Photosynthetic biogas upgrading to biomethane: Influence of the gas-liquid flow configuration in the absorption column on the biomass production and nutrients recovery

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Introduction

Anaerobic digestion

The most valuable byproduct from anaerobic digestion

Animal manure

Crops

Food waste

Sludge WWTP

ANAEROBIC DIGESTER

BIOGAS

$\text{CH}_4$ (40–75%)

$\text{CO}_2$ (25–60%)

$\text{H}_2\text{S}$ (0.005–2%)

$\text{N}_2, \text{O}_2, \text{H}_2$ and VOCs (trace level concentrations)

The most valuable byproduct from anaerobic digestion

BIOFERTILIZER

- $\text{NH}_4^+$ emission
- $\text{NO}_3^-$ leaching
- $\text{P}$ soil saturation

Digestate

Food waste

Animal manure

Crops

Sludge WWTP

WC
Introduction

Biogas: a renewable energy source

- Households heat
- Electricity & industrial heat
- Fuel cells
- Injection into natural gas grids
- Fine & bulk chemical bioconversion
- Vehicle fuel
Biogas production in Europe

- Number of biogas plants and total installed capacity in Europe (2010-2014)

- Production of Biogas in the EU28 will reach 18-20 billions Nm³ by 2030 (EBA)
  
  ➔ 3-4% Natural gas consumption in EU

- Biogas Electricity 63.6 TWh

- BIOGAS UPGRADING
Biomethane injection into natural gas grids or used 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). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Country         | Sweden          | Switzerland     | Germany         | France          | Austria         | Netherlands     | Spain           | Belgium         | Czech Rep       |
| CH₄ content (%) | 97±1 (Type A)   | > 96 (Type B)   | > 96            | > 95            | > 95            | > 85            | > 95            | > 95            | U.S.            |
|                 | 97±2 (Type B)   | > 50            | > 80            | > 85            | > 85            | > 88            |                 |                 |                 |
| Wobbe index (MJ Nm⁻³) | 44.7–46.4 (unlimited injection) | 47.9–56.5 | 46.1–56.5 | 48.2–56.5 | 47.7–56.5 | 43.46–44.41 | 13.40–16.06 kWh m⁻³ (48.25–57.81 MJ m⁻³) | 47.6–51.6 | 47.28–52.72 |
| Water dew point (°C) | < 8 (at 200 bar) | -8 at MOP | -5 at MOP (40 bar) | -8 | -10 | 2°C at 7 bar | < -10°C |        |
| Water content max. (mg Nm⁻³) | < 32 | < 32 | | | | | | |
| CO₂ (%) | < 4 (Type A) | < 6 (Type B) | < 6 | < 2.5 (Type B) | < 2 | < 6 | < 10–10.3 for regional grid | 2.5 | 2.5 | 5 | 3 |
| O₂ (%) | < 1 | < 0.5 | < 3 | < 0.01 (Type B) | < 0.5 | < 0.5 | 0.01 (0.3) | < 0.5 | < 0.2 | < 1 |
| CO₂+O₂+N₂ (%) | < 4 (Type A) | < 5 (Type B) | < 5 | < 5 | < 5 | < 5 | < 5 (CO₂+O₂+N₂) | 1.5–4.5 |
| H₂S (mg Nm⁻³) | < 15.2 | < 5 | < 5 | < 5 | < 5 | < 5 | < 5 | < 5 | < 7 | 88 |
| Total sulfur (mg Nm⁻³) | < 23 | < 30 | < 30 | < 30 | < 45 | 50 | < 30 | < 30 | < 265 |
| Mercaptans (mg m⁻³) | < 5 | < 6 | < 6 | < 6 | < 10 | 17 | < 6 | < 5 | 106 |
Biogas upgrading: CO$_2$ and H$_2$S removal

- Costs of compression and transportation decrease.
- Specific calorific value increases.

**CO$_2$ removal technologies**

- Not effective for H$_2$S.
- High environmental impact.
- High investment and operating costs.

(Bauer et al. 2013)
Biogas upgrading: \( \text{CO}_2 \) and \( \text{H}_2\text{S} \) removal

- Toxic
- Malodorous
- Corrosion of pipelines, engines, and storage structures

\( \text{H}_2\text{S} \) removal

**H\(_2\text{S} \) removal technologies**

1. **AT THE SOURCE**
   - Not realistic
   - Remove source of S

2. **END-OF-PIPE**
   - Physical-chemical techniques
   - Biological techniques
   - Not effective for \( \text{CO}_2 \) Contamination of biogas with \( \text{O}_2 \)

3. **AT PROCESS LEVEL**
   - Selective inhibitors of sulphidogenic bacteria
   - Raising the pH
   - Sulphide precipitation
   - Microaerobic

\( \text{ANAOBIC DIGESTER} \)

Sulphide
Photosynthetic biogas upgrading

**ALGAL-BACTERIAL PROCESSES**

Simultaneous biogas upgrading and nutrient recovery from digestate

Key operational parameter: Recycling Liquid/Biogas configuration

Co-current or counter-current?

High rate algal pond (HRAP) interconnected to an external absorption column (AC):

- **Treated digestate**
- **O₂-free CH₄ (g)**
- **CO₂ (L)**
- **H₂S (L)**
- **Microalgae Biomass**

**RAW BIOGAS**

- **CH₄ (g)**
- **CO₂ (L)**
- **H₂S (L)**

**BIOENERGY**

**Biomethane**

**Digestate**

**Upgraded biogas**

**Absorption column**

**Microalgae recycling**

**Treated Water**

**Harvested biomass**

**Sedimentation tank**

**Treated digestate**
Objectives

**Photosynthetic biogas upgrading to biomethane: co-current vs. counter-current**

**Objective 1**

Comparison of the influence of the gas/liquid flow configurations: **co-current and counter-current**

→ biomethane quality
→ nutrient recovery

**Objective 2**

Application of an **innovative operational strategy** based on decoupling the hydraulic retention time (HRT) from the solids retention time (SRT) to maximize

→ nutrient recovery in the harvested biomass
→ the control of the biomass concentration in the HRAP

**Objective 3**

**Minimization of effluent** to reduce the loss of carbon and nutrients in the treated effluent
Experimental set-up and operation

Liquid recirculation velocity: **20 cm/s**
Cultivation surface: **1.21 m²**

Light intensity: **1500 ± 600 µmol/m²/s**
Light /dark cycles: **14 : 10 hours**

- **CH₄** (70%)
- **CO₂** (29.5%)
- **H₂S** (0.5%)
- **IC** (1500±168 mg L⁻¹)
- **COD** (1745±413 mg L⁻¹)
- **NH₄⁺** (1668±249 mg L⁻¹)
- **TN** (1815±109 mg L⁻¹)
- **TP** (48±2 mg L⁻¹)
- **SO₄²⁻** (15±2 mg L⁻¹)

**Materials & Methods**

**Experimental set-up and operation**

- Liquid recirculation velocity: **20 cm/s**
- Cultivation surface: **1.21 m²**

- Light intensity: **1500 ± 600 µmol/m²/s**
- Light /dark cycles: **14 : 10 hours**

**Chemifloc CV-300**
- **120 mg/L**

**TAP WATER**

**Diagram**

- Absorption column
- Counter-current flow
- Cultivation broth recycling
- Co-current flow
- Biogas
- Digestate
- 1 L/d
- Effluent: 0.5 L/d
- L/G=1
- 1.6 m³/m²/h
- Bio-methane
- HRAP
- LED PCBs
- Biomass harvesting
- Coagulation-flocculation tank
- Biomass-free effluent
- Biomass-free cultivation broth recycling
- LED PCBs
- TAP WATER
- Chemifloc CV-300
- 120 mg/L
Experimental set-up and operation

**STAGE 1**

- CO-CURRENT: 94 days

**STAGE 2**

- COUNTER-CURRENT: 110 days
Operating conditions under co-current and counter-current flow configurations

Time course of the total suspended solids concentration in the HRAP

- Prevention of mutual shading by the high light irradiance
- Stabilization of the microalgae culture
- Absence of Mg limitation
- Microalgae growth limitation by trace metal availability due to their precipitation as sulphur-salts: O₂ deprivation
- Chlorella predation

Results & Discussion

- Co-current flow steady state
  - TSS: 2.6 g/L
  - Biomass productivity: 15 g/m²/d
  - pH: 10.2 ± 0.5
  - DO: 15.9 ± 1.6 mg/L

- Counter-current flow steady state
  - TSS: 1.4 g/L
  - Biomass productivity: 8.7 g/m²/d
  - pH: 9.5 ± 0.1
  - DO: 13.3 ± 1.1 mg/L

Micronutrients: Mg (20 mg L⁻¹), P (4 mg L⁻¹)
Digestate treatment under co-current and counter-current flow configurations

Digestate treatment: organic matter, inorganic carbon and nutrient removal efficiencies (RE)

<table>
<thead>
<tr>
<th></th>
<th>Stage I</th>
<th>Stage II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (%)</td>
<td>88±4</td>
<td>57±5</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>64±7</td>
<td>45±12</td>
</tr>
<tr>
<td>Phosphorus (%)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Sulfur (%)</td>
<td>38</td>
<td>24</td>
</tr>
</tbody>
</table>

Effluent concentrations: N-NO$_2^-$, N-NO$_3^-$ and SO$_4^{2-}$

Effluent flow rate: 0.5 L/d

LOW ENVIRONMENTAL IMPACT IN TERMS OF WASTEWATER DISCHARGE TO THE ENVIRONMENT
Biogas upgrading under co-current and counter-current flow configurations

**CO₂ removal efficiency**

**STAGE 1**

→ CO-CURRENT: $98.8 \pm 0.8\%$

**STAGE 2**

→ COUNTER-CURRENT: $96.9 \pm 1.6\%$

**CO₂ removal**

CO₂ removal highly depends on the photosynthetic activity of microalgae in spite of the high buffer capacity of the digestate.

**H₂S removal efficiency:**

≈ 100% regardless of the flow configuration

**H₂S removal**

H₂S removal highlighted the robustness of this biological technology for H₂S abatement.

Decrease in the pH mediated by the decrease in microalgae activity.
Results & Discussion

Biogas upgrading under co-current and counter-current flow configurations

Bio-methane composition under co-current and counter-current flow

<table>
<thead>
<tr>
<th>Nº stage</th>
<th>CO₂ (%)</th>
<th>O₂ (%)</th>
<th>N₂ (%)</th>
<th>CH₄ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STAGE I</td>
<td>0.4 ± 0.3</td>
<td>0.7 ± 0.4</td>
<td>2.7 ± 0.5</td>
<td>96.2 ± 0.7</td>
</tr>
<tr>
<td>STAGE II</td>
<td>0.9 ± 0.3</td>
<td>1.2 ± 0.3</td>
<td>2.6 ± 0.3</td>
<td>95.1 ± 0.2</td>
</tr>
</tbody>
</table>

Steady state

H₂S oxidation

SIMILAR VALUES DUE TO THE OPERATION AT THE SAME L/G RATIO
Conclusions

Photosynthetic biogas upgrading to biomethane: co-current vs. counter-current

- Counter-current operation decreased biomass productivity and the cultivation broth pH

- High C, N, P and S recoveries were achieved by decoupling the HRT from the SRT and by working at low effluent rate

- Successful nutrient recovery from the digestate regardless of the operational conditions

- EU standard bio-methane was obtained regardless of the gas-liquid flow configuration

- First systematic comparison addressing the influence of the biogas-recycling liquid flow configuration on bio-methane composition
THANK YOU FOR YOUR ATTENTION!

More information:

http://iqtma.uva.es/envtech/
http://gastreatment-microalgaeresearchgroup.blogspot.com.es/

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