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Industrial Decarbonization

Gap and opportunity for ammonia, bioproducts, and cement

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Senior Member of the Technical Staff

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U.S. DEPARTMENT OF ENERGY

NNSA

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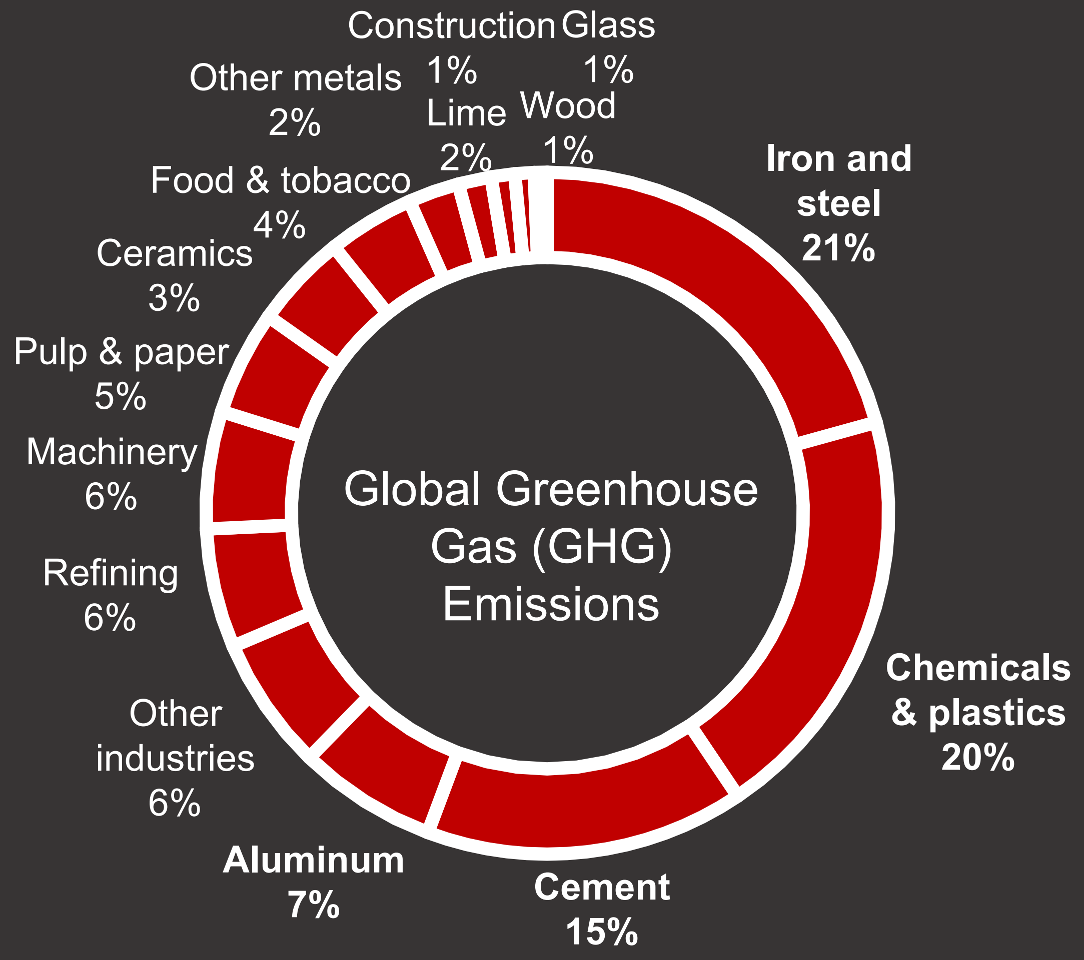
Research Interests



"The anticipated bottlenecks and ***constraints – in energy, water*** and other critical natural resources and infrastructure – are bringing ***new political and economic challenges***, as well as new and hard-to-manage instabilities.''

Research…

Seeks to understand the ***sustainability uncertainties and trade-offs of water, energy, and decarbonization systems*** and has developed new models, experimental data, and approaches to achieve a ***design and experiment loop between laboratory-scale experimentation and industrial-scale systems***

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Lee, B., & Ellinas, L. (2010). Water and energy security in tackling the world water crisis: reshaping the future of foreign policy. The Foreign Policy Centre and Nestle.
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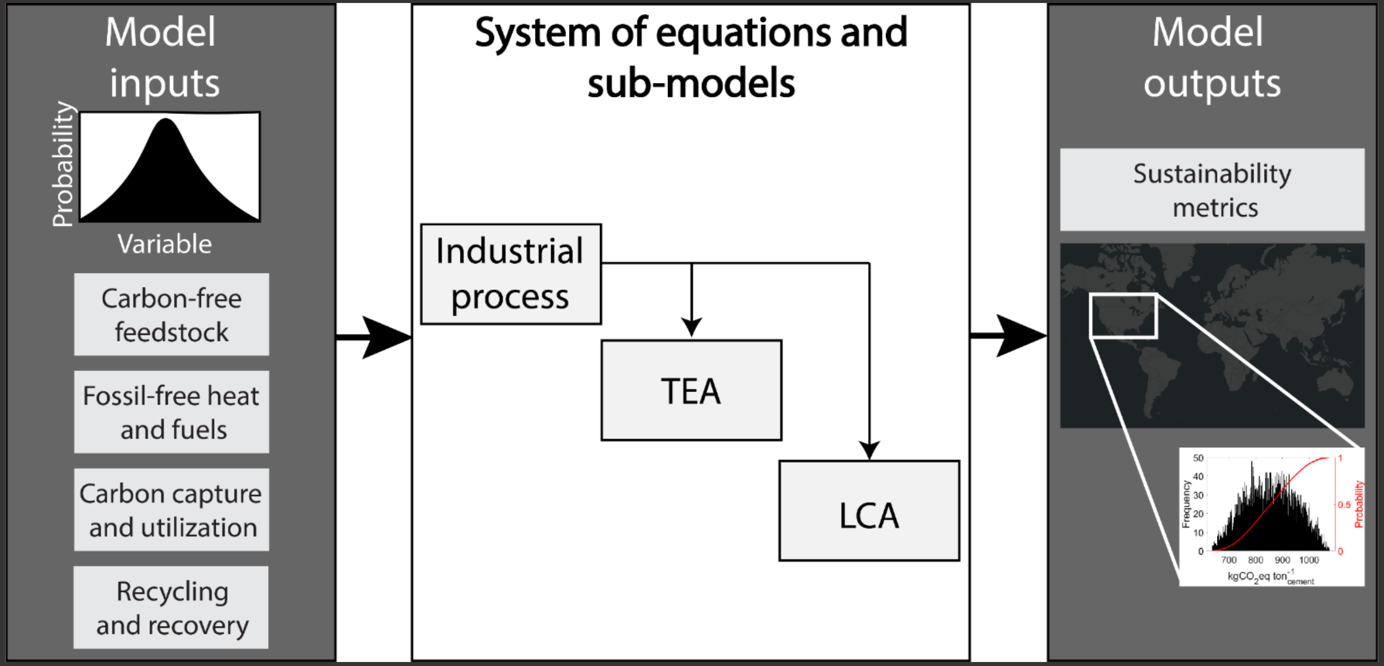
Rissman, Jeffrey, Chris Bataille, Eric Masanet, Nate Aden, William R. Morrow III, Nan Zhou, Neal Elliott et al. "Technologies and policies to decarbonize global industry: Review and assessment of mitigation drivers through 2070." Applied Energy 266 (2020): 114848.

Current work

Goal:
We seek to identify ***carbon-neutral and carbon-negative processes to decarbonize the U.S. economy*** within the opportunity space of ***i) hydrogen and ammonia production, ii) bioresources to bioproducts, and iii) cement***

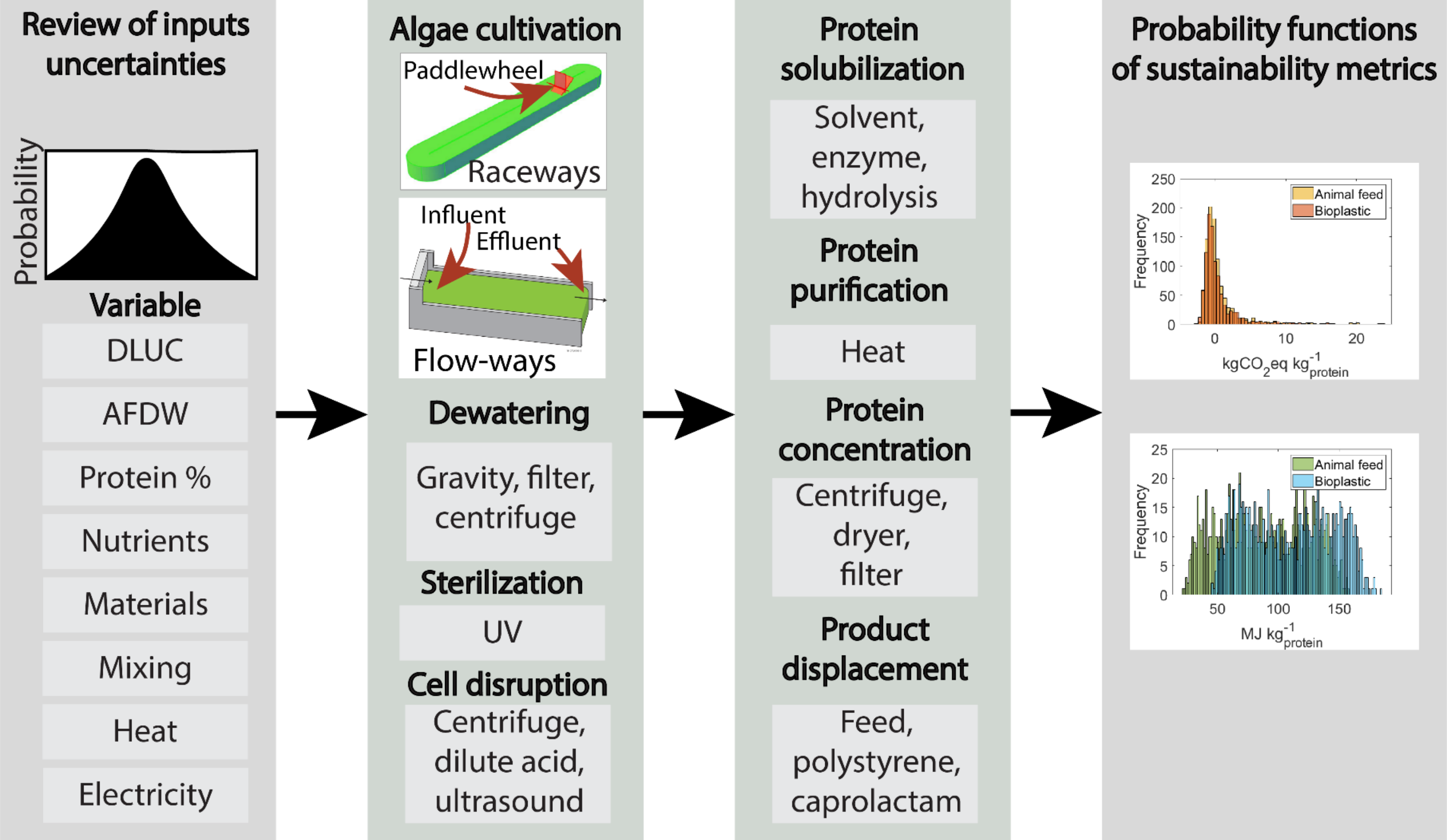


Approach:

- Our ***decarbonization framework consists of four categories***: i) carbon-free feedstocks and chemical processes, ii) fossil-free heating and electrification, iii) novel carbon sequestration, and iv) recycling, repurposing, and recovery
- The System of equations and outputs consisting of ***process and dynamical formulations, and probabilistic Techno-Economics Analysis (TEA)*** and ***Life Cycle Assessment (LCA)*** enable us to derive robust sustainability metrics

Ho, Clifford K., Carlos Quiroz Arita, Anthe George, Kristin Hertz, Jessica Rimsza, Erik D. Spoerke, and Andrea Ambrosini. "A Lifecycle Framework for Industrial Decarbonization." In *Proceedings of the American Solar Energy Society National Conference*, pp. 161-167. Springer, Cham, 2022.

Gap and opportunity space for decarbonization: bioproducts



To assess the ***risk associated with algal-protein bioproducts*** input variations, we used a Monte Carlo methodology to ***simulate scenarios with probabilities of sustainability performance:***

- Life cycle energy
- Life cycle carbon dioxide equivalent (CO_2eq) emissions

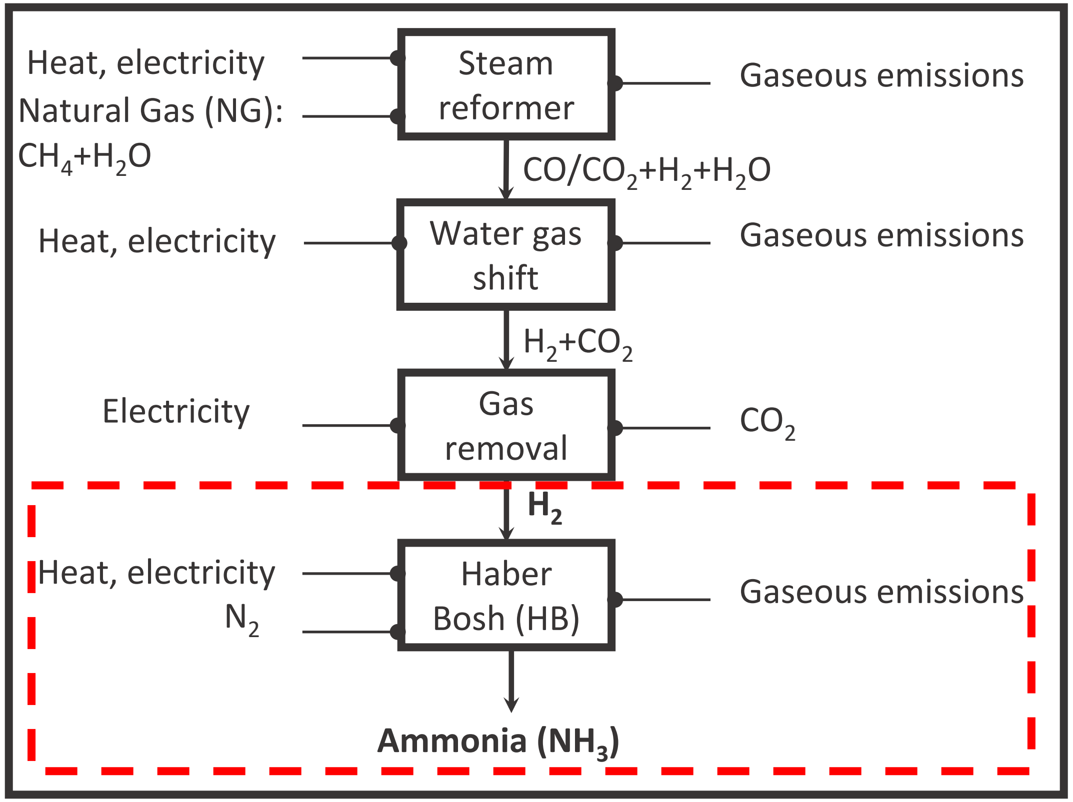
Life-cycle energy and ***CO_2eq emissions*** considers the energy use of ***direct, indirect, and supply chain*** processes

Direct land-use change (**DLUC**) in barren land areas

Ash-free dry weight (**AFDW**) algae productivity

Quiroz-Arita, C., Shinde, S., Kim, S., Monroe, E., George, A., Quinn, J. C., Nagle, N., Knoshaug, E., Kruger, J.S., Dong, T., Pienkos, P., Laurens, L.M., Davis, R. W. (2022). Bioproducts from high-protein algal biomass: An economic and environmental sustainability review and risk analysis. Sustainable Energy & Fuels.

Gap and opportunity space for decarbonization: bioproducts - nutrients



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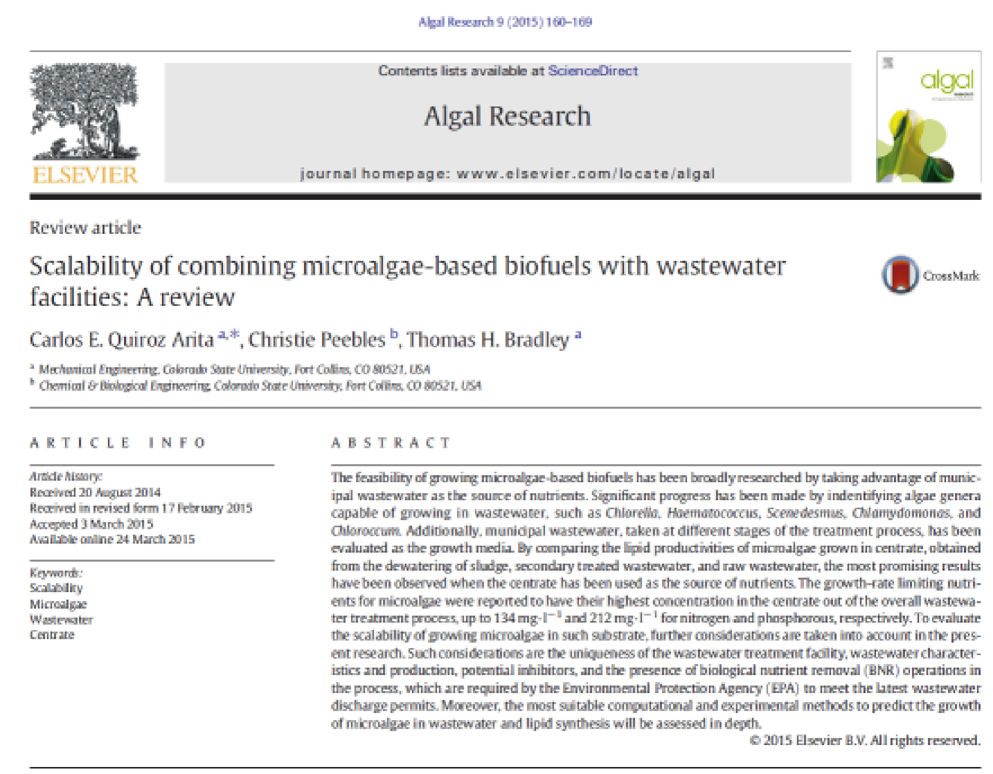
Michael C. Johnson, Ignasi Palou-Rivera, Edward D. Frank. Energy consumption during the manufacture of nutrients for algae cultivation. August 19, 2013.

de la Calle, A., et al., Solar-thermochemical ammonia production: system design and techno economic analysis, in 27th SolarPACES Conference. 2021.

- Conventional ***production of ammonia from Natural Gas***, demands heat and pressure energy that results in 450-550 kJ mol-NH_3^{-1} and ***emissions at 1.5 to 2.6 ton CO_2eq ton NH_3^{-1}***

- Recent studies reveal that ***resources used in the production of H_2***, i.e., natural gas and oil production and transmission, represent ***8 to 12% of global methane emissions, which exacerbates life cycle CO_2 emissions from ammonia***

Gap and opportunity space for decarbonization: bioproducts - nutrients



Algal Research 9 (2015) 160–169

Contents lists available at ScienceDirect

Algal Research

journal homepage: www.elsevier.com/locate/algal

ELSEVIER

Review article

Scalability of combining microalgae-based biofuels with wastewater facilities: A review

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ABSTRACT

The feasibility of growing microalgae-based biofuels has been broadly researched by taking advantage of municipal wastewater as the source of nutrients. Significant progress has been made by indentifying algae genera capable of growing in wastewater, such as *Chlorella*, *Haematococcus*, *Scenedesmus*, *Chlamydomonas*, and *Chlorococcum*. Additionally, municipal wastewater, taken at different stages of the treatment process, has been evaluated as the growth media. By comparing the lipid productivities of microalgae grown in centrate, obtained from the dewatering of sludge, secondary treated wastewater, and raw wastewater, the most promising results have been observed when the centrate has been used as the source of nutrients. The growth-rate limiting nutrients for microalgae were reported to have their highest concentration in the centrate out of the overall wastewater treatment process, up to 134 mg·l^{-1} and 212 mg·l^{-1} for nitrogen and phosphorous, respectively. To evaluate the scalability of growing microalgae in such substrate, further considerations are taken into account in the present research. Such considerations are the uniqueness of the wastewater treatment facility, wastewater characteristics and production, potential inhibitors, and the presence of biological nutrient removal (BNR) operations in the process, which are required by the Environmental Protection Agency (EPA) to meet the latest wastewater discharge permits. Moreover, the most suitable computational and experimental methods to predict the growth of microalgae in wastewater and lipid synthesis will be assessed in depth.

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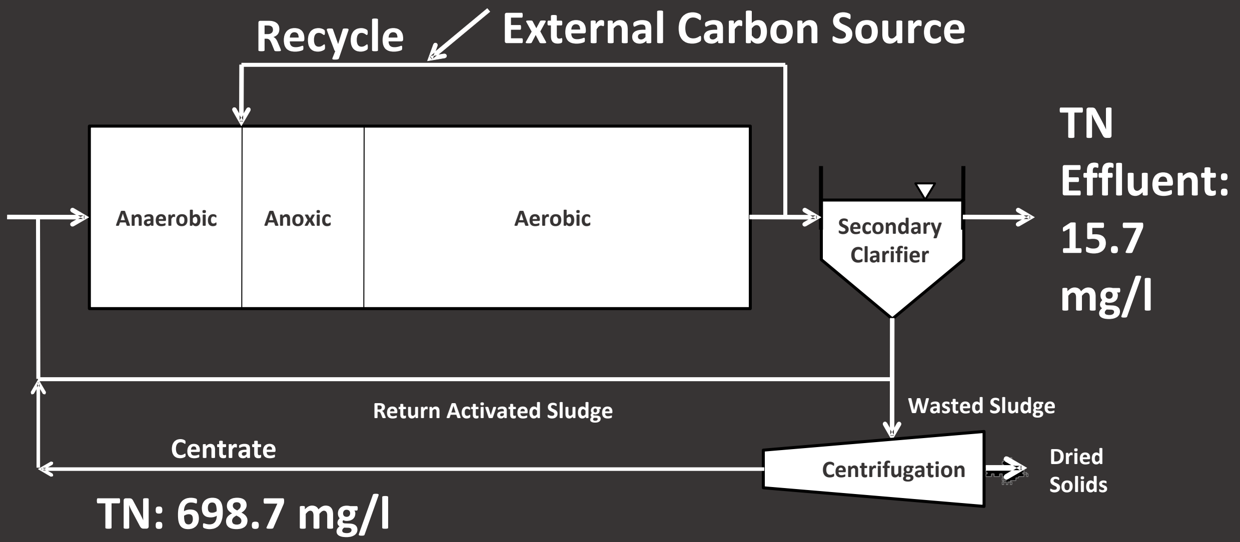
Arita, Carlos E. Quiroz, Christie Peebles, and Thomas H. Bradley. "Scalability of combining microalgae-based biofuels with wastewater facilities: a review." *Algal research* 9 (2015): 160-169.

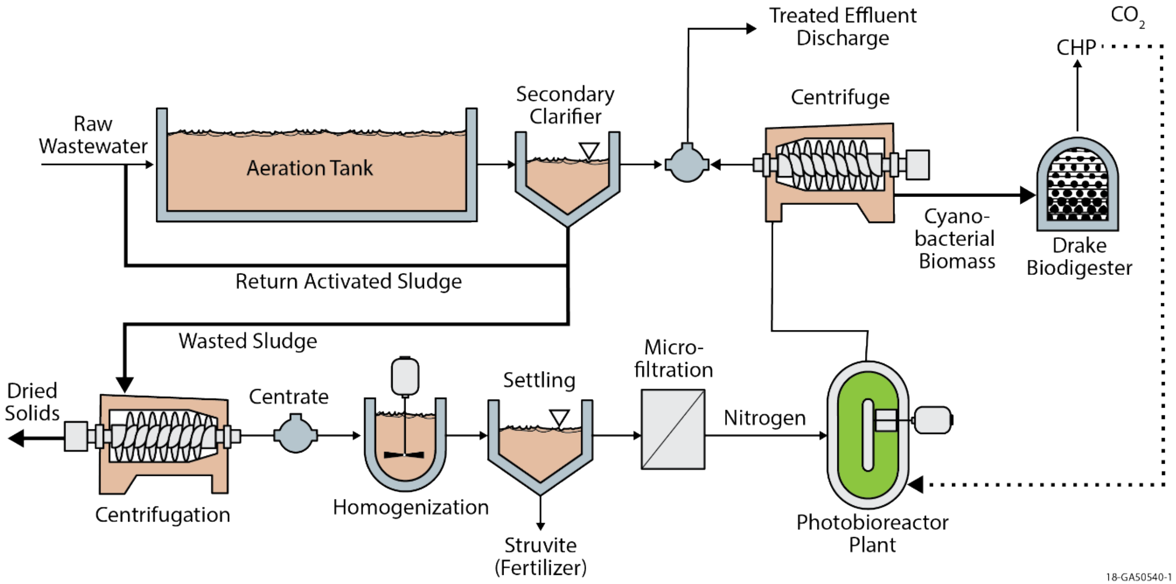
Challenges of Wastewater Treatment Facilities (WWTF):

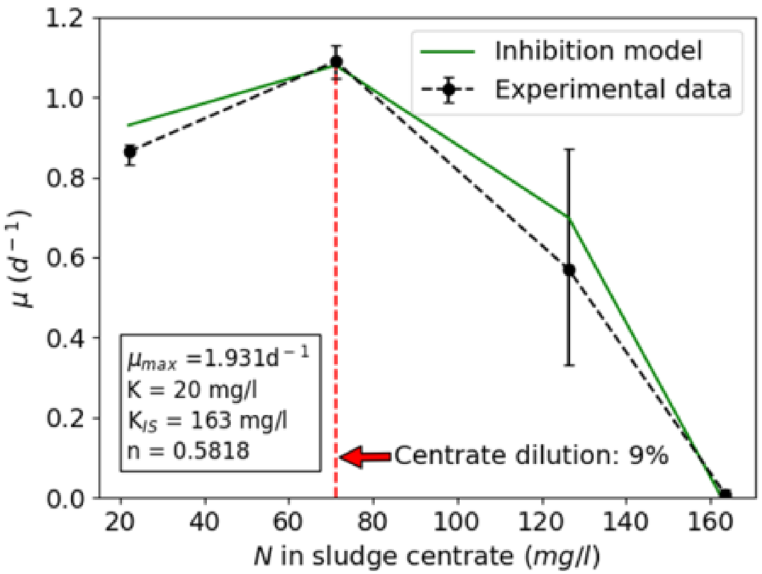
- Nitrogen ***(7mg.l^{-1})*** and phosphorous ***(0.7mg.l^{-1})*** **limits**
- Sidestream technologies ***(centrate)***
- Energy requirements



Adapted from Tchobanoglous, 2003 and Quiroz *et. al.* 2015

Gap and opportunity space for decarbonization: bioproducts - nutrients

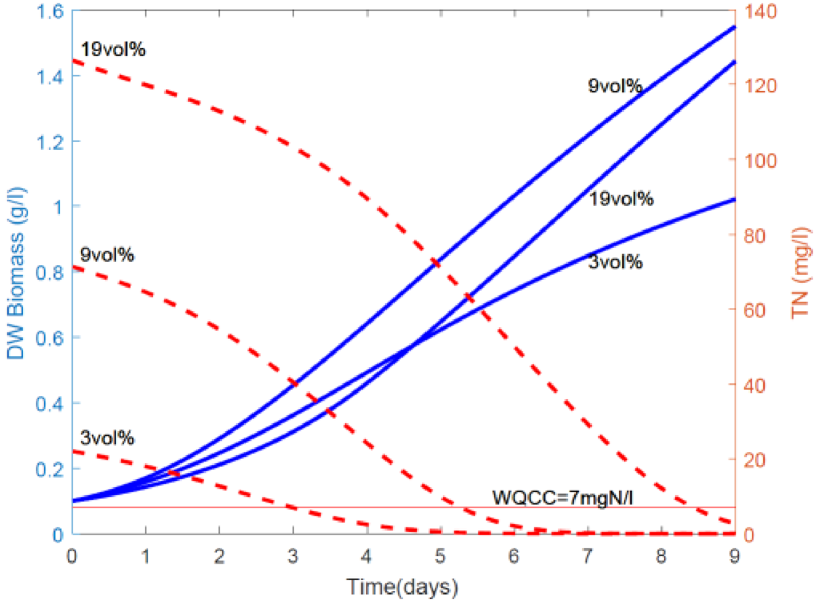


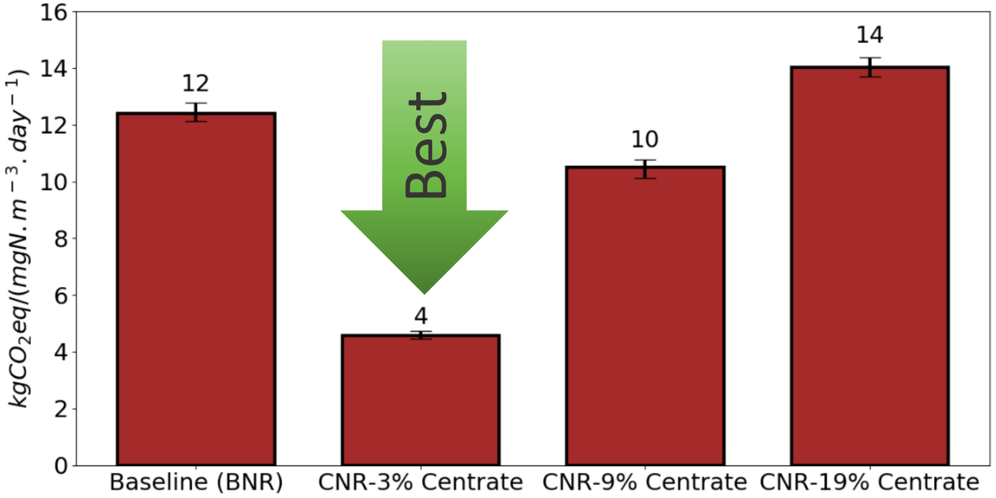


- The WW treatment system was validated in a laboratory environment at optimal nutrients, temperature, and radiation at TRL 4.
- We studied the mechanisms of WW treatment and ***inhibition of the strain Synechocystis sp. PCC6803 at high intracellular concentrations of nutrients*** due to damage to photosystem II.
- The ***highest μ value*** of *Synechocystis* sp. PCC6803 was obtained at sludge centrate concentration of ***71 mg TN l^{-1}***
- ***Centrate completely inhibits the growth*** of *Synechocystis* sp. when is greater than ***163 mg TN l^{-1}***

Adapted from: **Quiroz-Arita, Carlos**, John J. Sheehan, and Thomas H. Bradley. "Life cycle net energy and greenhouse gas emissions of photosynthetic cyanobacterial biorefineries: Challenges for industrial production of biofuels." Algal research 26 (2017): 445-452.

Gap and opportunity space for decarbonization: bioproducts - nutrients





To meet the Water Quality Criteria for the State of CO (WQCC) and produce dry weight (DW) biomass for co-digestion, the cultivation times are:

- Centrate dilutions at 3vol%: 4 days
- Centrate dilutions at 9vol%: 7 days
- Centrate dilution at 19 vol%: 9 days

$$GHG = \frac{(CO_{2,out} - CO_{2,in})}{N_r}$$

Where;

GHG = Greenhouse gas emissions to nitrogen removal ratio

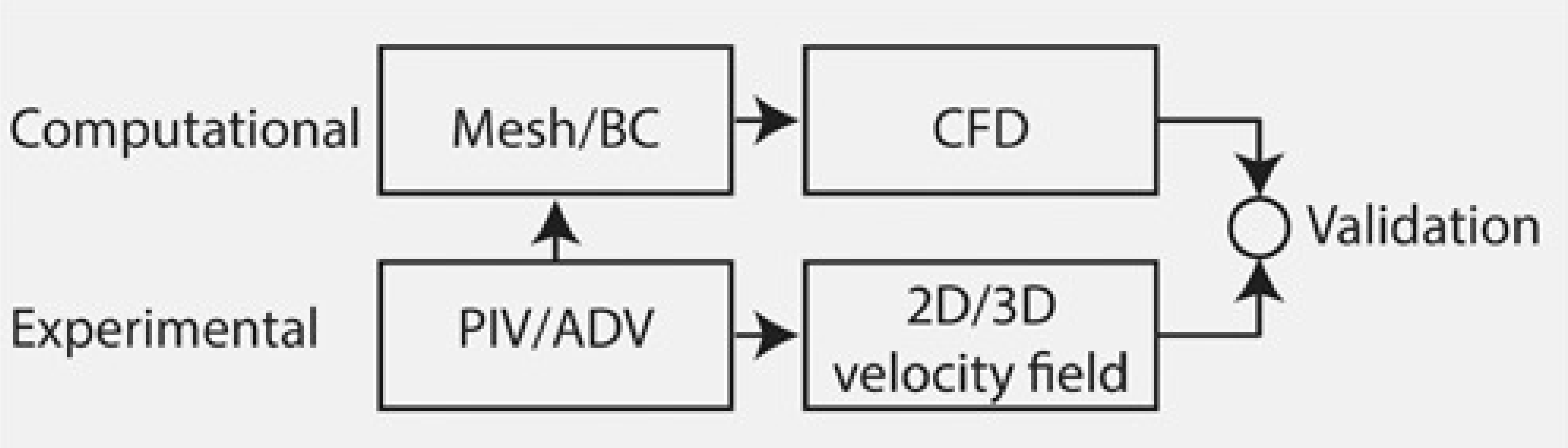
$CO_{2,out}$= GHG emissions produced by system, $kgCO_2$eq

$CO_{2,in}$= GHG emissions displaced by system, $kgCO_2$eq

N_r = Nitrogen removal rate, N.m^{-3}.day^{-1}

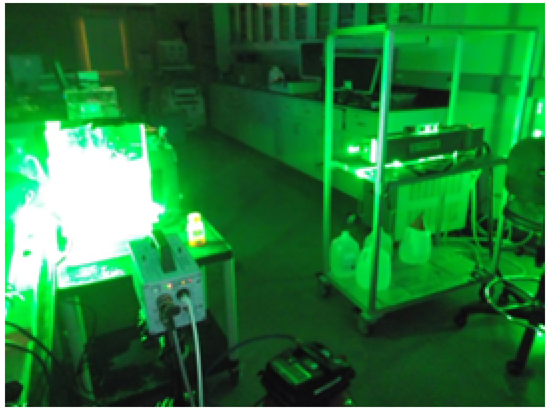
Adapted from: **Quiroz-Arita, Carlos**, John J. Sheehan, and Thomas H. Bradley. "Life cycle net energy and greenhouse gas emissions of photosynthetic cyanobacterial biorefineries: Challenges for industrial production of biofuels." Algal research 26 (2017): 445-452.

Gap and opportunity space for decarbonization: bioproducts – mixing energy

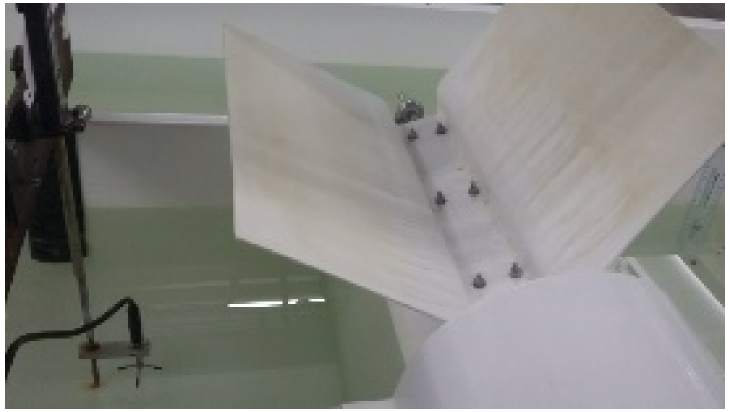


BC: Boundary Conditions
CFD: Computational Fluid Dynamics

PIV: Particle Image Velocimetry

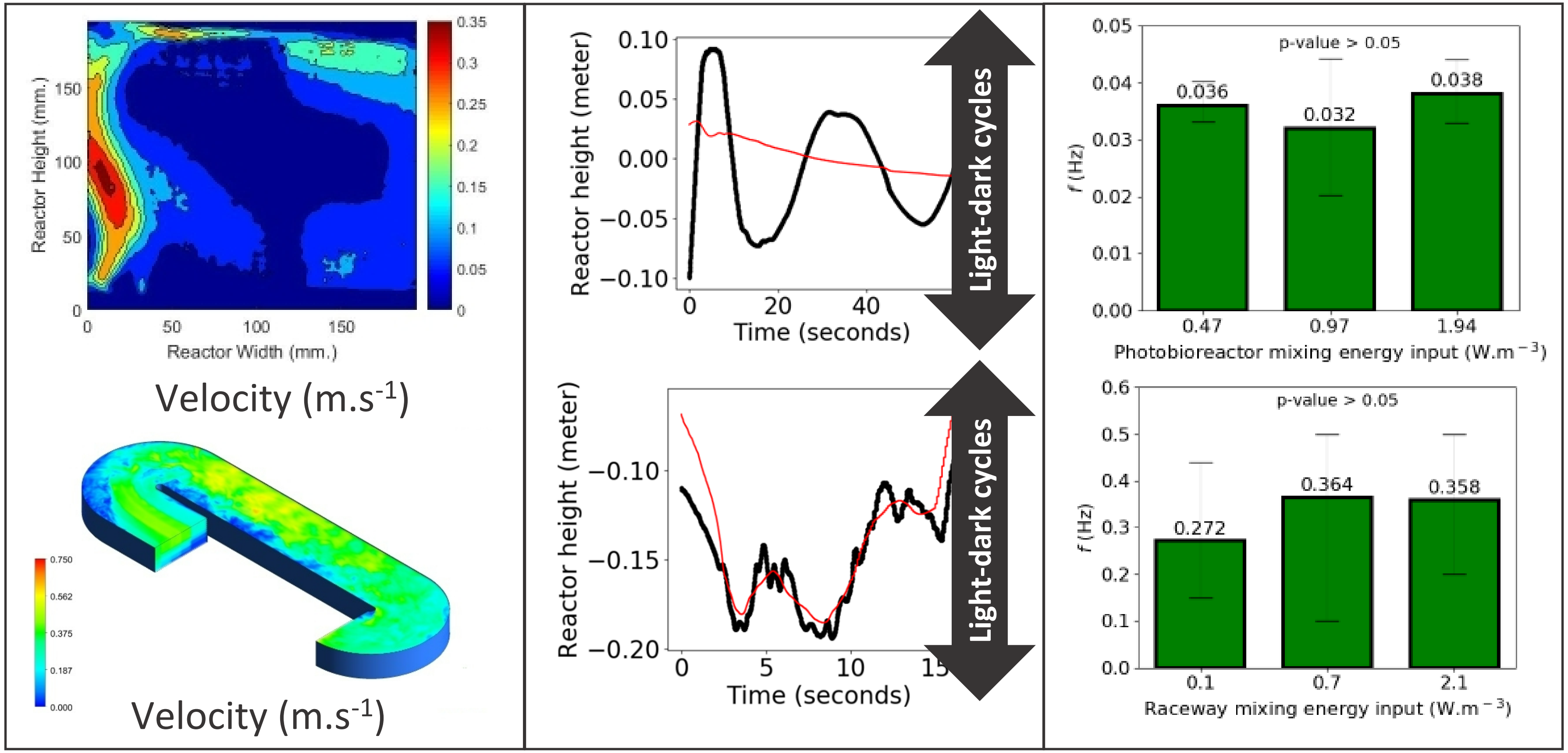


ADV: Acoustic Doppler Velocimetry



Quiroz-Arita, Carlos, Myra L. Blaylock, Patricia E. Gharagozloo, David Bark, Lakshmi Prasad Dasi, and Thomas H. Bradley. Biotechnology and Bioengineering 117, no. 4 (2020): 959-969.

Gap and opportunity space for decarbonization: bioproducts – mixing energy



Differences in mixing energy input do not significantly impact:

- Structure of turbulence
- Frequency of cells motion
- Light/dark cycling frequencies

Quiroz-Arita, Carlos, Myra L. Blaylock, Patricia E. Gharagozloo, David Bark, Lakshmi Prasad Dasi, and Thomas H. Bradley. Biotechnology and Bioengineering 117, no. 4 (2020): 959-969.

Gap and opportunity space for decarbonization: bioproducts – mixing energy

$$\text{Terminal velocity} = \frac{1}{18} * g * d^2 \left(\frac{\rho_{Water} - \rho_{Air\ Bubble}}{\mu}\right)$$

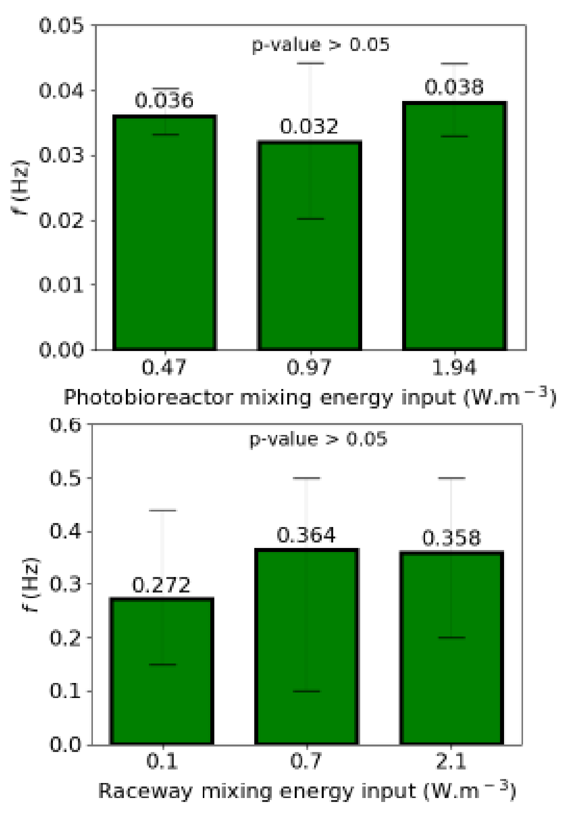
Where;

g: Gravitational acceleration

ρ: Density (Air Bubble/Water)

μ: Dynamic viscosity

d: Diameter of air bubble → **Variables are held constant regardless of mixing energy input**



- Air bubbles buoyancy drives flow circulation in flat-panel photobioreactors

Quiroz-Arita, Carlos, Myra L. Blaylock, Patricia E. Gharagozloo, David Bark, Lakshmi Prasad Dasi, and Thomas H. Bradley. Biotechnology and Bioengineering 117, no. 4 (2020): 959-969.

Gap and opportunity space for decarbonization: bioproducts – mixing energy

$$Terminal\ velocity = \frac{1}{18} * g * d^2 \left(\frac{\rho_{Water} - \rho_{Air\ Bubble}}{\mu}\right)$$

Where;

g: *Gravitational acceleration*

ρ: *Density (Air Bubble/Water)*

μ: Dynamic viscosity

d: Diameter of air bubble

→ **Variables are held constant regardless of mixing energy input**

$$L = \frac{4 * H * W}{2 * H + W}$$

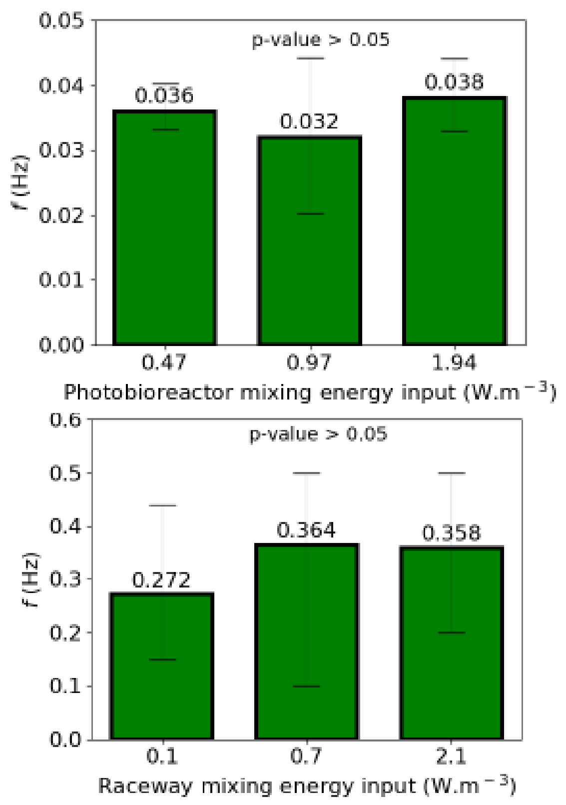
Where;

L: *Characteristic Length*

W: *Channel Width* ***(Constant)***

H: *Channel Height* ***(Constant)***

U: *Velocity Profile* ***(Initial Conditions for Motion)***



- Air bubbles buoyancy drives flow circulation in flat-panel photobioreactors
- The period of cells motion is the same order of magnitude of large-scale eddies (time scales)

Quiroz-Arita, Carlos, Myra L. Blaylock, Patricia E. Gharagozloo, David Bark, Lakshmi Prasad Dasi, and Thomas H. Bradley. Biotechnology and Bioengineering 117, no. 4 (2020): 959-969.

Gap and opportunity space for decarbonization: bioproducts – productivity

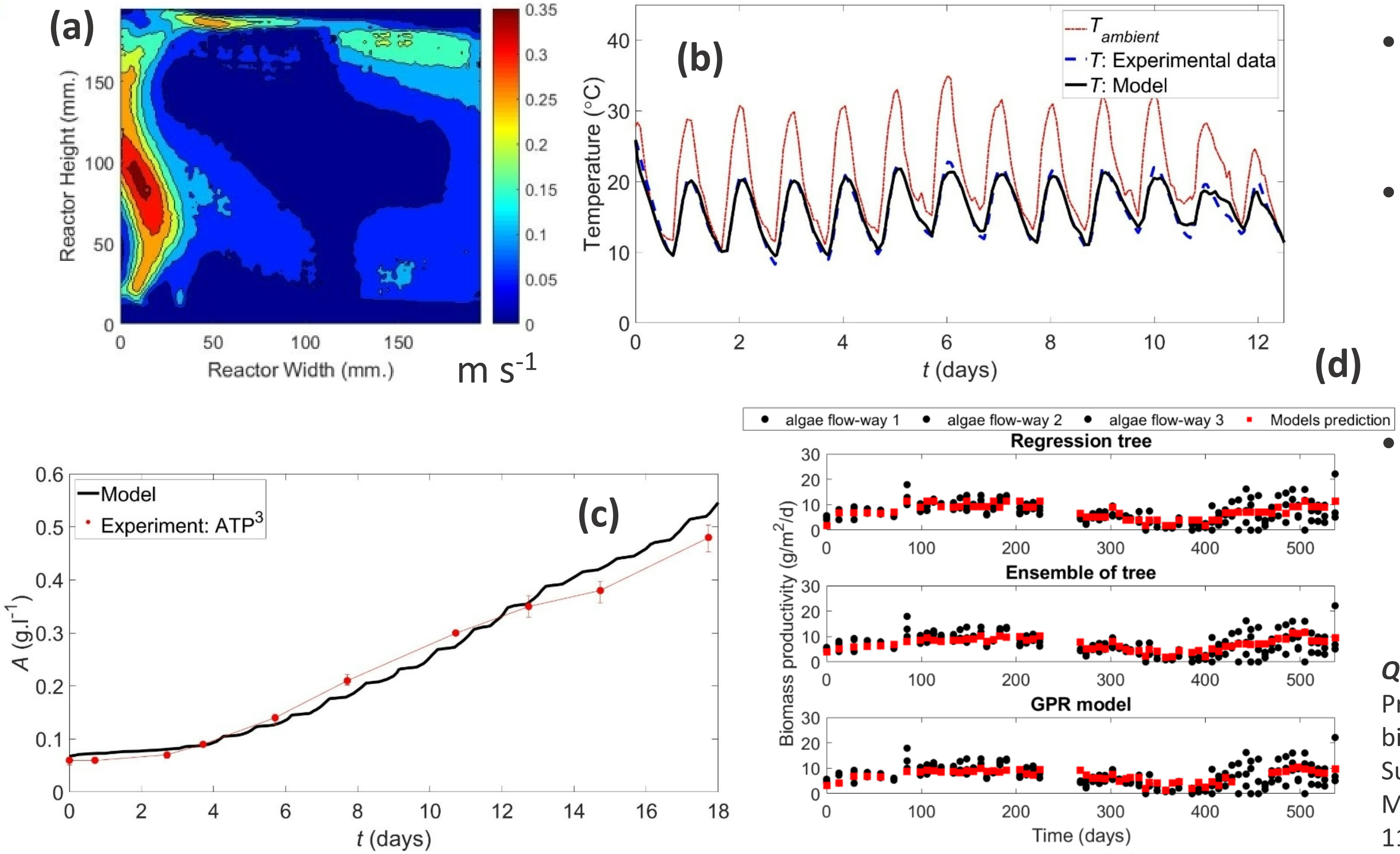
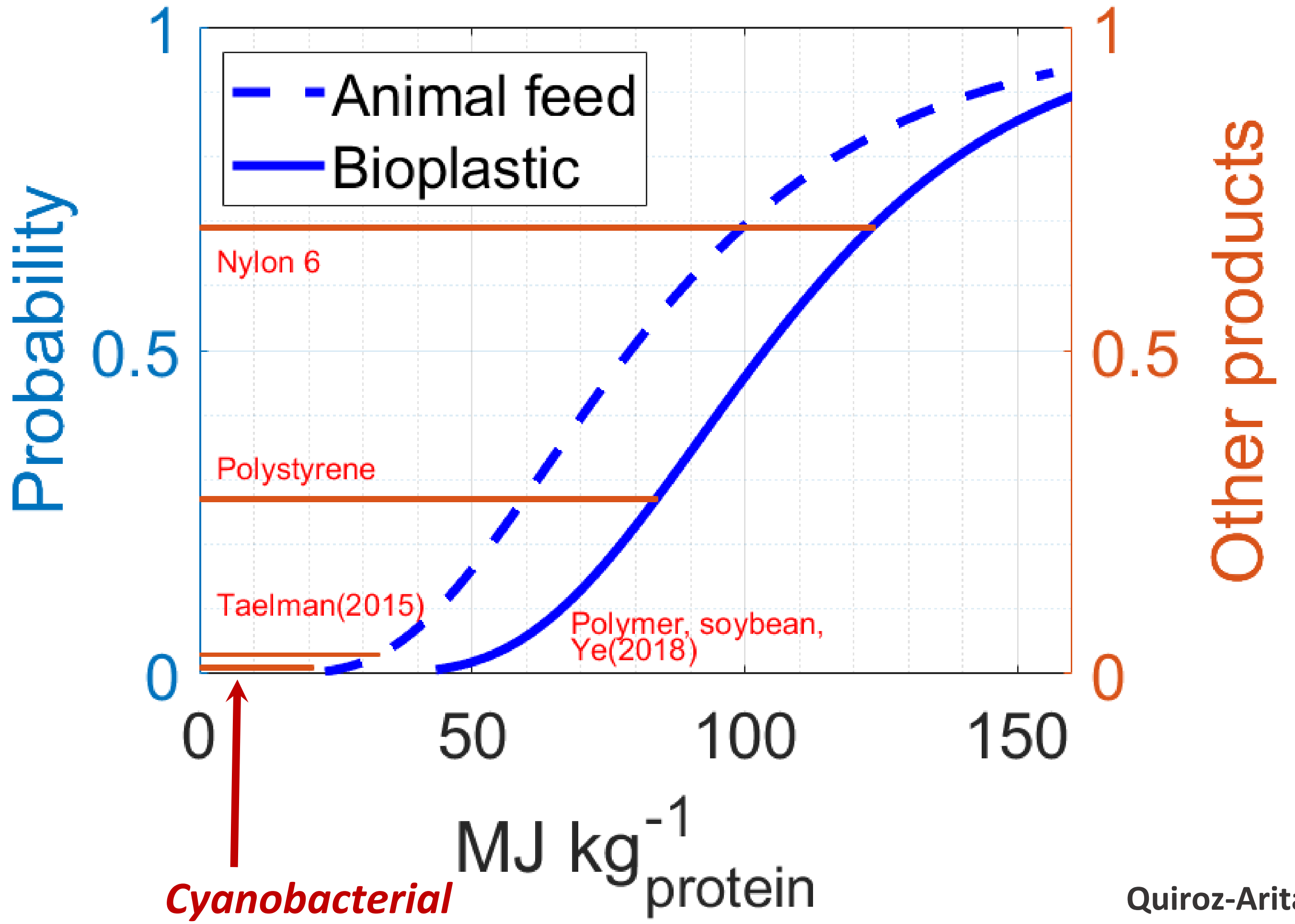


Illustration of biophysical research in algae systems: Mixing in photobioreactors **(a)**, thermal system **(b)**, biomass and carbon in algae raceways **(c)** and attached-polycultures flow-ways **(d)**.

- Demonstrated that ***well-mixed*** conditions exist, even for relatively ***low mixing energy inputs***
- The thermal system, algae growth rate limitations, and photoinhibition ***can be represented in a well-mixed raceway or photobioreactor dynamical formulation***
- Predicted ***thermal system***, algae growth rate limitations, ***and biomass (carbon)*** using well-mixed *dynamic systems and Machine Learning (ML) models*

Quiroz-Arita, C., Blaylock, M.L., Gharagozloo, P.E., Bark, D., Prasad Dasi, L., & Bradley, T.H. Biotechnology and bioengineering 117, no. 4 (2020): 959-969.
Sungwhan, K., ***Quiroz-Arita, C.***, Monroe, E.A., Siccardi, A., Mitchell, J. Huysman, N., and Davis, R.W. Water Research (2021): 116816.
Quiroz-Arita, C., Blaylock, M.L., Gharagozloo, P.E., Bradley, T.H., Dempster, T., McGowen, J., & Davis, R.W. Bioresource Technology Reports 10 (2020): p.100405.

Gap and opportunity space for decarbonization: bioproducts

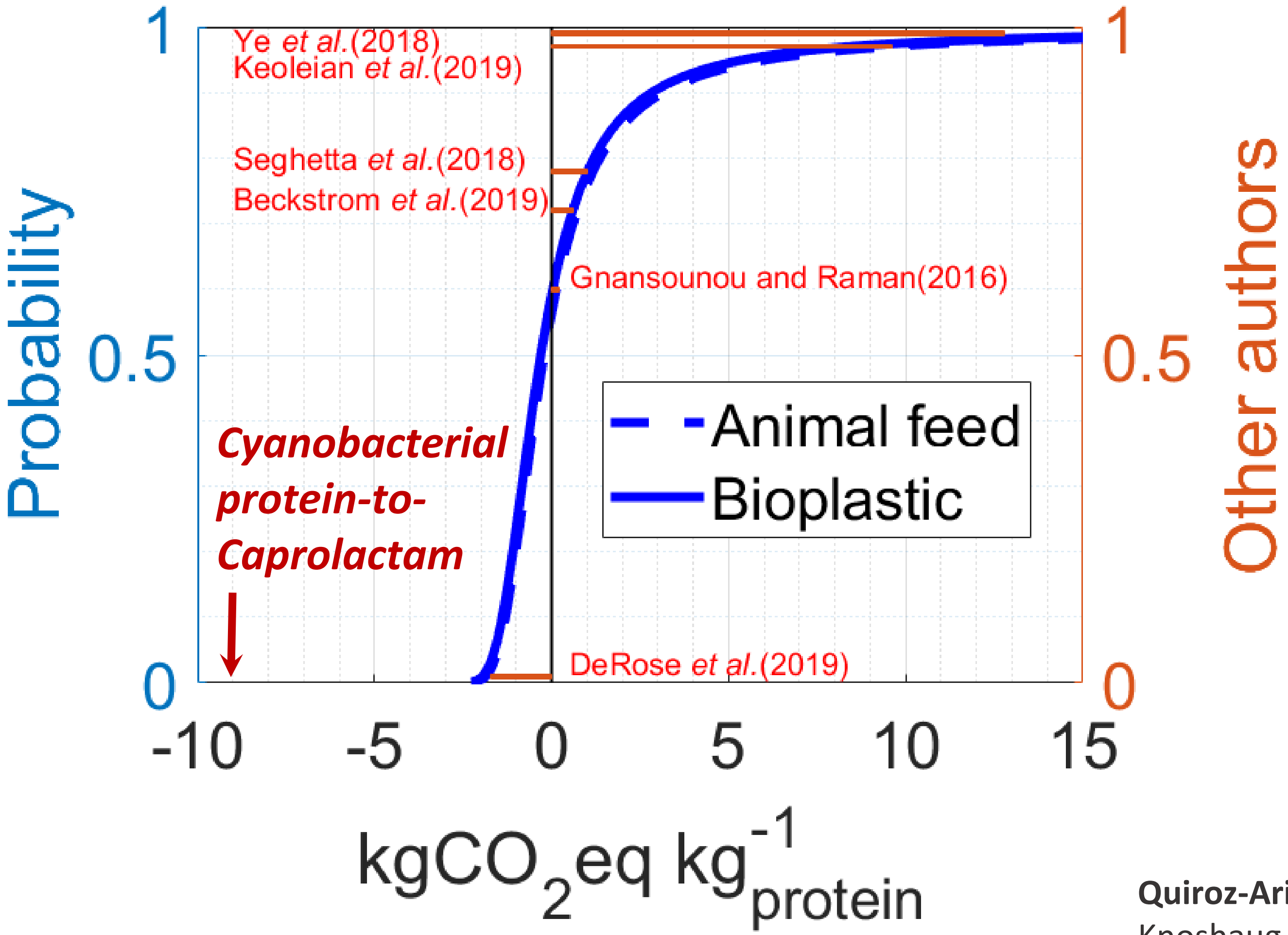


Cyanobacterial protein-to-Caprolactam

- ***Nylon 6*** life cycle energy values are ***equal to a 67% probability of algae-derived bioplastic***
- Algae-derived ***protein tablets*** reported in the literature ***assumed best-case scenario*** obtaining the ***lowest life cycle energy***
- The Monte Carlo analysis demonstrates that ***50% of algae-derived animal feed and bioplastics*** will consume ***life cycle energy less than 100 MJ kg^{-1}$_{protein}$***
- **Cyanobacterial protein-to-Caprolactam:**
  - Direct energy: 2.8 MJ kg^{-1}
  - Indirect energy: 5.3 MJ kg^{-1}
  - **Life cycle energy: 8.1 MJ kg^{-1}**

Quiroz-Arita, C., Shinde, S., Kim, S., Monroe, E., George, A., Quinn, J. C., Nagle, N., Knoshaug, E., Kruger, J.S., Dong, T., Pienkos, P., Laurens, L.M., Davis, R. W. (2022). Bioproducts from high-protein algal biomass: An economic and environmental sustainability review and risk analysis. Sustainable Energy & Fuels.

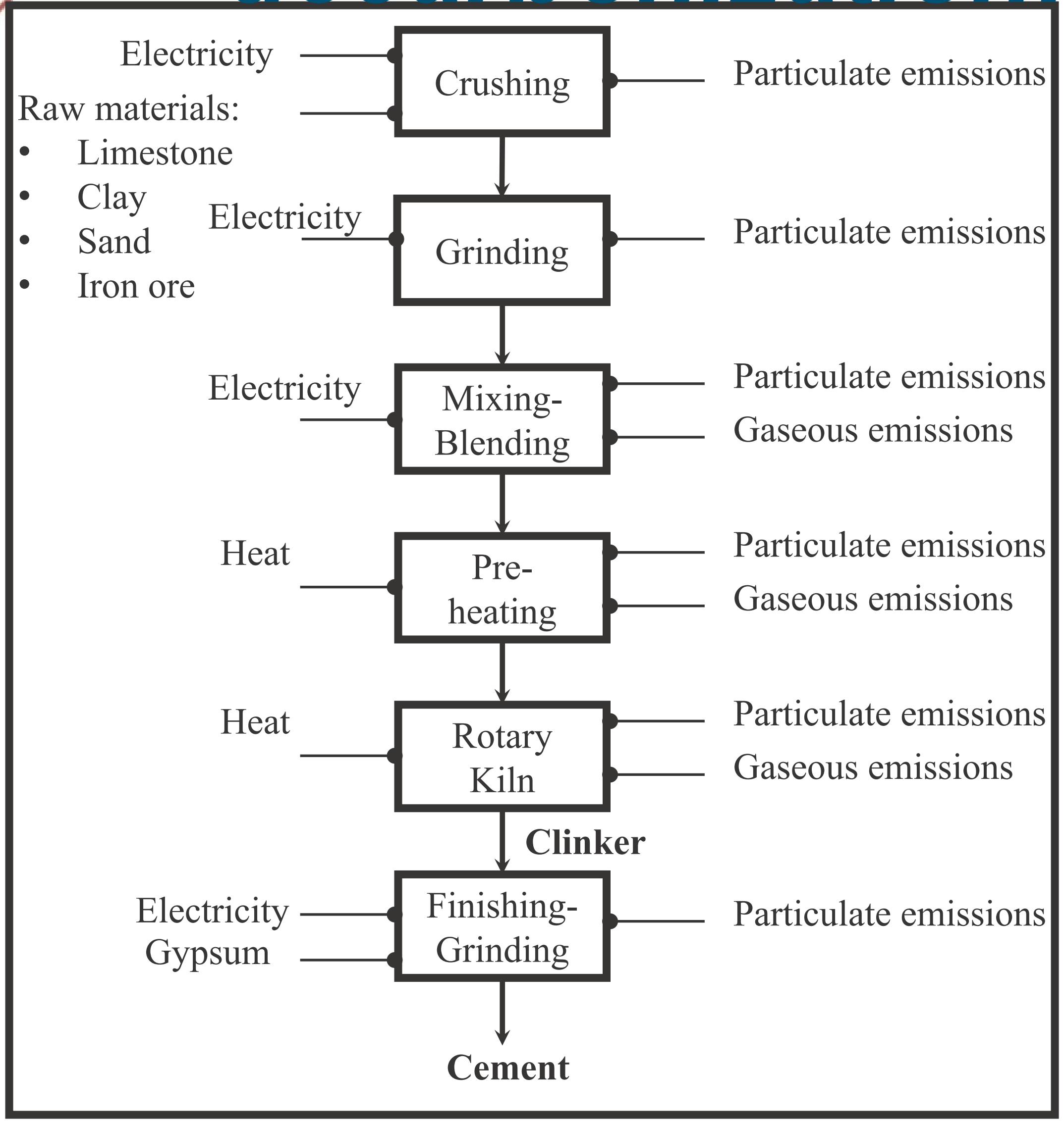
Gap and opportunity space for decarbonization: bioproducts



- Algae-derived protein tablets reported in the literature (**Chensong *et al.* 2018**) ***assumed the worst-case scenario*** obtaining the ***highest life-cycle CO_2eq***
- Protein recovery from ***benthic polyculture*** showed ***negative life-cycle CO_2eq (DeRose et al. 2019)***
- The Monte Carlo analysis demonstrates that ~***50% of algae-derived animal feed and bioplastics*** can produce ***CO_2eq lower than values reported by other authors***
- **Cyanobacterial protein-to-Caprolactam:**
  -9.2 kgCO_2eq kg^{-1}

Quiroz-Arita, C., Shinde, S., Kim, S., Monroe, E., George, A., Quinn, J. C., Nagle, N., Knoshaug, E., Kruger, J.S., Dong, T., Pienkos, P., Laurens, L.M., Davis, R. W. (2022). Bioproducts from high-protein algal biomass: An economic and environmental sustainability review and risk analysis. Sustainable Energy & Fuels.

Gap and opportunity space for decarbonization: cement production



- ***The kiln is the primary energy sink in cement*** production through chemical and physical principles that turn raw materials into clinker
- Standard ***fuels used for heat*** requirements in the kiln include ***natural gas, petroleum coke, and coal*** resulting in energy consumption between ***3000 and 6000 MJ per ton of cement***
- Based on equipment efficiencies, the ***electricity consumed per ton of cement*** in the process is 90 –150 kWh

Refernces

Salas, Daniel Andres, Angel Diego Ramirez, Carlos Raúl Rodríguez, Daniel Marx Petroche, Andrea Jael Boero, and Jorge Duque-Rivera. "Environmental impacts, life cycle assessment and potential improvement measures for cement production: a literature review." Journal of Cleaner Production 113 (2016): 114-122.
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ISO 14040:2006 Environmental management — Life cycle assessment — Principles and framework

Gap and opportunity space for decarbonization: cement production

Germany:
265-850

Russia:
859*

France:
899

Saudi Arabia:
850*

Japan:
779

United States:
862-930*

Spain:
799-987,
530 (PCC)

Iran:
851*

China:
734-1,000

India:
851*

Life Cycle CO_2eq:
Cement Production

Brazil:
858*

Units: kg CO_2eq/ton of Cement

PCC: Post-combustion carbon capture

*Values computed from the 2014 World Business Council for Sustainable Development, and the 2016 Global Cement Directory

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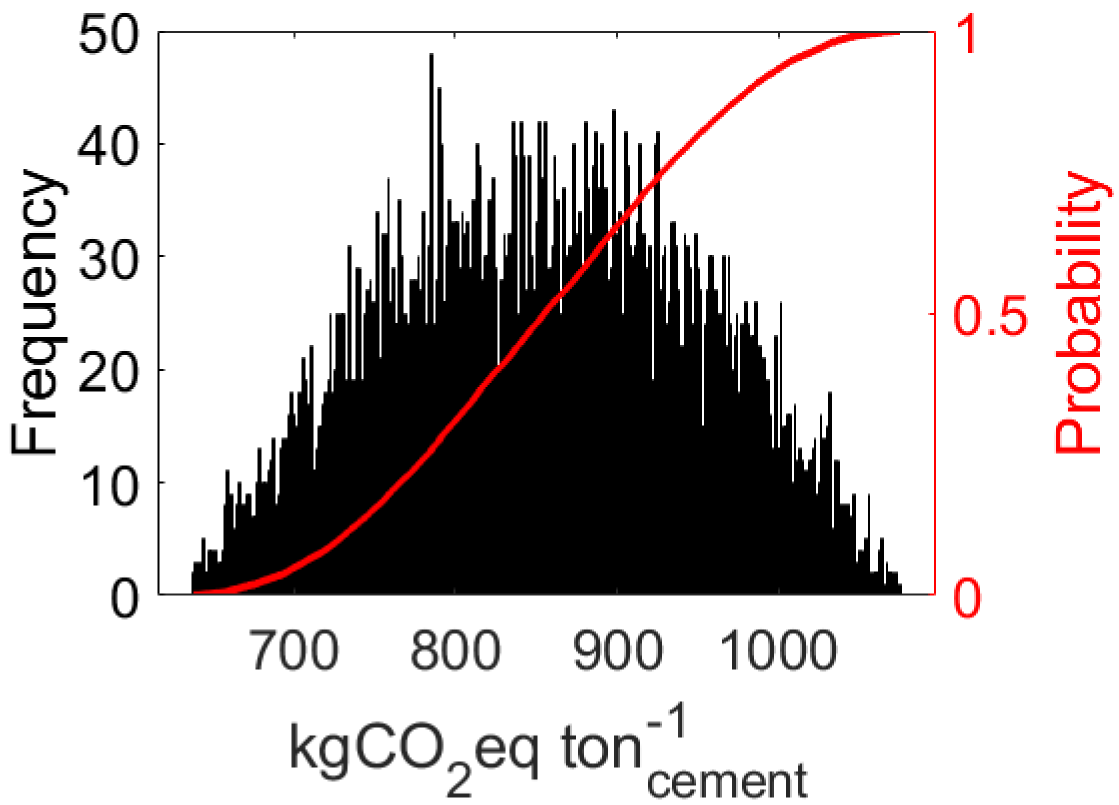
Farfan, Javier, Mahdi Fasihi, and Christian Breyer. "Trends in the global cement industry and opportunities for long-term sustainable CCU potential for Power-to-X." Journal of Cleaner Production 217 (2019): 821-835.

Gap and opportunity space for decarbonization: cement production



- The resulting probability distribution, varying from ***638 to 1,075 kgCO$_2$eq ton^{-1} of cement, is consistent with the literature*** reviewed

- Consistent with previous life cycle carbon emissions, we estimate that:
    - ***Direct emissions from calcination*** contribute ***50%***
    - ***Fuel consumption 40%***, and
    - **Indirect emissions from electricity** production ***10%***

- ***Decarbonization strategies*** that displace direct and indirect emissions ***in the kiln are priorities to improve the carbon footprint*** in these systems, ***including Bio-composites to replace reinforced concrete***

Path forward/ Ways to Collaborate

Summary

- ***Sustainable production of ammonia*** can displace ***indirect emissions from*** the highly energy-intensive ***conventional production, i.e., fossil-fuel***
- We need to ***accelerate current efforts in the green production of HB's feedstocks, e.g., H_2,*** through water splitting
- The ***sustainable production of ammonia (nutrients)*** will enable us ***to improve life cycle energy and CO_2eq emissions*** to decarbonize the supply-chain of bio-products
- Probabilistic life cycle CO_2eq emissions showed that ***negative-net carbon pathways are possible under low-energy intensity processes*** in bioproducts from high-protein algae systems
- In 2019 the US cement capacity was 120.8 Megatons (MTon) per year. We estimate that ***Nationwide CO_2 emissions would decrease from 111 to 49 Mton CO_2 per year*** using Sandia's decarbonization strategies

Path forward/ Ways to Collaborate

Collaboration opportunities

- ***Industry/Faculty partners*** with research interests in decarbonization of hydrogen, bioresources, cement, and other industries (e.g., waste, aviation)
- ***Cooperative Research and Development Agreement (CRADA), and Strategic Partnership Projects***
- ***Sandia University Partnership Network (SUPN) LDRD funds*** to begin preliminary work towards a future proposal
- Partner in response to ***upcoming Funding Opportunity Announcements (FOA)***
- Students: Potential ***internship opportunities*** if highly-motivated in decarbonization

Path forward/ Ways to Collaborate

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Questions?