Feasibility of biomethane production by supplying H₂ into a pressurized digester of sewage sludge

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Abstract: The operation of the anaerobic digestion at a larger pressure than the atmospheric, hence favoring CO₂ solubility and enrichment of CH₄ in the biogas, can increase the efficiency of in-situ upgrading with H₂ supply. On the one side, the driving force for H₂ mass transfer is raised and, on the other side, the expected decrease in pH caused by the higher CO₂ concentration in the liquid can be counteracted by a larger H₂ rate transferred and employed in methanogenesis for converting CO₂ into CH₄. The feasibility of such a process was evaluated by a continuous supply of H₂ to a mesophilic pilot-plant digester (35L) of sludge operated at HRT of 20 d and an absolute pressure up to 3 atm. H₂ was supplied to sludge recirculation and a static mixer was employed to facilitate H₂ solubilization. The efficiency of H₂ conversion increased while the operating pressure raised, and the CH₄ concentration in the gas from digestion reached 95% at 3 atm. pH was close to 7 under such conditions and organic matter removal proceeded without a significant accumulation of volatile fatty acids.

Keywords: biomethane, pressurized digestion, power-to-gas, sewage sludge

Session: Biomethane

Introduction
Power-to-gas strategy consists in the utilization of excess electricity produced by renewable energy sources, when demand does not match uncontrollable supply rate, to convert water into H₂ and O₂ through electrolysis and subsequent chemical or biological methanation of H₂ and CO₂ according to equation 1.

\[ 4 \text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \]  

(1)

The biological method can be performed in-situ, whereby H₂ is supplied directly to the anaerobic digester so that archaea can consume H₂ and CO₂, hence additional units for upgrading may be avoided. H₂ transfer to the liquid phase has been identified as the limiting step for the conversion and several reactor configurations have been applied to increase specific mass transfer coefficient (Lecker et al., 2017). Alternatively, operating pressure can be increased to enlarge gases solubility, thus reducing CO₂ content in biogas and facilitating H₂ transfer to the liquid phase. In this study, the feasibility of in-situ upgrading by supplying H₂ into a pressurized digester of sludge was evaluated.

Material and Methods
Digester was inoculated with anaerobic sludge from Valladolid WWTP to a working volume of 35L. It was operated at 35°C and fed with raw sludge, periodically collected from the same WWTP, at a HRT of 20 d. Peristaltic pumps were employed for feeding, discharge and mixing
(sludge recirculation at 0.5 L min⁻¹). Operating pressure was controlled with an electrovalve in the headspace of the digester. H₂ was continuously supplied to the sludge recirculation and a static mixer (Koflo, USA) was implemented to increase turbulence and facilitate H₂ transfer (Figure 1).

The experiment consists of 4 stages with increasing operating pressures and H₂ rates (Table 1). Gas flowrate leaving the digester was measured by liquid displacement and the composition by GC-TCD. VFA concentration in digested sludge was determined by GC-FID. pH was monitored online with a probe and VS content was measured by Standard Methods (APHA, 1998).

**Results and Conclusions**

After a set-up period of 12 d, the pressure set-point was increased in stages I-III up to 3 atm at a H₂ rate of 0.45 NL L⁻¹ d⁻¹. H₂ conversion efficiency increased firmly as operating pressure was increased so did the CH₄ concentration in the gas (Figure 2). In stage III, the average concentration of the gas produced was 85.7% CH₄, 12.6% CO₂ and 1.7% H₂ with a H₂ conversion efficiency larger than 99%. A lack of H₂ was detected at this stage to complete CO₂ removal and H₂ supply rate was increased in stage IV to 0.64 NL L⁻¹ d⁻¹ to cope with a larger than expected CO₂ concentration. As a consequence, CH₄ concentration reached an average concentration of 94.4% during the last 20 d of the experiment with a concentration larger than 95% in 3 out of 14 samples. CO₂ and H₂ concentrations dropped to an average 4.8% and 0.8% respectively. Then, it was feasible to obtain biomethane, with a CH₄ concentration up to 95% CH₄ in a digester of sludge operating at absolute pressure of 3 atm.

pH in the digester dropped to values around 6.5 during stage I of the experiment (Figure 3) but recovered later when CO₂ conversion increased, particularly, in stage IV (up to 7.2). In this regard, H₂ supply acted as a “CO₂ scavenger” to control the pH in the system and prevented acidification caused by CO₂ equilibrium displacement to the liquid phase observed at high operating pressures (Lindeboom et al., 2013).

The efficiency of organic matter removal was quantified at 40-50% of VS removal during the experiment, within the typical values for anaerobic digestion of sludge at atmospheric pressure (Appels et al., 2008) and, interestingly, only trace concentrations of VFA were detected, thus indicating a lack of undesired accumulation of H₂ in the form of acetate.

**References**


Figure 1. Process flow diagram of the pilot-plant employed in the study.

Table 1. Operating conditions studied during the experiment.

<table>
<thead>
<tr>
<th>Stage</th>
<th>0</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (d)</td>
<td>0</td>
<td>12</td>
<td>61</td>
<td>117</td>
<td>158</td>
</tr>
<tr>
<td>Absolute pressure (atm)</td>
<td>1.5</td>
<td>2.0</td>
<td>2.5</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>H₂ flowrate (NL L⁻¹ d⁻¹)</td>
<td>-</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
<td>0.64</td>
</tr>
</tbody>
</table>
Figure 2. Composition and flowrate of the gas obtained from the pressurized digester.

Figure 3. pH and efficiency of organic matter removal in the digester.