Carbon Utilization Efficiency in Marine Algae Biofuel Production Systems Through Loss Minimization and Carbonate Chemistry Modification

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March 2021

Algae Platform Review

DOE Bioenergy Technologies Office (BETO)
2021 Project Peer Review

This presentation does not contain any proprietary, confidential, or otherwise restricted information

WBS 1.3.2.440

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Project Overview

This team grew out of ongoing work with MAGIC (WBS 1.3.5.310), but represents a smaller group with one new member who brings specialized experience

Our focus here is to build on substantial team experience associated with outdoor algae cultivation and TEA/LCA of algae biofuels to develop and test approaches to minimize CO_2 use and losses and to enhance overall algae productivity

Our goal: ***Demonstrate enhanced algal growth with an overall reduced CO_2 requirement at an industrially relevant scale with a system that has improved economics and environmental impacts***

<u>Success means improved algae biofuel economics and broader siting potential</u>

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1 – Management (Structure)

Task 2: Cultivation / Strain assessment
Task 4: Integration / Demonstration

Task 3: CO_2 conversion
Task 4: Integration / Demonstration

Task 5: TEA / LCA & System Modeling

- Monthly all consortium calls, weekly within task meetings (other topic meetings in between)
- *Basecamp* project management (calendar, tasks, shared documents, etc.)
- Tasks and Milestones in SOPO (identify responsible party) and include SMART goals
- Group decisions by consensus
- Prime (Duke) has final responsibility

Major project risks: (1) performance of algae, (2) performance of converter, (3) uneven progress

2 - Approach – Major Tasks

Goal*: Demonstrate enhanced algal growth on high DIC water at industrially relevant scale with a system that has improved economics and environmental impacts*

- Task 1: Verification
- **Task 2: Strain assessment** (Cultivation) - ΣCO_2 threshold and HCO_3 enhancement (G/NG: ID of strains, enhancement, C use efficiency)
- **Task 3: CO_2 conversion** CO_2 to HCO_3 using $CaCO_3$ (G/NG: improvements in CO_2 conversion)
- **Task 4: Demonstration** - integrated system, industrially relevant scale
- **Task 5: TEA/LCA & System Modeling** (G/NG: incorporation of data)

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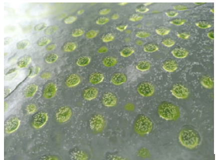
3 - Impacts

- **Productivity is the #1 driver of the economics of the economics of algae biofuels**
  - *demonstration of productivity enhancement would make algae-derived biofuels more economically feasible*
- **CO_2 limits siting of economically feasible algae biofuel production**
  - *Demonstration of conversion of CO_2 to HCO_3 would provide a CO_2 "integrator", expanding locations*
  - *Demonstration of uncoupling of CO_2 production and algae use would greatly expand locations*
  - *Identification of strains that have reduced [ΣCO_2] requirements could greatly reduce (or even eliminate) the requirement for CO_2, greatly expanding locations and lowering costs*
- **Results disseminated through peer-reviewed publications and other public presentations**



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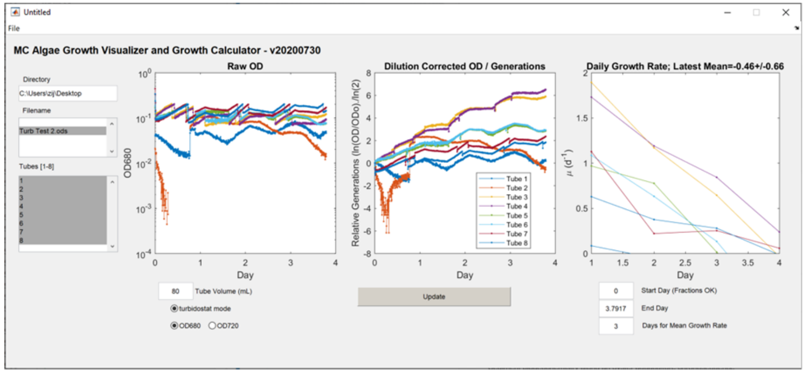
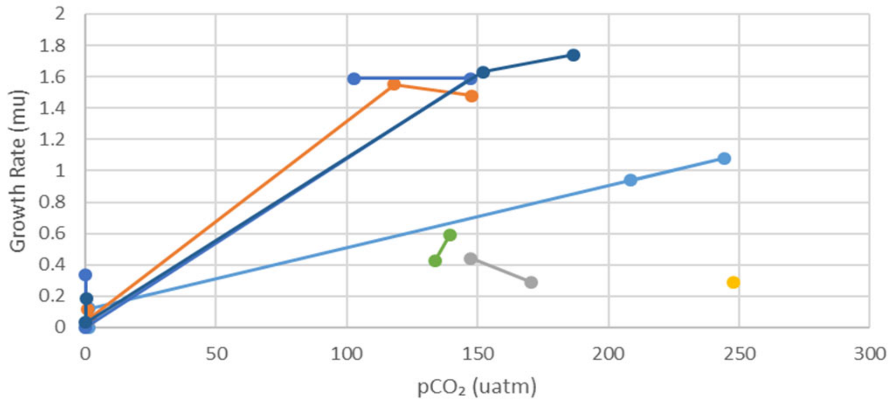
4 - Progress and Outcomes

Task 2: Strain assessment: *ID of strains with reduced pCO_2 threshold for growth*





In progress….but we have found some strains that grow fine at very low pCO_2!

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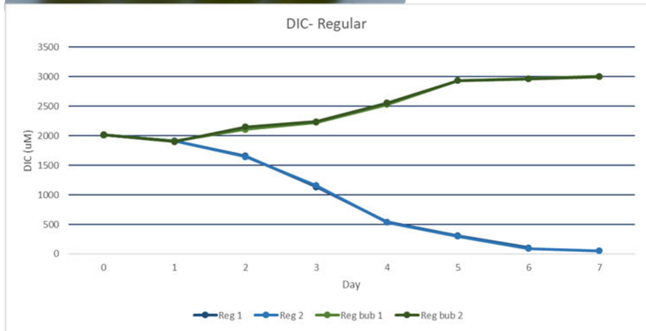
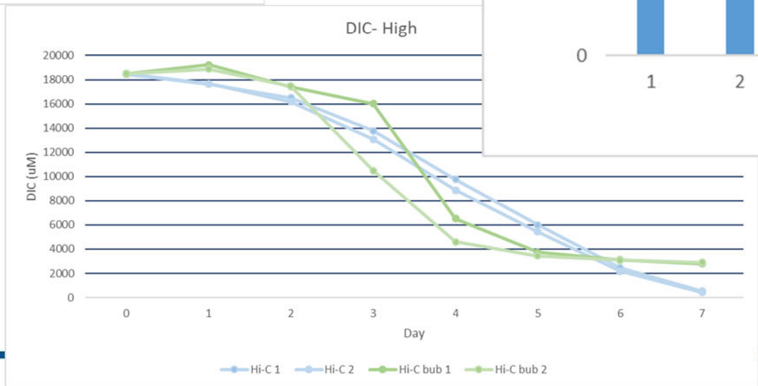
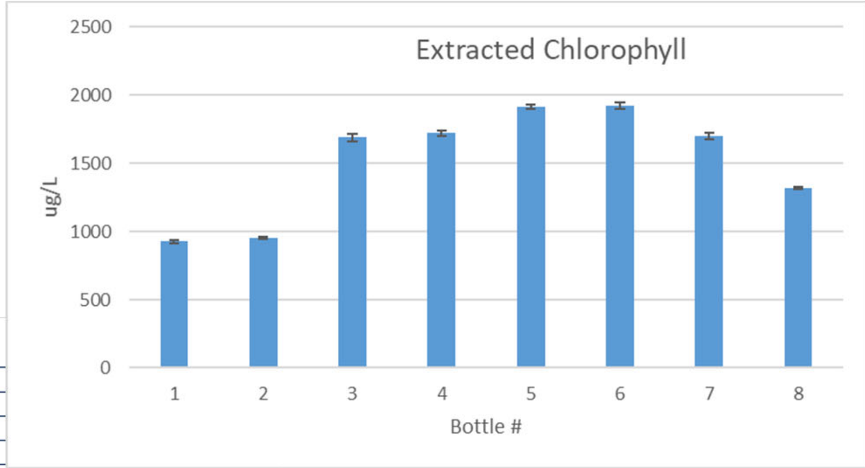
Task 2: Strain assessment: *Growth (enhancement) on high DIC waters*





In progress….multiple strains assessed.
At least one strain does better on high DIC than CO_2 bubbling



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Task 3 – CO_2 Conversion

Task Summary - The goal of this task is to demonstrate the "conversion" of CO_2 to Ca^{2+} + $2HCO_3^-$ using $CaCO_3$ mineral as a source of DIC with the hypothesized intent of increasing efficiency and lowering cost of algae culture. This task is based on an existing LLNL/DOE patent, but importantly has not yet been demonstrated for algae growth. In BP2, this task will involve construction of a pilot scale converter for testing with small scale (~100 L) raceway ponds.

Subtask 3.1: CO_2 conversion in lab/pilot (Q2-Q4)
A prototype CO_2 conversion system will be built in the laboratory and optimized to convert CO2 to HCO_3 using $CaCO_3$. This system will be optimized (in absence of algae) and delivered for trials for subtask 4.1

Milestone 3.1.1 CO_2 conversion in lab/pilot – start construction (m, Q3)
Milestone 3.1.2 CO_2 conversion in lab/pilot – working prototype (DP, Q4)

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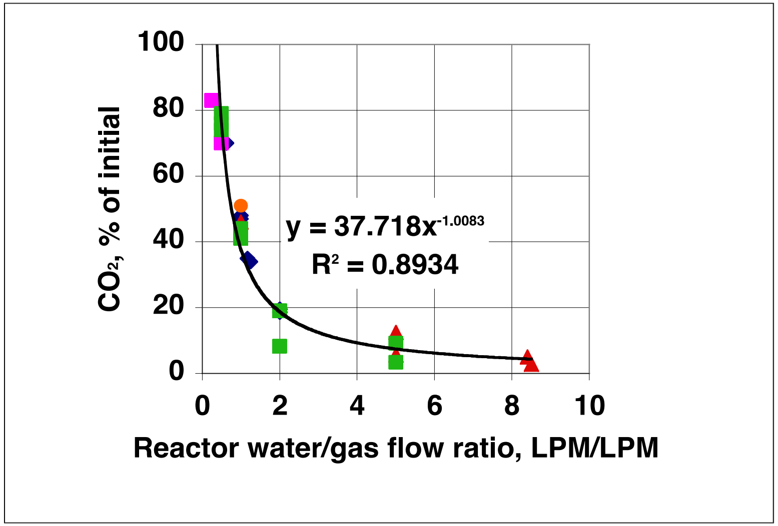
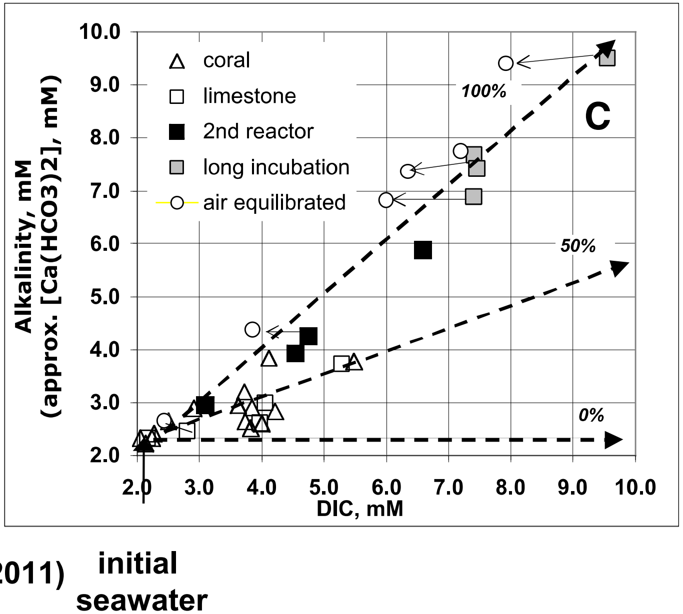
Task 3: Concept background

Spontaneous reaction under elevated CO_2 (Rau and Caldeira 1999, etc.):
$CO_2 + H_2O(sw) + CaCO_3$ (limestone) -----> $Ca^{2+} + 2HCO_3^- (+ CO_3^- + CO_2)$
with the intent of capturing and storing CO_2 from point sources





(from: Rau, *Environmental Science and Technology*, 2011)

So, could the high DIC seawater generated be used for cost-effectively supplying algal C substrate?

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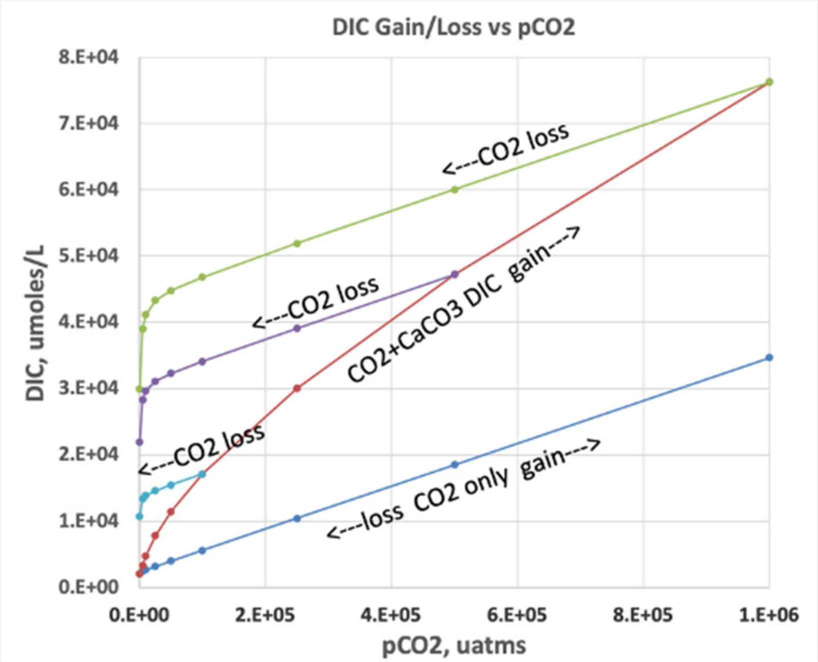
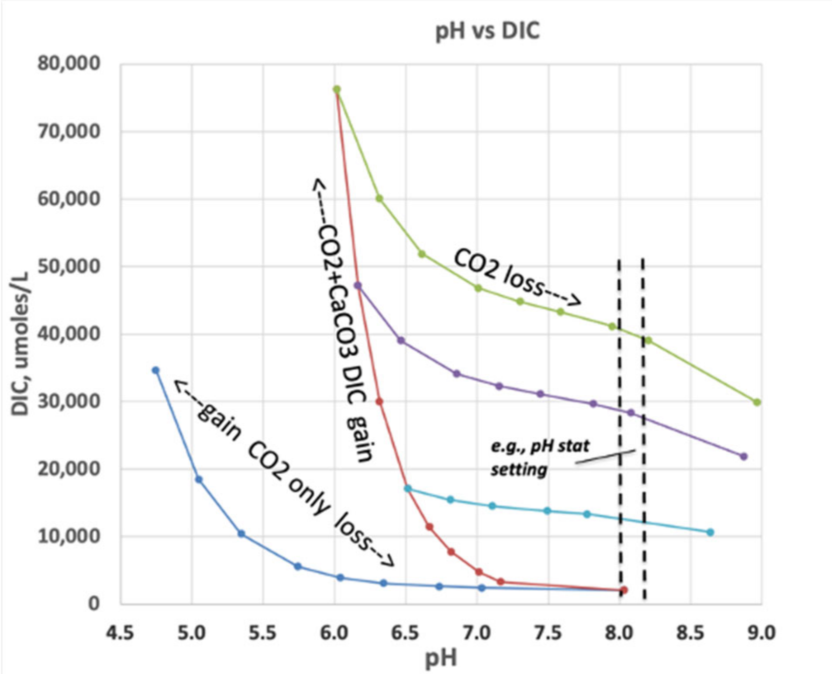
Task 3: DIC Modeling

Significant gain in DIC expected per amount of CO_2 added and pH achieved, relative to straight CO_2 bubbling:





Modeled DIC concentrations <u>at equilibrium</u> with a given pCO_2 and thus pH, with and without the presence of $CaCO_3$. Trajectories of DIC gain followed by CO_2 loss (degassing, algal uptake) are shown. Modeled using CO_2SYS.

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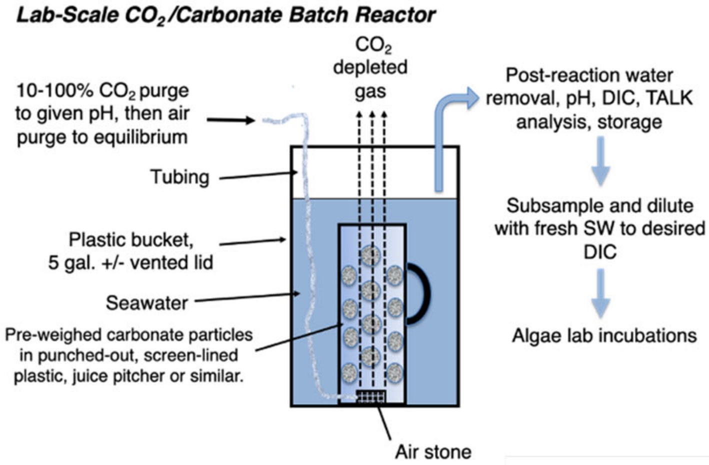
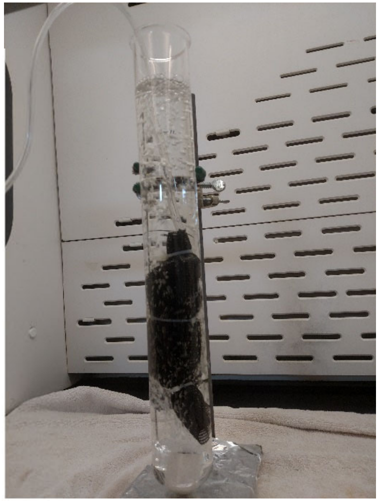
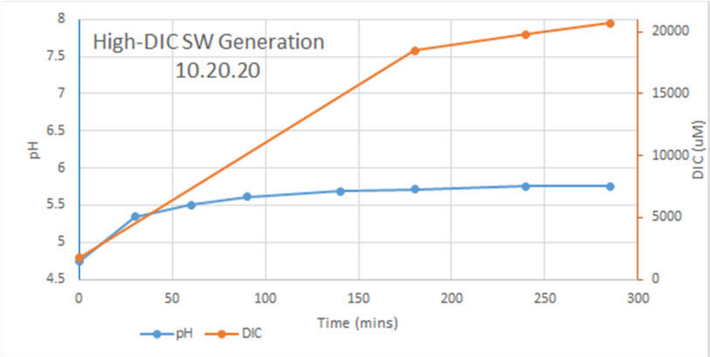
Task 3: DIC Generation Experiments

Various schemes used for initial DIC generation at lab scale



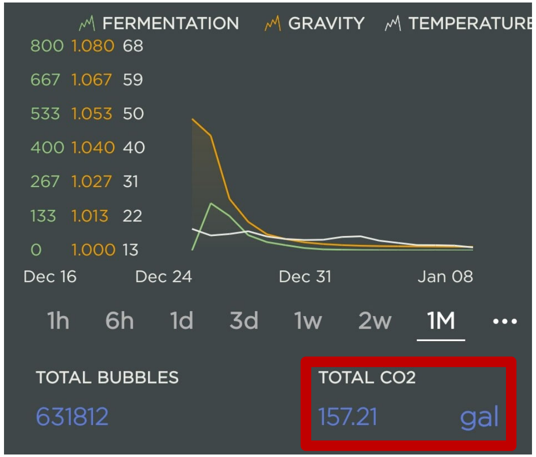




Generation of air stable >20mM ΣCO_2

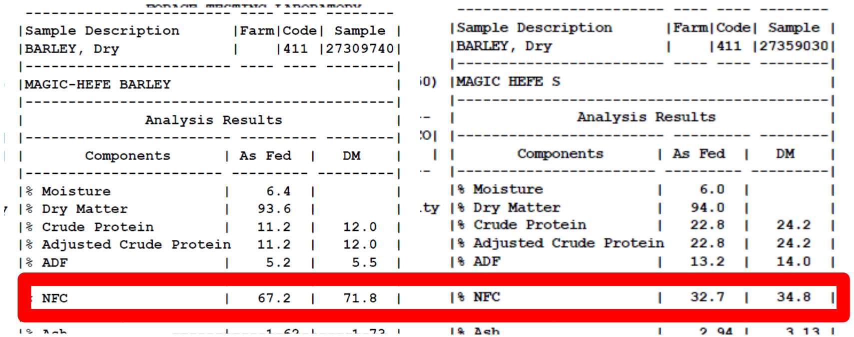
Task 4: Integration

Collection of commercial brewery CO_2, converting to high DIC solution, growing algae



~157 gallons CO_2 ≈ 0.5 kg C

Raw grain



Sample Description	Farm	Code	Sample
BARLEY, Dry		411	27309740
MAGIC-HEFE BARLEY			

Analysis Results

Components	As Fed	DM
% Moisture	6.4	
% Dry Matter	93.6	
% Crude Protein	11.2	12.0
% Adjusted Crude Protein	11.2	12.0
% ADF	5.2	5.5
NFC	67.2	71.8
% Ash	1.62	1.73

Spent grain

Sample Description	Farm	Code	Sample
BARLEY, Dry		411	27359030
MAGIC HEFE S			

Analysis Results

Components	As Fed	DM
% Moisture	6.0	
% Dry Matter	94.0	
% Crude Protein	22.8	24.2
% Adjusted Crude Protein	22.8	24.2
% ADF	13.2	14.0
% NFC	32.7	34.8
% Ash	2.94	3.13

4 kg of grain lost ~35% of mass in sugars → ~0.5 kg C

Prototyped a "femtoscale brewery", quantified CO_2 release, achieved mass balance with inputs

Next steps: collection / conversion of CO_2; trial algae growth

Task 5: ***Commercialization Analysis (TEA/LCA) - GOALS***

Task 5 – TEA/LCA (B&D and Bucknell)
The overall goal of this task is to ground experimental data in a larger commercialization and biofuel development framework to evaluate economic and environmental performance.

TEA/LCA efforts will focus on integrating CO_2 threshold reductions and CO_2 conversion results for algae grown at ~5000 L scale for end-to-end demonstration (CO_2 waste stream to algae growth).

Milestones: **Pending Final Results from Tasks 2 and 4**
5.1.1 TEA/LCA integration of milestone 2.1.2 (strain assessment) data (DP, Q6)
5.2.1 TEA/LCA integration of milestone 4.1.1 data (DP, Q6)
5.3.1 TEA/LCA integration of milestone 4.2.2 data - end (MS, Q12)
5.4.1 TEA/LCA integration of milestone 4.3.1 data - end (MS, Q12)

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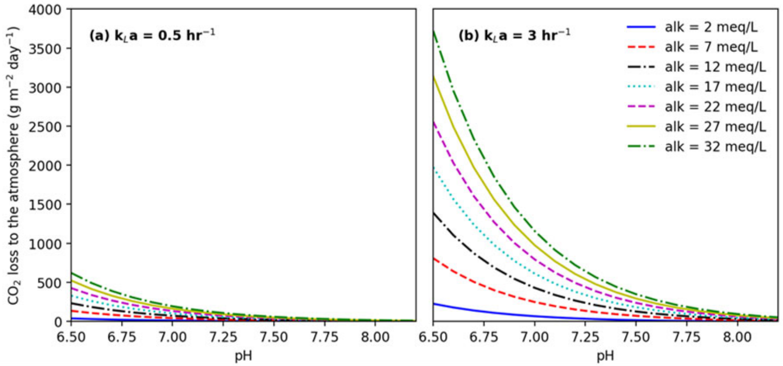
Task 5: ***Commercialization Analysis (TEA/LCA) - RESULTS***



<u>Modeling carbonate chemistry w/o algal growth (Bucknell)</u>

CO_2 loss is a function of pH, alkalinity, and the mass transfer rate coefficient, k_{La}.

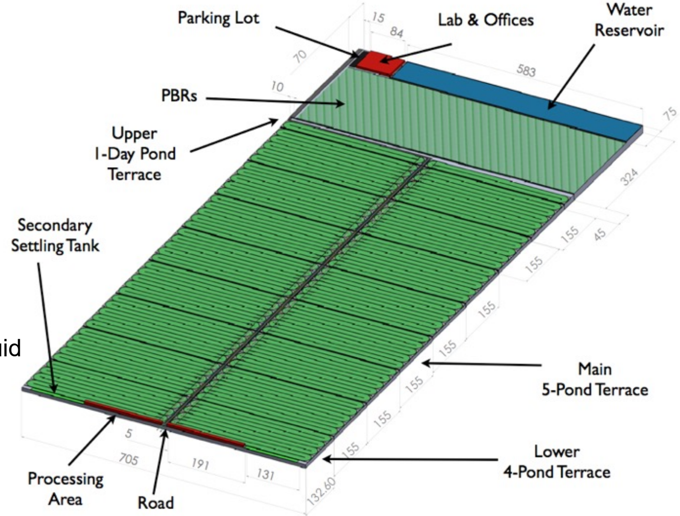
- As pH decreases, and k_La and alkalinity increase, CO_2 loss increases

<u>Process Modeling (B&D)</u>

Design of DIC generation system in 100-ha facility to replace conventional CO_2.

$$ln\left(\frac{c_i}{c_{out}}\right) = \frac{V}{F} k_v (1 - \epsilon)$$

C = concentration of reactant in entering and leaving liquid
V= volume of trickle bed packed with catalyst
F = liquid flow rate
K_v = 1st order reaction rate constant per vol. of catalyst
ϵ = void fraction in catalyst bed



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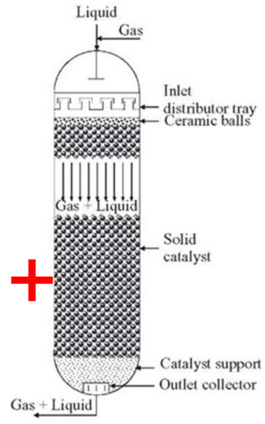

Trickle-bed reactor (Co-current flow)

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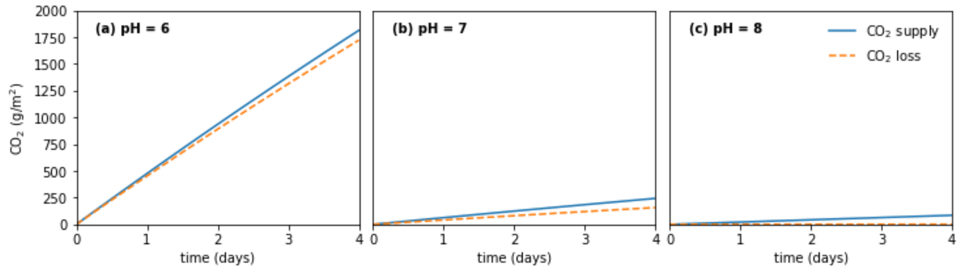
Task 5: ***Commercialization Analysis (TEA/LCA) - Ongoing***

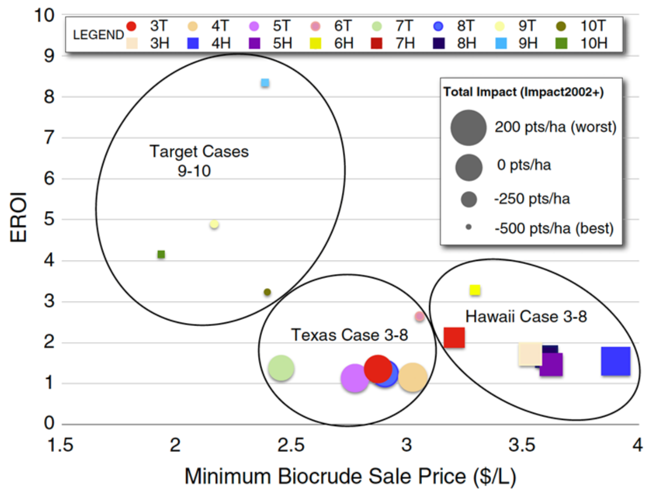


Modeling carbonate chemistry with algal growth (Bucknell)

Modeled CO_2 losses from open raceway ponds with constant algae growth.

- As pH increases from 6 to 8, loss of CO_2 decreases dramatically, indicating that CO2 losses can be minimized by careful control of pH
- This model is a basis for modeling DIC system

C.M. Beal et al. / Algal Research 10 (2015) 266–279

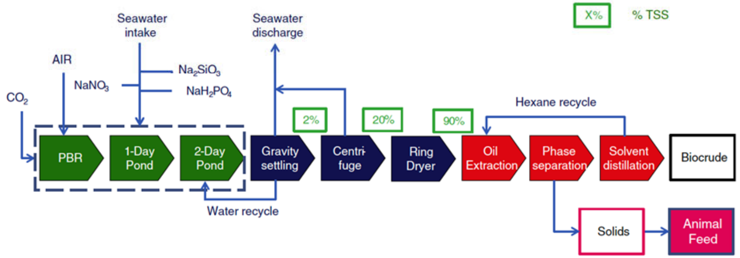


Process Modeling (B&D)

Conduct TEA/LCA of algae facility with DIC generation system at commercial scale based on experimental results from Task 2-4 to evaluate economic and environmental impacts

Technology Process Lineup: Case 1

Dry route to fuel and feed



Analysis Example:
Beal et al., 2015

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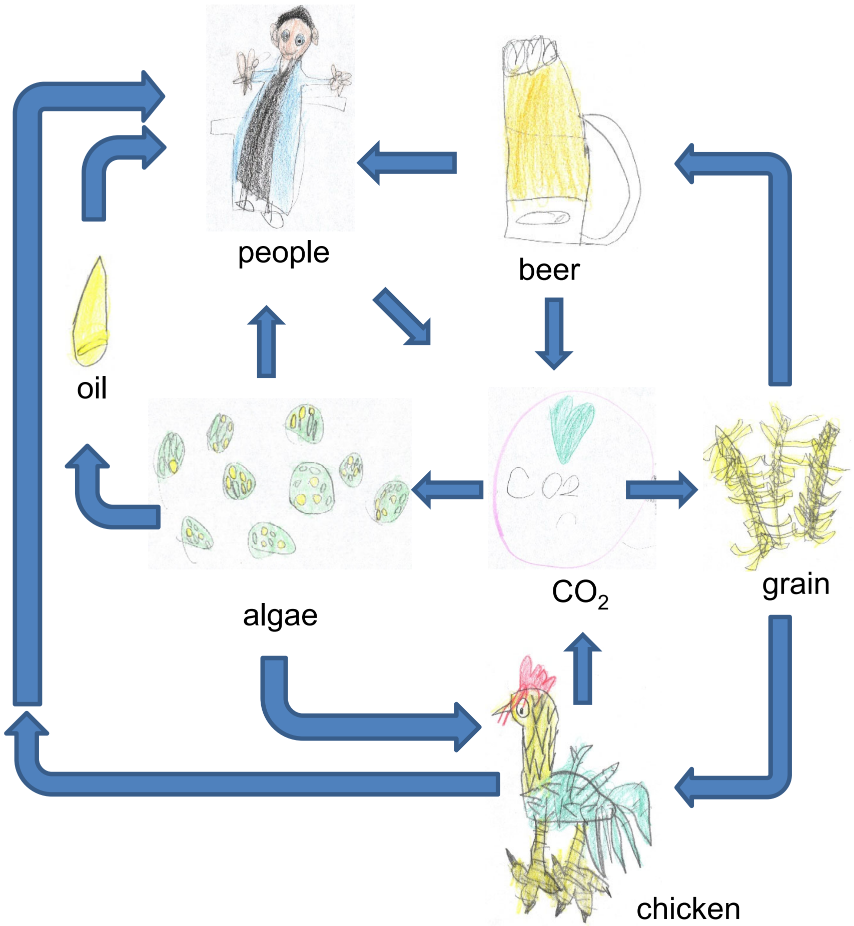
MAGIC-C(ircular Carbon) Summary



Task 2

- Demonstration of algae strains that grow under reduced ΣCO_2 environments → reduced CO_2 losses
- Demonstration of algae uptake and growth on converted carbon → reduced CO_2 losses, enhanced growth

Task 3

- Demonstration of high DIC waters from CO_2 + limestone reactor
- Modeling of improved high DIC generation process

Task 4

- Demonstration of biogenic CO_2 production and quantification (with mass balance)

Task 5

- Working model of carbonate chemistry with/without algae
- Process model of algae facility incorporating DIC generation

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MAGIC-C (EE0008518) - Quad Chart Overview

Timeline (approved period)

- October 1, 2019
- Sept 30, 2021

	FY20 Costed	Total Award
DOE Funding	*$183,243*	$1,511,515
Project Cost Share	*$37,395*	$416,780 (22%)

Project Partners

Partners: Bucknell, B&D Engineering, UCSC

Project Goals

Strain assessment of key algae strains - identify the pCO_2 threshold for growth, quantify the growth enhancement on high DIC medium, translate/verify these results in outdoor environment

CO_2 conversion – demonstration of conversion of CO_2 to bicarbonate at multiple scales

Integrated system – demonstration of coupled DIC generation (ultimately from industrial CO_2) + algae growth

TEA/LCA – translation of laboratory and field findings to nth plant design, TEA/LCA of findings to quantify impacts on environment and economics

End of Project Milestone

Demonstrate enhanced algal growth on high DIC water at industrially relevant scale with a system that has improved environmental impact and economics

Funding Mechanism

DE-FOA-0001908, Efficient Carbon Utilization in Algal Systems, 2018

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Thank you

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http://www.duke.edu/~zij
http://www.ml.duke.edu/webcam/algae/

We're a team!

B&D

Bucknell University

U.S. DEPARTMENT OF ENERGY
EERE #DE-EE0008518

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Additional Slides

Publications

Doo SS, Kealoha A, Andersson A, Cohen AL, Hicks TL, Johnson ZI, Long MH, McElhany P, Mollica N, Shamberger KEF, Silbiger NJ, Takeshita Y, Busch DS (2020). The challenges of detecting and attributing ocean acidification impacts on marine ecosystems. ICES Journal of Marine Science. DOI: https://doi.org/10.1093/icesjms/fsaa094

Loftus SE, Hunt DE, Johnson ZI (2020). Reused cultivation water from a self-inhibiting alga does not inhibit other algae but alters their microbiomes. Algal Research 51: 102067. DOI: https://doi.org/10.1016/j.algal.2020.102067

Hall ER, Wickes L, Burnett LE, Scott GI, Hernandez D, Yates KK, Barbero L, Reimer JJ, Baalousha M, Mintz J, Cai W-J, Craig JK, DeVoe MR, Fisher WS, Hathaway TK, Jewett EB, Johnson Z, Keener P, Mordecai RS, Noakes S, Phillips C, Sandifer PA, Schnetzer A, Styron J (2020). "Acidification in the U.S. Southeast: Causes, Potential Consequences and the Role of the Southeast Ocean and Coastal Acidification Network." Frontiers in Marine Science 7. https://doi.org/10.3389/fmars.2020.00548

Marra JF, Barber RT, Barber E, Bidigare RR, Chamberlin WS, Goericke R, Hargreaves BR, Hiscock M, Iturriaga R, Johnson ZI, Kiefer DA, Kinkade C, Knudson C, Lance V, Langdon C, Lee Z-P, Perry MJ, Smith WO, Vaillancourt R, Zoffoli L (2020). A database of ocean primary productivity from the 14C method. Limnology and Oceanography Letters. https://doi.org/10.1002/lol2.10175

Patents, Awards, and Commercialization

No patents have been applied for based on the work supported by DOE.

No special awards have been received.

All primary results from this project are being published in the open, peer-reviewed literature. The publications from this project – cited above – provide a comprehensive and detailed analysis of commercialization potential. This information will be available to anyone with access to the open literature.