Autogenerative high pressure digestion: anaerobic digestion and biogas upgrading in a single step reactor system

R. E. F. Lindeboom, F. G. Fermoso, J. Weijma, K. Zagt and J. B. van Lier

ABSTRACT

Conventional anaerobic digestion is a widely applied technology to produce biogas from organic wastes and residues. The biogas caloric value depends on the \( \text{CH}_4 \) content which generally ranges between 55 and 65%. Biogas upgrading to so-called ‘green gas’, with natural gas quality, generally proceeds with add-on technologies, applicable only for biogas flows >100 m\(^3\)/h. In the concept of autogenerative high pressure digestion (AHPD), methanogenic biomass builds up pressure inside the reactor. Since \( \text{CO}_2 \) has a higher solubility than \( \text{CH}_4 \), it will proportion more to the liquid phase at higher pressures. Therefore, AHPD biogas is characterised by a high \( \text{CH}_4 \) content, reaching equilibrium values between 90 and 95% at a pressure of 3–90 bar. In addition, also \( \text{H}_2\text{S} \) and \( \text{NH}_3 \) are theoretically more soluble in the bulk liquid than \( \text{CO}_2 \). Moreover, the water content of the already compressed biogas is calculated to have a dew point \(<–10 \, ^\circ \text{C} \). Ideally, high-quality biogas can be directly used for electricity and heat generation, or injected in a local natural gas distribution net. In the present study, using sodium acetate as substrate and anaerobic granular sludge as inoculum, batch-fed reactors showed a pressure increase up to 90 bars, the maximum allowable value for our used reactors. However, the specific methanogenic activity (SMA) of the sludge decreased on average by 30% compared to digestion at ambient pressure (1 bar). Other results show no effect of pressure exposure on the SMA assessed under atmospheric conditions. These first results show that the proposed AHPD process is a highly promising technology for anaerobic digestion and biogas upgrading in a single step reactor system.

Key words | anaerobic digestion, biogas upgrading, \( \text{CO}_2 \) solubility, high pressure

INTRODUCTION

Worldwide, the (re-)interest in anaerobic conversion processes is rapidly growing, due to the growing concerns on energy scarcity and green house gas emissions. Anaerobic digestion combines waste-(water) treatment and energy production by converting the chemically stored energy in organic waste constituents to energy-rich biogas, a mixture of the most reduced and most oxidised form of carbon, i.e. \( \text{CH}_4 \) and \( \text{CO}_2 \). For example, the Dutch society produces about 500 kton of organic waste annually through its sewer system. If this waste is anaerobically digested to methane and subsequently to electricity, with a 33% efficiency, it has a potential energy content of 6.5–7 P\( \text{J} \) (1.8×10\(^9\) kWh). Efficient technologies are searched for to cost-effectively convert this potential into an actual energy supply.

The characteristics of biogas produced by anaerobic digestion do not meet the requirements for injection in existing gas distribution systems (Wempe 2007; IEA 2005). The main reasons are:

- **Low pressure**: biogas should be pressurised up to 8 bar for injection in the local consumer-linked gas grid. For centralised conveyance systems pressures exceeding 40 bars are required.
- **Low caloric value**: with the currently applied technologies the biogas \( \text{CH}_4 \) content is 55–65%.

• **High CO₂-content**: the CO₂ content of biogas from organic waste varies between 35 and 45%, CO₂ concentration must remain below 6%, for injection into the regional gas grid.

• **High H₂S content**: under anaerobic conditions, H₂S is formed due to mineralisation of organic sulfur compounds and to the reduction of inorganic oxidised S compounds such as SO₄²⁻. For grid injection, the H₂S content should be <5 mg/Nm³, or 0.147 mmol/Nm³ (Total S = 45 mg/Nm³)

• **Restrictions to NH₃ content**: NH₃ may not exceed 3 mg/Nm³ = 0.167 mmol/Nm³

• **High water content**: biogas is saturated with water vapour. Dew point must be below −10 °C.

For injection in the natural gas grid and other high-grade applications, biogas upgrading units are necessary in order to increase the CH₄ content, decrease the H₂S, NH₃ and water content of the biogas. At this moment, most studies refer to external upgrading technologies, such as membranes, pressure swing adsorption and water scrubbing, which require external compressors and thus demand external energy input (IEA 2001; Welink et al. 2001). The generally applied technologies are economically feasible only on large scale, i.e. at biogas flows >100 m³/h). Consequently, lower biogas flows are so far disregarded for biogas upgrading techniques and its potential for high-grade use is generally lost. For example, biogas generation from small-scale digesters, mounted in the so-called Decentralised Sanitation and Reuse (DeSaR) systems, do not exceed 10 m³ biogas/person/y. The handling and upgrading of this low amount is a real constraint for further development of DeSaR systems (Zeeman et al. 2008).

We propose a novel anaerobic digestion concept for production of high-grade biogas in a single step: autogenerative high pressure digestion (AHPD). The objective is to digest organic matter under auto-generated high pressure to CH₄ and CO₂ (Zagt et al. 2010). Henry’s constants for CH₄, CO₂, H₂S, and NH₃ respectively are 0.0016, 0.0318, 0.115, and 62 mol/L/bar (Wang et al. 2003). With a higher constant, more dissolved gas can be present in the liquid phase. Consequently, the CH₄ content will increase to values comparable to natural gas. Moreover, the biogas is already at a suitable pressure for high-grade use. AHPD eventually aims to generate biogas that meets the demands for Synthetic Natural Gas (SNG), or in popular words ‘green gas’. Then, no additional upgrading technology is required. Although investments are needed to operate anaerobic digestion at high pressure, we expect that AHPD is cost-effective at small scales and therefore suitable for decentralised biogas production from organic waste. The aim of the work described here is to demonstrate the feasibility of this concept, focussing on auto-generative pressure build up and the impact of high pressures on methanogenic activity.

**METHODS**

**Reactor set-up**

All experiments were conducted in batch-fed high pressure reactors using different working volumes, i.e. 13.5 L, 1.7 L and 0.6 L (Figure 1(a)). Safe range of operation for the reactors is 0–100 bar and 4–125 °C. The 13.5 L reactor (property of Bureau) was equipped with a pH sensor (Büchi high pressure probe), a pressure sensor (Parker PTD & PTX) and temperature sensor (PT100). The 13.5 L reactor set-up is shown in Figure 1(b). The 1.7 and 0.6 L reactors were equipped with a pressure sensor. The temperature in these reactors was controlled by a water bath.

![Figure 1](https://iwaponline.com/wst/article-pdf/64/3/647/444295/647.pdf)
Online monitoring provided data for all experiments on total pressure, pH and temperature. A field point module functioned as receiver of data. Data was logged in Labview 7.1 (National Instruments).

Reactor operation

The reactor experiments were performed at different liquid/gas ratios, ranging from 14:1 to 200:1. These ratios were chosen based on the stoichiometric conversion of substrate into biogas and an estimation of the final pressure based on the added amount of substrate and the ideal gas law. The reactors were inoculated with different concentrations of methanogenic granular sludge obtained from a full-scale UASB reactor treating paper mill wastewater (pH 7.0, 30 °C) at Industriewater Eerbeek (Eerbeek, The Netherlands). Macronutrient stock solution (6 mL/L) and trace elements stock solution (0.6 mL/L) were added to the liquid medium (Table 1). Furthermore, different concentrations of sodium acetate trihydrate (NaCH₃COO·3H₂O) were added as substrate. An overview of all experiments is shown in Table 2.

Analyses

Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) were determined according to Standard Methods (APHA 2005), prior to bioreactor inoculation.

Gas composition was determined by taking biogas samples at the end of each run. A two valve system with a sampling port in between, connected to the high pressure reactor, was used to decompress the biogas during sampling. The two valve system was flushed and 100 μL gas samples were taken perpendicular to the flow direction by means of a gas syringe with sample-lock. Afterwards biogas was analyzed at atmospheric pressure by means of gas chromatography (Interscience 8430). The gas sample was directed over two different columns. One was equipped with Molsieve 5 A 30 m, having a diameter of 0.53 mm and the other with Pora-Bond Q 25 m, having a diameter of 0.53 mm. In the columns the gases were separated, using 4 bar of helium pressure as the carrier gas. Detection took place by a thermal conductivity detector. Further operational conditions were: the oven temperature was 53 °C, injection port temperature was 110 °C and the detector was operated at 99 °C.

The specific methanogenic activity (SMA) was determined by pressure increase following the protocol of Zandvoort et al. (2002). The online pressure sensor in the high pressure reactor allowed us to follow pressure increase every minute. Based on the total pressure and the gas

### Table 1 | Macronutrient stock and trace element stock solution

<table>
<thead>
<tr>
<th>Macronutrients stock solution</th>
<th>Trace elements stock solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>KH₂PO₄ (37 g/L)</td>
<td>FeCl₂·4H₂O (2 g/L)</td>
</tr>
<tr>
<td>MgSO₄·7H₂O (9 g/L)</td>
<td>MnCl₂·4H₂O (0.5 g/L)</td>
</tr>
<tr>
<td>NH₄Cl (170 g/L)</td>
<td>ZnCl₂ (50 mg/L)</td>
</tr>
<tr>
<td>KH₂PO₄ (37 g/L)</td>
<td>CoCl₂·6H₂O (2 g/L)</td>
</tr>
<tr>
<td>MgSO₄·7H₂O (9 g/L)</td>
<td>CuCl₂·2H₂O (30 mg/L)</td>
</tr>
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<td>NH₄Cl (170 g/L)</td>
<td>MnCl₂·4H₂O (0.5 g/L)</td>
</tr>
<tr>
<td>KH₂PO₄ (37 g/L)</td>
<td>Na₂SeO₃·5H₂O (100 mg/L)</td>
</tr>
<tr>
<td>MgSO₄·7H₂O (9 g/L)</td>
<td>NiCl₂·6H₂O (50 mg/L)</td>
</tr>
<tr>
<td>NH₄Cl (170 g/L)</td>
<td>EDTA (1 g/L)</td>
</tr>
</tbody>
</table>

### Table 2 | Overview of pressure experiments

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Reactor volume (L)</th>
<th>Gas volume (L)</th>
<th>Substrate (g acetate-COD/L)</th>
<th>P range (bar) initial/final</th>
<th>Final gas composition*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.55</td>
<td>0.04</td>
<td>1</td>
<td>3/7.5</td>
<td>CH₄ (%) 91 CH₄ (%) 1  CO₂ (%) 94 CO₂ (%) 1  N₂ (%) 94 N₂ (%) 1  Time (h) 30</td>
</tr>
<tr>
<td>2</td>
<td>0.55</td>
<td>0.04</td>
<td>1</td>
<td>31.5/36</td>
<td>Leakag</td>
</tr>
<tr>
<td>3</td>
<td>0.55</td>
<td>0.04</td>
<td>1</td>
<td>12/13.5</td>
<td>Leakage</td>
</tr>
<tr>
<td>4</td>
<td>1.68</td>
<td>0.04</td>
<td>3</td>
<td>0/23</td>
<td>Leakage</td>
</tr>
<tr>
<td>5</td>
<td>1.68</td>
<td>0.04</td>
<td>5</td>
<td>0/22</td>
<td>Leakage</td>
</tr>
<tr>
<td>6</td>
<td>1.68</td>
<td>0.01</td>
<td>14</td>
<td>0/58</td>
<td>Leakage</td>
</tr>
<tr>
<td>7</td>
<td>1.68</td>
<td>0.01</td>
<td>14</td>
<td>0/90</td>
<td>n.a.</td>
</tr>
<tr>
<td>8</td>
<td>13.5</td>
<td>0.10</td>
<td>7</td>
<td>0/26</td>
<td>n.a.</td>
</tr>
<tr>
<td>9</td>
<td>13.5</td>
<td>0.10</td>
<td>14</td>
<td>0/24</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

*All gas measurements have a 2% error margin.
To perform the SMA tests at atmospheric pressure 1 L batch bottles were filled with 500 mL of liquid medium. The liquid medium contained 1 g COD/L and similar concentrations of macronutrients and trace elements solution as described above. Inoculum (2 g VSS/L) was taken from the high pressure reactors after decompression. The gas phase was flushed with N₂ prior to the start of the experiments. Subsequently, the bottles were connected to an online pressure transducer and monitor (Pressdaq 2.0 and Pressdaq 2.0 software). Total gas phase of the bottle was determined by subtracting the liquid volume from the total volume of the bottle. Then, as for the high pressure experiments, molar CH₄ production could be calculated using the ideal gas law and the data on pressure increase.

Liquid samples were taken from the reactor medium after each experiment. Sampling during operation was not possible without interfering with the ongoing experiment. Samples were centrifuged at 10,000 rpm for 5 minutes and subsequently diluted by adding 0.5 ml 3% of formic acid to the 0.5 mL centrifuged sample. VFA was afterwards determined by a gas chromatograph (Hewlet Packard 5890 series II) with a flame ionisation detector (FID). A glass column (2 m × 6 mm × 2 mm) with a 10% Fluorad 431 coating on Supelco-port (mesh 100–120) was used. Further operating conditions were the FID was operated at 280 °C; oven temperature was 130 °C and injection temperature was 200 °C. The carrier gas was nitrogen saturated with formic acid.

**RESULTS**

**Autogenerative high microbiological pressure production**

Significant microbiological pressure production was achieved in nine independent batch-fed experiments using various gas and liquid volumes (Table 2). In seven out of nine reactor experiments, more than two times the pressure required for injection in the natural gas grid was achieved (Table 2). Other results show that pressure build up continues up to 90 bar. The final pressure is obviously limited by the amount of added substrate, the degree of stoichiometric conversion, and the chosen head space gas volume (liquid/gas ratio). The time required to reach the final pressure was less than a week in all experiments. The produced biogas in the head space reached CH₄ concentrations between 89 and 96%. The CO₂-content was below 6% in all experiments.

A gradual increase in pressure between 0 and 90 bar was observed in experiment 4 (Table 2) over a period of one week, after which the experiment had to be cancelled to ensure biological pressure production would not damage the equipment (Figure 2). Surprisingly, a 100-fold increase in pressure seems not to detrimentally harm the methanogenic inoculum coming from common UASB reactors for wastewater treatment. Very likely, the pressure could be increased even further, provided high-pressure resistant bioreactors would have been used.

**SMA under high pressure conditions**

SMA tests done with the granular sludge inoculum revealed an SMA of 0.6 g COD-CH₄/g VSS/d at atmospheric pressure (Figure 3(a)). When the SMA was measured with an initial pressure of 3 bar by adding a mixture of CO₂ 5% and CH₄ 95% to the head space, a moderate decrease in SMA to about 0.4 g COD-CH₄/g VSS/d was observed (Figure 3(b)). A third experiment was performed in which the reactor was pressurised up to 31.5 bar, using a similar gas composition (CO₂ 5% and CH₄ 95%). The observed SMA at 31.5 bar was in the same range as the SMA done at 3 bar (Figures 3(b) and (c)).

**The influence of pressure and/or decompression**

The impact of high pressures on the standardised SMA at atmospheric pressure was determined by assessing the standardised SMA after sludge exposure to high pressures. Results show that an exposure to 16 bars at 303 K for 4 days, apparently has no effect since SMA test values of the
inoculum and the SMA values after pressurised conditions were very similar (Figures 3(a) and 4(a)).

The SMA value with the inoculum exposed to 58 bar showed an unexpectedly high biogas yield in an SMA performed after decompression. More biogas was generated than expected based on the stoichiometric conversion of the added substrate (Figure 4(b)). Interestingly, in the liquid phase of the reactor at 58 bar, propionate, butyrate and valerate were measured with values of 272, 280 and 163 mg/L, respectively. Possibly, the increased soluble COD/VFAs is due to lysis of bacteria and/or Archaea cells resulting from the pressure increase or decompression, but this could not be confirmed. Similar results have been obtained with the sludge exposed to 90 bar (data not shown). After being exposed to the high pressures, the granular structure was completely disrupted and visually, the sludge made an emulsified impression. Sludge exposed to 58 and 90 bar appeared more viscous than sludge exposed to lower pressure, i.e. 7.5 and 16 bars.

**DISCUSSION**

To our knowledge, no experiments have been reported in which the anaerobic digestion is used for the auto-generative build up of up to 90 bar of pressure. The results presented in this study demonstrate that anaerobic granular sludge from a conventional wastewater treatment plant can autogenerate more pressure than required for injecting biogas into the regional or local gas grid.

This additional pressure could be used for direct mechanical work, e.g. in the AHPD process (pumping, membrane pressure, etc.), without the need for electrical equipment and electricity supply. It can be expected that use of the pressure for mechanical work is more efficient than methane conversion into electrical energy, which only has an efficiency of about 40%.

When comparing the gas composition results to the requirements for gas grid injection, it is clear that the integrated scrubbing mechanism is technically feasible and the gas composition (CO₂) is suitable for injection into the Dutch regional gas grid. Based on the higher Henry’s constants for both H₂S and NH₃, the internal scrubbing mechanism is expected to reduce gas concentration of both gases relatively more than CO₂. Regulation for these gases is much stricter than for CO₂ and further practical study is required to ensure no post-treatment is required.

Based on the headspace composition and the total pressure, a CH₄-COD balance was made. Unfortunately, the CH₄-COD retrieved in all high pressure experiments (Table 2) was only between 60 and 80% of the added COD as acetate. For every mole of acetate removed, one mole of CH₄ was expected based on the acetoclastic methanogenic conversion. In experiments 6 and 7, 14 g COD/L was added and a similar pressure was expected. However, experiment 6 resulted in an end-value of 58 bar, whereas experiment 7 ended at 90 bar when the experiment was...
cancelled due to equipment problems. In several experiments CH₄ was detected outside of the reactor, indicating that at higher pressures reactors started leaking and the procedure for sealing the reactor was not sufficiently effective. Based on the Henry’s constant of CH₄, it is also hypothesised that significant quantities of the produced CH₄ are being dissolved in the liquid phase. New experiments using different reactor heads and a method to measure CH₄ in the liquid phase are currently being conducted.

Pressure sensitivity of bacteria involved in the anaerobic digestion process and the impact of increased pressure on the methanogenic activity is hardly studied. However, methanogens have been studied and isolated from deep sea trenches where the pressure can be as high as 1,000 bar (Kato et al. 1998; Takai et al. 2008). Takai et al. (2008) isolated the thermophilic piezophilic Methanopyrus kandlerii, in a cultivated batch reactor at 4 and 400 bars. However, here it concerned hydrogenotrophic methanogenesis and not acetoclastic methanogenesis. But no impact of high pressures on the SMA is described for acetoclastic methanogens. Based on our results we can conclude that increased pressure has no detrimental effect on methanogenic sludge SMA using acetate as the substrate.

The observed disrupted granular structures and the emulsified liquid broth, combined with the increased level of propionate, butyrate and valerate give rise to an analogy with the presence of toxic compounds and/or sudden temperature increases beyond the respective range, which also results in increased levels of VFA and EPS in the liquid medium (van Lier et al. 1993; Aquino & Stuckey 2004). With pressure, gaseous and dissolved CO₂ also accumulate; for instance, the total inorganic carbon in the reactor was estimated at 0.36 mol in the 1.68 L reactor. Additionally, a relatively high concentration of 5 g Na⁺/L was present and the stirring mechanism required for CSTR conditions induced a high shear. Notably, in the 58 bar experiment the sludge was in the system for 96 h. After being released from the system, the granule structure was completely disrupted. So far, it is yet unclear to what extent the increased pressure is responsible as the sole stress factor causing an increased level of VFA and EPS. Further experimental studies are required to understand the limitations between micro-organisms in an AHPD reactor with an increasing pCO₂ and a high shear.

**CONCLUDING REMARKS**

It has been proven that anaerobic micro-organisms are able to digest acetate in high pressure reactors and build a pressure of up to 90 bar by means of their biogas production. In addition, the produced biogas was of very high quality, consisting of >90% CH₄ and <6% CO₂. It was also observed that less CH₄ was produced than expected based on reaction stoichiometry. Whether this was the result of leakage, CH₄ dissolvement due to Henry’s law or because of biological changes could not be determined. The measured rate of COD-conversion (SMA) decreased from 0.6 g COD/CH₄/g VSS/d to 0.4 g COD/g VSS/d at 5 and 31 bar. After decompression, propionate, butyrate and valerate were found in significant concentrations. It could not be determined if this was caused by the compression, decompression, the high stirring rate or the exposure to high free sodium concentrations. All parameter changes were involved with operating the reactor at higher pressure. Literature about piezophilic micro-organisms showed that operating pressures (up to 90 bar) are in the range where most piezo-sensitive and piezo-tolerant species can still survive. So, even though decay of certain microbes is likely as result of pressure increase, our experimental results and literature show that pressures applied in this study are unlikely to have a detrimental effect on the overall process. Therefore, we conclude that AHPD has great potential for making external gas upgrading equipment obsolete.

**REFERENCES**


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