Overview of Physical/Chemical & Biological Technologies for Biogas Upgrading

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The need for biogas upgrading

- Biogas upgrading is a function of the specifications of the final use of Biomethane

<table>
<thead>
<tr>
<th></th>
<th>Household Heat</th>
<th>Internal Combustion Engines</th>
<th>Turbines</th>
<th>Micro-turbines</th>
<th>Fuel Cells</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H₂S</strong></td>
<td>&lt; 1000 ppmv</td>
<td>&lt; 200-1000 ppmv</td>
<td>&lt; 10000 ppmv</td>
<td>&lt; 70000 ppmv</td>
<td>&lt; 10 ppmv</td>
</tr>
<tr>
<td><strong>Siloxanes</strong></td>
<td>-</td>
<td>&lt; 9-44 ppmv</td>
<td>&lt; 0.0068 ppmv</td>
<td>0.005 ppmv</td>
<td>1 ppmv</td>
</tr>
</tbody>
</table>

Bailon and Hinge (2012)

- No CO₂ removal required in internal combustion engines, turbines or micro-turbines & fuel cells
The need for biogas upgrading

- Higher Technical specifications for bio-methane for injection into natural gas grids or use as vehicle fuel

### Table 1. Technical specifications for injection of biogas in natural gas grid and use as a vehicle fuel (Marcogaz, 2006; Persson et al, 2006; Huguen and Le Saux, 2010; INN, 2010; Bailón and Hinge, 2012; BOE, 2013; Svensson, 2014).

<table>
<thead>
<tr>
<th>Country</th>
<th>Sweden</th>
<th>Switzerland</th>
<th>Germany</th>
<th>France</th>
<th>Austria</th>
<th>Netherlands</th>
<th>Spain</th>
<th>Belgium</th>
<th>Czech Rep</th>
<th>California U.S.</th>
<th>Chile</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ content (%)</td>
<td>&gt;97(1)</td>
<td>&gt;96(2)</td>
<td>&gt;96(3)</td>
<td>&gt;96</td>
<td>&gt;80</td>
<td>&gt;95</td>
<td>&gt;85</td>
<td>&gt;95</td>
<td>&gt;95</td>
<td>&gt;88</td>
<td></td>
</tr>
<tr>
<td>Type</td>
<td>Type A</td>
<td>Type B</td>
<td>Type B</td>
<td>Type B</td>
<td>Type A</td>
<td>Type B</td>
<td>Type B</td>
<td>Type A</td>
<td>Type A</td>
<td>Type A</td>
<td>Type B</td>
</tr>
<tr>
<td>Wobbe index (MJ Nm⁻³)</td>
<td>44.7 - 46.4 (Type A)</td>
<td>47.9 - 56.5 (unlimited injection)</td>
<td>46.1 - 56.5 (Type B)</td>
<td>48.2 - 56.5 (Type B)</td>
<td>47.7 - 56.5 (Type B)</td>
<td>43.46 - 44.41 (Type B)</td>
<td>12.40-16.06 kWh m⁻³ (48.25-57.81 MJ m⁻³)</td>
<td>47.6-51.6</td>
<td>47.28 - 52.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water dew point (°C)</td>
<td>&lt;9 (at 200 bar)</td>
<td>-8 at MOP</td>
<td>Ground temp.</td>
<td>&lt; -5 at MOP (40 bar)</td>
<td>&lt; -10 (8 bar)</td>
<td>2°C at 7 bar</td>
<td>&lt; -10°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water content max. (mg Nm⁻³)</td>
<td>&lt;32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt;32</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ (%)</td>
<td>&lt; 3</td>
<td>&lt; 4(2)</td>
<td>&lt; 6(3)</td>
<td>&lt; 2.5(7)</td>
<td>&lt; 6</td>
<td>2.5</td>
<td>&lt; 2.5</td>
<td>&lt; 5</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂ (%)</td>
<td>&lt; 1</td>
<td>&lt; 0.5</td>
<td>&lt; 1</td>
<td>&lt; 0.01(7)</td>
<td>&lt; 0.5</td>
<td>0.01 (0.3(8))</td>
<td>&lt; 0.5</td>
<td>&lt; 0.2</td>
<td>&lt; 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂+O₂+N₂ (%)</td>
<td>&lt; 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Type A</td>
<td>&lt; 5</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type B</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂S (mg Nm⁻³)</td>
<td>&lt; 15.2</td>
<td>&lt; 5</td>
<td>&lt; 5</td>
<td>&lt; 5</td>
<td>&lt; 5</td>
<td>&lt; 5</td>
<td>&lt; 5</td>
<td>&lt; 5</td>
<td>&lt; 7</td>
<td>88</td>
<td>-</td>
</tr>
<tr>
<td>Total sulfur (mg Nm⁻³)</td>
<td>&lt; 23</td>
<td>&lt; 30</td>
<td>&lt; 30</td>
<td>&lt; 30</td>
<td>&lt; 10</td>
<td>&lt; 45</td>
<td>50</td>
<td>&lt; 30</td>
<td>&lt; 30</td>
<td>265</td>
<td>&lt; 35</td>
</tr>
<tr>
<td>Mercaptans (mg m⁻³)</td>
<td>&lt; 5</td>
<td>&lt; 6</td>
<td>&lt; 6</td>
<td>&lt; 6</td>
<td>&lt; 10</td>
<td>17</td>
<td>&lt; 6</td>
<td>&lt; 5</td>
<td>106</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The biogas upgrading market

- Distribution of Biogas upgrading plants in the Task37 countries

Germany: 161
Sweden: 52
United Kingdom: 27
The Netherlands: 21
Switzerland: 19
France: 9
Austria: 12
Finland: 9
Denmark: 7
South Korea: 8
Brazil: 4
Ireland: 1

(IKEA Bioenergy)
The cost of biomethane production

Biomethane production Costs

- Biogas Production
- Biogas Upgrading
- Biomethane Injection

2015 Natural gas 0.31 € m⁻³

(IEA Bioenergy 2014)
The biogas upgrading market

Today....

- Water scrubber: 41%
- Chemical scrubber: 22%
- PSA: 21%
- Membrane: 10%
- Organic physical scrubber: 6%
- Cryogenic separation: 0.4%

(IEA Bioenergy 2014)
Physical/Chemical CO$_2$ removal Technologies

(Bauer et al. 2013)
Physical/Chemical CO₂ removal Technologies

Energy demand: 3-12 % energy content of Biogas
Coste del biometano

Need to develop innovative low-cost & environmentally friendly technologies for a sustainable Biogas upgrading
Photosynthetic Upgrading

- Photosynthetic fixation of CO₂ as algal biomass using digestates as nutrients source
Biological CO\textsubscript{2} removal Technologies

Photosynthetic Upgrading

\[ \text{CH}_4 > 95 \%, \ \text{CO}_2 < 1 \%, \ \text{N}_2 < 3\%, \ \text{O}_2 < 0.5 \% \]
Photosynthetic Upgrading

Key operational parameter: Recycling Liquid/Biogas ratio
Biological CO₂ removal Technologies

Photosynthetic Upgrading

Graphs showing the concentration changes of CO₂, CH₄, O₂, and N₂ as a function of L/G for different flow rates of BM (5 mL/min, 15 mL/min, 30 mL/min).
Upgrading Fotosintético de Biogás

Photosynthetic Upgrading
Photosynthetic Biogas Upgrading

Upgrading of 300 Nm$^3$/h.............

Annual Microalgae Production ≈ 1000 Tn/year

Total Energy Consumption = 0.085 kwh/Nm$^3$ <<<< 0.2-0.3 kwh/Nm$^3$

Energy Produced as Biogas = 0.82 kwh/Nm$^3$ → 0.3 kwh/Nm$^3$ electricity >>>> 0.085 kwh/Nm$^3$ (Microalgae biodegradability of 40 %)

Investment cost ≈ 2800 €/(Nm$^3$/h) << 4000 € / (Nm$^3$/h)

Land requirements = 300 m x 350 m
Biological $H_2S$ removal Technologies

**Biotrickling Filtration**

- **Aerobic**
  \[ H_2S + 0.5O_2 \rightarrow S + H_2O \]
  \[ H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+ \]

- **Anoxic**
  \[ 3H_2S + NO_3^- \rightarrow 3S + 0.5N_2 + 3H_2O \]
  \[ 3H_2S + 4NO_3^- \rightarrow 3SO_4^{2-} + 2N_2 + 6H^+ \]

- Based on the action of lithoautotrophs: $H_2S$ as energy source & $CO_2$ carbon source
- $e^-$ acceptor: $O_2$ or $NO_3^-$
- No significant $CO_2$ associated
- EBRT: 2-16 min ($H_2S$-RE: 99%)
- Full Scale Technology
Biological $H_2S$ removal Technologies

Biotrickling Filtration

- Upgraded biogas
- Biotrickling filter
- Raw biogas
- Nitrate solution
- pH control
- Nutrient solution

$\text{NO}_3^-$

High Robustness

![Graph showing $H_2S$ removal over time with high robustness.](image)
Biological $H_2S$ removal Technologies

Photosynthetic Upgrading

- The high pH value $\rightarrow$ High $H_2S$ mass transfer
- $RE-H_2S > 99\%$

![Diagram showing the process of biological $H_2S$ removal technologies with photosynthetic upgrading.](Diagram)
Biological $H_2S$ removal Technologies

Microaerobic AD

- No need for external desulfurization
- No impact in AD
- EBRT $> 5$ h for $H_2S$-RE $> 97$
- Periodical cleaning of AD headspace
Biological $H_2S$ removal Technologies

**Graph 1:**
- **Y-axis:** $H_2S$ concentration (%)
- **X-axis:** Time (d)
- **Sections:**
  - Anaerobic
  - $O_2$ supply into Feeding Pipeline
  - $O_2$ supply into Headspace

**Graph 2:**
- **Y-axis:** CH$_4$ and CO$_2$ (%)
- **X-axis:** Time (d)
- **Sections:**
  - CH$_4$
  - CO$_2$
Biological $H_2S$ removal Technologies

Operational cost (€ m$^{-3}$)

- Chemical Precipitation
- Adsorption
- Aerobic biofiltration
- Anoxic biofiltration
- Microaerobic
- Photosynthetic Upgrading
Biogas Upgrading market dominated by physical/chemical Technologies → High Operating Cost & Environmental Impact

✓ Biological Processes have shown a similar CO₂ and H₂S removals & high robustness but at:
  - Lower operating costs and environmental impacts
  - No need for previous removal of particles/H₂O/siloxanes
  - Tested at pilot and full scale
  - Use of residual nutrients from digestate

✓ Photosynthetic upgrading allows for simultaneous H₂S & CO₂ removal