Improving hydrogen biomethanation in a CSTR reactor fed with primary sludge: (preliminary) results of a pilot-scale test

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**Goal:**
- Storage and transformation of excess renewable energy
- Alternative process to upgrade biogas to biomethane
- Optimization of the anaerobic digestion process due to the hydrogen biomethanation exothermic reaction
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**HOW?**

Power to Gas

Power to Methane

**Hydrogen biomethanation**
**H₂ biomethanation <--> exothermic reaction catalysed by hydrogenotrophic methanogenic archaea**

**HOW?**

\[ 4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \quad \Delta H^\circ = -164.9 \text{ kJ/mol} \]

**Limiting factors <--> challenges**

- pH increase due to the bicarbonate consumption could inhibit Hydrogenotrophic Methanogenesis
  - H₂ partial pressure increase could inhibit VFAs oxidation
    - Poor gas-liquid H₂ mass transfer (low solubility)
  - Effective applicability of the in-situ process at full scale (existing reactors: kLa)
In this work:

- In-situ H₂ biomethanation process energy assessment
- A.D. pilot scale test with preliminary results
Energy assessment

$4H_2 + CO_2 \rightarrow CH_4 + H_2O \quad \Delta H^o = -164.9 \text{ kJ/mol}$

HYPOTHESIS:
- lower heating value of $H_2$: 11,890 kJ/m³
- TS of the sludge: 4%, VS/TS ratio 0,74
- boiler efficiency $\eta$: 0.9
- Sludge specific heat capacity $C$: 4.18 kJ/kg/°C
- ambient temperature: 15°C
- Heat transfer digester walls $k$: 0.8 W/m²/°C
- volume and surface digester → radius to height ratio: 1:1

Primary s. $38 \, ^oC$

$11680 \, \text{kJ/Nm}^3\text{CH}_4$

Boiler $\eta=90\%$
Primary s. biodegradability: 50%

HEATING 38 °C - 96,3 MJ

Exergonic reaction

H₂
26,4
Nm³/d

15,9 m³ biogas
58% CH₄
42% CO₂

CO₂ theoretically available
6,6 Nm³
Pilot scale test
Materials and Methods

**Semicontinuous digestion test**

**Electrolyser**

10 L C.S.T.R. MESOPHILIC DIGESTER – HRT 20 days

PRE-THICKENED PRIMARY SLUDGE
(sCOD before TS, VS, pH, FOS / TAC)

Biogas recirculation

Biogas (CH\textsubscript{4}, CO\textsubscript{2}, H\textsubscript{2}, Other)

DIGESTATE
(TS, VS, pH, FOS / TAC, VFAs characterization)

H\textsubscript{2} (320 mL/d)
Materials and Methods

Substrate: Primary sludge

Ruffino B., et al; Energy Conversion and Management; 223 (2020)

\[ tCOD = \frac{8(4n + a - 2b - 3d)}{(12n + a + 16b + 14d)} \times \left( \frac{gCOD}{gC_nH_aO_bN_d} \right) = 1.65 \times \frac{g O_2}{g VS} \]

\[ \frac{sCOD}{tCOD} = 5 \% \]

Castiglione Torinese SMAT WWTP 2,300,000 e.p.

Average elemental composition of the PS used in the study.

<table>
<thead>
<tr>
<th></th>
<th>N (%)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS</td>
<td>4.568</td>
<td>41.819</td>
<td>6.048</td>
<td>46.994 (*)</td>
</tr>
<tr>
<td>FS</td>
<td>&lt;DL</td>
<td>0.546</td>
<td>0.253</td>
<td>ND</td>
</tr>
</tbody>
</table>

FS, fixed solids (TS – VS); DL, detection limit; ND, not determined

(*) The oxygen amount was calculated as 100 minus the sum of the amounts of C, N, H.

Primary sludge samples

Thickened from 2.5 to 3.1% TS
Results: Process stability

**mg tVFAs / mg TA vs pH**

- tVFAs / TA: Blue circles
- pH: Orange circles

**H₂ injection**

**tVFAs [mg HAeq / L] vs TA [mg CaCO₃ / L]**

- tVFAs: Blue circles
- TA: Orange circles

**H₂ injection**
**H₂ injection**

![Graph showing tVFAs and TA over time (day)](image)

**VFAs characterization and quantification**

Lighter species accumulation during the week which were degraded during the weekend when the primary sludge was not fed.
Results

Biogas production

Injected H₂ is on average the 5% that stoichiometrically could react with the CO₂ produced.

Conversion rate of H₂ in CH₄ 99%
Results
Methane cumulative production

- Injected $H_2$
- Unreacted $H_2$

- $CH_4$ by bCOD conversion
- $CH_4$ by $H_2$ conversion
Hydrogen biomethanation contributes for the 2% to the methane production increase

Conclusions

• The in-situ hydrogen biomethanation process has a positive effect in a lower thermal energy consumption;

• The pilot scale test conditions allowed a conversion rate of $\text{H}_2$ in $\text{CH}_4$ of 99%. However, in order to understand the system limiting factors, increasing steps of $\text{H}_2$ flow rate should be investigated;

• Experimental data (VFAs characterization) could be elaborated with the Anaerobic Digestion Model 1 to predict process inhibitory factors
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*Thank you for your attention!*

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