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Improving the biomethane yield from food waste by boosting hydrogenotrophic methanogenesis

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HIGHLIGHTS

- Hydrogen addition improved biomethane yield and biogas quality from food waste.
- Biogas was upgraded from 65% to 77.2% CH_4 using a gas mixture of 5%-H_2 and 95%-N_2.
- No inhibition to volatile fatty acids production and decomposition was observed.
- High acidification potential of food waste helped to buffer excessive pH increase.

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ABSTRACT

Anaerobic digestion of food waste is usually impacted by high levels of VFAs, resulting in low pH and inhibited methane production from acetate (acetoclastic methanogenesis); however, this could be harnessed for improving methane production via hydrogenotrophic methanogenesis (biomethanation). In this study, batch anaerobic digestion of food waste was conducted to enhance biomethanation by supplying hydrogen gas (H_2), using a gas mixture of 5%-H_2 and 95%-N_2. The addition of H_2 influenced a temporal microbial shift in substrate utilisation from dissolved organic nutrients to H_2 and CO_2 and was perceived to have enhanced the hydrogenotrophic methanogenic activity. As a result, with the release of hydrogen as degradation progressed (secondary fermentation) hydrogenotrophic methanogenesis was further enriched. This resulted in an enhancement of the upgrading of the biogas, with a 12.1% increase in biomethane (from 417.6 to 468.3 NmL-CH_4/gVS_{added}) and 38.9% reduction in CO_2 (from 227.1 to 138.7 NmL-CO_2/gVS_{added}). Furthermore, the availability of hydrogen gas at the start of the process promoted faster propionate degradation, by the enhanced activity of the H_2-utilisers, thereby, reducing likely propionate-induced inhibitions. The high level of acidification from VFAs production helped to prevent excessive pH increases from the enhanced hydrogenotrophic methanogenic activity. Therefore, it was found that the addition of hydrogen gas to AD reactors treating food waste showed great potential for enhanced methane yield and biogas upgrade, supported by VFAs-induced pH buffer. This creates the possibility to optimise hydrogenotrophic methanogenesis towards obtaining biogas of the right quality for injection into the gas grid.

1. Introduction

Anaerobic digestion (AD) follows four distinct but interconnected biochemical steps occurring in syntrophy: (i) Hydrolysis – Breakdown of complex polymers (proteins, carbohydrates and lipids) into smaller molecules (amino acids, simple sugars and fatty acids); (ii) Acidogenesis (primary fermentation) – Production of organic acids; (iii) Acetogenesis (secondary fermentation) – Degradation of organic acids to acetic acid; and (iv) Methanogenesis – Production of methane from acetic acid (acetoclastic methanogenesis – AM) and the combination of hydrogen and carbon dioxide (hydrogenotrophic methanogenesis – HM). The enzymatic activities of all acting microorganisms at each step is principally governed by different optimal pH ranges; a pH lower than 5 for hydrolysis/acidogenesis, 6.8–7.6 for acetogenesis and 6.5–7.2 for methanogenesis [1]. However, an optimal pH range of 6.8–7.4, has been suggested as suitable for a good working anaerobic digester, to

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allow for a good degree of metabolism among all acting microorganisms [1].

The addition of hydrogen to serve as the electron donor to boost hydrogenotrophic methanogenesis is known as chemoautotrophic biological CO_2 conversion [2], otherwise known as, and henceforth referred to as biomethanation. Biomethanation however, leads to a rise in pH as CO_2 is removed; especially significant with feedstock having low organic acids potential such as cattle slurry [3]). High organic-based feedstock with a higher potential for organic acid production such as food waste, could help to reduce this effect. In fact, the fermentation of high protein- and lipid-containing substrates present in food waste results in the release of volatile fatty acids (VFAs), ammonia, CO_2 and H_2 [4]. The release of VFAs leads to an initial reduction in pH and alkalinity; however, ammonia and CO_2 helps to retain a high amount of bicarbonate in the liquid as ammonium bicarbonate [5], thereby, regaining the lost alkalinity (such as in Eq. (1)) and buffering the pH.

$$NH_3 + CO_2 + H_2O \leftrightarrow NH_4HCO_3 \quad (1)$$

Ammonium bicarbonate is soluble in water (24.8 g/100 mL at 25 °C) and can easily be dissociated especially in the presence of organic acids into NH_4^+ and HCO_3^-. In aqueous solution inorganic ammonia is available in two forms: the ionic form as ammonium nitrogen (NH_4^+-N) and the free form as free ammonia nitrogen (NH_3-N, FAN). The latter is deemed inhibitory to AD, because it can penetrate into the cell walls of microorganisms and cause proton imbalance, change extracellular pH and inhibit specific enzymatic reactions [6]. The concentration of FAN is however, controlled by pH and temperature changes; an increase in either or both can result in an increase in FAN, which becomes predominant when pH > 9.25 [7]. More so, the maximum concentration of FAN in aqueous solution is limited by its solubility in water (31 g/100 mL at 25 °C) and the overall mass transfer coefficient in the liquid phase (K_{OL}).

The dissolved CO_2 (in the form of bicarbonates) and hydrogen is utilised by the hydrogenotrophic methanogens to produce methane (Eq. (2)), this CO_2 removal causes an increase in pH, which also helps to buffer the low pH induced by high VFAs load.

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \quad (2)$$

The reaction in Eq. (2), together with ammonia release results in an increase in pH, buffering the low pH induced by VFAs production. Hence, the pH during AD is controlled by bicarbonate, ammonia and VFAs production and degradation. However, because of the high levels of VFAs produced and relatively low levels of hydrogen released (and utilised by hydrogenotrophic methanogens), food waste digesters are often prone to high levels of VFAs and ammonia concentrations, which have potential inhibitory effects especially on the acetoclastic methanogens, thus leading to reduced methane yield or eventual digester breakdown after a period of time [8,9]. Different studies have been conducted to improve digester stability and biomethane yield from food waste, including ammonia stripping [10–12], selective trace elements (TEs) dosing (see Table 1) [13–18] and more recently, the addition of biochar [19,20].

It is very clear that these approaches have mainly focused on improving acetoclastic methanogenesis, which results in the production of CH_4 and CO_2, hence, the quality of biogas produced remains relatively unchanged (i.e. ~ 65% CH_4 content). The HM route, however, improves both CH_4 yield and quality of biogas, and has been relatively underexplored, particularly with food waste as feedstock. Biomethanation has been tested with other substrates such as cattle manure [21], maize leaf [22], co-digestion of cattle manure and whey [23] and anaerobic cultures [24], however, no previous work was found on the use of biomethanation to improve the AD of food waste at the time of writing this paper. This study therefore, explores the use of biomethanation to enhance hydrogenotrophic methanogenesis during food waste anaerobic digestion, to achieve both an increase in biomethane and biogas upgrade (i.e. CO_2 reduction) and presents an in-depth analysis of the

Table 1
Previous approaches to improve biomethane yield from mono-digestion of food waste.

Biogas upgrade method	Reactor design	Methane yield without treatment	Methane yield with treatment (mL/gVS_{added})	Reference
Trace elements	Semi-continuous mesophilic reactor	NR	352–459	[17]
Trace elements	Semi-continuous mesophilic reactor	55[a]	58[a]	[13]
Trace elements	Semi-continuous mesophilic reactor	467[b]	461–491[b]	[16]
Trace elements	Batch mesophilic	338–434	342–566	[14]
Trace elements	Batch mesophilic	372	~504	[15]
Biochar in nutrient medium-supported food waste digestion	Batch reactor	340–490	460–530	[19]
Biochar addition to biowaste	Solid-state batch mesophilic reactor	449.6–453.3	447.0–546.2	[20]

[a] Actual values not given, presented as percentage of methane in biogas.
[b] Yield at an organic loading rate of 1.0 gVSL-1d-1, but digester failed when OLR was increased to 4.0 gVSL-1d-1, while TE treated reactor had a mean yield of 465.5 for OLR of 1 – 5 gVSL-1d-1.

changes induced on key process parameters (such as pH, VFAs and Ammonia) during anaerobic degradation.

2. Materials and methods

2.1. Food waste sampling

Samples of food waste were obtained from the University of Leeds' student refectory, collected over a period of five days in a separately monitored bin. Samples were sorted daily after each collection, to separate out the food waste fraction, and stored at 4 °C until the last day of sampling, after which all samples were thoroughly mixed and ground to a paste, using a Nutribullet food processor. The homogenised sample was then sieved through a 1 mm sieve, to obtain a substrate particle size range of ≤1 mm that was characterised and stored at −20°C. Frozen samples were thawed at 4 °C a day before the tests were setup and then acclimatised to room temperature before testing, hence, no heat was applied to defrost the samples.

2.2. Inoculum

The inoculum used in this study was obtained from a mesophilic anaerobic digester treating sewage sludge at Yorkshire Water's Esholt Waste Water Treatment Work (Bradford, UK). The inoculum was filtered through a 1 mm sieve, to remove large materials and grits. Fresh digestate samples were first stored at 37 °C for two weeks to remove residual biogas from the digestate, followed by an acclimation with food waste for 30 days, achieved by adding 0.2 g of food waste sample (as Volatile Solids – VS) per day in each litre of inoculum.

2.3. Hydrogen leak tests

Experiments were performed in Wheaton bottles (160 mL) (see Section 2.4), previously leak tested for their ability to retain hydrogen throughout the digestion period using distilled water. The same hydrogen addition procedure used in the leak test was employed to add hydrogen to AD tests. Samples of gas were monitored by gas chromatography at regular sampling times by measurement of the headspace gas. Hydrogen leak experiments were setup using reactors containing 75 mL distilled water and involve the bubbling of a N_2-H_2 mixture through the water for five minutes followed by immediate sealing with rubber seals and aluminium crimps. The reactors were then placed in a water bath set to 37 °C for 21 days to simulate the actual experiment. All reactors were prepared in duplicate for seven analytical points as sacrificial samples, such that samples taken for each analysis were not returned to the system.

2.4. Experimental setup for anaerobic digestion tests

Batch mesophilic tests were conducted using 160 mL (absolute volume) Wheaton bottles as anaerobic reactors. The reactors had a working volume of 75 mL and were maintained at a temperature of 37 °C (Fig. 1), using a 3:1 inoculum to substrate ratio (ISR). Blank (inoculum), control (food waste plus inoculum with no hydrogen added) and test (food waste plus inoculum with hydrogen added) were tested. Hydrogen was added into the test reactors on the day of setup (Day 0) using a gas mixture of 5%-hydrogen and 95%-nitrogen. The gas was bubbled through the samples using a ceramic diffuser for 5 min each and immediately sealed with rubber seals and aluminium crimps. All reactors were prepared in duplicate for each analytical point (7 in total per test) as sacrificial samples, while all experimental analyses were conducted in triplicate. The overall experimental setup is described in Fig. 1.

2.5. Analytical methods

2.5.1. Headspace gas analysis

The headspace gas composition was measured by a gas chromatograph (GC) (Agilent Technology, 7890A) equipped with a thermal conductivity detector (TCD) and a Carboxen 1010 PLOT column – i.e., length 30 m, diameter 0.53 mm and film thickness 30 μm. The GC-TCD was operated at 200 °C inlet temperature and 230 °C detector temperature with Argon as a carrier gas (3 mL/min). Gas samples (G_v) were collected from the headspace of the anaerobic reactors to analyse their composition using a 500 μL glass syringe. Two full syringes were drawn and expelled through a bottle of distilled water to flush the syringe and also ensure the needle was not blocked with septa cores. With the needle in the reactor, the syringe was pumped about seven times to mix the headspace gas sample and a full syringe was drawn, which was then set to 200 μL (bubbled through distilled water) and manually injected into the GC inlet column. The GC was calibrated with three standard gas mixtures; 50%CH_4:3%H_2:47%N_2; 20%O_2:80%N_2; and 10%CO_2:90%N_2 at predetermined intervals. After sample collection for headspace gas composition analysis, the remaining gas volume in each of the reactors was measured by using a water displacement method according to the setup described in Fig. 2. The water displacement setup was calibrated with 10 mL of air before each analysis to ensure the system pressure was maintained.

2.5.2. Liquid sample analysis

The pH of the remaining liquor was measured immediately after opening the reactor, using a HACH pH meter (HQ 40d). Alkalinity was analysed immediately after pH measurement using a METTLER TOLEDO Auto-titrator (T50), with 0.05 mol-H_2SO_4/L as the titrant. The pH and alkalinity analyses were conducted immediately after opening the reactors to minimise changes due to atmospheric oxidation. Standard analytical methods used for the examination of wastewaters and sludge were employed [25] to characterise liquid samples, including the following parameters: total solids – TS (Method 2540 B), volatile solids – VS (2540 E), ammonia nitrogen – NH_3-N (4500-NH_3 B-C), total Kjeldahl nitrogen – TKN (4500-N_{org} B) and chemical oxygen demand – COD (5220 C). Liquid samples were also processed for dissolved organic carbon (DOC) analysis by the differential method with HACH IL550 TOC-TN equipment.

The volatile solids (VS) for all reactor contents were examined within four hours of sampling, following the opening of the reactors. Liquid samples for the analysis of soluble COD (sCOD) and DOC were initially centrifuged at 2000 RPM (775*g*) for 5 min, using an Eppendorf 5810R centrifuge; the supernatants were filtered through 0.45 μm filters and diluted with deionised water (DIW) prior analysis.

Total VFAs concentration was measured using a GC (Agilent Technologies, 7890A) equipped with a flame ionization detector (FID), auto-sampler and DB-FFAP column – i.e., length 30 m, diameter 0.32 mm and film thickness 0.5 μm, and Helium as a carrier gas. The GC-FID operating conditions were: 150 °C inlet temperature and 200 °C FID temperature. Liquid samples were adjusted to pH 2.0 using phosphoric acid and allowed to rest for 30 min and then centrifuged at 14,000 RPM (16,000*g*) for 5 min, using a Technico Maxi micro-centrifuge. After centrifuging, the supernatant was filtered through a 0.2 μm filter and the liquid analysed for VFAs. The GC was calibrated with a SUPELCO Volatile Acid Standard Mix, which includes acetic-, propionic-, iso-butyric-, butyric-, iso-valeric-, valeric-, iso-caproic-, caproic- and heptanoic- acids. The remaining solid fraction was first dried at 40 °C for two days and ground to a powder using a mortar and pestle, before being processed for elemental analysis. Elemental carbon, hydrogen, nitrogen and sulphur (CHNS) were measured on dry samples using a Thermo Scientific FLASH2000 Organic Elemental Analyser.

2.5.3. Statistical analysis

The experiment was set up with duplicates for each sampling point

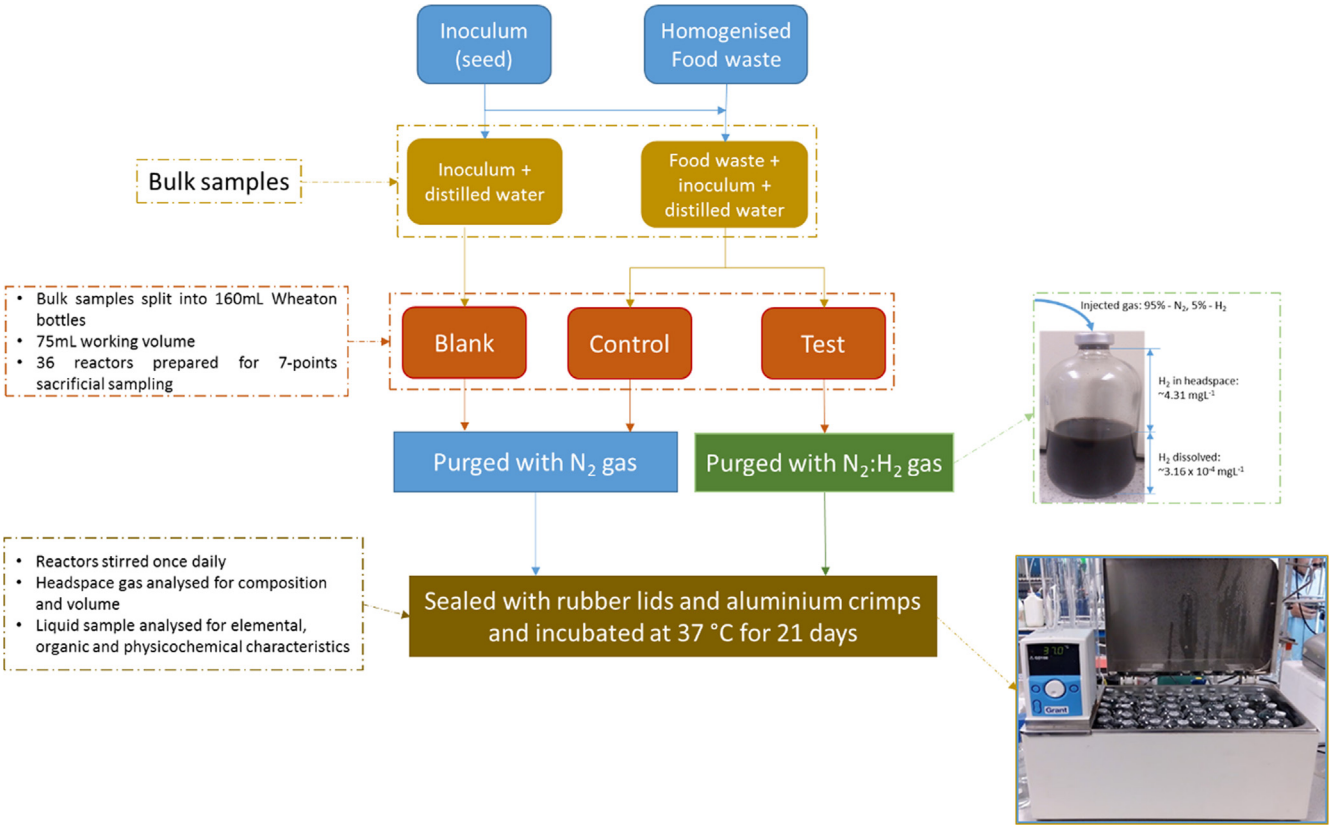

Fig. 1. Experimental setup showing the preparatory stages for anaerobic digestion with hydrogen addition.

and the analysis conducted on the reactor content (liquid content) was carried out in triplicates (except for DOC that was measure in duplicates), to give a total of 6 readings (4 for DOC) from each sampling point. Experimental data was subjected to descriptive statistical analysis – i.e., normality test, mean and standard deviation. All results from each group of assays (control and test) were first individually analysed for statistical significance, using a one sample *t*-test. Where the results showed significant difference, further outlier test was conducted to remove outliers, before final analysis and graphical representations. Analysis of Variance (ANOVA) on VFA concentrations between the control and test reactors (for $\alpha = 0.05$; $n = 12$) were conducted for data collected between Day1 and Day3; during which period hydrogen was measured in the headspace of the reactors.

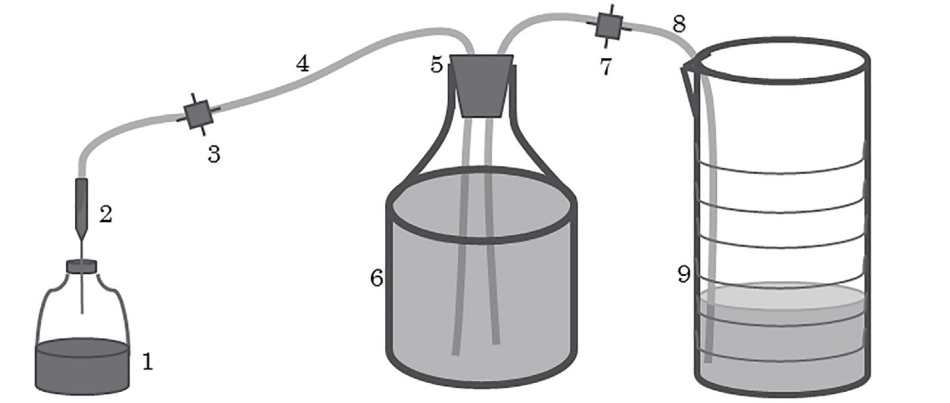

Fig. 2. Schematic setup for headspace gas volume measurement by water displacement.

Table 2
Characteristics of inoculum and food waste samples used in batch anaerobic digestion experiments.

Parameter	Inoculum	Food waste	
		This study[c]	Other studies
Moisture content – MC (%)	96.2	68.6(0.02)	61.3–85.7[a]
TS (g/kg)	38.1	314.3(0.2)	217.5–294.0[a]
VS (g/kg)	21.6	295.0(0.3)	178.7–257.0[a]
VS/TS (%)	56.7	93.9	80.6–98.2[a]
COD (g-O_2/kg)	38.6	469.7(0.0)	248.2–260.0[a]
TKN (g/kg)	2.68	7.51(0.6)	11.9[a]
Total VFAs (g/kg)	–	1.39(0.01)	Not reported
N (% of TS)	4.00	4.44(0.10)	2.35–3.42[b]
C (% of TS)	29.40	53.19(2.12)	32.85–48.42[b]
H (% of TS)	4.20	7.87(0.23)	6.90–7.03[b]
S (% of TS)	1.30	0.33(0.18)	0.15–0.44[b]
O (% of TS)	61.20	34.17(2.51)	34.13–34.30[b]
C/N	7.35	11.98	14.0–19.3[b]

[a] Cited Refs. [27,28,48–50,16,51].
[b] Measurements reported on dry basis, cited references include [27,28,16].
[c] Mean value and standard deviation in brackets, $n = 3$.

3. Results and discussion

3.1. Inoculum and food waste sample characteristics

The characteristics of the inoculum used in this study are summarised in Table 2. Furthermore, characteristics of food waste used in this study are also presented in Table 2, which are within the range of values reported in other studies for food waste. The high VS percentage and COD values demonstrate its suitability for AD; however, the C/N ratio (11.98) was found to be below the optimal range suggested for anaerobic digesters (25–30) [26] and lower than values reported for food waste samples by other studies (14.0–19.3) [27,28,15]. This suggests that the sample poses a potential risk of toxicity due to the potential for production of high ammonia levels during AD, especially if the pH was to increase.

3.2. Hydrogen leak test

Hydrogen leak tests were conducted to make certain hydrogen was not going to leak from the reactors during the duration of the experiment. As this study was performed in batch reactors using a predetermined amount of hydrogen (being very light), in order to estimate the efficiency of hydrogen conversion to biomethane, it was important to ensure there were no leaks from the test reactors. Hydrogen could leak through the tiniest orifice, hence, this experiment was conducted to confirm that the hydrogen injected and generated during feedstock breakdown, was directly consumed by microorganisms and not lost to the atmosphere. Since the reactors were subjected to the same process conditions as in the actual experiments; except the reactor content containing only distilled water, the gas withholding capacity of the system was assumed to be the same as the actual experiments containing food waste. From a total of 13 data samples, a confidence interval for the percentage of hydrogen in the headspace of 4.60–4.86% at 95% confidence level and a mean of 4.73% H_2 was obtained from a one-sample *t*-test using Minitab 17 statistical software (i.e. initial gas mixture: 5%-H_2 and 95%-N_2). The apparent 0.27% loss could have been a result of human error, assumed to have either occurred when the gas injection pipe was withdrawn, when the bottles were sealed and/or when the gas was injected to the GC, or perhaps from loss due to hydrogen dissolved in the liquid. It was however, confirmed that there was no direct hydrogen leak during the entire test period from the reactors, whereby, most of the measured percentage hydrogen was between 4.7 and 4.9%.

Table 3
Reactor characteristics obtained in this study at Day 0.

Parameter	Reactor		
	Blank	Control	Test
pH	8.64(0.00)	8.49(0.00)	8.49(0.00)
TS (g/L)	10.46(0.26)	14.25(0.23)	14.25(0.23)
VS (g/L)	6.05(0.27)	9.02(0.21)	9.02(0.21)
Total VFAs (mg/L)	32.6(4.6)	52.1(11.3)	52.1(11.3)
NH_3-N (mg/L)	336(0)	364(0)	364(0)
Total COD (g/L)	13.81(0.41)	26.06(0.46)	26.06(0.46)

Mean values with standard deviation in brackets, $n = 3$.

3.3. Effect of hydrogen addition on biomethane yield

3.3.1. Initial experimental conditions

Table 3 summarises the characteristics of the samples prepared for the blank, control and test anaerobic reactors, hence, the contents of the control and test reactors had the same liquid phase characteristics before the addition of hydrogen gas to the test reactors.

3.3.2. Biomethane yield

The volumetric change in CH_4 and CO_2 yields in comparison with the removal of gas-phase hydrogen of the control and test reactors are presented in Fig. 3.

The detection of hydrogen gas in the headspace of the control and test reactors within the first two days implies a hydrogen-saturated liquid, and the continuous increase in acetic acid (discussed further in Section 3.4.1) for the same period, suggests that at the early stage, methane production from both the control and test reactors was primarily through HM. Since hydrogen gas was not measured at Day3, the mass balance for hydrogen utilisation was limited to the data collected at Day1 and Day2.

The percentage gaseous hydrogen utilisation (U_H) was 7.1% in the test reactor at Day1; the U_H was not calculated for the control reactor, because, it had no hydrogen in the headspace at Day0. After the subtraction of the methane yield from the blank reactors (inoculum) from the control and test reactors, the concentration of CH_4 in the headspace of the control and test reactors was 12.0 mg/L and 15.2 mg/L, and with a CH_4:H_2 mass ratio of 1.99 (Eq. (2)), the predicted amount of hydrogen utilised was 6.0 mg-H_2/L and 7.7 mg-H_2/L respectively. However, from Fig. 3a, we observe that the hydrogen concentration in the headspace of the test reactor reduced from 3.9 mg/L by Day0 to 3.6 mg/L by Day1. This implies that out of the 7.7 mg-H_2/L consumed in the test reactor, 7.4 mg-H_2/L was produced directly from substrate degradation. This value was higher than the amount of hydrogen utilised in the control by 23.7% (1.4 mg-H_2/L), which gives an indication of a higher rate of hydrogenotrophic methanogenic activity (HMA) in the test reactor.

The U_H by Day2 was calculated as the percentage reduction of the headspace hydrogen concentration in comparison with the concentration at Day1 – i.e. (Day2 – Day1)/Day1. By Day2, 11.5 and 17.6 mg-H_2/L were consumed in the control and test reactors respectively, and the U_H was 27.6% and 71.7% respectively, confirming a more rapid HMA in the test reactor, at approximately three times the activity of the control reactor. Evidently, the gas-liquid hydrogen mass transfer rate was influenced by the higher hydrogen partial pressure, when hydrogen was added. Therefore, the addition of hydrogen is believed to have increased the HMA, which consequently, increased hydrogen gas-liquid transfer rate in the test reactor. Hence, the reduction in gaseous hydrogen, translated into an increase in CH_4 yield, especially by Day2 (Fig. 3b); when the highest U_H of 71.7% was achieved.

Low gas-liquid mass transfer of hydrogen was said to influence the increase in methane yield, owing to limited inhibition on the system [29] and high mixing rates above 150 rpm was thought to have influenced fast gas-liquid hydrogen transfer and flocs breakage, which led to

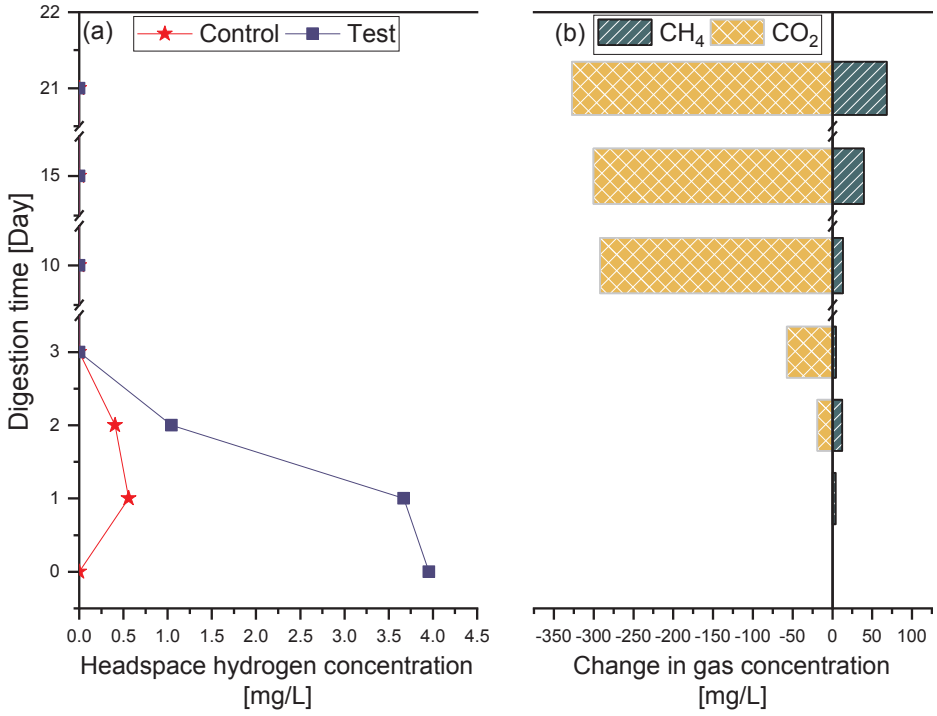

Fig. 3. (a) Hydrogen concentration in the headspace of the control and test reactors and (b) Change in CH_4 and CO_2 concentration, taken as difference between concentrations from test and control reactors (e.g., $CH_{4\ test} - CH_{4\ control}$).

low methane production rates [6,23]. However, in this study, the gas-liquid mass transfer was observed to increase through time based on the U_H, which led to an increase in methane yield. This could have been influenced by the optimised HMA, extensively removing dissolved hydrogen, and therefore, inducing a higher rate gas-liquid hydrogen transfer.

As the hydrogen concentration dropped and with further biological processes, the margin between the concentration of CH_4 in the control and test reactors consequently reduced. Furthermore, the high increase in U_H observed by Day2 only accounted for about 7% of the cumulative yield, so that the continuous increase in methane yield after the injected hydrogen had depleted was attributed directly to the continuous degradation of acids. The CO_2 yield in the test reactor continued to decrease, believed to be as a result of the improved HMA, with possible occurrence of syntrophic acetate oxidation (SAO); a process whereby, acetate is first oxidised to CO_2 and H_2, followed by hydrogenotrophic methanogenesis [30]. In addition, around 6.4–8.5% of CO_2 was reportedly lost during biomethanation for biomass growth [31–34], which could also have contributed to the decrease in CO_2 yield from the test reactor in this study.

Hydrogen produced during AD is almost immediately consumed by the hydrogen consumers; relative to their abundance, such that excess dissolved hydrogen is transferred to the headspace; because of low H_2 solubility (15.5 mg/L at 25 °C). Additionally, until the dissolved and gaseous hydrogen are equilibrated to a very low partial pressure, the high hydrogen partial pressure could inhibit VFAs degradation [35] and consequently, have a negative impact on acetoclastic methanogenesis as a result of possible backward VFAs-induced inhibition [36]. Hence, hydrogen in the headspace gas could pass as an indication of dissolved hydrogen inhibition on AM. Based on this premise, the methane production from the day of setup (Day0) both in the control and test reactors until the point at which no hydrogen was detected in the headspace (Day3) can be attributed primarily to HM. The negative change in CO_2 from Day1 indicates that a lower CO_2 was obtained in the test reactor right after initial hydrolysis. This could either be an indication of inhibition of hydrolysis (and/or fermentation) or enhanced HM, since substrate solubilisation leads to the formation of hydrogen and carbon dioxide. However, the bacterial community within the AD system is autocatalytic, in that the amount produced will always be proportional to the flux of the substrates within the system [4], which implies the needed bacteria cannot limit the reaction, but the substrate or nutrient concentration. Hence, the hydrogenotrophic methanogenesis route was believed to have been enhanced right from the early stages of digestion owing to the availability of H_2 and CO_2 to facilitate their metabolism.

After Day3 however, the digestion was believed to progress typically without possible inhibition from high hydrogen concentration on microbial groups present. And the probable competition for available nutrients by active microorganisms was perceived to have shrunk the margin of increase in the CH_4 yield during the later days of digestion. Perhaps, continuous addition of hydrogen could help to increase the CH_4 yield and as well reduce the CO_2 throughout the process. Luo and Angelidaki, [3] made a similar observation, with a study on an enriched methanogenic culture, whereby, with continuous hydrogen injection, they achieved up to 95% CH_4 in the biogas at steady state, at an injection rate of 6 L/L/day.

The final biogas from the test reactor composed of 77.2% CH_4 and 22.8% CO_2 (468.3 $NmLCH_4/gVS_{added}$ and 138.7 $NmLCO_2/gVS_{added}$), while the biogas from the control reactor composed of 64.8% CH_4 and 35.2% CO_2 (417.6 $NmLCH_4/gVS_{added}$ and 227.1 $NmLCO_2/gVS_{added}$) respectively, resulting in 12.1% biomethane increase and 38.9% CO_2 reduction.

3.4. Effect of hydrogen addition on the stability of the anaerobic digestion process

3.4.1. Acids fermentation

Acidogenesis was analysed by VFAs concentration in the reactors up until Day3. The total VFAs (TVFAs) recorded here comprised acetate, propionate, butyrate, iso-butyrate, valerate and iso-valerate. ANOVA ($\alpha = 0.05$; $n = 12$) conducted for the control and test reactors by Day1 and Day2 are presented in Table 4. The TVFAs concentration was

Table 4
p-values for 2 sample t-tests analysis of volatile fatty acids in the control and test reactors from Exp1 ($\alpha = 0.05$, $n = 12$).

Day	Acetate	Propionate	Butyrate	Total VFA
Day 1	0.773	0.010	0.088	0.394
Day 2	0.848	0.774	0.118	0.721

635.0 mg/L in the control and 644.6 mg/L in the test reactor, respectively by Day1; with acetate, propionate and butyrate higher in the test reactor by 0.5%, 6.0% and 4.2% respectively. According to Mosey [37], asides acetate, VFAs produced during AD are mere bacteria responses to hydrogen surge loads. It was therefore, not surprising that propionate and butyrate levels were higher in the test reactor by Day1, due to an initial system adjustment; supported by the relatively lower *p*-values presented in Table 4. Furthermore, extremely low level of H_2 partial pressure ($< 10^{-4}$–10^{-5}) is thermodynamically required to allow for non-inhibited butyrate and propionate degradation [38]. Hence, the initial high concentration of H_2 in the test reactor led to a slight increase in butyrate (Day1) and propionate (up until Day3) (also presented in Fig. 4).

By Day2, the concentrations of acetate, propionate and butyrate within the control and test reactors increased to about the same levels in both reactors. The increased rate of hydrogen consumption in the test reactor was believed to have slowed further propionate and butyrate accumulation in the test reactor. While in the control reactor, hydrogen surge from primary fermentation enriched higher accumulation of propionate and butyrate. For instance, by Day2, while propionate and butyrate increased between Day1 and Day2 by 67% and 11% in the control reactor, they increased by 59% and 4% in the test reactor respectively, which explains the increase in *p*-values by Day2 (Table 4). The *p*-values by Day2 suggest that there was no significant difference in the VFA intermediates produced during acidogenesis.

In agreement with the findings in this study, H_2 injection into anaerobic biogas reactors was believed to have initial negative impact, until the H_2 consumption rate becomes equal to or greater than the hydrogen production (or injection) rate, in order to balance the process [6,23]. Similarly, Fukuzaki et al. [35] found H_2 addition to inhibit propionate degradation; relative to hydrogen partial pressures, however, an increase in the hydrogenotrophic methanogens reversed this inhibition. This means VFAs degradation by obligate hydrogen producers (OBHP) to acetate can be affected if the hydrogen consumers are not commeasurably present to consume the available hydrogen. This mechanism is especially controlled by the inter-species hydrogen transfer (IHT) between the hydrogenotrophic methanogens and the OBHP [39,40]. Therefore, the increase in dissolve H_2 consumption rate in the test reactor; as a result of a higher HMA, influenced an increased rate of butyrate and propionate degradation in the test reactor afterwards, leading to higher acetate level in the test reactor by Day10 (Fig. 4b). In agreement, Yang et al. [39] related high propionate removal rate during AD of sludge with activated carbon to the enrichment of hydrogen-utilising methanogens, which could have influenced a forward push of propionate degradation.

The non-detection of hydrogen by Day3 in the headspace of both test and control reactors, implies methane formation from this time was mostly related to improved VFAs degradation. By the end of the experiment, only acetic acid was available in both the control and test reactors at concentrations of 15 mg/L and 14 mg/L, respectively. As such, there was neither inhibition in acetogenesis nor acetate accumulation at the end of the experiment with hydrogen addition. A

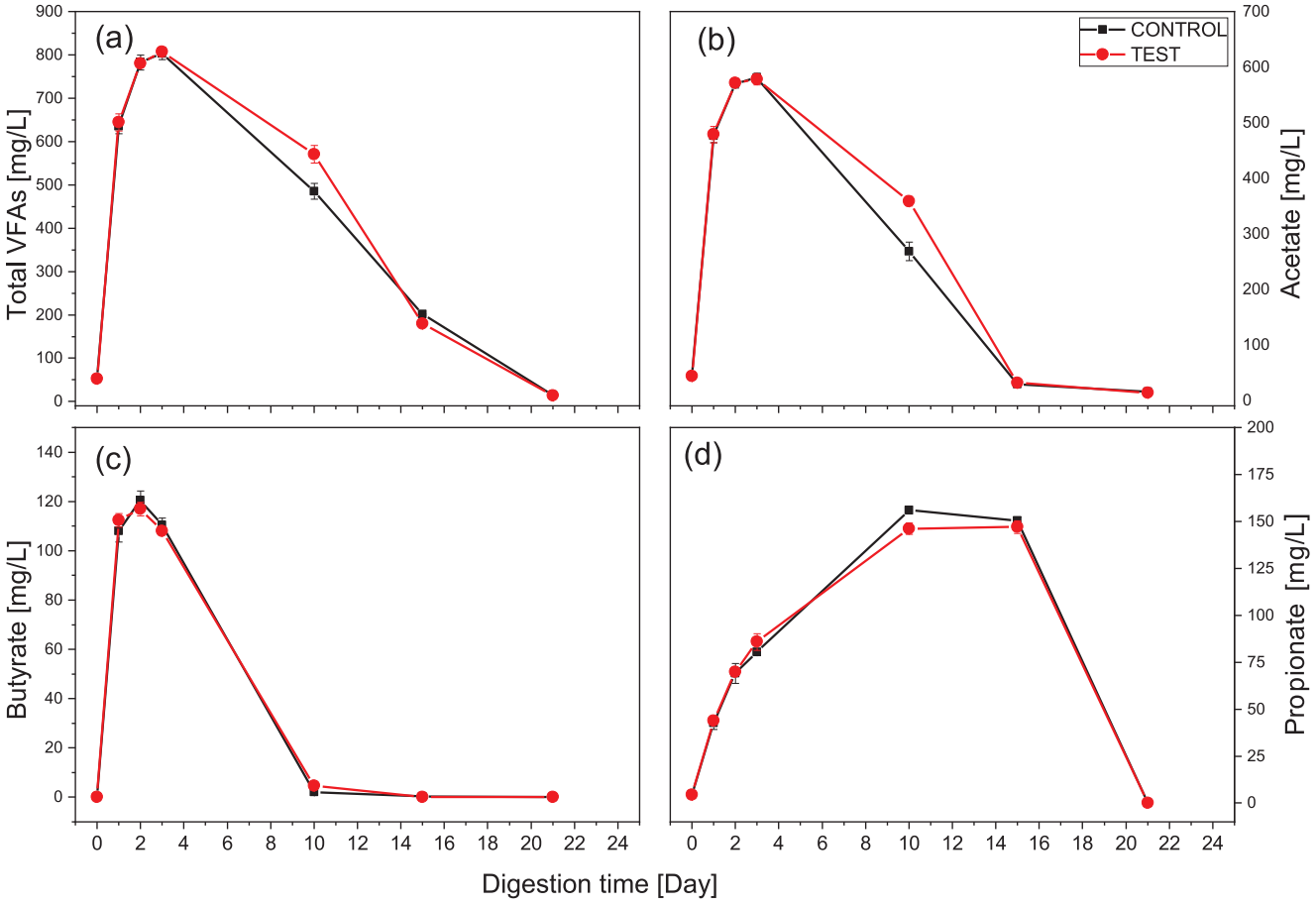

Fig. 4. VFA concentrations comparison between the test and control reactors. Error bars are the standard deviation from the mean.

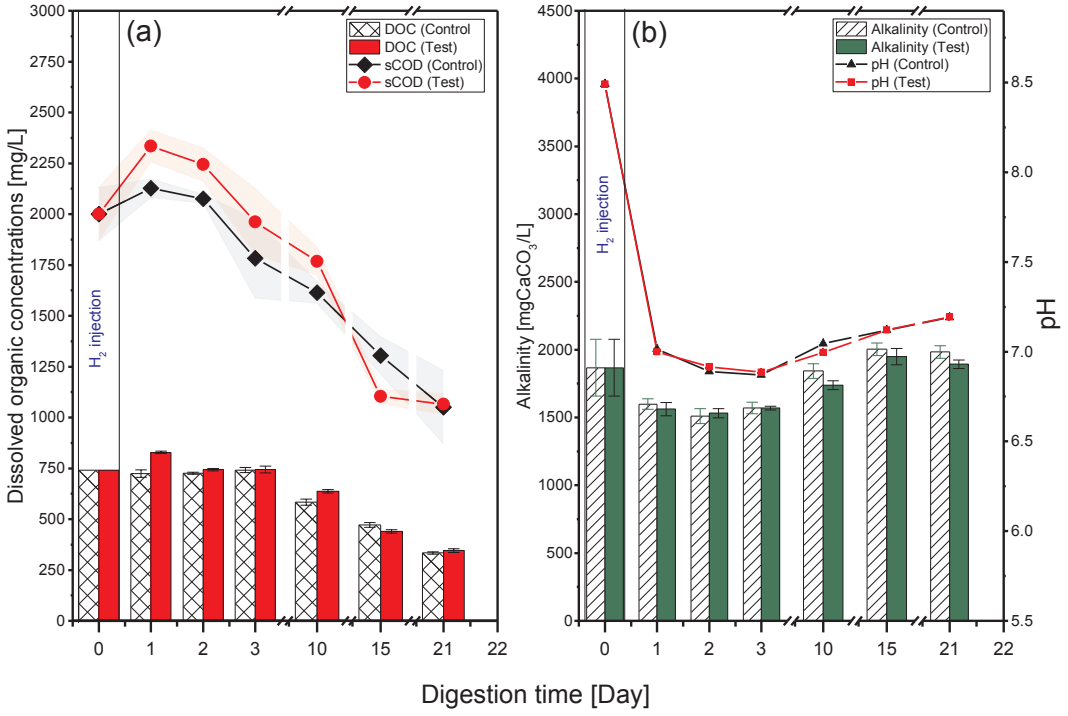

Fig. 5. (a) Dissolved organic concentrations (sCOD and DOC) in the reactors. Shaded areas in sCOD plots indicate error margin based on standard deviations from mean; (b) Alkalinity (column graphs) and pH pattern during the experimental period.

similar observation was made during the co-digestion of manure and acidic whey for in-situ biogas upgrading by the addition of H_2, whereby, Luo and Angelidaki, [23] observed that there was no obvious acetogenesis inhibition with increases in hydrogen. Furthermore, they observed an increase in the key enzyme responsible for methane production from acetate and H_2/CO_2 consumption (Coenzyme F_{420}) by 20%, with hydrogen addition.

3.4.2. Organic compounds degradation

Dissolved organic concentrations (sCOD and DOC), pH and alkalinity measured in both the control and test reactor contents during the digestion period are shown in Fig. 5. High levels of sCOD and DOC were measured in the test reactor by Day1 (Fig. 5a), but since there was no VFAs accumulation for the same time period, it means organic carbon consumption stalled in the test reactor, due to readily available food forms (H_2 and CO_2) for HM. However, the sharp decrease in DOC and sCOD between Day1 and Day2 in the test reactor depicts increased microbial activity, which also corresponds with the high methane yield in the test reactor by Day2 as earlier presented in Fig. 3.

The production of VFAs led to a sharp reduction in pH by Day1 both in the control and test reactors (Fig. 5b), and it continued to reduce as the VFAs accumulated. The hydrogen added did not greatly affect the pH, which remained between pH 6.87 and 7.20 in both reactors throughout the digestion period. This was probably due to the low concentration of hydrogen injected relative to the concentration of VFAs produced. Hydrogen addition to AD systems have been reported to increase the pH due to bicarbonate consumption, with values exceeding pH 8.0 [3,6,33]; however, the use of acidic substrates was able to buffer the rise in pH [23]. That seems to be the case for AD of food waste as in this study.

Between pH 6.3 and pH 10.4 dissolved CO_2 is predominantly as bicarbonate [41]. Considering pH of the test and control reactors remained between pH 6.87 and 7.20, it is expected that the CO_2-induced alkalinity was mainly as bicarbonate and its removal will influence a reduction in alkalinity. Hence, the increase in bicarbonate consumption in the test reactor impacted a reduction in the alkalinity throughout the digestion period (Fig. 5b).

3.4.3. Ammonia concentration

The concentration of total ammonia-nitrogen (TAN) and the FAN during the digestion period for both the control and test reactor is shown in Fig. 6. TAN in both the control and test reactors reduced by Day1, which could be attributed to a higher rate of ammonium nitrogen utilisation by the microorganisms for cell growth before the release of ammonia from substrate hydrolysis/degradation.

The further reduction in TAN in the test reactor by Day2 was therefore, because of the enhanced HMA, during which the highest hydrogen gas utilisation was recorded at 71%. Seeing that the alkalinity in the test reactor by Day2 also increased, it is possible that some of the TAN was also used to regain alkalinity in the form of ammonium bicarbonate. With a shift from organic substrates utilisation to the available H_2 and CO_2, the release of ammonia could also have temporarily stalled, so that, as the gaseous hydrogen diminished and organic substrate degradation progressed, the concentration of TAN increased for both the control and test reactors (as observed in Fig. 6a). The FAN calculated according to the formula detailed in Rajagopal et al. [42] and presented in Fig. 6b, remained relatively similar in both the control and test reactors throughout the digestion period; in the range of 2.9–4.8 mgNH_3-N/L and 2.7–5.0 mgNH_3-N/L respectively. The proportion of FAN in the TAN is highly dependent on the pH of the system; such that, higher pH enriches higher FAN levels [7]. Hence, higher TAN levels observed in the control reactor between Day1 and Day2 did not culminate in higher FAN levels in the control reactor, because, the pH of the test reactor was slightly higher than the control for the same time period. As such, the FAN was not significantly different between the control and test reactors. This would imply the initial reduction in TAN observed in the test reactor, with hydrogen addition was impacted more by ammonium nitrogen reduction, which further elucidates the increase in HMA in the test reactor for the period hydrogen was measured in the headspace.

It can, therefore, be inferred that hydrogen injection prior to hydrolysis can provide short term reduction in TAN, and continuous

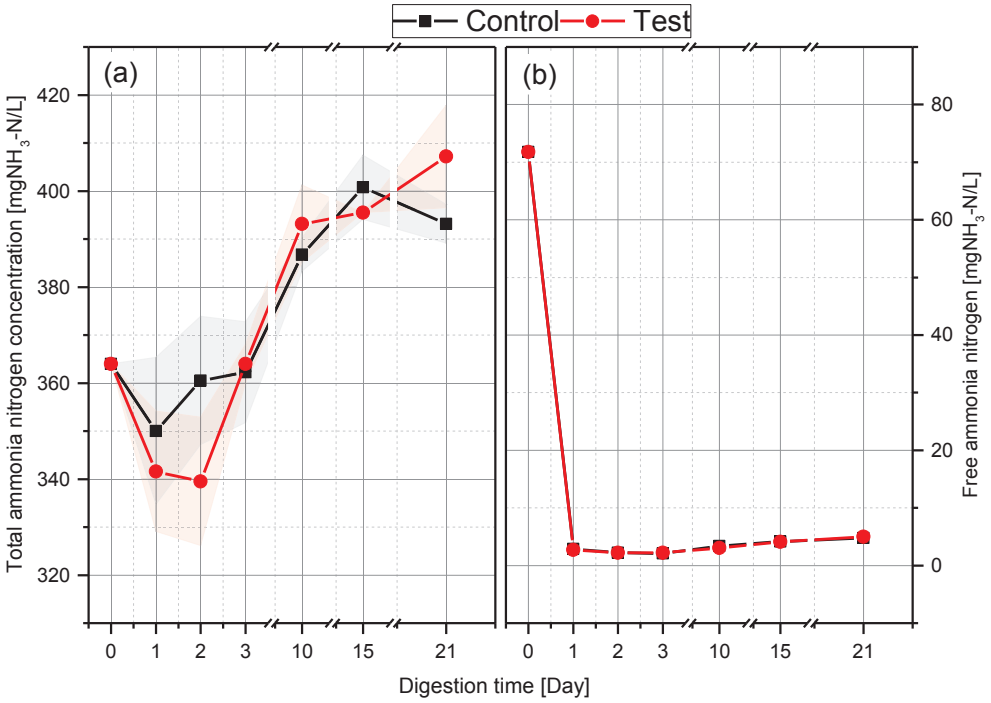

Fig. 6. Ammonia-nitrogen concentration; (a) total ammonia nitrogen (TAN), where shaded portion indicates magnitude of standard deviation from the mean, (b) free ammonia nitrogen (FAN) calculated from the corresponding TAN and pH using formula detailed in [42].

hydrogen addition could help to sustain low levels within the reactor; however, the substrate degradation must be closely monitored, so as to prevent incomplete digestion. Despite the subsequent increase in TAN levels after the complete removal of gaseous hydrogen, the biomethane yield in the test reactor continued to increase, which could be attributed to the system becoming more resistant to the ammonia toxicity, as a result of increase in hydrogenotrophic methanogens [3,6,23,33]. Substrates with high initial protein and TAN concentrations can be treated anaerobically using an acclimated sludge with ammonia levels corresponding to 3 gNH_4^+-N/L (ammonium nitrogen) or 0.15 gNH_3-N/L (FAN), above which methanogenesis is inhibited, regardless of pH and temperature levels [43]. In this study FAN was always below 0.15 gNH_3-N/L and hence, ammonia toxicity was not observed. SAO become the dominant pathway for the degradation of acetic acid under such high ammonia levels [13,43,44]. Although, ammonia levels recorded here are lower than inhibition levels reported by Fotidis et al. [43], the continuous decrease in CO_2 yield in the test reactor, is an indication of an enhanced hydrogenotrophic methanogens in the test reactor compared to the control, and since the hydrogen injected had been completely utilised, SAO becomes a more viable route for HM.

3.5. Possibility for hydrogen integration into active food waste anaerobic digestion plants and future works

Biomethanation processes induce increase in pH because of bicarbonate removal; however, large scale food waste digesters are prone to low pH due to high VFA levels. This particularly makes the adoption of biomethanation in such systems feasible, as shown from the results in this study, since the high VFAs content becomes useful to buffer the excessive pH increase resulting. Depending on the process optimisations, percentage biomethane yield from single stage AD of food waste could range from 55 to 73% [13,45,46], and to be injected into the gas grid, it has to be purified to obtain over 95% biomethane (typically 97–98%; [47]. The current decrease in incentives for electricity generation from biogas and a more robust incentive for its upgrade to biomethane, has inspired the optimisation of biogas from AD to fully exploit its potential as a renewable energy source [2].

With biomethanation, considering there is an existing infrastructure the only areas for additional energy input would be for hydrogen production, transport and storage (if necessary) and injection mechanism. Hydrogen production would impact about the most energy demand and must be from a renewable source too, in order not to contradict the overall aim. In this regard, further studies on the influence of hydrogen injection time and increase in hydrogen concentration added in anaerobic digesters are needed to fully understand and optimise the use of hydrogen towards food waste biogas upgrade for injection into the gas grid and possible transport fuel.

4. Conclusions

The addition of hydrogen showed great potential to improve food waste AD. This influenced an increased hydrogenotrophic methanogenesis activity, as suggested by a higher percentage hydrogen utilisation of 71.7% measured in the test reactor, compared to 27.6% in the control. This likely allowed competition for the hydrogen produced during secondary fermentation in favour of hydrogenotrophic methanogenesis. This was also supported by the continuous removal of CO_2 in the test reactor during the digestion period, suggesting the progression of hydrogenotrophic methanogenesis. There was an initial increase in the dissolved organic contents when hydrogen gas was available in the headspace due to a temporary shift in the substrate's utilisation to the readily available H_2 and CO_2; indicating an increased activity of hydrogenotrophic methanogens. Consequently, an initial increase in propionate and butyrate accumulation rates was observed with hydrogen injection. The gas-liquid mass transfer also increased through time, which likely improved the interspecies hydrogen transfer between the hydrogenotrophic methanogens and the hydrogen producing acetogens, thus, reducing the potential for propionate-induced inhibition. Despite high concentrations of nitrogen in the feedstock (low C/N ratio), ammonia toxicity was not present, as a result of acidification from the production of VFAs. Therefore, the pH was maintained below thresholds that should impact on a thermodynamic shift towards free ammonia nitrogen. With the addition of hydrogen, the final biogas was upgraded, yielding 12.1% increase in biomethane (from 417.6 to 468.3

NmL-CH_4/gVS_{added}) and 38.9% reduction in CO_2 (from 227.1 to 138.7 NmL-CO_2/gVS_{added}). It is expected that by increasing the concentration of hydrogen gas injected and/or intermittent hydrogen injection, the biogas can further be upgraded to obtain a gas suitable for injection into the gas grid. This, and the microbial analysis of the systems should be studied in future to further investigate the impact of injecting hydrogen on the microbial population.

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