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 15-19, 2022

Susie Dai
Texas A&M University

August 15, 2022

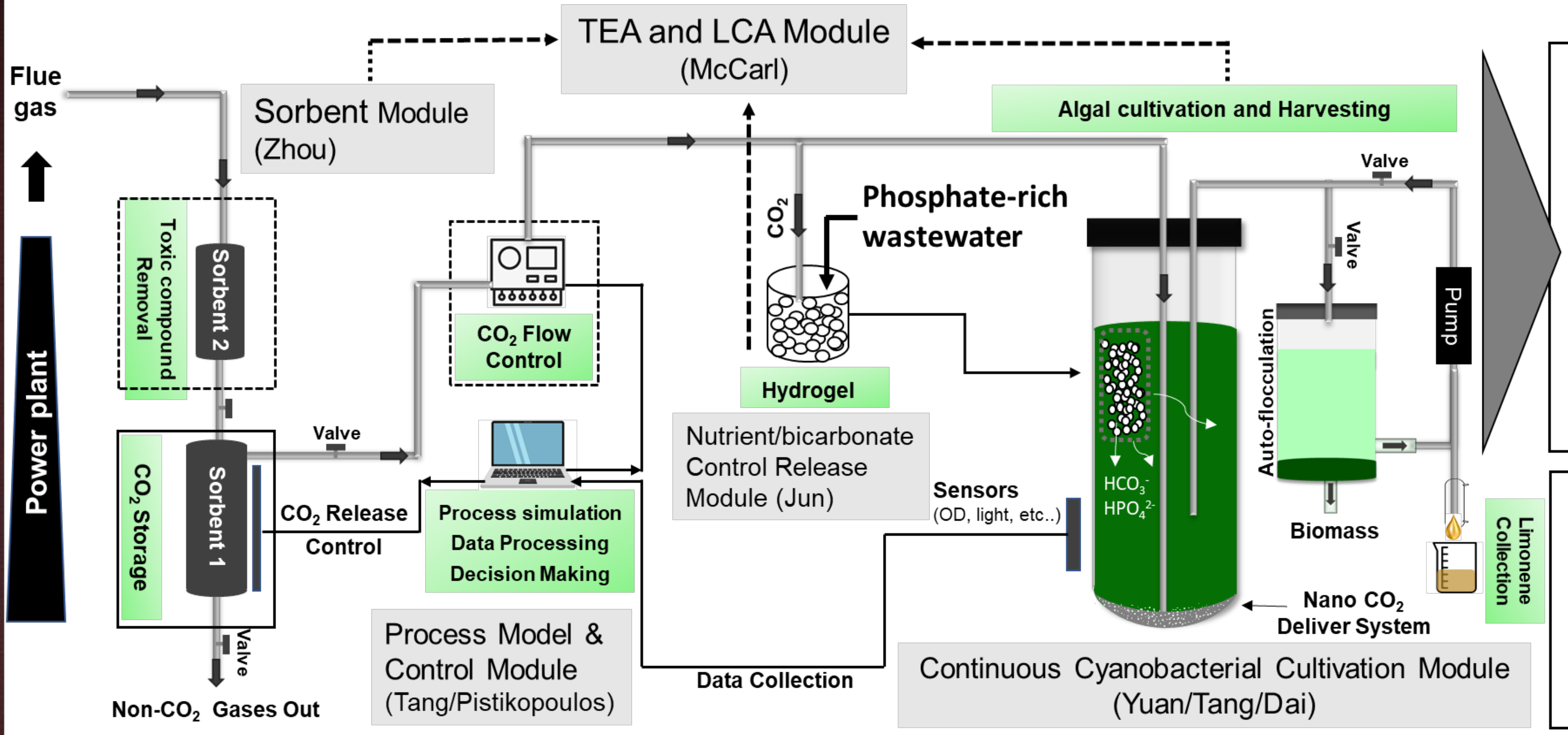
Project Overview

- 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 CO_2 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 CO_2, bicarbonate, and nutrient capture and delivery to the low-cost harvest-empowered continuous algal cultivation system with ultra-high productivity and CO_2 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



Outcomes

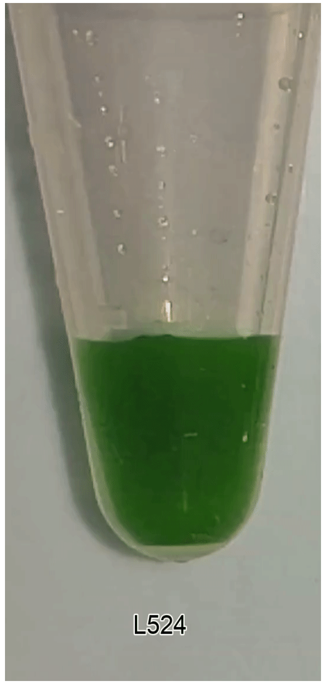
- Sorbent CO2 capture
- Gel nutrient release
- Fast algal growth
- Easy Biomass harvest
- Process integration
- Optimal Design
- Process control
- Capital Cost
- Operating Cost
- Biomass profit
- Environmental benefits

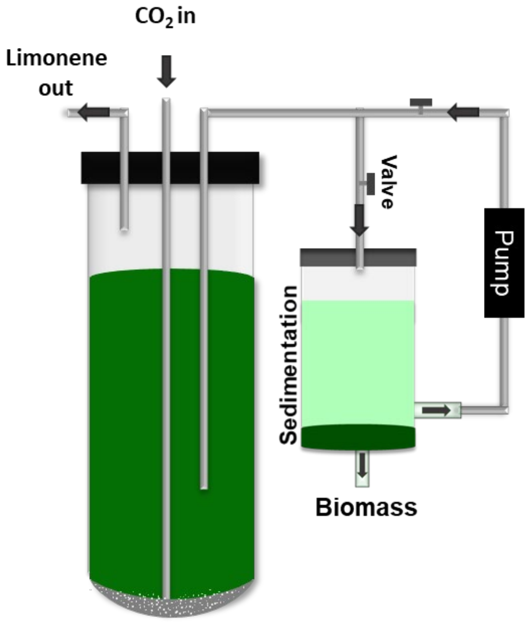
Milestones

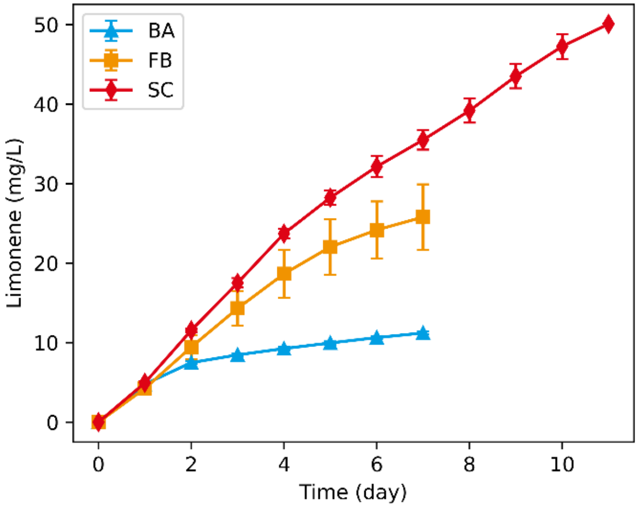
Year 1: Small scale lab tests (bio and abiotic studies)
Year 2: 20~100 L PBR test
Year 3: Outdoor tests and TEA/LCA (>100 L)

The integrated CACCU system

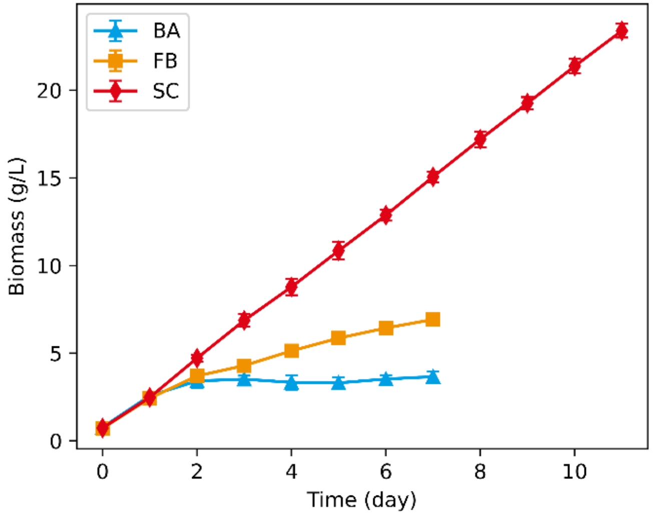
Sustainable co-production of limonene and biomass by semi-continuous cultivation







~5 mg/L/day



~2.2 g/L/day

Record productivities and yields in limonene productivity

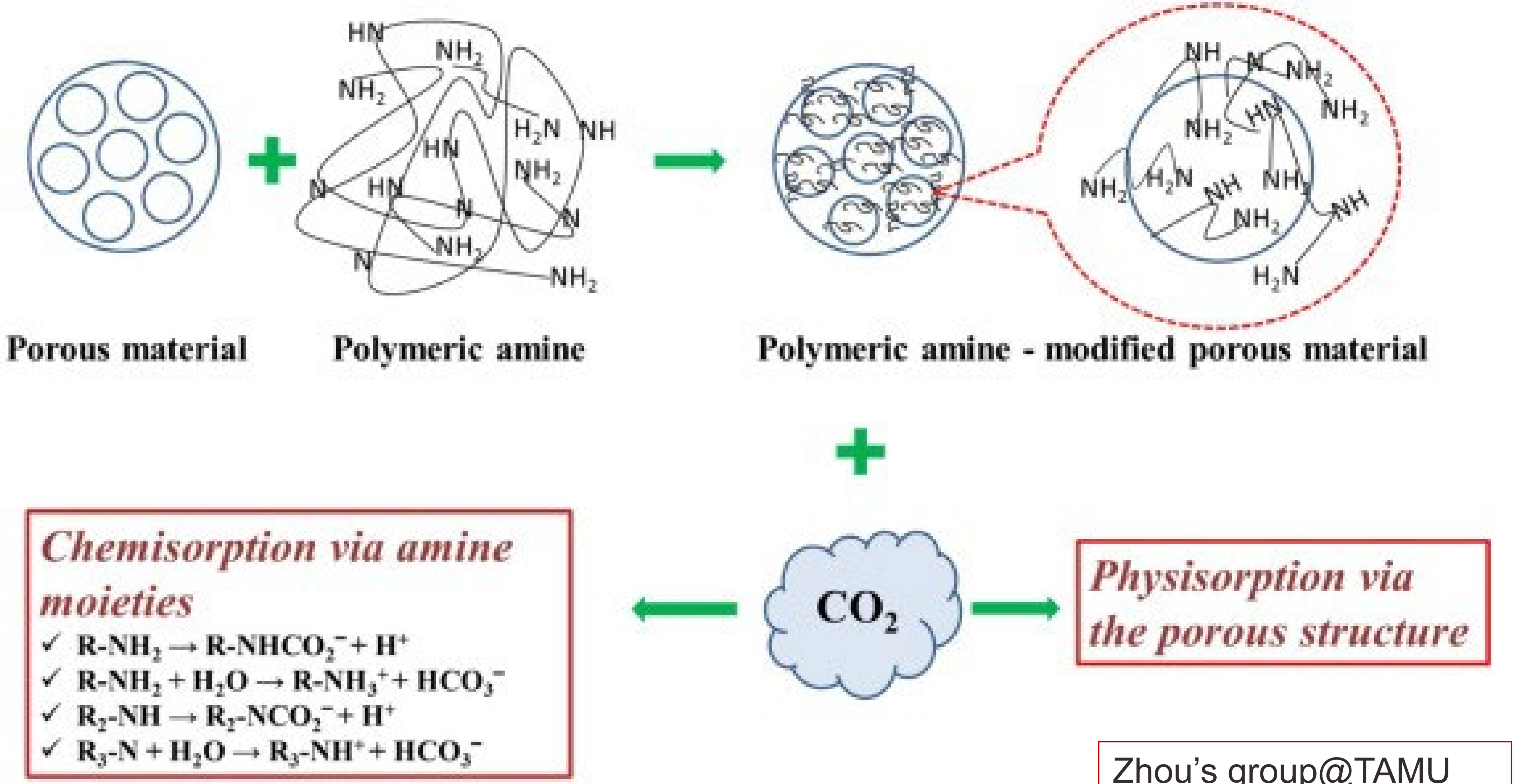
Sustainable biomass accumulation at about 1-2g/L/Day for a long period of time.

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



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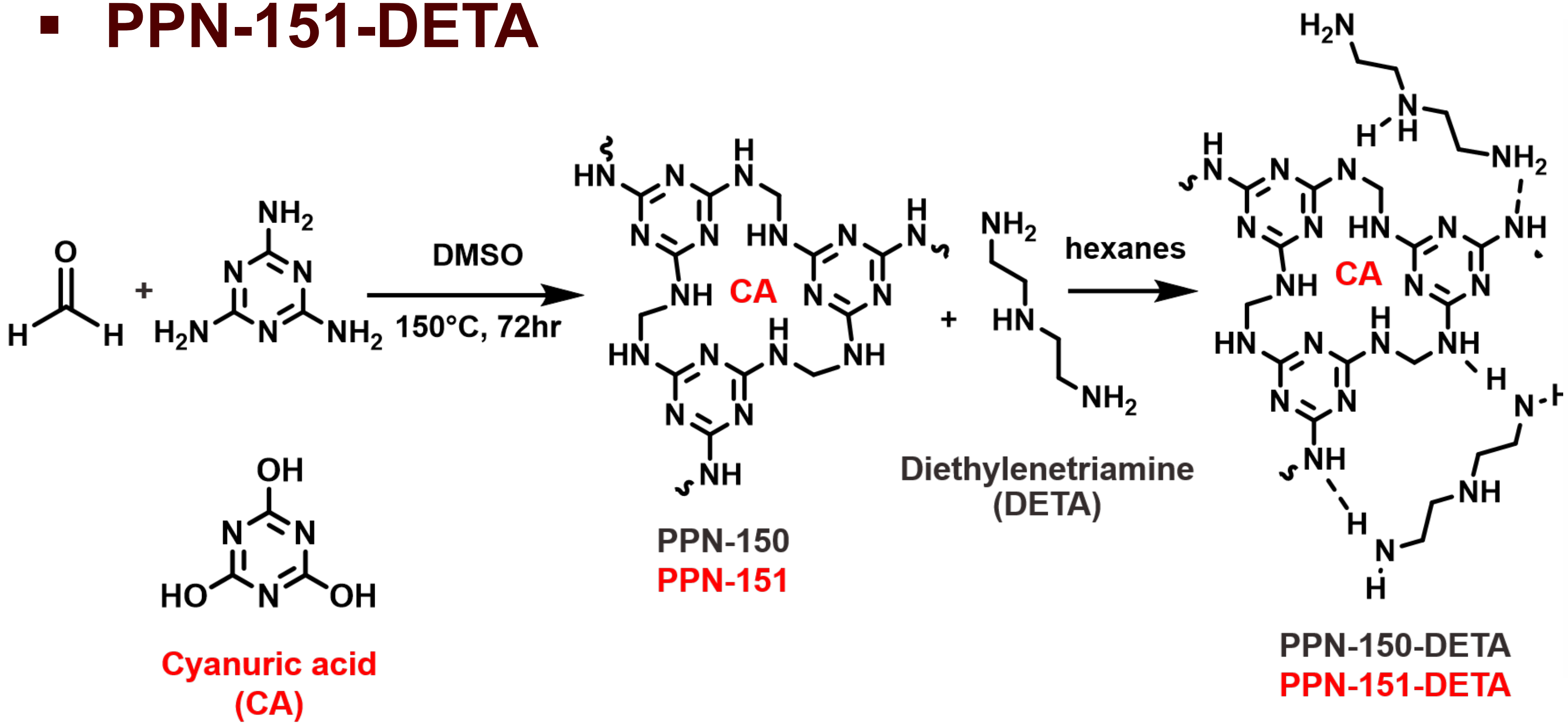
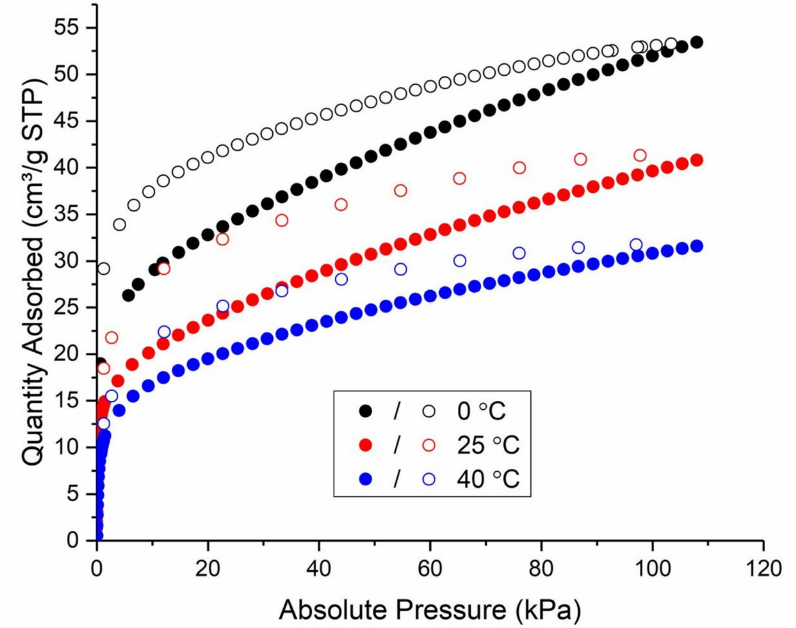
Previous results and materials on carbon capture

- **PPN-151-DETA**





CO_2 adsorption of 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

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Mineral-seeded mineral hydrogel composites for nutrient delivery and pH control

Adding salts or P and P-rich wastewater

Struvite ($NH_4MgPO_4 \cdot 6H_2O$)

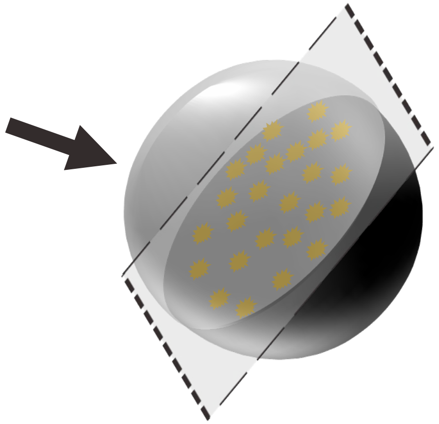
CO_2 capture/dissolution

Ca^{2+}

HPO_4^{2-}

NH_4^+

HCO_3^-



Calcium-Alginate Hydrogel (Ca-Alg)

Mineral seed

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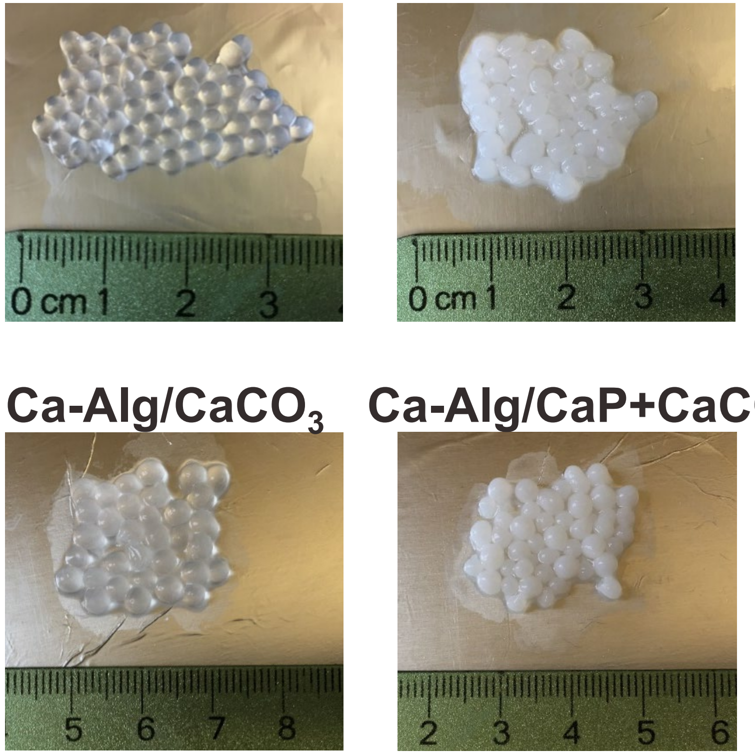


Kim, D and Jun, Y.-S., *Green Chemistry* **2018,** *20* (2), 534-543.

- 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)

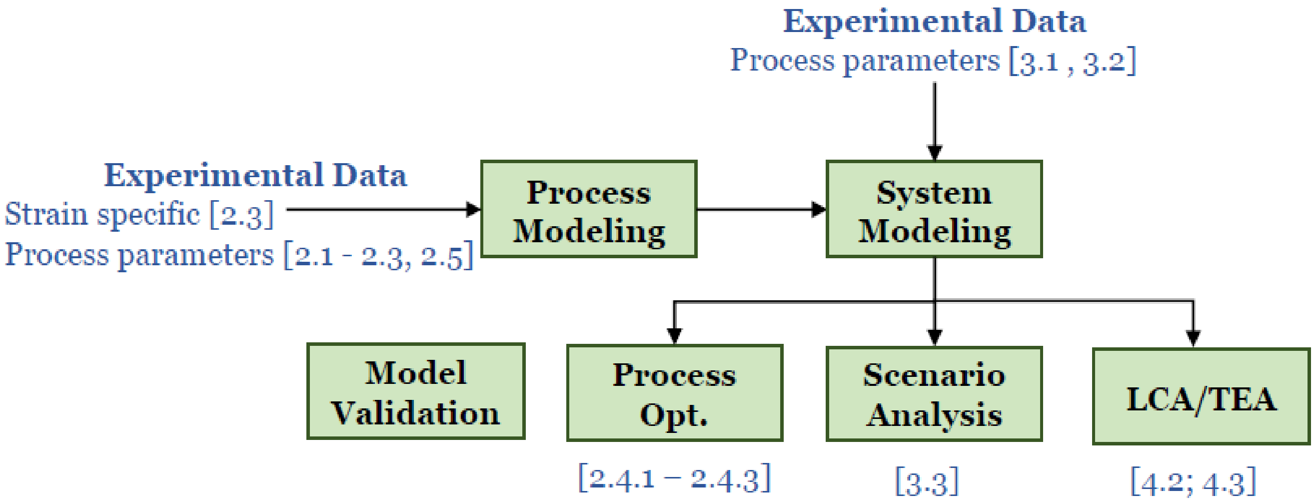
MIPs can be optimized to multiple objectives

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)



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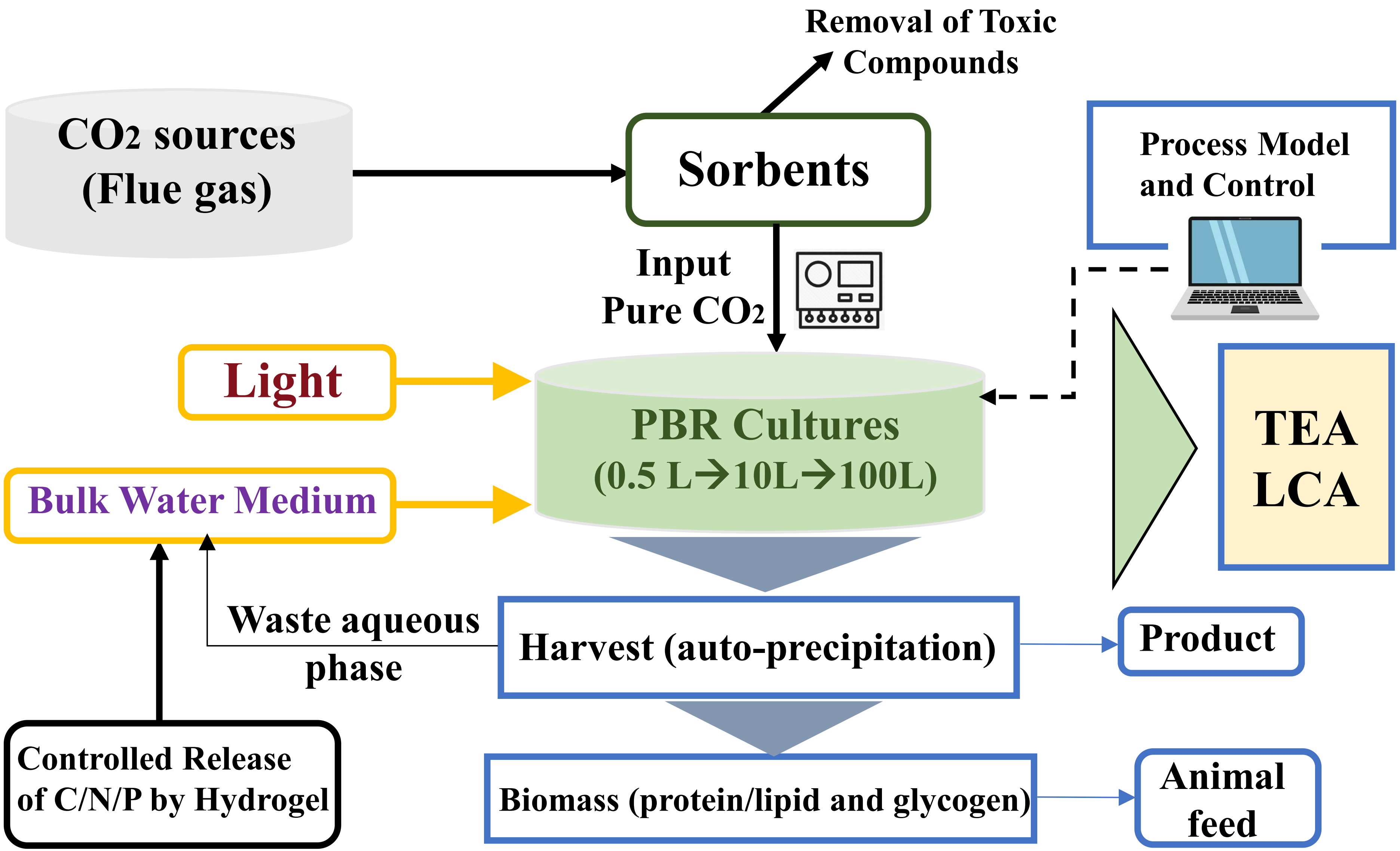
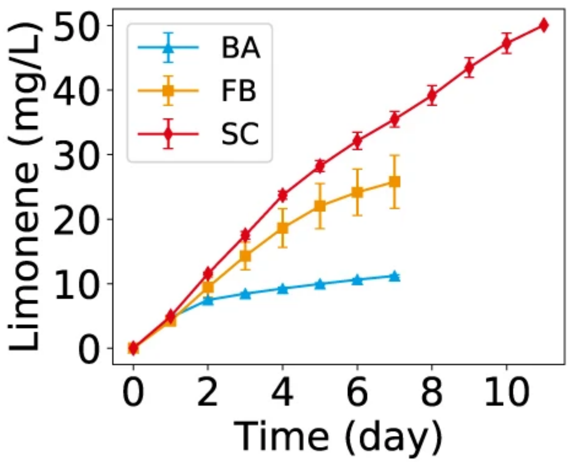
Technical Approach/Project Scope

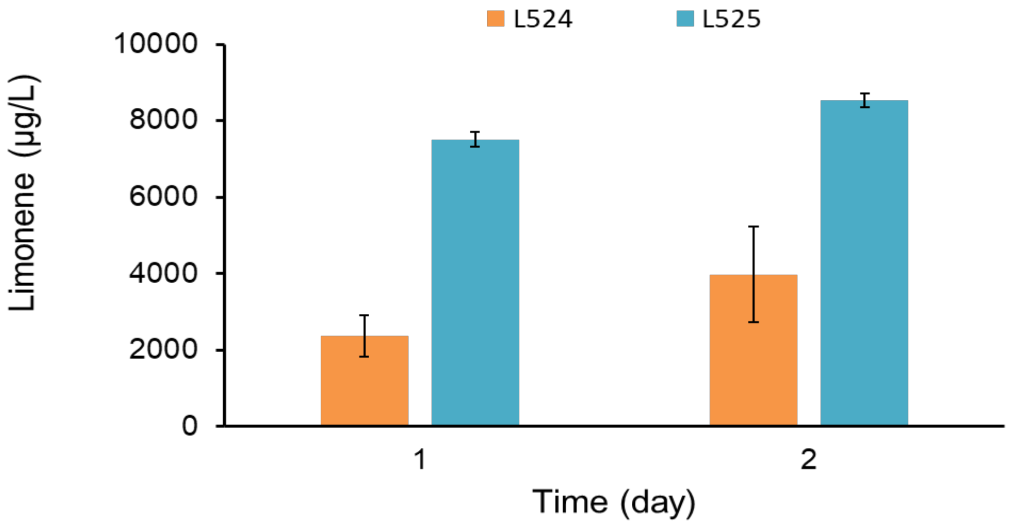


Progress

- We have successfully engineered Synechococcus UTEX 2973 to produce limonene

L524





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

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

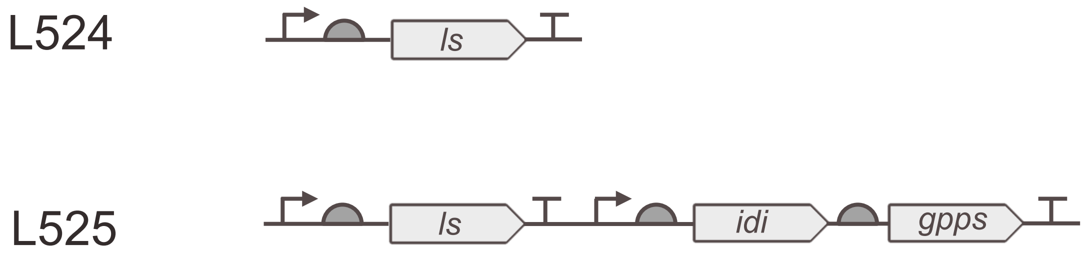
Dai, Yuan's groups@TAMU

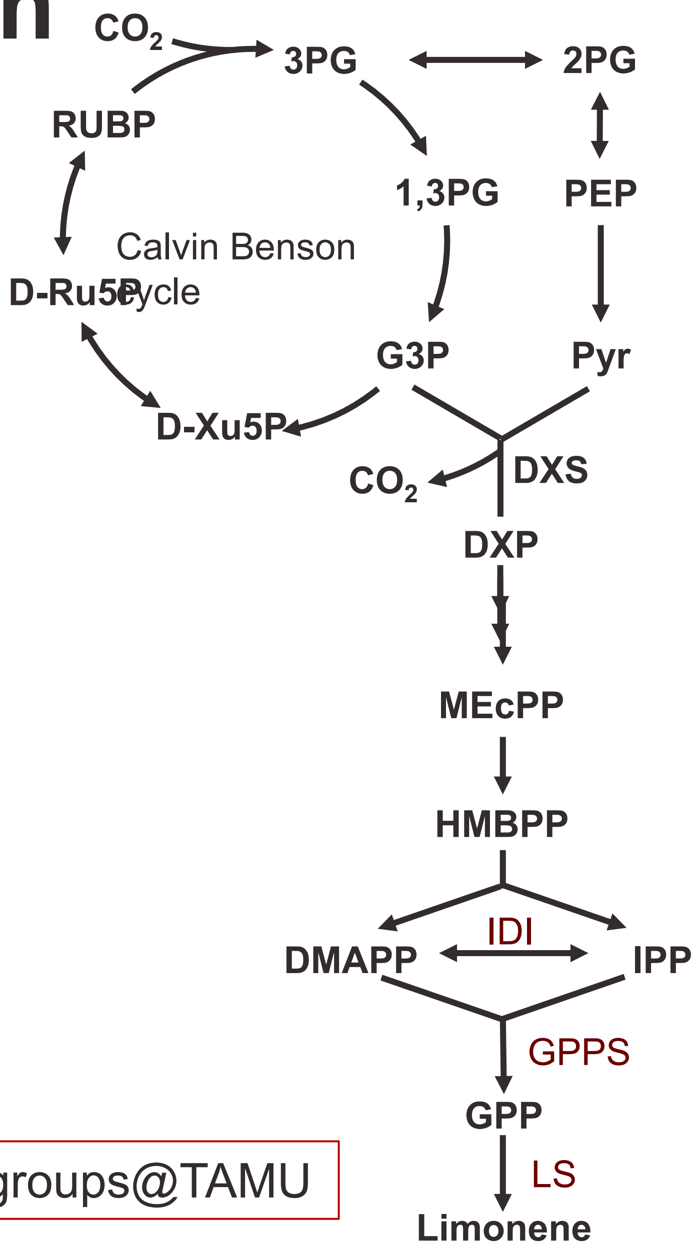
Long et al., Nature Communications, 2022, 13:541

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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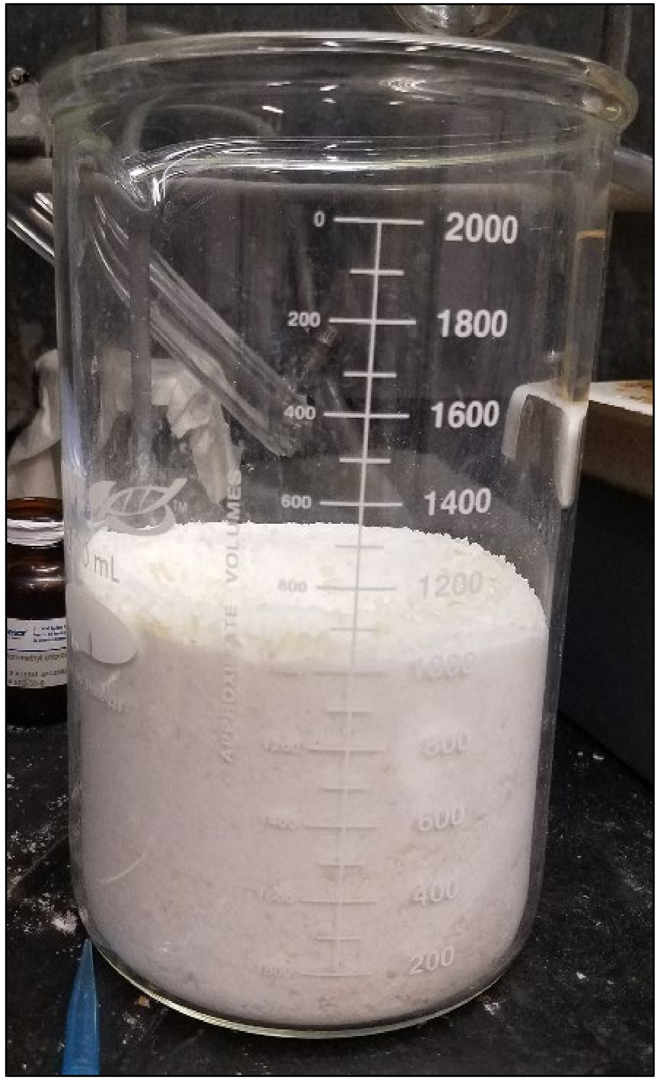
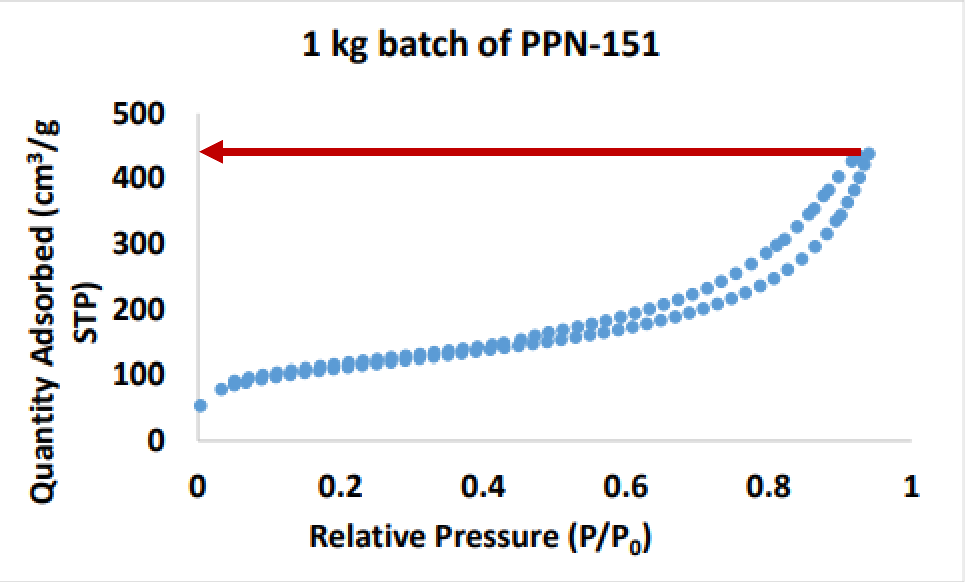
Initial 50g Scale-up

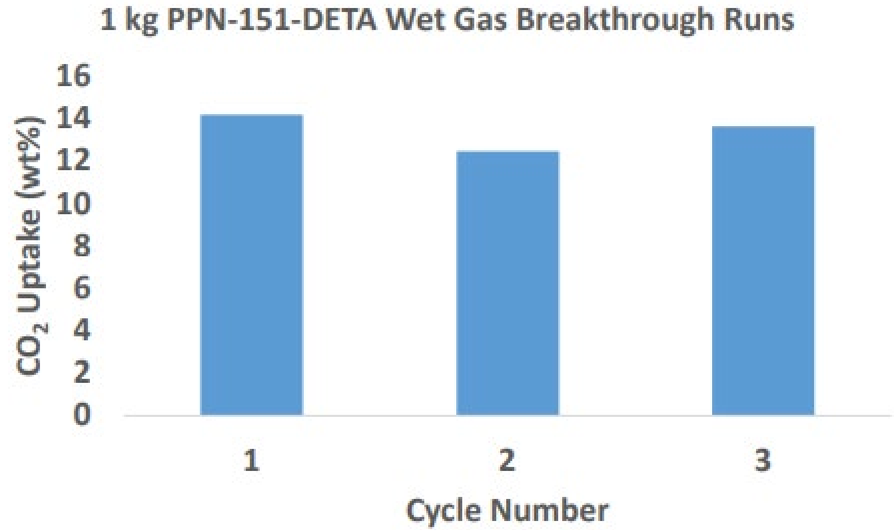


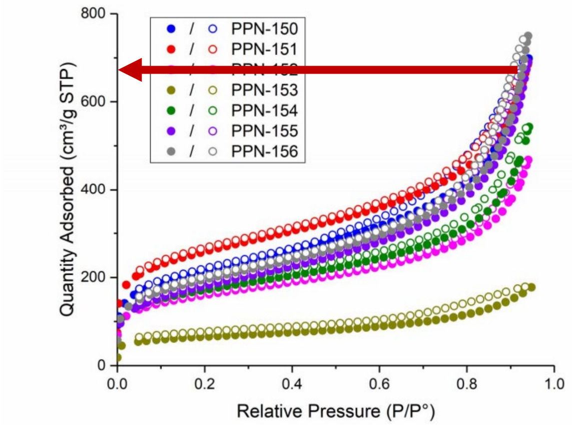
200g Scale-up

1kg Scale-up

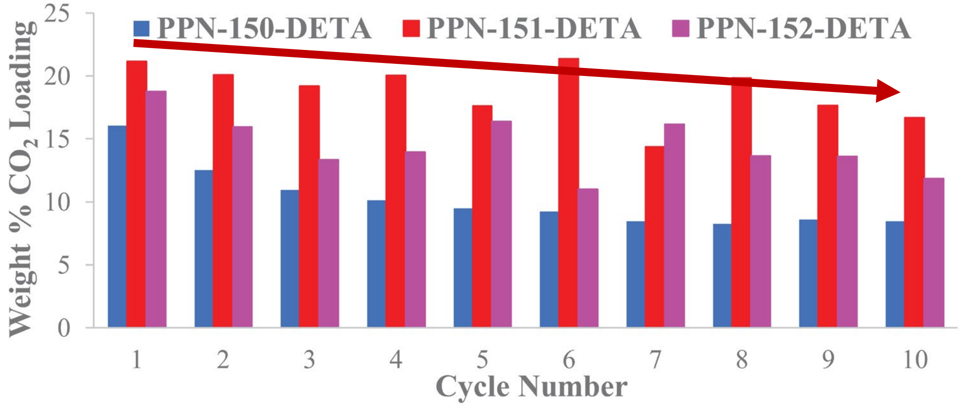
1 Kg Scale-up Test Run







~40% lower performance than bench scale



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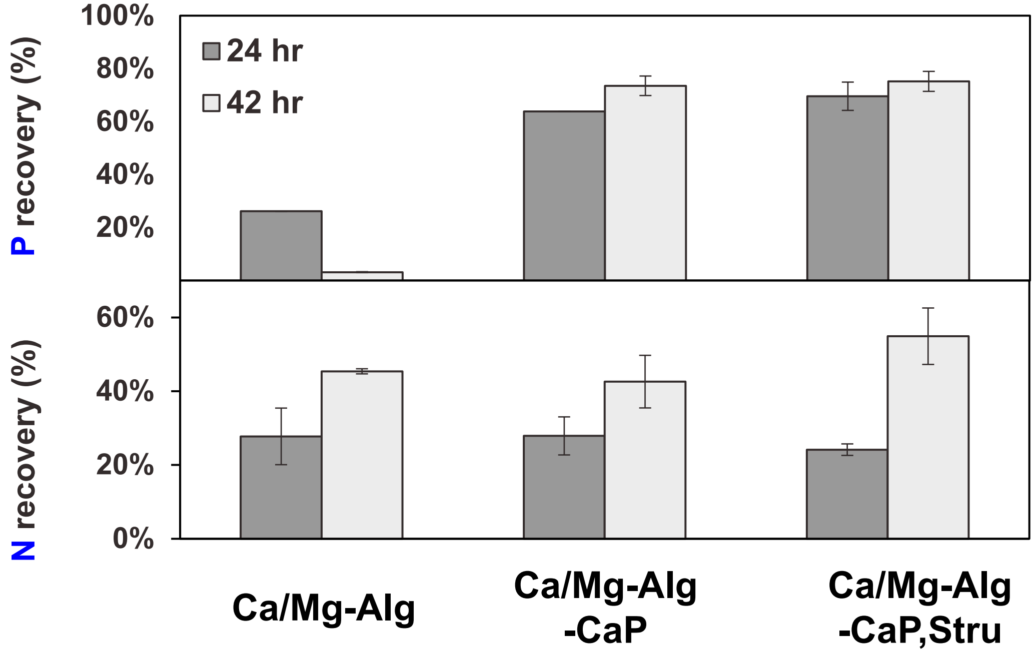
Breakthrough using 15% CO_2, **2% H_2O**, 83% N_2,
around 1 g of loosely packed material

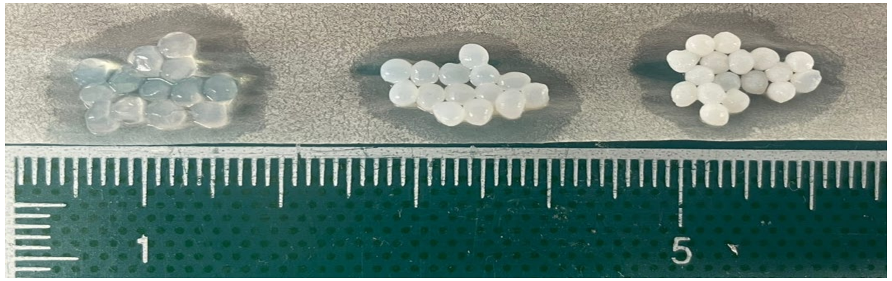
P and N recovery using mineral-hydrogel composites

P and N recovery efficiency of mineral-hydrogel composites



Composites	40 mM Mg	40 mM Mg 20 mM P	40 mM Mg 40 mM P 20 mM N

After 42 hrs



Ammonium Recovery capacity (mg/g)

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

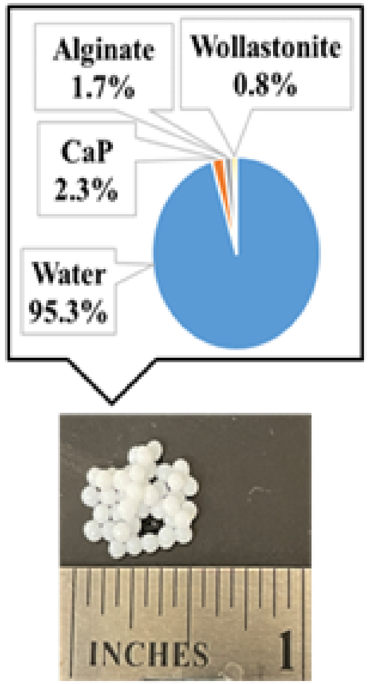
Mineral hydrogel	La-magnetic biochar	As based Bentonite
134.67 (24hr) **232.52 (48hr)**	101.67	5. 7
This study	LI, Ting, et al. *Bioresource technology*, 2018	ZAINI et al. *Advanced Powder Technology*, 2021

- **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

P Release as fertilizer

CO_2 fixation

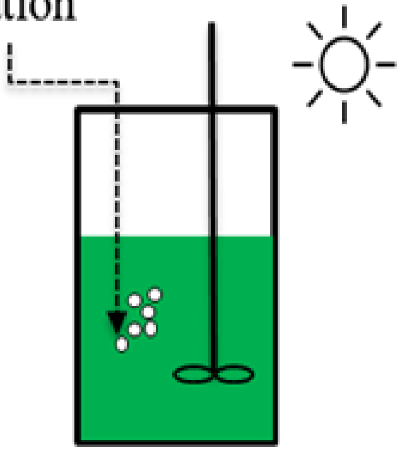
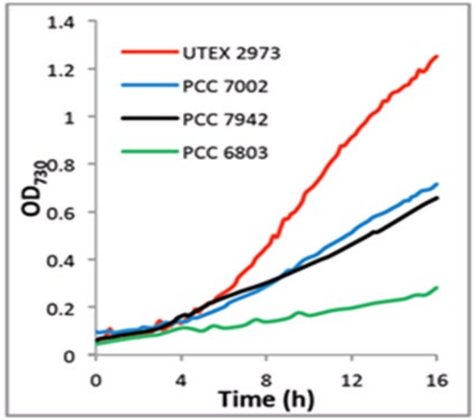


Photo-biorefinery

Algae biomass & Fatty acids Carbon neutral fuel



Fast growth in optimal PBR: 41 ^oC, 1500 $\mu mol/m^2/sec$ of light, 50mL, 5% CO_2

Xiao et al., Sci Total Environ. 2022. 847:157533.

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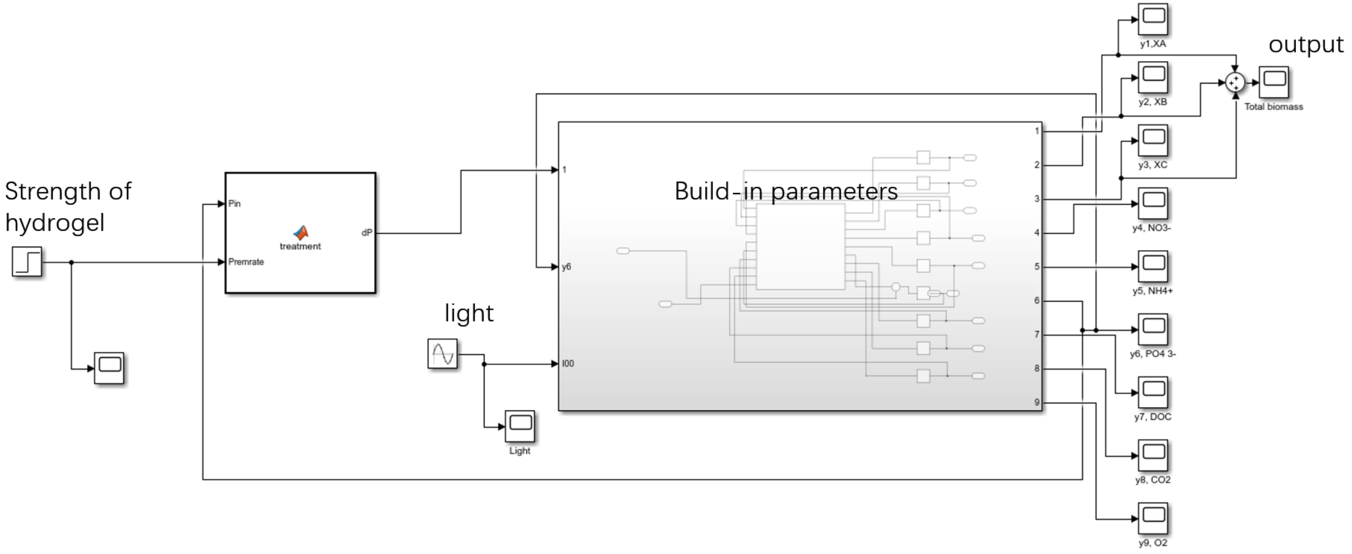
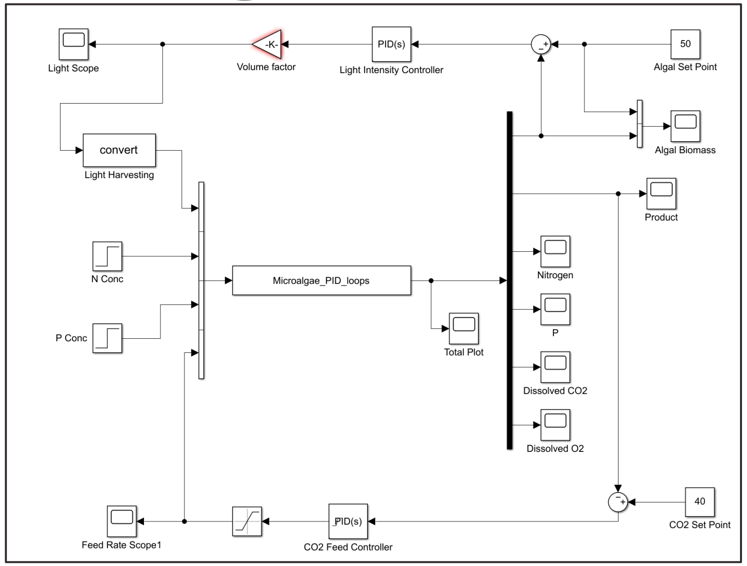
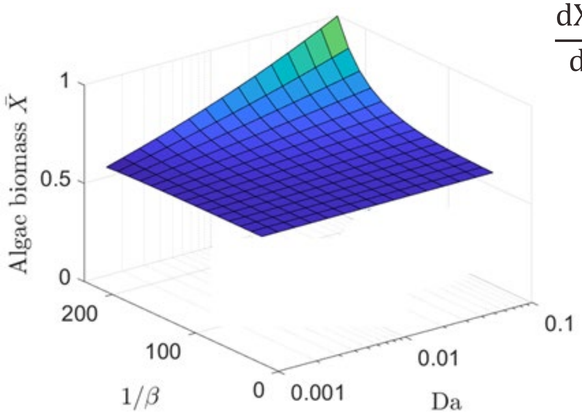
Integrated Modeling







$$\frac{dX_A}{dt} = \frac{\mu_{max,A} S_{CO_2}}{S_{CO_2} + K_{CO_2}} \frac{I}{I + K_L} \frac{N}{N + K_N} X_A - k_{d1} X_A \quad - DX_A \quad (Eq\ 1)$$

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

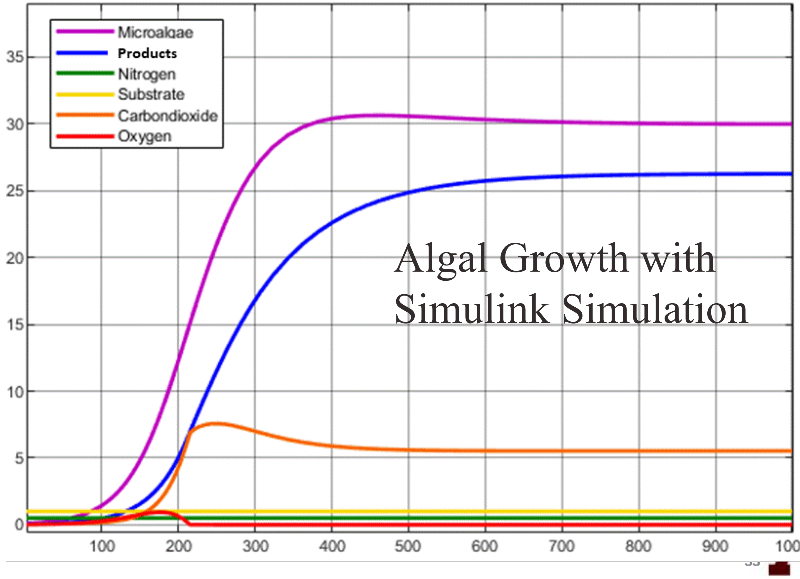
$$\frac{dP_L}{dt} = Y_L \frac{dX_A}{dt} + aX_A \quad (Eq\ 3) \quad (Biofuel)$$

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

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

The light function I can be described as:

$$I = \frac{I_0}{A(X_A + X_B)} (1 - e^{-A(X_A)}) \qquad (Eq. 6)\ .$$



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System modeling

Modeling components

Input parameters
1. Total salt content of water
2. Cell composition
3. Nutrient sources
4. Nutrient release rates

Measured
1. pH
2. Nutrient levels
3. Temperature
4. Chlorophyll fluorescence

Control variables
1. Light intensity
2. Nutrient feed rates
3. CO_2 feed rates

Optimization
1. Biomass production
2. Lipid production
3. CO_2 utilization
4. Harvest Schedule

Experimental data

[Zhou] CO_2 release rates
[Yuan] Strain specific data
[Jun] Nutrient release rates

Process dynamics

[Tang] Algae production model

Process optimization and control

Phases of algae growth
1. **Lag** - initial delay in growth
2. **Exponential** – contingent on supply of nutrients and light
3. **Linear**
4. **Stationary** – constant growth rate
5. **Death** – accumulation of waste, decrease in nutrients

Quantify impact of strain characteristics and process design considerations on phases and composition of algae growth

- Develop appropriate control scheme
- Identify bottlenecks
- Propose experiments

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

Pistikopoulos and McCarl's groups@TAMU&WUSTL

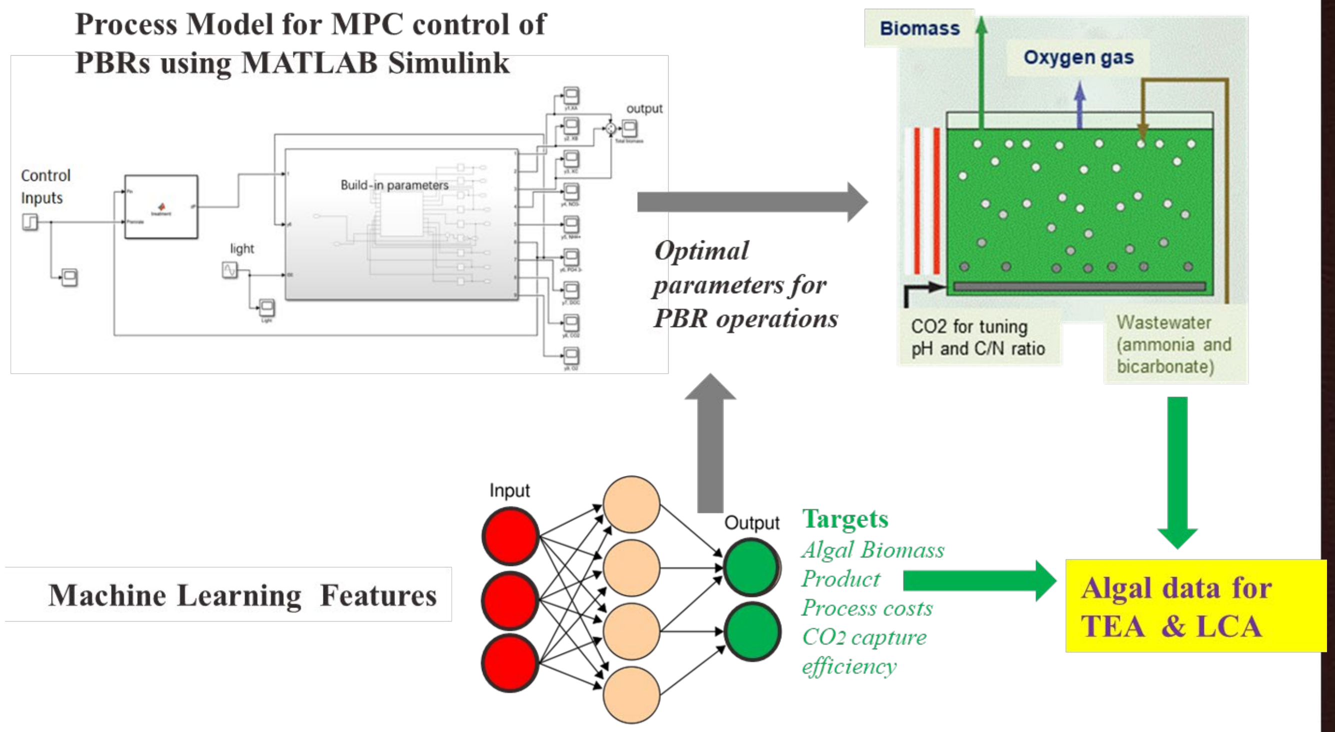
ATM

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

Dai

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

McCarl

TAMU Agriculture Economics
Life cycle analysis and environmental analysis

NCCC at Southern Company
Scale up and on-site testing

Morten

Pistikopoulos

Chemical Engineering
System modeling and TEA

Zhou

TAMU Chemistry
Amine-based porous sorbent advancement

Yuan

Jun

Tang

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

Acknowledgement

- DOE Office of Fossil Energy
- Dr. Lei Hong

- Questions?