COMMUNICATION TO THE EDITOR

BIOTECHNOLOGY and BIOENGINEERING

Simultaneous Hydrogen Utilization and In Situ Biogas Upgrading in an Anaerobic Reactor

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Received 14 August 2011; revision received 27 October 2011; accepted 28 October 2011

Published online 8 November 2011 in Wiley Online Library (wileyonlinelibrary.com). DOI 10.1002/bit.24360

ABSTRACT: The possibility of converting hydrogen to methane and simultaneous upgrading of biogas was investigated in both batch tests and fully mixed biogas reactor, simultaneously fed with manure and hydrogen. Batch experiments showed that hydrogen could be converted to methane by hydrogenotrophic methanogenesis with conversion of more than 90% of the consumed hydrogen to methane. The hydrogen consumption rates were affected by both P_{H_2} (hydrogen partial pressure) and mixing intensity. Inhibition of propionate and butyrate degradation by hydrogen (1 atm) was only observed under high mixing intensity (shaking speed 300 rpm). Continuous addition of hydrogen (flow rate of 28.6 mL/(L/h)) to an anaerobic reactor fed with manure, showed that more than 80% of the hydrogen was utilized. The propionate and butyrate level in the reactor was not significantly affected by the hydrogen addition. The methane production rate of the reactor with H_2 addition was 22% higher, compared to the control reactor only fed with manure. The CO_2 content in the produced biogas was only 15%, while it was 38% in the control reactor. However, the addition of hydrogen resulted in increase of pH (from 8.0 to 8.3) due to the consumption of bicarbonate, which subsequently caused slight inhibition of methanogenesis.

Biotechnol. Bioeng. 2012;109: 1088–1094.

KEYWORDS: hydrogen; methane; anaerobic digestion; biogas upgrading

Wind and bioenergy are two of the most promising renewable energy sources. Commercial wind power has been produced in Denmark since the 1970s, and wind power currently accounts for nearly 20% of the Danish electricity supply (Mason, 2008). Due to varying wind conditions and electricity demand over the years, up to 40% of the electricity from wind is judged to be a temporary surplus. Although some surplus electricity is exported to neighboring countries (Sharman, 2005), the potential of wind mills is not fully utilized. An attractive way of exploiting surplus wind mill production is to electrolyze water for hydrogen production (Sherif et al., 2005). Hydrogen is a clean fuel and can be used in fuel cells. However, hydrogen utilization has several unsolved bottlenecks such as hydrogen transport, storage, as well as utilization in fuel cells. It is a very light gas and contains much lower volumetric energy content (10.88 MJ/m^3) compared to the energy content of methane (36 MJ/m^3). Storage costs of hydrogen are consequently high. In anaerobic digesters, hydrogen can be converted to methane by the action of hydrogenotrophic methanogens according to Equation (1) (Ako et al., 2008; Wise et al., 1978).

$$4H_2+CO_2= CH_4+2H_2O \quad \Delta G^0= -130.7\,\text{kJ/mol} \quad (1)$$

Conversion of hydrogen in a biogas plant would provide several advantages, such as utilization of the existing infrastructure of biogas plants. Additionally, conversion of hydrogen in a biogas reactor would consume some CO_2 in the biogas and, thereby, result in upgraded biogas with lower CO_2 content. This partial removal of CO_2 from the biogas would decrease the costs for the upgrading of biogas to natural gas quality, which could provide additional utilization opportunities of biogas, for example, as vehicle fuel (Deng and Hägg, 2010), as well as improving energy density and transmission capacity of the CH_4 enriched biogas. Finally, possible unconverted hydrogen mixed with methane, would improve the combustion properties of biogas as fuel (5–30% hydrogen by volume) (Akansu et al., 2004). The storage costs for methane is at least a three times lower compared to hydrogen (Balat, 2008), due to the higher boiling point and higher volumetric energy density of

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Contract grant sponsor: Vestforsyning A/S

Contract grant sponsor: Shanghai Tongji Gao Tingyao Environmental Science & Technology Development Foundation

gaseous methane. Additionally, a number of countries already have natural gas infrastructure, which would make distribution of upgraded biogas feasible.

However, adding hydrogen to a biogas reactor might cause problems due to the increase of the hydrogen partial pressure (P_{H_2}) in the biogas reactor, which theoretically could lead to inhibition of VFA (propionate and butyrate) degradation and, thereby, potential process disturbance or break down (Fukuzaki et al., 1990; Siriwongrungson et al., 2007).

Therefore, the present study tested the feasibility of conversion of hydrogen to methane and the potential inhibition of hydrogen on VFA degradation in batch experiments. Furthermore, methane production from hydrogen in an anaerobic reactor continuously fed with cattle manure and hydrogen was investigated.

The hydrogen consumption and methane production under different P_{H_2} are shown in Figure 1. The hydrogen consumption rates under all tested initial P_{H_2} decreased with the decrease of P_{H_2}, at shaking speed 100 rpm. After 25 h, around 70% of the hydrogen was consumed under all tested P_{H_2}. However, the hydrogen consumption rates under all tested initial P_{H_2} were almost constant (independent of the P_{H_2}) at shaking speed 300 rpm, as reflected by the linearly decrease of hydrogen in the headspace. Besides, hydrogen was almost fully consumed after 6 h. The above results clearly showed that the effect of P_{H_2} on hydrogen consumption rates was strongly associated with the shaking speed. Gas–liquid mass transfer is crucial for hydrogenotrophic methanogenesis, since it determines the dissolved substrate available for hydrogenotrophic methanogens. Carbon dioxide was shown to be in quasi-equilibrium under normal operating conditions, while hydrogen gas–liquid or liquid–gas transfer limitations were always observed in anaerobic reactors (Pauss et al., 1990). When the hydrogen gas–liquid mass transfer is the limiting factor during the process of hydrogenotrophic methanogenesis, Equation (2) could be used to describe the kinetics of hydrogen consumption in the batch experiment.

$$\frac{dV_{H_2}}{dt} = V_g \frac{dP_{H_2}}{dt} = -V_g K_L a (P_{H_2} - P^*_{H_2}) \quad (2)$$

$$\frac{dV_{H_2}}{dt} \approx -V_g K_L a P_{H_2} (P^*_{H_2} \approx 0) \quad (3)$$

Assuming hydrogen is consumed fast by hydrogenotrophic methanogenesis once solubilized, $P^*_{H_2}$ could be neglected (Equation 3). By integration of Equation (3), V_{H_2} can then be expressed as Equation (4).

$$V_{H_2} = V^0_{H_2} e^{(-K_L a t)} \quad (4)$$

From Equation (3), it is obvious that the hydrogen consumption rate is proportional to P_{H_2}. This dependency was experimentally observed at shaking speed 100 rpm as previously mentioned. Equation (4) was used to simulate the variation of hydrogen with time at shaking speed 100 rpm (Fig. 1). Higher hydrogen consumption rates could be obtained by increasing the P_{H_2} as shown in Table I. The $K_L a$ values for 0.25, 0.5, and 1.0 atm were very similar to each other (0.038, 0.036, and 0.039 h^{-1}, respectively). It is because all the reactors had the same configuration and operated under the same condition (temperature, inoculum, mixing intensity, etc.). $K_L a$ is specific to a given reactor and mode of operation, but independent on gas pressure (Pauss et al., 1990). Hydrogen consumption rate could be increased by increasing $K_L a$ (Equation 3). One way to increase $K_L a$ is increasing the mixing of the reactor (Kramer and Bailey, 1991).

When the gas–liquid mass transfer is not the limiting factor, the hydrogen consumption rate will be determined by the hydrogen uptake rate by hydrogenotrophic methanogens (Equation 5).

$$\frac{dV_{H_2}}{dt} = 11.2 V_l \frac{dS}{dt} = -11.2 V_l X Y_{S/X} \mu_{max} \frac{S}{(K_s + S)} \quad (5)$$

$$\frac{dV_{H_2}}{dt} \approx -11.2 V_l X Y_{S/X} \mu_{max} (K_s << S) \quad (6)$$

K_s usually corresponds to a P_{H_2} around 0.02 atm (Ahring and Westermann, 1987). Assuming hydrogen distribution between gas and liquid phase is in equilibrium, K_s could be neglected since it is much lower than S (in the P_{H_2} range of 0.25–1 atm in our study). By integration of Equation (6), V_{H_2} could be expressed as Equation (8).

$$V_{H_2} = V^0_{H_2} - 11.2 V_l X Y_{S/X} \mu_{max} t \quad (7)$$

Under non-limiting gas–liquid mass transfer conditions, the hydrogen consumption rate is constant in the initial phase because the concentration X could be assumed constant (Equation 6). The linear decrease of hydrogen partial pressure with time at shaking speed 300 rpm (Fig. 1) indicated that hydrogen was under non-limiting gas–liquid mass transfer conditions. Therefore, the experimental results fitted well by Equation (7) (Fig. 1). Similar hydrogen consumption rates (Table I) were obtained under different initial P_{H_2}, which was in accordance with Equation (6). The hydrogen consumption rates (260–280 (mL/(L/h)) were much higher than those obtained at shaking speed 100 rpm (lower than 70 mL/(L/h)). At shaking speed of 300 rpm, increase of the P_{H_2} or mixing would not be beneficial for higher hydrogen consumption rates, since the limiting factor was the microbial activity and not the hydrogen transfer rate. Increase of the microbial concentration might lead to higher hydrogen consumption rate (Equation 6).

No accumulation of liquid metabolites was observed during anaerobic digestion, indicating that hydrogen was directly consumed for methane production. The direct

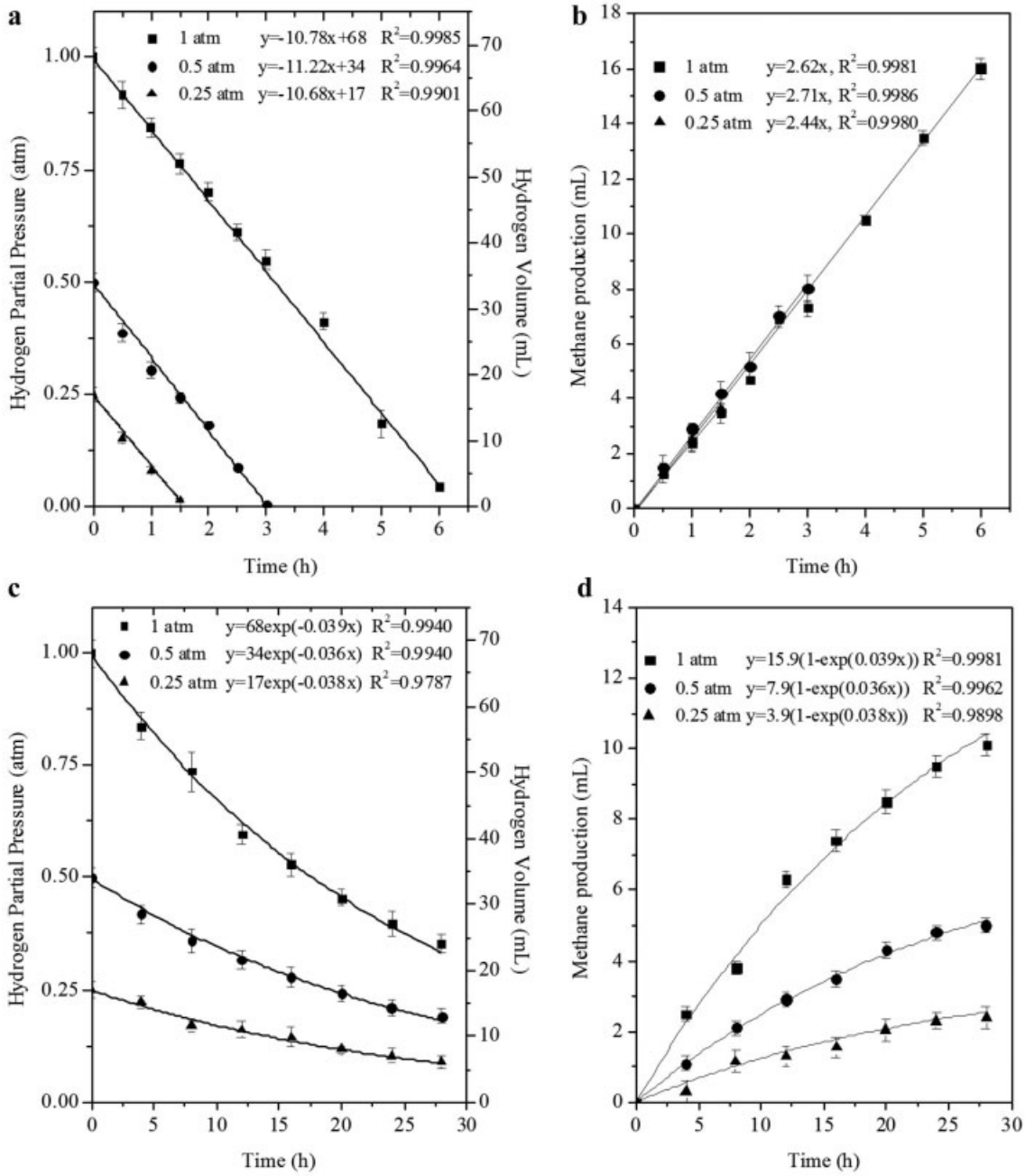

Figure 1. Variations of hydrogen and methane with digestion time in batch experiment 1. **a**: Hydrogen consumption at shaking speed 100 rpm. **b**: Methane production at shaking speed 100 rpm. **c**: Hydrogen consumption at shaking speed 300 rpm. **d**: Methane production at shaking speed 300 rpm.

Table I. Hydrogen consumption and methane production rates in batch experiments 1 and 2[a]

	100 rpm			300 rpm		
Initial hydrogen partial pressure (atm)	0.25	0.50	1.00	0.25	0.50	1.00
Hydrogen consumption rate (mL/(L/h))	16.2	30.6	66.3	267	281	270
Methane production rate (mL/(L/h))	3.7	7.11	15.5	61	67.8	65.5
$Y_{p/s}$ (%)	91.7	92.9	93.5	91.4	96.6	97.2

[a]The data were calculated by fitting the curves to Equation (4) or Equation (6). At shaking speed 100 rpm, the hydrogen consumption rate and methane production rate shown in the table were the initial values since they varied with time.

conversion of H_2 with CO_2 to CH4 by hydrogenotrophic methanogenesis is the most common conversion pathway of hydrogen at anaerobic conditions (Wise et al., 1978). The following two Equations (8) and (9) were used to simulate methane production at shaking speed 100 and 300 rpm.

$$V_{CH_4} = \eta \frac{V^0_{H_2}}{4}(1 - e^{(-K_L at)}) \quad (8)$$

$$V_{CH_4} = \eta \frac{11.2 V_l X Y_{S/X} \mu_{max} t}{4} \quad (9)$$

The conversion efficiency of hydrogen to methane (η) were higher than 90%, indicating that the consumed hydrogen was almost stoichiometrically converted to methane (Table I) with only a minor fraction consumed for cell synthesis.

The profiles of hydrogen, propionate, and butyrate from batch experiment 2 are shown in Figure 2. At shaking speed 100 rpm under P_{H_2} 1 atm, both propionate and butyrate had similar degradation trends as control experiments, and no obvious inhibition by hydrogen was observed. However, based on thermodynamic considerations, degradation of propionate and butyrate needs very low hydrogen concentration (generally lower than 10^{-4} atm (Fukuzaki et al., 1990; Siriwongrungson et al., 2007)) to make the reactions (Equations 10 and 11) thermodynamically feasible. The absence of obvious inhibition of propionate and butyrate degradation observed in this experiment, could be explained by the slow mass transfer of H_2 from gas to the liquid phase, along with fast consumption of the dissolved hydrogen by hydrogenotrophic methanogens, a combination which would keep the dissolved hydrogen level adequately low for propionate and butyrate degradation (Fukuzaki et al., 1990). In contrast, no obvious degradation of propionate and butyrate was observed until the hydrogen was fully consumed at the shaking speed 300 rpm.

$$CH_3CH_2CH_2COOH + 2H_2O \rightarrow 2CH_3COOH + 2H_2 \quad \Delta G^0 = 45.4\,kJ/mol \quad (10)$$

$$CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + 3H_2 + CO_2 \quad \Delta G^0 = 72.7\,kJ/mol \quad (11)$$

The above results showed that lower mixing intensity is crucial to achieve hydrogen utilization without inhibiting propionate and butyrate degradation. For anaerobic reactors, lower mixing intensity or intermediate mixing was recommended considering the higher methane yield and stability of the process compared to higher mixing intensity (Kaparaju et al., 2008; Stroot et al., 2001). Low mixing intensity will also reduce the cost for the operation of full-scale anaerobic reactors. Besides, previous reports showed there were liquid–gas mass transfer limitations in anaerobic reactors. For example, the actual dissolved hydrogen concentration in a biomethanation process can be as much as 80-fold higher than the equilibrium value calculated from the P_{H_2} in the gas phase (Kuroda et al., 1991; Pauss and Guiot, 1993). However, the lower mixing intensity may result in lower hydrogen consumption rate. Therefore, it will be a challenge to obtain higher hydrogen consumption rate and at the same time avoid the inhibition of propionate and butyrate degradation. Close monitoring of VFA concentrations would provide early warning for process imbalance (Ahring et al., 1995). In case of starting accumulation of propionate and butyrate, inhibition can be prevented to progress further, by reducing hydrogen flow rate.

Both reactors A and B were started up at the same time, with manure as the only substrate. Steady-state was achieved in both reactors, after about 1.5 months (approx. three retention times) of operation. There was no significant difference of methane yields between reactors A and B during this period. The methane yields were around 200 mL/gVS, which was within normal range of 180–250 mL/gVS for cattle manure (Ahring et al., 2001; Kaparaju et al., 2008). Thereafter, hydrogen was added to reactor A at a flow rate of 28.6 (mL/(L/h)). Both reactors were operated for another 1.5 months until a new steady-state was achieved in reactor A. The results obtained at steady-states are summarized in Table II. In reactor A, 80% of the added hydrogen was consumed. The hydrogen consumption rate was around 22.8 (mL/(L/h)), which was close to the values obtained in batch experiment 1 at shaking speed 100 rpm. The result indicated there was gas–liquid mass transfer limitation in the anaerobic reactor. It was further demonstrated by the VFA distribution since there was only minor elevation of propionate and butyrate, even though the hydrogen gas phase concentration in the reactor was around 20% equivalent to $P_{H_2} = 0.2$ atm. The CO_2 content in the biogas of reactor A was only 15% which was significantly lower compared to that in reactor B (38%). The methane production rate in reactor A was 18.9 mL/(L/h), which was 22% higher than in reactor B. The following Equation (12) was used to calculate the theoretical methane production rate:

$$r_{CH_{4A}} = r_{CH_{4B}} + \frac{(r_{H_{2A}} - r_{H_{2D}})}{4} \quad (12)$$

The theoretical methane production rate in reactor A was calculated as 21.2 ± 1.1 (mL/(L/h)). ANOVA analysis showed that the methane production rate of 18.9 mL/(L/h) was significantly lower (10%) than the theoretical value. The missing 10% methane could be partly explained by the biomass production during methanogenesis. Additionally, the difference could have been due to the increased VFA

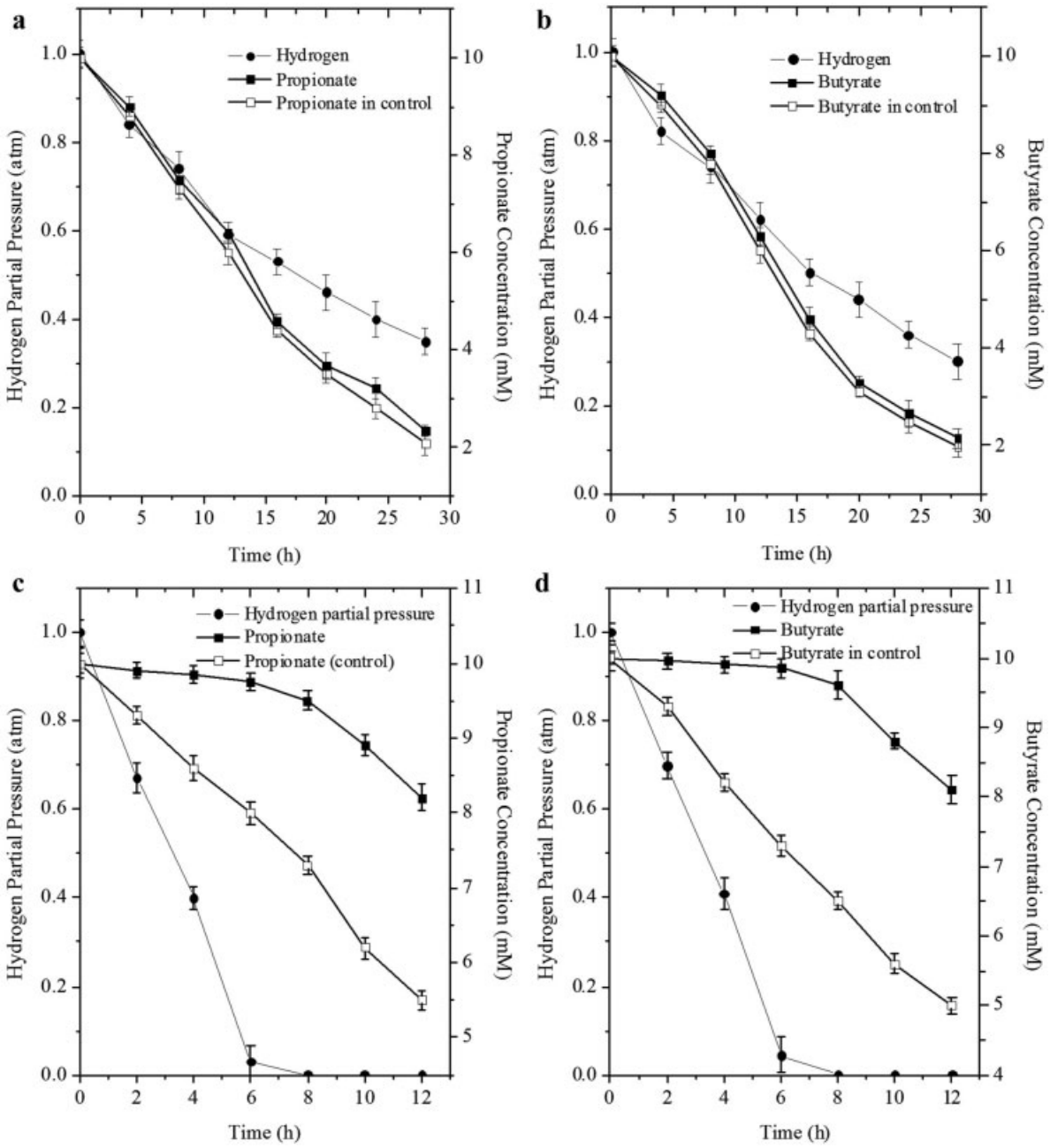

Figure 2. Variations of hydrogen, propionate, and butyrate with digestion time in batch experiment 2. **a**: Propionate degradation at shaking speed 100 rpm. **b**: Butyrate degradation at shaking speed 100 rpm. **c**: Propionate degradation at shaking speed 300 rpm. **d**: Butyrate degradation at shaking speed 300 rpm.

concentration in reactor A, especially acetate (Table II). By specific methanogenic activity (SMA) tests we demonstrated that the increased acetate concentration in reactor A was due to the slight inhibition of aceticlastic methanogenesis. The SMA results based on acetate were 25.6 mL CH_4/(L/h) for reactor A and 32.5 mL CH_4/(L/h) for reactor B. The inhibition could be attributed to the higher pH 8.3 in reactor A compared to pH 8.0 in reactor B. O'Flaherty et al. (1998) demonstrated that the optimal pH for the growth of aceticlastic methanogens were between 7.0 and 7.5, and the maximum growth rate of aceticlastic methanogens could decrease from 0.07 day^{-1} at pH 8.0 to around 0.04 day^{-1} at pH 8.3. The increase of pH was due to the consumption of bicarbonate by hydrogenotrophic methanogens, since the inorganic carbon (mainly bicarbonate at pH around 8) in the anaerobic reactor with addition of hydrogen (around 300 mg/L) was much lower that in the reactor without hydrogen (around 600 mg/l). The increased VFA

Table II. Profiles of gas and liquid phases during steady-state periods in the continuous experiments.

	Reactor A	Reactor B	Difference[a]
Biogas production (mL/(L/h))	29.1 ± 2	25.1 ± 1.8	*
Biogas composition			
CH_4 (%)	65 ± 3.3	62 ± 2.5	—
H_2 (%)	20 ± 2.5	0	*
CO_2 (%)	15 ± 2.1	38 ± 3.2	*
CH_4 production (mL/(L/h))	18.9 ± 0.9	15.5 ± 1.1	*
CO_2 production (mL/(L/h))	4.3 ± 0.6	9.5 ± 0.9	*
H_2 consumption (mL/(L/h))	22.8 ± 1.2	0	*
pH	8.3 ± 0.1	8.0 ± 0.1	*
Acetate (mM)	24 ± 0.93	7.2 ± 0.73	*
Propionate (mM)	4 ± 0.35	1.3 ± 0.25	*
Butyrate (mM)	0.8 ± 0.1	0.21 ± 0.08	*
NH_4^+ (g/L)	1.28 ± 0.21	1.21 ± 0.24	—

"—" Means not significant with $P > 0.05$.

[a] "Difference" means the significance of difference between reactor A and B by ANOVA analysis at $P = 0.05$ level.

*Means significant with $P < 0.05$.

concentration in reactor A compared to reactor B corresponded to about 1.3 mL/(L/h). If it was added to the total methane production from reactor A, 20.2 mL/(L/h) could be obtained, which was near to the theoretical value (only 4.7% difference).

The above results demonstrated that it was possible to convert hydrogen to methane in an anaerobic reactor. Moreover, reducing the content of CO_2 in the produced biogas may reduce the cost for biogas upgrading. Further study should be conducted to improve the hydrogen utilization efficiency by controlling pH and other process conditions (H_2 dispersion, mixing intensity, etc.). It could be expected that by decreasing pH to 7–8 in reactor A, the hydrogen utilization efficiency could be increased, the VFA elevation minimized, and the hydrogen and CO_2 content in the produced biogas could be decreased (O'Flaherty et al., 1998). Hydrogen could perhaps with advantage be added to anaerobic reactors together with other acidic organic wastes (e.g., stillage and household solid waste), which could probably maintain the pH between 7 and 8.

Materials and Methods

Batch Experiments

Two series of batch experiments were conducted. Batch experiment 1 aimed to investigate the effect of P_{H_2} on the conversion efficiency from hydrogen to methane under different mixing conditions. Hydrogen partial pressures of 0.25, 0.5, and 1 atm were tested. Inoculum was obtained from a lab-scale thermophilic biogas reactor treating cattle manure. One hundred eighteen milliliter of serum bottles were used as reactors. Forty milliliters of inoculum was added to each bottle. The bottles were then sealed with butyl rubber stoppers and aluminum crimps and purged with nitrogen for 10 min. The bottles were incubated in a rotary shaker at 55°C for 1 h. After that, different volumes of hydrogen were injected to the bottles to obtain different P_{H_2} (0.25, 0.5, and 1 atm). CO_2 was also injected into each bottle with 1/4 volume of the injected hydrogen, corresponding to the stoichiometric ratio according to Equation (1). Two different shaking speeds (100 and 300 rpm) were tested. Batch experiment 2 was carried out to investigate the effect of P_{H_2} on VFA degradation. The experiments were also conducted in 118 mL serum bottles with 40 mL inoculum. Butyrate and propionate were added to a final concentration of 10 mM. Initial pH was measured and adjusted to 8. P_{H_2} was set at 1 atm. The same experimental procedure was adopted as batch experiment 1 and two shaking speeds (100 and 300 rpm) were tested. Gas and VFA liquid samples were taken regularly. Both experiments were performed with triplicate bottles, and bottles containing only inoculum and propionate or butyrate without hydrogen were used as controls.

Continuous Experiments

Two identical 4.5 L continuously stirred tank reactors (CSTR) with working volume of 3.5 L were used. The reactors have previously been described (Kaparaju et al., 2008). Both reactors were filled with inoculum, which was digested manure from Snertinge biogas plant, in Denmark, operating under thermophilic conditions (55°C). Temperature in reactors was controlled at 55°C by recycling hot water through a water jacket surrounding the reactors. Raw cattle manure was sieved through a net with opening of 5 mm × 5 mm, in order to remove the largest particles to avoid blocking of the tubing, and used as feed. The TS content of the raw sieved manure was 6% and it was diluted with tap water to a final TS content of 3% (VS 2.6%) in order to facilitate pumping. The pH, ammonium, and total nitrogen of the diluted manure were 7.2 g-NH_4-N/L, 0.9 g-NH_4-N/L, and 2.1 g-N_{tot}/L, respectively. Sixty milliliters of diluted manure were pumped to each reactor four times per day giving a HRT of 14 days. Both reactors (A and B) were fed with only manure at identical operating conditions, until steady-state was established. Then, hydrogen was continuously added to Reactor A, while reactor B was operated as control, without hydrogen injection. The H_2 injection flow rate in reactor A was initially chosen to be around four times higher than CO_2 production rate in the reactor, corresponding to the stoichiometric ratio of H_2:CO_2 for production of CH_4 (Equation 1). After calibration, the hydrogen flow rate was 28.6 mL/(L/h). The hydrogen gas was injected to the bottom of reactor A, from a gas cylinder via a pressure regulation valve and a peristaltic pump. Hydrogen was entering the liquid phase through two ceramic gas diffusers to distribute the gas into small bubbles for better contact with the liquid. Continuous mechanical stirring at 65 rpm was used.

Specific Methanogenic Activity (SMA) Tests

When reactor A and B reached steady-state after hydrogen was added to reactor A, their content was tested for SMA, for specific substrates according to our previous study (Luo et al., 2011).

Analyses

The analytical methods for all parameters could be found in our previous study (Luo et al., 2010). Analysis of variance (ANOVA) at 0.05 level was used to analyze the data.

Nomenclature

V_{H_2}	hydrogen volume in the headspace (mL)
$P^*_{H_2}$	the hydrogen partial pressure equivalent to the dissolved hydrogen in the liquid phase at thermodynamic equilibrium (atm)
V_g	the volume of headspace (mL)
K_La	the global volumetric mass transfer coefficient for the bioreactor (h^{-1})
V_l	liquid volume (mL)
11.2	a coefficient for conversion of mass (2 g/mol for hydrogen) to volume (22.4 L/mol for hydrogen) (L/g)
μ_{max}	the maximum specific growth rate in the absence of inhibition (h^{-1})
S	the dissolved hydrogen concentration (g/L)
K_s	the growth saturation constant (g/L)
$Y_{s/x}$	the yield coefficient for cell production (g substrate/g cell)
X	the cell mass concentration (g/L)
$V^0_{H_2}$	the initial hydrogen volume (mL)
$r_{CH_{4A}}$	the theoretical methane production rate from reactor A (mL/(L/h))
$r_{CH_{4B}}$	the methane production rate from control reactor (reactor B) (mL/(L/h))
$r_{H_{2A}}$	the added hydrogen rate to reactor A (mL/(L/h))
$r_{H_{2D}}$	the hydrogen rate leaving reactor A with the produced biogas (mL/(L/h))
η	conversion efficiency of hydrogen to methane (%)

This study received support from Vestforsyning A/S. Gang Luo would like to thank for the financial support from the Shanghai Tongji Gao Tingyao Environmental Science & Technology Development Foundation. The authors would like to thank Hector Garcia for his technical assistance with the experiments.

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