# A Microalgae-based Platform for the Beneficial Reuse of $CO_2$ Emissions from Power Plants

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# Project Overview

## (DE-FE0026396)

- **Funding:**
  DOE: $990,334
  Cost share: $261,110
  Total project: $1,251,444

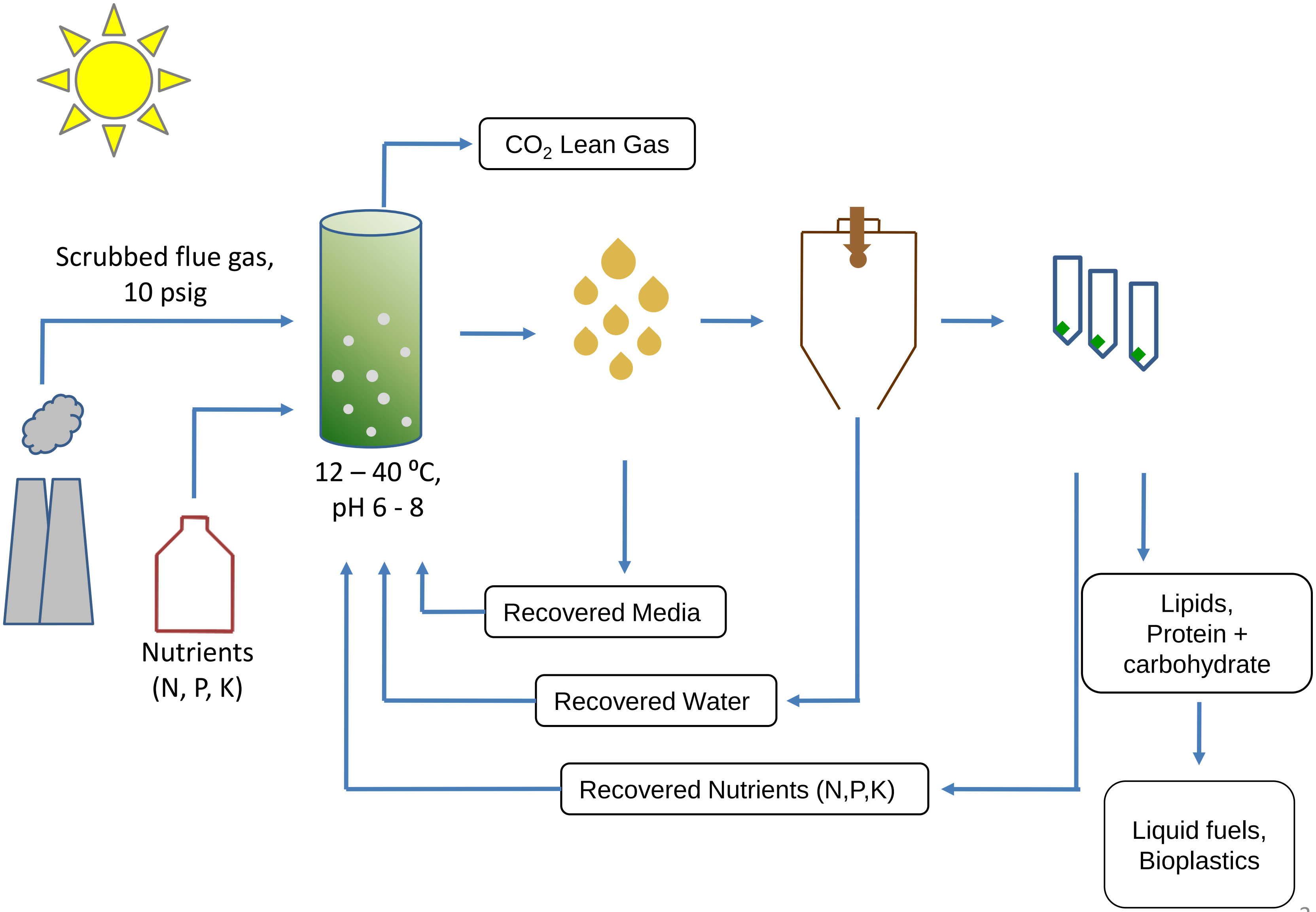
- **Performance dates:**
  10/1/2015 – 9/30/2017

- **Project Participants:**
  - University of Kentucky
  - University of Delaware
  - Algix LLC
  - Duke Energy

**Project Objectives:**

- Optimize UK's technology for microalgae cultivation and processing with respect to cost and performance, particularly with regard to harvesting and dewatering
- Develop strategies to monitor and maintain algae culture health
- Develop a biomass utilization strategy which produces lipids for upgrading to fuels and a proteinaceous feedstock for the production of algal-based bioplastics
- Perform techno-economic analyses to calculate the cost of $CO_2$ capture and recycle, and life cycle analyses to evaluate the GHG emission reduction potential.

# Technology Background: Process Schematic



$CO_2$ Lean Gas

Scrubbed flue gas,
10 psig

12 – 40 °C,
pH 6 - 8

Nutrients
(N, P, K)

Recovered Media

Recovered Water

Recovered Nutrients (N,P,K)

Lipids,
Protein +
carbohydrate

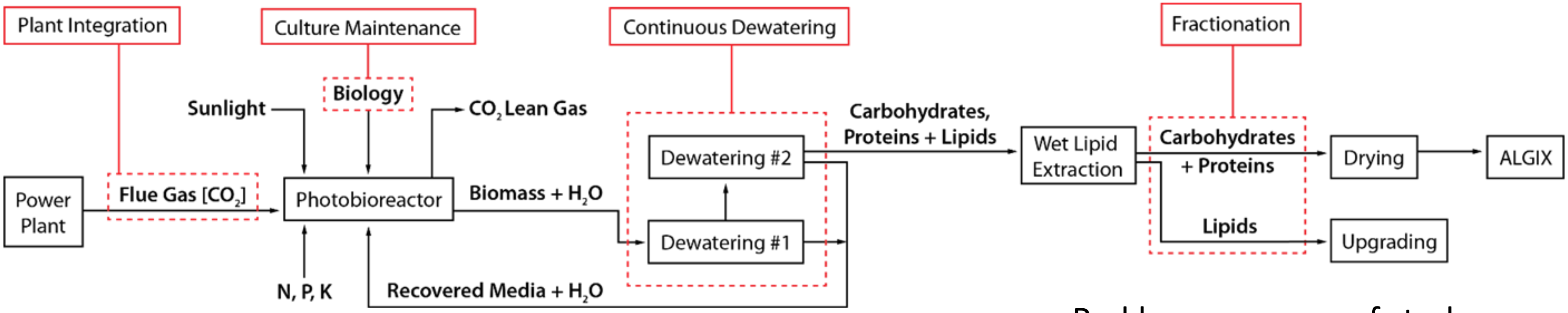
Liquid fuels,
Bioplastics

# 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)

# Technical Approach/Project Scope



Red boxes = areas of study

**Year 2:**

- **Task 5: Engineering Analysis and Testing (UK)**
  - dewatering system refinement
  - life cycle assessment
  - techno-economic analysis
  - field testing and biomass production
  - develop models to assess power plant integration opportunities
  - update LCA/TEA with process data
- **Task 6: System Biology (UD):**
  - alternative carbon supply system testing
  - optimization of abiotic parameters for production of lipids and protein
- **Task 7: Biomass Valorization (UK/Algix)**
  - profiling and upgrading of extracted lipids
  - biomass fractionation and upgrading
  - bioplastics evaluation
  - heavy metals fate analysis

# Key Milestones / Success Criteria

| Decision Point | Date | Success Criteria | Status |
|---|---|---|---|
| **Lipid extraction** | 9/30/16 | >50 wt% total lipid recovery demonstrated for wet extraction | >80% lipid recovery achieved |
| **Demonstration of continuous dewatering** | 9/30/16 | Solids recovery of >95% demonstrated | >95% solids recovery achieved |
| **Verification of methodology for culture maintenance** | 9/30/17 | Maintenance of culture viability for 2 weeks without flue gas | Achieved |
| **Validation of bioplastic properties** | 9/30/17 | Mechanical properties of bioplastics derived from defatted algae better or equal to bioplastics based on whole cell algae | On-going |
| **Lifecycle analysis** | 9/30/17 | Lifecycle analysis shows net positive greenhouse gas emission reduction | Achieved |

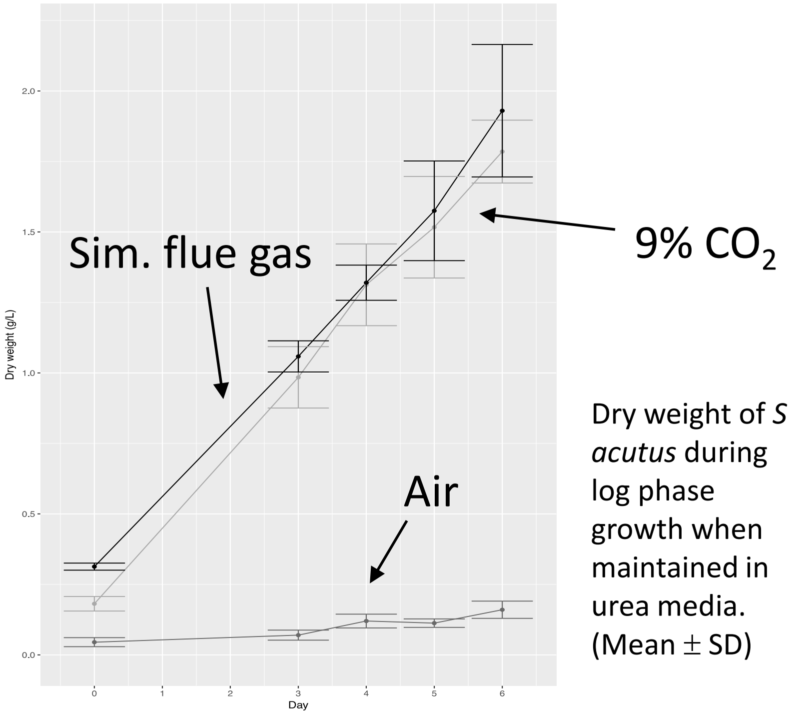
# System Biology: Effect of Flue Gas Constituents on Algae Growth

**Experimental Design:**

- Three gas treatments: Air/Control (400 ppm $CO_2$), 9% $CO_2$, and simulated flue gas (9% $CO_2$, 55 ppm NO, 25 ppm $SO_2$).
- Four replicate cultures for each treatment
- Flow rates were maintained between 2.3-2.5 ml/min for each replicate for all treatments.
- Cultures were acclimated to the gases for two batch cycles before starting experiment (transferred before reaching stationary phase)

**Results:**

- There was no statistical difference in productivity between simulated flue gas and $CO_2$-grown cultures.

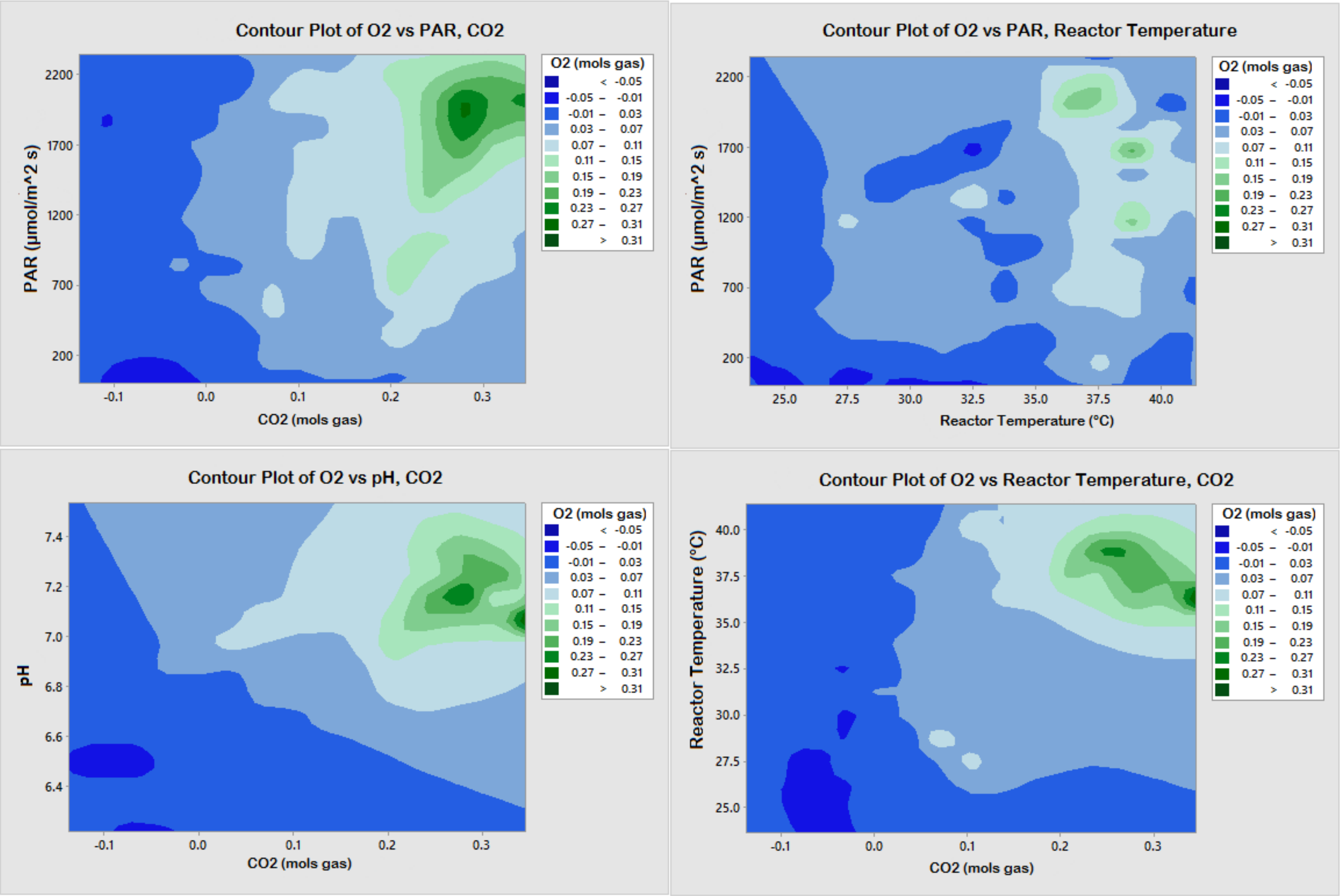


Dry weight of *S. acutus* during log phase growth when maintained in urea media. (Mean ± SD)

Productivity and specific growth rates during log phase growth when maintained in urea media

| | **Treatment** | | |
|---|---|---|---|
| | Air | $CO_2$ | Flue Gas |
| **Productivity (g $L^{-1}$ $Day^{-1}$)** | 0.018 | 0.268 | 0.266 |
| **Specific growth (μ)** | 0.22 | 0.389 | 0.307 |

# Engineering Analysis: East Bend Station Data (1100 L PBR)
# $O_2$ Production vs. Process Temperature, PAR & pH

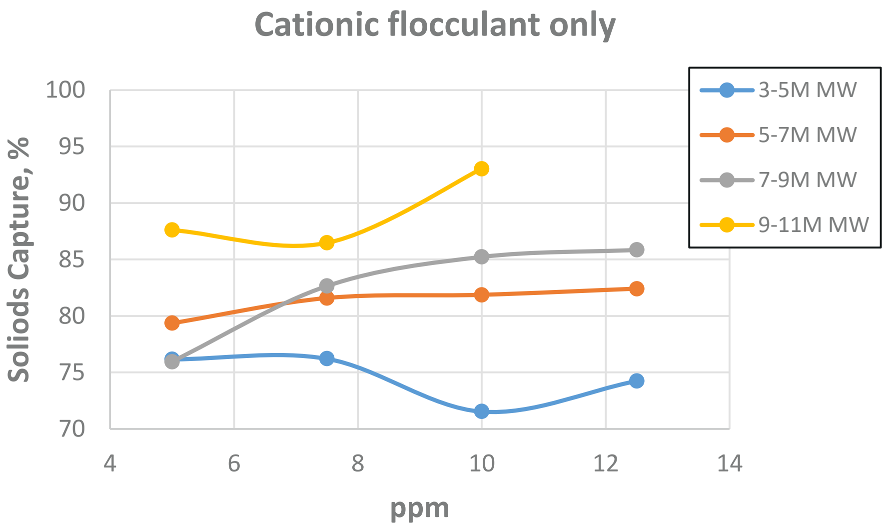


- Optimal $O_2$ production is more temperature dependent than previously thought
- Highest $O_2$ production trend occurs at process temperatures and PAR values of 35-38.5 °C and 1200-2000 μmol/($m^2$s), respectively

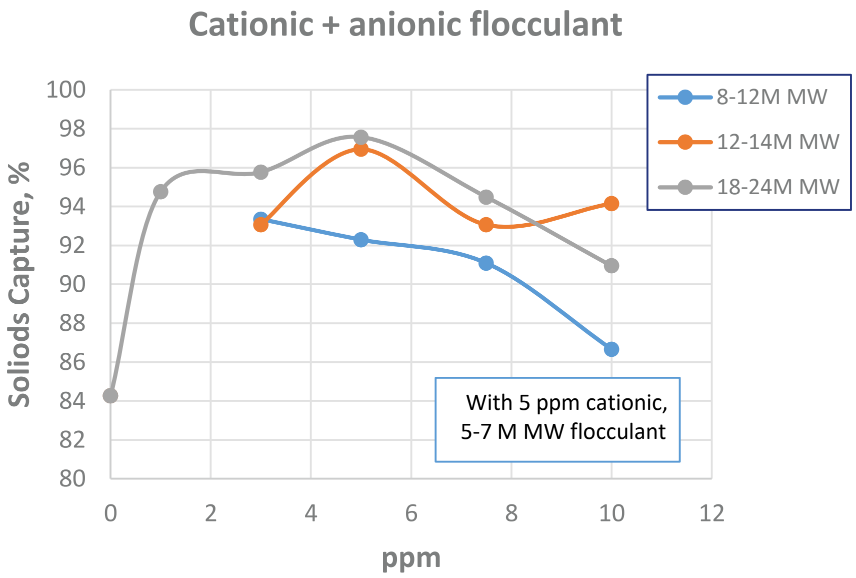
# Biomass Harvesting:

# Optimization of Flocculation Procedure

## (Residence Time = 10 Min)



Effect of cationic flocculant dosage and molecular weight on solids capture of harvested algae (0.456 g/L)



With 5 ppm cationic, 5-7 M MW flocculant

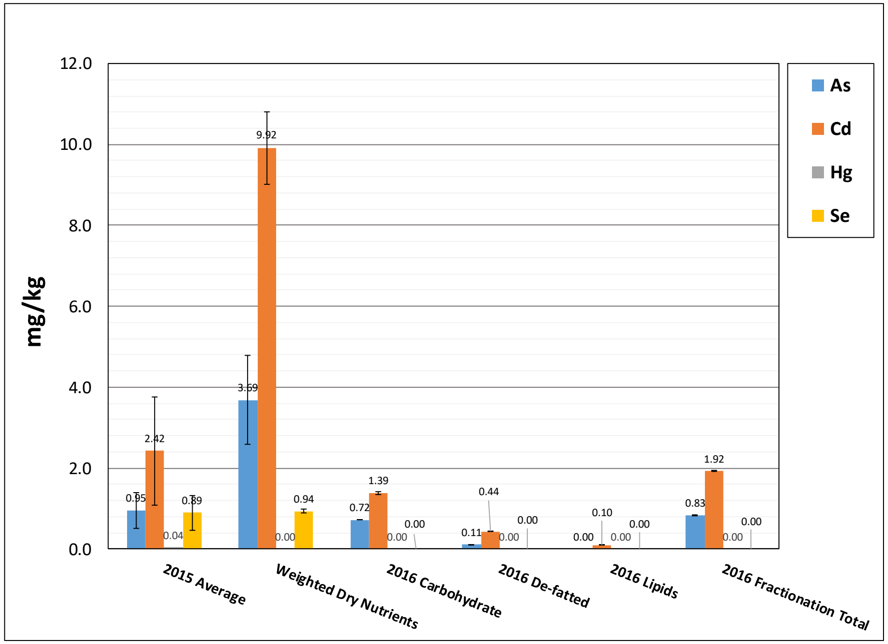
Effect of anionic flocculant dosage and molecular weight on solids capture of harvested algae pretreated with 5 ppm cationic flocculant

- Extent of solids capture is limited if only cationic flocculant is used (regardless of flocculant mol. wt.)

- Anionic flocculants by themselves are not effective
- However, 95% solids capture is possible by addition of 1 ppm of anionic flocculant to algae pre-flocculated with 5 ppm cationic flocculant

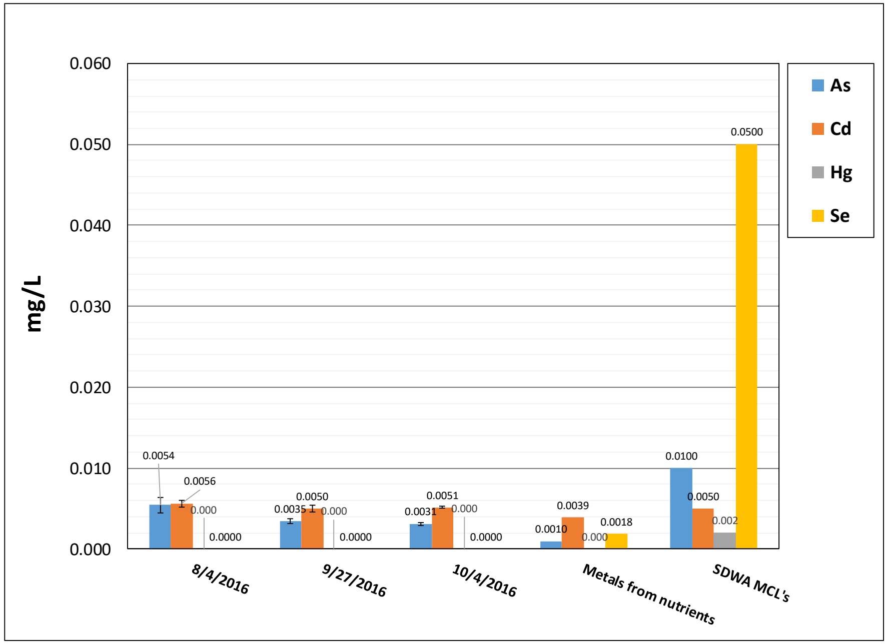
# Heavy Metals Analysis

## Analysis of solids



- 2015 averages are average of five samples of dry algae grown on flue gas at East Bend Station in 2015
- Weighted Dry Nutrients numbers represent the sum of all metals present in dry nutrients, weighted to reflect the nutrient mixture as it is added to the PBR

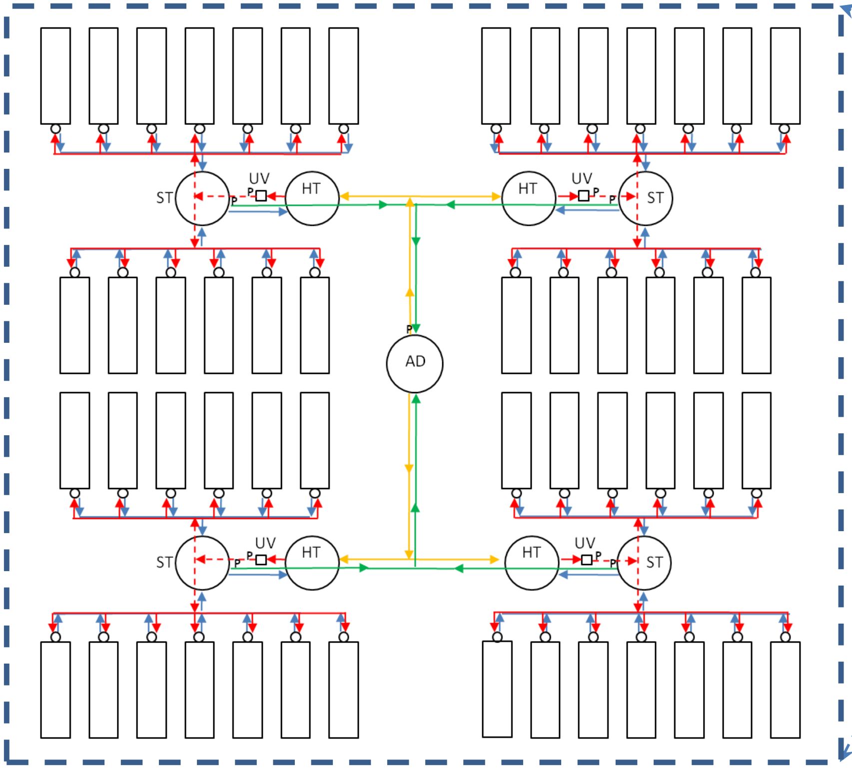
## Analysis of nutrient broth in PBR



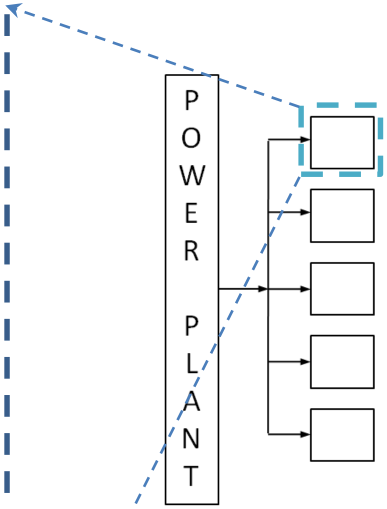
- "Metals from Nutrients" represents weighted calculation based on metals in dry nutrients and their respective target concentrations in algae media
- SDWA MCL's represent the Maximum Contaminant Levels (MCL's) for drinking water as regulated by the Safe Drinking Water Act of 1974

- Very low heavy metal concentrations detected in harvested algae – levels are consistent with heavy metals incorporation from supplied nutrients

# Life Cycle Assessment



Schematic of a section of the algae system consisting of 52 PBR modules, 4 settling tanks (ST), holding tanks (HT), and UV sterilizers (UV).



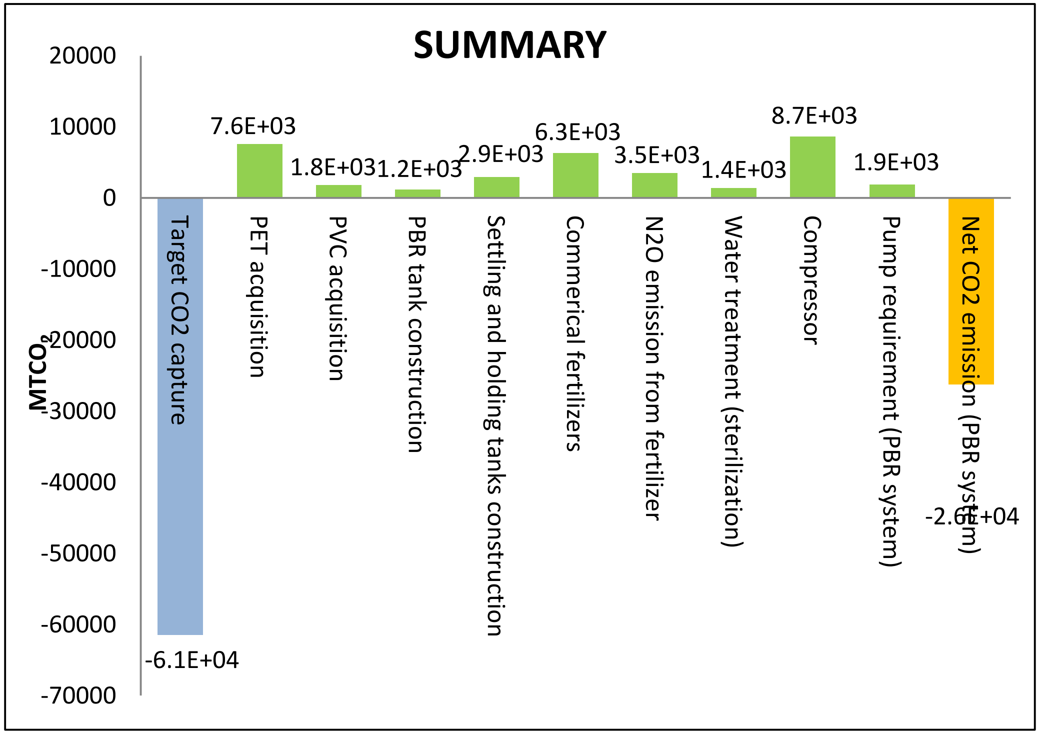
A schematic of the algae system (260 PBR modules; 260 individual feed tanks, feed pumps, and compressors; 20 individual settling tanks, holding tanks, and UV sterilizers)

- A life cycle assessment (LCA) was developed for an algae system based on UK's cyclic flow PBR, **mitigating 30% of the $CO_2$ emitted by a 1 MW coal-fired power plant**.
- Operation of the algae system included cumulative process requirements and energy consumption associated with algae cultivation, harvesting, dewatering, nutrient recycling, and water treatment.

# Life Cycle Assessment: Results

- $CO_2$ emission associated with the gas compressor was 8.7 x $10^3$ metric tons, due to the large amount of flue gas (4422 $m^3/h$) being compressed at full capacity for 12 h per day.
- PBR feed pumps emitted a lesser amount of $CO_2$ (1.9 x $10^3$ metric tons) on account of the cyclic flow operation mode.
- The PBR system was able to capture 43% (2.6 x $10^4$ metric tons) of the target $CO_2$ emission (6.1 x $10^4$ metric tons).
- The LCA results demonstrate that a PBR algae system can be considered as a $CO_2$ capture technology.

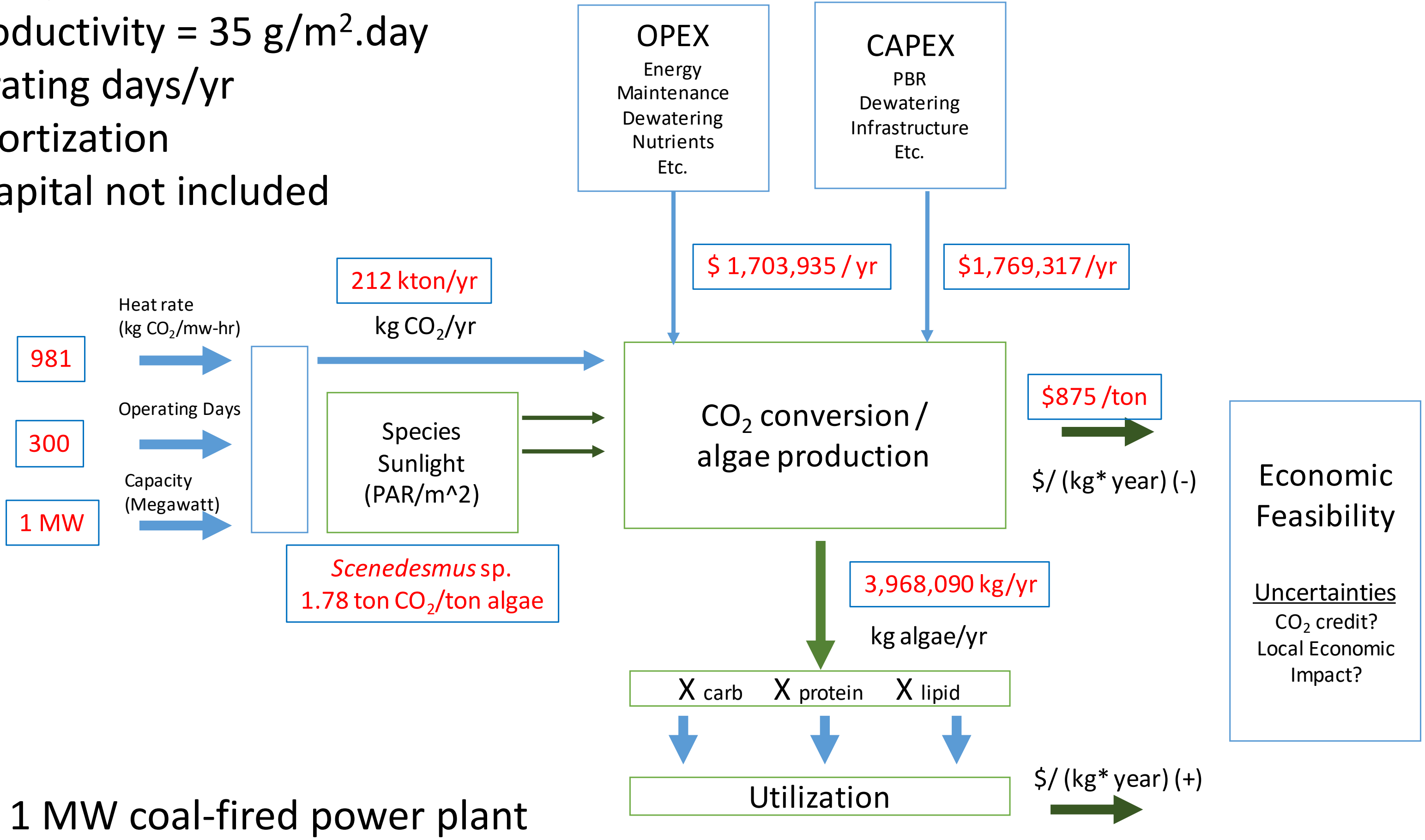
| **POWER PLANT** | | |
|---|---|---|
| Capacity | 1 | MW |
| $CO_2$ emission | 22.76 | ton/day |
| $CO_2$ capture | 30 | % |
| $CO_2$ emission mitigated | 6.83 | ton/day |
| Operation | 300 | day/year |
| **ALGAE** | | |
| Strain | *Scenedesmus acutus* | |
| Growth rate | 0.15 | g/L/day |
| Culture density at harvest | 0.8 | g/L (dry weight) |
| Algae required for 30% $CO_2$ capture | 3.88 | ton/day |



# Techno-economic Analysis

**US Scenario (best case):**

- 30% $CO_2$ capture
- Algae productivity = 35 $g/m^2$.day
- 300 operating days/yr
- 30 yr amortization
- Cost of capital not included



OPEX
Energy
Maintenance
Dewatering
Nutrients
Etc.

CAPEX
PBR
Dewatering
Infrastructure
Etc.

$ 1,703,935 / yr

$1,769,317 /yr

212 kton/yr

kg $CO_2$/yr

981

Heat rate
(kg $CO_2$/mw-hr)

300

Operating Days

1 MW

Capacity
(Megawatt)

Species
Sunlight
(PAR/m^2)

*Scenedesmus* sp.
1.78 ton $CO_2$/ton algae

$CO_2$ conversion / algae production

$875 /ton

$/ (kg* year) (-)

3,968,090 kg/yr

kg algae/yr

X carb X protein X lipid

Utilization

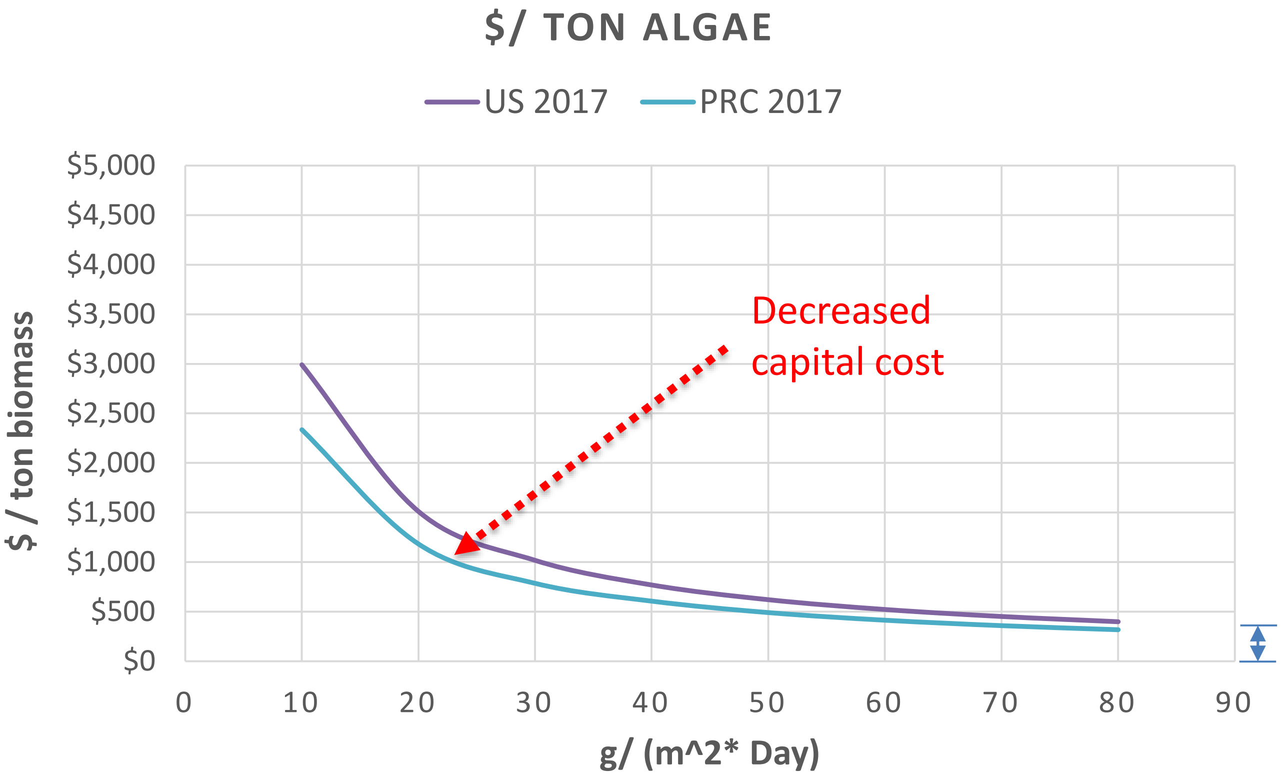
$/ (kg* year) (+)

Economic Feasibility

Uncertainties
$CO_2$ credit?
Local Economic Impact?

Base case: 1 MW coal-fired power plant
Estimated min. algae production cost = **$875/ton**
(biomass dewatered to 10-15 wt% solids)

# Techno-economic Analysis (cont.)

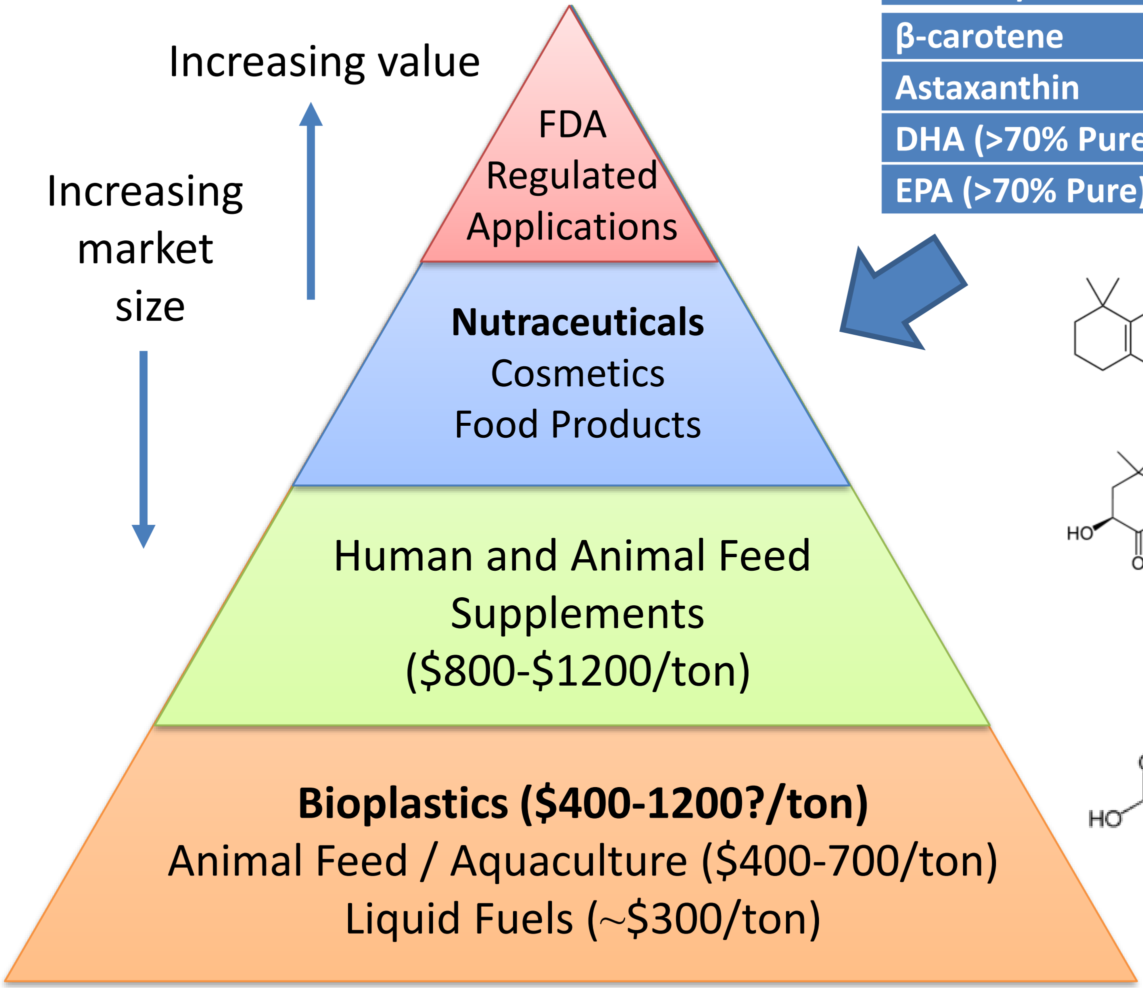


Decreased capital cost

Operating costs; note asymptote

- Cost estimates (2017) are consistent with projections from prior analysis (2013), showing considerable progress toward economic viability
- Asymptote relates to operating costs

# Algal Biomass Utilization



Increasing value

Increasing market size

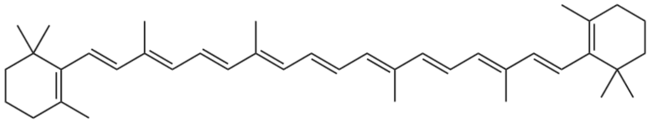
FDA Regulated Applications

**Nutraceuticals**
Cosmetics
Food Products

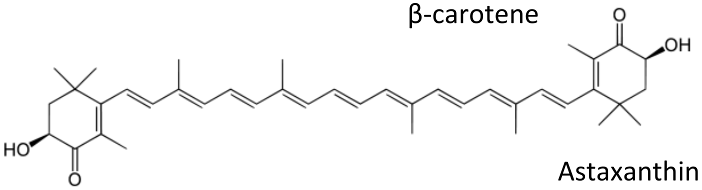
Human and Animal Feed Supplements ($800-$1200/ton)

**Bioplastics ($400-1200?/ton)**
Animal Feed / Aquaculture ($400-700/ton)
Liquid Fuels (~$300/ton)

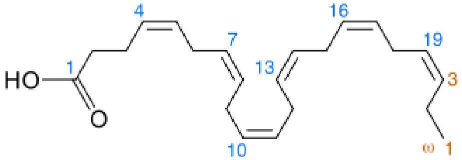
| Product/extract | Selling price | Wt% in algae |
|---|---|---|
| **β-carotene** | $300-3000/kg | 14% |
| **Astaxanthin** | $2500-7150/kg | 3% |
| **DHA (>70% Pure)** | ~$12,540/kg | 7.8% |
| **EPA (>70% Pure)** | ~$12,540/kg | 4% |



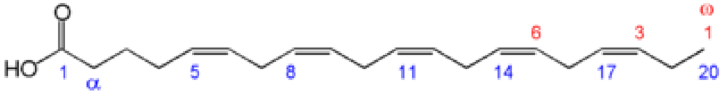
β-carotene



Astaxanthin



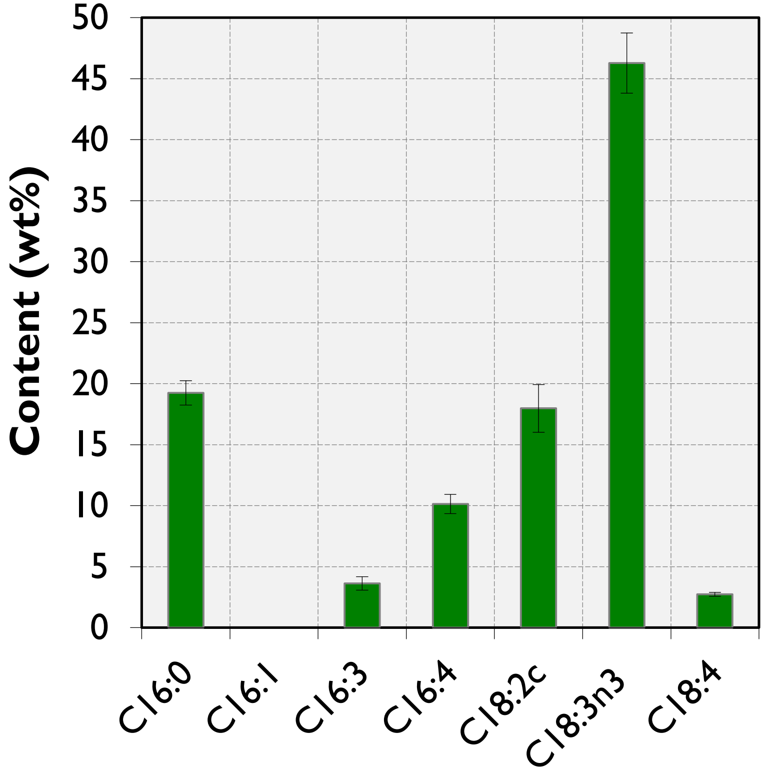
DHA



EPA

# Lipid Extraction and Characterization

- Wet *Scenedesmus*, typically ~15 wt% solids
- Ultrasound, microwave irradiation and bead beating all proved ineffective for cell lysing
- Acidification to pH 1-2 using aq. HCl/MeOH results in cell lysing and simultaneous lipid (trans)esterification*
- Yield of esterifiable lipids = 6.3 (+/- 0.1) wt%, close to value reported previously for dry *Scenedesmus***
- Lipids from this strain of *Scenedesmus acutus* are highly unsaturated: ALA (α-linolenic acid) accounts for almost 50% of total lipids



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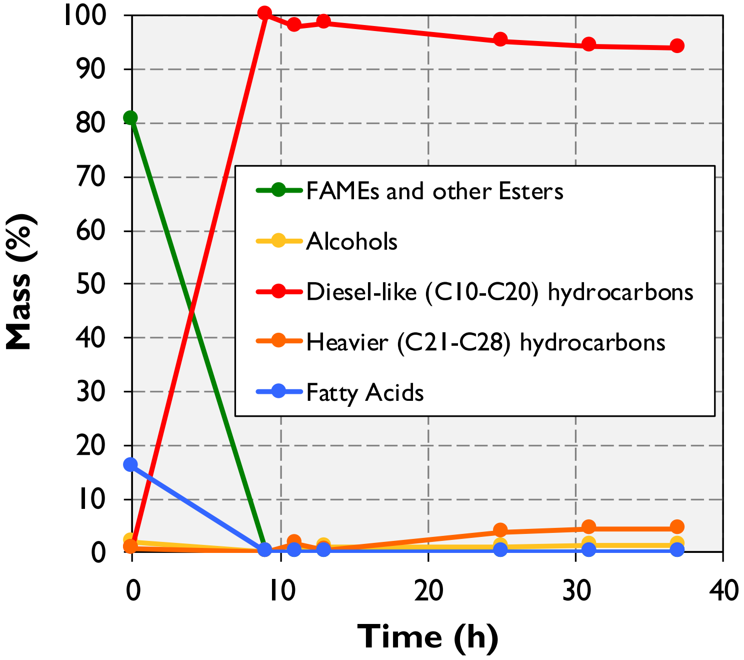
* L.M.L. Laurens, M. Quinn, S. Van Wychen, D.W. Templeton, E.J. Wolfrum, *Anal. Bioanal. Chem.*, 403 (2012) 167-178.

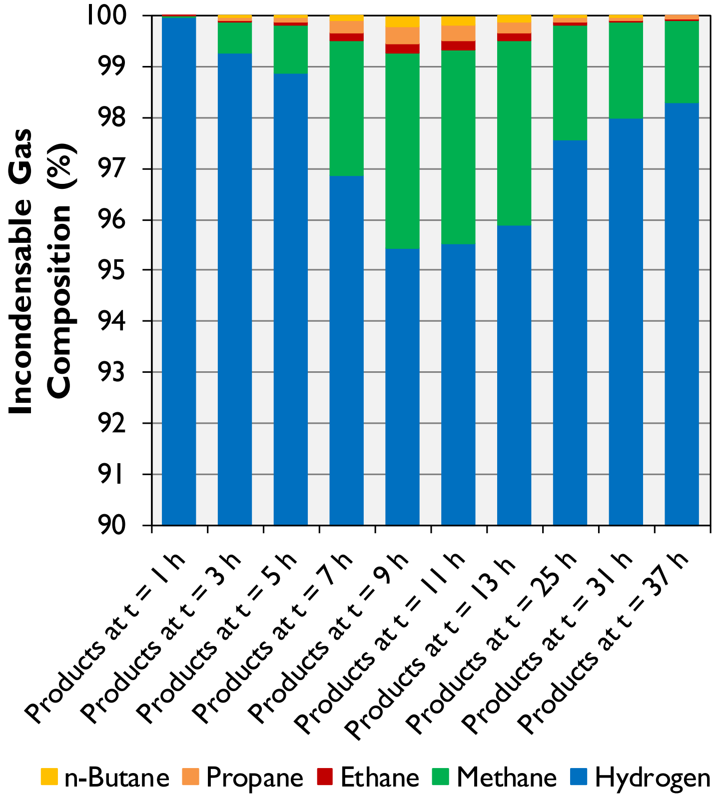
**E. Santillan-Jimenez, R. Pace, S. Marques, T. Morgan, C. McKelphin, J. Mobley, M. Crocker, *Fuel* 180 (2016) 668-678.

# Upgrading of Extracted Algal FAMES to Hydrocarbons

**75 wt% algal FAMEs in dodecane, WHSV = 1 h$^{-1}$, Temp. = 375 °C**

**20% Ni – 5% Cu/Al$_2$O$_3$ catalyst**





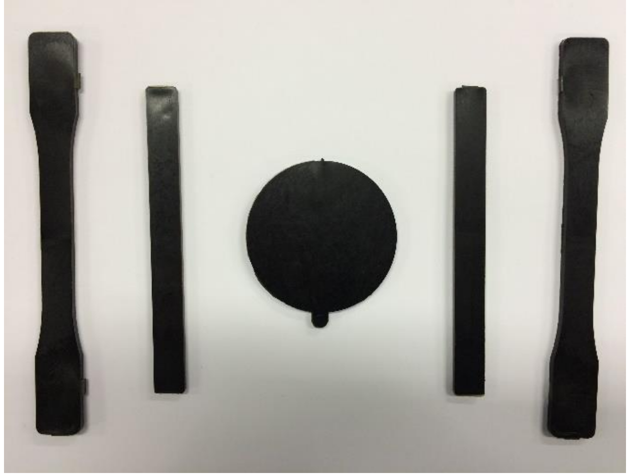
- >90% liquid products are diesel-like hydrocarbons at all reaction times
- Methane yield decreases after induction period, indicating poisoning of cracking sites

E. Santillan-Jimenez, R. Loe, M. Garrett, T. Morgan, M. Crocker, *Catal. Today*, 2017, http://dx.doi.org/10.1016/j.cattod.2017.03.025.

# Composition of Whole and Defatted Algae

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

# Summary

- An improved protocol for algae harvesting was developed, based on the use of cationic + anionic flocculants
- Very low heavy metal concentrations detected in harvested algae – levels are consistent with heavy metals incorporation from supplied nutrients
- LCA showed that the cyclic flow PBR qualifies as a net $CO_2$ capture technology
- TEA indicates a best case scenario production cost of $875/ton for *Scenedesmus acutus* biomass
- A procedure was developed for lipid extraction from wet *Scenedesmus* biomass
- Extracted lipids were upgraded to diesel-range hydrocarbons
- Defatted biomass possessed improved odor properties for bioplastic applications

# Acknowledgements

- Department of Energy / National Energy Technology Laboratory:
  Andy Aurelio
- University of Kentucky:
  Michael Wilson, Dr. Jack Groppo, Aubrey Shea, Stephanie Kesner, Daniel Mohler, Robert Pace, Dr. Eduardo Santillan-Jimenez, Tonya Morgan, Dr. Czarena Crofcheck
- University of Delaware:
  Dr. Jennifer Stewart, Jenna Schambach, Dr. Mark Warner
- Algix:
  Dr. Ashton Zeller, Ryan Hunt
- Duke Energy:
  Doug Durst