Harnessing Algal Biomass to Contain Power Plant Emissions

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Outline

- Current challenges of biological CO₂ capture from power industry
- Our strategy - The combined biological and chemical solution
- The pilot-scale photobioreactor algal cultivation
- The algal amino acid salt solution of CO₂ capture
- Mass and energy balance of the combined solution

100 MW T.B. Simon Power Plant, MSU
160 MW Erickson Power Plant, Lansing, MI

Algal cultivation on flue gas and wastewater from the power plant
1. Current challenges of biological CO₂ capture from flue gas

- Algal biomass yield and algal biomass productivity
  - Very good biomass yield (considering photosynthesis)
  - Unmatched biomass productivity (considering the rate of CO₂ emission)

- Land and water demands for large algal cultivation systems required to completely capture CO₂ from a commercial coal-fired power plant
  - Erickson Power Plant (150 MW): ~3,000 metric ton CO₂ per day requires ~150,000,000 m² area for the open pond reactor and ~45,000,000 m³ volume for the photobioreactor (based on the current algae biomass productivity of 20 g/m²/day)

- Stability and robustness of algal strains for long-term cultivation on flue gas
2. Our Strategy – A combined biological and chemical solution

Synergistically integrating biological and chemical processes to efficiently capture CO₂ from flue gas and completely utilize the algal biomass for value-added chemical and fuel production

Objectives:
1. The selected algal strain to maximize biomass accumulation from the coal-fired flue gas
2. A cascade biomass utilization to produce amino acid absorbents, polyurethanes, biodiesel, and methane
3. Techno-economic analysis (TEA) and life cycle assessment (LCA)
2. Our Strategy – A combined biological and chemical solution

The flowchart of the biological and chemical solution*

- **A robust algal species**
  - Nutrients (P/N)
  - Water

1. **High-rate algae photobioreactor**
   - Raw flue gas (CO₂, SO₂, NOₓ, O₂, and N₂)
   - Power

2. **Cascaded biomass utilization**
   - Algal biomass
   - Amino acid salt absorption
   - Pure CO₂

- **Biofuels**
  - Carbohydrates and lipids
  - Protein

- **High-efficiency amino acid absorbents**
  - Spent amino acid salt solution

The pilot photobioreactor system in the MSU power plant

- **CO₂**
- **Pumping unit**
- **Electrolysis**
- **Heat**
- **Centrifuge**
- **Dryer**
- **Power Plant**
- **Phyco2 Photobioreactor**

- **Liquid**
- **Wet algal biomass**
- **Dry algal biomass**

*a. T.B. Simon power plant; b. Flue gas pumping unit; c. Photobioreactor; d. Algae growing in the reactor; e. Centrifuge; f. Dryer*

*: Solid black lines are the mass flow. Dashed blue lines are the energy flow. The red frame is the system that will be studied by this project.
3. The Pilot-scale photobioreactor algal cultivation

A. A robust algal strain from the Great Lakes region

- A robust alga, *Chlorella sorokiniana* MSU, has been selected from the Great Lake region.

![Algal community assemblages](image)

Changes of the algal assemblage during 5 months continuous culture

- Original seed
- 5 months: 40 g m\(^{-3}\) TN
- 5 months: 100 g m\(^{-3}\) TN
- 5 months: 200 g m\(^{-3}\) TN

*Pseudanabaena* • *Phormidium* • *Limnothrix* • *Synechocystis* • *Scenedesmus* • *Chlorella*

![Effects of different wavelengths on algae](image)

![Flask culture (250 ml)](image)

![Bench scale photobioreactor (2 L)](image)

![Bench scale photobioreactor (10 L)](image)

Algal community assemblages before (a) and after (b) cultured in AD effluent for 5 months, and (c) SEM picture of the pure *Chlorella sorokiniana* MSU
3. The Pilot-scale photobioreactor algal cultivation

B. Pilot operation

- This task optimizes and validates continuous algae cultivation using the pilot photobioreactors

- Pilot experiments
  - **The algal strain:**
    - The selected *Chlorella sorokiniana* MSU with several bacteria
  - **Culture system preparation:**
    - The boiler water (12 mg/L TP) is the water source for the culture.
    - The flue gas from the T.B. Simon power plant is the CO₂ source.
    - Na₂SO₃ and NH₄NO₃ are used to mimic SO₂ and NO₂ in the flue gas.

- **Operation of the algal cultivation:**
  - Flue gas flow rate: 120 L/1000 L solution/min
  - The reactor volume: 100 L
  - Harvesting frequency: 12 hours and 24 hours
  - Harvesting amount: 30 L/harvesting, 50 L/harvesting, 60 L/harvesting, 70 L/harvesting
  - Water recirculation: 50 L/harvesting and recirculation
3. The pilot-scale photobioreactor algal cultivation

B. Pilot operation

Biomass concentration under different culture conditions (from March 2018 to June, 2019)
3. The pilot-scale photobioreactor algal cultivation

B. Pilot operation

Nitrogen consumption (from March 2018 to June 2019)

Phosphorus consumption (from March 2018 to June 2019)

pH (from March 2018 to June 2019) a, b

a: A strategy using ammonia and nitrate to balance pH has been developed applied to control pH without acid and alkali usages
b: NxO in the flue gas can be beneficial for the pH control.

Cq ratio of alga and bacteria (from March 2018 to June 2019) a

a: Cq is the number from qPCR analysis.
3. The pilot-scale photobioreactor algal cultivation

B. Pilot operation

Biomass concentration and productivity

- 50 L harvesting twice per day had the highest (P<0.05) biomass productivity of 1.45 g/L/day.
- 50 L harvesting with SO₂ supplement had the highest (P<0.05) biomass concentration of 1.36 g/L.
- 50 L harvesting with SO₂ and water cycle had the biomass productivity and biomass concentration of 0.36 g/L/day and 0.72 g/L.
### C. Harvested biomass from the pilot operation

#### Characteristics of algal biomass from the pilot operation

<table>
<thead>
<tr>
<th>Elements</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (% dry biomass)</td>
<td>48.2</td>
</tr>
<tr>
<td>Nitrogen (% dry biomass)</td>
<td><strong>9.1</strong></td>
</tr>
<tr>
<td>Sulfur (% dry biomass)</td>
<td>0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Components</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude proteins (% dry biomass)</td>
<td><strong>56.8</strong></td>
</tr>
<tr>
<td>Lipids (% dry biomass)</td>
<td>6.8</td>
</tr>
<tr>
<td>Carbohydrates (% dry biomass)</td>
<td>30.4</td>
</tr>
<tr>
<td>Ash (% dry biomass)</td>
<td>6.0</td>
</tr>
</tbody>
</table>

#### Amino acids

<table>
<thead>
<tr>
<th>Amino acids</th>
<th>Content (Mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>histidine</td>
<td>1.63</td>
</tr>
<tr>
<td>isoleucine</td>
<td>4.24</td>
</tr>
<tr>
<td>leucine</td>
<td>8.52</td>
</tr>
<tr>
<td><strong>lysine</strong></td>
<td><strong>10.32</strong></td>
</tr>
<tr>
<td>methionine</td>
<td>3.90</td>
</tr>
<tr>
<td>phenylalanine</td>
<td>3.58</td>
</tr>
<tr>
<td>threonine</td>
<td>3.62</td>
</tr>
<tr>
<td>tryptophan</td>
<td>-</td>
</tr>
<tr>
<td>valine</td>
<td>7.96</td>
</tr>
<tr>
<td>arginine</td>
<td>4.88</td>
</tr>
<tr>
<td>cysteine</td>
<td>1.43</td>
</tr>
<tr>
<td><strong>glycine</strong></td>
<td><strong>11.04</strong></td>
</tr>
<tr>
<td>proline</td>
<td><strong>5.66</strong></td>
</tr>
<tr>
<td>tyrosine</td>
<td>1.00</td>
</tr>
<tr>
<td>alanine</td>
<td><strong>13.35</strong></td>
</tr>
<tr>
<td>aspartic Acid</td>
<td>5.79</td>
</tr>
<tr>
<td>glutamic Acid</td>
<td>10.51</td>
</tr>
<tr>
<td>serine</td>
<td>2.53</td>
</tr>
</tbody>
</table>
4. The algal amino acid salt solution of CO₂ capture

A. Flowchart

- Wet algal biomass
- Mechanical alkali protein extraction and hydrolysis
- Mixed amino acid salt solution
- CO₂ capture
- Spent amino acids

2 L ball mill unit for mechanical alkali protein extraction

2 L Parr reactor for protein hydrolysis

Bench-scale CO₂ absorption unit

Bench-scale CO₂ desorption unit
4. The algal amino acid salt solution of CO₂ capture

B. Protein extraction and amino acid CO₂ absorption results

Mechano-chemical protein extraction process*

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Ball material</th>
<th>Ball:Biomas s mass ratio</th>
<th>Reaction time (min)</th>
<th>KOH</th>
<th>Protein extraction efficiency (%)</th>
<th>Amino acid conversion efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zirconia</td>
<td>4:1</td>
<td>60</td>
<td>KOH</td>
<td>87</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>Zirconia</td>
<td>4:1</td>
<td>30</td>
<td>KOH</td>
<td>41</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>Agate</td>
<td>4:1</td>
<td>30</td>
<td>KOH</td>
<td>81</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>Agate</td>
<td>2:1</td>
<td>30</td>
<td>KOH</td>
<td>17</td>
<td>7</td>
</tr>
</tbody>
</table>

*: The effects of selected ball/biomass ratio, reaction time on protein extraction efficiency of ball mill treated algal biomass. The milled slurry was treated under 130°C for 2 hours before using for absorption.

- Both agate and zirconia had high protein extraction efficiency.
- Amino acid conversion efficiency is still low.
- Major amino acids from algal biomass can efficiently absorb CO₂ and release them under an elevated temperature.

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Total carbon of original solution (mol carbon/L)</th>
<th>Total carbon after absorption (mol carbon/L)</th>
<th>Total carbon after desorption (mol carbon/L)</th>
<th>Total carbon captured (mol carbon/mol amino acid salt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycine salt</td>
<td>1.82</td>
<td>2.69</td>
<td>1.68</td>
<td>1.01</td>
</tr>
<tr>
<td>Alanine salt</td>
<td>2.37</td>
<td>4</td>
<td>2.73</td>
<td>1.27</td>
</tr>
<tr>
<td>Lysine salt</td>
<td>5.08</td>
<td>5.75</td>
<td>5.14</td>
<td>0.61</td>
</tr>
<tr>
<td>Proline salt</td>
<td>4.34</td>
<td>5.35</td>
<td>4.51</td>
<td>0.84</td>
</tr>
<tr>
<td>KOH (control)</td>
<td>0</td>
<td>0.43</td>
<td>0.28</td>
<td>0.15</td>
</tr>
</tbody>
</table>

*: the amino acid solution used for this test is 1 M.

Chemical reactions of amino acid salt CO₂ absorption

- Amino formation: \( \text{OOC-R-NH}_2 + \text{KOH} \rightarrow \text{K}^+ + \text{OOC-R-NH}_2 + \text{H}_2\text{O} \)
- Carbonate formation: \( \text{CO}_2 + 2 \text{OOC-R-NH}_2 \leftrightarrow \text{OOC-R-NH}_2 + \text{OOC-R-NH}_2^+ + \text{HCO}_3^- \)
- Carbonate hydrolysis: \( \text{OOC-R-NH}_2 + \text{H}_2\text{O} \leftrightarrow \text{OOC-R-NH}_2 + \text{HCO}_3^- + \text{bicarbonate} \)
- Biocarbonate formation: \( \text{CO}_3 + \text{OOC-R-NH}_2 + \text{H}_2\text{O} \rightarrow \text{OOC-R-NH}_2^+ + \text{HCO}_3^- + \text{HCO}_3^- \)
4. The algal amino acid salt solution of CO₂ capture

B. Amino acid salt CO₂ absorption

Kinetics of absorption and desorption of single amino acids
4. The algal amino acid salt solution of CO$_2$ capture

B. Amino acid salt CO$_2$ absorption

NMR results of absorption and desorption of single amino acids
4. The algal amino acid salt solution of CO₂ capture

B. Amino acid salt CO₂ absorption

Kinetics of repeated absorption and desorption of algal amino acids salt solution

<table>
<thead>
<tr>
<th>Solution</th>
<th>Average CO₂ amount absorbed (mol carbon/L)</th>
<th>Average CO₂ amount desorbed (mol carbon/L)</th>
<th>Total CO₂ captured (mol CO₂/mol algal amino acids)</th>
<th>Total CO₂ captured (g CO₂/g algal amino acids)</th>
<th>Total CO₂ captured (g CO₂/g dry algal biomass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algal amino acid salt solution</td>
<td>0.2</td>
<td>0.19</td>
<td>2.2</td>
<td>0.88</td>
<td>0.044</td>
</tr>
</tbody>
</table>

- Algal amino acid salt solution shows much better CO₂ absorption capacity than single amino acid salt solution.
- Increasing amino acid conversion is a critical step for producing high-efficiency algal amino acid salt solution.
- Repeatability of algal amino acid salt solution is very good and still under investigation.
The mass balance analysis is based on a system sized for a 150 MW coal-fired power plant. The power plant burns subbituminous coal and generates 1.2 million metric tons of CO₂, 6,000 metric tons of N₂O, and 3,000 metric tons of SO₂ per year.

A. Preliminary mass balance analysis

- **CO₂ from the coal-fired power plant**
  - The amount: 3,000,000 kg/day

- **CO₂ for the algal cultivation**
  - The amount of CO₂ pumped into the algal system: 76,510 kg/day

- **Water recycled**
  - Volume: 1394 m³/day
  - Nitrogen: 5 mg/L
  - Phosphorous: 2 mg/L

- **Harvesting and dewatering**
  - Harvesting volume: 1,400 m³/day

- **Algae biomass**
  - Amount: 2,800 kg/day, wet basis
  - Dry matter: 25%

- **Amino-acid salt CO₂ capture**
  - CO₂/amino acid mass ratio: 0.88
  - Amino acid amount: 250,000 kg
  - Solvent amount: 1,000,000 kg
  - Solvent flow rate: 8 m³/tCO₂

- **The remained CO₂ after the algal culture**
  - The amount: 75,287 kg/day

- **Amino acid**
  - The amount: 420 kg/day

- **Amino acid in the spent absorbent**
  - Amount: 420 kg/day

- **Pure CO₂**
  - Amount: 2,990,000 kg/day

- **Water added**
  - Volume: 6 m³/day

- **The remained CO₂ from the power plant**
  - The amount: 2,923,490 kg/day

- **CO₂ from the coal-fired power plant**
  - The amount: 3,000,000 kg/day

a. The repeatability of the algal amino acid salt solution is still under investigation. The current calculation is based on single amino acid salt solution.
5. Mass and energy balance

A. Preliminary mass balance analysis

- The mass balance analysis is based on a system sized for a 150 MW coal-fired power plant.
- The power plant burns subbituminous coal and generates 1.2 million metric tons of CO₂, 6,000 metric tons of N₂O, and 3,000 metric tons of SO₂ per year.

- 1,220 kg CO₂ captured by algae
- 2,800 m³ of the algal reactor volume at a productivity of 0.5 g/L/day
- 2.9 million kg CO₂ captured by algal amino acid salt solution

a. The repeatability of the algal amino acid salt solution is still under investigation. The current calculation is based on single amino acid salt solution.
The energy balance analysis is based on the previous mass balance.

The 150 megawatts coal-fired power plant generates 14,416,457 GJ/year for both electricity and heat.

The studied system consumes 19% of the total energy generated from the power plant to near-completely capture CO₂ in the flue gas, compared to 35% of MEA process.

### System components

<table>
<thead>
<tr>
<th>Energy value (GJ/year)</th>
<th>The studied system (^b)</th>
<th>The amino acid salt process (^c)</th>
<th>MEA process (^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical production</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy input</td>
<td>-2,184</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Energy output</td>
<td>2,920</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>CO₂ capture</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy input</td>
<td>-2,759,055</td>
<td>-2,759,055</td>
<td>-5,040,044</td>
</tr>
<tr>
<td>Energy output</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total energy input</td>
<td>-2,761,389</td>
<td>-</td>
<td>-5,040,044</td>
</tr>
<tr>
<td>Total energy output</td>
<td>1,920</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Net energy</strong></td>
<td>-2,759,469</td>
<td>-2,759,055</td>
<td>-5,040,044</td>
</tr>
</tbody>
</table>

a. Data used in the calculation are from the pilot scale algal cultivation and previous lab-scale utilization experiments. The energy input is assigned as negative. The energy out is assigned as positive.

b. The studied system consists of algae photobioreactor cultivation, cascade biomass utilization, and CO₂ capture.

c. The single amino acid salt process only includes amino acid salt absorption.

d. The MEA process only includes MEA CO₂ capture.
Summary

- Long-term culture stability (~17 months and counting) of the selected algal strains was achieved using flue gas as the carbon source.

- A pH control strategy was achieved to enhance algal growth.

- Algal biomass productivity reaches **0.2-1.4 g/L/day** at a biomass concentration of **0.6-1.4 g/L** from the pilot operation.

- Algal amino acid salt solution shows better performance (**0.88 g CO₂/g algal amino acids**) on CO₂ capture than single amino acid solutions (**average 0.65 g CO₂/g amino acid**).

- The combined biological and chemical flue gas utilization leads to a **technically sound system** to efficiently capture CO₂ in the flue gas.
Next step

- A cascade algal biomass conversion process
  - CO$_2$ absorbent
  - polyurethane
  - Diesel
  - Methane

- Comprehensive techno-economic analysis and life cycle assessment
Acknowledgments

- NETL FE0030977

- Erickson Power Plant
Thank You

Go Green!!