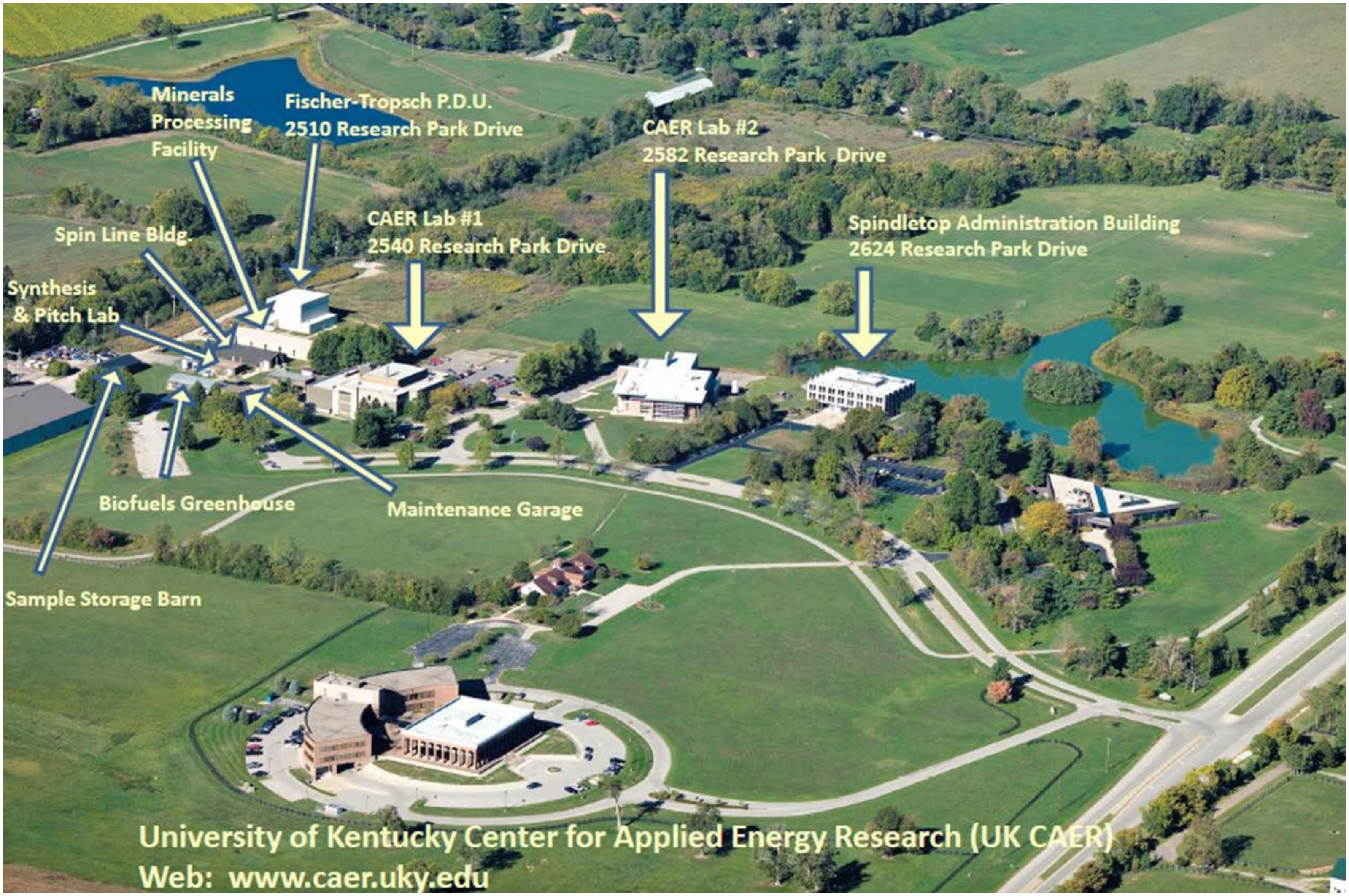
Beneficial Re-use of Industrial Carbon Dioxide Emissions using Microalgae

Mark Crocker
Center for Applied Energy Research
University of Kentucky

University of Kentucky Center for Applied Energy Research



Project Timeline

- 2008: UK approached by Kentucky Department of Energy Development and Independence to investigate the techno-economic feasibility of algae-based CO_2 mitigation
- 2011-2012: initial demonstration work started at EKPC's Dale Station
- **2012-present: demonstration project at Duke Energy's East Bend Station**
- 2011-present: part of US-China Clean Energy Research Center (CERC)
- August, 2015: NETL Biological CO_2 Utilization Award - $1,257,415

Research Focus
Power plant integration, PBR design, low cost/low energy dewatering, utilization studies, techno-economic modeling

Utilization Studies
Anaerobic digestion, lipid extraction, catalytic upgrading, bio-polymers, pyrolysis, etc.

Why Algae?

- Biodiversity – over 30,000 known species (eukaryotic, unicellular organisms)
- High productivity per acre
  - Fastest growing photosynthetic organism on the planet
- Minimizes competition with conventional agriculture
  - Doesn't need good land or fresh water
- Compatible with integrated production of fuels and co-products within bio-refineries

S.L. Nielsen, S. Enriquez, C.M. Duarte, K. Sand-Jensen, *Functional Ecology* **1996,** *10* (2), 167-175.
T.M. Mata, A.A. Martins, N.S. Caetano, *Renew. Sustain. Energy Rev.* **2010,** *14* (1), 217-232.

Screening for Optimal Algae Strain
(Dr. Jim Dawson, Pittsburg State U.)

- 150 candidate strains identified from literature
- Screening for specific growth rate at pH 5.5 and 35 ^{o}C
- Four different growth media used

- Promising strain of *Scenedesmus* identified – native to KY; currently our strain of choice

Scenedesmus acutus

Media Optimization

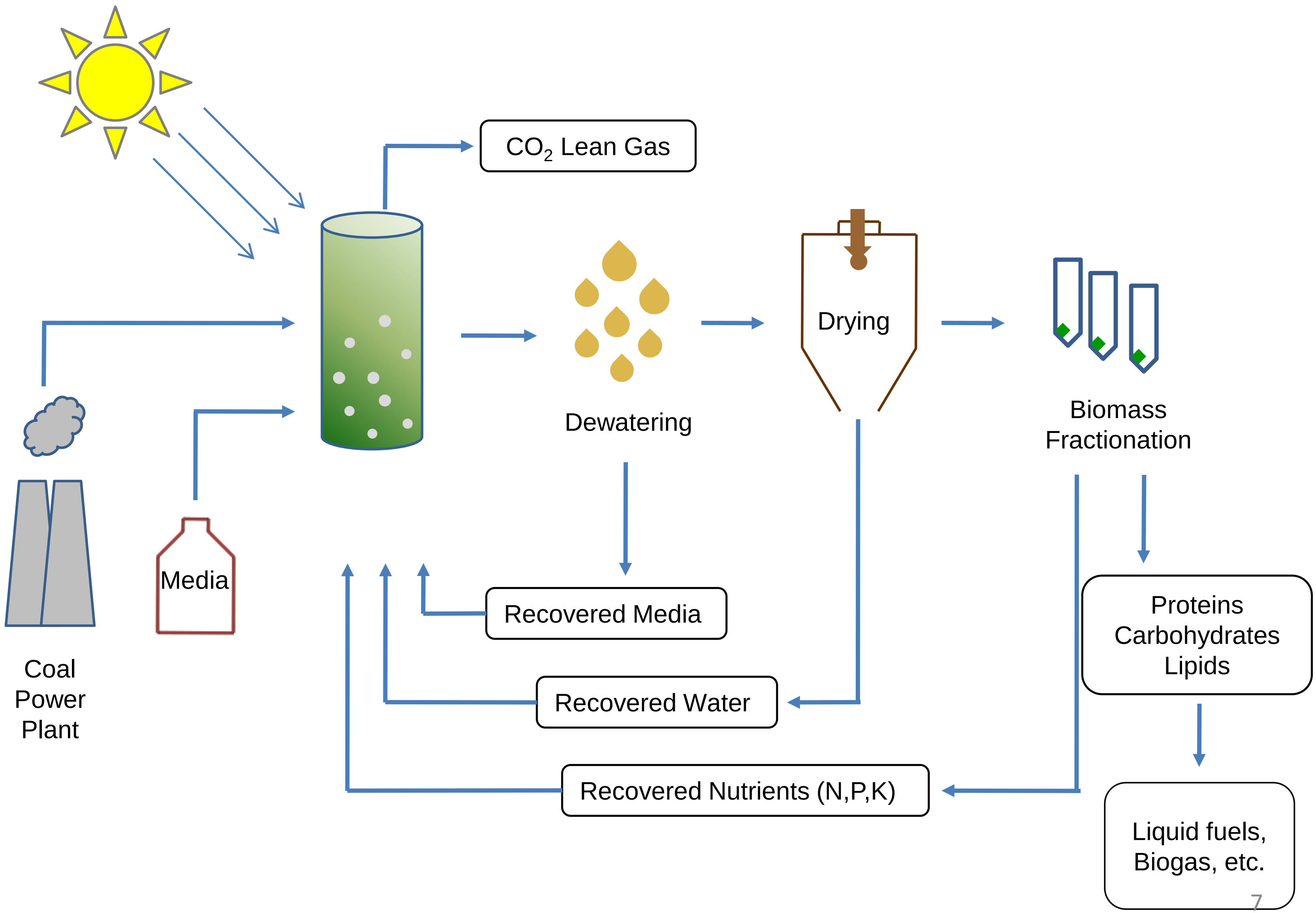
Elemental Composition of *Chlorella*			
Element % by weight	% by weight	Elemental composition % by weight	
		Min[a]	Max[a]
Macro-elements			
N	7.7	6.2	7.7
P	2.0	1.0	2.0
K	1.62	0.85	1.62
Mg	0.8	0.36	0.8
S	0.39	0.28	0.39
Fe	0.55	0.04	0.55
Micro-elements			
Ca	0.080	0.005	0.080
Zn	0.005	0.0006	0.005
Cu	0.004	0.001	0.004
Mn	0.01	0.002	0.01
B	0.0026	-	0.0026
Mo	0.001	-	0.001
Co	0.001	-	0.001

- Starting with the elemental analysis of *Chlorella*, *Scenedesmus* and recipes from the literature, an optimized urea-based medium was developed

Ingredient (g/L)	M-8 75%, Literature	LPP results
KNO_3	0.75	0.75
KH_2PO_4	0.185	0.1185
$NaHPO_4$	0.065	not included
$CaCl_2.2H_2O$	0.00325	0.0004
$FeSO_4.7H_2O$	0.0325	0.037
$MgSO_4.7H_2O$	0.1	0.10925
Micronutrients		
$MnCl_2.4H_2O$	0.003245	0.000486
$CuSO_4.5H_2O$	0.000458	0.000212
$ZnSO_4.7H_2O$	0.0008	0.000298

C. Crofcheck, X. E, M. Montross, M. Crocker, R. Andrews, *J. Biochem. Tech*. 2012, 42, 589-594.

Overall Process



Large-Scale Algae Cultivation

Open Ponds

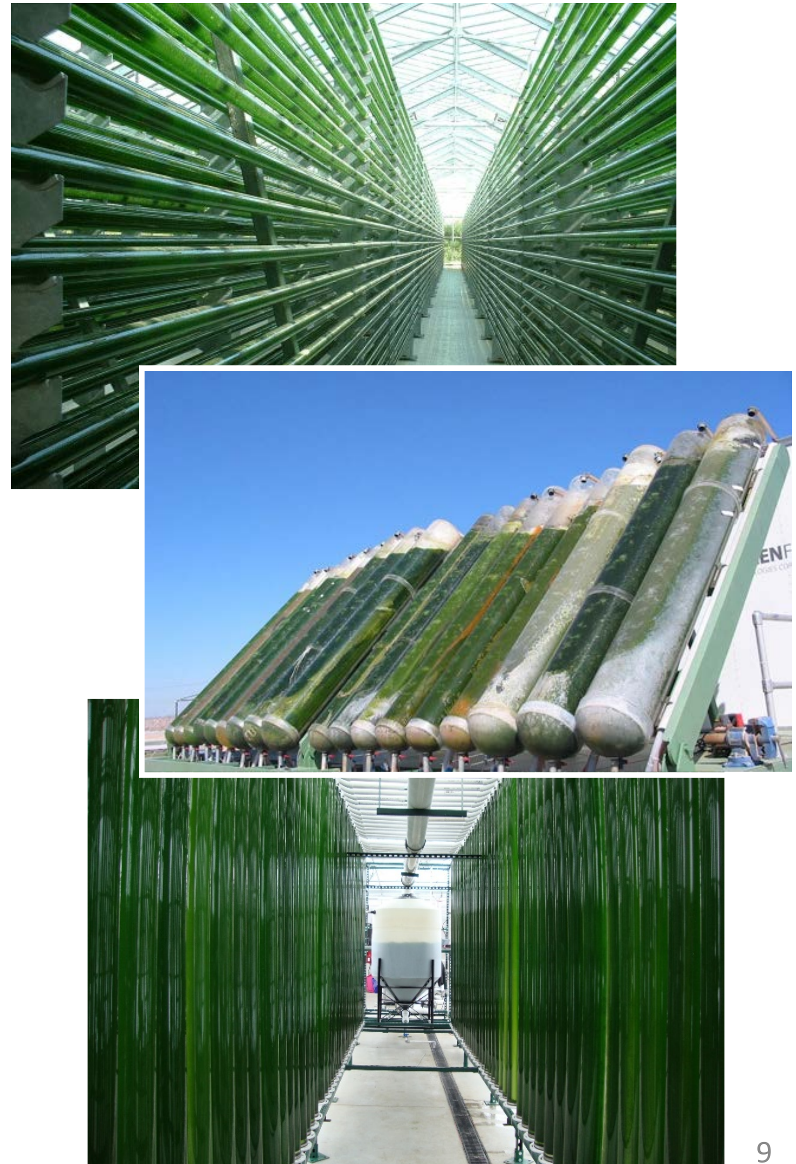
- *Pros*
  - Relatively low capital cost
  - Technology is mature (commercial facilities exist)
  - Operationally simple
- *Cons*
  - Significant evaporative losses
  - Large area requirements
  - Subject to external pollutants, contamination, and conditions.
  - Low CO_2 and light utilization efficiency

Large-Scale Algae Cultivation

<u>Photobioreactors</u>

- *Pros*
  - Potentially high yield of biomass per unit area
  - Low water loss
  - Can cultivate a broad and variable array of algal cultures (based on needs)
  - Can be further optimized?

- *Cons*
  - High capital cost
  - Technology is not mature (few demonstrations exist beyond the lab)
  - Operational costs could be a concern



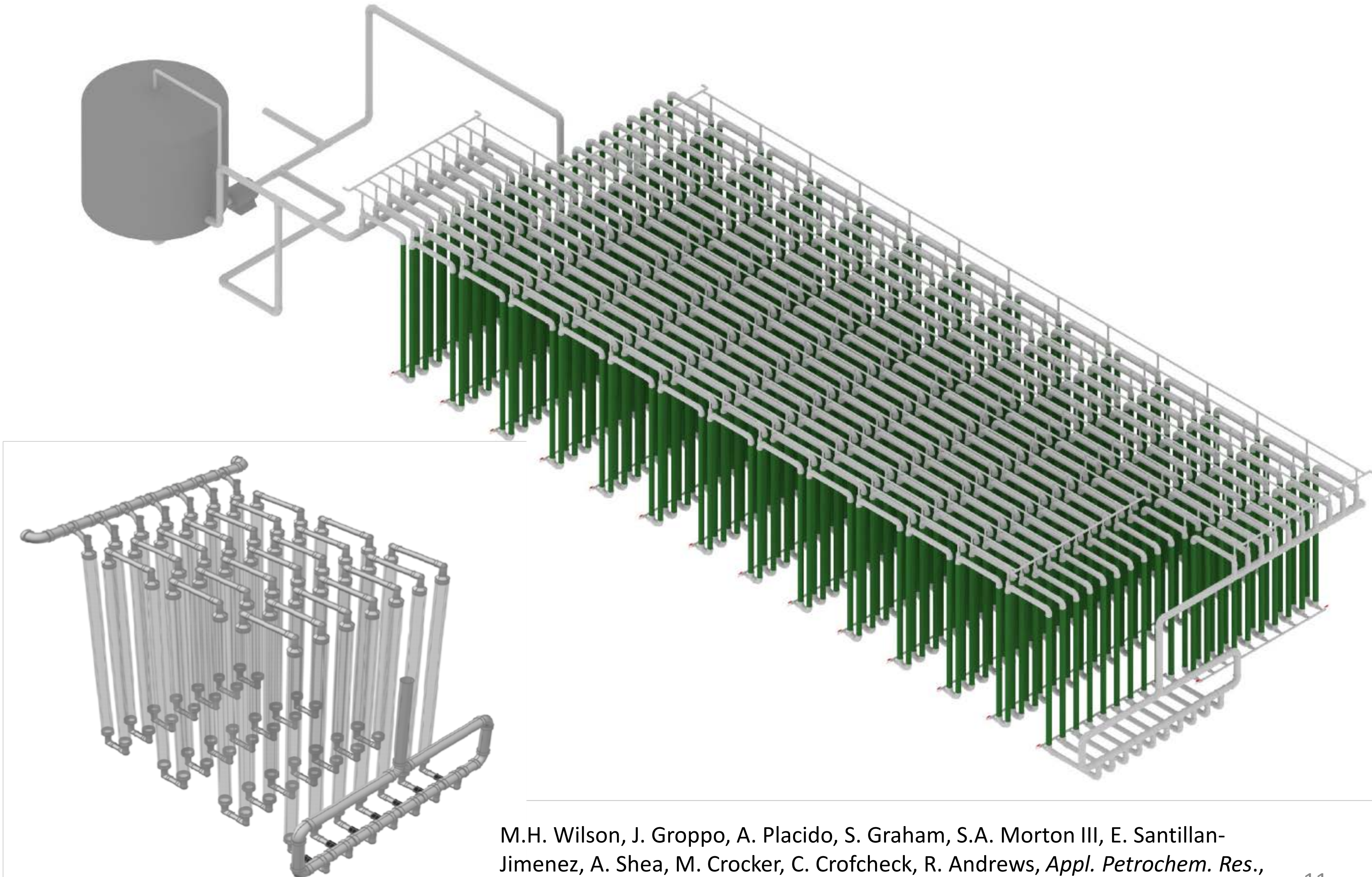
System Sizing

- 1 MWh of coal based power generation produces 1 ton of CO_2/h
- Elemental composition of algae shows that 1 ton of algae produced is equivalent to *ca.* 1.8 tons of CO_2

Areal Productivity	**Land Required**	**Production**
(g algae/m²/day)	*(Acres)*	*(Tons algae/acre/day)*
10	269	0.04
20	134	0.09
30	89.5	0.13
40	67.3	0.18
50	53.8	0.22
60	44.8	0.27

- The dramatic effect of areal productivity on required land drove the team toward the development of a low-cost photobioreactor

1st Generation UK CAER Photobioreactor



M.H. Wilson, J. Groppo, A. Placido, S. Graham, S.A. Morton III, E. Santillan-Jimenez, A. Shea, M. Crocker, C. Crofcheck, R. Andrews, *Appl. Petrochem. Res.*, 2014, 4, 41-53.

East Bend Station Demonstration Facility

DUKE ENERGY®

650 MW Scrubbed Unit (SCR, FGD, ESP)

<u>MAIN GOALS</u>

- Define kinetics of process
  - Monitor dissolved CO_2 and O_2 to determine photosynthetic rate
  - Help size large system and next generation design
- Gain understanding of real capital and operating costs
  - Minimize energy consumption
- Measure biomass composition to track heavy metals and other flue gas constituents

	CO_2 %	NO_x ppm	SO_2 ppm
Average	8.9	53.4	28.0
Minimum	7.2	14.5	6.5
Max.	9.6	97.2	84.3

East Bend Photobioreactor (18,000 L)

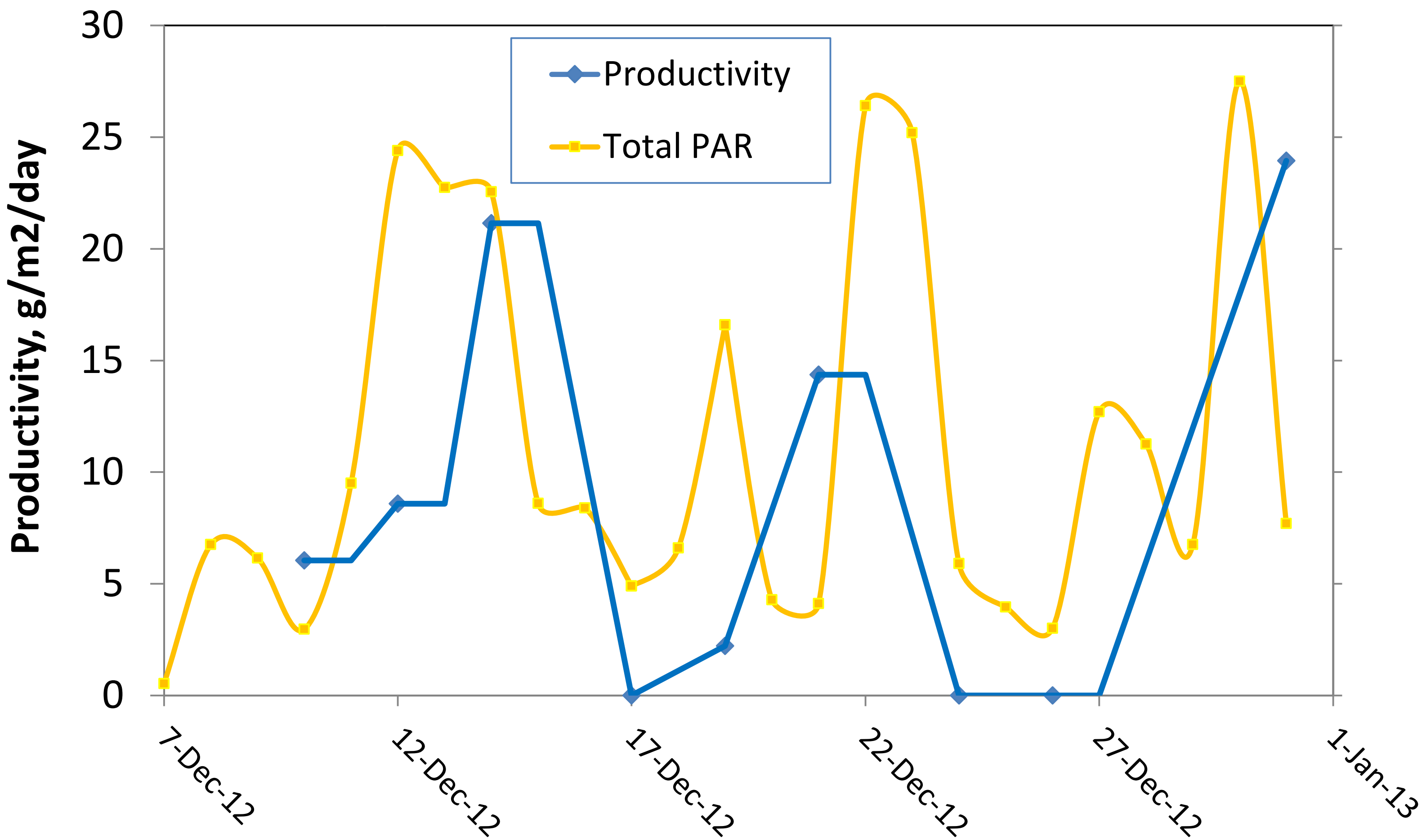
End view

Side view

M.H. Wilson, J. Groppo, A. Placido, S. Graham, S.A. Morton III, E. Santillan-Jimenez, A. Shea, M. Crocker, C. Crofcheck, R. Andrews, *Appl. Petrochem. Res.*, 2014, 4: 41-53.

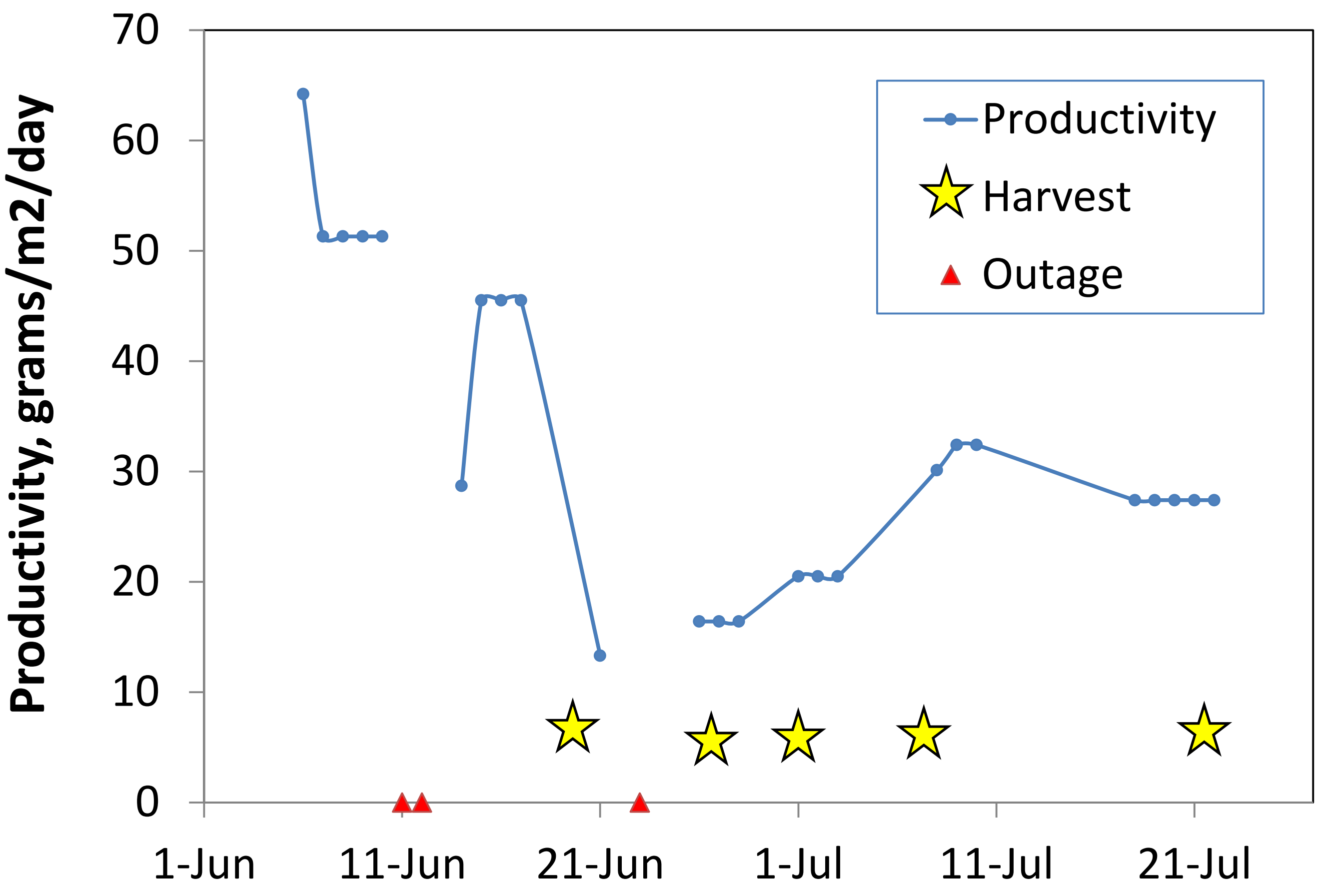
East Bend Growth Study: Winter 2012

Productivity & Photosynthetically Active Radiation (PAR)



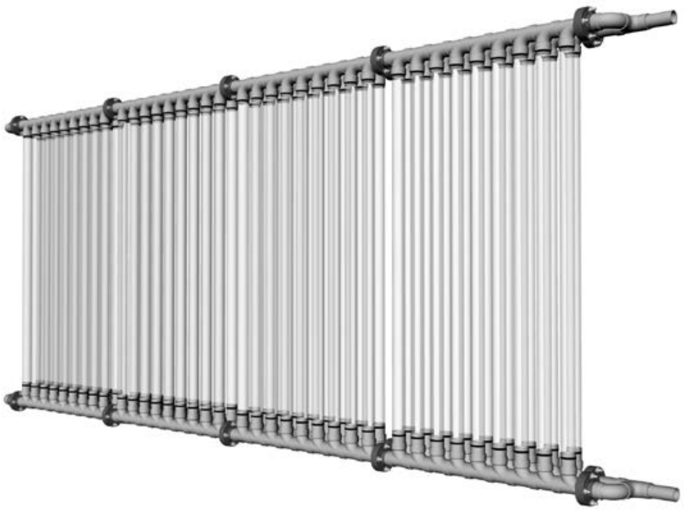
Average growth rate = 10 g/(m^2.day)

East Bend Growth Study: Summer 2013



Average growth rate = 39.4 g/(m^2.day)

"Cyclic Flow" Photobioreactor (1100 L) Installed at East Bend (2nd Generation PBR)

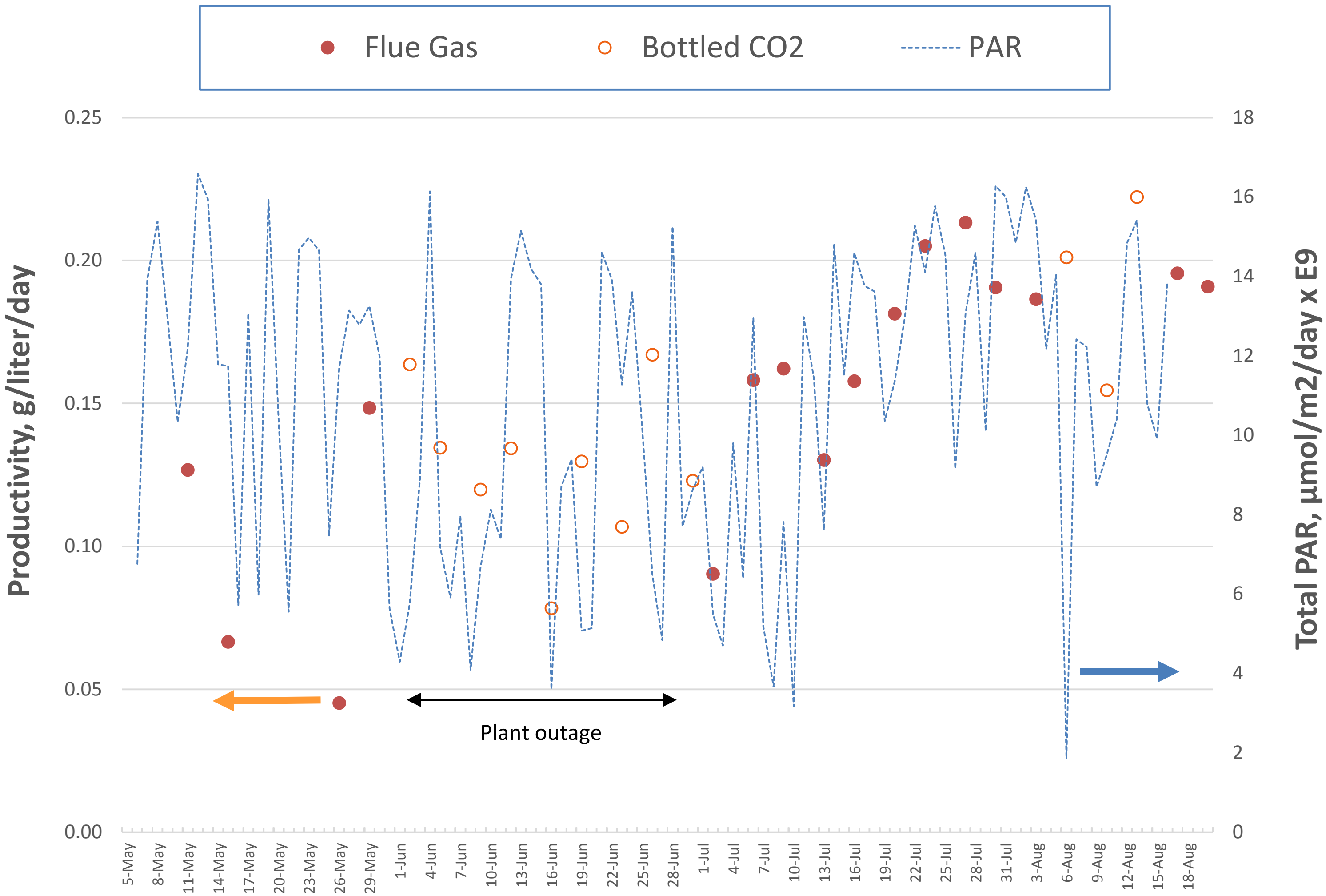


Summer 2014

May 2015

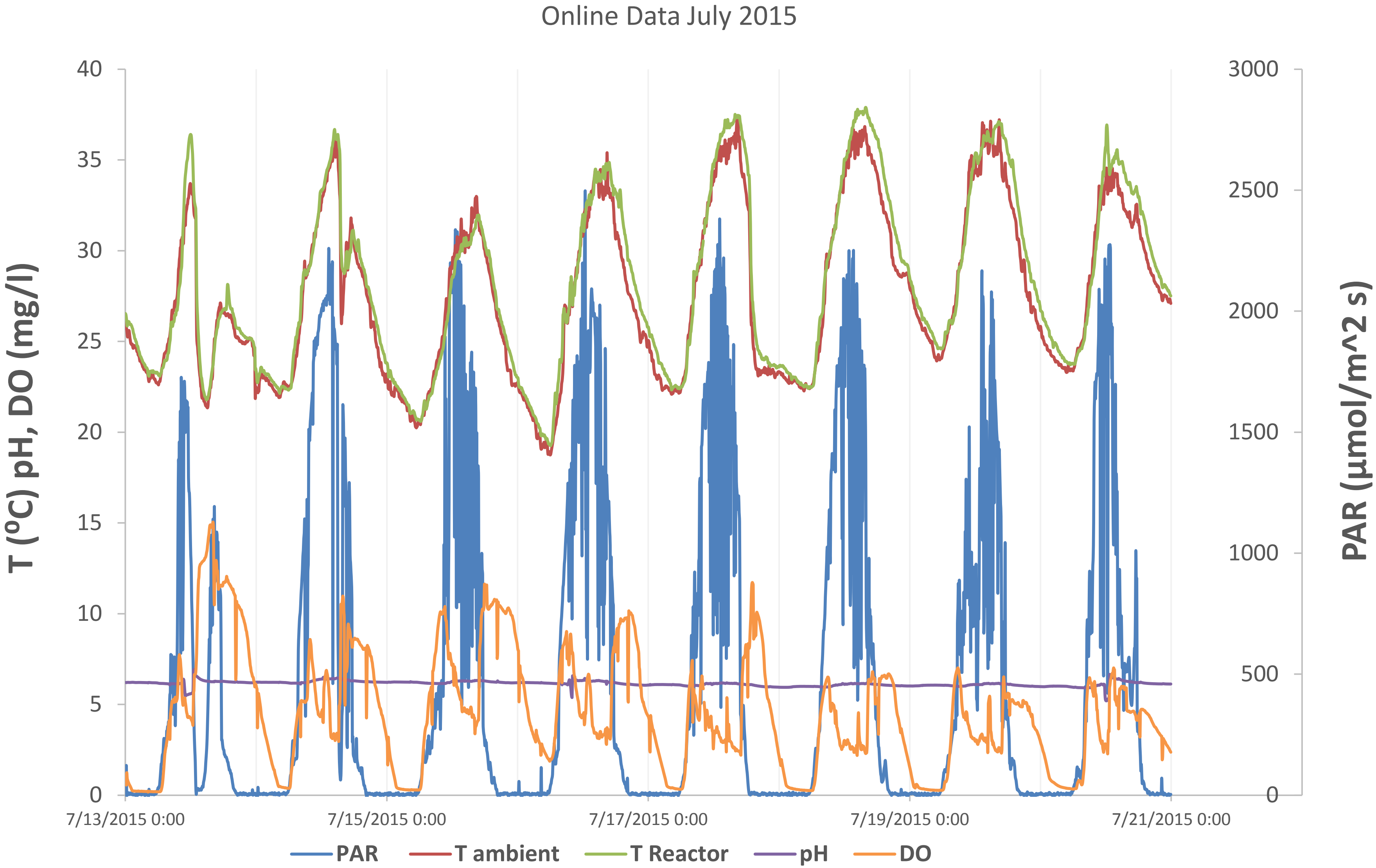
East Bend Algae Productivity

Summer 2015

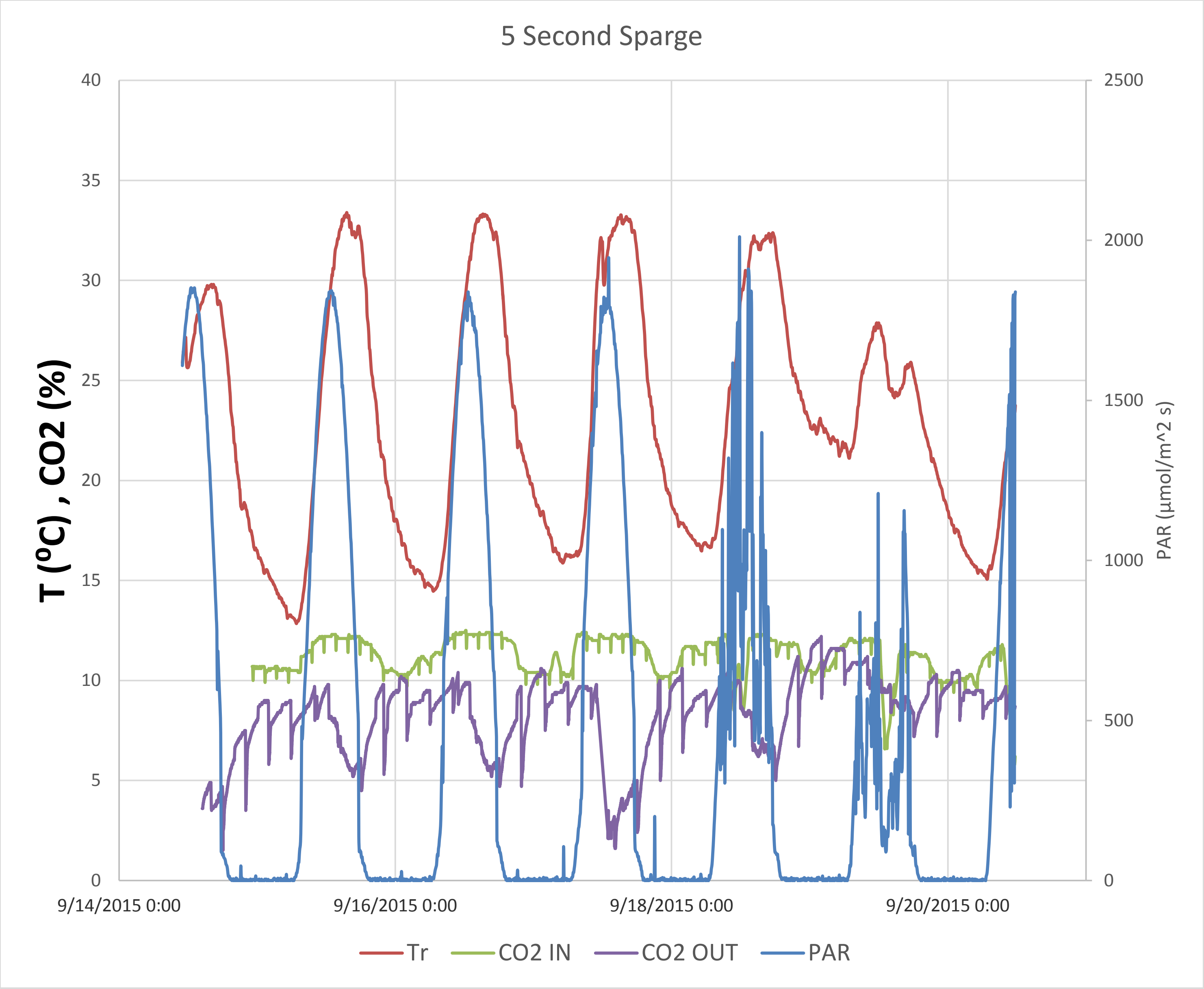


- Consistent growth of *ca*. 30 $g/m^2/day$ observed

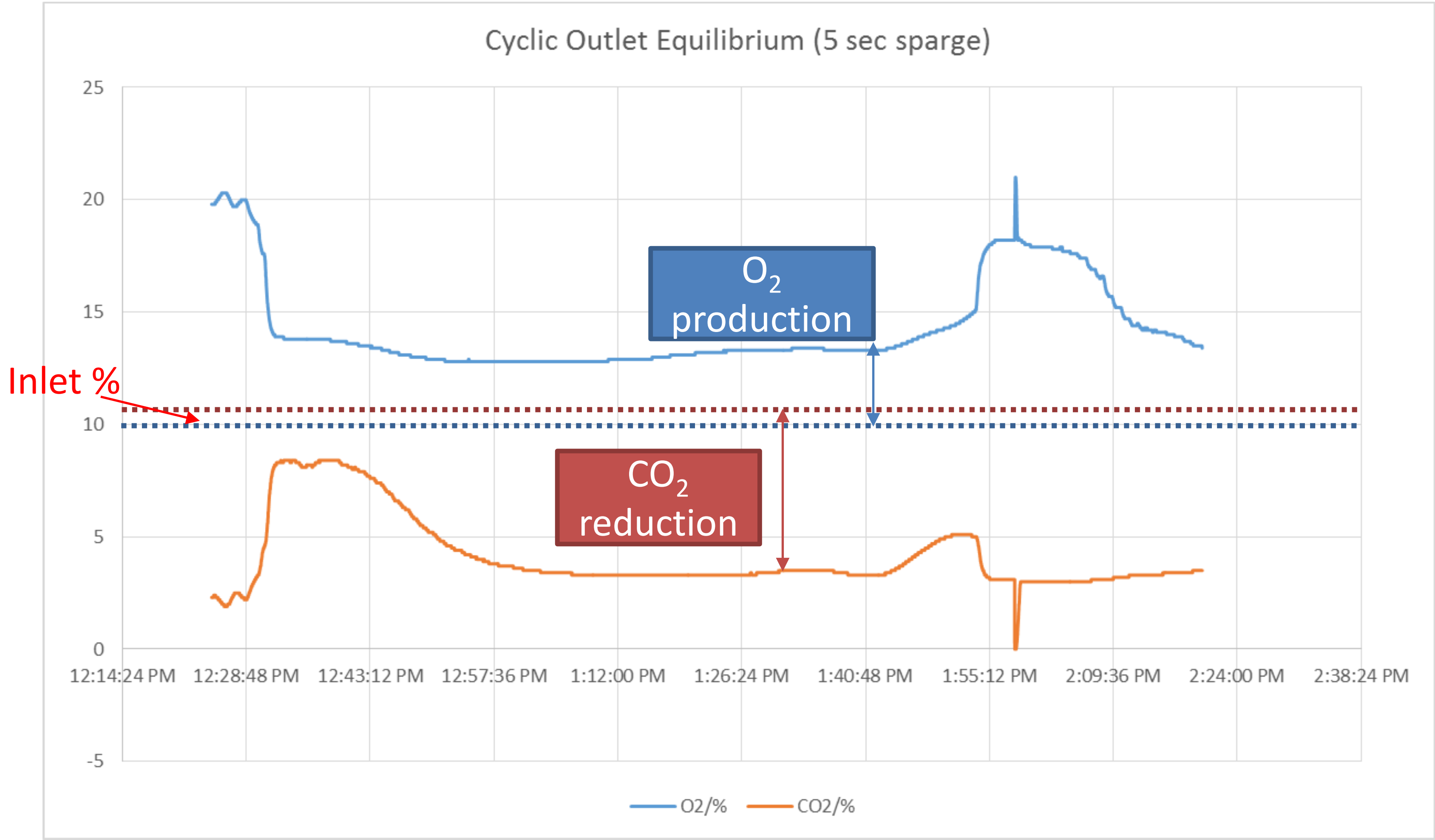
Typical Data Set



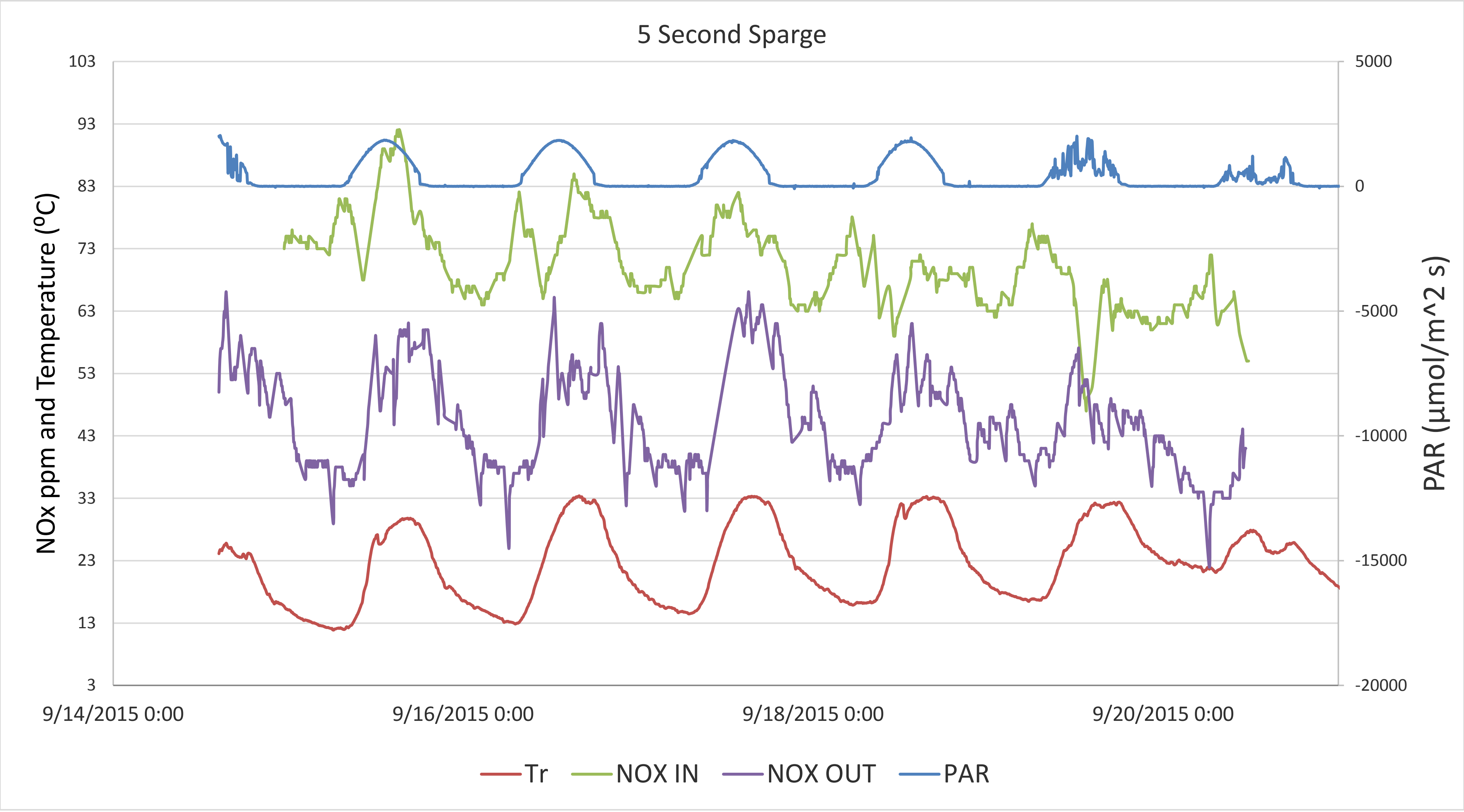
CO_2 in *versus* CO_2 out



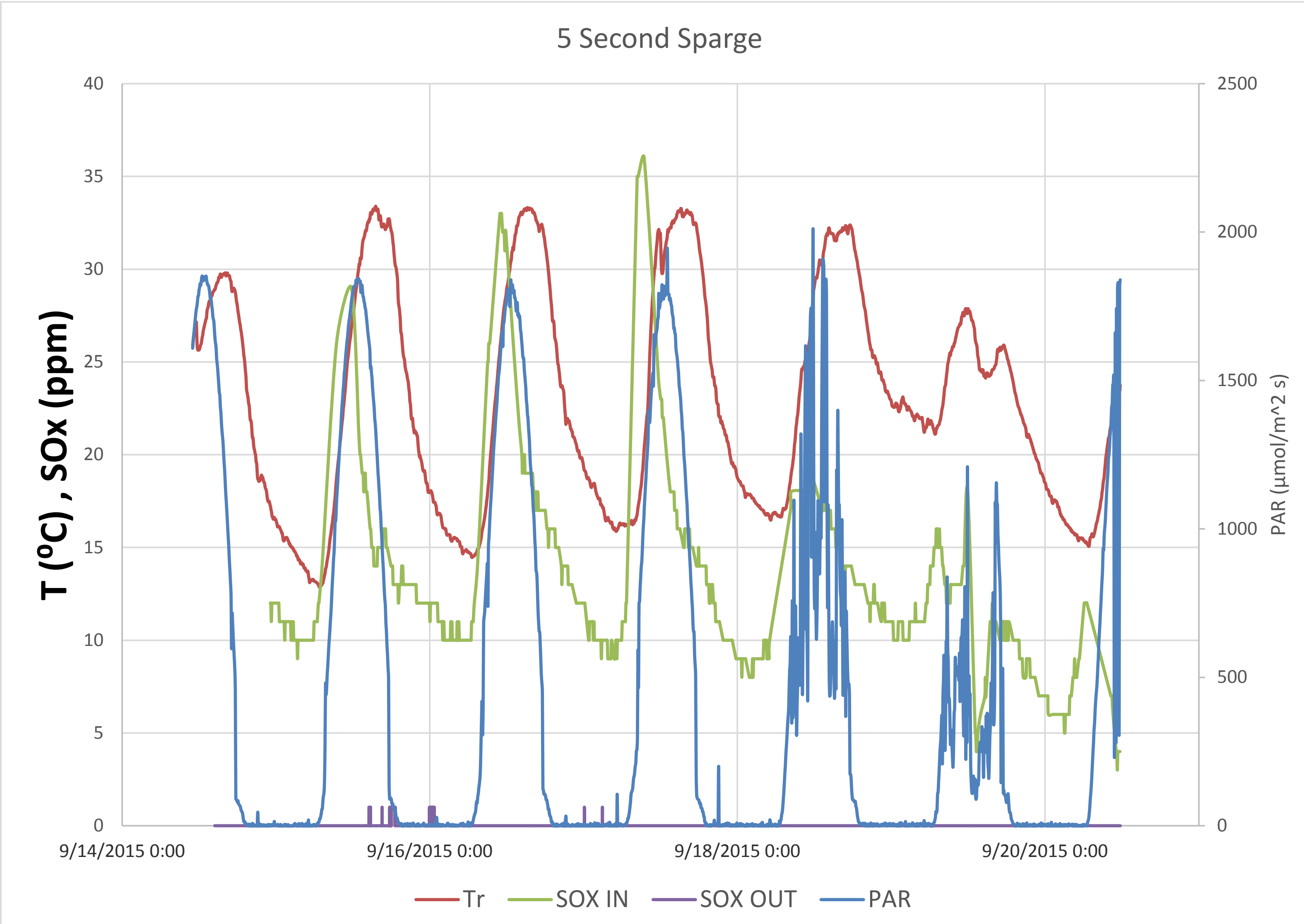
Comparison of Measured CO_2 and O_2 Concentrations



NOx in *versus* NOx out



SOx in *versus* SOx out



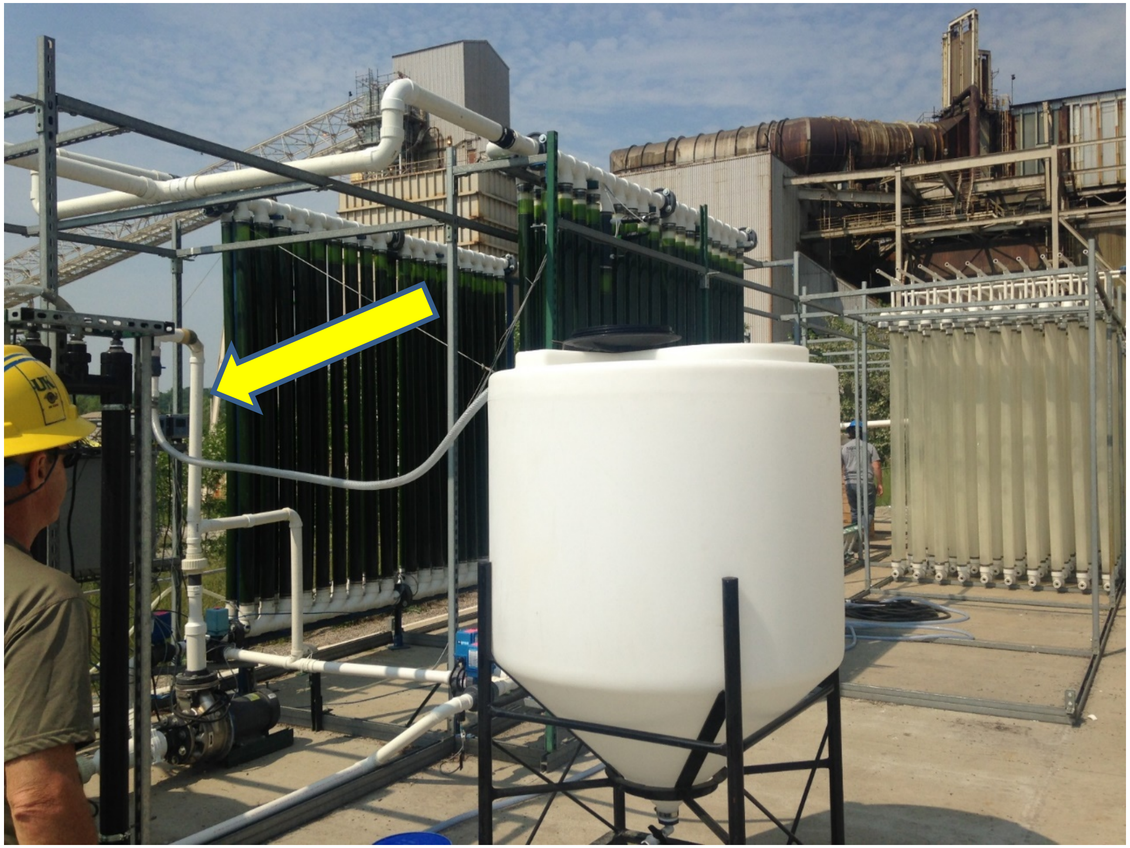
East Bend Station: Mass Balance Calculations

- Two ways to measure carbon capture directly:
  - 1. Measure culture density at the beginning and end of the growth period. Use this difference, volume of the reactor and mass percent carbon of harvest to find mass of carbon captured.
  - 2. Measure the inlet and outlet gas composition. Use pressure, temperature and volumetric flow rate to calculate the amount of carbon captured.

Mass Balance Calculations

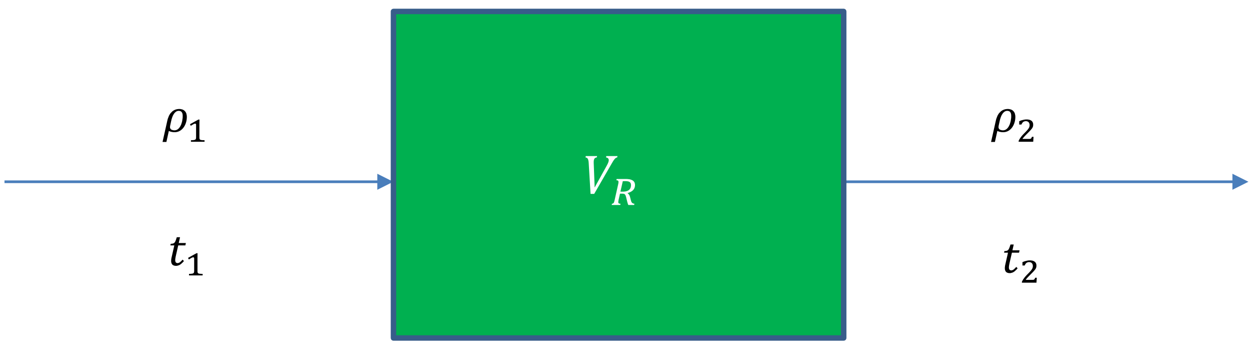
- Sep. 14 – Sep. 17, 2015

- Samples taken directly before and after harvest. Filtered w/a 0.45 µm filter.
- Dry mass analysis results reported in mass/volume (g/L)



Carbon Capture using Culture Density Measurements

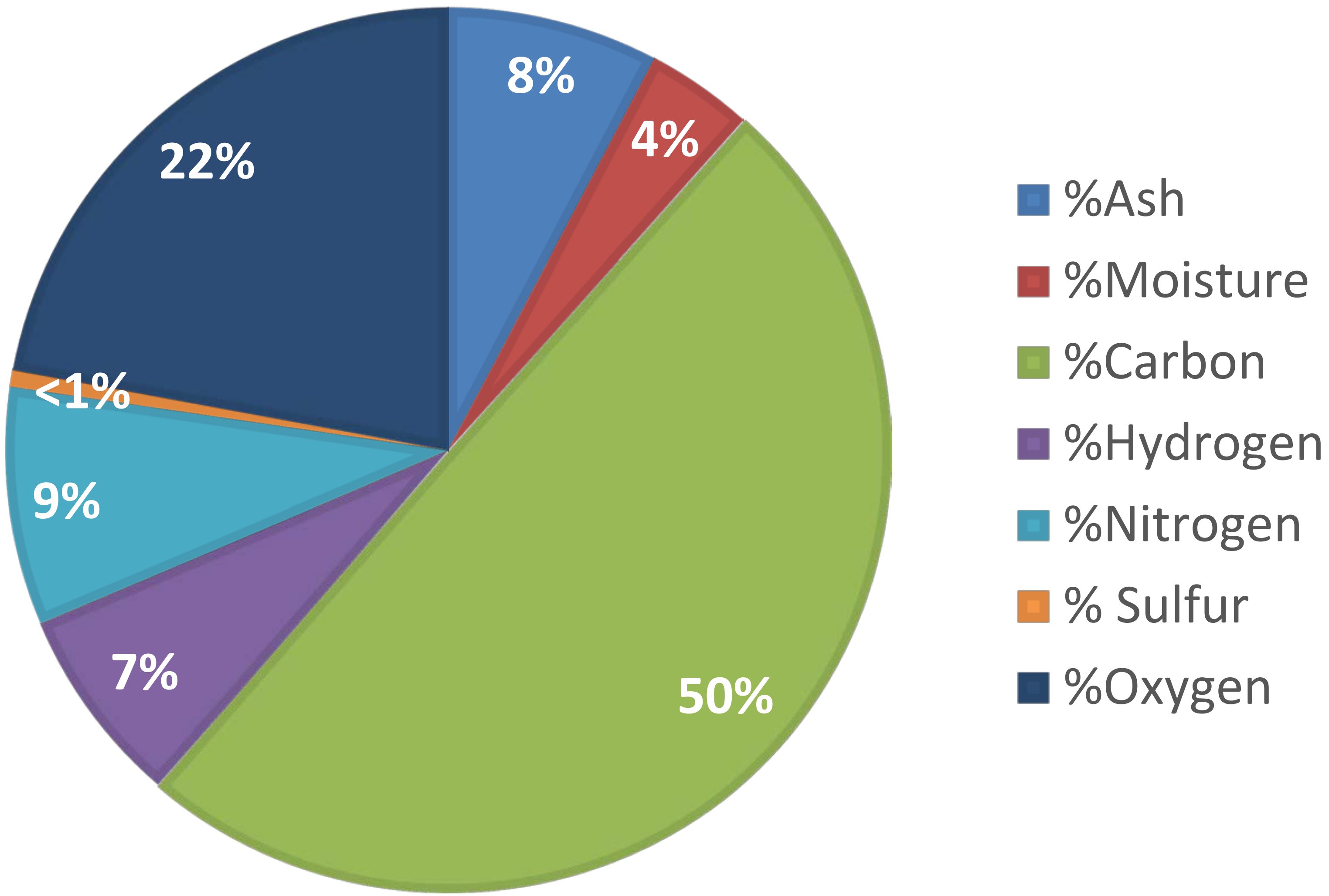
$\boldsymbol{t_i} = date\ and\ time\ sample\ taken\ (mm{:}\,dd{:}\,yyyy, hh{:}\,mm{:}\,ss)$
$\boldsymbol{V_R} = liquid\ volume\ of\ reactor\ (L) = 1136\ L$
$\boldsymbol{m_{c_{accum}}} = mass\ accumulated\ carbon\ (g)$
$\boldsymbol{\rho_i} = Algae\ culture\ density\ \left(\frac{g}{L}\right)$
$\boldsymbol{w_c} = mass\ fraction\ carbon$



$$m_{c_{accum}} = (\rho_2 - \rho_1)V_R w_c$$

$$m_{c_{accum_{algae}}} = \left(\frac{0.653g\ Algae}{L} - \frac{0.200g\ Algae}{L}\right)(1136\ L)\left(\frac{0.5g\ C}{1\ g\ Algae}\right) = \mathbf{257g\ Carbon}$$

Composition of Harvested Algae



Carbon Accumulation Based on Culture Density Measurements

Sparge Setting (sec/min)	Accumulated Algae Mass (g)	Accumulated Carbon Mass (g)	Accumulation Rate (g Carbon/hr)	Time period (days)	Daylight time (min)
5	514	257	7.79	3	1980

- Assumptions
  - Daylight hours are based on measured PAR > 10 µmol/(m^2.s)

Flue Gas Measurements

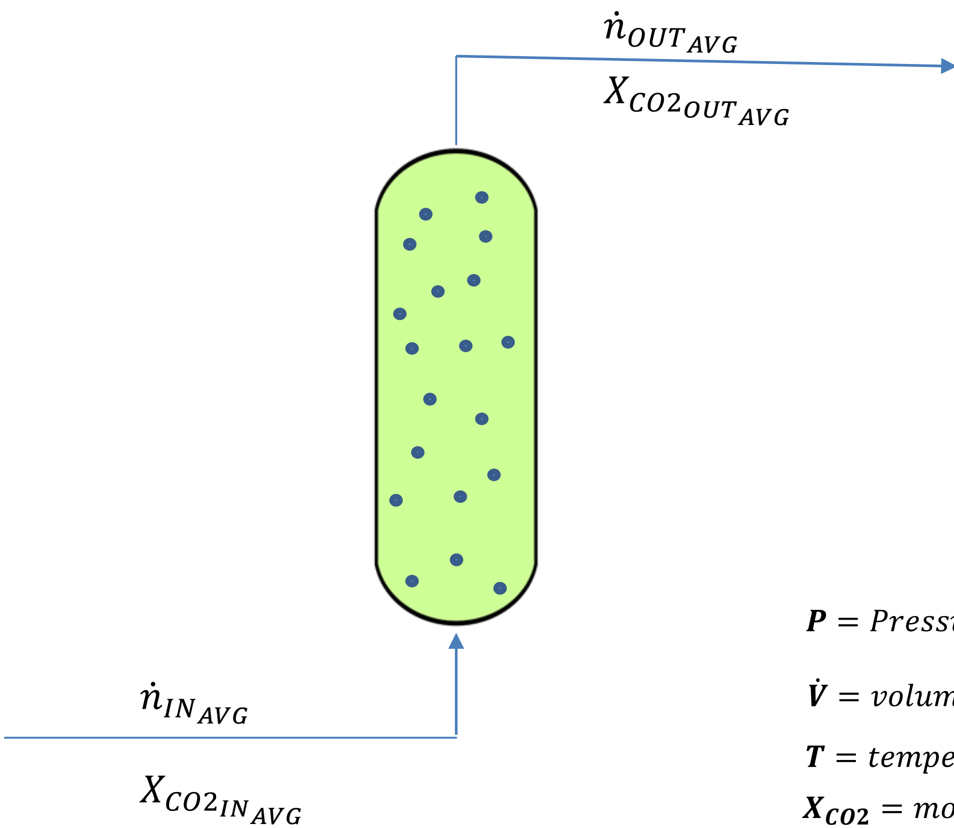
- Temperature measured and averaged (inlet and outlet of PBR)
- Pressure measured and averaged (inlet and outlet of PBR)
- Volumetric flow rate measured with low accuracy

Calculation of Carbon Capture using Flue Gas Measurements

$P_{OUT} = 1.0\ atm$

$\dot{V} = 5.25\ L/min$

$T_{OUT_{AVG}}\ (K)$



Flue Gas

$P_{IN} = 1.5\ atm$

$\dot{V} = 5.25\ L/min$

$T_{IN_{AVG}}\ (K)$

$\boldsymbol{P} = Pressure\ (atm)$

$\boldsymbol{\dot{V}} = volumetric\ flow\ rate\ (L/min)$

$\boldsymbol{T} = temperature\ (K)$

$\boldsymbol{X_{CO2}} = mole\ fraction\ of\ CO2$

} ***measured***

$\boldsymbol{\dot{n}} = molar\ flow\ rate\ (mols/min)$ } ***calculated***

Calculation of Carbon Capture using Flue Gas Measurements

$$\dot{n}_i = \frac{P_i \dot{V}}{RT_{AVG_i}}$$

$$n_{CO2_{accum}} = \left(\dot{n}_{IN}\, X_{CO2_{IN_{AVG}}} - \dot{n}_{OUT}\, X_{CO2_{OUT_{AVG}}}\right)\Delta t$$

$$\Delta t = daylight\ hours\ (Min)$$

$$m_{C_{accum}} = n_{CO2_{accum}}\left(\frac{1mol\ C}{1mol\ CO_2}\right)\left(\frac{12.01g\ C}{mol\ C}\right)$$

$$\boldsymbol{m_{C_{Total}}} = \sum_{\boldsymbol{i=Day\ 1}}^{\boldsymbol{Day\ n}} \boldsymbol{m_{C_{accum_i}}} = m_{C_{accum_{Day\ 1}}} + m_{C_{accum_{Day\ 2}}} + \cdots + m_{C_{accum_{Day\ n}}}$$

$$Where\ Day\ n = Day\ harvested$$

Calculation of Carbon Capture using Flue Gas Measurements

	T AVG IN (K)	T AVG OUT (K)	n IN (mols/min)	n OUT (mols/min)	XCO2 IN AVG	XCO2 Out AVG	Time span	Time (min)	nCO2 IN (mol)	nCO2 Out (mols)	Δn CO2 (IN-OUT) (mols)	Accumulated C (g)
14-Sep	300.234	301.340	0.329	0.213	0.1216	0.043	14:30-19:30	300.000	12.003	2.721	9.3	111.4
15-Sep	302.887	301.038	0.326	0.211	0.1197	0.075	07:30-19:30	720.000	28.105	11.328	16.8	201.3
16-Sep	299.872	297.799	0.329	0.213	0.1220	0.078	07:30-19:30	720.000	28.936	11.949	17.0	203.8
17-Sep	302.005	300.925	0.327	0.212	0.1218	0.075	07:30-11:30	240.000	9.561	4.812	4.7	57.0
Total								1980.000			47.8	**585.5**

Carbon in Solution
(Sep. 17, at time of harvest)

- <u>Total carbon in solution per CHN analysis:</u>

$$\boldsymbol{m_{C_{soln_{Total}}}} = \left(\frac{48.5\ mg\ C}{L}\right)(1136\ L\ soln) = \mathbf{55.1\ \boldsymbol{g\ carbon\ in\ solution}}$$

- <u>Carbon as urea in solution:</u>

$$\boldsymbol{m_{C_{soln_{Urea}}}} = \left(\frac{105\ mg\ Urea}{L}\right)(1136\ L\ soln) = 119\ g\ Urea\left(\frac{12gC}{60gUrea}\right) = \mathbf{23.0\ \boldsymbol{g\ carbon\ as\ urea}}$$

Carbon in Solution, cont.
(Sep. 17, at time of harvest)

- CO_2 in solution using Henry's Law (gas in equilibrium is ~75,000 ppm CO_2):

$$[CO_2(aq)] = \frac{P_{CO2}}{K_{H_{CO_2}}} = \frac{75{,}000\ E^{-6}\ atm}{\frac{28.20\ atm\ L}{mol}} = \mathbf{0.00265\ mol}\ \boldsymbol{CO_2/L}$$

$$\boldsymbol{m_{C_{soln_{CO2}}}} = \left(\frac{0.00265\ mol\ CO_2}{L}\right)(1136\ L\ soln)\left(\frac{1mol\ C}{1mol\ CO_2}\right)\left(\frac{12.01g\ C}{mol\ C}\right) = \boldsymbol{36.3\ g\ carbon\ as\ CO_2}$$

• CO_2 in Solution using Henry's Law, cont.

- 100 gallons (378 L) of fresh water was added to this harvest on Sep. 14 at the beginning of the growth phase, the other 200 gallons assumed to be already saturated.

$$m_{c_{accum\ new\ water}} = \left(\frac{100 gallons}{300 gallons}\right) * 36.3\ g\ carbon\ as\ CO_2 =$$

$$12.1\ g\ carbon\ accumulated\ in\ solution\ from\ flue\ gas$$

CO_2 in Solution: Comparison of Measured and Calculated Values

$$\boldsymbol{m}_{C_{soln_{CO2}}}(calculated\ ) + \boldsymbol{m}_{C_{soln_{Urea}}}(measured) = \mathbf{59.3}\boldsymbol{g\ carbon\ in\ soln}$$

$$\boldsymbol{m}_{C_{soln_{Total}}}(measured) = [C] * V_R = \left(\frac{48.5\ mg\ C}{L}\right)(1136\ L\ soln) = \mathbf{55.1}\ \boldsymbol{g\ carbon\ in\ soln}$$

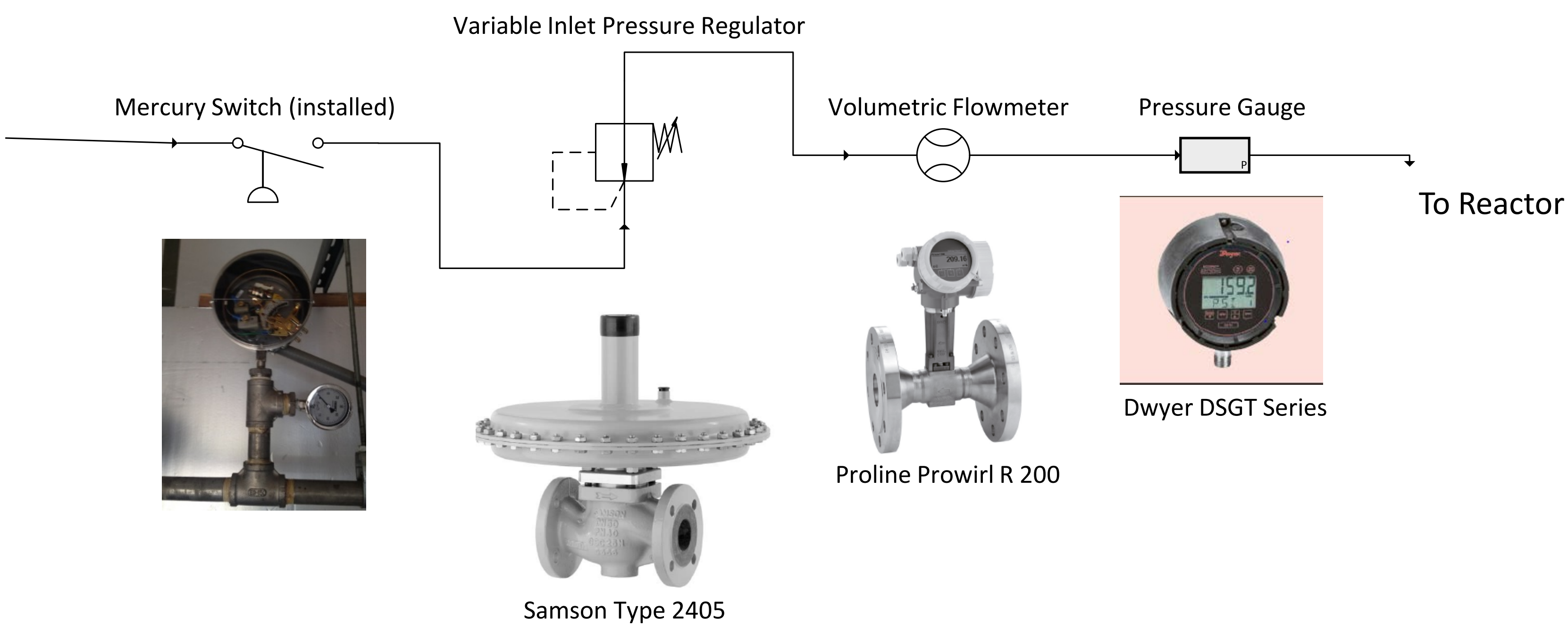
Comparison of Calculated Carbon Capture

Carbon Accumulation Comparison				
	Flue Gas Measurements		Culture Density Measurements	
Sparge time	**Carbon Accumulation (g)**	**Rate (g Carbon/hr)**	**Carbon Accumulation (g)**	**Rate (g Carbon/hr)**
5 sec	586	17.4	257	7.79

- Pressure changes consistently as gas is cyclically bled into the system.
  - Hence, the volumetric flow rate has a large error associated with it
- Significant biofilm formation occurred during the period of this study. The associated carbon is unaccounted for
- Night losses were not examined in calculations done with flue gas measurements

Future Work

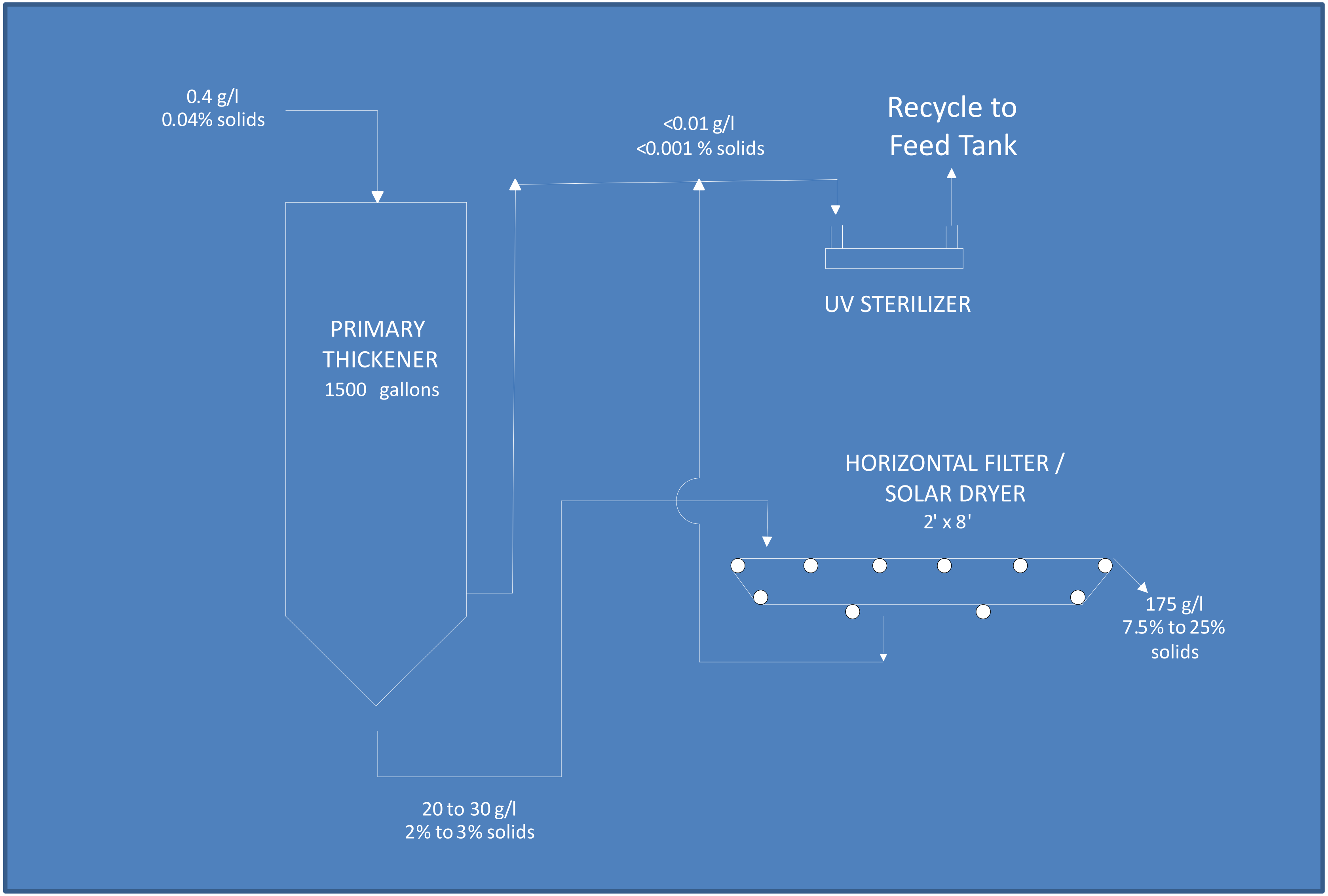
- Purchase and installation of gas flow regulation and monitoring system.
- More accurate volumetric and subsequently mass flow rates.



Algae Harvesting

1. Flocculation and sedimentation
    - Leverages experience in coal preparation and waste products utilization
    - Low molecular weight cationic flocculant (3 ppm)
2. Decanting tank increases density of biomass (2-10% solids)
3. Further dewatering via filtration (up to 25% solids)

Harvest/Dewatering Flowsheet



Prototype Gravity Filter/Solar Dryer

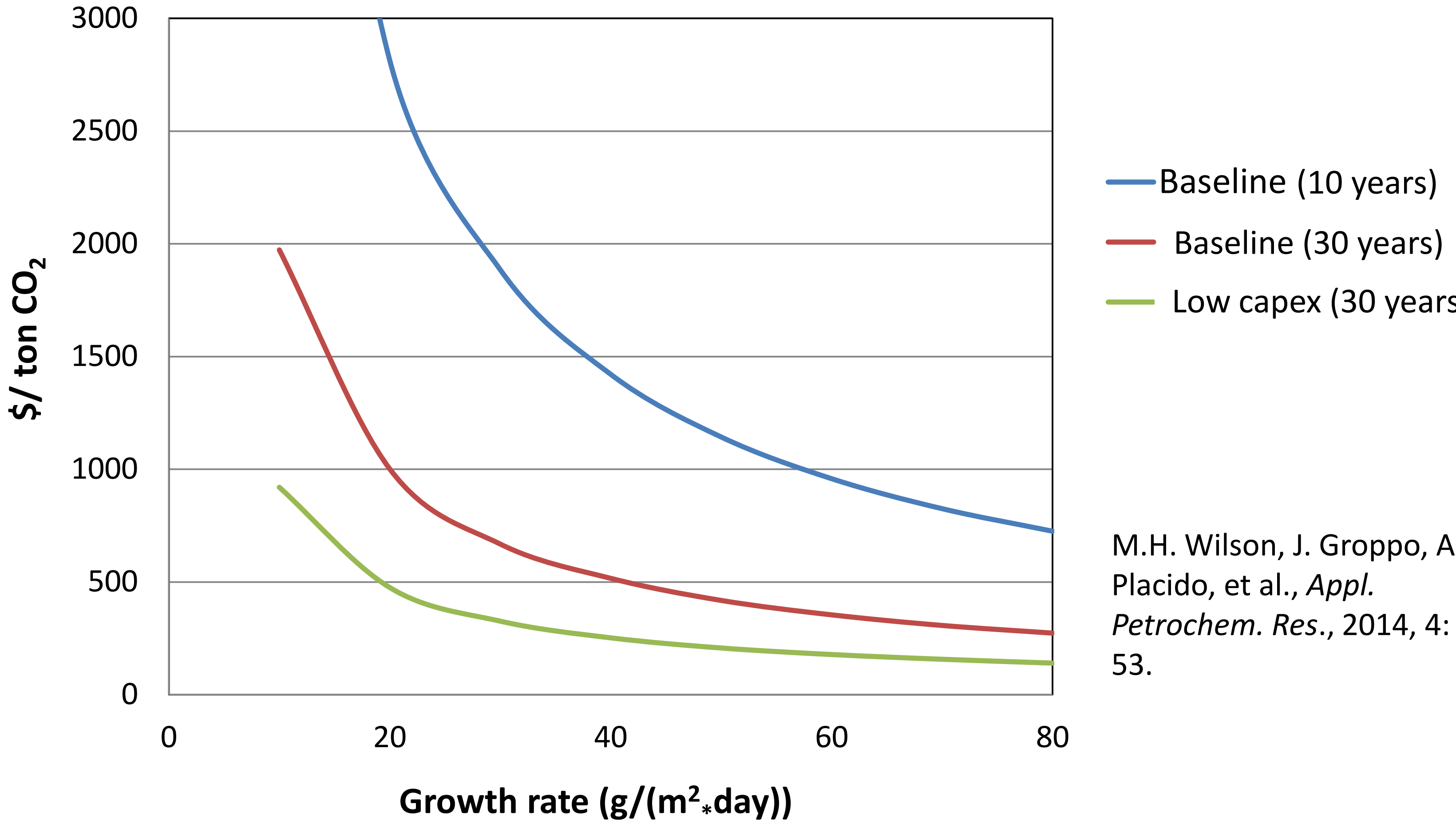
- Multifilament nylon fiber weave allows for cake formation
- Allows separation and recycling of all free water containing unused nutrients
- Short vacuum pulse can improve throughput

- Yields product with 10-25% solids content
- If desired, subsequent drying can be performed in solar oven (can reach 60 ºC in summer)

Techno-economic Analysis

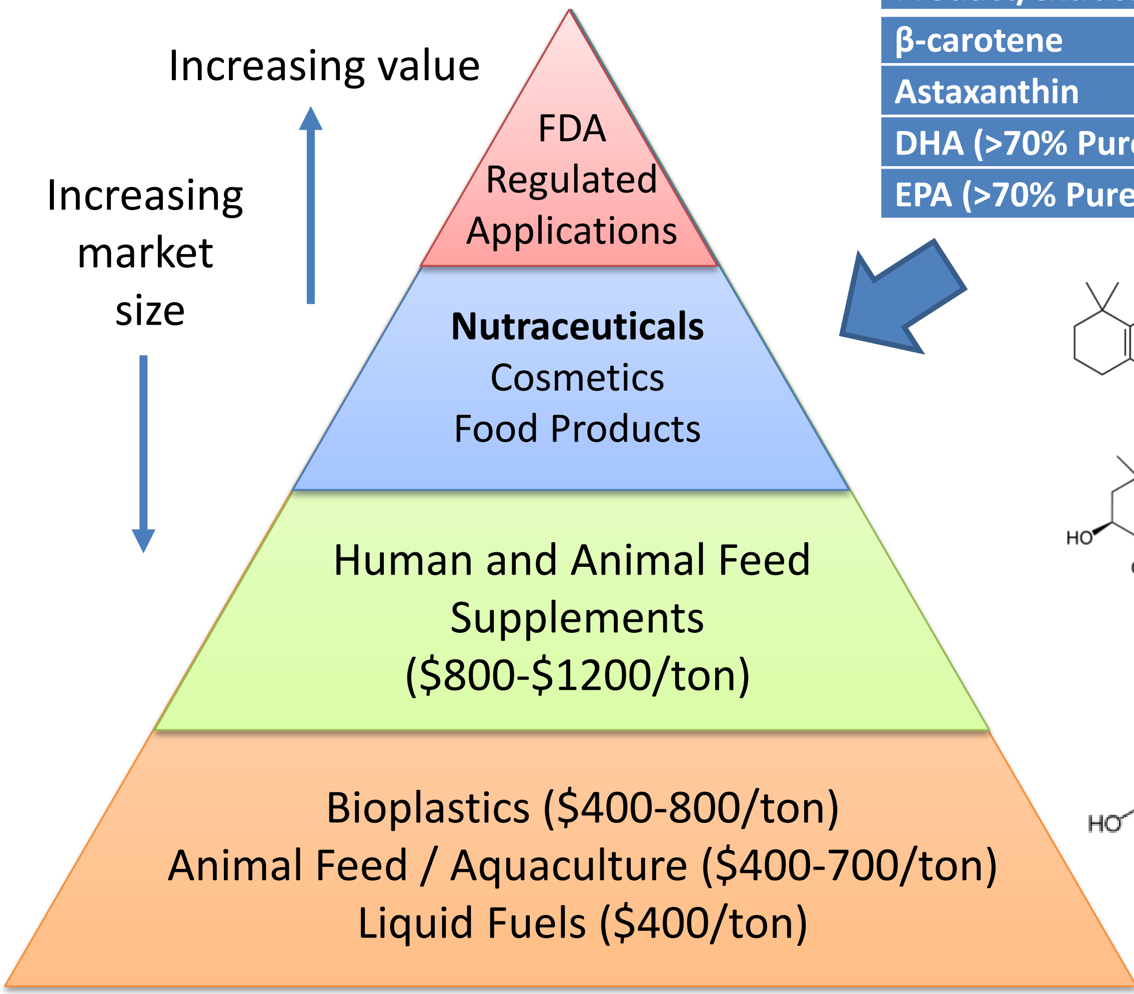
1st Generation PBR

Effect of payback period (10 vs. 30 years), capital cost reduction and algae growth rate (value of biomass produced not included in calculation)

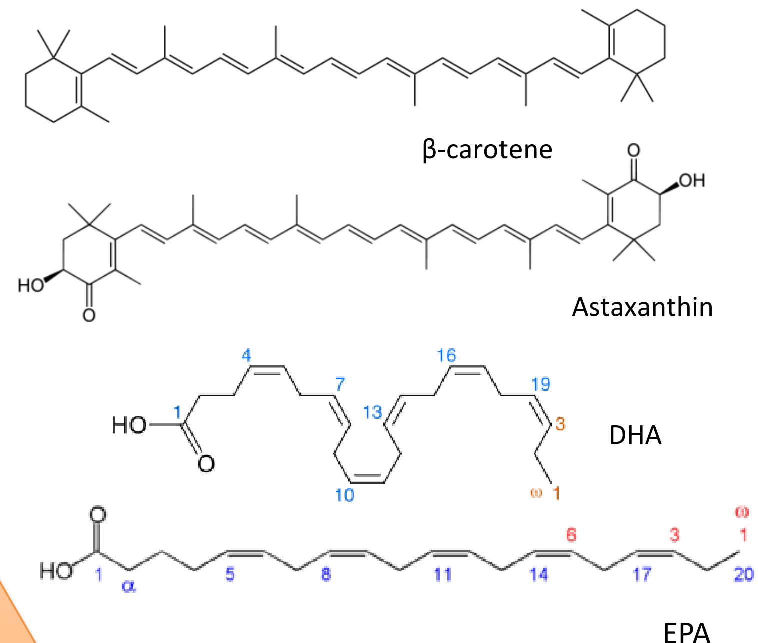


M.H. Wilson, J. Groppo, A. Placido, et al., *Appl. Petrochem. Res.*, 2014, 4: 41-53.

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%

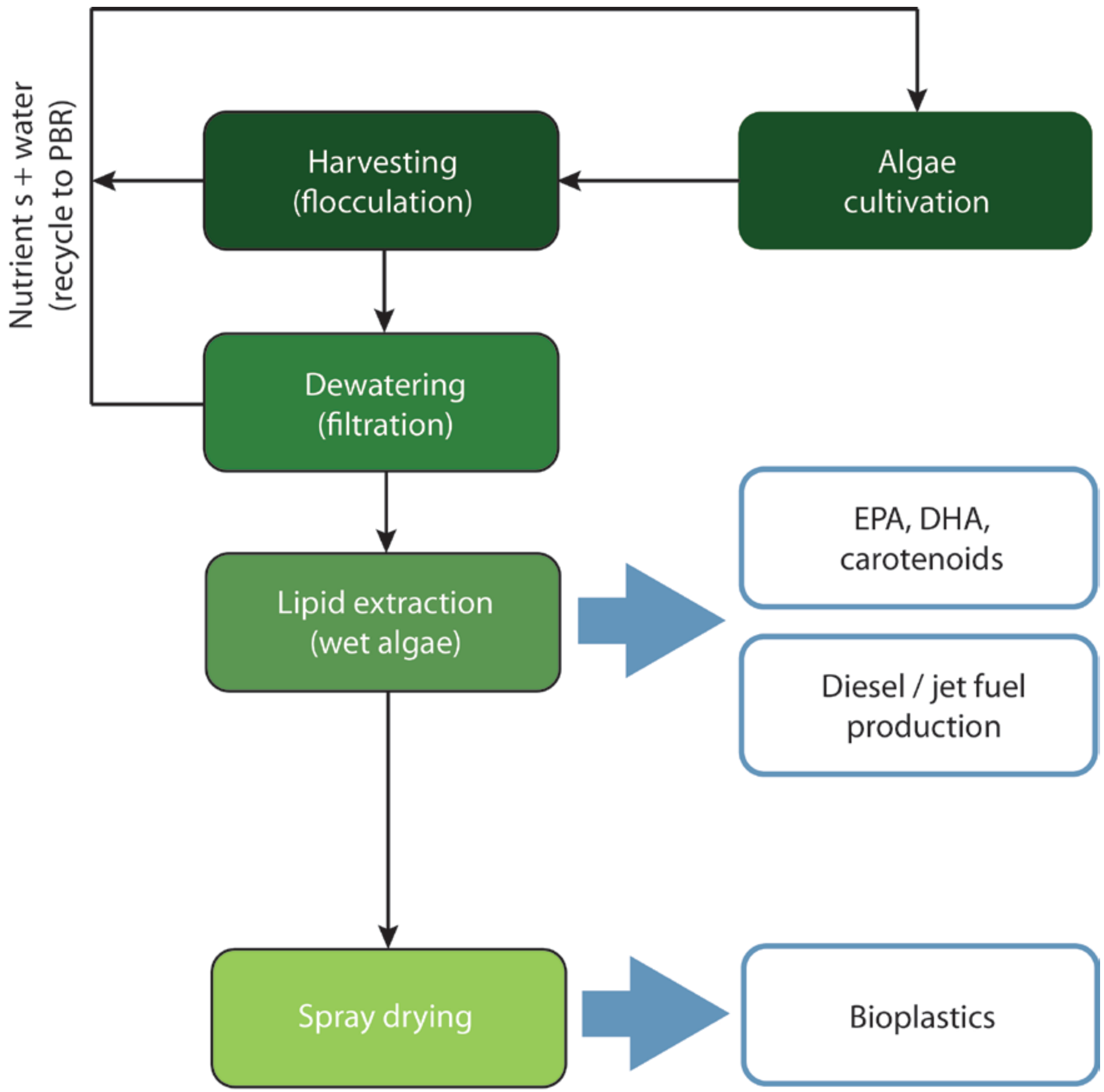


Utilization of Algae for Bioplastics

- Algae can substitute for up to 50 wt% of polymer
- High protein content in algae beneficial for polymer properties
- "Sequestration" of CO_2 in durable plastics such as HD polypropylene
- Enhancement of biodegradability when added to polylactic acid, polybutylene adipate terephthalate
- Targeting applications in horticulture, automotive industry, consumer packaging, etc.

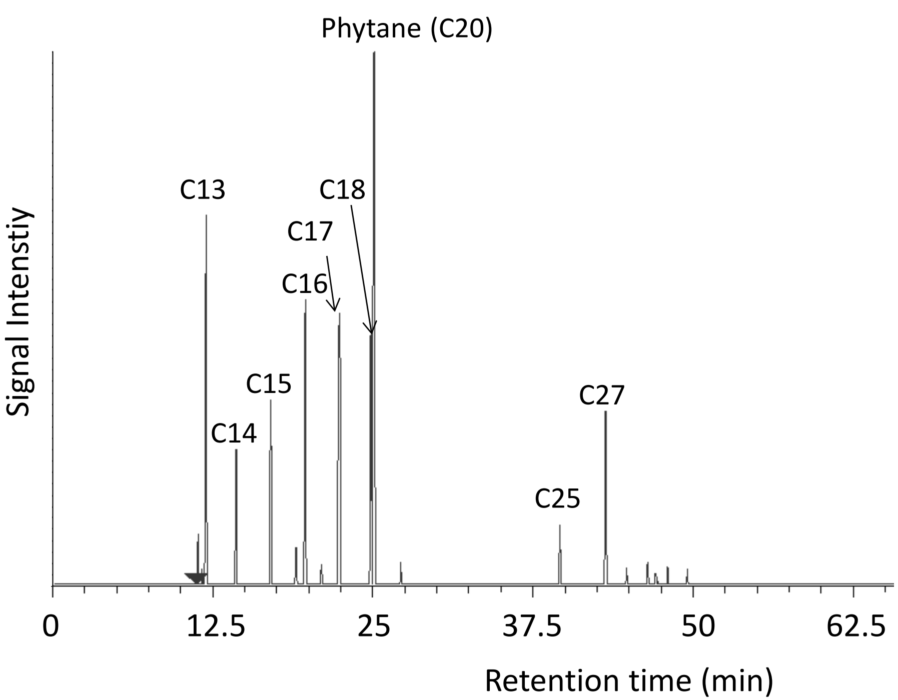
Photos courtesy of ALGIX LLC

Current UK Concept for CO_2 Capture/ Algae Utilization

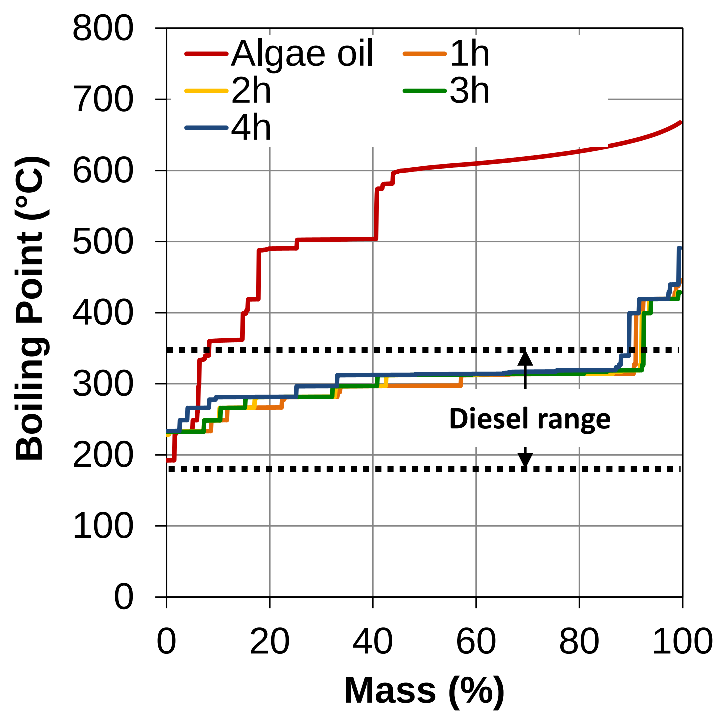


Conversion of Algal Lipids to Fuel-Like Hydrocarbons via Decarboxylation/Decarbonylation

Ni catalyst, 260 °C, 580 psi H_2, fixed bed reactor, dodecane as solvent, algae oil WHSV = 0.25 h^{-1}



Gas chromatogram



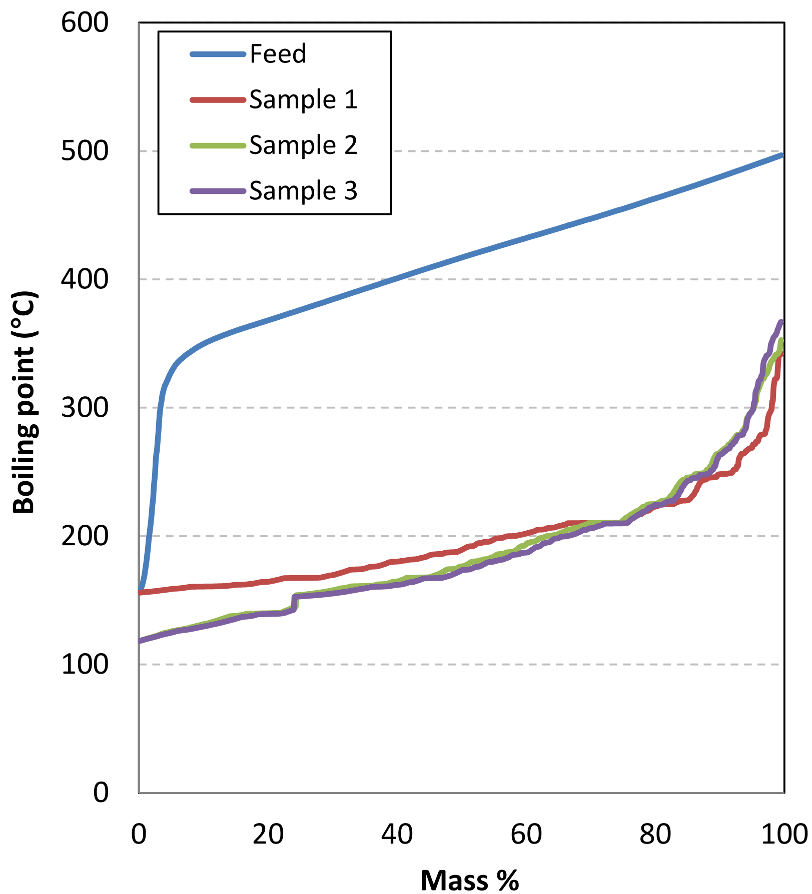
Simulated-distillation GC:
Boiling point distribution plot

T. Morgan, D. Grubb, E. Santillan-Jimenez, M. Crocker, *Top. Catal*. 53 (2010) 820;
B. Peng, X. Yuan, C. Zhao, J.A. Lercher, *J. Am. Chem. Soc*. 134 (2012) 9400;
T. Morgan, E. Santillan-Jimenez, A.E. Harman-Ware, M. Crocker, *Chem. Eng. J.* 189-190 (2012) 346;
E. Santillan-Jimenez, T. Morgan, J. Lacny, S. Mohapatra, M. Crocker, *Fuel* 103 (2013) 1010.

Conversion of Algal Lipids to Fuel-Like Hydrocarbons via FCC

- 10% algae oil in HVGO as feed; provided by Sapphire Energy
- Commercial catalyst, procedure based on ASTM D-3907 (reaction temp. = 482 °C)
- 3 successive tests w/ catalyst regeneration in between (740 °C, 5 min, air)

	Sample 1	Sample 2	Sample 3
Total LPG, vol%	5.3	30.5	22.7
Gasoline, vol %	57.0	62.9	65.7
Light cycle oil (200-340°C), vol%	41.7	35.3	30.9
Heavy cycle oil (340-455°C), vol%	0.3	1.4	2.5
Coke, wt%	19.5	19.5	13.4
Conversion, vol% (bp>216°C)	77.7	76.5	77.7



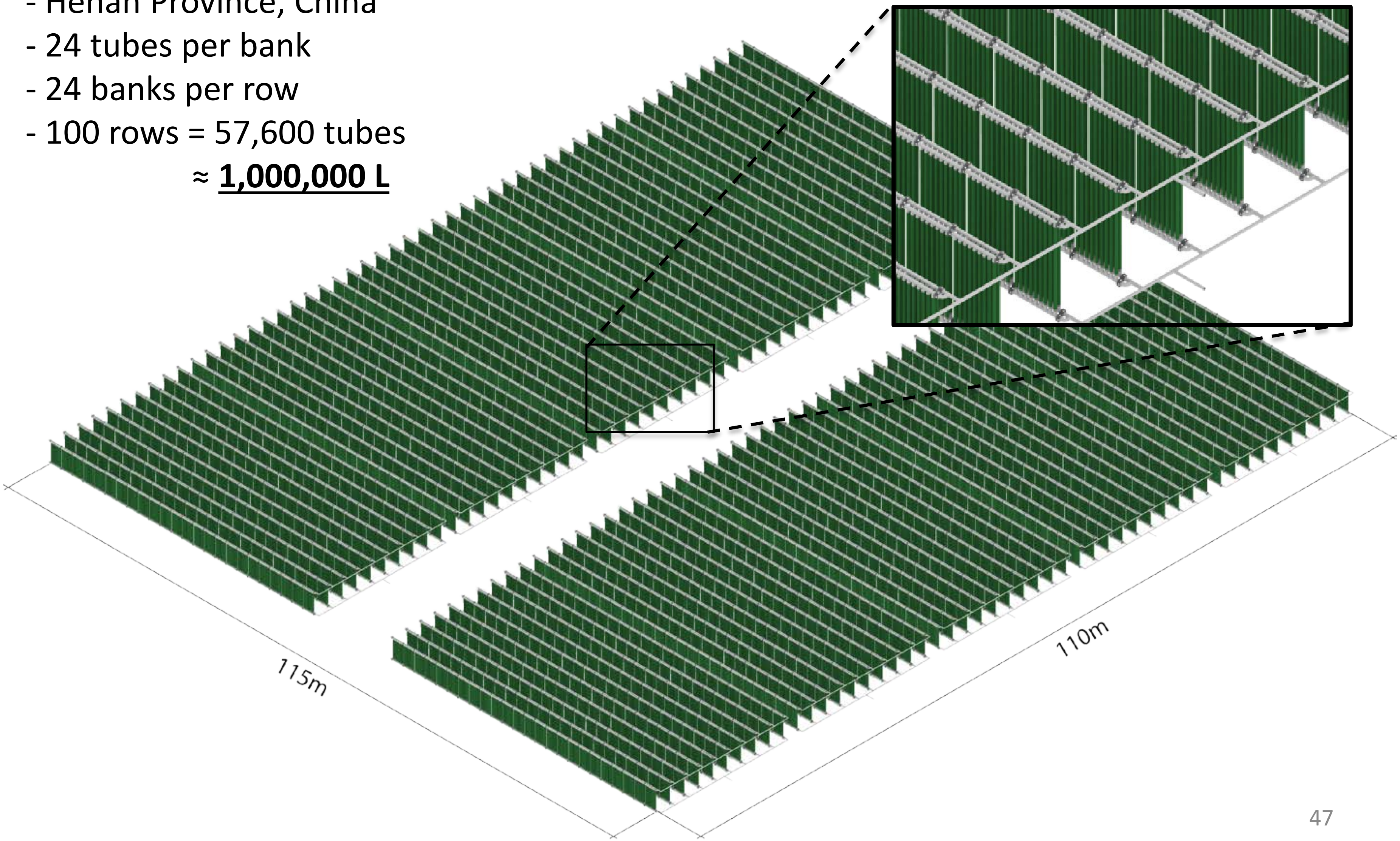
- ➢ Good yields of gasoline and LCO; results unaffected by presence of 10% algae oil
- ➢ No heteroatom-containing compounds detected in product (GC/MS)

Proposed Layout of 3-Acre Cyclic Flow PBR System

5-acre site under construction utilizing UK's cyclic flow PBR technology

- Henan Province, China
- 24 tubes per bank
- 24 banks per row
- 100 rows = 57,600 tubes

≈ **<u>1,000,000 L</u>**



Henan Site under Construction

Conclusions

- A new “cyclic flow” photobioreactor has been designed and built in order to reduce liquid pumping requirements; areal productivity of routinely ≥ 30 $g/m^2/day$ has been demonstrated since early May 2015
- A low cost algae harvesting and dewatering system has been developed
- Conversion of algal lipids to gasoline/diesel range hydrocarbons has been demonstrated using catalytic DeCOx and FCC approaches
- On-going developments focused on the production of medium to high value products will continue to drive down algae production costs, and in turn, the cost of CO_2 capture using algae
- Lifecycle assessments (data not shown) indicate that liquid pumping and gas compression requirements are the largest sources of CO_2 emissions from algae cultivation systems (PBRs and ponds)

Acknowledgements

- KY Department of Energy Development and Independence
- Duke Energy
- Department of Energy: U.S.-China Clean Energy Research Center
- The UK algae team:

Michael Wilson
Dr. Jack Groppo
Stephanie Kesner
Thomas Grubbs
Robert Pace
And….. ca. 30 students

Dr. Czarena Crofcheck
Aubrey Shea
Daniel Mohler
Dr. Eduardo Santillan-Jimenez
Tonya Morgan

AOI 4: A MICROALGAE-BASED PLATFORM FOR THE BENEFICIAL REUSE OF CO_2 EMISSIONS FROM POWER PLANTS

Project Objectives

- Optimize UK's current technology with respect to cost and performance, particularly with regard to harvesting and dewatering operations and enhanced power plant integration;
- Develop strategies to monitor and maintain algae culture health, based on a sound understanding of algal biology;
- Develop a biomass utilization strategy which simultaneously produces lipid feedstock for the direct upgrading to fuels and a proteinaceous feedstock for the production of algal-based bioplastics, thereby maximizing the value of the algal biomass;
- Perform techno-economic analyses to calculate the cost of CO_2 capture and recycle using this approach, and lifecycle analyses to evaluate the greenhouse gas emission reduction potential.

Project Timeline

GANTT CHART

	Task Mode	Task Name	Duration	Start	Finish	Prede
1		**1.0 Project Management**	**523 days**	**Thu 10/1/15**	**Sun 10/1/17**	
2		1.11 Stakeholder Meeting	1 day	Thu 10/1/15	Thu 10/1/15	
3		1.12 Stakeholder Meeting	1 day	Sat 10/1/16	Sat 10/1/16	
4		1.2 Reporting	**523 days**	**Thu 10/1/15**	**Sun 10/1/17**	
5		1.3 Go/No go reviews	33 days	Thu 8/25/16	Mon 10/10/16	
6		**2.0 Engineering Analysis & Testing**	**263 days**	**Thu 10/1/15**	**Sat 10/1/16**	
7		2.1 Harvesting and Dewatering System Design	77 days	Thu 10/1/15	Fri 1/15/16	
8		2.2 Power plant integration resources assessment	131 days	Thu 10/1/15	Thu 3/31/16	
9		2.3 Harvesting and dewatering Prototype Construction/Testing	87 days	Fri 1/1/16	Sat 4/30/16	
10		2.4 Operation and Field Testing	131 days	Wed 3/30/16	Wed 9/28/16	
11		**3.0 System Biology**	**262 days**	**Thu 10/1/15**	**Fri 9/30/16**	
12		3.1 Plant outage mitigation system design	129 days	Thu 10/1/15	Tue 3/29/16	
13		3.2 Effect of flue gas constituents on biomass composition	130 days	Fri 4/1/16	Thu 9/29/16	
14		**4.0 Biomass utilization /Benefication baseline**	**262 days**	**Thu 10/1/15**	**Fri 9/30/16**	
15		4.1 Scale up of extraction/Lipid evaluation	113 days	Thu 10/1/15	Mon 3/7/16	
16		4.2 Baseline characterization of production biomass	131 days	Sat 4/2/16	Fri 9/30/16	
17		4.3 Bioplastics formation development	88 days	Wed 6/1/16	Fri 9/30/16	
18		**5.0 Engineering Analysis and testing II**	**262 days**	**Sat 10/1/16**	**Sat 9/30/17**	
19		5.1 Dewatering system design refinement	67 days	Sat 10/1/16	Sat 12/31/16	
20		5.2 Life cycle assessment	130 days	Sat 10/1/16	Thu 3/30/17	
21		5.3 Techno economic analysis	130 days	Sat 10/1/16	Thu 3/30/17	
22		5.4 Field testing & Biomass production	132 days	Sat 4/1/17	Sat 9/30/17	
23		5.5 Develop model to assess power plant integration strategies	87 days	Sat 4/1/17	Sun 7/30/17	
24		5.6 Update LCA/TEA with process data	45 days	Tue 8/1/17	Sat 9/30/17	
25		**6.0 Systems Biology II**	**262 days**	**Sat 10/1/16**	**Sat 9/30/17**	
26		6.1 Plant outage mitigation system testing	131 days	Sat 10/1/16	Fri 3/31/17	
27		6.2 Aboitic parameter optimization for production of lipids, protiens	132 days	Sat 4/1/17	Sat 9/30/17	
28		**7.0 Biomass utilization/Valorizaiton study**	**262 days**	**Sat 10/1/16**	**Sat 9/30/17**	
29		7.1 Upgrading & profiling of estracted lipids	130 days	Sat 10/1/16	Thu 3/30/17	
30		7.2 Lipid extraction/biomass fractionation and upgrading	152 days	Sun 1/1/17	Sun 7/30/17	
31		7.3 Bioplastic coumpounding & evaluation	152 days	Sun 1/1/17	Sun 7/30/17	
32		7.4 Heavy metals fate analysis	88 days	Thu 6/1/17	Sat 9/30/17	

T CHART

Task 1: Project Management

Task Summary: To manage a project of this technical complexity a combination of meetings, reporting, milestone/deliverable tracking, and go/no-go reviews will be employed.

1.1 Stakeholder Meetings

- Who: UK, UD, Algix

Regular communication between members of the project team will be facilitated through scheduled teleconferences, emails, and face-to-face meetings. A kick-off meeting will be held at the start of the project, involving all the participants, in order to review the technical scope and the project management plan. To ensure the smooth coordination of activities, throughout the duration of the project conference calls will be held on a bi-monthly basis, with the purpose of informing participants about the latest results, planning forthcoming activities and addressing new issues as they arise. Project members will also meet in person at least once a year to review the progress made and plan for the next period.

Milestone 1.1 Project Kick off meeting held at UK CAER

Milestone 1.2 Presentation at NETL < 90 Days from project start date

Milestone 1.3 Presentation at NETL in final quarter of project

1.2 Reporting

- Who: UK, UD, Algix

Reports and other deliverables will be provided in accordance with the Federal Assistance Reporting Checklist following the instructions included therein. Additionally, technical progress for the project will be reported in scholarly journals, and more rapidly at appropriate scientific meetings and workshops.

Milestone 1.2.1 Final Report to NETL

Milestone 1.2.2 Presentation of project work at 2016 Algal Biomass Annual Summit

DELIVERABLE: Final Report

1.3 Go/No-Go Review

- Who: UK, UD, Algix

Project reviews will be made at the end of year 1 to assess project progress versus the project schedule. Stakeholders will either meet at NETL headquarters or schedule a webinar conference to present progress made, major obstacles encountered, and future plans. During this meeting, all stakeholders will assess the project progress and determine whether the work plan should be continued as planned, altered based on lessons learned, or terminated.

Milestone 1.3.1 Year 1 Go/No-Go Review

Task 2: Engineering Analysis & Testing

Task Summary: Engineering analysis will be brought to bear to tackle a variety of technical challenges associated with biological beneficial re-use of carbon emissions, including many of the technical bottlenecks highlighted in previous research.

2.1 Harvesting & Dewatering System Design

- Who: UK (Jack Groppo)

Existing low cost/low energy dewatering processes, currently performed in batch mode, will be converted to a continuous process, thereby linking algae production with biomass processing to provide a feedstock for utilization processes. A static thickener equipped with lamella plates will be sized and designed to perform the primary dewatering of the harvested algal biomass in a continuous fashion. A range of cationic flocculants and co-flocculent systems will be evaluated and optimized to enhance settling rates. Additionally, the outflow of this stage of processing will be matched with the inflow to the secondary dewatering step, gravity filtration. The flow rate and solids content of the primary dewatering will be characterized and used to determine the size and feed rate of the secondary dewatering stage. Prototypes of technical pinch points will be built and tested to inform design modifications and construction efforts.

2.2 Power Plant Integration Assessment

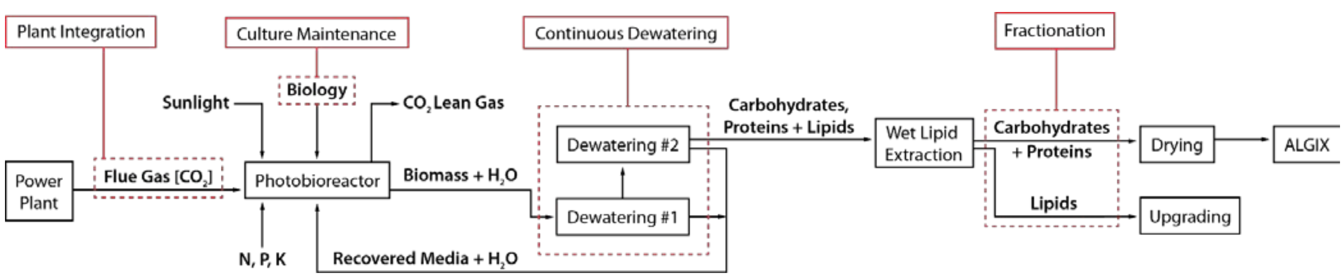
- Who: UK (Michael Wilson)

Opportunities to further integrate with power plants, beyond serving as a carbon source, will be evaluated. The team will work with Duke Engineers to evaluate the potential of leveraging large volumes of low grade waste heat to elevate the temperatures of algae cultures, thereby increasing productivity or extending the growing season. Aspen will be used to facilitate these efforts. In addition, the method of introducing flue gas to algae cultures will be extensively studied, comparing compression and sparging (using a variety of techniques to enhance mass transfer while minimizing energy costs) with liquid-driven gas venturis/eductors and with countercurrent spray columns.

2.3 Harvesting and Dewatering Prototype Construction/Testing

- Who: UK (Jack Groppo)

Full prototypes of an integrated, two-stage dewatering process will be built, tested, and operated. The biomass processing equipment designed in Task 2.1 will be constructed and integrated to enable the continuous separation of biomass and culturing media. The scale of the design will be determined by combining the needs of the biomass utilization strategies downstream and the algae cultivation technologies upstream of the process.



Block diagram of proposed beneficial re-use strategy.

2.4 Operation & Field Testing

- Who: UK, UD (Michael Wilson, Jen Stuart)

The improved harvesting system will be demonstrated through the cultivation of *Scenedesmus acutus* algae. A 2500 L cyclic flow PBR will be operated on flue gas containing 9-12% CO_2 by volume. Seed cultures will be scaled up, and maintained, in the CAER greenhouse to facilitate biomass production in the larger reactors. Culture health will be continually tracked and evaluated using standard techniques and biomass will be regularly harvested using a two-stage dewatering process based on flocculation/sedimentation and gravity belt filtration. Clarified water will be circulated back to the PBR in order to maintain a closed water balance and recycle any unused nutrients via a UV sterilizer to prevent bacterial contamination. The dewatered biomass (20 - 25% solids) will then be assessed and characterized in Task 4. Flue gas conversion efficiency and rates of nutrient utilization will be analyzed to inform comprehensive mass balances on the most important species.

Milestone 2.1: Demonstration of continuous dewatering system

Task 3: System Biology

Task Summary: The productivity, health, and stability of *Scenedesmus* will be optimized for large-scale growth when integrated for CO_2 utilization at a coal-fired power plant.

3.1 Plant Outage Mitigation System Design

- Who: UD (Jen Stuart)

Algae culturing typically relies on CO_2 to control the pH of the system and maintain an environment conducive to algae productivity, and thereby carbon consumption. Plant outages, both scheduled and unplanned pose a risk to long-term culture health. Approaches for storing carbon and delivering it to algae cultures will be designed and evaluated for their suitability for large-scale implementation. Specifically, using lab-scale experiments conducted at UD, the productivity, health, and biochemical composition of *Scenedesmus* cultures will be assessed when switched from simulated flue gas as the CO_2 source to (1) compressed air (containing 390 ppm CO_2), (2) CO_2 stored from flue gas emissions as an aqueous sodium bicarbonate solution or 3) direct bicarbonate supplementation. In this manner, the best alternative CO_2 source for culture maintenance during plant outages will be determined.

3.2 Effect of Flue Gas Constituents on Biomass Composition

- Who: UD (Jen Stuart)

The effect of CO_2 and O_2 concentration on algae productivity, as well as NOx and SOx, will be studied using simulated flue gas, blended from bottled gases using mass flow controllers, in a controlled laboratory environment. *Scenedesmus acutus* (UTEX B72) will be maintained on urea media optimized for this strain (Crofcheck et al. 2012). Replicate cultures (n=4) will be grown in 800 mL bubble columns at room temperature and an irradiance of ~70 µmol quanta $m^{-2}s^{-1}$ on a 16:8 h light:dark cycle. Cultures will be continuously sparged with the following compressed gas mixtures: air (as a control), 9% CO_2 in air, and a simulated flue gas blend of 9% CO_2, 55 ppm NO, 20 ppm SO_2, 3.5% O_2 and N_2 as the balance. Cultures will be transferred every 10 days while maintained in batch growth under these conditions for 30 days, and then cultured semi-continuously until steady state growth is achieved. Samples for biomass characterization will be taken from replicate cultures during steady state growth. Lipid, protein, and carbohydrate partitioning, based on different flue gas constituents, will be evaluated using standard analytical techniques. Initial results will inform further experiments varying the concentration of both SOx and NOx as a sensitivity analysis to better understand the potential effects of a scrubber unit temporarily going out of commission. These results will also be compared with biomass grown in the field in Task 2.5 on industrial flue gas.

Milestone 3.1: Study of flue gas component effect on biomass composition completed

Task 4: Biomass Valorization/Utilization

Task Summary: The methods intended for use during this project for dewatering, drying, and lipid extraction will be evaluated and baselines will be determined regarding biomass composition.

4.1 Scale-up of Extraction/ Lipid Evaluation

- Who: UK (Robby Pace)

Lipid extraction will be accomplished according to the method of Shen et al. and will be scaled up to 10 lb capacity. The defatted algae and the whole cell algae will then undergo milling and compounding to create algae plastic resin pellets for analysis. Studies will be performed to determine the effect of the extraction step on the resulting algae residues with regard to plastic compounding. Additionally, the extracted lipids will be characterized for their suitability for biofuel production in task 7.1.

4.2 Baseline Characterization of Production Biomass

- Who: UK (Daniel Mohler)

Algae biomass will be characterized with respect to biomass quality, consistency, and potential for biofuel and bioproduct conversion. Compositional analysis will include protein, fats/lipids, carbohydrates (starch and soluble carbs), ash/mineral, elemental analysis, heavy metal analysis, and moisture. Preliminary polymer testing will include compression molding samples and qualitative analysis. Odor profile analysis will be performed using GC-MS to separate and detect potential odorous compounds from the algae feedstock that may require odor neutralization in the final compound.

4.3 Bioplastic Formulation

- Who: Algix

Characteristic compositional evaluations of the biomass performed in Task 4.1 will be used to design resin formulations from both whole and defatted algal biomass. The algae characterization from Task 4.1 will be used to develop at least 3 formulations for extrusion compounding for whole and defatted algae. These formulations will vary key ingredients and loading levels such as the algae loading level and particle size, base resin type, melt flow index and loading level, surfactant type and loading level, compatibilizer type and loading level, moisture scavenger type and loading level, and odor mitigation package type and loading level.

Milestone 4.1: Successfully scaled-up lipid extraction demonstrated
DELIVERABLE 4.1: Bioplastic formulations for both whole and defatted algal biomass will be developed based on biomass composition.

Task 5: Engineering Analysis & Testing II

Task Summary: Lessons learned during the field testing of process equipment will be used to inform design modifications. Additionally, LCA and TEA will be performed to assess the greenhouse gas emission reduction benefits and the economic viability of beneficial CO_2 reuse with bioplastic production.

5.1 Dewatering System Design Refinement

- Who: UK (Jack Groppo)

Data and operating experience gained during Task 2.4 will be used to inform design modifications and improvements. Refinements to the system design will be made in order to integrate the continuous dewatering process with biomass production to provide dewatered biomass for both biofuels and bioplastics production. Operating data from this task will enable determination of appropriate scale-up criteria for full scale design.

5.2 Lifecycle Analysis

- Who: UK (Aubrey Shea)

A preliminary lifecycle analysis will be performed on the entire process encompassing contributions from cultivation in PBRs, harvesting/dewatering, extraction, and algae plastic compounding to determine the greenhouse gas emission reduction benefits of this utilization strategy. Input for the LCA will use the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation Model (GREET) to inform assumptions, while maintaining consistency with previous work. The boundaries of the LCA will include cultivation, harvesting/dewatering, drying, and processing into algae bioplastics, while the scope of the LCA will encompass the energy and emissions going into and out of the boundaries. The net energy ratio (NER = energy contained in the outputs divided by the energy used within the boundaries) will be calculated for comparison with other studies (taking care to make comparisons with only those studies which are applicable, i.e., studies incorporating the same boundaries). The NER for each of the unit operations will help determine where additional improvements in the system can be made. Particular attention will be paid to ensure the energy requirements for PBR operation are well understood. Additionally, the process will be evaluated to determine the improvements contributed by both enhanced systems biology and improved operational strategies.

5.3 Techno-economic Analysis

- Who: UK (Michael Wilson)

The economic feasibility of biological-based carbon mitigation using microalgae will be assessed. Special attention will be paid to capital, operating, and biomass processing costs. A previous TEA will be extended and refined to include the updated processing steps linking biomass production with the utilization pathways. Changes to the dewatering and cultivation stages of the process will be captured and their impact evaluated.

5.4 Field Testing and Biomass Production

- Who: UK (Michael Wilson)

Scaled-up operations for algae cultivation (similar to Task 2.4) paired with an improved dewatering system will be operated to provide feedstock for lipid extraction and larger scale algae plastic compounding trials described in Task 7. Operating data will be collected including: electricity consumption, CO_2 conversion efficiency, PAR, pH, and temperature to include in the LCA and TEA (Tasks 5.2, 5.3, 5.6). Systematic sampling will occur in order to assess overall productivity, biomass composition, and flue gas constituent accumulation.

5.5 Develop Models to assess Power Plant Integration Opportunities

- Who: UK (Michael Wilson)

Integration concepts generated from the completion of Task 2.2 will be further developed to better understand their potential impact on the LCA and TEA. Implementation of system integration variations will be used as input to Task 5.6.

5.6 Update LCA/TEA with Process Data

- Who: UK (Michael Wilson, Aubrey Shea)

The LCA and TEA models developed in Tasks 5.2 and 5.3 will be updated with up to date operational data from Task 5.4 in order to accurately quantify the magnitude of the GHG emission reductions that can be achieved using a microalgae-based process for producing fuels and biopolymers.

Milestone 5.1: A preliminary LCA of the process
Milestone 5.2: Preliminary TEA
DELIVERABLE 5.1: A comparative LCA highlighting the overall greenhouse gas budget
DELIVERABLE 5.2: TEA of process including production of bioplastics and biofuels.

Task 6.0: System Biology II

Task summary: Flue gas availability impacted by power plant outages (both planned and unplanned) has a potentially large impact on large scale algaculture. The methodology developed in Task 3 will be scaled up, tested, and its impacts evaluated. Additionally, the effect of abiotic parameters (e.g., pH, temperature, and light intensity) on biomass productivity and composition will be evaluated.

6.1 Alternative Carbon Supply System Testing

- Who: UD (Jen Stuart)

The most promising approach identified in task 3.1 to sustain large scale culture health in the event of flue gas unavailability, due to both long planned and short unplanned power outages, will be scaled up and tested at a pilot scale. Dr. Stewart from UD will advise the UK CAER team in developing a scaled up version of the methodology. Multiple cycles between normal operation (using real or simulated flue gas) and the alternative carbon delivery system will be performed with special attention paid to effects on algae health, growth rate and composition.

6.2. Optimization of Abiotic Parameters for the Production of Lipids and Proteins

- Who: UD (Jen Stuart)

Scenedesmus acutus (UTEX B72) will be maintained as described in Task 3. We will sample for biochemical characterization, photochemical measurements, and RNA analysis while batch cultures are in early to late stage log phase growth and during stationary phase. Cultures will then be cultivated in a pH-controlled cyclostat system. The cyclostat system will allow us to keep cells in steady-state at a specific growth rate, density and C:N [30]. This cyclostat system will be set for continual pH control, with CO_2 and growth media addition. Cellular C:N quotas as well as N:P and dissolved inorganic carbon concentrations of the growth media will be recorded from our batch growth experiments and will be used as the set points for continuous culturing. This will allow us to keep cultures in steady state growth under N-replete and N-limited conditions, similar to the sampling points analyzed during exponential and stationary phase growth. In this manner, we can conduct a well-controlled analysis of the effects of pH, temperature, and light intensity during nutrient replete and deplete conditions. CO_2 concentrations in captured outlet gases will be measured with a Vaisala CARBOCAP Carbon Dioxide Transmitter GMT221 (Vaisala, Boulder, CO) to calculate %CO_2 captured. CO_2 assimilation rates will also be calculated from oxygen exchange rates and particulate carbon according to the method of Toledo-Cervantes et al. Optimal conditions for the production of lipid and protein fractions will then be validated at a volume of 300 L in a cyclic photobioreactor located at University of Delaware under conditions that simulate cultivation at the East Bend field site, including bubbling with 9% CO_2 and 55 ppm NO. Growth and photochemistry will be monitored and biomass characterization will include total lipid, protein, and carbohydrate quantification, CHN, and FAME analysis.

Milestone 6.1: Multiple cycles of normal operation and operation with alternative carbon delivery system completed
DELIVERABLE 6.1: A comprehensive comparative analysis of the effects of flue gas constituents and growth conditions on biomass productivity and composition

Task 7.0: Biomass/Valorization

Task Summary: In order to realize the maximum potential value of the algal biomass produced, a fractionation scheme will be implemented. Wet lipid extraction will be employed to separate the lipid fraction from the protein and carbohydrate portions of the biomass, while avoiding an energy intensive drying step. The extracted lipids will be characterized, processed into fuel using cutting edge catalytic techniques, and the products analyzed. The protein rich algae meal will be delivered to ALGIX, LLC for compounding into bioplastics and subsequent bioplastic evaluation. The plastics developed using the defatted algae will be compared to similar compounding consisting of whole algal biomass.

7.1 Upgrading and profiling of extracted lipids

- Who: UK (Robby Pace, Eduardo Santillan-Jimenez)

Lipids, extracted in Task 4.1 will be profiled through transesterification to fatty acid methyl esters followed by gas chromatography analysis to determine their suitability as a feedstock for the production of fuels and chemicals. In addition, the suitability of the lipids for upgrading to diesel-range hydrocarbons by means of catalytic decarboxylation/decarbonylation will be evaluated, using catalysts previously developed at the UK CAER. Specific points of interest will include elemental analysis of the extracted lipids (prior to upgrading) for the possible presence of heavy metals, and the yield of hydrocarbons produced during upgrading, in order to calculate the carbon efficiency. Additionally, runs will be made with lipids produced in Task 7.2 in order to produce plastics and fuels from the same feedstock.

7.2 Lipid Extraction/Biomass Fractionation and Upgrading

- Who: UK (Robby Pace)

Lipid extractions will be performed on 10 lb batches of wild type *Scenedesmus acutus* to determine the effect of lipid extraction on the production of bioplastics. After lipid extraction, the resulting algae residues will be subjected to compounding trials (in addition to whole cells, which will function as a reference). Algae will undergo milling and compounding to create algae plastic resin pellets in 10 lb batches. Algae processing includes using two milling techniques to micronize the feedstock, i.e., hammer mill and jet mill. The output of the two milling techniques will be characterized using laser diffraction particle size analysis to determine the mean particle size, and particle size distribution. The top selected formulations, developed in Task 4.3, will be run on a 16 mm co-rotating twin screw extrusion compounder with dual gravimetric feeders. A screw design and extruder barrel temperature profile will be selected and can be optimized during the campaign to create algae plastic pellets for molding and characterization. The compounded algae resin pellets will then be injection molded for conversion into ASTM testing specimens for material performance characterization and analysis. The algae plastic resin pellets will be used directly and can be let down with virgin base resin to vary the final algae loading levels in the test specimen part. The output will be ASTM grade tensile dogbones, flexbars, impact bar and round disc at selected final algae loading levels (15-45%).

7.3 Bioplastic Evaluation

- Who: Algix

The algae plastic molded test specimens will be used for mechanical performance and material characterization. The mechanical performance testing includes: tensile strength and modulus, flexural strength and modulus, impact strength, and melt flow indexing. The material characterization includes: moisture uptake/susceptibility, odor profile, and color analysis. A detailed report for each feedstock and formulation tested will be compiled and recommendations made for the top performing formulations for future pilot testing.

7.4 Heavy Metal Fate Analysis

- Who: UK (Daniel Mohler)

Inductively Coupled Plasma-Mass Spectrometry will be used to determine the concentrations of various heavy metals (As, Hg, Se) commonly associated with coal combustion. The various fractionation streams (lipids and defatted algae) as well as whole biomass will be subject to analysis. Additionally, the final products (bioplastic pellets) will also be analyzed. Other potential sources of heavy metals, such as the agricultural fertilizers used to ensure appropriate levels of N,P, and K in the system and the water used for algae cultivation, will also be sampled and analyzed along with the recycled nutrient media. Finally, a market analysis will be conducted to assess the acceptable ranges of heavy metals in the various products that could be made from the fractionation streams.

Milestone 7.1: Deliver 10 lb defatted algae and 10 lb whole algae biomass to Algix for evaluation
Milestone 7.2: Create algae bioplastic resins, injection molded samples and performance characterization for defatted and whole algae biomass.
DELIVERABLE 7.1: A comparative analysis of bioplastics made from whole and defatted algae
DELIVERABLE 7.2: Heavy metals fate analysis (biomass, bioplastics, biofuels, etc.)

SOPO Deliverables (1)

- The Recipient will provide reports in accordance with the Federal Assistance Reporting Checklist and the instructions accompanying the Checklist:

  ➔ Quarterly and annual reports

- A minimum of one presentation will be given at a National Conference. Potential venues include CO_2 utilization conferences, the annual Algal Biomass Summit, or the annual Algal Biomass Biofuels & Bioproducts conference.

- An annual presentation will be given at DOE's carbon capture conference

- <u>The Recipient will provide the following data during project execution through the Final Technical Report and/or other project deliverables</u> as outlined in the Federal Assistance Reporting Checklist (see following slides)

SOPO Deliverables (2)

- Conceptual design for coupling the proposed biological CO_2 use/conversion process with a coal-fired power plant, including advanced concepts for process footprint reduction, heat and water management, and maximum CO_2 emissions reductions (Subtask 5.3)
- Impact of flue gas contaminants, such as heavy metals, NO_x, SO_x, VOC, PM, etc., on organism growth rates and biomass composition (i.e., lipid, protein and carbohydrate) (Subtask 6.2)
- Anticipated fate of flue gas contaminants, such as heavy metals, NO_x, SO_x, VOC, PM, etc., in the proposed process and resultant value-added product(s) (i.e., disposition between biomass produced, waste water, and air emissions; and further between specific value-added products produced from the biomass) (Subtask 7.4)
- Updated Performance, Cost, Emissions, Market, and Safety Metrics for the process, as defined in NETL's *Cost and Performance Metrics Used to Assess Carbon Utilization and Storage Technologies* (Subtask 5.3)
- Updated Life Cycle Analysis further demonstrating the potential of the proposed process to be a substantive CO_2 mitigation option, by verifying that the CO_2 emissions of the proposed process are less than that of processes currently producing similar products (Subtask 5.6)

SOPO Deliverables (3)

- A high-level technical and economic feasibility study with a high-level return-on-investment (ROI) analysis based on experimental and modeling results. Key components of this study shall include:
  - Detailed accounting of capital costs
  - Detail accounting of operation and maintenance (O&M) costs
  - Detailed market assessment for all value-added product(s), including assessment of all revenue streams and assumed unit costs
    (Subtask 5.3)
- Technology Gap Analysis (as described in SOPO Appendix A) (Subtask 1.2)
- Experimental results, including, as appropriate (Subtask 2.4):
  - measured heat and mass transfer data
  - measured reaction kinetics data
- Recommended operating pressures (in units of bar) and temperatures (in units of ^{o}C) for coal-fired flue gas delivery (Subtask 5.6)
- Preliminary concepts for flue gas conditioning and delivery, and any novel unit operations, such as mass/heat transfer equipment (Subtasks 2.2 and 5.3)
- Description of models used to predict process performance and capacity (Subtask 5.3)

Questions?

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