis	Fri 5/14/21	Sun 12/19/21
6.2 Design Package	Mon 12/20/21	Thu 6/30/22
7.0 Test Plan	Fri 10/1/21	Thu 3/31/22
Budget Period 2	Fri 7/1/22	Sat 9/30/23
8.0 Process Equipment Purchase	Fri 7/1/22	Fri 9/30/22
9.0 Assembly	Sat 10/1/22	Sat 12/31/22
10.0 Integrated Process Parametric Campaign	Sun 1/1/23	Tue 2/28/23
11.0 Long-term Campaign	Wed 3/1/23	Sat 9/30/23
12.0 TEA	Fri 7/1/22	Sat 9/30/23
12.1 Process Flow and Modeling	Fri 7/1/22	Sat 9/30/23
12.2 Membrane Modeling	Thu 12/1/22	Fri 3/31/23
12.3 Equipment Sizing and Cost Estimation	Sat 4/1/23	Wed 5/31/23
12.4 TEA	Thu 6/1/23	Sat 9/30/23
13.0 TGA	Sat 4/1/23	Fri 6/30/23
14.0 LCA	Tue 11/1/22	Mon 7/31/23