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

Susie Dai
Texas A&M University
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National Energy Technology Laboratory
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Project Overview

• Funding
  • DOE $2,000,000; Cost Share $510,583

• Overall Project Performance Dates
  • 10/01/2021-09/30/2024

• Project Participants
  • TAMU: Susie Dai, Bruce McCarl, Stratos Pistikopoulos
  • 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 at with flue-gas coupled 100 L photobioreactors (PBRs).
Technology Background

The integrated CACCU system

Outcomes
- Sorbent CO₂ capture
- Gel nutrient release
- Fast algal growth
- Easy Biomass harvest
- Process integration
- Optimal Design
- Process control
- Capital Cost
- Operating Cost
- Biomass profit
- Environmental benefits

Milestones
- Year 1: Small scale lab tests (bio and abiotic studies)
- Year 2: 20–100 L PBR test
- Year 3: Outdoor tests and TEA/LCA (>100 L)
Sustainable co-production of limonene and biomass by semi-continuous cultivation

Record productivities and yields in limonene productivity

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

Machine learning informed semi-continuous cultivation.

Dai and Yuan’s groups@TAMU

Long et al., Nature Communications, 2022, 13:541
Amine Grafted Porous Polymer Network

Porous material + Polymeric amine → Polymeric amine - modified porous material

Chemisorption via amine moieties:
- R-NH₂ → R-NHCO₂⁻ + H⁺
- R-NH₂ + H₂O → R-NH₃⁺ + HCO₃⁻
- R₂-NH → R₂-NCO₂⁻ + H⁺
- R₃-N + H₂O → R₃-NH⁺ + HCO₃⁻

Physisorption via the porous structure

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Previous results and materials on carbon capture

- **PPN-151-DETA**

  - **Physically impregnated amines**
  - **CA - noncovalent anchoring sites for alkylamines**

_Working capacity: 5 wt% (dry), 18 wt% (wet)
Regenerative energy: 82.8 kJ/mol CO$_2$ (MEA, 185 kJ/mol CO$_2$)
Low cost, large scale preparation_

*Adv. Sustain. Syst., 2019, 3, 1900051*
Mineral-seeded mineral hydrogel composites for nutrient delivery and pH control

Adding salts or P and P-rich wastewater

Calcium-Alginate Hydrogel (Ca-Alg)

Mineral seed

Ca-Alg/CaP

Calcium-Alginate Hydrogel

CO₂ capture/dissolution

Struvite (NH₄MgPO₄·6H₂O)

Ca²⁺

HPO₄²⁻

NH₄⁺

HCO₃⁻

Jun and Tang’s groups@WUSTL

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)
Technical Approach/Project Scope

CO₂ sources (Flue gas) → Sorbents

Light → PBR Cultures (0.5 L → 10L → 100L)

Input Pure CO₂ → Harvest (auto-precipitation)

Controlled Release of C/N/P by Hydrogel

Waste aqueous phase → Biomass (protein/lipid and glycogen)

Process Model and Control

TEA LCA

Product

Animal feed

Removal of Toxic Compounds

Flue gas

Harvest (auto-precipitation)

Biomass (protein/lipid and glycogen)

CO₂ sources (Flue gas)
Progress

- We have successfully engineered Synechococcus UTEX 2973 to produce limonene

- Limonene productivity at ~ 5mg/L/day.

- Limonene productivity by L525: 8.5 mg/L/day

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

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Pull strategy to increase carbon flux towards limonene

- A number of publications suggest IDI and GPPS are bottlenecks in terpene biosynthesis;
- Our previous results suggest that fusion of GPPS and LS could enhance limonene productivity;

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Breakthrough using 15% CO₂, 2% H₂O, 83% N₂, around 1 g of loosely packed material.

~40% lower performance than bench scale

Zhou’s group@TAMU
P and N recovery using mineral-hydrogel composites

**Ammonium Recovery capacity (mg/g)**

<table>
<thead>
<tr>
<th>Mineral hydrogel</th>
<th>La-magnetic biochar</th>
<th>As based Bentonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca/Mg-Alg</td>
<td>134.67 (24hr)</td>
<td>101.67</td>
</tr>
<tr>
<td>Ca/Mg-Alg-CaP</td>
<td>232.52 (48hr)</td>
<td>5.7</td>
</tr>
<tr>
<td>Ca/Mg-Alg-CaP, Stru</td>
<td>This study</td>
<td></td>
</tr>
<tr>
<td>40 mM Mg, 20 mM P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 mM Mg, 20 mM P, 20 mM N</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Dry weight of Ca/Mg-Alg-CaP, Stru: 0.082 g

- Struvite can recover phosphate and ammonium simultaneously
- With a longer time, we can form more CaP and struvite and recover P and N from nutrient-rich resources.
- Homogeneous precipitation of these minerals without hydrogels is lower than 10%

Jun’s group@WUSTL
Integration of hydrogel in algal system

P/N-rich water

CaP + Wollastonite mineral hydrogel composite

Tang’s group@WUSTL

CO₂ fixation

P Release as fertilizer

Photo-biorefinery

Fast growth in optimal PBR: 41 °C, 1500 μmol/m²/sec of light, 50mL, 5% CO₂

Integrated Modeling

\[
\frac{dX_A}{dt} = \frac{\mu_{\text{max}} A S_{\text{CO}_2}}{S_{\text{CO}_2} + K_{\text{CO}_2} I + K_N N} - k_{d1} X_A - DX_A \quad (\text{Eq 1})
\]

\[
\frac{dP_O}{dt} = Y_g \frac{dX_A}{dt} \quad (\text{Eq 2}) \quad (\text{Oxygen})
\]

\[
\frac{dP_L}{dt} = Y_L \frac{dX_A}{dt} + aX_A \quad (\text{Eq 3}) \quad (\text{Biofuel})
\]

\[
\frac{dN}{dt} = -Y_N \frac{dX_A}{dt} \quad (\text{Eq 4}) \quad (\text{N or P nutrient sources})
\]

\[
\mu_{\text{max}} = A e^{-Ea/RT} \quad (\text{Eq 5}). \quad (\text{Growth rate})
\]

The light function can be described as:

\[
I = \frac{I_0}{A(X_A + X_B)} (1 - e^{-A(X_A)}) \quad (\text{Eq 6})
\]

Jun, Tang and Yuan's groups@WUSTL
System modeling

- Life Cycle Assessment
  - Land usage
- Techno-economics assessment
- Market penetration
  - The market responses
- Integrated market analysis
  - Byproducts and substitution

Pistikopoulos and McCarl’s groups@TAMU&WUSTL
Future Plans

• Further strain engineering to improve photosynthesis efficiency, biomass and high value product yield
• Optimization of sorbents by covalently attaching amines
• Examine a high dose of composites to recover N and P and leave the treated water to have low total N and P.
• Nutrient (N, P) tests for algal growth with struvite hydrogels
• System integration and outdoor testing
Future Plans

- Multiscale scenario Analysis: to identify synergies between disparate value chains, find optimal network configuration, and determine potential bottlenecks
- Integrate ML model and process model
- TEA/LCA
Our Team

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

TAMU Chemistry
Amine-based porous sorbent advancement

TAMU Agriculture Economics
Life cycle analysis and environmental analysis

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

NCCC at Southern Company
Scale up and on-site testing

Dai
Pistikopoulos
Chemical Engineering
System modeling and TEA

McCarl
Zhou
Yuan
Jun
Tang
Morten

ATM
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• Questions?