An operational strategy to produce Bio-hydrogen: the use of digestate for process control

*Andrea Schievano**[1], Alberto Tenca[2], Roberto Oberti[2], Fabrizio Adani[1]*
[1]*Dipartimento di Produzione Vegetale, University of Milano, Milano (I)*
[2]*Istituto di Ingegneria Agraria, University of Milano, Milano (I)*
***andrea.schievano@unimi.it**

Summary

A semi-continuous digester was fed twice a day with a concentrated solution of glucose (100 g l^{-1}) and monitored for a 30-days period, with the aim of testing the possibility of utilizing the digestate of a traditional biogas plant, after a heat-shock at 100ºC, for controlling process parameters (organic loading rate OLR, pH, volatile fatty acids VFA concentration), by adding it to the fresh substrate at a ratio R of the total feeding volume. The process resulted instable for OLR=10 g_{VS} $L^{-1}$and R=0.7, while more stable for OLR of 5 g_{VS} $L^{-1}$and R=0.85. The maximum bio-hydrogen production rate in stable conditions was 100 NmL_{H2} h^{-1} and the conversion yields were 1.7 - 1.8 mol_{H2} $mol^{-1}{}_{glucose}$. The produced biogas showed always complete absence of methane.

Riassunto

Un digestore semi-continuo è stato alimentato 2 volte al giorno con una soluzione concentrata di glucosio (100 g l^{-1}) e monitorato per 30 giorni, con lo scopo di testare la possibilità di utilizzare il digestato di un tradizionale impianto di biogas, dopo shock termico a 100ºC, per controllare i parametri di processo (carico organico OLR, pH e concentrazione di acidi grassi volatili VFA), aggiungendolo al substrato fresco nel rapporto R del volume totale di alimentazione. Il processo è risultato instabile per OLR=10 g_{VS} L^{-1} e R=0.7, mentre più stabile per OLR=5 g_{VS} L^{-1} e R=0.85. La velocità di produzione massima di bio-idrogeno in condizioni di processo stabili è risultata di 100 $NmLH_2$ h^{-1}, con rendimenti di conversione di 1.7 - 1.8 mol_{H2} $mol^{-1}{}_{glucosio}$. Il biogas prodotto ha mostrato sempre una completa assenza di metano.

1. Introduction

Hydrogen has been always recognized as an ideal alternative energy source to substitute fossil fuels. Hydrogen produced directly from organic materials by bacteria, i.e. bio-hydrogen, has considerable potential in defining hydrogen's future use [1].

In anaerobic conditions, organic matter is converted to methane and carbon dioxide via a series of interrelated microbial metabolisms, including hydrolysis/fermentation, acetogenesis, and methanogenesis. Fermentative bacteria hydrolyze and ferment carbohydrates, proteins, and lipids to volatile fatty acids, which are further converted to acetate, and CO_2/H_2 by acetogenic bacteria. The products of acetogenesis, i.e. acetate and CO_2/H_2, are finally converted to methane by methanogenic bacteria [2]. A bioreactor could possess significant capacity for the transformation of organics into hydrogen gas when bioactivity of hydrogen consumers contained in a bioreactor was inhibited [3–6]. Some methods have been reported to inhibit methanogens and to harvest anaerobic spore-forming bacteria such as *Clostridium*, capable to produce hydrogen. One is a heat shock of the inoculum at 100ºC for 2 hours, which favours only spore-forming microrganisms. Other method is the pH control in the interval 5<pH<6, which has been shown to be optimal for hydrogen-type fermentation and to inhibit methanogenic activity [7 - 9]. In literature, the pH control has been always achieved by the use of chemicals such as NaOH or KOH and HCl [7-10]. On the other hand, the use of large amounts of reagents wouldn't be possible in a full scale-process.

Besides, high concentrations in the digester of volatile fatty acids (VFA), forming during fermentation, are responsible of both inhibiting the hydrogen-producing bacteria and dropping the pH below pH 5 [11]. The concentrations of VFA in the digester are proportional to the organic loading rate (OLR) and at the same time to the hydraulic retention time (HRT). The higher the OLR is, the faster the wash-out of the VFA produced should be, i.e. low HRT.

Han et al. [11] suggested diluting the liquid phase of food waste during its anaerobic fermentation by leaching pure water through the solids (leaching–bed reactor), so that the high concentration of VFA is washed out. The result was an optimal dilution *D* (*D* = flow rate / operating volume) of 4.5

d^{-1} [11]. On the other hand, this solution, applied on full-scale, would imply huge water consumption and problems in environmental and economical feasibility.
Traditional biogas plants produce abundant effluents, i.e. digestates, which have normally a pH of 7-8, a considerable alkaline buffer-capacity and low concentrations of volatile fatty acids, as they were transformed into methane.
This paper aims to investigate the use of pre-heated (100ºC) digestates to control the hydrogen production process in a semi-continuous thermophilic bio-digester, by diluting the liquid medium and buffering the pH to the desired values.

2. Methods

2.1. *Seed microorganisms*

The seed sludge was the digestate taken from an anaerobic digester biogas plant and boiled (100ºC) for 2 hours to inactivate hydrogenotrophic bacteria and to harvest anaerobic spore-forming bacteria such as Clostridium sp. [7]. This procedure was carried out twice a day, before feeding. The pH, alkalinity, total VFA concentration and volatile solids (VS) concentration of the sludge were respectively 8.1, 7470 mg $_{CaCO_3}$ l^{-1}, 1190 mg l^{-1} and 750 mg l^{-1}.

2.2. *Feedstock for feeding*

A solution of 100 g l^{-1} of pure glucose (99%) was used as feeding mixture, in order to represent an extreme condition for concentration of sugar-type substrate in the feedstock. The glucose was also chosen as known substrate for better understanding the process performances.

2.3. *Experimental setup and procedure*

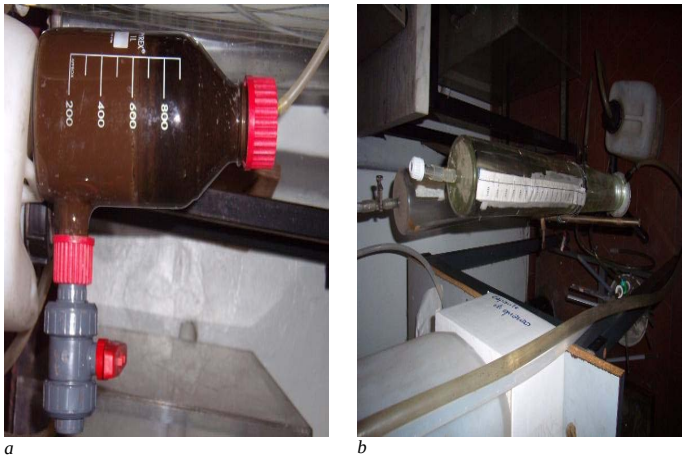
A completely mixed reactor with working volume of 600 ml was operated in a semi-continuous mode by feeding twice a day a mix of the glucose solution and the heat-shocked digestate by a syringe (Fig. 1). The digester was operated at a temperature of 55ºC (thermophilic conditions) and a HRT of 3 days. Output digestate was withdrawn twice a day before each alimentation.

2.4. *Experimental conditions*

Two experiments were performed to test the process behaviour in producing biohydrogen. The aim was to find the maximum OLR and the minimum recirculation ratio (*R*), i.e. the digestate input volume divided by the total input volume. The digester was fed in the first two-week period with an OLR of 10 g_{VS} l^{-1} d^{-1} and in the second period with an OLR of 5 g_{VS} l^{-1} d^{-1}. The recirculation ratios were of 0.7 and 0.85 respectively.

2.5. *Analytical procedures*

The biogas production was measured using a volumetric gas meter column connected to the headspace of the digester. Biogas composition was analyzed by a gas chromatograph (Agilent, Micro GC 3000A) equipped with two thermal conductivity detectors (TCD) and two columns, using Nitrogen and Helium as carriers.



a *b*

Fig. 1 – *Experimental set up.*
[a] *digester*
[b] *column for biogas measurement*

3. **Results and discussion**

3.1. *H_2 production*

In Fig. 2 are reported the results of the process performance in terms of H_2 production per mole of glucose added and the hydrogen production rate. Methane was never found in the biogas, indicating complete inhibition of the hydrogen-consumers microrganisms. Fig.3 shows the pH trend and the total VFA concentration in the digester.

3.2. *First two-week period (OLR=10 g_{VS} l^{-1} d^{-1})*

The first period (hours 0 to 250) was characterized by a lag-phase during the first week (hours 0 to 115), in which few biogas was produced (Fig. 2). This drove to low hydrogen yields, if compared with the second week, when the process yielded 1.5-1.8 $molH_2$ $mol^{-1}_{glucose}$. This result was quite satisfactory, if compared to the maximum yields of 2.45 and 2.6 mol_{H2} $mol^{-1}_{glucose}$ achieved in controlled batch cultures by Van Ginkel et al. and Taguchi et al. [12 - 13]. Hang-sik and Jong-Ho [10] obtained a calculated value of 2.2 mol_{H2} mol^{-1}_{exose}, feeding mixed food waste continuously, with an operative HRT of 5 days and adjusting the pH with specific pure reagents (KOH and HCl).
The hydrogen production rate showed notable imbalance, showing, during the second week, maximum peaks around 150 and 200 ml_{H2} l^{-1} $h^{-1}$and null values. The obtained maximum rates were four times higher than those measured by Hang-sik and Jong-Ho [10], in fermenting mixed food waste, with similar OLR. This was probably caused by the high availability of glucose to microrganisms, if compared to more complex organic molecules that must be hydrolyzed before fermentation.
On the other hand, the use of glucose meant higher shock due to the high-loading. The fast production of VFA partially inhibited the fermentation because of high concentrations (around 10 g l^{-1}) (Fig. 3) and dropped twice the pH to 4.7 and 4.8 (Fig. 3), causing process imbalance. The addition of digestate in the feeding with the ratio *R*=0.7, resulted non-sufficient to control the process parameters. Because the digester was semi-continuously fed, this effect was probably more evident than what would happen in a continuously-fed system.

3.3. *Second two-week period (OLR=5 g_{VS} l^{-1} d^{-1})*

From hour 250 to 500, the OLR was lowered to 5 g_{VS} l^{-1} d^{-1}. The hydrogen production gave yields almost constantly around 1.7 – 1.8 mol_{H2} $mol^{-1}_{glucose}$ and rates following a relatively stable trend, with maximum peaks around 80 ml_{H2} l^{-1} h^{-1} (Fig. 2). The variations were probably caused by the semi-continuous feeding. The pH was maintained always higher than in the first period (Fig. 3), between pH 5.4 and 6.2, meaning that the *R* ratio (0.85) was the upper limit for a satisfactory control of the process pH. The VFA concentration resulted in lower values than in the first period (Fig. 3).

These results revealed that the digestate added to the feeding (at the ratio *R*) has a remarkable effect on the process control, for both diluting VFA concentration and buffering the pH to desired values (5<pH<6). This strategy would probably work better in a continuously-fed system.

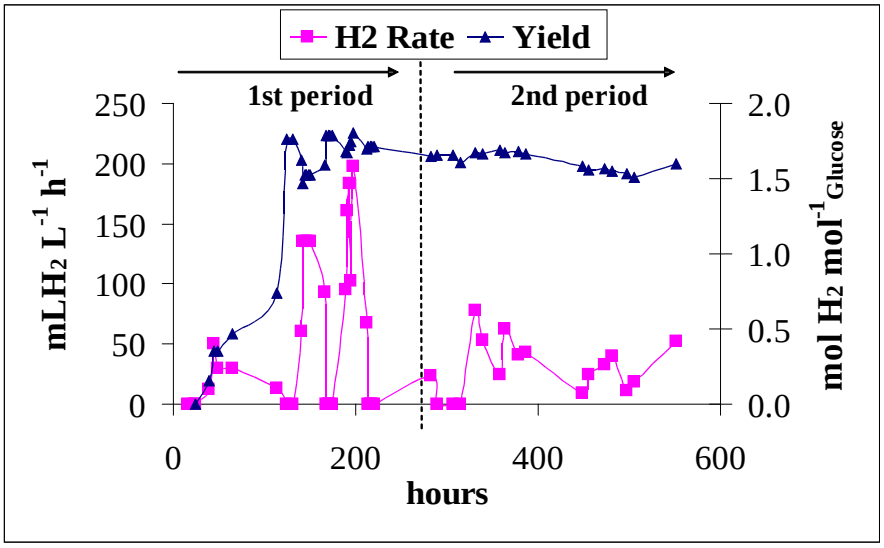


Fig. 2 – Process yield and hydrogen production rate

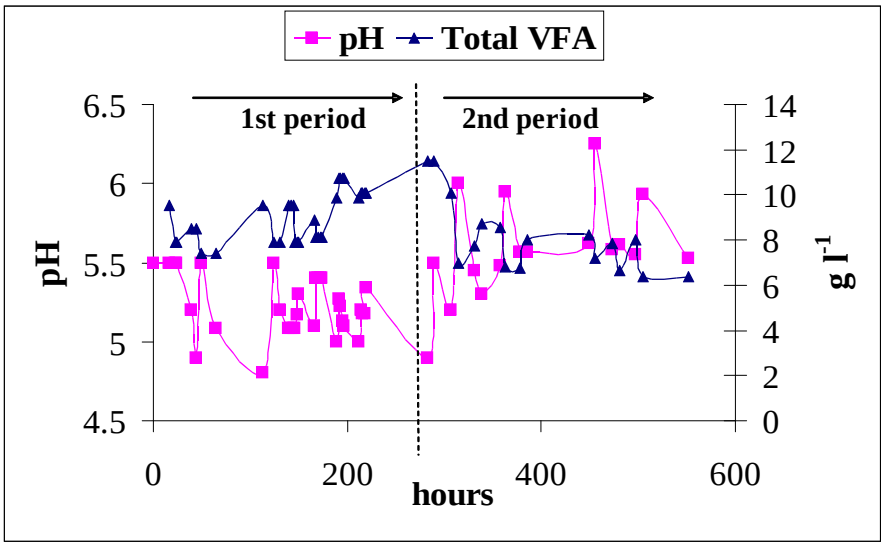


Fig. 3 – Trends of the pH and the total VFA concentrations, measured during the test

4. Conclusions

The studied semi-continuous process, with a fixed HRT of 3 days, showed imbalance conditions for *R* between 0.7 and 0.85 and for OLR between 5 and 10 g_{VS} l^{-1} d^{-1}. Comparing this process to the one proposed by Han et al. [11], the dilution ratio (*D*) for optimal operation, in the present case, would be 0.3 d^{-1}. Using pure water in a leaching-bed system, Han et al. found optimal *D*s between 2 and 5 so that high water consumptions were needed. The use of digestate instead of water would probably

give a better option to both control the pH and dilute the VFAs, also in a leaching-bed system. Further research should be carried out to test this strategy for fermenting various kinds of organic substrates, with different operational conditions.

5. References

[1] ZAJIC, J.E., KOSARIC, N., BROSSEAU, J.D.: Microbial production of Hydrogen. Adv Biochem Eng, 7, 57-109 (1978).

[2] BITTON, G.: Wastewater microbiology. New York: Wiley-Liss, 1994.

[3] SPARLING, R., RISBEY, D., POGGI-VAMIDO, H.M.: Hydrogen production from inhibited anaerobic composters. Int J Hydrogen Energy, 22(6), 563–6 (1997).

[4] LAY, J.J., LEE, Y.J., NOIKE, T.: Feasibility of biological hydrogen production from organic fraction of municipal solid waste. Water Res, 33(11), 2579–86 (1999).

[5] LAY, J.J.: Modeling and optimization of anaerobic digested sludge converting starch to hydrogen. Biotechnol Bioeng, 68, 269–78 (2000).

[6] LAY, J.J.: Biohydrogen generation by mesophilic anaerobic fermentation of microcrystalline cellulose. Biotechnol Bioeng, 74(4), 280–7 (2001).

[7] LIU, D., LIU, D., ZENG, R.J., ANGELIDAKI, I.: Hydrogen and methane production from household solid waste in the two-stage fermentation process, Water Research, 40, 2230-2236 (2006)

[8] CHANG, F.Y., LIN, C.Y.: Biohydrogen production using an upflow anaerobic sludge blanket reactor. Int. J. Hydrogen Energy, 29 (1), 33–39 (2004).

[9] OH, S.E., VAN GINKEL, S., LOGAN, B.E.: The relative effectiveness of pH control and heat treatment for enhancing biohydrogen gas production. Environ. Sci. Technol., 37 (22), 5186–5190 (2003).

[10] HANG-SIK, S., JONG-HO, Y.: Conversion of food waste into hydrogen by thermophilic acidogenesis, Biodegradation, 16, 33–44 (2005).

[11] HAN, S.K., SHIN, H.S.: Biohydrogen production by anaerobic fermentation of food waste, International Journal of Hydrogen Energy, 29, 569 – 577 (2004).

[12] TAGUCHI, F.; YAMADA, K.; HASEGAWA, K.; TAKI-SAITO, T.; HARA, K.: J. Ferment. Bioeng., 82(1), 80 (1996).

[13] VAN GINKEL, S., SUNG, S., L A Y, J.J.: Biohydrogen production as a function of pH and substrate concentration, Environ. Sci. Technol., 35, 4726-4730 (2001).