Carbon capture and culture pH in microalgal cultures

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Carbon Capture and Storage R&D Program (CCSP)

  - Volume: 15 M€, main part of the funding from Tekes
- Targets
  - Technological readiness for pilots and demonstrations
  - Strong scientific basis for development of CCS
- http://ccspfinalreport.fi
**Why algae?**

- CO₂ is captured, but not necessarily stored (relatively short term).
  - CO₂ is released when the biomass is converted to fuel or digested as feed.
  - CO₂ may be stored longer term in novel chemicals.
- Many microalgae have higher growth rates than plants – this means they can also capture more CO₂ than the plants.
  - Note: not all algae grow faster than plants!
- Feeding CO₂ can increase the rate of algal growth – i.e. CO₂ is limiting in the atmosphere.
  - Industrial CO₂ (flue gas) and industrial fermentations (e.g. bioethanol) can provide CO₂ for algal growth.
  - There are many studies on the toxicity and use of flue gases.
  - Need to consider how to transport and feed CO₂.

<table>
<thead>
<tr>
<th>Organism</th>
<th>μ (d⁻¹)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanobacteria</td>
<td>0.2 - 3</td>
</tr>
<tr>
<td>Purple bacteria</td>
<td>0.5 - 3.3</td>
</tr>
<tr>
<td>Microalgae (pH &gt; 7)</td>
<td>0.1 - 2</td>
</tr>
<tr>
<td>Microalgae (pH &lt; 7)</td>
<td>0.1 - 5.5</td>
</tr>
<tr>
<td>Macroalgae</td>
<td>0.02 - 0.8</td>
</tr>
<tr>
<td>Moss</td>
<td>0.2 - 0.8</td>
</tr>
<tr>
<td>Plant cells</td>
<td>0.1 - 0.5</td>
</tr>
<tr>
<td>Plant</td>
<td>&lt;0.01 - 0.3</td>
</tr>
</tbody>
</table>

* Approximate μ of a limited variety of strains, based on published values – CO₂ feeding and light limitation are not taken into account.
CO₂ supply for production of algae

1) Direct injection of CO₂ (e.g. flue gas)
   - CO₂ diffuses passively across algal cell membranes
   - injection of gas provides mixing and removes oxygen
   - only the CO₂ which dissolves into the liquid is available to the cells and much CO₂ is lost to the atmosphere
   - injection of flue gas causes a reduction in culture pH

2) Indirect feeding of bicarbonate solutions
   - CO₂ is captured as bicarbonate in separate absorbers / scrubbers (aqueous or chemical, e.g. utilising cultivation medium)
   - bicarbonate (HCO₃⁻) requires transporters to cross the cell membrane
   - bicarbonate should be fed at pH values above 7.

The pH of the culture system is important when considering how to supply the CO₂ to the algae
Algal growth and extreme pH

- Most algal cultivation is carried out at pH values between ~6.5 and 8 – can species which grow outside this range be exploited to better understand the options for CO₂ provision?

- For pH ranges both below 6 and above 8, there are several species which grow at relatively high rates (>1 d⁻¹).

- Physiologically, there is no inherent benefit (improved solubility) or disadvantage (energy costs) to feeding either bicarbonate (high pH) or soluble CO₂ (low pH).
Algal growth and extreme pH

- Using known acidophilic and alkaliphilic algae we wanted to measure the effect of pH on carbon uptake.
  - \( \mu \) and CO\(_2\) consumption were determined at near neutral and extreme pH values

<table>
<thead>
<tr>
<th>Strain</th>
<th>pH</th>
<th>expected ( \mu ) (d(^{-1}))</th>
<th>Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Euglena gracilis</em> UTEX753</td>
<td>3</td>
<td>(~1.1) *</td>
<td>23</td>
</tr>
<tr>
<td><em>Euglena mutabilis</em> UTCC451</td>
<td>3</td>
<td>(~0.8) *</td>
<td>23</td>
</tr>
<tr>
<td><em>Coccomyxa anubensis</em> UTCC508</td>
<td>3</td>
<td>(~0.4) †</td>
<td>23</td>
</tr>
<tr>
<td><em>Thalassiosira pseudonana</em> CMP1335</td>
<td>9</td>
<td>(~1.8) ‡</td>
<td>23</td>
</tr>
<tr>
<td><em>Phaeodactylum tricornutum</em> SYKE</td>
<td>&gt;9</td>
<td>?**</td>
<td>23</td>
</tr>
<tr>
<td><em>Chlamydomonas</em> sp. CCMP2294</td>
<td>9</td>
<td>(~0.4) ††</td>
<td>4</td>
</tr>
</tbody>
</table>

* Olaveson & Nalewajko 2000, † Vaquero et al. 2014, ‡ Chen & Durbin 1994, ** unpublished (SYKE), †† Søgaard et al. 2011
Each of the species was able to grow at essentially the same rate at the extreme pH (pH 3 or pH 9) as at pH 6-7.5.

- Exception: *E. mutabilis* grew very poorly at pH 7
- Biomass production was higher at pH 9 than at pH 7, but measurement could include inorganic precipitates

Although the alkaliphilic algae could grow as well as acidophilic algae, they stopped growing earlier and did not produce as much biomass (diatoms not ideal for these conditions).
CO₂ uptake and extreme pH – growth & CO₂ consumption

- Alkaliphilic algae produced less biomass than the acidophilic algae.
  - At pH 7, supplementation of air with CO₂ did not enhance growth of the diatoms and CO₂ uptake was difficult to measure since they generally consumed less than 5% of the input CO₂.
  - CO₂ feeding (1.8%) at pH 9 resulted in excessive precipitate formation.

- Alkaliphilic algae were thus fed air (0.04% CO₂) and did not require additional CO₂ at pH 7 or 9.
CO₂ uptake and extreme pH – CO₂ consumption

- Measurement of CO₂ consumption and specific growth rate both support the conclusion that uptake of CO₂ at pH 3 or bicarbonate at pH 9 can be very efficient.

- CO₂ consumption was similar at pH 3 and pH 6-7 (except for *E. mutabilis* which consumed most CO₂ at pH 6)

- Total CO₂ consumption was similar at pH 7 and pH 9 (except for *Chlamydomonas* sp., which consumed most CO₂ at pH 9)

  - Alkaliphilic algae consumed a higher percentage of the fed CO₂ partly because they were fed less CO₂. However, *E. mutabilis* and *Coccomyxa* sp. when grown on air consumed only 38% of the CO₂, whereas the diatoms consumed >60%.

  - Total uptake of CO₂ was higher for acidophilic algae.
CO₂ uptake and extreme pH – bicarbonate feeding

- Bicarbonate feeding (without air sparging) increased the uptake of CO₂ at both pH 7 and pH 9.
  - Only 1-6% CO₂ was lost to the atmosphere.
  - More CO₂ consumed per day and per gram biomass.
  - Precipitation of magnesium salts still a problem at high pH.

Growth and CO₂ uptake parameters for *E. gracilis* (blue, pH 7.3) and *P. tricornutum* (green, pH 9) grown in photobioreactors fed with either CO₂ in the gas stream (solid bars) or with sodium bicarbonate (open bars).
CO₂ uptake and extreme pH – bicarbonate feeding

- Improved CO₂ utilisation comes at a cost – specific growth rate and biomass production were both lower than in cultures fed with gas.
- Accumulation of dissolved oxygen limits growth.
- Sparging with air results in loss of CO₂ to the atmosphere.

Growth and CO₂ uptake parameters for *E. gracilis* (blue, pH 7.3) and *P. tricornutum* (green, pH 9) grown in photobioreactors fed with either CO₂ in the gas stream (solid bars) or with sodium bicarbonate (open bars).

Dissolved O₂ in an *E. gracilis* culture fed with sodium bicarbonate (or 2.3% CO₂, green). Agitation was increased to reduce DOT at 3 times in the bicarbonate culture.
**CO₂ uptake and extreme pH – conclusions**

- Algae which are tolerant to either high or low pH are able to grow and consume CO₂ equally well in the extreme condition as they do at near neutral pH.
  - For these strains, CO₂ capture is not critically dependent on pH.
  - Alkaliphilic algae may capture a higher percentage of fed CO₂ than acidophilic algae.
  - Acidophilic algae can capture a lot of CO₂, even if the percentage of captured CO₂ is lower than for alkaliphilic strains.

- Bicarbonate feeding can be used to increase the proportion of CO₂ consumed, even at pH 7 – but removal of dissolved oxygen is also important.
  - Coupling of alkali scrubbers with algal cultivation should be further developed so that loss of CO₂ to the atmosphere from systems currently using direct injection of CO₂ can be reduced.

- Production strains are chosen based on a variety of properties, but their pH tolerance should be considered when planning the mode of delivery of CO₂.
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