

Autogenerative High Pressure Digestion: Future Potentials and Constraints

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Abstract

Biogas generated in waste (water) treatment facilities is increasingly regarded as an important source of renewable energy. However, generally, the CH₄ content in biogas ranges between 55-70%, depending waste(water) composition, and cannot be applied directly for high grade applications such as gas grid injection or vehicle fuel. Conventional biogas upgrading technologies are only cost-efficient when treating biogas flows exceeding 100 Nm³/h. Therefore, cost-effective external biogas upgrading, to remove H₂O, CO₂, H₂S and other trace impurities, was assumed to pose a major challenge for the further dissemination of small-scale decentralized anaerobic digestion technology.

Consequently, an integrated CO₂-scrubbing mechanism, denominated as Autogenerative High Pressure Digestion (AHPD) was introduced. Previous work already showed that working pressures up to 90 bar and >95% CH₄-content of the biogas are feasible. This work explores the future potential of AHPD by discussing constraints on the requirement of Acid Neutralizing Capacity (ANC), and the role of mineral addition. Although not the main focus of this work, insights on kinetics and population dynamics are used to support the findings. The fact that a continuous AHPD 1.5 m³ reactor is currently in operation brings the technology very close to practice.

Keywords

Pressure digestion; biogas upgrading; mineral supplementation; Acid neutralizing capacity, kinetics; population dynamics; microbial diversity

INTRODUCTION

Conventional anaerobic digestion is a commonly used technology worldwide and external biogas upgrading is well documented (Wellinger and Lindberg, 2001). However, literature on in-situ biogas upgrading and high-pressure digestion is limited (Richards et al., 1991; Zagt et al., 2010). Our recent work (Lindeboom et al. 2011, 2012, 2013) explores the interactions between the partial biogas pressures, the chemical equilibria, bio-kinetics in the liquid and solid phase and the microbiology. Obtained results show that natural gas quality biogas can be directly recovered from AHPD reactors locally, requiring little or no further upgrading.

MATERIALS AND METHOD

Presented results were obtained in 0.6 and 8 L pressure reactors (Lindeboom et al. 2012, 2013). Reactors were inoculated with anaerobic granular sludge from a full scale Upflow Anaerobic Sludge Blanket treating paper mill wastewater (Industriewater Eerbeek, The Netherlands) and an Expanded Granular Sludge Bed treating fruit juice waste water (Friesland Campina Riedel, The Netherlands). Varying concentrations of acetate, acetic acid and glucose were used. Biogas, VFA and ion composition, ANC, pressure and pH were measured (Lindeboom et al. 2012, 2013).

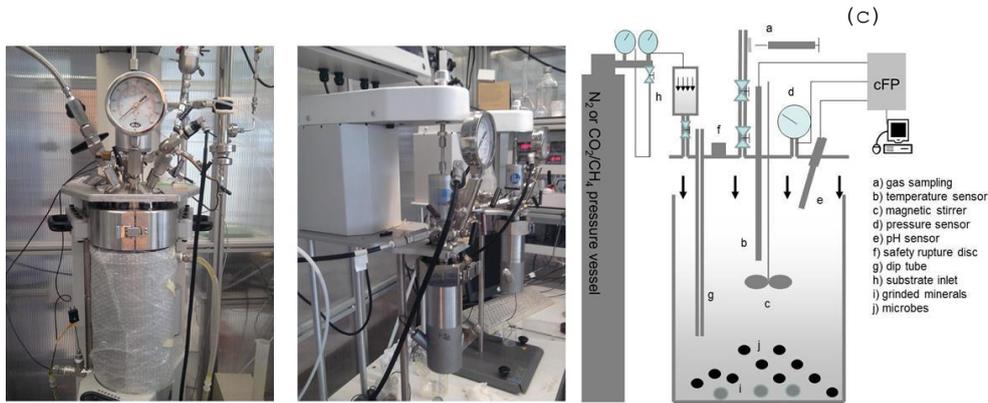


Figure 1 AHPD-reactors of 8 (a) and 0.6 L (b) and (c) overview of setup (adjusted from Lindeboom et. al 2012)

EXPERIMENTS 1: LIQUID TO CONTROL THE GAS QUALITY

By digesting sodium acetate 20 bar pressure was achieved in 3 phases (figure 2a). The CH_4 produced, dissolved according to Henry's law with a respective value of $0.0016 \text{ mol L}^{-1} \text{ bar}^{-1}$ at 30°C (Lindeboom et al., 2012). The ratio between Acid Neutralizing Capacity (ANC) and Total Inorganic Carbon_{produced} (TIC) was essential to explain CO_2 dissolution and biogas composition (Figure 2b). Furthermore, acetotrophic methanogenic activity on undissociated acetic acid was only marginally suppressed at reduced ANC/TIC ratio, resulting in a $\text{pH} < 5$ (figure 2c), a final pressure of 13 bar and a CO_2 -content of 19% at 9 bar of total pressure. This indicates that pressure alone can be used to produce high quality biogas from undissociated fatty acids. Strikingly, CO_2 dissolved according to equilibrium calculations in demi water, but exceeded equilibrium values, in experiments in which the liquid medium was inoculated with granular sludge (figure 2d). It was thus anticipated that the inoculum sludge provided additional ANC, e.g. by means of minerals and proteins, which was likely responsible for sequestering more CO_2 as HCO_3^- and providing a protective pH-micro gradient around the micro-organisms at decreasing pH.

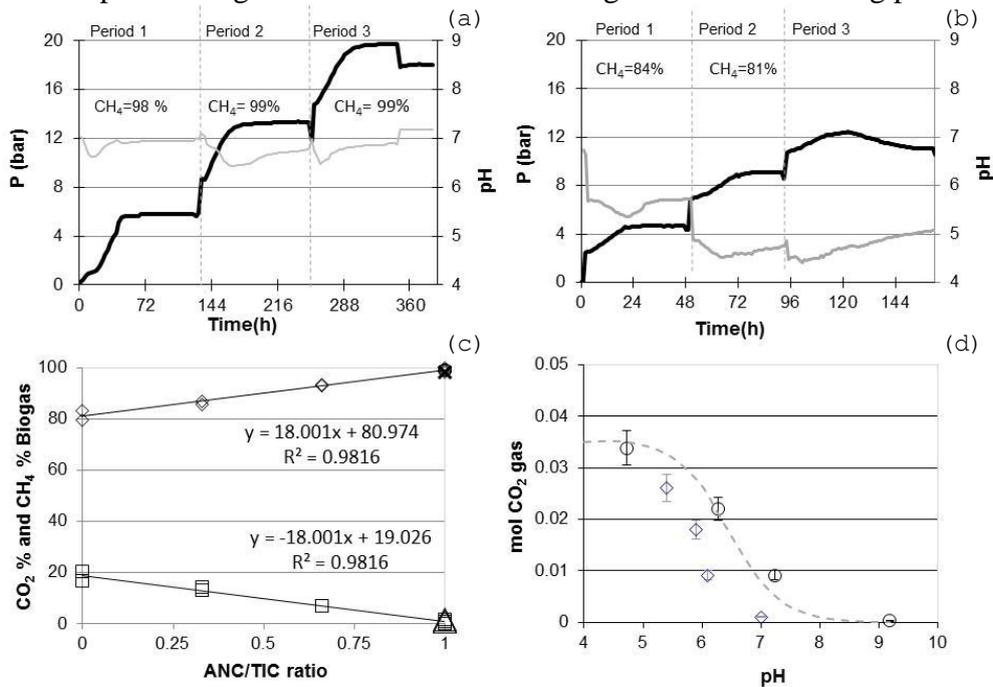
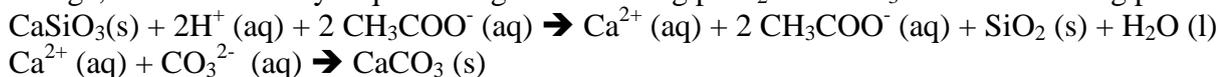


Figure 2 (a) pressure and pH profile of acetate digestion at ANC/TIC =1, (b) pressure and pH profile during acetate digestion at decreasing ANC/TIC (c) effect of ANC/TIC ratio experiment III and IV on biogas quality, and (d) difference in CO_2 -content of the biogas using demiwater, inoculated medium and theoretical values (adjusted from Lindeboom et al., 2012)

EXPERIMENTS 2: EARTH ALKALI METALS TO CONTROL THE LIQUID

For many substrates, the available ANC is insufficient to sequester all CO₂ inside the reactor liquid and, therefore, leads to a drop in pH and reduced methane production rates, rendering in situ CO₂-removal very difficult. Therefore, we hypothesized that in-situ mineral weathering and secondary carbonation of natural silicate minerals, could provide a low-cost alternative to conventional caustic dosage, thus additionally sequestering accumulating pCO₂ as CaCO₃ via the following pathways:



It was experimentally verified that olivine (Mg_{1.8}Fe_{0.16}Ni_{0.04}SiO₄) and wollastonite (CaSiO₃) could buffer the pH of undissociated acetic acid additions to the reactor. Furthermore, olivine and wollastonite improved the biogas quality up to a maximum of 70 and 96% ± 2% CH₄, respectively during acetic acid digestion compared to a conventional phosphate buffer (figure 3a, b). Other experiments showed that biogas quality from glucose digestion improved from the stoichiometric 50% CH₄ and 50% CO₂ to 88 ± 2% CH₄ by wollastonite addition at autogenerated pressures of 3 - 10 bars (Lindeboom et al., 2013). It was however also observed that average CH₄-production rates decreased by 50% in the 10 bars experiment. Although no hydrogen accumulation was detected above 60 Pa (the detection limit), the reduced CH₄-production rates, coincided with elevated concentration of propionate up to 2.8 g COD L⁻¹, more than 50% of total COD.

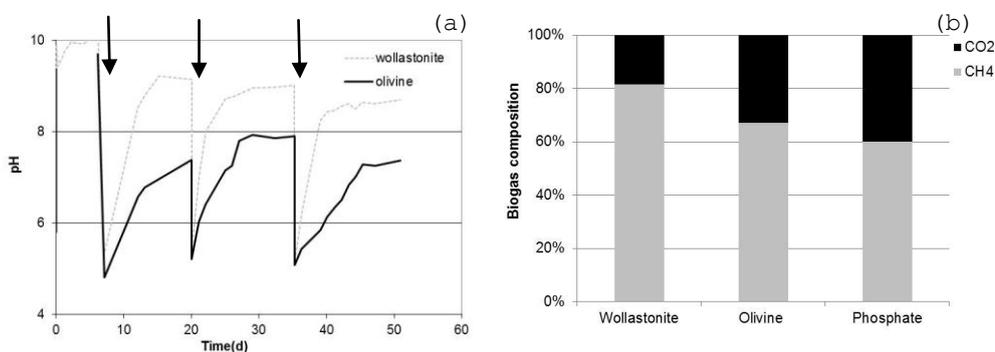


Figure 3 (a) Typical pH-profile of olivine and wollastonite leaching. Arrows indicate undissociated acetic acid additions and (b) biogas composition at the different applied ANC sources (grey: CH₄; black: CO₂).

Both the results in figure 2 and 3 indicate that the Acid Neutralizing Capacity can protect the microbes from acidification and thereby provide suitable pH-conditions for CH₄-production. But despite continued CH₄-production, methanogenic activity showed to be sensitive to the conditions associated with pressure autogeneration. This is in line with the results from the pressure experiments performed with neutralized VFA, in which also a ~30% reduction in degradation rates was observed at circumneutral pH (Lindeboom et al., 2011). So, although from a physicochemical point of view any biogas composition can be attained by using Henry's law in combination with a form of ANC, the loss of biological activity or the change in formed intermediates still poses a constraint that cannot be neglected. Most recent unpublished results of a long term glucose fed batch experiment in which the population dynamics were studied by using Denaturing Gradient Gel Electrophoresis (DGGE), cloning and sequencing, showed that detailed insights into the bacterial and archaeal population dynamics under AHPD conditions are essential to fully explain CH₄-production rates and accumulation of intermediates.

CONTINUOUS 1.5 M³ EXPERIMENTS

At a selected operational pressure of 20 bars, Bateau operated continuous trial experiments on glycerol and primary sewage sludge (from municipal WWTP Drachten, The Netherlands). Currently, research on blackwater and organic solid waste are being performed (Zagt et al., 2012).

DISCUSSION

The presented overview of the results, indicate that in situ biogas upgrading is possible applying the AHPD process. By using the ANC/TIC ratio or addition of wollastonite, the CO₂-content of the biogas can be reduced to below 5 % at moderate pressures (3-20 bar) from different substrates in a single step. However, it should be emphasized that the requirement of ANC for formation of HCO₃⁻ could potentially inhibit the microbiology due to increasing salt concentrations and scaling risks. This could, depending on the substrate, pose an upper limit to an ANC based strategy. At pressures up to 20 bars dissolved CO₂ can be used as 2nd major CO₂ sink without affecting the pH if sufficient HCO₃⁻ is present. It can furthermore be calculated that the dew point of the pressurized biogas (based on water vapour only), can be reduced from 30°C at atmospheric pressure to 12, -6 and -14 °C after decompression from 3, 10 and 20 bar, respectively. Finally, the higher Henry's constant of H₂S compared to CO₂, 0.115 versus 0.032 mol L⁻¹ bar⁻¹ will theoretically also facilitate improved in-situ H₂S scrubbing at much lower pressures than 20 bars (Zagt et al. 2010). Fixation of sulphide could then be obtained by the addition of FeCl₃ or olivine e.g. conventional FeS precipitation.

As described above, a small shift in the carbonate equilibrium due to the addition of biomass and a reduction in methanogenic activity were observed in accumulating pressure experiments. Although the biological implications of pressure accumulation are not fully understood yet, it is clear they are essential to the selection of the operational pressure. Besides physicochemical disadvantages of pressure elevation should be taken into account. Owing to simultaneously increasing CH₄-dissolution, CH₄ losses could be experienced when decompressing liquid effluents from higher pressures. For example, increasing the operational pressure from 10 to 20 bars results in a doubling of CH₄ dissolution from 1 g COD CH₄ L⁻¹ to 2 g COD CH₄ L⁻¹ of treated effluent. Nevertheless, atmospheric digesters are also reported to have CH₄ losses. Furthermore, minimizing the operational pressure would facilitate the construction of more cost-effective reactor designs.

In order to optimally benefit from AHPD in practice it is therefore essential that depending on the type and concentration of the substrate and the desired biogas quality, a suitable operational pressure is chosen. This should combine ANC management and storage of dissolved CO₂ and thereby minimize the negative effects of pressure accumulation and ANC addition. Besides, a combined approach leaves opportunity to adjust AHPD technology to required biogas quality and available resources of rural communities, making the technology more widely applicable.

ACKNOWLEDGEMENTS

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