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CO_2 to Bioplastics: Beneficial Re-use of Carbon Emissions from Coal-Fired Power Plants Using Microalgae

University of Kentucky

ALGIX

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DUKE ENERGY

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Project Overview
(DE-FE0029623)

- **Funding:**
  DOE: $999,742
  Cost share: $258,720
  Total project: $1,258,462

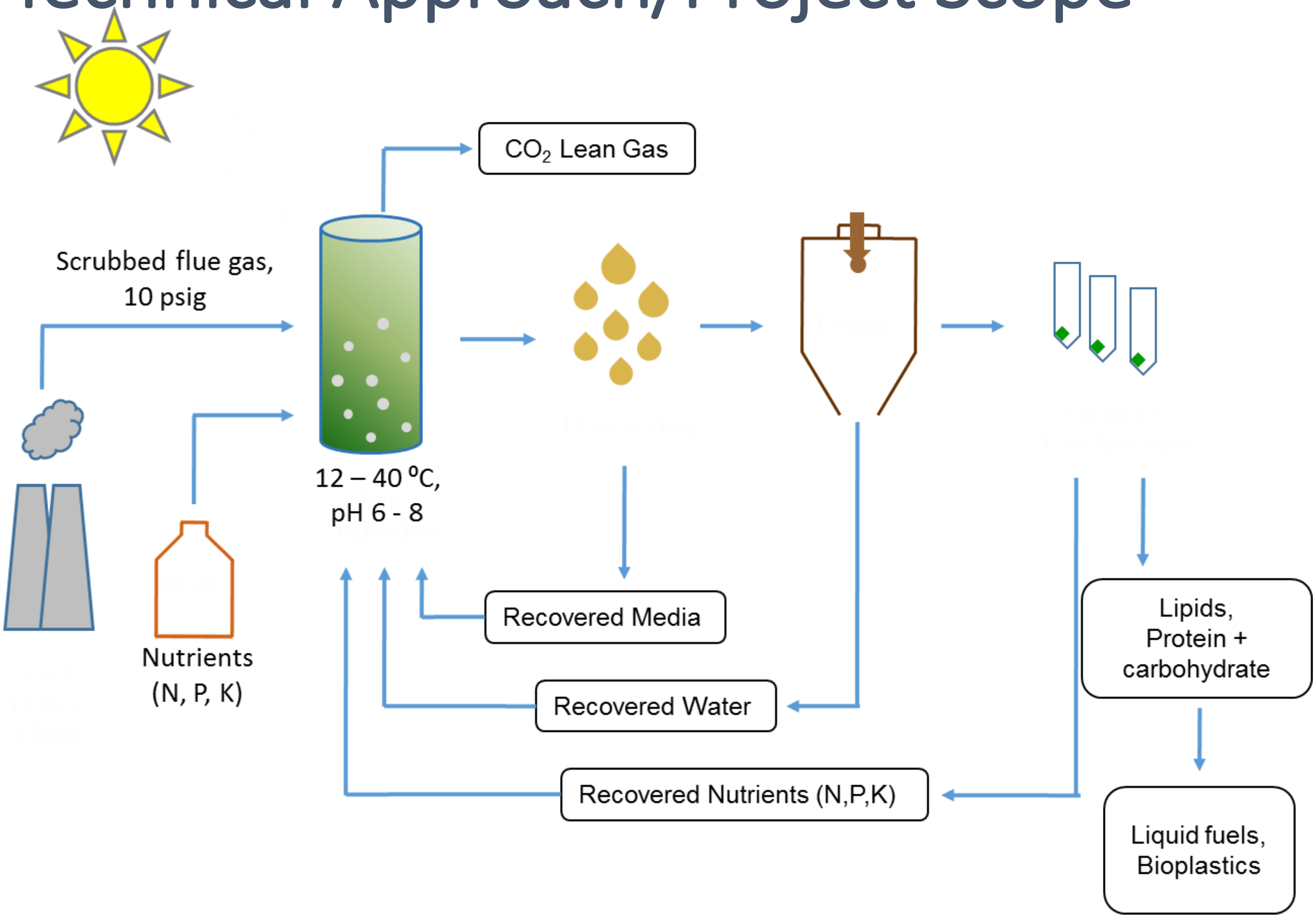
- **Performance dates:**
  6/1/2017 – 5/31/2020

- **Project Participants:**
  - University of Kentucky
  - Colorado State U.
  - Algix LLC
  - Duke Energy

Project Objectives:

- A dual PBR/pond cultivation system will be evaluated with respect to capital and operational costs, productivity, and culture health, and compared to pond-only cultivation systems
- A high-value biomass utilization strategy will be developed to simultaneously produce a lipid feedstock for the production of fuels, a carbohydrate feedstock for conversion to chemicals and/or bio-ethanol, and a protein-rich meal for the production of algal-based bioplastics
- Techno-economic analyses will be performed to calculate the cost of CO_2 capture and recycle using this approach, and a life cycle assessment will evaluate the potential for reducing greenhouse gas emissions.

DE-FE0029623: Technical Approach/Project Scope



Advantages and Challenges

- Ability to generate a valuable product, thereby off-setting costs of CO_2 capture (potential for new industry)
- No need to concentrate CO_2 stream
- Potential to polish NOx and SOx emissions

- Areal productivity such that very large algae farms required for significant CO_2 capture
- CO_2 capture efficiency modest for conventional systems (<50%)
- Challenging economics: cost of algae cultivation is high (currently >$1,000/MT), hence require high value applications for produced algae biomass
- Market size generally inversely related to application value (hence risk of market saturation)

Key Issues to be Resolved

1) Can algal biomass production costs be lowered by the use of a combined PBR + pond cultivation system?

   → Combine the low capex of ponds with the high productivity of PBRs

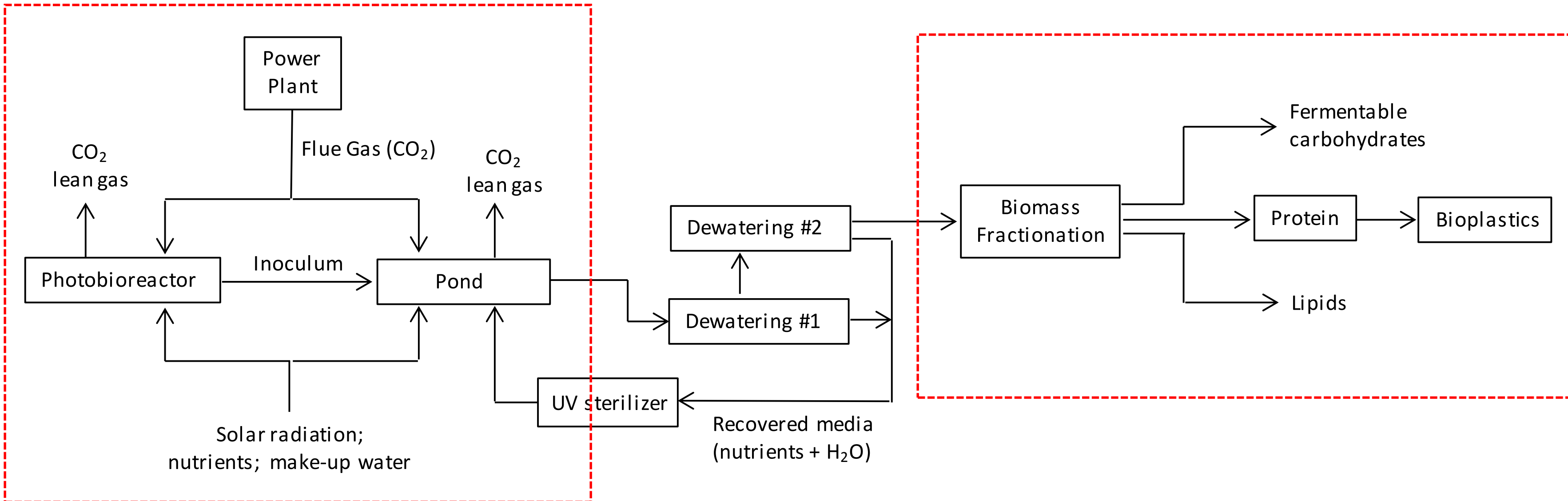
   → Comparison of pond, PBR, and PBR/pond systems (TEA and LCA)

2) In the case of algae-based bioplastic production, which processing scheme offers the greatest potential for revenue generation and large-scale application?

   → Whole biomass vs. wet lipid extraction vs. combined algal processing (CAP)

3) From a TEA and LCA perspective, which cultivation system and processing scheme(s) offer the greatest potential?

Technical Approach/Project Scope (1)



- Focus on algae cultivation (maximize productivity / minimize cost) and biomass fractionation (maximize value of produced biomass)
- Algae cultivation studies at UK CAER in Year 1, transitioning to Duke Energy's East Bend Station in Year 2

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Technical Approach/Project Scope (2)

Year 1:

- Task 1: Project Management
- Task 2: LCA and TEA
  - develop engineering process model for ponds, PBR and PBR/pond hybrid system
- Task 3: Algae Cultivation
  - pond and PBR installation
  - pond operation: comparison of pond and PBR/pond hybrid system
  - monitor hydrolysate quality and composition
- Task 4: Biomass Processing
  - wet lipid extraction with carbohydrate recovery
  - combined algal processing evaluation
  - bioplastic compounding

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Project Timeline

				Budget period 1				Budget period 2				Budget period 3			
				6/1/17-5/31/18				6/1/18-5/31/19				6/1/19-5/31/20			
Tasks and Milestones	Start	End	Cost	Q 1	Q 2	Q 3	Q 4	Q 1	Q 2	Q 3	Q 4	Q 1	Q 2	Q 3	Q4
1.0 Project Management	6/1/2017	5/31/2020	$119,845												
1.1 Stakeholder Meetings															
1.2 Reporting	6/1/2017	5/31/2020													
Milestone 1: Project kick-off meeting															
2.0 LCA/TEA I	9/1/2017	2/28/2018	$76,166												
2.1 Engineering Process Modeling	9/1/2017	2/28/2018													
Milestone 2.1: Engineering system model completed															
3.0 Algae Cultivation I: Lab/Pilot Scale Investigation	6/1/2017	5/31/2018	$192,928												
3.1 Pond Installation	6/1/2017	8/31/2017													
3.2 PBR + Pond Operation	9/1/2017	2/28/2018													
3.3 Monitor Hydrolystate Quality and Composition	12/1/2017	5/31/2018													
Milestone 3.1: Pond and PBR/pond systems operational															
4.0 Biomass Processing I: Biorefinery Concept Development	6/1/2017	5/31/2018	$109,453												
4.1 Optimization of Wet Lipid Extraction	6/1/2017	11/30/2017													
4.2 Combined Algal Processing Evaluation	12/1/2017	5/31/2018													
4.3 Bioplastic Compounding	12/1/2017	5/31/2018													
Milestone 4.2: > 50% sugars & >80% lipids recovered															
5.0 LCA/TEA II	6/1/2018	5/31/2019	$149,341												
5.1 Initial Techno-economic Analysis	6/1/2018	11/30/2018													
5.2 Initial Life Cycle Assessment	12/1/2018	5/31/2019													
Milestone 5.2: Initial LCA showing net CO_2 capture															
6.0 Algae Cultivation II: Demonstration	6/1/2018	5/31/2019	$211,779												
6.1 Site Preparation	6/1/2018	8/31/2018													
6.2 PBR and Pond Operation	9/1/2018	2/28/2019													
6.3 Monitor Culture Health and Identify Contaminants	12/1/2018	5/31/2019													
Milestone 6.1: Ponds and PBR/ponds installed at East Bend															
7.0 Biomass Processing II: Valorization and Scale Up	6/1/2018	5/31/2019	$133,244												
7.1 Market Analysis (sugars & lipids)	6/1/2018	11/30/2018													
7.2 Bio-Plastic Material Characterization	12/1/2018	5/31/2019													
Milestone 7.2: Bioplastic fiber vs film comparison															
8.0 LCA/TEA III	6/1/2019	5/31/2020	$264,037												
8.1 PBR Temperature and Growth Modeling	6/1/2019	11/30/2019													
8.2 Resource Assessment	12/1/2019	5/31/2020													
8.3 Data Incorporation	9/1/2019	2/28/2020													
8.4 Technology Gap Analysis	3/1/2020	5/31/2020													
Milestone 8.3: CO_2 capture cost & revenue stream quantified															
Milestone 8.4: Technology gap analysis complete															

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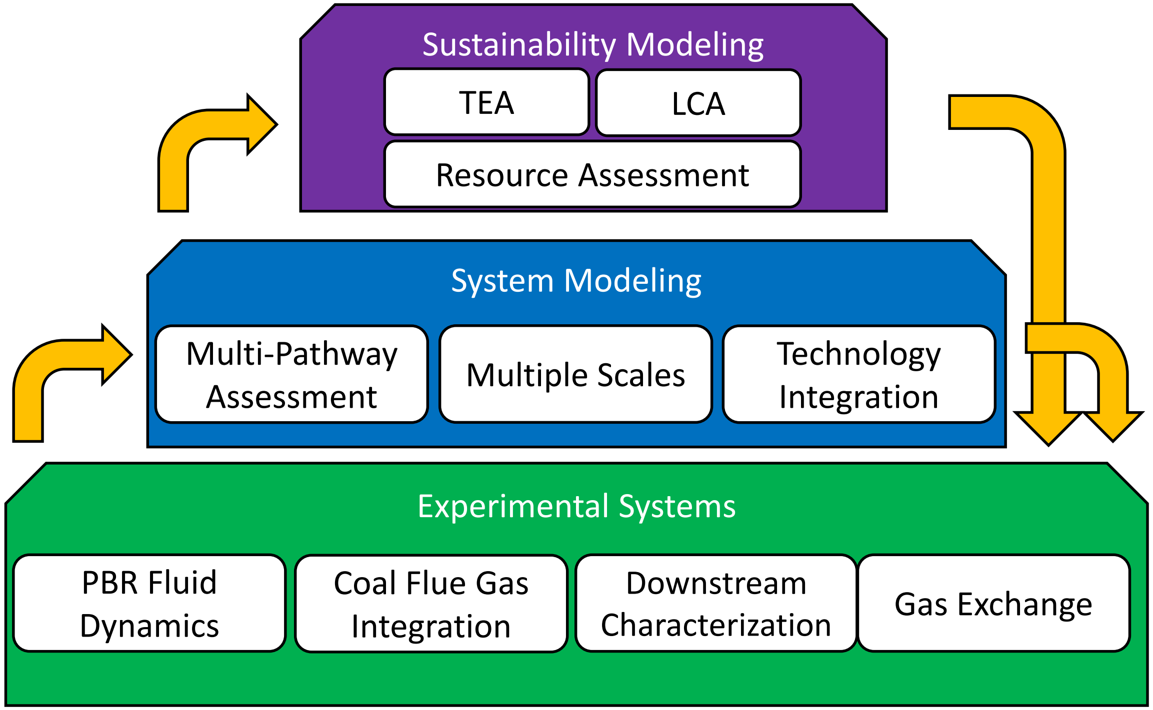
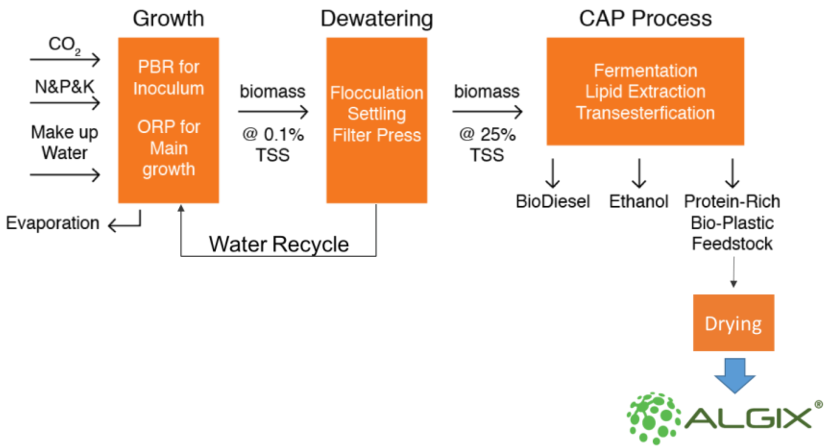
DE-FE0029623:
Year 1 Results

Task 2: Sustainability Modeling

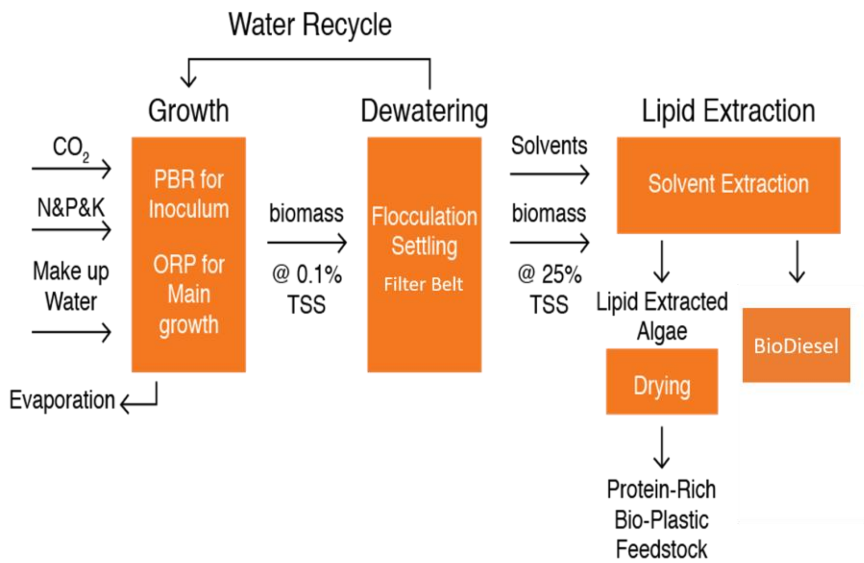


CAP Pathway



- Established NREL method
- Similar to previous extraction at CAER
- Simultaneous production of lipids, proteins, and carbohydrate streams

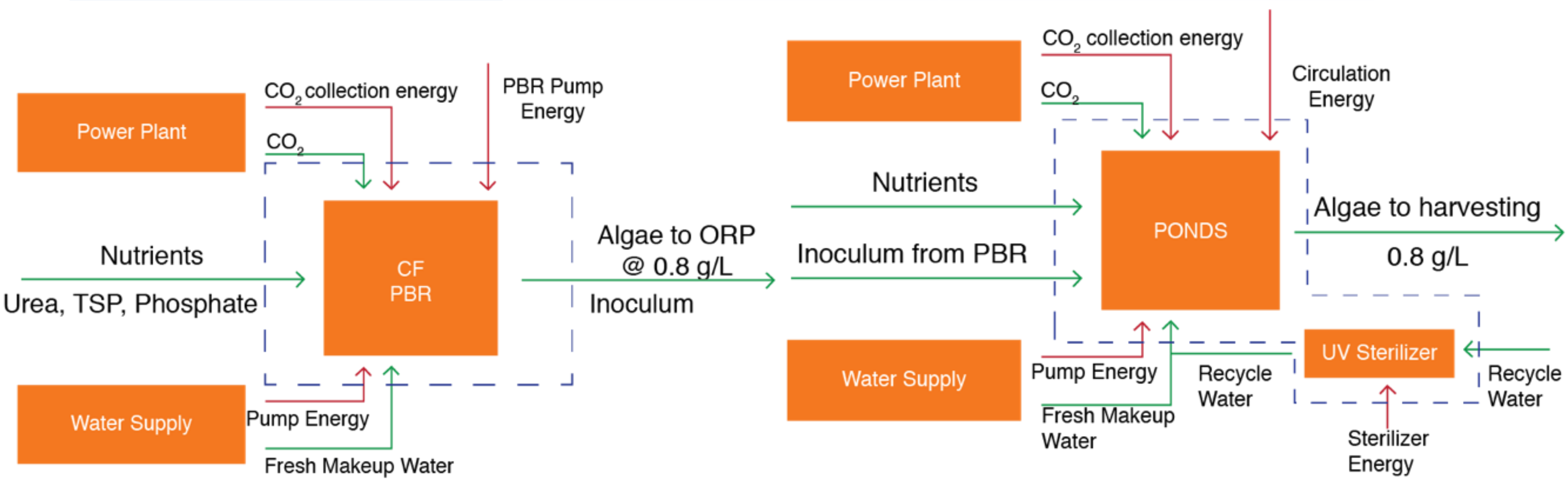
CAER Wet Lipid Extraction Pathway



- Developed at UK CAER
- Optimized approach
- Produced fractions can be tuned based on conditions
- Yields more proteinaceous solids for biopolymers

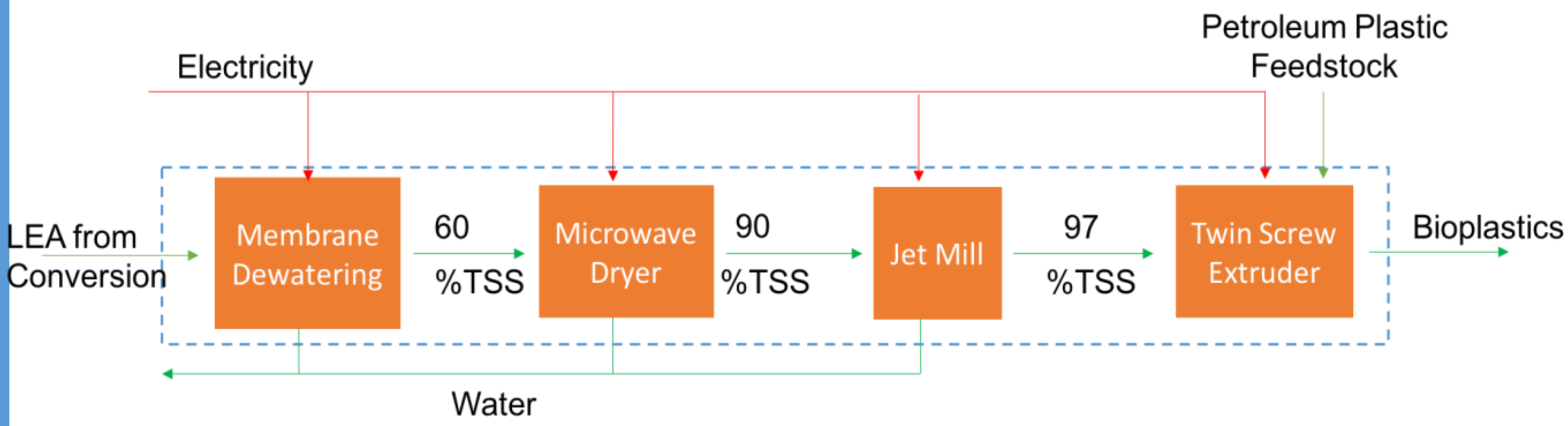
Growth Assumptions

PBR and ORP growth sub-process assumptions		
Land Area Ratio	0.167	m^2 PBR/ m^2 ORP
Fertilizer Requirements:		g/kg algae produced
Triple Super Phosphate	84.6	
Urea	169.9	
Potash	15.6	
CO_2 Requirement	1.83	kg/kg algae
Make-up Water Pumping Power Demand	1130	kWh/MMgal
CO_2 Delivery Power	37	kJ/kg
UV Sterilization Power	23.75	Wh/m^3
Circulation Energies:		
ORP	1.167	kW/ha
PBR	836.236	Wh/day module
ORP evaporation Rate	0.4	Cm/day
Individual Pond Size	40,000	m^2
PBR Module Size	100	m^3



Algix BioPlastics Assumptions

Algix Bioplastic Sub-Process Assumptions		
Membrane Electricity Demand	88.2	Wh/kg algae
Microwave Dryer Electricity Demand	0.485	kWh/kg algae
Jet Mill Electricity Demand	0.485	kWh/kg algae
Screw Extruder Electricity Demand	0.507	kWh/kg algae
Fraction of Bioplastic:		
Biomass	0.45	kg/kg bioplastic
Petroleum	0.55	kg/kg bioplastic



Model Outputs

Upstream Sub-Process		
CO_2 Consumed	2253.9	Tonnes
Growth Areas: ORP PBR	 264,002 (7 ponds) 33,000 (70 modules)	 m^2 m^2
Fertilizer Requirements: TSP Urea Potash	 92,146.74 184,657.69 178,59.713	 kg kg kg
Make-up Water Requirement	525,488.65	m^3
Electrical Consumption: PBR ORP Dewatering LE CAP	 234.48 782.66 39.20 312.33 355.52	MWh
LE Pathway		
Material	Produced	Consumed
Methanol		74,408 L
HCl		54,450.34 kg
Hexane		40,838 L
Petroleum Plastic Feedstock		897,302 kg
BioPlastic	1,631,459 kg	
BioDiesel	63,495 kg	
CAP Pathway		
Material	Produced	Consumed
Methanol		16,007 kg
KOH		31,785 kg
NaOH		2,052 kg
HCl		11,629 kg
Petroleum Plastic Feedstock		764,041 kg
BioPlastic	1,389,165 kg	
BioDiesel	78,761 kg	
Glycerin	9,451 kg	
Citric Acid	112,374 kg	Fermentation product

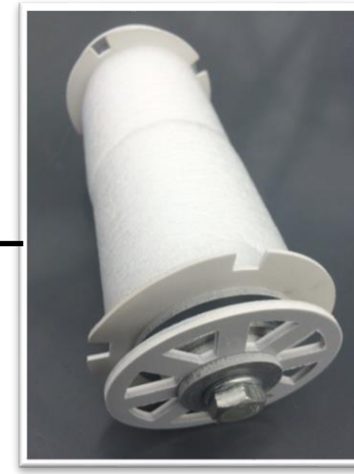
Task 3: Installation of Ponds

- *4 x 1100 Liter raceway ponds were installed and commissioned in first week of September 2017, along with 200 Liter seed pond*
- *Total growing capacity now > 8,000 Liters:*
    - *2 x 1200 L cyclic flow*
    - *4 x 1100 L ponds*
    - *1 x 200 L seed pond*
    - *2 x 150 L seed reactor*
    - *1 x 800 L Varicon biofence PBR*

Ponds and cyclic flow PBR installed at UK CAER (10/6/2017)

Task 3: Construction of Updated Cyclic Flow Photobioreactor

A.



B.

System Info:

- 2 rows of tubes @ 36 tubes per row (72 tubes)
- 1140 L total system volume

Improvements:

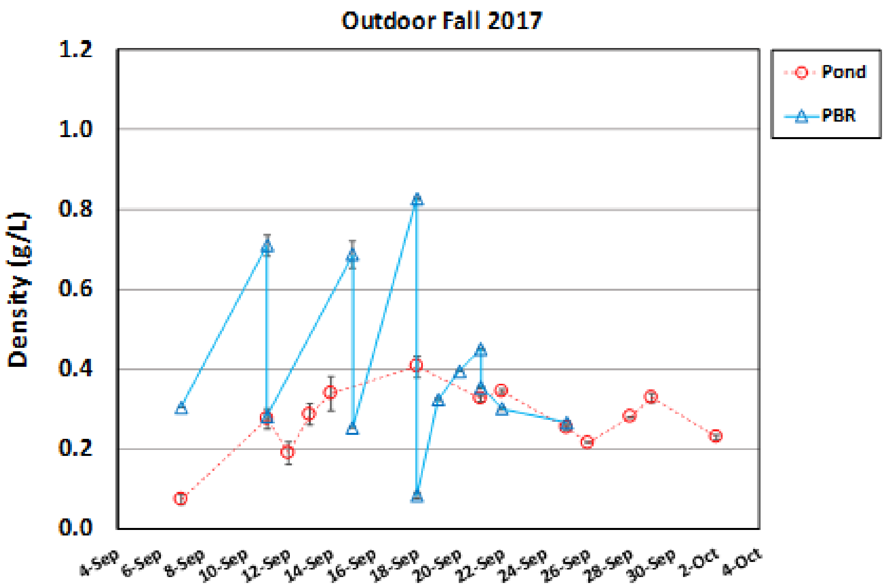
- New PBR features several Chinese-made components:
  - Pipe-cleaning pigs (**A**) are now mass produced.
  - PVC stubs (**B1**) used to mount the PET tubes now utilize rubber O-rings (**B2**) instead of the previously used rubber bands, creating a more leak resistant connection.
- Improved gas delivery system with more consistent bubble column.

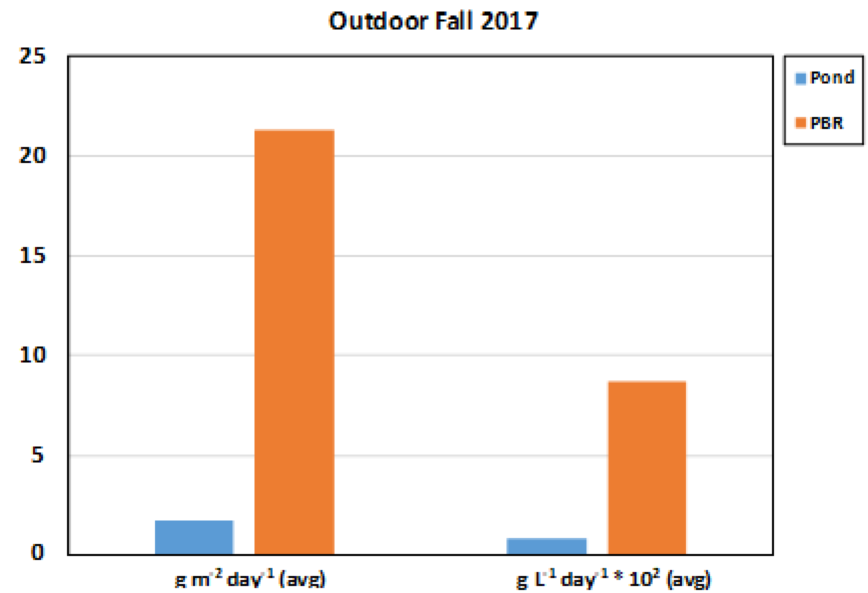
Installation of Ponds: Algae Lab Systems (ALS) Water Quality Monitoring

- *Latest technology integrated with growth systems to continuously monitor temperature, pH, dissolved oxygen, and optical density*
- *ALS Spark boxes are modular, swappable, and commute wirelessly to a central hub to facilitate data visualization and export*
- *Representatives from Commercial Algae Professionals and Algae Lab Systems were on site to help with the installation and to train CAER research staff*

Clockwise from top left: ALS Spark box, software interface, wireless calibration of probes, ALS and Commercial Algae Professionals working on system installation

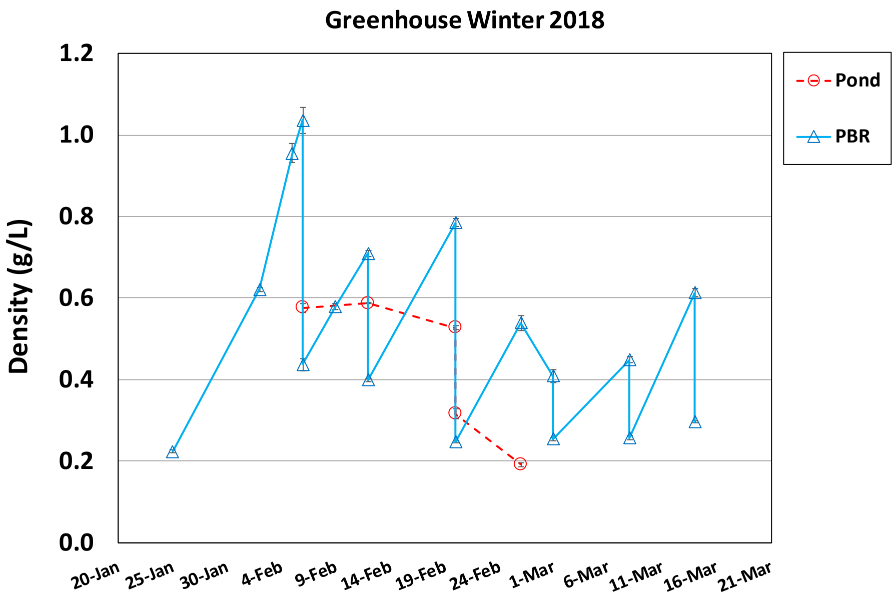
Task 3: Algae Cultivation

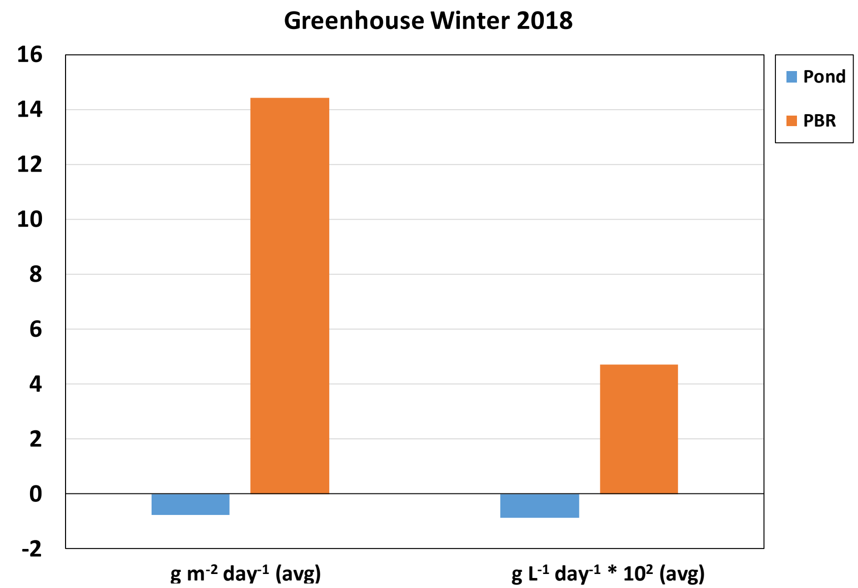




- Algae were cultivated in the cyclic flow PBR, as well as in 2 x 1100 L ponds, in September 2017
- The superior performance of the PBR was reflected in average growth rates for the PBR and ponds of 0.087 and 0.009 g L^{-1} day^{-1}, respectively
- Average areal productivities for the PBR and ponds were 21.3 and 1.74 g m^{-2} day^{-1}, respectively

Task 3: Algae Cultivation



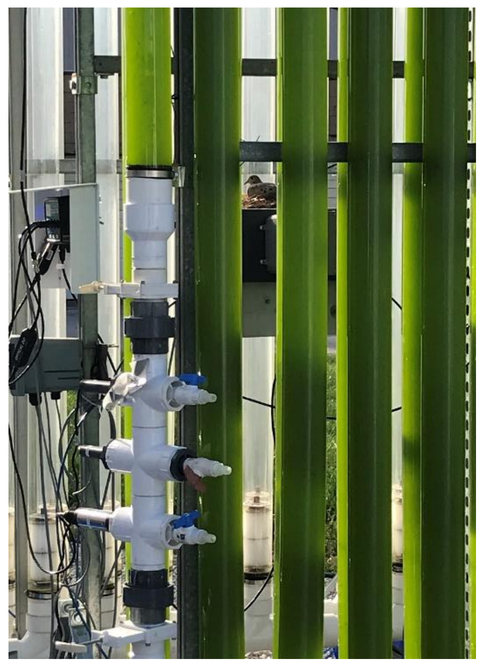


- Algae were cultivated in the cyclic flow PBR, as well as in a 200 L seed pond, in the CAER greenhouse during January-March 2018
- Average indoor daily PAR values for Jan – March 2018 were 269 µmol m^{-2} s^{-1} with a max value of 1075 µmol m^{-2} s^{-1}. The average daily reactor temperature was 23 ^{o}C with a range of 7 ^{o}C – 42 ^{o}C.
- Average growth rates for the PBR and pond for January-March were 0.047 and -0.008 g L^{-1} day^{-1}, respectively
- Average areal productivity for the PBR and pond for January-March were 14.5 and -0.889 g m^{-2} day^{-1}, respectively

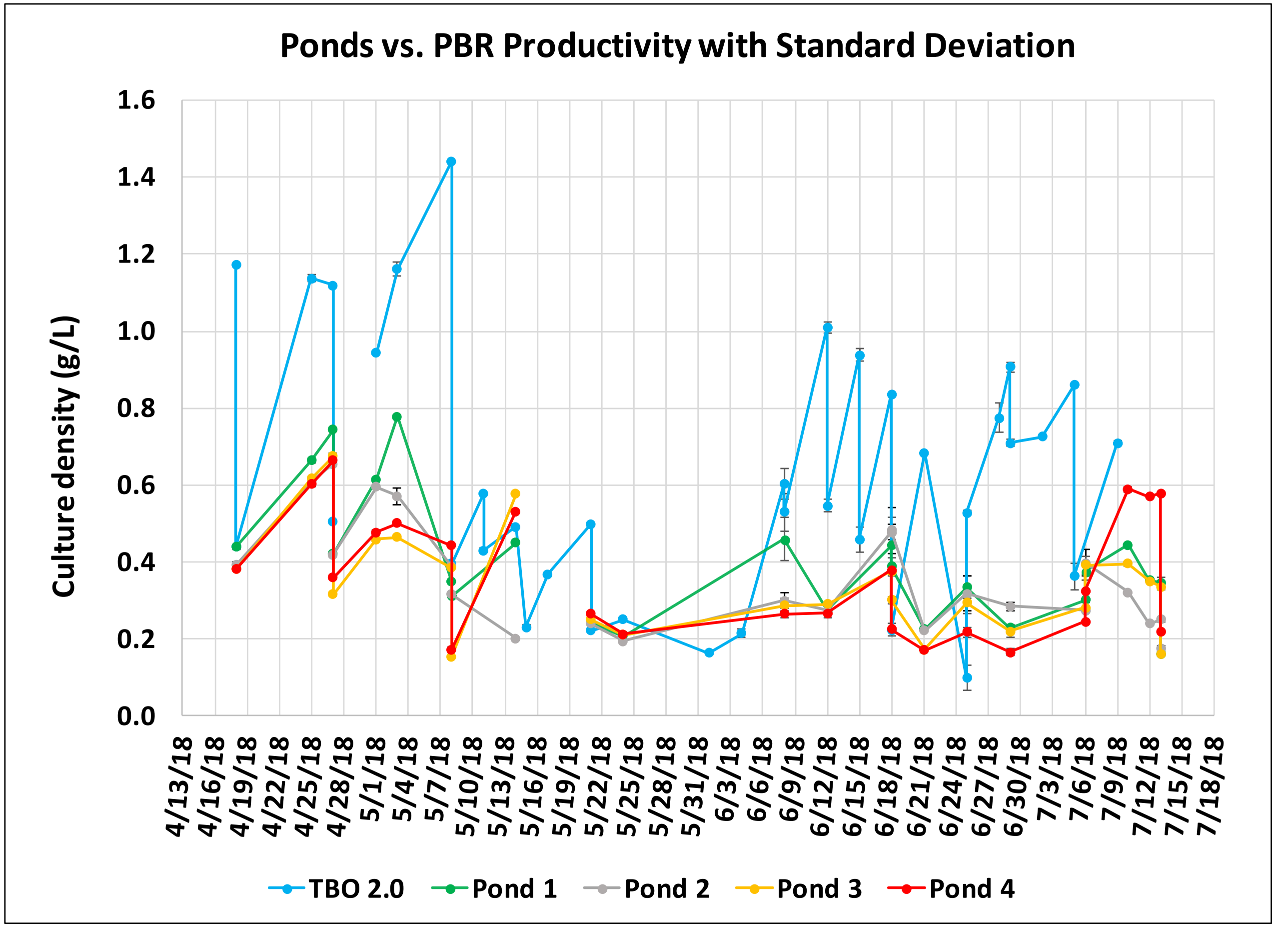
Task 3: Algae Cultivation

- Unseasonable spring weather delayed growth campaign
- Outdoor cultivation was commenced on March 27th in the newest cyclic flow PBR, seeded from the greenhouse seed reactor
- Two dissolved oxygen probes were installed (at top and bottom of tube) to determine the most appropriate measurement location in the PBR
- The outdoor ponds were seeded from the PBR on 4/18/18 to commence the growth campaign

Clockwise, starting top right: (i) Cyclic flow PBR seeded on 3/27/2018; (ii) algae test bed on intended seed date of 3/20/2018; (iii) installed bio-interface panel and a nesting mourning dove

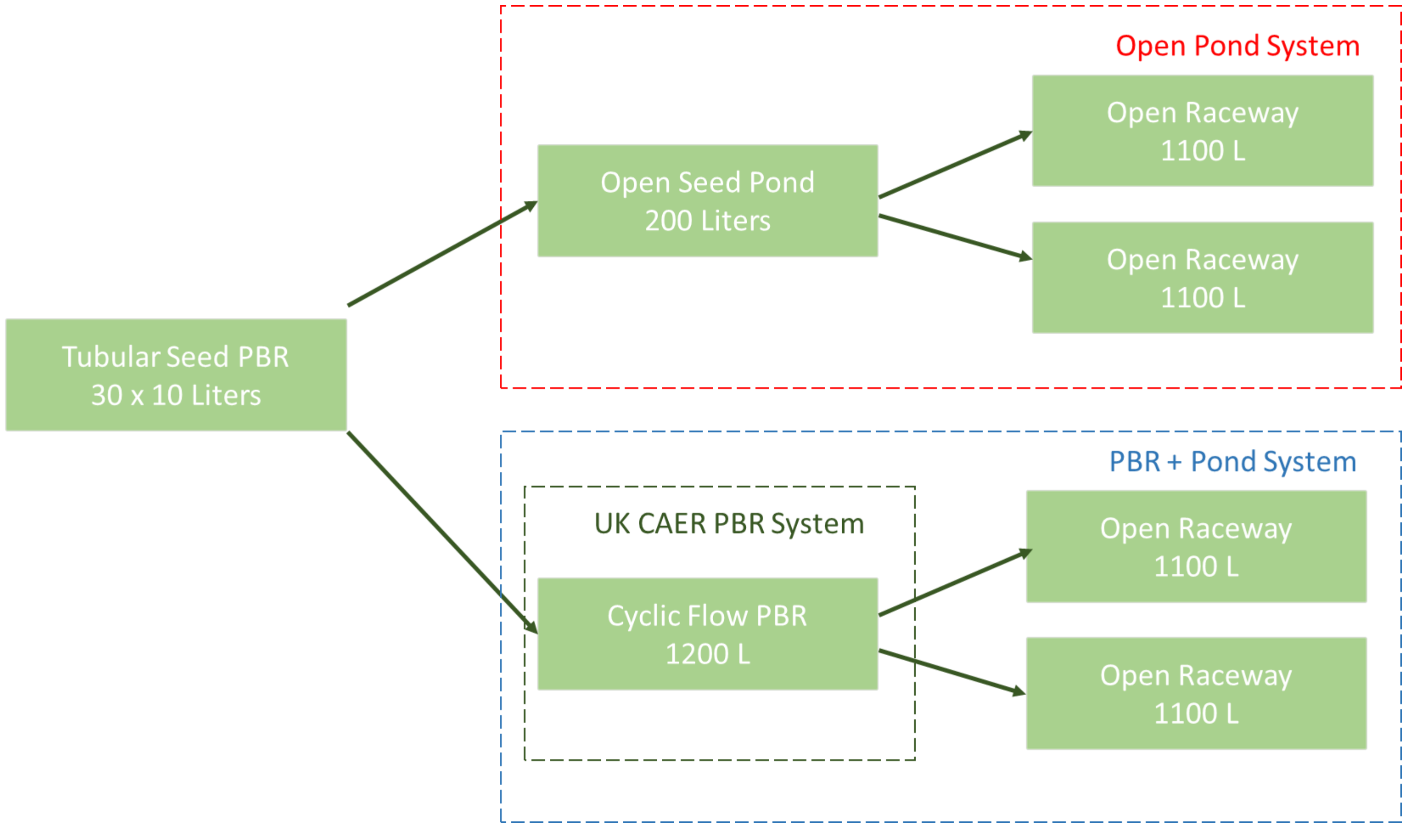


Task 3 / 6 : Algae Cultivation



- Poor pond productivity to date hampering PBR/pond vs. pond-only evaluation
- Lessons learned will be transferred to East Bend Station (e.g., increase degree of pond over-seeding from PBR)
- PBR/pond vs. pond-only culturing experiments continuing at UK CAER
- PBR continues to show vastly superior productivity

Task 3: Growth Comparison Study

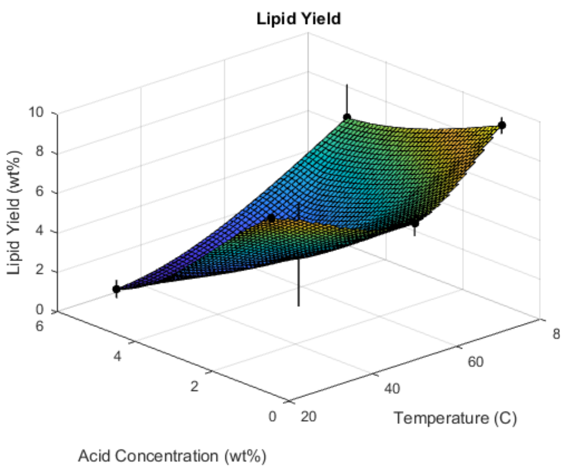


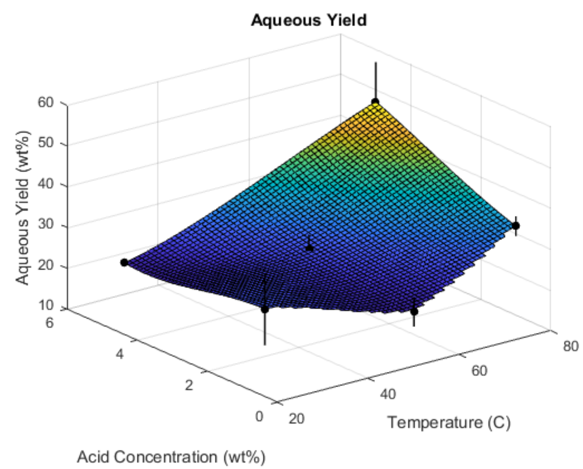
Operating Conditions

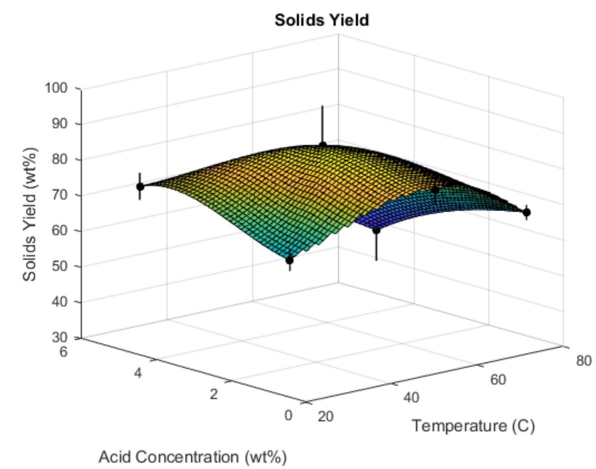
- Open Pond System seeded from seed pond and operated traditionally in semi-batch mode, with harvesting and dilution from 0.8 g/l to 0.2 g/l
- PBR + Pond system will be harvested at 0.8 g/l to 0.1 g/l with an additional 'over seed' of 0.1 g/l from PBR
- PBR system will then be harvested to match the other systems at 0.2 g/l
- Similar data sets will be maintained for all systems

Task 4: Optimization of Algae Fractionation – Wet Lipid Extraction

- Lipids isolated from wet algae biomass via *in situ* transesterification/esterification using MeOH/HCl. Lipids recovered via hexane washing, solids via filtration. Aqueous phase contains mainly dissolved sugars.
- DoE: T = 25, 50, 80 °C; [HCl] = 0, 1, 3, 5 wt% of MeOH used; MeOH = 50, 100, 200 ml. Fixed: 100 g algae slurry (20 wt% solids); extraction time 2 h. Triplicate runs.



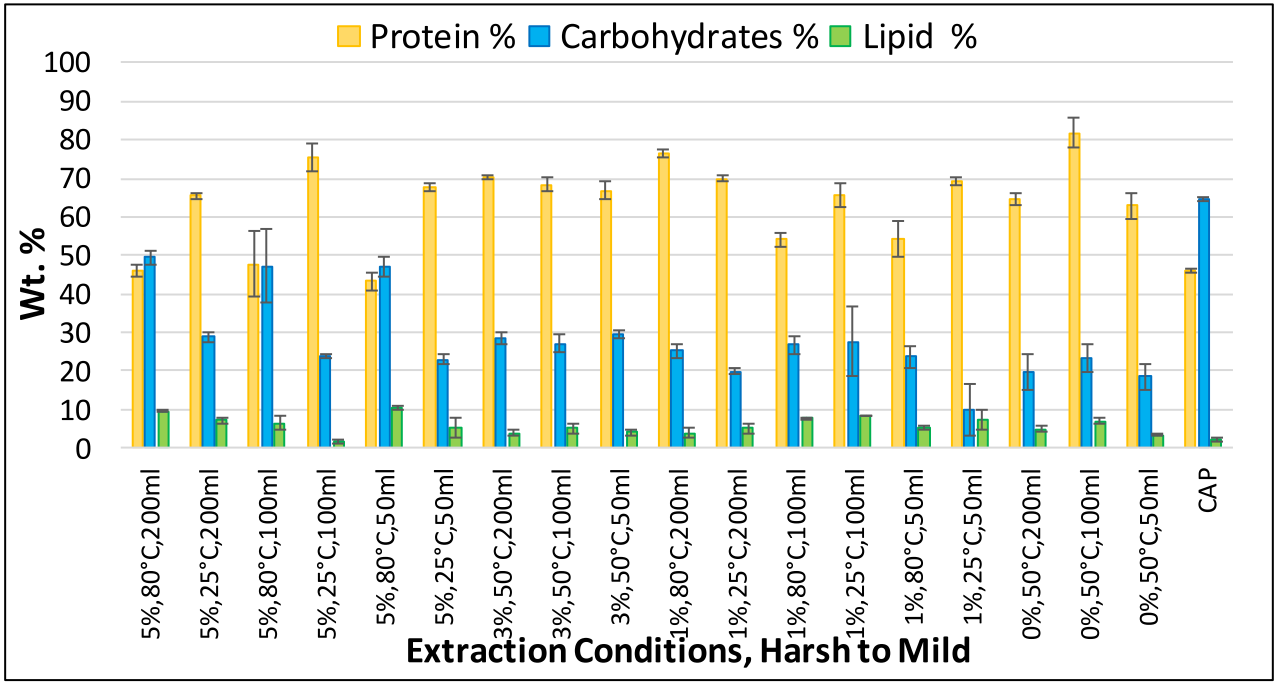




- ➢ Increasing temperature and acid concentration lead to higher aqueous phase yield and lower solids yield
- ➢ Increasing acid concentration decreases lipid yield while increasing temperature leads to increased lipid yield
- ➢ Volume of MeOH (not shown) has little effect on the yields of all fractions

Task 4: Optimization of Algae Fractionation – Summary

Wet lipid extraction and CAP results



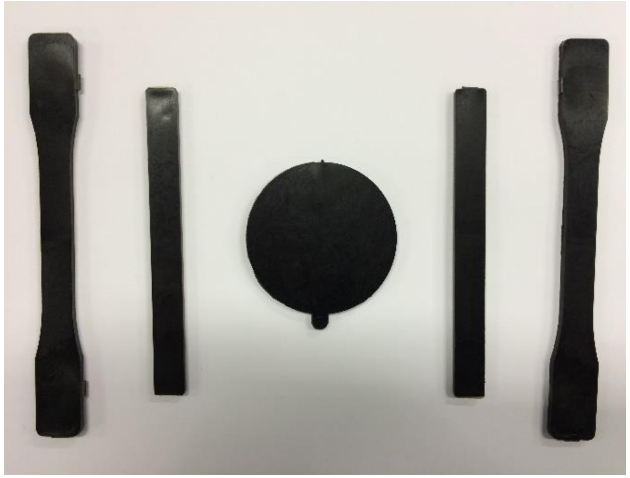
Wt% of fractions obtained from CAP

	Defatted solids (wt%)	Carbohydrate fraction (wt%)	Organic fraction (wt%)	Recovery %
Average	45.9	64.5	2.0	112.4
STDV	0.5	0.6	0.4	1.5

Composition of Whole and Defatted Algae

Sample	Ash (wt%)	Protein (wt%)	Volatiles (GC/MS)
Whole	11.1	44.2	16 peaks at 140 °C; 196 peaks at 200 °C
Defatted	15.6	50.7	12 peaks at 140 °C; 121 peaks at 200 °C

- Increase in protein and ash content consistent with removal of lipids
- Fewer compounds were released upon heating to 200 °C for the defatted algae, suggesting that lipid extraction may have improved thermal stability
- Defatted algal biomass has improved odor properties
- Defatted algae used for production of maleic anhydride compatibilized EVA (ethylene vinyl acetate) composite, containing 30 wt% algae



EVA composite test parts

Task 5: LCA TEA II

- A more in-depth LCA for both Combined Algal Processing (CAP) and Lipid Extraction (LE) pathways has been completed.
  - Shown in Figures 1 & 2. Added co-product credits and material consumption emissions.

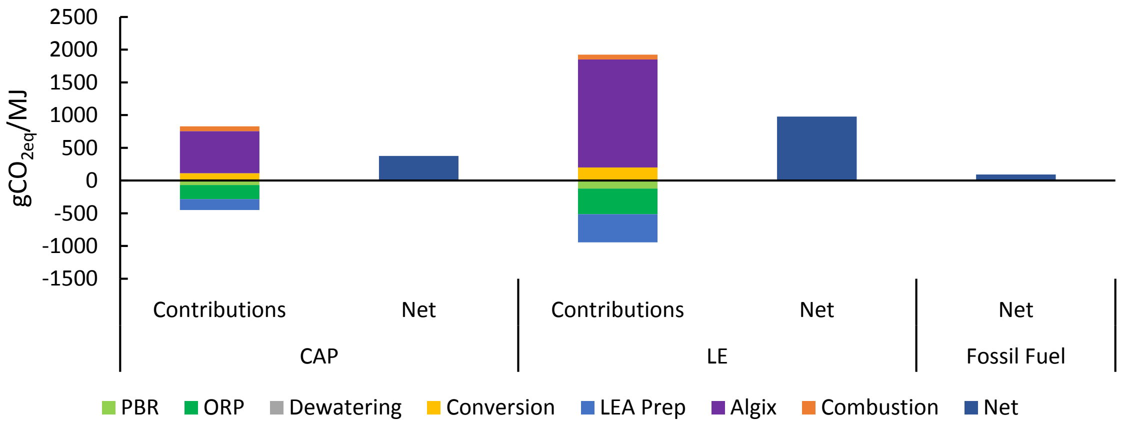
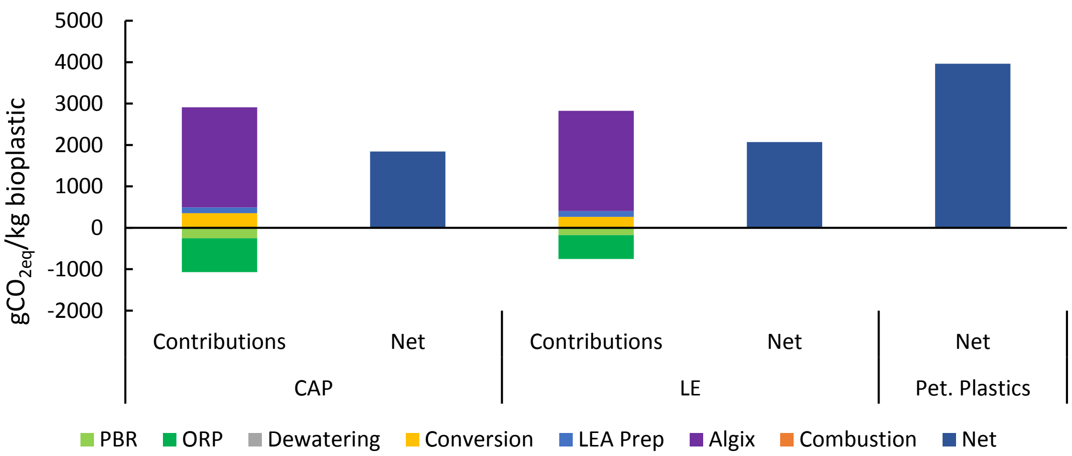


Figure 1.LCA for a fuels focused process. Results for each sub-process, along with the net for the pathway, are compared with fossil fuel emissions. Results show fuels produced are not sustainable.

Figure 2. LCA for a bioplastic focused process. Results for each sub-process, along with the net for the pathway, are compared with petroleum plastic emissions. Results show bioplastics are environmentally favorable.



Task 5: Preliminary TEA Results

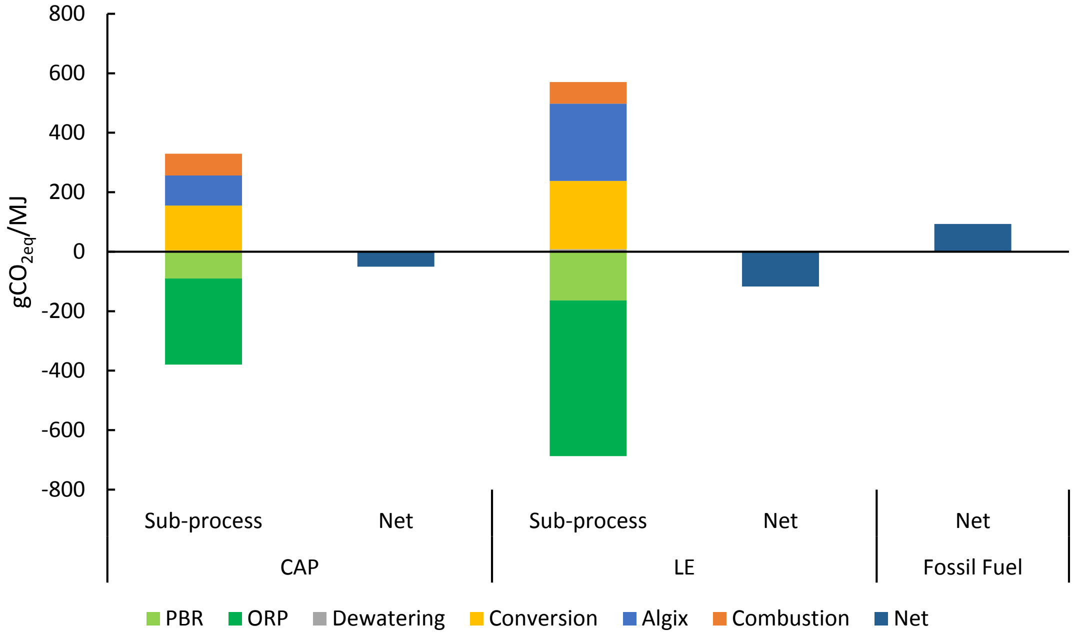


Figure 1.Basic LCA completed for both Pathways. Results for each sub-process, along with net for the pathway is compared with Fossil Fuel emissions.

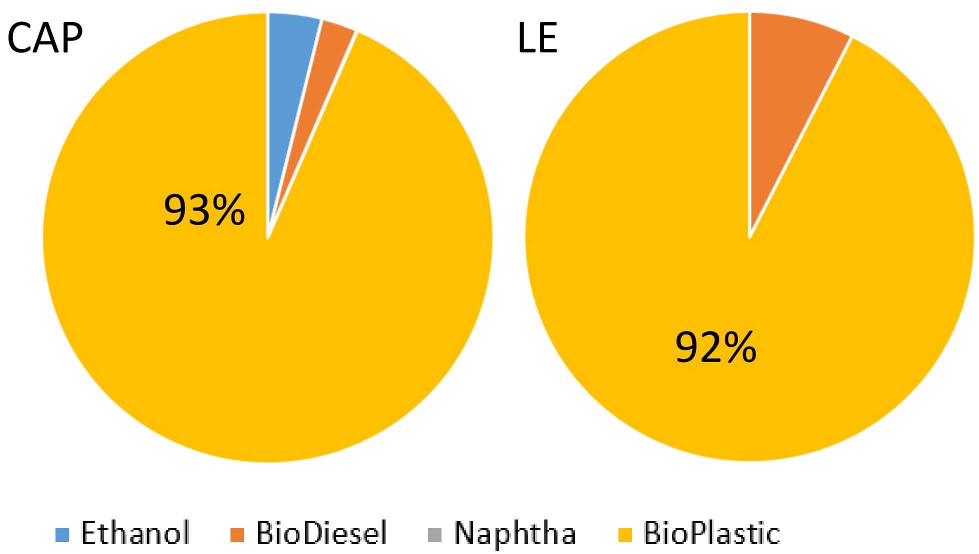


Figure 2. Shows the fraction of value in the biomass from each revenue stream. BioPlastics account for >90% in both cases.

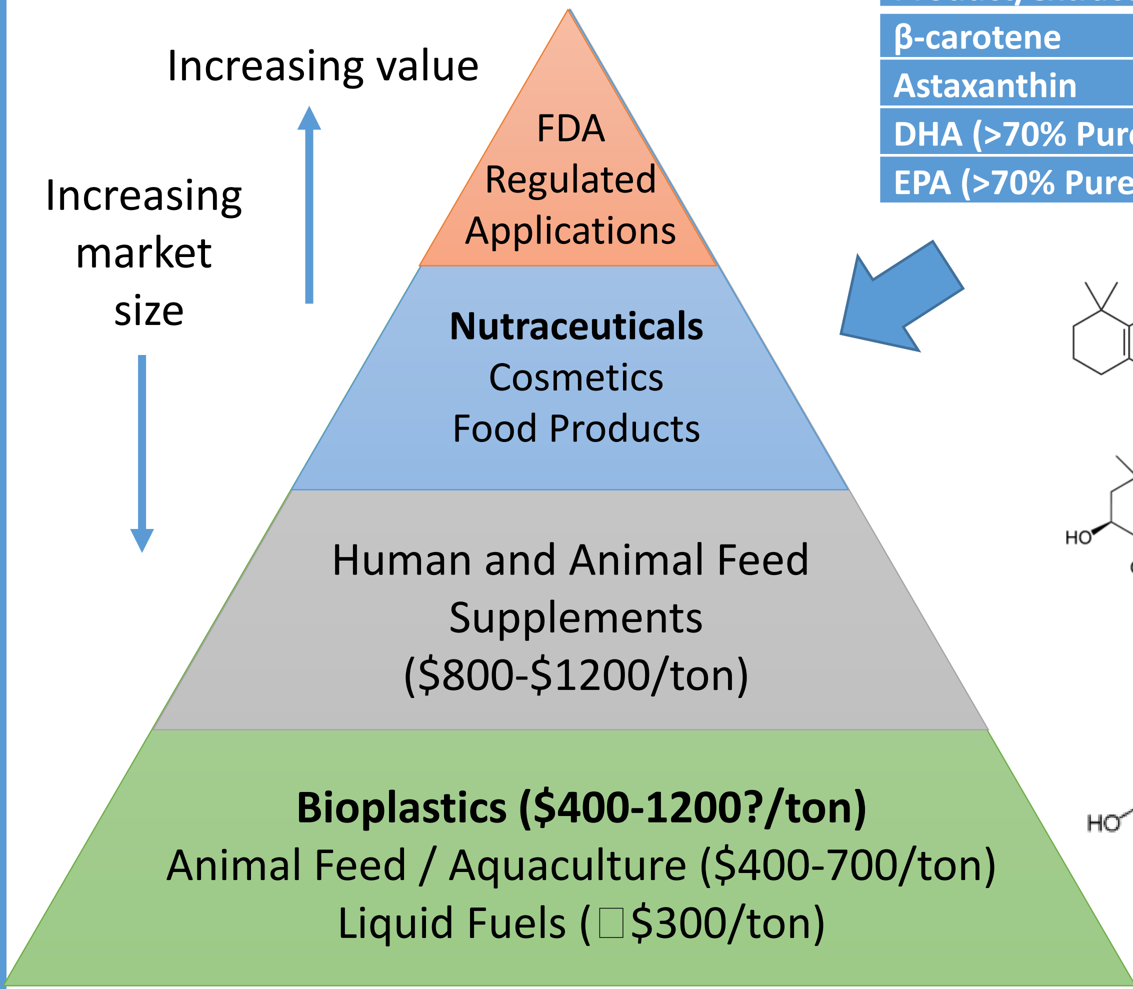
Summary of Progress to Date

- Engineering model constructed for algae cultivation, harvesting, dewatering and fractionation
- 1200 L cyclic flow PBR installed at UK CAER, together with 4 x 1100 L ponds and monitoring equipment
- Superior productivity of UK PBR with respect to open raceway ponds demonstrated indoors and outdoors
- Wet lipid extraction process optimized
- Fractions obtained from combined algal processing characterized

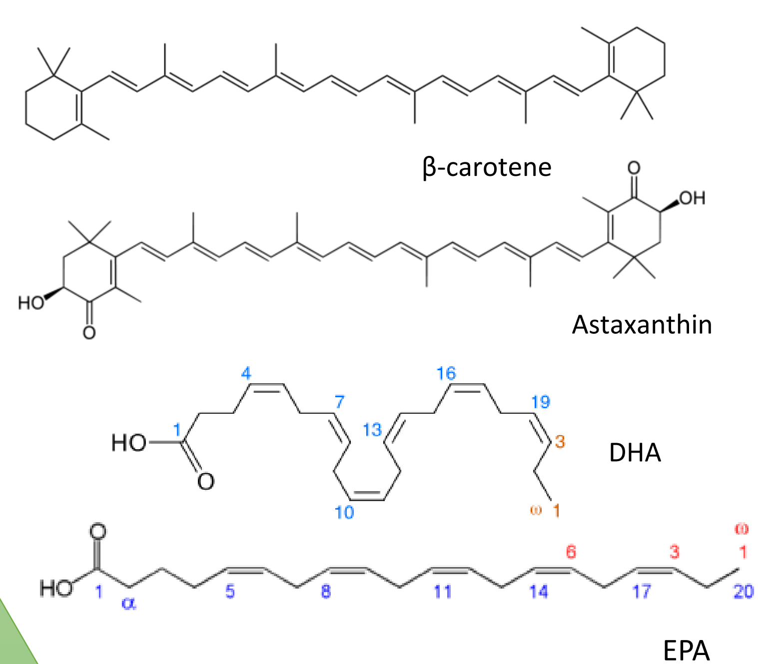
Next Steps

- Continuation of productivity study at UK CAER
- Transfer of productivity study to East Bend Station in June 2018 (EB maintenance shutdown scheduled for March-May)
- Monitor ponds for invasive species (community sequencing analysis)
- Bioplastic compounding using defatted *Scenedesmus*
- Continued refinement of engineering process model
- Continue TEA and LCA studies

Algal Biomass Utilization

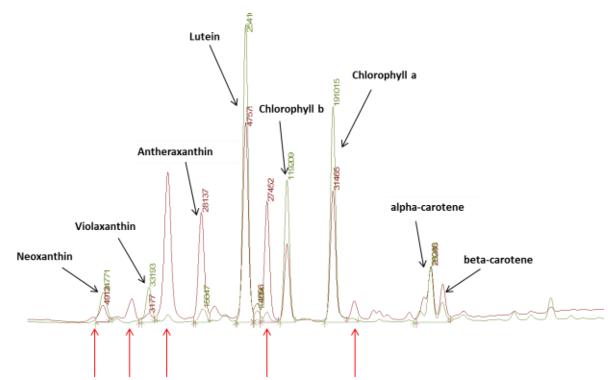


Product/extract	Selling price	Wt% in algae
β-carotene	$300-3000/kg	14%
Astaxanthin	$2500-7150/kg	3%
DHA (>70% Pure)	~$12,540/kg	7.8%
EPA (>70% Pure)	~$12,540/kg	4%



Commercialization Pathway

Clockwise from top left: 100,000 Liter cyclic flow PBR in Zhenzhou China, Red pigment production experiments, HPLC carotenoid analysis showing the production of high value chemical such as lutein / astaxanthin



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- Algix:
  Ashton Zeller, Ryan Hunt
- Duke Energy:
  Doug Durst, Joe Clark

Questions?

http://greenchicgeek.blogspot.com/2009_08_01_archive.html