Recent advances in **biological biogas upgrading and valorization**

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Change in AD perception

Waste Reduction Technology

Electricity production

Multi-product Bio-refinery
AD as a multi-product Biorefinery

- Anaerobic Digestion as an effective Carbon and Nutrient recycling platform

- Electricity & Industrial Heat
- Biomethane for Natural Gas Grids
- Biofertilizers
- Fine & Bulk Chemicals
- Biomethane for Vehicles
Biogas production plants in Europe

(EBA, 2018)
Primary energy production from Biogas in Europe

- Legal limitations in the use of energy crops
- Lower tax incentives to electricity production

Evolution of primary biogas energy production in European union (EU 28) since 2000 (in ktoe)

Source: EurObserv'ER 2017
Annual production of biogas in the EU will reach 41 Mtoe in 2030 (EBA)

Estimated annual production potential of biogas in the world can reach 658 Mt CH₄

Other sources
Livestock waste, urban solid waste, energy crops, etc

(EBA, 2018)
Electric capacity from Biogas in Europe

(EBA, 2018)
Biogas quality requirements

**INTERNAL COMBUSTION ENGINES**
- Siloxanes < 9.44 ppm
- \( \text{H}_2\text{S} < 200 - 1000 \text{ ppm} \)

**TURBINES & MICRO TURBINES**
- Siloxanes < 0.006 ppm
- \( \text{H}_2\text{S} < 10000 \text{ ppm} \)

**FUEL CELLS**
- Siloxanes < 1 ppm
- \( \text{H}_2\text{S} < 10 \text{ ppm} \)

**VEHICLE FUEL**
- Standard EN 16723-2

**INJECTION INTO NATURAL GAS GRIDS**
- Standard EN 16723-1
Biogas upgrading plants in the IEA Bioenergy Task 37 group countries

*(IEA Bioenergy 2018)*
Biomethane production in Europe

(EBA, 2018)
Distribution of Biogas upgrading plants in the IEA Task 37 group countries 2017

(EBA, 2018)
The price of Biomethane

(Biosurf, 2016)
CO$_2$ Removal Technologies
CO₂ Removal Technologies

A large portfolio of technologies

Scrubbing
- Water
- Chemical
- Organic solvent

Physical

Chemical
- Cryogenic Separation
- Pressure Swing Adsorption

ABAD Bioenergy®

Electromethanogenesis

Photosynthetic

Hydrogenotrophic

Biological

Others
- Enzymatic
- Fermentative
- PPB-assisted
Distribution of CO₂ removal technologies in IEA Task 37 group countries

2012
- Water scrubber 41%
- Membrane 10%
- Chemical scrubber 22%
- PSA 21%
- Organic physical scrubber 6%
- Cryogenic separation 0.4%

2017
- Water Scrubber 30%
- Membrane 25%
- Chemical Scrubber 18%
- PSA 16%
- IEA, 2018

(IEA, 2014)
Biological CO₂ Removal Technologies

Photosynthetic Upgrading

Treated Water

O₂-free CH₄(g)

BIOFERTILIZER

BIOENERGY

Microalgae Biomass

Wastewater

CO₂(g)

H₂S(g)

SO₄²⁻(aq)

O₂(l)

CO₂(l)

H₂(l)

Bioenergy
Photosynthetic Upgrading

Seasonal variation of biogas upgrading coupled with digestate treatment in an outdoors pilot scale algal-bacterial photobioreactor

David Martín, Esther Pousadas, Patricia Cane, Víctor Pérez, Saul Blanco, Raquel Lebredo, Raúl Muñoz
Biological CO$_2$ Removal Technologies

Photosynthetic Upgrading

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

Photosynthetic Upgrading

Diagram showing the percentage of CO₂, O₂, N₂, and CH₄ over the ratio L/G.
Biological CO₂ Removal Technologies

Photosynthetic Upgrading

Universidad de Valladolid

INCOVER

HORIZON 2020
Photosynthetic Upgrading

IChemE Sustainability Metrics

Economic  Social  Environmental

Photosynthetic vs physical/chemical processes

Bio-methane

HRAP

Absorption column

Activated carbon filter

Water scrubber

**Upgrading Capacity**: 300 Nm³/h of biogas
Photosynthetic Upgrading

Biological CO₂ Removal Technologies

A comparative analysis of biogas upgrading technologies: Photosynthetic vs physical/chemical processes

Alma Toledo-Cervantes, José M. Estrada, Raquel Lebrero, Raúl Muñoz
Hydrogenotrophic Upgrading

**Key players**

\[ 4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \]
\[ \Delta G^0 = -130.4 \text{ kJ mol}^{-1} \]
Biological CO₂ Removal Technologies

Hydrogenotrophic In-situ Upgrading

Excess Electricity → Electrolysis of Water → H₂ → Anaerobic Digester → CH₄ → Gas Rate

Renewable Energies
Seasonal surpluses
Hydrogenotrophic *Ex-situ* Upgrading

**Biological CO₂ Removal Technologies**

**Influent Biogas Composition**

<table>
<thead>
<tr>
<th>CH₄:CO₂ (vol/vol)</th>
<th>30:70</th>
<th>45:55</th>
<th>60:40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final [CH₄] (%)</td>
<td>98</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>Final [CO₂] (%)</td>
<td>1.2</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Upgrading Capacity (m³/m³ d⁻¹)</td>
<td>13</td>
<td>11</td>
<td>9.5</td>
</tr>
</tbody>
</table>
Hydrogenotrophic *Ex-situ* Upgrading

Biological \( \text{CO}_2 \) Removal Technologies

![Graph showing the removal of \( \text{CO}_2 \) over time with different materials.](Image)

- Glass Rings
- PU - loose
- PU - compact

![Image of experimental setup](Image)
Hydrogenotrophic **Ex-situ** Upgrading

**Pilot Scale**

**Full Scale: in 2-3 years**

- BioUpgrade Project - Lemvig Biogas plant
- eFUEL Project - Midtfyn Biogas Plant
Biological CO₂ Removal Technologies

Electromethanogenesis

\[ \text{CH}_4 \]

Methanation

\[ \text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 \]

\[ \text{CH}_4 : \text{CO}_2 : \text{H}_2 \]

Electromethanogenesis

8:1 (e⁻ : CO₂)

Renewable Energy
Electromethanogenesis

- $\text{HCO}_3^-$ as main charge balancing ion

Simultaneous desulphurization
Biological CO$_2$ Removal Technologies

**Electromethanogenesis**

![Graph showing CO$_2$ removal efficiency vs. current density](image)

- CO$_2$ loading rate:
  - 1000 L CO$_2$ m$^{-2}$ d$^{-1}$
  - 2000 L CO$_2$ m$^{-2}$ d$^{-1}$
  - 4000 L CO$_2$ m$^{-2}$ d$^{-1}$

![Diagram illustrating biogas composition](image)

- Biogas composition (%):
  - Time (days):
    - 0
    - 1
    - 2
    - 3
  - Components:
    - CO$_2$
    - H$_2$
    - CH$_4$
Biological CO₂ Removal Technologies

PPB-assisted Upgrading

Assessing the potential of purple phototrophic bacteria for the simultaneous treatment of piggery wastewater and upgrading of biogas

David Martín a, Esther Poucel a, Diana García a, Daniel Puyol a, Raquel Labrador a, Reif Medkour a

Bioresource Technology
journal homepage: www.asn.org/journals/bioresotech

Biomethane (%)  

TOC (mg L⁻¹)
H$_2$S Removal Technologies
Based on the action of lithoautotrophs: \( \text{H}_2\text{S} \) as energy source

- \( \text{e- acceptor: O}_2 \) or \( \text{NO}_3^- \)
- \( \text{EBRT} = 2\text{–}16 \text{ min} \rightarrow \text{H}_2\text{S-RE} = 99\% \)

**Aerobic**

\[
\text{H}_2\text{S} + 0.5\text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O}
\]

\[
\text{H}_2\text{S} + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} + 2\text{H}^+
\]

**Anoxic**

\[
3\text{H}_2\text{S} + \text{NO}_3^- \rightarrow 3\text{S} + 0.5 \text{N}_2 + 3\text{H}_2\text{O}
\]

\[
3\text{H}_2\text{S} + 4\text{NO}_3^- \rightarrow 3\text{SO}_4^{2-} + 2\text{N}_2 + 6\text{H}^+
\]
Biological H$_2$S Removal Technologies

**Biotrickling Filtration**

- **NITRIFICATION TANK**
- **BIOTRICKLING FILTER**

$\text{NH}_4^+ + 2.5 \text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}_2\text{O}$

- $\text{H}_2\text{S-EC} = 280 \text{ gS m}^{-3} \text{ h}^{-1}$ (RE = 96%)
- $\text{EBRT} = 3 \text{ min}$
Biological H₂S Removal Technologies

- No need for external desulfurization
- No impact on AD
- Periodical cleaning of AD headspace

Microaerobic AD

H₂S- free Biogas

O₂
Biological H₂S Removal Technologies

Microaerobic AD

O₂ generator

93 ± 3 % O₂

2400m³ sludge digester

O₂ injection into the headspace

WWTP for 100,000 p.e.

Biogas composition

Infra-red & electrochem.

(CH₄, CO₂, O₂, N₂, H₂S)

Biogas flow rate

Ultrasonic flowmeter
Biological H$_2$S Removal Technologies

Microaerobic AD

Initial H$_2$S: 1900 ppm (anaerobic conditions)

O$_2$ Dosing Rate (m$^3$ d$^{-1}$)

- O$_2$ rate
- H$_2$S concentration

H$_2$S (ppm)

Concentration (% v.)

- CH4 concentration
- CO2 concentration

Time (d)
Biological H$_2$S Removal Technologies

Microaerobic AD

- H$_2$S removal over 99%
- Minimum N$_2$ or O$_2$ contamination of biogas
- Minimum sulfur deposits outside the membrane surface
Operating Cost of $H_2S$ Removal Technologies
Siloxanes Removal Technologies
Biological Siloxane Removal Technologies

- Siloxanes are biodegradable
- Siloxanes removal is limited by gas-liquid mass transfer

Two-Phase Partitioning Bioreactors

TPPBs are based on the addition to a bioreactor of an immiscible, non-volatile, biocompatible and non-biodegradable organic solvent with a high affinity for the target gas pollutant.....

e. g.
Silicone oil
Heptamethylnonane
Biological Siloxane Removal Technologies

Two-phase partitioning Bioreactors

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**Graph 1:**
- **Y-axis:** RE (%)
- **X-axis:** L2, L3, D4, D5, Total VMS
- **Legend:**
  - 2P-BTF
  - 1P-BTF

**Graph 2:**
- **Y-axis:** EC (g/m³·h)
- **X-axis:** L2, L3, D4, D5, Total VMS
- **Legend:**
  - 2P-BTF
  - 1P-BTF
Biogas bioconversion into commercial bioproducts
Biogas bioconversion into commercial bioproducts

- Biopolymers
- Ectoine
- Single cell protein
- Exopolysaccharides
- Chemical building blocks
Biogas bioconversion into commercial bioproducts

<table>
<thead>
<tr>
<th>Culture condition</th>
<th>PHA content (wt %)</th>
<th>HB fraction (mol %)</th>
<th>HV fraction (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogas</td>
<td>43.1 ± 1.8</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Biogas + Acetic acid</td>
<td>52.3 ± 0.7</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Biogas + Propionic acid</td>
<td>47.9 ± 0.7</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>Biogas + Butyric acid</td>
<td>52.2 ± 2.1</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Biogas + Valeric acid</td>
<td>53.8 ± 0.8</td>
<td>75</td>
<td>25</td>
</tr>
</tbody>
</table>
Biogas bioconversion into commercial bioproducts

- 100% biogas to CHP
- 1000 Nm³ biogas h⁻¹
- 100% biogas to PHA
- 55% biogas to CHP + 45% biogas to PHA
Biogas bioconversion into commercial bioproducts

- PHA production: ~1,900 kg PHA d⁻¹
- PHA selling price: ~7,1 € kg⁻¹

- PHA production: ~800 kg PHA d⁻¹
- PHA selling price: ~4,4 € kg⁻¹
Biogas bioconversion into commercial bioproducts

Biogas (CH₄, CO₂) → Exhaust gases

Biogas recirculation

Hyposmotic Shock (0% NaCl)

High mass transfer bacterial reactor (6% NaCl)

Biomass

Ectoine is an osmotic cell protector with a high market value (> 1000 € kg⁻¹)

Anaerobic digester

TLR 5 → DEEP PURPLE → TLR 7
TAKE HOME MESSAGES

- Anaerobic digestion can be engineered as a multi-product biorefinery
- Biotechnologies for biogas upgrading are being successfully scale-up and validated
- Power-to-gas has attracted most research efforts in the field of biological biogas upgrading
- Biological desulfurization methods provide high H₂S-REs at low operating costs
- TPPB can support an effective siloxane removal
- Biogas represents a valuable feedstock for the production of commodities and high-added value products
Acknowledgements

Co-authors

Funding agencies:
Thank you for your Attention

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