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# Effect of operating pressure on direct biomethane production from carbon dioxide and exogenous hydrogen in the anaerobic digestion of sewage sludge

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## HIGHLIGHTS

- In-situ $CO_2$ biomethanation improved with increasing operating pressure.
- Exogenous $H_2$ was fed to an anaerobic sludge digester with stepwise pressure increase.
- $H_2$ conversion reached 99% as driving force for gas-liquid mass transfer increased.
- Biomethane concentration increased with pressure, up to 95.2% at 300 kPa.
- Neutral pH was attained without persistent volatile fatty acids accumulation.

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## ABSTRACT

The development of biological Power-to-Methane in-situ technologies aimed at producing biomethane directly in a single anaerobic digestion unit by the supply of external hydrogen, find its limiting step in the gas-to-liquid mass transfer of poorly soluble hydrogen. Increasing the operating pressure with an exogenous hydrogen supply could enhance transfer rates of hydrogen and carbon dioxide (enriching gas phase with methane) and simultaneously control the liquid media pH because the methanation of hydrogen and carbon dioxide prevents the acidification caused by carbon dioxide/bicarbonate equilibrium displacement. Thus, the feasibility of operating the anaerobic digestion of sludge at a pressure higher than the atmospheric pressure with an exogenous hydrogen supply to improve the solubilisation of hydrogen and subsequent bioconversion of hydrogen and carbon dioxide into methane by methanogenic *archaea* was studied. A mesophilic sludge digester (35 L) was operated at variable absolute pressure up to 300 kPa. Hydrogen was continuously supplied through the sludge recirculation stream, coupled to a static mixer. Hydrogen conversion increased with the operating pressure (up to 99%), and the methane concentration in the digester off-gas averaged 92.9 ± 2.3% at 300 kPa (maximum of 95.2%). pH approached 7 under such conditions, and the efficiency of organic matter removal was similar to that observed during conventional anaerobic digestion at atmospheric pressure without a detrimental accumulation of volatile fatty acids. This study confirmed that increasing the system pressure (mass transfer driving force) can be a viable alternative to high energy-consuming mixing methods to enhance the hydrogen gas-liquid mass transfer.

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# 1. Introduction

## 1.1. Anaerobic digestion, biogas production and utilisation

Biomass is one of the largest sources of carbonaceous material available to produce renewable energy. Anaerobic digestion (AD) is a popular method for waste treatment that produces biogas and stabilises organic waste into a digested biomass that can find uses as fertiliser and for soil reclamation. Biogas is regarded as an alternative renewable energy source and can be considered to be carbon-neutral [1–3]. In 2016 the biogas production in the EU was equivalent to 16,000 ktoe which corresponds to approximately 8% of the total primary energy produced by renewable energy sources. This biogas is produced in plants of varying sizes ranging from 2 kW to 20 MW [4].

Based on the chemical composition of the substrate and pH of the digester, biogas is a mixture of $CH_4$ (50–70%) and $CO_2$ (30–50%), with low concentrations of $H_2S$, $N_2$, $O_2$, $NH_3$, CO, siloxanes and volatile organic compounds (VOCs) [5]. The high $CO_2$ content limits the uses of biogas that in practice are restricted to the production of heat and electricity. Combined Heat and Power (CHP) engines are commonly used to produce electricity with efficiency above 40%, depending on the type of gas engines and size. Biogas played a pivotal role in producing 61 TWh (219 PJ) of electrical energy within the European Union (EU), and in 2015 about 26.6 PJ heat energy was distributed to the district heating networks [4].

The new policies put in place to mitigate the environmental impact of the use of fossil fuels are hinged on the use of alternative renewable energy sources. The EU has ambitiously pronounced the goal of creating a competitive low carbon economy realising between 80% and 95% GHG emission reduction by 2050. Moreover, the production of alternative renewable energy sources can be between 55% and 75% of gross final energy use [6].

To expand the potential uses of biogas, it is imperative to implement upgrading technologies to improve its characteristics and turn it into a product with more valuable uses. As a means to upgrade biogas to fuel of high calorific value, there are two major technologies, those that eliminate $CO_2$ and those that transform (valorise) it, preferably into methane. The leading $CO_2$ removal physical/chemical established technologies are water scrubbing, organic solvents or chemical solutions, pressure swing adsorption, membrane separation and cryogenic $CO_2$ separation. These removal technologies dominate the biogas upgrading processes nowadays although they have both economic and environmental limitations; in particular, the evacuation to the atmosphere of between 1 and 2% of the methane fed in the process.

The biological $CO_2$ valorisation process is based on $CO_2$ transport from the bulk of the biogas to a microbial medium followed by different pathways of autotrophic uptake of $CO_2$. $CO_2$ can be used as a substrate for the growth of photosynthetic microalgae, which can later be used as a feed for the generation of biofuels or valuable products [5,7]. Alternatively, a biological reduction of $CO_2$ to $CH_4$ can be performed through $H_2$ injection into a bioreactor rich in *archaea* (hydrogenotrophic methanogenesis). To produce biomethane, a two-stage process is carried out: Firstly, $H_2$ is generated by electrolysing water using surplus electricity and, secondly, the yielded $H_2$ is injected to the anaerobic bioreactor to react with $CO_2$ in the biogas to produce $CH_4$.

The latter technology has been eased by the increasing implementation of renewable energy production technologies, particularly solar and wind power. One of the limitations of these technologies is the difficulty encountered in storing excess electrical energy during peak production periods. The storage of electrical energy can be achieved in the form of chemical energy. Thus, the aim of different Power to Gas (PtG) processes is to link the power grid to the gas grid by the conversion of excess power into gas which meets the legislative gazetted gas quality to be injected into the grid. Reviews highlighting the essence of PtG technologies for dealing with renewable energies can be found elsewhere [8–9]. One of the main ways of converting electricity into gas is based on the conversion of biogas into biomethane.

## 1.2. Biological $CO_2$ methanation

Biological Power to Methane (PtM) processes are based on the reaction (Eq. (1)):

$$CO_{2\,(g)} + 4\,H_{2\,(g)} \rightarrow CH_{4\,(g)} + 2\,H_2O_{\,(g)}\ \Delta G = -165\ \mathrm{kJ\ mol^{-1}} \tag{1}$$

When hydrogenotrophic methanogenic archaea perform this exergonic reaction, it is known as the biological $CO_2$-methanation process [10]. From an energetic point of view, the stoichiometry of the reaction is adverse because 2 mol of $H_2$ are lost to form 2 mol of $H_2O$; in fact, from 4 mol of $H_2$ only form 1 mol of $CH_4$. Taking into account the combustion heats of $H_2$ ($\Delta H^0{}_C = -286$ kJ mol$^{-1}$) and $CH_4$ ($\Delta H^0{}_C = -889$ kJ mol$^{-1}$), the formation of 1 mol of $CH_4$ from 4 mol of $H_2$ represents a loss of 22% of the $H_2$ energy potential.

Biogas from AD is the natural source of $CO_2$ for biological conversion to $CH_4$; thus, biogas can be upgraded to biomethane whose characteristics and composition can meet the legislative quality required to be injected in the grid and considered as a substitute of natural gas [9]. Most applications are conducted in "ex-situ" using an external biological reactor that is fed with a mixture of $H_2$ and biogas that exits the digester [11–13]. At the lab-scale $CH_4$ formation rates (MFR) up to 40 L $L_R^{-1}$ $d^{-1}$ have been reported in plug-flow bioreactors [14]; at this rate, effective integration of ex-situ upgrading was estimated in WWTP [15]. Nonetheless, at pilot and demo scales, long-term and stable production was achieved only in biotrickling filters at MFR of 3.1 L $L_R^{-1}$ $d^{-1}$ [11].

## 1.3. In-situ biomethane production by $H_2$ supply to the anaerobic digester

In recent years, "in-situ" systems in which $H_2$ is directly injected into the anaerobic digester so that *archaea* directly utilise $H_2$ to deplete $CO_2$ from the biogas have been applied at laboratory or pilot scale. With an efficient conversion, biomethane could be directly produced from the digester or after refining in an ex-situ stage [16]. The gas-to-liquid mass transfer has been reported to be the limiting step of the process in increasing the purity of biomethane to 55–96% [17].

The first experimental work in which $H_2$ is directly charged into the bioreactor was carried out in 2012 at laboratory scale, in batch operation mode, and thermophilic (55 °C) range [18]. The initial results were modest, the $CH_4$ production rate was 22% higher in comparison to the control digester, and $CO_2$ composition in the biogas was reduced to 15%, while the control system reported 38%. Also in 2012, it was demonstrated that the additional supply of $H_2$ had an encouraging effect on the methanogenesis, but had no properly defined effect on the acetogenic process. The $H_2$ injection mechanism (diffusers with different pore sizes) and the degree of liquid mixing were shown to have an impact on the gas-liquid mass transfer of $H_2$ and the biogas content. The $CH_4$ concentration increased from 55 to 75% [19].

A continuous setup composed of two-stage reactors was presented in [20]. Biogas was upgraded to an average methane composition of 89% in the mesophilic digester and 85% in the thermophilic. The upsurge of hydrogenotrophic methanogenic microbes and syntrophic *Desulfovibrio* and the reduction of acetoclastic methanogens showed an $H_2$-mediated shift towards the hydrogenotrophic pathway improving biogas upgrading. A similar behaviour revealing the shift toward the hydrogenotrophic pathway and the significant effect on reactor performance of the $H_2$: $CO_2$ ratio to avoid process instability were the main conclusions presented in [21]. Keeping the topic of $H_2/CO_2$ ratio, the systematic isotope analysis presented in [22] showed that surplus $H_2$ injection caused an increase in dissolved $H_2$ to a thermodynamic limit that inhibits the decomposition of VFA and stimulates homoacetogens for the generation of acetate from $CO_2$ and $H_2$.

Maintaining continuous operation, the setup operated in [20] comprised of a granular digestor coupled to a separate chamber in which

$H_2$ was added. To bolster gas-liquid mass transfer, the recirculated liquid and gas, and chamber orientation were optimised, $CO_2$ composition in the biogas dwindled from 42 to 10%, and the end product was upgraded from 58 to 82% methane composition.

Conversely, pH increase was noted in several studies (8–9) due to the consumption of bicarbonate [16,18,23–25], and eventually, VFA accumulation and inhibition of methanogenesis. The acid-base equilibrium between dissolved $CO_2$ and $HCO_3^-$ at pH around 7, in which AD naturally occurs (Fig. 1.a), is altered by exogenous $H_2$ supply. $CO_2$ consumption in Eq. (1) causes a decrease in dissolved $CO_2$ concentration and the subsequent displacement of acid-base equilibrium with $HCO_3^-$ (Eq. (2)), consuming protons, and increasing pH (Fig. 1.b).

$$CO_{2(aq)} + H_2O \leftrightarrow HCO_3^-{}_{(aq)} + H^+{}_{(aq)} \tag{2}$$

The only real-scale study was carried out in a 1.110 $m^3$ thermophilic digester treating manure, and a conventional Venturi device was used to inject by pulses the exogenous $H_2$ [26]. The performance was very modest, reaching an $H_2$ consumption rate of 15 $LH_2\ m^{-3}{}_r\ h^{-1}$ and consuming only 26% of the injected $H_2$. In this sense and also for an in-situ system with pulse $H_2$ addition, [27] underlines the relevance of methanogen adaption.

### *1.3.1. Driving-force oriented mass transfer of $H_2$ by increasing the operating pressure*

The low solubility of $H_2$ in water and poor mass transfer from the gas to the liquid phase is the limiting-step for the conversion. The rate of $H_2$ transferred to the liquid phase can be described as:

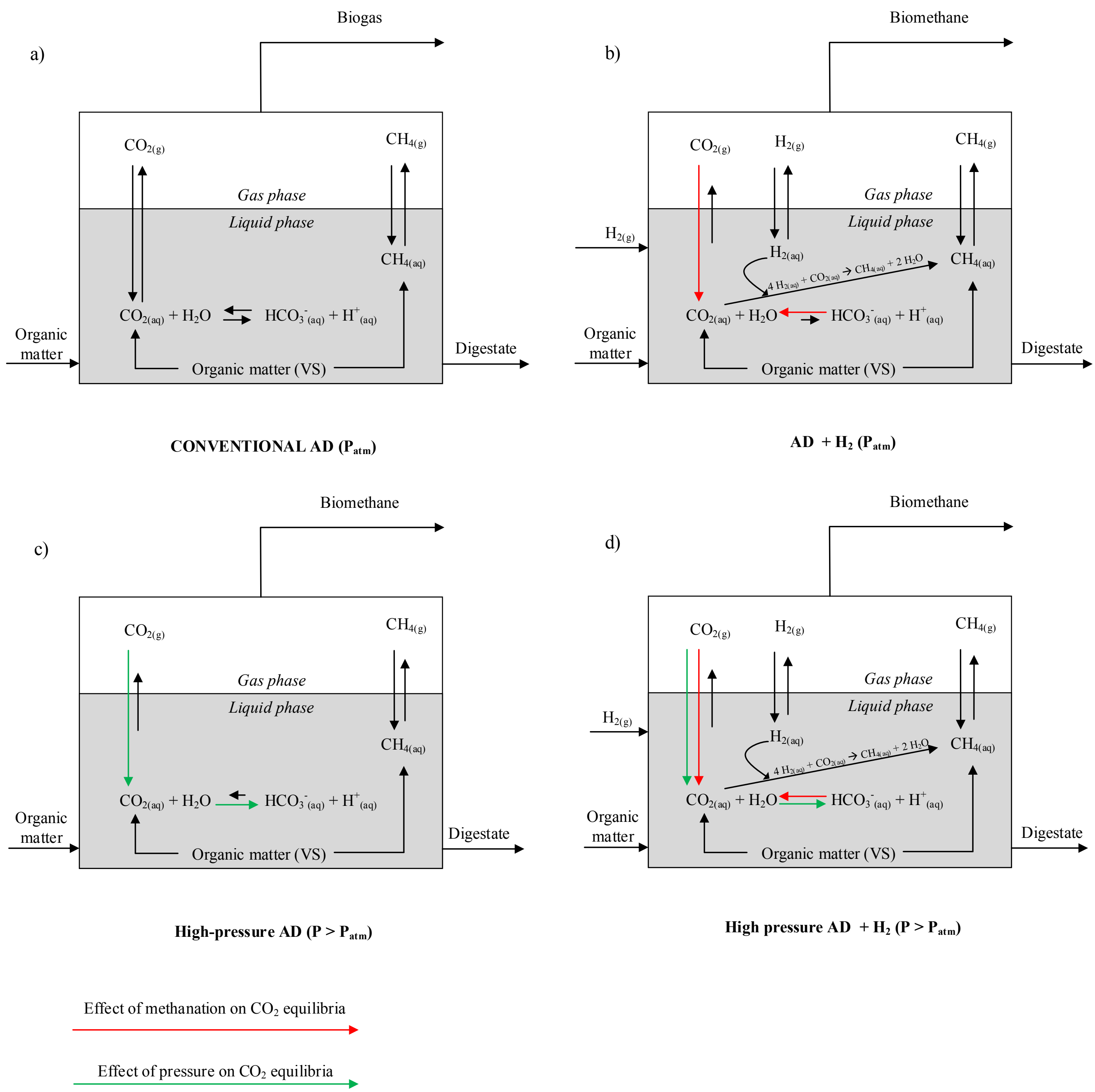


**Fig. 1.** Effect of pressure and exogenous $H_2$ supply on gas-liquid and acid-base equilibria of $CO_2$. a) Conventional AD at atmospheric pressure. b) Equilibria displacement by methanation of $H_2$ and $CO_2$ at atmospheric pressure. c) Equilibria displacement by increasing operating pressure. d) The combined effect on $CO_2$ equilibria of methanation and increased operating pressure.

$$r_{H2} = V\,k_La\,(P_{H2,G}/H - c_{H2,L}) \tag{3}$$

where $r_{H2}$ is the molar rate of $H_2$ transferred to the liquid phase (mol $h^{-1}$), V is the volume of the reactor (L), $k_La$ is the specific mass transfer coefficient for $H_2$ ($h^{-1}$), $P_{H2,\,G}/H$ is the concentration of $H_2$ (mol $L^{-1}$) in the gas-liquid interphase in equilibrium with the gas phase according to Henry's Law ($H_{H2}$ (35 °C) = $7.5 \cdot 10^{-5}$ mol $L^{-1}$ $atm^{-1}$) and $C_{H2,\,L}$ is the concentration of dissolved $H_2$ in the global liquid phase (mol $L^{-1}$). For a given volume of reaction, the rate of $H_2$ can be increased, whether by increasing the mass transfer coefficient or by increasing the partial pressure of $H_2$ in the bioreactor.

As mentioned in Section 1.3, several studies have shown different approaches to facilitate biomethanation of $H_2$ and $CO_2$ by increasing the specific mass transfer coefficient; nonetheless, there is a knowledge gap regarding the effect of the concentration gradient. On this subject, a higher operating pressure increases the concentration gradient (driving force for gas-to-liquid mass transfer) and, thus, the solubility of gases in water. The solubility of $CO_2$ ($H_{CO2}$ (35 °C) = $2.7 \cdot 10^{-2}$ mol $L^{-1}$ $atm^{-1}$) is notably more significant than that of $CH_4$ ($H_{CH4}$ (35 °C) = $1.2 \cdot 10^{-3}$ mol $L^{-1}$ $atm^{-1}$); then, an increase in the operating pressure can directly enrich biogas in $CH_4$ (Fig. 1.c). This was confirmed in [28]; where high-pressure (up to 1100 kPa) AD of acetate was accompanied by an enhancement in the concentration of $CH_4$ (74–86%) in the off-gas, owing to the greater solubility of $CO_2$, at the expense of a lower pH ·(3–5). Further, an increase in the operating pressure also can improve $H_2$ mass transfer to the liquid phase by increasing $P_{H2}$ (Eq. (3)). This has been confirmed in the biological methanation carried out in pressurised single-culture CSTRs [29] and biotrickling filters [11,30], performed in a separate unit (ex-situ upgrading).

### 1.4. Objectives, experimental hypothesis and novelty

This study aims to evaluate the feasibility of producing biomethane from a digester of sewage sludge supplied with $H_2$ at operating pressures higher than the atmospheric pressure. In this regard, an increase in the operating pressure of AD with exogenous $H_2$ supply can synchronously increase the driving force for $H_2$ mass transfer (Eq. (3)) and, hypothetically, counteract the expected decrease in pH because of $CO_2/HCO_3^-$ equilibrium displacement (Eq. (2)) with a larger $H_2$ rate transferred to convert $CO_2$ into $CH_4$ according to Eq. (1) (Fig. 1.d).

Reported studies on exogenous $H_2$ injection to anaerobic digesters have focused on increasing the specific mass transfer coefficient to ease the solubilisation of $H_2$ at atmospheric pressure while the effect of increasing the concentration gradient of $H_2$ at high pressure remains unexplored in anaerobic digesters; no in-situ studies have been reported about combined $H_2$ supply and pressure increase. If feasible, a new pathway to apply the Power-to-Methane concept could be developed and optimised, in which mass transfer of $H_2$ does not rely on high energy-demanding methods to increase the specific mass transfer coefficient, hence reducing the parasitic energy consumption in $CO_2$-methanation and improving energy conservation.

## 2. Materials and methods

### 2.1. Experimental setup

The digester had a cylindrical configuration (OD: 315 mm and H: 800 mm), built of high-density polyethene (PE100 PN10, AENOR-N 001/34 UNE EN 12201) with a working volume of 35 L (total volume of 48 L). The digester was insulated with polystyrene while the temperature was regulated and maintained using electric resistance coiled between the walls of the digester and the insulation material. Mixing was achieved by recirculating the sludge from the midpoint height to the bottom of the digester. $H_2$ flowrate was controlled with a mass flow controller (GFC Aalborg, USA) and injected through the sludge recirculation stream. A static mixer (1/2-40C-4-12-2 Koflo, USA) was installed after the $H_2$ dosing point to avoid the formation of large $H_2$ bubbles (Fig. 2). The operating pressure was controlled with an electrovalve (N263DVC M&M international, Italy) embedded in the headspace of the digester and a gauge pressure probe (Cerabar PMC21 Endress Hausser. Switzerland). A vessel (3L) was used for gas expansion at the outlet of the digester.

### 2.2. Operating conditions

The digester was inoculated with anaerobic sludge from the WWTP of Valladolid (Spain). Inoculum presented a pH of 7.1 and the following concentrations: VS = 1.0% w., Total alkalinity = 4400 mg $CaCO_3$ $L^{-1}$, TKN (Total Kjeldahl Nitrogen) = 1648 mg $L^{-1}$, N-$NH_4^+$ = 725 mg $L^{-1}$. The digester was operated under mesophilic conditions (35 ± 1 °C) and fed semi-continuously with mixed sludge, periodically collected from the same WWTP. Mixed sludge, from the primary clarifier and activated sludge, showed a variable concentration of organic matter according to seasonal changes, VS concentration was 1.3–2.8% (w.) and total COD between 19.9 and 45.4 g $L^{-1}$ during the study. Feeding and discharge pumps were activated four times per day to achieve an HRT of 20 d. Mixing was provided by sludge recirculation at a rate of 20 L $L_r^{-1}$ $d^{-1}$.

The experiment consisted of 4 stages (I, II, III, IV) governed by the increasing operating pressures and $H_2$ rates (Table 1). The pressure was increased until an average CH4 concentration in the off-gas was larger than 90%. HRT was fixed, and OLR varied (between 0.80 and 1.31 gVS $L_r^{-1}$ $d^{-1}$) based on the concentration of collected raw sludge. After a setup period of 12 d at ~150 kPa, the pressure was increased to 200 kPa in stage I, 250 kPa in stage II, and 300 kPa in stage III at a fixed $H_2$ rate of 0.45 NL $L_r^{-1}$ $d^{-1}$. In stage IV, the pressure was kept at 300 kPa, and $H_2$ flowrate was raised to 0.64 NL $L_r^{-1}$ $d^{-1}$. $H_2$ flowrate was below the stoichiometric requirement for the full conversion of expected $CO_2$ during the whole experiment.

### 2.3. Monitoring

The experiment was monitored as follows: gas leaving the digester passed through an expansion vessel to measure daily flowrate by the liquid displacement method at atmospheric pressure. Gas composition ($CH_4$, $CO_2$, and $H_2$) was measured daily by GC-TCD (3800 VARIAN, USA), as reported elsewhere [31]. VFA concentration in digested sludge was determined weekly by GC-FID [32]. pH was monitored online with a probe (5364 Crison, Spain), and VS content, TKN, and N-$NH_4^+$ in raw and digested sludge were weekly measured by using Standard Methods [33]. The total alkalinity of the inoculum and the total COD of raw sludge were also determined by Standard Methods [33].

### 2.4. Calculations

The calculations performed to estimate the mass flowrate of $CH_4$ in the effluent stream assumed an ideal equilibrium according to Henry's law and a dimensionless Henry's constant of $1.2 \cdot 10^{-3}$ mol $L^{-1}atm^{-1}$ at 35 °C [34].

The specific mass transfer coefficient of $H_2$ was calculated according to Eq. (3), where $P_{H2,G}$ was assumed to be the operating pressure in every stage of the study; since pure $H_2$ was supplied through the sludge recirculation stream, bubbles of pure $H_2$ were assumed to bubble up in the digester while mass transfer occurred. The amount of $H_2$ transferred from the gas headspace to the liquid phase was neglected because of the low $H_2$ concentration and the lack of gas recirculation for mixing. Dissolved $H_2$ concentration ($C_{H2,\,L}$) was also neglected assuming that kinetics of Eq. (1) did not limit the $CO_2$-methanation process. Molar rate of $H_2$ transferred to the liquid phase ($r_{H2}$, mol $h^{-1}$) was calculated as the difference between $H_2$ molar supply rate ($\dot{n}_{H2,IN}$, mol $h^{-1}$) and the molar rate of $H_2$ leaving the digester ($\dot{n}_{H2,OUT}$, mol $h^{-1}$) (Eq. (4)):

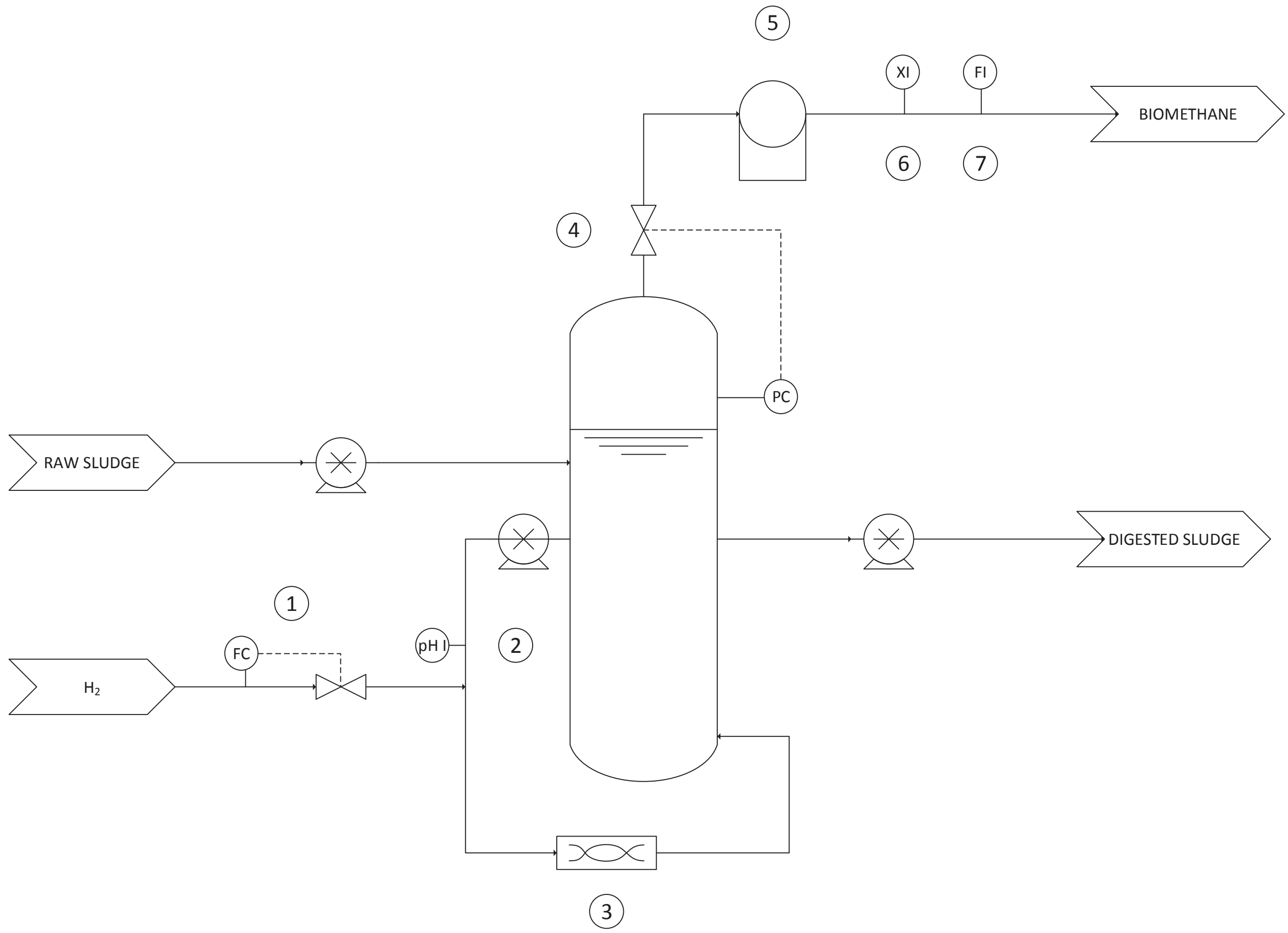


**Fig. 2.** Process flow diagram of the experimental setup. 1. $H_2$ Mass flow controller, 2. pH probe, 3. Static mixer, 4. P control valve, 5. Gas expansion vessel, 6. Gas sample point, 7. Gas flowmeter.

**Table 1**
Overview of operating conditions and biomethane production during the experiment.

| Stage | I | II | III | IV |
|---|---|---|---|---|
| Time (d) | 12 | 61 | 117 | 158 |
| Absolute pressure (kPa) | 200 ± 10 | 250 ± 10 | 300 ± 10 | 300 ± 10 |
| $H_2$ flowrate (NL $L_r^{-1}$ $d^{-1}$) | 0.45 | 0.45 | 0.45 | 0.64 |
| Average OLR (gVS $L_r^{-1}$ $d^{-1}$) | 0.92 ± 0.23 | 0.80 ± 0.15 | 1.31 ± 0.08 | 1.20 ± 0.18 |
| Average gas productivity (NL $L_r^{-1}$ $d^{-1}$) | 0.44 ± 0.10 | 0.36 ± 0.06 | 0.51 ± 0.12 | 0.54 ± 0.06 |
| Average gas composition (% v.) | | | | |
| $CH_4$ | 69.4 ± 5.8 | 79.7 ± 3.7 | 85.7 ± 4.1 | 92.9 ± 2.3 |
| $CO_2$ | 15.2 ± 4.0 | 12.8 ± 1.6 | 12.6 ± 3.0 | 6.3 ± 2.4 |
| $H_2$ | 15.4 ± 5.1 | 7.5 ± 3.1 | 1.8 ± 2.5 | 0.8 ± 0.3 |

$$rH2 = \dot{n_{H2,IN}} - \dot{n_{H2,OUT}} \tag{4}$$

The efficiency of $H_2$ conversion ($\eta_{H2}$, %) was calculated through Eq. (5):

$$\eta_{H2} = \frac{\dot{n_{H2,IN}} - \dot{n_{H2,OUT}}}{\dot{n_{H2,IN}}} \hat{A}\cdot 100 \tag{5}$$

Data from [23] was pegged as the reference for conventional AD to establish comparisons; a lab-scale digester (20 L) inoculated and fed with sludge from the same WWTP, operated at mesophilic conditions, at the same HRT to this study (20 d) and an average OLR of 1.3 ± 0.2 gVS $L_r^{-1}$ $d^{-1}$ during the 119 d period. A biogas productivity of 0.65 ± 0.16 NL $L_r^{-1}$ $d^{-1}$ or 0.50 ± 0.12 L $gVS_{fed}^{-1}$ (65.7% $CH_4$ and 34.3% $CO_2$) and a VS removal efficiency of 48.2 ± 7.5% were recorded. $H_2$ concentration in the biogas was below the detection limit during the whole period. To elucidate whether VS removal efficiency was different in this experiment with respect to the reference AD, an unequal variances *t*-test (one tail) was applied in Microsoft Excel to compare the averages of both samples at a confidence level of 95% ($\alpha = 0.05$). Atmospheric pressure considered for calculations (1 atm).

## 3. Results and discussion

### 3.1. Consumption of $CO_2$ to biomethane-rich gas

During the experiment, the concentration of $CH_4$ in the off-gas increased with operating pressure at a constant $H_2$ supply rate (stages I, II and III) as shown in Fig. 3; from an average 69.4% at 200 kPa (stage I) to 79.7% at 250 kPa (stage II) and 85.7% at 300 kPa. Contrarily, $CO_2$ and $H_2$ concentrations dropped accordingly (Table 1). The drop was relatively larger in the $H_2$ concentration than that observed in $CO_2$; this is a consequence of the stoichiometry of the $CO_2$-methanation reaction (Eq. (1)) which requires 4 mol of $H_2$ to convert 1 mol of $CO_2$. Given the fact that a constant $H_2$ flowrate was supplied during stages I to III, the increase in the operating pressure resulted in a higher $CH_4$ concentration and lower $CO_2$ and $H_2$ concentrations.

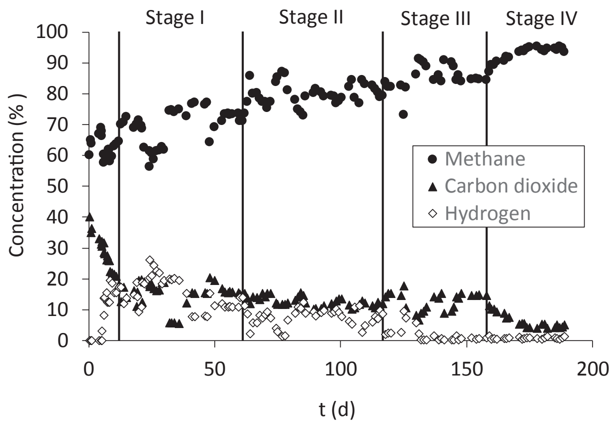


**Fig. 3.** Evolution of the gas composition.

A lack of $H_2$ for further $CO_2$ conversion was detected at stage III; $H_2$ concentration averaged 1.8% while $CO_2$ concentration was 12.6% (Table 1). $H_2$ was clearly the limiting reactant for higher $CO_2$ removal; then, $H_2$ supply rate was increased in stage IV to 0.64 NL $L_r^{-1}$ $d^{-1}$. Consequently, $CH_4$ concentration reached an average concentration of 92.9% during stage IV and a maximum of 95.2%.

Then, biomethane with a $CH_4$ concentration up to 95% in a digester of sludge operating at an absolute pressure of 300 kPa was obtained. Increasing the operating pressure could be advantageously used to improve the overall $H_2$ transference to the liquid phase. Due to this, an upsurge in the operating pressure brought about a positive effect on the efficiency of $H_2$ conversion ($\eta_{H2}$). During stage I, $\eta_{H2}$ was, on average, 78.8 ± 8.4% and increased to 91.0 ± 4.5%, 97.1 ± 4.3% with operating pressure in stages II and III, respectively. When $H_2$ flowrate was increased in stage IV, the $\eta_{H2}$ observed was 99.0 ± 0.4%.

Total gas productivity in the digester (Fig. 5) was mainly affected by two factors. Firstly, OLR, which was variable during the study according to the VS concentration in raw sludge as in full-scale sludge digesters and, secondly, the efficiency of the conversion of $H_2$ and $CO_2$ to $CH_4$ (Fig. 4). In this regard, greater gas productivity can be expected when OLR increases (OLR was higher in stages III and IV than in stages I and II) and, additionally, a more significant $\eta_{H2}$ causes a reduction in the total gas production rate because 5 mol of gases (4 mol of $H_2$ and 1 of $CO_2$) produce only 1 mol of $CH_4$ (Eq. (1)). In contrast, the flowrate of $CH_4$ is increased both by increasing OLR and $\eta_{H2,}$ and this was the trend observed during the study. From an average $CH_4$ flowrate of 0.30 ± 0.07 $NL_{CH4}$ $L_r$ $d^{-1}$ in stage I, a similar flowrate (0.29 ± 0.05 $NL_{CH4}$ $L_r$ $d^{-1}$) was detected in stage II despite the greater $\eta_{H2}$ presumably because of a slight decrease in OLR. Later, $CH_4$ flowrate increased to 0.43 ± 0.10 $NL_{CH4}$ $L_r$ $d^{-1}$ in stage IV and to 0.50 ± 0.06 $NL_{CH4}$ $L_r$ $d^{-1}$ because of both the higher OLR and $\eta_{H2}$ observed.

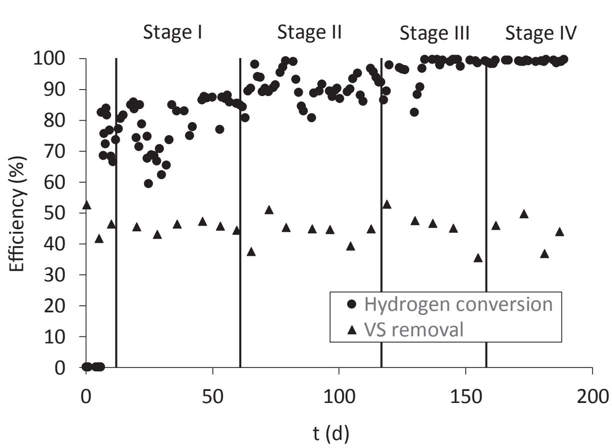


**Fig. 4.** Efficiencies of $H_2$ conversion and organic matter removal.

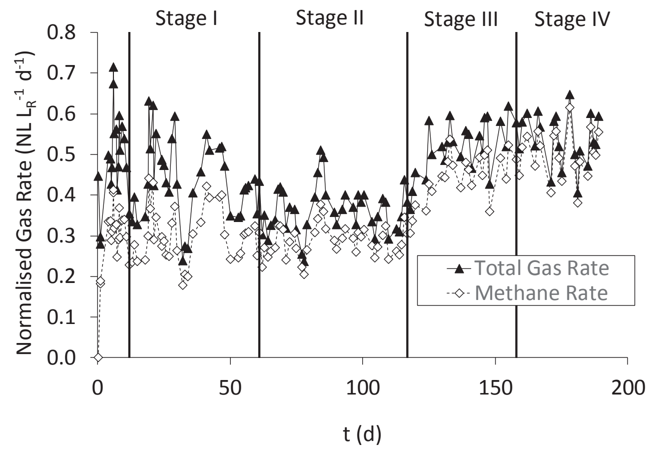


**Fig. 5.** Normalised gas productivity during the experiment.

The average gas productivity during stage IV was 0.54 ± 0.06 NL $L_r^{-1}$ $d^{-1}$, lower than that observed during the reference conventional AD at atmospheric pressure (0.66 ± 0.16 NL $L_r^{-1}$ $d^{-1}$); however, $CH_4$ productivity (0.50 ± 0.05 $NL_{CH4}$ $L_r^{-1}$ $d^{-1}$) was 16% higher than that of conventional AD (0.43 ± 0.08 NL $L_r^{-1}$ $d^{-1}$). Under the hypothesis that the conditions applied in stage IV did not alter significantly VS removal (discussed in Section 3.4), the complete conversion of $H_2$ to $CH_4$ according to the stoichiometry of hydrogenotrophic methanogenesis could result in maximum $CH_4$ productivity of 0.59 NL $L_r^{-1}$ $d^{-1}$ (0.43 NL $L_r^{-1}$ $d^{-1}$ from VS removal plus 0.16 NL $L_r^{-1}$ $d^{-1}$ from $H_2$ and $CO_2$ conversion) for stage IV. Despite the large $H_2$ conversion efficiency during stage IV (99.0 ± 0.4%), as shown in Fig. 3, the $CH_4$ productivity was approximately 15% lower than the maximum. A slightly lower OLR in stage IV in comparison to the reference period (1.20 vs. 1.3 gVS $L_r^{-1}$ $d^{-1}$) and the utilisation of $H_2$ for microbial growth, estimated at 16–19% of consumed $H_2$ [23], are the main reasons behind this discrepancy.

Dissolved $CH_4$ calculated according to Henry's Law ($3.8 \cdot 10^{-3}$ NL $L_r^{-1}$ $d^{-1}$ for 300 kPa and 95% $CH_4$) can be neglected for mass balances purposes because it is infinitesimally small and represents less than 1% of total $CH_4$ production. However, this value is 4.3 times the value calculated for conventional AD (atmospheric pressure and 66% $CH_4$), and supersaturation of dissolved $CH_4$ has been previously reported in effluents from AD [35]. To prevent diffuse emissions of $CH_4$ from digested sludge, dissolved $CH_4$ should be quantified in future research for appropriate management and recovery of dissolved $CH_4$.

### *3.2. Estimation of the specific mass transfer coefficient ($k_La$)*

The specific mass transfer coefficient of $H_2$ was estimated (Eq. (3)) considering a simplified plug flow regime in the recirculation stream (laminar flow), pure $H_2$ dispersed bubbles ascending in the digester ($P_{H2}$ is the operating pressure for every stage) and a negligible concentration of dissolved $H_2$ ($C_{H2L} = 0$). Estimated values are quite low in the range of 0.4–0.5 $h^{-1}$ (Fig. 6). Reported $k_La$ values for $H_2$ in lab-scale digesters supplied with exogenous $H_2$ are between 6.6 $h^{-1}$ and 16 $h^{-1}$ employing diffusers and mechanical stirring [19] and 25 $h^{-1}$ in digesters mixed by gas recirculation through membranes and bubbling [23]. The low $k_La$ values observed in this study suggest that the contribution of the static mixer to increase mass transfer was poor. Nonetheless, kLa value in this study could be slightly underestimated chiefly because of two reasons: the continuous desorption of $CH_4$ generation might have reduced the $P_{H2}$ in ascending bubbles and because of neglecting the concentration of dissolved $H_2$ ($C_{H2L}$). However, it should be noted that for low to moderate OLR rates and large HRT, such as in this study, a $H_2$ flowrate of 0.64 NL $L_r^{-1}$ $d^{-1}$ would require $k_La$ values around ~5 $h^{-1}$ at atmospheric

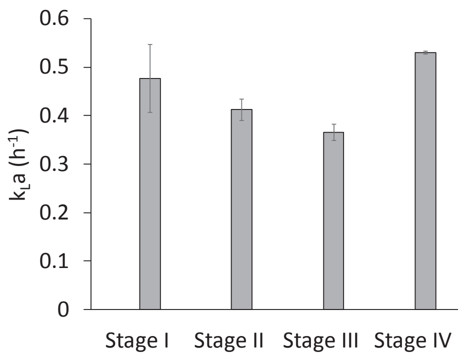


**Fig. 6.** Estimated mass transfer coefficients in various stages.

pressure to achieve a concentration of $CH_4$ of 95% according to simulations performed elsewhere [36]. The increase in the driving-force provoked by a greater operating pressure would result in very low $k_{La}$ values, sufficient to achieve high conversion efficiencies by employing low-efficiency mixing devices at laminar flow regimes in the sludge recirculation stream, such as the static mixer used in this research or with Venturi-type mixers as in [26].

### 3.3. Evolution of pH

pH in the digester dropped to an average value of 6.6 ± 0.2 (down to 6.4) during stage I of the experiment (Fig. 7.a) but later recovered when $H_2$ conversion increased, to 6.8 ± 0.1 in stage II and III and, particularly, in stage IV to 7.0 ± 0.1. In this regard, the hypothesis that $H_2$ supply controlled the pH in the pressurised system was confirmed and prevented acidification caused by $CO_2$ equilibrium displacement in the liquid phase observed at high operating pressure values [37]. The drop in pH during the first stages of the experiment, particularly in stage I, was presumably as a result of the $CO_2/HCO_3^-$ equilibrium displacement at low $H_2$ utilisation rates (60–85%, Fig. 4). Conversely, concentration of $CH_4$ greater than 90% was observed at pH 7.0 in stage IV at 300 kPa, while reported pH in studies of anaerobic digesters was higher than 8 [16,18,23–25] (Fig. 7.b). Higher solubilisation of $H_2$ contributed to pH stabilisation around 7 at stages III and IV.

It should be pointed out that, even when a neutral pH was observed in the latter stages, at high $H_2$ conversion rates and 300 kPa, the system reached a state of very low alkalinity because of $CO_2$ methanation. In this regard, previous studies reporting the evolution of pH under the supply of exogenous $H_2$ to anaerobic digesters were performed at OLR between 1.6 and 1.9 gVS $L^{-1}$ $d^{-1}$ [18,23–25] and 4 gVS $L^{-1}$ $d^{-1}$ [16]. Sudden increases in the OLR, intrinsic to the sludge generation process in the WWTP, could result in a breakdown of the process because of no or inferior buffer capacity.

### 3.4. Organic matter removal and VFA accumulation

The efficiency of VS removal (Fig. 4) was, on average, 45.2 ± 4.3% (26 observations) throughout the experiment, within the typical values for AD of sludge at atmospheric pressure [38] for low OLR. The average VS removal of the reference data for conventional AD was 48.2 ± 7.5% (14 observations). For a confidence level of 95% ($\alpha = 0.05$), the hypothesis of no difference between both averages adopting an unequal variances *t*-test gave a *p*-value of 0.08, larger than α; then, the hypothesis cannot be rejected, and VS removal efficiency during the experiment was similar to that observed during the conventional AD.

Combining the observations in Section 3.1 and the performance of the organic matter removal, the estimated productivity of $CH_4$ (mL $gVS_{fed}^{-1}$) from organic matter during stage IV was ~ 93% of expected (44.8% VS removal vs. 48.2% in the reference AD) and that from methanogenesis of exogenous $H_2$ and $CO_2$ was stoichiometrically approximately 82% of the maximum (~0.13 vs. 0.16 NL $L_r^{-1}$ $d^{-1}$). Therefore, $CH_4$ productivity in stage IV (0.50 ± 0.05 $NL_{CH4}$ $L_r^{-1}$ $d^{-1}$) was the sum of ~ 0.37 $NL_{CH4}$ $L_r^{-1}$ $d^{-1}$ from VS removal (74%) and ~ 0.13 $NL_{CH4}$ $L_r^{-1}$ $d^{-1}$ from the methanation of $H_2$ and $CO_2$. In this sense, the contribution of the different metabolic pathways of $CH_4$ production (hydrogenotrophic and acetoclastic) is of interest because methanogenic microbial communities have shown adaptation to exogenous $H_2$ as well as a significant production of acetate through homoacetogenesis [27]. While the methods here employed do not allow distinguishing the rate at which hydrogenotrophic and acetoclastic methanogenesis took place, an equilibrium was observed because of the lack of VFA accumulation.

Acetate concentration was below 40 mg $L^{-1}$ in 18 out of 20 observations and two peaks of 650 and 240 mg $L^{-1}$ were found on days 19 and 125 respectively (Fig. 8.a). These peaks were attributed to transient states and, overall, acetate accumulation was not observed thus indicating a lack of undesired conversion of $H_2$ into acetate. Propionate and butyrate concentrations were below 18 and 38 mg $L^{-1,}$ respectively, during the whole experiment (20 observations). Variations in the OLR could be the reason behind these peaks; an increase in VS concentration in raw sludge occurred on days 19 and 125. To a lesser extent, a similar behaviour was observed in day 42 (Fig. 8.a). In this regard, sludge digestion is sharply limited by the hydrolysis step and overloads are less common than in anaerobic bioreactors processing readily biodegradable substrates.

With respect to the evolution of N species during the experiment, TKN and $N\text{-}NH_4^+$ concentrations remained within the typical values in the conventional AD of sludge (Fig. 8.b); inlet and outlet TKN were practically equal and $N\text{-}NH_4^+$ concentrations increased during AD (up to 875 mg $L^{-1}$). Inhibition by ammonia is favoured at high pH, where equilibrium is displaced to form $NH_3$; the operation at a neutral pH

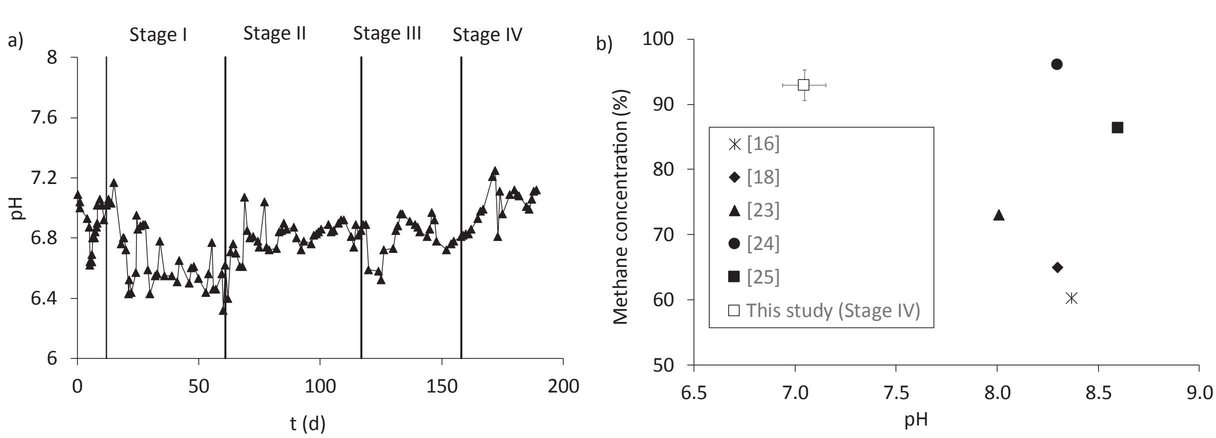


**Fig. 7.** Evolution of pH during the study (a). pH and $CH_4$ concentration in anaerobic digesters with exogenous $H_2$ supply (b).

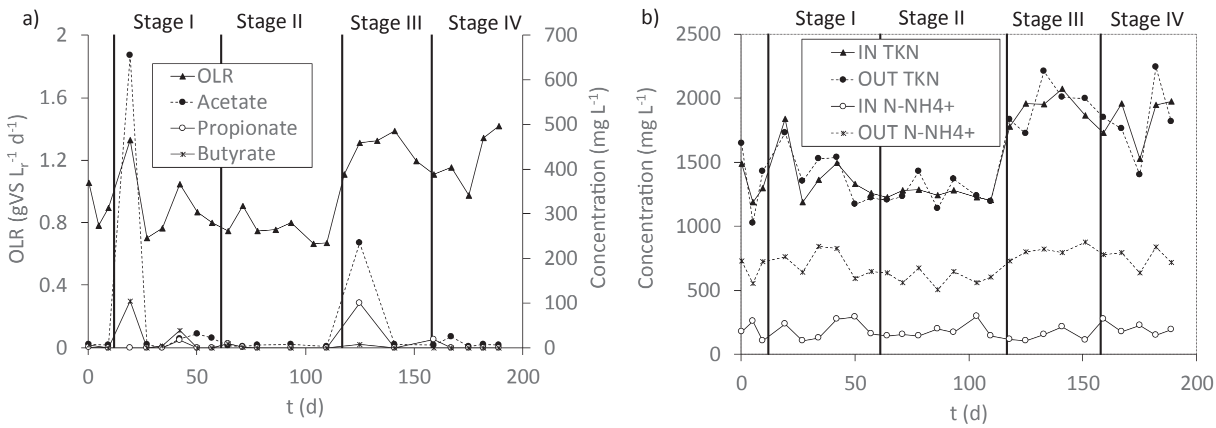


**Fig. 8.** OLR and concentrations of volatile fatty acids (acetate, propionate and butyrate) during the study (a). Evolution of TKN and N-$NH_4^+$ (b).

assists to prevent inhibition by $NH_3$.

Essentially, no evidence was found to support that methanogenesis was inhibited by the pressure increase or the supply of exogenous $H_2$. In this regard, methanogens had also shown tolerance to moderate operating pressures (up to 900 kPa) before [37], and the high $P_{H2}$, which thermodynamically could inhibit syntrophic fermentations [36], did not show an accumulation of VFA during the study. The latter effect might be favoured because sludge digestion is limited by the hydrolysis step. The low VFA concentration observed is in agreement with the lack of inhibition of syntrophic fermentation indicating that the methanogenesis/homoacetogenesis rates were high enough to cope with $H_2$ production from organic matter and to sustain both organic matter removal and $CO_2$ methanation. Therefore, most of the $H_2$ content in the gas is presumably the result of the exogenous supply.

### 3.5. Perspectives and future work

It was feasible to achieve a high concentration of $CH_4$ (greater than90%) directly from the anaerobic digester and a neutral pH with a continuous supply of exogenous $H_2$ by increasing the operating pressure. However, several challenges arise for the scale-up of the process. The absence of buffer capacity could result in process inhibition and accumulation of VFA at higher OLR than this study, and stationary operation of the system must be assessed. Further, a higher OLR might require higher operating pressure to transfer enough $H_2$ for a greater $CO_2$ flowrate or alternatively, an increase in the specific mass transfer coefficient. Apart from that, the extension of this application (high pressure and $H_2$ supply) to other kinds of anaerobic bioreactors such as UASB or similar treating soluble organic matter, limited by methanogenesis rather than hydrolysis, could be infeasible because of the greater intermediate concentration of dissolved $H_2$ associated to syntrophic fermentations.

From an energetic point of view, the pressure is autogenerated by gas generation from VS, and a moderate operating pressure was required in this study to achieve high $H_2$ conversion (300 kPa, implying a lower energy requirement; only additional power for pumping the sludge and the $H_2$ stream to a higher pressure can be expected), in contrast to forcing the conversion of $H_2$ using high biogas or liquid recirculation rates in the reactor or sophisticated $H_2$ transfer systems with the consequent increase in the net energy consumption of the process. Therefore, lower operating costs can be expected by raising the operating pressure (driving-force) than those of increasing the specific mass transfer coefficient ($k_La$) by mixing. On the contrary, fixed costs are expected to increase notably in because of the wall thickness necessary to withstand a pressure higher than the atmospheric. In this regard, the better pressure distribution expected in egg-shaped digesters or a reduced diameter to length ratio (D/L) could also help to contain fixed costs.

## 4. Conclusions

Biomethane with a concentration above 90% was produced directly from an anaerobic digester of sewage sludge with exogenous hydrogen supply by raising the operating pressure to 300 kPa. Hydrogen mass transfer to the liquid phase was favoured by increasing the driving force, and hydrogen conversion reached 99% under such conditions. The contribution of the removal of organic matter to methane production was approximately 74% and that from the methanation of hydrogen and carbon dioxide the remaining 26%. The expected decrease in pH, caused by the higher carbon dioxide concentration in the liquid, was counteracted by the utilisation of hydrogen in methanogenesis, hence converting carbon dioxide into methane, and pH could be maintained around neutral values (7) when a high hydrogen conversion was achieved. Besides, the efficiency of organic matter removal during the experiment was not significantly different from that of conventional anaerobic digestion at atmospheric pressure, and no persistent accumulation of volatile fatty acids or inhibition of methanogenesis was observed.

## CRediT authorship contribution statement

**Israel Díaz:** Conceptualization, Methodology, Writing - original draft, Writing - review & editing, Formal analysis, Investigation, Validation. **Fernando Fdz-Polanco:** Conceptualization, Methodology, Writing - original draft, Writing - review & editing, Supervision, Funding acquisition. **Boldwin Mutsvene:** Investigation, Writing - original draft, Writing - review & editing. **María Fdz-Polanco:** Conceptualization, Writing - review & editing, Supervision, Funding acquisition, Project administration.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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