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Parameters affecting acetate concentrations during in-situ biological hydrogen methanation

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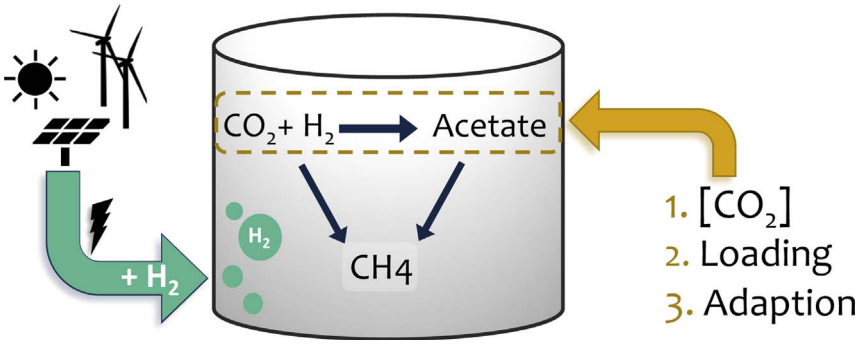
GRAPHICAL ABSTRACT



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ABSTRACT

Surplus electricity may be supplied to anaerobic digesters as H_2 gas to upgrade the CH_4 content of biogas. Acetate accumulation has been observed following H_2 injections, but the parameters determining the degree of acetate accumulation are not well understood. The pathways involved during H_2 consumption and acetate kinetics were evaluated in continuous lab reactors and parallel batch ^{13}C experiments. Acetate accumulation increased during initial H_2 injections as organic loading rate increased and CO_2 levels decreased below 7%. The share of CH_4 in H_2 and ^{13}C mass balances increased after repeated H_2 injections, which corresponded with the increase of *Methanomicrobiales* observed via qPCR. The organic loading rate, the inorganic carbon level and level of methanogen adaption hence determine acetate kinetics during biomethanation of H_2. The three identified parameters may form the base of a decision tool to assess acetate accumulation during H_2 injections to an anaerobic digester.

1. Introduction

The 2015 Paris Climate Agreement sets out a global action plan to keep global temperature increase below 2 °C. One of the key elements is the transition to a low-carbon society with an increased share of renewable power sources (United Nations, 2015). The European Union has set a binding target for renewable power sources to account for 27% of the energy demand in 2030 (European Council, 2014), while California will likely meet it's 2030 goal of 50% energy production by renewable sources in 2020 (California Public Utilities Commission,

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2017). An important challenge related to renewable sources such as wind and solar power is their inherently fluctuating character, resulting in periods with an imbalance between power production and demand. This jeopardizes a stable and secure operation of the power grid (Götz et al., 2016) and decreases the economic viability of renewable power producers. In Germany, the amount of hours with negative electricity prices nearly doubled in 2017 as compared to 2016 (Amelang and Appunn, 2018) demonstrating the growing demand for local electricity buffers (IEA Bioenergy Task 37, 2015). A potential storage strategy is biomethanation of surplus electricity to CH_4 by using the existing infrastructure of anaerobic digesters. Surplus electricity can be injected into anaerobic digesters in the form of H_2 gas, where the inherent microbial community readily converts it to CH_4, which can be stored or injected into the natural grid system (Luo and Angelidaki, 2012). Biomethanation of surplus electricity has sparked great interest amongst industry and academia and been the focus of intensive research. Biogas upgrading to a CH_4 content as high as > 95% has been achieved in both mesophilic and thermophilic set-ups using an in-situ or ex-situ H_2 injection configuration (e.g. Bassani et al., 2015a; Luo and Angelidaki, 2013; Rachbauer et al., 2016; Savvas et al., 2017; Strübing et al., 2017b) and three recent reviews give an overview of the biogas upgrading potential of biomethanation obtained in different reactor set-ups (Angelidaki et al., 2018; Lecker et al., 2017; Zabranska and Pokorna, 2018).

During biomethanation, the conversion of H_2 to CH_4 can happen directly via hydrogenotrophic methanogenesis (HM), or indirectly via homoacetogenesis (HA) followed by acetoclastic methanogenesis (AM, Table 1). Homoacetogens are a metabolic versatile community (Saady, 2013), but are generally outcompeted by hydrogenotrophic methanogens due to their lower H_2 affinity (Poehlein et al., 2012). The high H_2 levels caused by H_2 injections removes this disadvantage, and opens up the possibility for homoacetogenesis (Liu et al., 2016). During homoacetogenesis, CO_2 (apparent pKa = 6. 35) is converted to the stronger acetic acid (pKa 4.76). At a pH of 7.5 this pathway results in the release of 4.4 times more protons compared to protons consumed during hydrogenotrophic methanogenesis. A stimulation of homoacetogenesis in a reactor with limited buffering capacity or a set-up maximizing the gas-liquid contact surface may further enhance the acidifying effect of homoacetogenesis. The pH of a trickle bed reactor has been found to decrease to below 6 at increasing H_2 injection rates to a trickle-bed reactor, resulting in a sharp decline of the biogas upgrading rate (Strübing et al., 2017a). Similarly, acetate accumulation has been observed during H_2 injection rates at a 4:1 H_2:CO_2 ratio (Mulat et al., 2017) or higher ratios (Agneessens et al., 2017; Luo and Angelidaki, 2013). In contrast, other studies reported no or only a transient acetate accumulation at injection ratios ≥4:1 H_2:CO_2 (Bassani et al., 2015b; Rachbauer et al., 2016). Hydrogen injections hence seem to affect acetate kinetics during biomethanation, but the parameters steering this process are not well understood. If acetate accumulation during hydrogen injections remains below the reactor's acidification threshold, then acetate will merely act as a storage compound for H_2 and gradually be converted to CH_4. If the increase of acetate is however too sudden and pronounced, it may negatively affect the reactor performance due to a pH drop or inhibition of upstream processes and acetoclastic methanogenesis (Ahring et al., 1995; Dupla et al., 2004). Identifying the parameters that favor acetate accumulation during hydrogen injections is hence vital to ensure stable reactor performance and optimal biogas upgrading during biomethanation. This study therefore aimed to evaluate acetate kinetics during H_2 additions to an anaerobic digester, by identifying the microbial communities involved during the conversion of H_2 to ultimately CH_4 and the parameters that affect these communities. It was hypothesized that the sudden increase in H_2 levels, combined with the lower abundance of hydrogenotrophic methanogens, creates an opportunity for homoacetogens to convert the injected H_2 to acetate. Alternatively, if the microbial community receives H_2 injections on a regular basis, it was hypothesized that an upregulation of an adapted methanogen community would reduce the observed acetate accumulation.

Table 1
Gibbs free energy change of hydrogenotrophic methanogenesis (HM), homoacetogenesis (HA) and acetoclastic methanogenesis (AM) at standard and experimental conditions**.

Pathway	Reaction	ΔG^{0*}	$\Delta G_{high\ H_2,\ low\ CO_2}$	$G_{high\ H_2,\ high\ CO_2}$	$\Delta G_{low\ H_2,\ low\ CO_2}$	$\Delta G_{low\ H_2,\ high\ CO_2}$
		[kJ/mol]				
HM	$4\ H_2 + CO_2 \rightarrow CH_4 + 2\ H_2O$	−135.6	−114.3	−118.0	−76.6	−80.3
HA	$4\ H_2 + 2\ CO_2 \rightarrow CH_3COOH + 2\ H_2O$	−104.6	−88.6	−93.0	−50.9	−55.3
AM	$CH_3COOH \rightarrow CH_4 + CO_2$	−31.0	−27.9	−24.3	−27.9	−24.3

* Calculated at standard conditions at 25 °C and pH 7.

** Initial experimental conditions amounted to temperature = 38 °C, p_{CH4} = 0.17 bar, $[CH_3COO^-]$ = 2.84 mM, high p_{H2} = 0.38 bar, low p_{H2} = 0.01 bar, high p_{CO2} = 0.40 (30% of headspace), low p_{H2} = 0.09 bar (7% of headspace), pH = 7.8 and 8.36 at high and low p_{CO2}, respectively.

2. Material and methods

2.1. Lab-scale reactor set up

Sludge was collected from a mesophilic, manure-based biogas plant (Bånlev, Denmark) operated at 38–40 °C and a hydraulic retention time (HRT) of 21 days. The sludge was sieved over a 0.8 mm sieve to remove large particles and avoid obstructions in the experimental set-up. The pH, dry matter content (DM) and volatile solids content (VS) of the sieved sludge was 7.9 ± 0.1, 3.7 ± 0.2% on a fresh matter base, and 2.2 ± 0.1% on a fresh matter base. The sludge was used as inoculum for six 1.4 L lab reactors with a working volume of 0.3 L. The temperature and hydraulic retention time (HRT) of the lab reactors were set at respectively 38 °C and 20 days to reflect the full-scale reactor conditions. The remainder of the collected sludge was stored at −20 °C. Before feeding it to the lab reactions, it was thawed and mixed with finely ground straw (< 0.5 mm particle size). This straw was added to compensate for it's removal during sieving of the sludge. The reactors were fed semi-continuously every 24–48 h at an organic loading rate (OLR) of 0.5, 1.5 or 2.0 g VS/L_{sludge}/day. The reactor headspace was flushed with a gas mixture (60% CH_4, 30% CO_2, 10% N_2) or with pure N_2 to obtain headspace CO_2 levels > 25% or < 7%, respectively.

Pulsed H_2 injections were started after at least 8 days during which the variation in biogas production was smaller than 10% after changing the OLR or CO_2 levels. The H_2 gas was pulse injected directly into the headspace of the reactors at a rate of 1.3 L_{H2}/L_{sludge}/d. To maximize the contact between the sludge and the H_2 gas in the gas phase 0.3L of sludge was added to 0.15 m broad bottles, resulting in a 1:10 surface to volume ratio. The sludge was stirred intensely at 450 rpm to further minimize gas-liquid mass transfer limitations. The headspace overpressure was released 24 h after a H_2 injection to avoid buildup of overpressure above 0.7 bar due to biogas production. Hydrogen was injected 2–3 times per week.

2.2 Stable isotope analysis.

To evaluate the pathways involved during H_2 consumption a parallel experiment was set up, measuring the incorporation of $NaH^{13}CO_3$ into CH_4 or acetate following a H_2 injection. To identify the contribution of homoacetogenesis to H_2 consumption, the inhibitor fluoromethane (CH_3F) was added to avoid the acetoclastic conversion of acetate to CH_4. As the use of an inhibitor can disturb the prevailing