Integrated algae-based biomethane fuel purification and hydrothermal carbonisation of digestate

Jonathan Wagner, Tanja Radu, Uttam Roy
Overview

• Introduction and process concept
• Proof-of-concept study results
• HTC of digestate and nutrient recovery

Dr Uttam Roy
Dr Tanja Radu
Anaerobic digestion

- Biomass feed, e.g. food waste, sewage sludge
- AD
- Biogas: ~60% CH₄ / 40% CO₂
- CHP
- CO₂ removal
- Electricity
- Biomethane export
- Dewatering
- Digestate
- Land application

Loughborough University

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UK AD market

- >670 operational plants
- 11% of UK bioenergy / > 2.5% of UK electricity
- ~ 150M€
- 19% growth in 2016/17
- Potential to decarbonise UK economy by 6% by 2030
- UK net zero requires trebling of current levels of biomethane grid injection by 2030
Current challenges

• Biogas purification
  – High infrastructure costs
  – Use of recovered CO$_2$?
    $\sim$1.8 kg(CO$_2$) kg$^{-1}$(methane)

• Digestate
  – High water content
  – Insufficient land capacity
  – Potential contamination
  – Ammonia emissions

⇒ Use recovered CO$_2$ for algae cultivation
  - Biomethane value $\sim$70% higher than electricity
  - Enhanced biogas production from algae recycle

⇒ Combine AD with HTC
  - Reduced or negative carbon emissions from existing plants
  - Carbon credits for biochar
Algae-based biogas purification

\[
\text{CO}_2 \text{ absorption:} \quad \text{CO}_3^{2-} + \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow 2\text{HCO}_3^{-}
\]

\[
\text{Algae growth:} \quad 12\text{HCO}_3^- \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{CO}_3^{2-} + 6\text{O}_2
\]
Algae selection and characterisation

Cultivation of D. tertiolecta CCAP 19/30 in bicarbonate solution

<table>
<thead>
<tr>
<th>Selected strain</th>
<th>Tolerance of strains to NaHCO₃ (g L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.02 2.5 5 10 20 40</td>
</tr>
<tr>
<td>D. tertiolecta CCAP 19/30 (MA)</td>
<td><img src="green_cube.png" alt="" /></td>
</tr>
<tr>
<td>D. tertiolecta CCAP 19/27 (MA)</td>
<td><img src="yellow_cube.png" alt="" /></td>
</tr>
<tr>
<td>N. Vigenis CCAP 254/3 (MA)</td>
<td><img src="red_cube.png" alt="" /></td>
</tr>
<tr>
<td>Euhalothece sp. CCAP 1421/1 (CB)</td>
<td><img src="white_cube.png" alt="" /></td>
</tr>
<tr>
<td>Synechococcus elongatus CCAP 1479/1B (CB)</td>
<td><img src="gray_cube.png" alt="" /></td>
</tr>
</tbody>
</table>
CO₃⁻ regeneration and product yields

Bicarbonate conversion (20 g L⁻¹)

Carbon content, g L⁻¹

Cultivation time, days

Regenerated CO₂ absorption capacity

CO₂ absorption capacity, g L⁻¹

Cultivation time, days

Product distribution

Product yields / conversion

Bicarbonate concentration, g L⁻¹

Carbonate, Algae, CO₂, Conversion
CO₂ absorption

Na₂CO₃ + CO₂ + H₂O → 2 NaHCO₃
Algae culture in spent absorbent

- Cell density, $1 \times 10^6$ cells mL$^{-1}$
  - Control
  - Spent absorbent

- Culture carbon content, g L$^{-1}$

CO$_2$ uptake in algae effluent

- Cumulative carbon uptake, g L$^{-1}$
  - JM medium
  - Spent culture
  - Recycled absorbent

- Carbon concentration, g L$^{-1}$
  - Carbonate C
  - Bicarbonate C
  - Total C
  - Expected C
**AD and HTC**

Feed: Sewage Sludge  
Volume: 9L  
Hydraulic retention time: 36 days  
Organic loading rate: 1.56 g VS L$^{-1}$ Day$^{-1}$  
P$\text{H}$: 7.96  
Temperature: 36°C  
Agitation: 100ppm

- Cumulative Volume, L
  - Methane
  - CO$\text{2}$

Solid loading: 10wt%  
Reaction time: 1h

**HTC Carbon balance**

<table>
<thead>
<tr>
<th>Carbonisation temperature, °C</th>
<th>Product yields</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td></td>
</tr>
<tr>
<td>220</td>
<td></td>
</tr>
<tr>
<td>240</td>
<td></td>
</tr>
</tbody>
</table>

**Figure:**
- HTC Carbon balance
- Hydrochar
- Aqueous phase

#InspiringWinners since 1909
Overall carbon balance

- Based on AD of sewage sludge
- PBR yields based on bicarbonate concentration of 32 g L\(^{-1}\)
- HTC yields extrapolated from literature
- Carbon captured in biochar represent \(~14.8\%\) of methane revenue (carbon price of € 20 t\(^{-1}\)CO\(_2\)).

**HTC of centrifuged digestate**

- High increase in metal concentrations
  - Recoveries of Cu, Al, Ca, Fe, Ba, Mn and Sr exceed 98%
  - Lower recoveries for Cd, Bi, Mo and Co, but very low initial concentrations (<0.1 mg g⁻¹)

### Total Mass balance

<table>
<thead>
<tr>
<th>Carbonisation temperature, °C</th>
<th>200</th>
<th>220</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Product yields</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Proximate analysis of hydro-char (wt%)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Digestate</th>
<th>HC200</th>
<th>HC220</th>
<th>HC240</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ash</strong></td>
<td>32.26 ± 3.66</td>
<td>49.35 ± 0.61</td>
<td>47.89 ± 0.03</td>
<td>48.08 ± 0.07</td>
</tr>
<tr>
<td><strong>C</strong></td>
<td>35.48 ± 5.10</td>
<td>33.72 ± 0.57</td>
<td>34.53 ± 1.12</td>
<td>34.01 ± 0.12</td>
</tr>
<tr>
<td><strong>H</strong></td>
<td>5.24 ± 0.057</td>
<td>4.34 ± 0.062</td>
<td>4.33 ± 0.157</td>
<td>4.07 ± 0.012</td>
</tr>
<tr>
<td><strong>N</strong></td>
<td>4.89 ± 0.035</td>
<td>2.80 ± 0.003</td>
<td>2.78 ± 0.044</td>
<td>2.73 ± 0.026</td>
</tr>
<tr>
<td><strong>P</strong></td>
<td>3.77</td>
<td>5.64</td>
<td>5.16</td>
<td>4.47</td>
</tr>
<tr>
<td><strong>S</strong></td>
<td>1.79</td>
<td>2.09</td>
<td>1.76</td>
<td>1.43</td>
</tr>
<tr>
<td><strong>O</strong></td>
<td>22.12 ± 1.85</td>
<td>9.79</td>
<td>10.47</td>
<td>11.10</td>
</tr>
</tbody>
</table>

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HTC nutrient distribution

Macronutrient concentrations in aqueous phase (g L⁻¹)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>AP200</th>
<th>AP220</th>
<th>AP240</th>
<th>Johnson medium</th>
<th>Ratio to medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic C</td>
<td>16.06</td>
<td>15.36</td>
<td>14.68</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Inorganic C</td>
<td>0.80</td>
<td>1.37</td>
<td>1.71</td>
<td>4.86*</td>
<td>0.2 – 0.4</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>3.89 ± 0.33</td>
<td>7.36 ± 3.13</td>
<td>5.80 ± 1.41</td>
<td>0.034</td>
<td>114.4 – 216.5</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.16 ± 0.08</td>
<td>0.27 ± 0.17</td>
<td>0.21 ± 0.12</td>
<td>0.614</td>
<td>0.3 – 0.4</td>
</tr>
<tr>
<td>Total N</td>
<td>3.06</td>
<td>5.77</td>
<td>4.55</td>
<td>0.181</td>
<td>16.9 – 31.9</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>0.71 ± 0.28</td>
<td>1.28 ± 0.62</td>
<td>1.20 ± 0.60</td>
<td>0.028</td>
<td>25.4 – 45.7</td>
</tr>
<tr>
<td>Total P</td>
<td>0.453</td>
<td>0.434</td>
<td>0.459</td>
<td>0.009</td>
<td>48.3 – 51.1</td>
</tr>
</tbody>
</table>

*Based on bicarbonate concentration of 34 g L⁻¹
### Trace nutrients in aqueous phase, mg L$^{-1}$

<table>
<thead>
<tr>
<th>Element</th>
<th>AP200</th>
<th>AP220</th>
<th>AP240</th>
<th>Johnson medium</th>
<th>Ratio to medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>710</td>
<td>595</td>
<td>545</td>
<td>64.1</td>
<td>8.5 – 11.1</td>
</tr>
<tr>
<td>Na</td>
<td>140</td>
<td>129</td>
<td>132</td>
<td>4598</td>
<td>0.03</td>
</tr>
<tr>
<td>K</td>
<td>482</td>
<td>443</td>
<td>460</td>
<td>504</td>
<td>0.9 – 1.0</td>
</tr>
<tr>
<td>Ca</td>
<td>26.4</td>
<td>20.5</td>
<td>24.3</td>
<td>56.1</td>
<td>0.4 – 0.5</td>
</tr>
<tr>
<td>Mg</td>
<td>5.75</td>
<td>22.6</td>
<td>59.5</td>
<td>228</td>
<td>0.03– 0.26</td>
</tr>
<tr>
<td>Fe</td>
<td>29.3</td>
<td>12.1</td>
<td>6.00</td>
<td>0.497</td>
<td>12.1 – 59.0</td>
</tr>
<tr>
<td>Mo</td>
<td>2.2</td>
<td>2.15</td>
<td>2.2</td>
<td>0.21</td>
<td>10.2 – 10.5</td>
</tr>
<tr>
<td>Mn</td>
<td>0.35</td>
<td>0.35</td>
<td>0.45</td>
<td>0.011</td>
<td>31.8 – 40.9</td>
</tr>
<tr>
<td>B</td>
<td>8.7</td>
<td>7.2</td>
<td>7.3</td>
<td>0.107</td>
<td>67.3 – 81.3</td>
</tr>
<tr>
<td>Zn</td>
<td>1.45</td>
<td>0.85</td>
<td>1.05</td>
<td>0.019</td>
<td>44.7 – 76.3</td>
</tr>
<tr>
<td>Co</td>
<td>0.35</td>
<td>0.3</td>
<td>0.3</td>
<td>0.012</td>
<td>25.0 – 29.2</td>
</tr>
<tr>
<td>Cu</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
<td>0.015</td>
<td>n/a</td>
</tr>
</tbody>
</table>

- Sodium present as NaCl and NaHCO$_3$
- Large excess of most trace nutrients
Cultivation of *D. tertiolecta* in HTC AP

**Growth curves**

Cell density, $1 \times 10^6$ cells mL$^{-1}$

**Chlorophyll content in cultures**

Chlorophyll content (μg mL$^{-1}$)

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>1% AP200</th>
<th>2% AP200</th>
<th>3% HTC AP200</th>
<th>1% AP220</th>
<th>1% AP240</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth rate ($\mu$, d$^{-1}$)</td>
<td>0.80 ± 0.17</td>
<td>0.95 ± 0.13</td>
<td>0.63 ± 0.17</td>
<td>0.26 ± 0.05</td>
<td>0.71 ± 0.08</td>
<td>0.62</td>
</tr>
<tr>
<td>Biomass content (g L$^{-1}$)</td>
<td>1.01 ± 0.04</td>
<td>1.14 ± 0.06</td>
<td>1.05 ± 0.04</td>
<td>0.28 ± 0.08</td>
<td>1.11 ± 0.08</td>
<td>0.355</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>20.74 ± 0.31</td>
<td>21.13 ± 5.14</td>
<td>20.19 ± 5.08</td>
<td>47.29 ± 8.06</td>
<td>19.15 ± 4.94</td>
<td>23.00 ± 5.98</td>
</tr>
</tbody>
</table>
CO$_3^{2-}$ regen. in supplemented cultures

**Bicarbonate conversion**

- Control
- 1% AP200
- 2% AP200
- 3% AP200
- 1% AP220
- 1% AP240

**Culture pH**

- Control
- HTC200 (1%)
- HTC200 (2%)
- HTC200 (3%)
- HTC220 (1%)
- HTC240 (1%)

**Cell density, 1 x 10^6 cells mL$^{-1}$**

- Control
- HTC200 (1%)
- HTC200 (2%)
- HTC200 (3%)
- HTC220 (1%)
- HTC240 (1%)
Conclusions and future work

• Successful proof-of-concept study
  – Reversible algae-based CO₂ absorption and utilisation
  – Preliminary carbon balance suggests high degree of carbon utilisation

• HTC of digestate could provide required growth nutrients
  – Large excess of N (17 – 32x), S (11x) and P (50x)
  – Large excess of most trace nutrients (10 – 80x)
  – Low heavy metal concentrations (< 1 mg L⁻¹)

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