A Microalgae-based Platform for the Beneficial Reuse of CO₂ 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

Scrubbed flue gas, 10 psig

12 – 40 °C, pH 6 - 8

CO₂ Lean Gas

Recovered Media

Recovered Water

Recovered Nutrients (N,P,K)

Lipids, Protein + carbohydrate

Liquid fuels, Bioplastics

Nutrients (N, P, K)
Advantages and Challenges

➢ Ability to generate a valuable product, thereby off-setting costs of CO₂ capture (potential for new industry)
➢ No need to concentrate CO₂ stream
➢ Potential to polish NOx and SOx emissions

▪ Areal productivity such that very large algae farms required for significant CO₂ capture
▪ CO₂ 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)
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

<table>
<thead>
<tr>
<th>Decision Point</th>
<th>Date</th>
<th>Success Criteria</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lipid extraction</td>
<td>9/30/16</td>
<td>&gt;50 wt% total lipid recovery demonstrated for wet extraction</td>
<td>&gt;80% lipid recovery achieved</td>
</tr>
<tr>
<td>Demonstration of continuous dewatering</td>
<td>9/30/16</td>
<td>Solids recovery of &gt;95% demonstrated</td>
<td>&gt;95% solids recovery achieved</td>
</tr>
<tr>
<td>Verification of methodology for culture maintenance</td>
<td>9/30/17</td>
<td>Maintenance of culture viability for 2 weeks without flue gas</td>
<td>Achieved</td>
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<tr>
<td>Validation of bioplastic properties</td>
<td>9/30/17</td>
<td>Mechanical properties of bioplastics derived from defatted algae better or equal to bioplastics based on whole cell algae</td>
<td>On-going</td>
</tr>
<tr>
<td>Lifecycle analysis</td>
<td>9/30/17</td>
<td>Lifecycle analysis shows net positive greenhouse gas emission reduction</td>
<td>Achieved</td>
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</tbody>
</table>
Experimental Design:
• Three gas treatments: Air/Control (400 ppm CO₂), 9% CO₂, and simulated flue gas (9% CO₂, 55 ppm NO, 25 ppm SO₂).
• 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 CO₂-grown cultures.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Productivity (g L⁻¹ Day⁻¹)</th>
<th>Specific growth (μ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>0.018</td>
<td>0.22</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.268</td>
<td>0.389</td>
</tr>
<tr>
<td>Flue Gas</td>
<td>0.266</td>
<td>0.307</td>
</tr>
</tbody>
</table>

Dry weight of *S. acutus* during log phase growth when maintained in urea media. (Mean ± SD)
• 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/(m²s), 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)

- 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
A life cycle assessment (LCA) was developed for an algae system based on UK’s cyclic flow PBR, mitigating 30% of the CO₂ 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\textsubscript{2} emission associated with the gas compressor was \(8.7 \times 10^3\) 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\textsubscript{2} (\(1.9 \times 10^3\) metric tons) on account of the cyclic flow operation mode.

- The PBR system was able to capture 43\% (\(2.6 \times 10^4\) metric tons) of the target CO\textsubscript{2} emission (\(6.1 \times 10^4\) metric tons).

- The LCA results demonstrate that a PBR algae system can be considered as a CO\textsubscript{2} capture technology.

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**POWER PLANT**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>1 MW</td>
</tr>
<tr>
<td>CO\textsubscript{2} emission</td>
<td>22.76 ton/day</td>
</tr>
<tr>
<td>CO\textsubscript{2} capture</td>
<td>30 %</td>
</tr>
<tr>
<td>CO\textsubscript{2} emission mitigated</td>
<td>6.83 ton/day</td>
</tr>
<tr>
<td>Operation</td>
<td>300 day/year</td>
</tr>
</tbody>
</table>

**ALGAE**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain</td>
<td><em>Scenedesmus acutus</em></td>
</tr>
<tr>
<td>Growth rate</td>
<td>0.15 g/L/day</td>
</tr>
<tr>
<td>Culture density at harvest</td>
<td>0.8 g/L (dry weight)</td>
</tr>
</tbody>
</table>

Algae required for 30\% CO\textsubscript{2} capture 3.88 ton/day

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**SUMMARY**

- Target CO\textsubscript{2} capture: -6.1E+04
- PET acquisition: 7.6E+03
- PVC acquisition: 1.8E+03
- PBR tank construction: 1.2E+03
- Commerical fertilizers: 2.9E+03
- Commercial fertilizer: 6.3E+03
- N2O emission from fertilizer: 3.5E+03
- Water treatment (sterilization): 1.4E+03
- Compressor: 8.7E+03
- Pump requirement (PBR system): 1.9E+03

Net CO\textsubscript{2} emission (PBR system): -2.6E+04
Techno-economic Analysis

US Scenario (best case):
- 30% CO₂ capture
- Algae productivity = 35 g/m².day
- 300 operating days/yr
- 30 yr amortization
- Cost of capital not included

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

<table>
<thead>
<tr>
<th>Product/extract</th>
<th>Selling price</th>
<th>Wt% in algae</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-carotene</td>
<td>$300-3000/kg</td>
<td>14%</td>
</tr>
<tr>
<td>Astaxanthin</td>
<td>$2500-7150/kg</td>
<td>3%</td>
</tr>
<tr>
<td>DHA (&gt;70% Pure)</td>
<td>~$12,540/kg</td>
<td>7.8%</td>
</tr>
<tr>
<td>EPA (&gt;70% Pure)</td>
<td>~$12,540/kg</td>
<td>4%</td>
</tr>
</tbody>
</table>

- **Bioplastics ($400-1200$/ton)**
- **Animal Feed / Aquaculture ($400-700$/ton)**
- **Liquid Fuels (~$300$/ton)**
- **Human and Animal Feed Supplements ($800-1200$/ton)**
- **Nutraceuticals**
  - Cosmetics
  - Food Products
- **FDA Regulated Applications**
- **Increasing value**
- **Increasing market size**

Increasing value

1. **β-carotene**
2. **Astaxanthin**
3. **DHA (>70% Pure)**
4. **EPA (>70% Pure)**

Increasing market size
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

Upgrading of Extracted Algal FAMES to Hydrocarbons

75 wt% algal FAMEs in dodecane, WHSV = 1 h⁻¹, Temp. = 375 °C

20% Ni – 5% Cu/Al₂O₃ catalyst

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

Composition of Whole and Defatted Algae

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ash (wt%)</th>
<th>Protein (wt%)</th>
<th>Volatiles (GC/MS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole</td>
<td>11.1</td>
<td>44.2</td>
<td>16 peaks at 140 °C; 196 peaks at 200 °C</td>
</tr>
<tr>
<td>Defatted</td>
<td>15.6</td>
<td>50.7</td>
<td>12 peaks at 140 °C; 121 peaks at 200 °C</td>
</tr>
</tbody>
</table>

➢ 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 CO₂ 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
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