Continuous Algae-based Carbon Capture and Utilization (CACCU) to Transform Economics and Environmental Impacts: DE FE 0032108

Texas A&M University Washington University in St Louis NCCC at Southern Company



U.S. Department of Energy National Energy Technology Laboratory Carbon Management Project Review Meeting August, 2023

Susie Dai Texas A&M University August 29, 2023



Project Overview

- Funding
 - DOE \$2,000,000; Cost Share \$510,583
- Overall Project Performance Dates
 - Original 10/01/2021-09/30/2024
 - Currently: with six-month extension due to late start of the entire project
- Project Participants
 - TAMU: Susie Dai, Bruce McCarl, Stratos Pistikopoulos, Chengcheng Fei
 - WUSTL: Young-shin Jun, Yinjie Tang, Joshua Yuan
 - NCCC at Southern Company: Frank Morten



Overall Project Objectives

- The project integrates novel CO₂ capture/controlled release sorbent with a breakthrough continuous algal cultivation system, assisted by hydrogel technology to reduce media cost, fertilize the algae with controlled nutrient delivery.
- Objective 1: Project management.
- Objective 2: Integrates CO₂, bicarbonate, and nutrient capture and delivery to the low-cost harvest-empowered continuous algal cultivation system with ultra-high productivity and CO₂ uptake plus valuable chemical bioproduct production. We also advance algal strain, sorbent, and hydrogel technologies to enhance carbon capture and yields of limonene, biomass, and glycogen.
- Objective 3: Scale up the sorbent technology and integrate it with algal cultivation.
- Objective 4: Test the prototype CACCU system with flue-gas coupled 100 L photobioreactors (PBRs).



Technology Background



The integrated CACCU system



Sustainable co-production of limonene and biomass by semicontinuous cultivation



Record productivities and yields in limonene productivity

Sustainable biomass accumulation at about 1-2g/L/Day for a long period of time.

Dai and Yuan's groups@TAMU

Machine learning informed semi- continuous cultivation.



Long et al., Nature Communications, 2022, 13:541

Amine Grafted Porous Polymer Network

the porous structure



Chemisorption via amine

 \checkmark R-NH₂ + H₂O \rightarrow R-NH₃⁺+ HCO₃⁻

 \checkmark R-NH₂ \rightarrow R-NHCO₂⁻+ H⁺

 \checkmark R₂-NH \rightarrow R₂-NCO₂⁻+ H⁺ \checkmark R₃-N+H₂O \rightarrow R₃-NH⁺+HCO₃⁻

moieties









CO₂ adsorption of PPN-151-DETA





Mineral-seeded mineral hydrogel composites for nutrient delivery and pH control Ca-Alg Ca-Alg/CaP





Ca-Alg/CaCO₃ Ca-Alg/CaP+CaCO₃ Ca-Alg/CaP+CaCO₃

Kim, D and Jun, Y.-S., Green Chemistry 2018, 20 (2), 534-543.

- Calcium phosphate, calcium carbonate, or ammonia-containing mineral seeds formed during alginate crosslinking.
- When placed into calcium phosphate/carbonate supersaturated solution, mineral seeds grow, collecting and incorporating phosphate, bicarbonate, and ammonia-containing minerals.



Translating process models into a process systems engineering framework at scale involves some critical steps

- 1) Accurate modeling of process dynamics
- 2) Reduced order approximation of nonlinear dynamics
- Surrogate linear models can tame computational complexity
- Linear programs can provide certificates of optimality
- 3) Design of control scheme

4) Formulation of a network design as a mixed integer program (MIP)

MIPs can be optimized to multiple objectives

Network decisions can be modeled as binary variables

Scheduling can be integrated (multiscale approach)

5) Integration of lifecycle tools

OpenLCA data integration with MIP framework (MIP)



Tang, Pistikopoulos and McCarl's groups@TAMU&WUSTL

Technical Approach/Project Scope





Progress

Task	Milestone Title	Baseline	Complete Date	Status
2.1.1	Achieve average algae biomass yield 1.2g/L/D using sorbent-released CO_2 , with optimized release rate and composition, along with nutrient optimization, at 0.5 Liter scale	1g/L/Day with 5% of CO ₂ from commercial source	Q6(03/31/2023) (previous version: Q4)	Completed 1.94 g/L/D at 0.5L scale, using CO ₂ released from PPN-151-DETA
2.1.2	Obtain 2 alternative pathways	Report the pathways and mechanisms	Q7(06/30/2023) (previously Q5)	Completed Acquired alternative strains in Q4
2.2.1	Achieve average dry weight percent of carbonate/P/N-containing minerals mineral 40 wt.% at 50g scale		Q7(06/30/2023) (previously Q5)	Completed Hydrogel-based nutrient release technology (P, N and bicarbonate) has been tested
2.3	Achieve average algae biomass yield >1.5 g/L/D using engineered strains and sorbent-released CO_2 , with optimized release rate and composition, along with nutrient optimization, at 0.5 Liter scale	1g/L/Day with 5% of CO ₂ from commercial source	Q8(09/30/2023) (previous version Q6)	Completed 1.94 g/L at 0.5L scale, using CO ₂ released from PPN-151-DETA





Sorbent-Algae integration system–Version 1



33 °C for 24h



- Significant inhibition was observed in the sorbent group
- Cell toxicity from leached amine (DETA)





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To be improved: General Scale to 0.5L Cultivation setups

□ Sorbent heating





Biomass productivity: 1.56 g/L/d (in 16h) at 0.5L scale. → surpassed Q6 and Q8

milestones

- Light is close to optimal
- CO₂ is not optimal
- No growth monitoring system







Achieved real-time monitoring & data logging of

CO₂, sorbent temperature, and algae growth.

□ Biomass productivity: 1.94 g/L/d.

Milestones: Q6—1.2g/L/d; Q8—1.5g/L/d; Q10—1.8g/L/d
 (2L).





Zhou's group@TAMU





Physically Attached Amines in PPN-151-DETA



Advantage: Easy recycle of PPN-151 backbone; Disadvantage: Potential amine loss during application.



PPN Design – Substoichiometric Strategy

Condensation Reaction



Advantages: 1. Commercially available starting materials;

2. Easy functionalization.



Porosity and CO₂ Uptake Study



After DETA tethering:

- 1. BET surface area decrease from 580 to 409 m^2/g
- 2. CO₂ adsorption increased slightly.



Substoichiometric Strategy – New Scaffold

Friedel-Crafts Acylation Reaction





Unpublished results

Porosity and CO₂ Uptake Study



After DETA tethering:

1. BET surface area decrease from 615 to 477 m²/g

2. CO₂ adsorption increased significantly both at low and high relative pressure

Unpublished results

All Carbon PPN Scaffold



Porosity Optimization







Jun's group @WashU

Simultaneous N/P Recovery: Ca-Alg/CaP+Struvite



Nitrogen and Phosphate Recovery Capacity



For N & P recovery, mineral-hydrogel composites showed the highest capacity among other recent techniques

Simultaneous N and P Recovery: Ca-Alg/CaP+Struvite





Dose- 2.5%	composites (v/	/v)
Initial conc.		

- 28 ppm N, 6.2 ppm P
- 80 ppm Ca, 46 ppm Mg

Interference	Initial conc. (ppm)
Fe	2
NO ₃	10
SO ₄	50
As	0.1 (much higher than environmental conditions)
SRDOM	25

- Phosphate is not much affected by interference (within 2%).
- The interference of iron, nitrate, and sulfate on ammonium is insignificant, but arsenic and SRDOM have some interference.
- Adsorption of As on struvite might hinder the struvite growth, so
 24 hrs efficiency is identical, but 42 hrs efficiency is low.
- Mineral-hydrogel composites are applicable for nutrient recovery from wastewater without significant interprese

Phosphate Delivery by Composites for Algal Growth: Ca-Alg/CaP+Wollastonite



Media: BG11 Media without P Dose: 1% (wet weight of hydrogel /v of media)



Xiao et al. Science of the total environment, 2022, 247, 157533

In our recent study, we found Ca-Alg/CaP+Wollastonite composites can release phosphate to grow algal species.



N/Phosphate Delivery: Dissolution Rates of Ca-Alg/CaP+Struvite N, P in BG11 media were already subtracte

Media • Medium #1: BG11 Medium #2: 32 mM NaNO₃ (same ionic strength as BG11) Medium #3: BG11 without critical elements (Ca, Mg, NH_4 , PO_4)

pH did not change (media #1,3: 8.08 and medium# 2: 7.25)

Dose 2.5 % (v of hydrogel precursor/v of media)

With a 2.5 % dose, P has released **1.2 ppm** for 24 hrs in BG11 without critical elements

To reach the original BG11 P level, around 4 times of the hydrogel dose is required.

Insufficient nitrogen concentration can be solved by adding nitrate salts.



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Capability of Mineral-Hydrogel Composites for Algal growth: Ca-Alg/CaP+Struvite

Struvite hydrogels nutrient release and algal growth: log phase (day 3)

Conditions	Phosphate	Ammonium	Nitrate	Relative	OD730 (over sta	andard	BG11	culture
1	BG11	BG11	BG11						
2	BG11+20% CaP+Stru Alg	BG11+20% CaP+Stru Alg	BG11						
3	BG11+40% CaP+Stru Alg	BG11+40% CaP+Stru Alg	BG11					ŀ	1
4	-	-	-						
5	20% CaP+Stru Alg	20% CaP+Stru Alg	-						
6	40% CaP+Stru Alg	40% CaP+Stru Alg	-				1		
7	-	-	BG11						
8	20% CaP+Stru Alg	20% CaP+Stru Alg	BG11						
9	40% CaP+Stru Alg	40% CaP+Stru Alg	BG11		н				
	•	· · · · ·	()% 20%	40%	60%	80%	100%	120%

- With the addition of 40% v/v struvite hydrogel composites in BG11, UTEX 2973 culture can increase the OD by 7% compared to standard BG11 (conditions 1 (OD: 1.32) and 3 (OD: 1.42) in the same batch).
- With 40% v/v struvite hydrogels as the only phosphate and ammonium source, UTEX 2973 can reach 73.4% agal growth in standard BG11 (conditions 1 and 6).



• Still, we need the nitrate source for comparable algal growth with BG11 (conditions 5 and 8).

Impacts of Mineral-Hydrogel Composites for Algal Growth: Ca-Alg/CaP+Struvite with Ca-Alg/NaNO₃ Composites

Nitrate embedded hydrogel nutrients release and agal growth: log phase (day 3)



- 1 2 3 4 5 6 7 8 9
- By using struvite and nitrate mineral-hydrogel composites as the only P and N sources, the growth of UTEX 2973 growth improves 32% more than standard BG11 (conditions 1 and 6).
- Balancing N/P ratio and ammonium toxicity are the main key factors for future optimization.



Modeling



Algae Cultivation Process



Equations Based Process modeling



Equations Based Process modeling



- Nonlinear dynamic modeling framework for algae cultivation in *pyomo.dae* package
- Understand the interaction between carbon, nitrate, phosphate, light intensity, and their impact on biomass yield.
- Parameter estimation
- Design of explicit control scheme

Multi-scale systems engineering framework

- Develop linear surrogate of dynamic process model
- Append to energy systems framework
- Scenario analysis to understand the at scale impact of process
- Benchmark against competing technology pathways: system costs, carbon intensity, circularity
- Post-validation of solutions against process model



Process model dynamics

Modeling components



Process Dynamic Model



- Model performs better under low light intensities than under high light intensities
- To add design equations within the model to improve the prediction
- Model requires more experimental data at different operating points to improve the accuracy of parameter estimation



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Multi-parametric

Integrated TEA and LCA Framework



Hierarchical modeling paradigm

Features

- Self-contained and modular modeling blocks
- Tailored generation of set, variables, and constraints

Advantages

- Seamless translation to object-oriented scripts
- Minimizes redundancy
- Generalizable approach

- Makes use of Component based approach in *energiapy*
- Processes are represented as a set of States/Resources and Tasks/Processes
- Capability to evaluate alternative options for each tasks



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Multi-parametric Optimization & Control

Initial Techno Economic Analysis

Assumptions:

- Number of adsorbent cycles is assumed to be 10.
- Number of times DMSO Solvent can be reused to produce the adsorbent is 100
- There are no downstream or upstream processing costs considered
- Fixed Capital cost data was estimated from the Algae Farm Model report [1]



Levelized Cost of Biomass is estimated to be \$475/ton of Biomass which is much lower than \$1137/ton estimation by the Algae Farm Model [1]



Parameters	Value	Unit
Algae Growth Rate	1.94	g/L/day
Adsorbent Efficiency	0.05	kg CO ₂ captured/kg adsorbent
Photobioreactor Bag Life	5	years
Photobioreactor Bag Volume	50	L
Photobioreactor Bags per module	18000	# of Bags
Module Area	5	acres
Payback Period	10	years
Interest Rate	8	%
No. of working days in a year	330	days
Cultivation Land area	1000	acres
Composition of Carbon in Biomass	0.53	kg carbon/kg biomass
Number of Adsorbent Cycles	10	# of cycles

Table 1: List of Parameters

Parameter	Cost	Unit
Melamine	0.7	\$/kg
Paraformaldehyde	0.8	\$/kg
Cyanuric Acid	1.3	\$/kg
DMSO Solvent	1.1	\$/kg
Cost of Bioreactor	43748	\$/acre
Unit CO ₂ Price	15	\$/ton
Photobioreactor Bag Cost	10	\$/Bag
Photobioreactor Structure Cost	20	\$/Bag
Cleaning in Place(CIP) chemical cost	1000	\$/acre

Table 2: Cost of Materials and Equipment's

Material	Quantity	Unit
Melamine	201.62	g
Paraformaldehyde	108	g
Cyanuric Acid	15.48	g
DMSO Solvent	2080	mL

Table 3: Chemicals required to produce PPN-151-DETA

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TEA Sensitivity analysis – Bioreactor Design

- Lowering the bioreactor bag cost and structure cost improves the levelized cost of biomass considerably
- At low biomass growth rates, the effect of parameters is more pronounced



TEA Sensitivity analysis – Cultivation Land

- Increasing the Cultivation Land area has a large influence on levelized cost of biomass
- At low biomass growth rates, the effect of parameters is more pronounced
- The TEA is more sensitive to cultivated area compared to land cost



DOE Meeting- 28th August 2023

LCA Goal and Scope Definition





Inventory Analysis

- The pond level algae cultivation system with CO₂ intake efficiency of 65%, and 90%
- To produce algae in the lab or pond, CO₂, NH₃, and DAP associated with electricity input are required
- Main products from this system are limonene, and algae biomass (may use as animal feed etc.)

		Low CO2 Efficiency	High CO2 Efficiency
		Rate	Rate
	Efficiency	65%	90%
	Pond (m2)	1	1
	Algae (g/m2/day)	43	43
	CO2 100% Intake	79.11	79.11
	CO2 with Efficiency Counted (g)	121.71	87.90
Input	Electricity Use per m2 (kwh)	0.10	0.10
-	NH3 (g)	0.86	0.86
	DAP (g)	0.42	0.42
	CO2 rate	35%	10%
Output	Limonene (g)	0.086	0.086
-	Biomass (g)	43	43

Input and Output Information of 1 squared meter pond in a day with various CO2 intake Efficiency

Notes: SAC unleashes cyanobacterial growth potential with 0.1 g/L/hour biomass productivity and 0.2 mg/L/hour limonene productivity over a sustained period in photobioreactors.

Source: https://www.nature.com/articles/s41467-021-27665-y



Impact Assessment

- Net carbon emission reduction
- Benchmark: Corn Stover ~0g CO₂eq emission per gram (GREET)

CO₂ Sequestration Associated with Efficiency

Emission from Electricity (g CO2eq)	42.06
Emission from NH3 (g CO2eq)	2.05
Emission from DAP (g CO2eq)	0.59
Net Emission (g CO2eq)	-34.41
Carbon Utilization Rate	56%
(counting Non-Carbon)	



Interpretation

- Current technology by Dai/Yuan group can produce 43.3g algae and about 86 mg limonene per day per squared meter pond
- It can sequestrate 34.4 g CO₂ equivalent per day into the algae biomass and limonene
- The carbon utilization rate is 56%
- In this LCA analysis, we didn't consider the emissions from CO₂ production and transporting the materials.



Algae Farm Supply Chain

- Optimum sites to cultivate algae
- Determine the optimum size of algae farm designs
- The objective is to simulate the algae supply chain, including production (from current TEA), operating, and transportation costs, the impacts on input and output markets, farm profits and the carbon credit.





Supply Chain Design Considerations

- Factors:
 - Farm design with land requirements and yields
 - Solar duration
 - Solar radiation
 - Temperature
 - Water resources
 - Photobioreactor (PBR) costs etc.
 - Power plant capacity (source for CO2)
 - Distance to the algae farm
 - Sorbent efficiency and reuse
 - Alternatives to ship sorbent and CO2
 - Nutrients from wastewater treatment
 - Distance from hydrogel producing facility to the algae farm
 - Hydrogel efficiency and reuse
 - Limonene and biomass processing
 - Emission and Reduction from all processes



Supply Chain Model

- The model has three layers
 - Layer 1 connects the CO2 supply locations i to algae farm p
 - Layer 2 connects algae cultivations to the byproduct production site k
 - Layer 3 connects the products to the potential market j





Future Plans

• Integration of different modules

• Scale-up to 2 liter, 20 liter and 100 liter



Our Team



TAMU Plant Pathology & Microbiology Microbial engineering and development of continuous algal cultivation platform



NCCC at Southern Company Scale up and on-site testing

Jun

Morten



TAMU Agriculture **Economics** Life cycle analysis and environmental analysis



Pistikopoulos

Chemical Engineering System modeling and TEA Zhou

TAMU Chemistry Amine-based porous sorbent advancement

Yuan

WUSTL Chemical, **Energy & Environmental** Engineering Unique hydrogel technologies and process design



Tang



Acknowledgement

- DOE Office of Fossil Energy
- Dr. Lei Hong

• Questions?



- Ca-Alg/CaP + Wollastonite can achieve P recovery up to 97% at 72 hr.
- Ca-Alg/CaP + Struvite can recover N and P simultaneously.
- Mineral-hydrogel composites can recover nutrients from wastewater without significant interference.
- With 10% (v of hydrogel precursor/v of media) dose, composites can deliver sufficient P for algal growth.
- Without BG11, 40% (v/v) Ca-Alg/CaP + Struvite can make 73.4% of algal growth with BG11 media.
- The ammonium dissolution rate of Ca-Alg/CaP + Struvite is slow. To provide N in a nitrate form, we developed Ca-Alg/NaNO₃ composites.
- Adding Ca-Alg/NaNO₃ composites can improve the algal growth by 2.3 for a compared to only N, P recovered mineral hydrogels.

Task 2.2 Hydrogel advancement and cultivation integration

Achieve average dry weight percent of carbonate/ P/ N-containing minerals -- mineral 40 wt.% at 50g scale by 6/30/2023

Ca-Alg/CaP: 41.7% dry weight of CaP/dry weight of the composites

Current status

Milestone

- Ca-Alg/CaP + Struvite: 68% dry weight of CaP + Struvite/dry weight of the composites;
 34.6%CaP/composites and 19.2% struvite/composites
 Ca-Alg/CaCO₃: 14.7% dry weight of CaCO₃/dry weight of
- the composites(This would be sufficient for algal growth)
- ✓ We successfully made composites at 50g scale.

Why algae farm supply chain design?

- Improve productivity
- Profit maximization
- Location Selection
- Facility Investment
- Carbon credit
- R & D
 - resource efficiency of laboratory experiments
 - identify cost-saving opportunities in procuring laboratory supplies and equipment
 - support informed decision-making (environmental impacts etc.)



Algae Farm Design Alternatives

- Open systems: tanks, circular ponds, raceway ponds
- Closed systems: flat-plate, tubular, vertical-column enclosed systems

Table 2: Factor comparison of different systems **Closed systems Parameters Open systems** Contamination High Low Process control Difficult Possible Species control Not possible Possible Not uniform Uniform Mixing Extremely high Foot-print Very low Low (5 to 10 m^{-1}) High $(20-200 \text{ m}^{-1})$ Area/volume ratio Capital cost Low High Costs Operation cost Low High **Minimum Biomass** Water losses Very high Low Selling Price Light utilization Low High Productivity Low High (3-5 times) Biomass conc. High (3-5 times) Low

Table 1: Comparison of open and closed systems for growth of algae

Leidos Horizont Open Helical Flat Factors Hangin Ponds al Tubes Panel Tubular g Bags Productivity high medium low low high Cultivation Area medium high high low low **Total Area** high high medium medium low Annual Power Usage medium medium medium high low **Installed Capital Costs** medium medium high low high Variable Operating medium medium high low Fixed Operating Costs low medium high low medium

Notes: We compared five different algae farm type, the data is from NREL (NREL, 2019).

low

medium medium high

high

Source: https://www.e-education.psu.edu/egee439/node/695

Low

High

Mass transfer

Land Requirements

Biomass productivity: 43.3 g/m²/Day in the open pond. Algae productivity can be improved using integrated systems (NREL, 2019)

Table 3: The land usage for a 50,000 dry tons/year algae farm



Notes: The estimated acre for each algae farm design is based on the annual productivity compared to the open pond system (NREL, 2019).



CO2 Utilization and Power Plant

- 1g algae biomass can utilize 0.21 grams of CO2
- A 50,000 dry ton capacity algae farm can capture 10,500 tones of CO₂ per year
- which is equivalent to **23.86 GWh** of electricity generated from natural gas
- which is approximately 50% of the total electricity generation in a year from a 10 MW natural gas combined cycle power plant with a capacity factor of 54.4%
- To match up such a 10 MW power plant's CO2 emissions, it requires **961 -3,000** acres for the algae farm.

Reference: https://www.eia.gov/tools/faqs/faq.php?id=74&t=11 https://www.eia.gov/tools/faqs/faq.php?id=667&t=2



Land Availability and Power Plant

• Ideally, the location of algae farm should be with land availability with lower rents and be closer to the natural gas power plant.

C

- Average rents in 2022 (non-irrigated cropland \$/acre):
 - A: \$36.58
 - B: \$25.46
 - C: \$17.47-\$25.46
 - D: \$25.46

and ents ural e):								8	
LAND USE/LAND COVER	AREA (km²)	% OF STATE	Y.				-		
Rangeland	314,823	45.26				X			
Agricultural Lands	224,924	32.33		1	1 mil	Y	0	300M	W
Forest Areas	114,020	16.39		5	141		\bigcirc	900141	
Urban/Built-up Areas	17,136	2.46		Y	7	11	\leq	000101	vv
Water	13,747	1.98		2	-	Hert	(1500M	1W/
Barren or Rocky Lands	4,283	0.96			V	- Jul	\bigcirc	10001	

Notes: all the points are for natural gas combined cycle power plants; the steam plants are not included.



Supply Chain Model

- Objective Function: Maximize social welfare to simulate market equilibrium
 - Integral of demand curves
 - Simulate market equilibrium price and quantity
 - Costs (capital and operating, land, pumping, transportation etc.)
 - Carbon credits
- Constraints
 - CO2 and other inputs supply: emission capacity and transport distance
 - Algae cultivation: cultivation types associated with land requirements, total land availability, water requirements, energy consumption, yields with factors like temperature, solar condition etc.
 - Byproduct production: extraction efficiency, transport distance
 - Demand: all products shipped should meet the demand



Ongoing work

- Integrating the algae farm design parameters (light, farm type etc.) within TEA and supply chain model (with Prof. Tang's group and Prof. Pistikopoulos's group)
- Developing the TEA and LCA for the nutrients from wastewater treatment process (with Prof. Jun's group and Prof. Pistikopoulos's group)
- Developing the supply chain model to incorporate all relevant processes and ensure a comprehensive market perspective for the project
- Scenario analysis (with Prof. Pistikopoulos's group and Prof. Tang's group)
- Multi-Objective formulation to assess tradeoffs between economic and environmental objectives

