Received: 21 August 2020 | Revised: 8 March 2021 | Accepted: 6 April 2021

DOI: 10.1002/fes3.288

Food and Energy Security Open Access WILEY

ORIGINAL RESEARCH

Enhancing bioenergy production from food waste by in situ biomethanation: Effect of the hydrogen injection point

Cynthia Kusin Okoro-Shekwaga[1,2] | **Andrew Ross**[3] | **Miller Alonso Camargo-Valero**[1,4]

[1]BioResource Systems Research Group, School of Civil Engineering, University of Leeds, Leeds, UK

[2]Department of Agricultural and Bioresources Engineering, Federal University of Technology, Minna, Nigeria

[3]School of Chemical and Process Engineering, University of Leeds, Leeds, UK

[4]Departamento de Ingeniería Química, Universidad Nacional de Colombia, Campus La Nubia, Manizales, Colombia

Correspondence
Miller Alonso Camargo-Valero, BioResource Systems Research Group, School of Civil Engineering, University of Leeds, Leeds, UK.
Email: M.A.Camargo-Valero@leeds.ac.uk

Funding information
University of Leeds

Abstract

The increasing rate of food waste (FW) generation around the world is a growing environmental concern, notwithstanding, its valorisation through anaerobic digestion (AD) makes it a potential resource. Moreover, there is a growing demand to optimise the biomethane from AD for gas-to-grid (GtG) and vehicular applications. This has spurred researches on hydrogen gas (H_2) injection into AD systems to enhance the biological conversion of H_2 and carbon dioxide (CO_2) to methane (CH_4), a process known as biomethanation. A simplistic approach for biomethanation is to add H_2 directly into working AD reactors (in situ biomethanation). However, a competition for the injected H_2 towards other biological reactions besides H_2/CO_2 conversion to CH_4 could follow, thus, reducing the efficiency of the system. Hence, this study was conducted to understand how different H_2 injection points would affect H_2/CO_2 conversion to CH_4 during FW in situ biomethanation, to identify an optimal injection point. Experiments were designed using H_2 equivalent to 5% of the head-space of the AD reactor at three injection points representing different stages of AD: before volatile fatty acids (VFA) accumulation, during VFA accumulation and at depleted VFA intermediates. Lower potential for competitive H_2 consumption before the accumulation of VFA enabled a high H_2/CO_2 conversion to CH_4. However, enhanced competition for soluble substrates during VFA accumulation reduced the efficiency of H_2/CO_2 conversion to CH_4 when H_2 was added at this stage. In general, 12%, 4% and 10% CH_4 increases as well as 39%, 25% and 34% CO_2 removal were obtained for H_2 added before VFA accumulation, during VFA accumulation and at depleted VFA intermediates, respectively. For immediate integration of biomethanation with existing AD facilities, it is suggested that the required H_2 be obtained biologically by dark fermentation.

KEYWORDS

anaerobic digestion, biological CO_2 conversion, food waste, hydrogen injection point, in situ biomethanation

1 | INTRODUCTION

A third of the food crops cultivated annually (about 1.3 billion tonne—Bt) for human consumption is reportedly wasted or lost at some level within the food supply chain from production to consumption (FAO, 2011); accounting for 44% of global waste (Kaza et al., 2018). It is reported that annual global solid waste generation will increase from the 2.01 billion tonnes estimate of 2016 to 2.59 billion tonnes in 2030 and 3.40 billion tonnes in 2050 (Kaza et al., 2018), consequently, FW increases are expected. Although this increasing rate of FW generation around the world is a growing environmental concern, its valorisation through anaerobic AD makes it a potential resource.

Biological upgrade of AD biogas to biomethane (biomethanation) provides more opportunities to fully exploit biogas potentials through GtG applications and use as vehicle fuel. Hence, biomethanation is becoming a highly researched area within the AD community.

Biological enrichment of CH_4 using anaerobic microorganisms that can convert H_2/CO_2 to CH_4 (also known as biomethanation) is increasingly being explored, to replace the conventional physicochemical technologies. Physicochemical technologies for biogas upgrade separate CO_2 in the biogas from CH_4 and includes processes such as absorption, adsorption and cryogenic and membrane separation (Angelidaki et al., 2018). These technologies are associated with a 20%–72% elevation in CH_4 production cost due to high energy, chemical and water demand, and up to 8% CH_4 losses (Linville et al., 2016). Also, additional waste is generated from these processes (Ullah Khan et al., 2017) and the regeneration of the adsorbent media releases the entrapped CO_2 into the atmosphere (Aryal et al., 2018; Linville et al., 2016), thus, reducing the carbon savings from biogas applications (Bright et al., 2011). However, biomethanation has the potential to double the original mass of CH_4 and can effectively remove CO_2 from the biogas for use in microbial metabolism, such that the CO_2 is not released into the atmosphere (Muñoz et al., 2015; Ryckebosch et al., 2011). Additionally, impurities in the biogas such as ammonia, carbon monoxide and hydrogen sulphide (H_2S) can be harnessed by the microorganisms during CH_4 enrichment (Aryal et al., 2018).

Typically, biomethanation can be mediated either ex situ (supply of H_2 into an external reactor enriched with hydrogenotrophic methanogens), in situ (direct supply of H_2 into the anaerobic digester treating a feedstock) or a combination of both ex situ and in situ (hybrid; Angelidaki et al., 2018; Zabranska & Pokorna, 2018). In situ biomethanation allows for efficient use of available hydrogenotrophic methanogens and volumetric space, thus, eliminating the extra cost for a post AD biogas treatment infrastructure (Aryal et al., 2018).

Low gas–liquid H_2 mass transfer due to its low solubility (15.5 mg/L at 25°C) is a common limitation to biomethanation (Angelidaki et al., 2018). In this regard, academic researches have increasingly focused on process modifications to improve gas–liquid H_2 mass transfer including, the mixing regime (Luo & Angelidaki, 2012; Yun et al., 2017), packing materials such as alumina ceramic sponge and rushing rings (Bassani et al., 2016) and the H_2 injection approach. H_2 injection approaches include pulse injections (Agneessens et al., 2017; Wahid et al., 2019), trickling filters (Rachbauer et al., 2016), hollow fibre membranes (Alfaro et al., 2019; Luo & Angelidaki, 2013a) and ceramic and column diffusers (Luo & Angelidaki, 2013b). While these processes have recorded significant CH_4 enrichment (up to 100%), the efficiency of H_2/CO_2 conversion for in situ biomethanation as influenced by the digestion stages (according to the VFA regime) during which H_2 is injected has not been studied.

AD progresses by the complex interaction of microorganisms according to four stages: hydrolysis, acidogenesis (primary fermentation), acetogenesis (secondary fermentation) and methanogenesis (hydrogenotrophic and acetoclastic), which have different reactions to a surge in H_2 and potentials for a competitive H_2 consumption (Kumaran et al., 2016; Schink et al., 2017). By implication, the reactive stage during which H_2 is injected will affect the rate of H_2/CO_2 conversion to CH_4. A competition for the added H_2 by other H_2 consumers could occur, through other H_2 sinks, such as acetate production by homoacetogenesis and sulphides production (sulphidogenesis), leading to low H_2/CO_2 to CH_4 conversion efficiency.

According to the AD process thermodynamics, H_2 utilisation would follow the order: sulphidogenesis > hydrogenotrophic methanogenesis > homoacetogenesis. The metabolism of each process, however, would depend on some factors including, the degraded state of the substrate; availability of combining elements such as CO_2 for hydrogenotrophic methanogens and homoacetogens and sulphur/sulphate for sulphate-reducing bacteria (SRB); the presence of inhibitors (including H_2) and operating conditions like pH (Chen et al., 2014). Hence, considering the underlying complexities associated with H_2 production, storage and transportation, it is important to optimise the process such that most (if not all) of the H_2 used for *in situ* biomethanation is efficiently utilised for CO_2 conversion to CH_4.

Biomethanation have been highly researched using low-organic substrates such as cattle manure, sewage sludge and glucose. Researches on biomethanation using FW are relatively under-developed, limited to recent studies (Okoro-Shekwaga et al., 2019; Tao et al., 2020; Yang et al., 2020). Moreover, Okoro-Shekwaga et al. (2019), suggested that FW was a suitable substrate for in situ biomethanation due to a high potential for volatile fatty acids (VFA)-induced pH buffer. The authors reported that using FW, pH levels

were maintained within an optimal pH range of 6.8 to 7.4 (Kumaran et al., 2016).

The highly organic and heterogeneous characteristic of FW makes it behave differently from other typical substrates during AD. Therefore, it can be expected to behave differently with biomethanation, so that, findings from biomethanation studies on other typical substrates might not be directly applicable to FW. Also, high-organic substrates, such as food and green waste, are on a global increase and thus, hold great potential as a resource for in situ biomethanation in the future. In the United Kingdom (UK), for instance, FW remains the largest AD feedstock (asides from other liquid feedstock such as sewage sludge), with about 22.9% of the FW generated annually processed through AD (WRAP, 2015).

Therefore, this study explores FW in situ biomethanation, with H_2 injection at different AD stages; analysing its stability and the possibility of a competitive H_2 utilisation for other processes besides biomethane production. Three H_2 injection points were selected, which correspond to periods before VFA accumulation (hydrolysis), during VFA accumulation (fermentation) and with depleted VFA intermediates. The findings from this study posit that FW in situ biomethanation has a great potential to become the game-changer modification aimed at enhancing biological CO_2 capture and valorisation for the production of bio-based renewable energy from FW.

2 | METHODOLOGY

2.1 | Food waste characterisation

Waste samples were collected from the University of Leeds' student refectory for 5 days in separately monitored bins. FW sorting, storage and characterisation method follow the methods described in a previous study (Okoro-Shekwaga et al., 2020). The characteristics of the FW used in this study are presented in Table 1, which includes pH, total solids (TS), volatile solids (VS), total chemical oxygen demand (TCOD) and total VFA (TVFA). FW samples were diluted by predetermined factors before some analyses, including 1 in 5 ml dilution for pH and VFA and 1 in 1000 ml dilution for COD. The final COD and VFA results were corrected by the respective dilution factors, while pH was reported without conversion. The analytical methods employed are described in Section 2.4.2.

2.2 | Inoculum preparation

Digestate collected from an anaerobic digester fed with sewage sludge at mesophilic temperature was used as inoculum. The inoculum was collected from Yorkshire Water's Esholt

TABLE 1 Characteristics of FW used in this study and the reactor content (liquid phase) before H_2 addition

	Food waste used	Exp1			Exp2			Exp3		
		Blank	Control	Test	Blank	Control	Test	Blank	Control	Test
pH	4.8 (0.0)	8.6 (0.0)	8.5 (0.0)	8.5 (0.0)	7.7 (0.0)	7.1 (0.0)	7.0 (0.0)	8.2 (0.0)	7.0 (0.0)	7.0 (0.0)
TS (g/L)	314.3 (0.2)[a]	10.5 (0.3)	14.3 (0.2)	14.3 (0.2)	10.3 (0.3)	11.6 (0.2)	11.6 (0.2)	9.8 (0.0)	10.3 (0.0)	10.3 (0.0)
VS (g/L)	295.0 (0.3)[a]	6.1 (0.3)	9.0 (0.2)	9.2 (0.2)	6.0 (0.10	6.9 (0.1)	6.9 (0.1)	6.3 (0.2)	7.2 (0.1)	7.2 (0.1)
TVFA (mg/L)	5111 (354)[a]	32.6 (4.6)	52.1 (11.3)	52.1 (11.3)	8.9 (2.0)	626.5 (3.5)	626.5 (3.5)	5.1 (1.4)	35.6 (2.5)	35.6 (2.5)
sCOD (g/L)	–	1.2 (0.1)	2.0 (0.1)	2.0 (0.1)	1.3 (0.1)	2.1 (0.1)	2.1 (0.1)	0.7 (0.0)	0.8 (0.0)	0.8 (0.0)
TCOD (g/kg)	469.7 (0.0)	–	–	–	–	–	–	–	–	–

Values in brackets are the corresponding standard deviations from triplicate samples.

[a]TS and VS reported as g/kg and TVFA reported as mg/kg.

Waste Water Treatment Work (Bradford, UK). It was then processed and adapted to FW as described in a previous study (Okoro-Shekwaga et al., 2019).

2.3 | Experimental set-up

Wheaton bottles (160 ml) were used as batch anaerobic reactors with 75 ml working volumes and held in a water bath to maintain reactor temperature at 37°C. An inoculum-to-substrate ratio (ISR) of 3:1 based on VS was adopted according to previous ISR optimisation tests (Okoro-Shekwaga et al., 2020). The experiments were set up to include a blank (inoculum only), control (inoculum and FW without H_2 injection) and test (inoculum and FW with H_2 injection) reactors. Blank reactors were set up to assess biogas contribution from the inoculum. Hence, the biogas yield from the blank was subtracted from the respective biogas yields of the control and test and reported accordingly. The control and test were prepared from the same bulk sample, such that, the only difference between both reactors was the injection of H_2 to the test. Three H_2 injection points were chosen according to VFA regimes during batch FW anaerobic digestion in a previous study (Izumi et al., 2010). The authors reported that VFA accumulation peaked 1–3 days after the start of the experiment and decreased rapidly within 6 days (except for propionate). Therefore, the three injection points chosen were Day 0, Day 3 and Day 6 representing periods before VFA accumulation, during VFA accumulation and depleted VFA intermediates and labelled Exp1, Exp2 and Exp3, respectively. The amount of H_2 used was equivalent to 5% of the head-space of the reactor. A relatively low amount of H_2 was used because this study aims to understand the adjustment of the system to in situ biomethanation using FW AD systems. The blank and control reactors were purged with nitrogen gas (N_2) for 1 min to obtain anaerobic environment and sealed with rubber stoppers and aluminium crimps. H_2 was added to all test reactors by flushing the reactors with a gas mixture of 5%-H_2:95-N_2 for 1 min. Exp2 and Exp3 bulk samples of the blank and substrate (FW plus inoculum) were prepared in 1 L Duran bottles, with rubber corks and set up to digest anaerobically up till Day 3 and Day 6, respectively. Afterwards, the generated biogas volume and composition from these reactors were measured at the respective days. The bulk samples were then split into Wheaton reactors, followed by a purge with N_2 for 1 min to regain an anaerobic environment and H_2 addition into the test reactors. Hydrogen addition to the reactors follows the method developed by Okoro-Shekwaga et al. (2019), which included hydrogen leak testing. The assays were prepared as sacrificial samples in triplicates for each analytical point (seven per assay), and the characteristics of each reactor are presented in Table 1.

2.4 | Analytical methods

2.4.1 | Analysis of head-space gas

The volume of the head-space gas was measured by water displacement, according to previously developed methods by Okoro-Shekwaga et al. (2019). The composition of the head-space gas was measured by gas chromatography (GC – Agilent Technology, 7890A), which uses a thermal conductivity detector (TCD) and a Carboxen 1010 PLOT column with the following dimensions: length 30 m, diameter 0.53 mm and film thickness 30 μm. A detailed description of the oven and detector temperatures, carrier gas, injection methods and calibration is described in Okoro-Shekwaga et al. (2019).

2.4.2 | Analysis of liquid samples

Standard analytical methods used for the examination of wastewaters and sludge were employed for liquid sample analysis: TS and VS were measured by the gravimetric method as described in 2540 B and 2540 E of standard methods, respectively, and VFA composition was analysed by gas chromatography (GC) analyser (Agilent Technologies, 7890A) as described in 5660 B of standard methods, COD was analysed by the titrimetric method as described in 5220 C of standard methods (APHA, 2005). Soluble COD (sCOD) was conducted on samples' filtrate, by centrifuging the samples at 2000 rpm (775 ***g***) for 5 min using an Eppendorf Centrifuge and filtering the supernatant through 0.45 μm Whatson filter paper, followed by the standard methods for analysing COD (5220 C). The pH was measured using a pH meter (HACH, 40d) and sulphur content was measured using a Thermo Scientific FLASH2000 Organic Elemental Analyzer on samples oven-dried at 40°C and ground to powder.

2.5 | Statistical analysis

Descriptive statistical analysis including normality test, mean and standard deviation was conducted on all experimental data. The data from each assay were first subjected to analysis for statistical significance, using a one-sample *t* test. Where significant differences were observed, an additional test was conducted to eliminate outliers.

3 | RESULTS AND DISCUSSION

3.1 | Hydrogen utilisation

The biogas composition for the periods H_2 was measured in the head-space of the reactors were analysed; test and

control represent reactors with and without H_2 addition, respectively (Table 2). The low solubility of H_2 in water means that changes in the head-space H_2 would be a consequence of gas–liquid H_2 transfers mediated by active microorganisms associated with H_2 consumption or production. The head-space of the control in Exp1 recorded some H_2 up to 48 h after set-up, indicating the production of H_2 for which the rate of consumption was lower than the rate of production and the excess H_2 was transferred to the head-space. Assuming similar H_2 production in the test, then, in addition to the H_2 injected, 4.6 mg-H_2/L would have been expected in the biogas of the test after 24 h. Instead, the head-space H_2 was lower than the external H_2 added by 0.3 mg-H_2/L. For the same period, biomethane concentration in the test was higher than the control by 7.8%, while CO_2 concentration was lower by 1.7%.

The difference in the H_2 of the test between 0 and 48 h was 3.0 mg-H_2/L, which should yield 6.0 mg-CH_4/L, using a stoichiometric CH_4:H_2 mass ratio of 1.99 (Okoro-Shekwaga et al., 2019). Adding this value to the biomethane concentration from the control within 48 h, 27.7 mg-CH_4/L would be expected, which was similar to the actual concentration measured (27.8 mg-CH_4/L). Furthermore, comparing the yields of the test and control between 24 and 48 h, biomethane concentration was higher by 26.9%, while CO_2 concentration was lower by 10.4% in the test. This follows an H_2 utilisation of 2.7 and 0.2 mg-H_2/L in the test and control, respectively, thus, implying enhanced biomethanation in the test as AD progressed, which would also suggest that the H_2 added in Exp1 was mostly utilised for CH_4 production.

A recent study revealed that despite excess H_2 loading, uptake of H_2 by fermenting microorganisms will only be to a very small fraction considering H_2 penetration from saturation into an active methanogenic substrate is less than 1 mm (Aryal et al., 2018). Also, the utilisation of H_2 for sulphate reduction mainly depends on intermediates from anaerobic fermentation/hydrolysis (Hao et al., 2014)—See Section 3.3, which means H_2 added in Exp1 was primarily utilised towards H_2/CO_2 conversion to biomethane in the test.

In Exp2, H_2 was neither measured in the test nor the control reactors by the next day after addition, believed to be because of heightened competition for common substrates at the fermentation stage (Schink et al., 2017). From Table 2, if all of the added H_2 was utilised to produce biomethane, then the biomethane concentration in the test would have been higher than the control by 7.9 mg-CH_4/L.

However, the difference between the test and the control was 5.4 mg-CH_4/L; being less by 31%. According to Schink et al. (2017), primary fermenters use up the bulk of the energy available during AD (about −280 kJ per mol-glucose) to ferment compounds such as amino acids to glucose, with the excess electrons released in the form of H_2. After primary fermentation, however, soluble substrates become available for the vast group of microorganisms actively present. As only a small amount of energy is available for secondary fermenters and the cooperating methanogens and sulphate reducers, extensive competition for available energy (substrates) is enriched during secondary fermentation (Schink et al., 2017), which would explain the rapid H_2 utilisation observed in Exp2. As would be discussed later in Section 3.3, results from the sulphur degradation suggest the utilisation of H_2 for other H_2-influenced processes, thus, buttressing a high competition for the added H_2 Exp2.

Exp3 demonstrated an ultimate consumption of the added H_2 for CO_2 conversion to biomethane. At the time of H_2 addition in Exp3, only trace amounts of acetate and propionate were remaining in the liquid reactor content (see Section 3.2). Thus, little or no competition was expected due to insufficient co-substrates. After 24 h, only 0.20 mg-H_2/L was measured in the test, suggesting a high H_2 uptake of 94.9%. Similarly, Wahid et al. (2019) reported a rapid H_2 uptake of 93% within 24 h, when H_2 was added on Day 9 of in situ biomethanation with glucose. During in situ biomethanation with 5-day pulse H_2 addition, which was started after Day 6 and sewage sludge

TABLE 2 Mean concentration of biogas components (at STP) in initial days immediately following H_2 addition ($n = 3$)

Experiment	Digestion time (h)	Control (mg/L)			Test (mg/L)		
		H_2	CH_4	CO_2	H_2	CH_4	CO_2
Exp1	0	0.0	0.0	0.0	4.0	0.0	0.0
	24	0.6	11.5	108.6	3.7	12.4	106.8
	48	0.4	21.9	200.7	1.0	27.8	179.8
	72	0.0	37.2	350.2	0.0	41.6	293.0
Exp2	0	0.0	0.0	0.0	4.0	0.0	0.0
	24	0.0	63.1	70.1	0.0	68.6	38.5
Exp3	0	0.0	0.0	0.0	4.0	0.0	0.0
	24	0.0	29.4	49.8	0.2	36.3	0.0
	48	0.0	53.4	69.4	0.0	57.9	35.9

Abbreviation: STP, Standard Temperature (273 K) and Pressure (1 atm).

as substrate, Agneessens et al. (2017) reported a high H_2 uptake immediately after H_2 was added, which was completely consumed within 24 h.

For 3.8 mg-H_2/L consumed within 24 h, the biomethane yield in the test was expected to be higher than the control by 7.5 mg-CH_4/L, to give a biomethane concentration of 36.9 mg-CH_4/L. Instead, 36.3 mg-CH_4/L was measured in the test; being less than the expected yield by only 1.4%, which indicates extensive H_2 uptake for methane production. Also, while the concentration of CO_2 in the control was 49.8 mg/L in 24 h, no CO_2 was measured in the test, to further buttress the assertion that the added H_2 was ultimately utilised for methane production. A comparatively high H_2 in Exp3 might be because at steady-state methane production, hydrogenotrophic methanogens are only starved of H_2 and can increase their metabolism to several orders of magnitudes should the substrates be non-limiting (Aryal et al., 2018).

After the complete uptake of the H_2 injected, CO_2 levels were lower than expected in the test of all three experiments. Supposing all the added H_2 were utilised for biomethane production, the CO_2 in the test would be expected to be less by 21.6 mg/L. However, the CO_2 in the test of Exp1, Exp2 and Exp3 was lower than the corresponding control by 57.2, 31.6 and 33.5 mg/L, respectively. Reportedly, around 0.28%–0.42% H_2 and 3% CO_2 are said to be converted to biomass during biomethanation, such that, the stoichiometric ratio of 4:1 (H_2:CO_2) for 1 mole of CH_4 production becomes 4:1.085 (Lecker et al., 2017). Consequently, 6.4%–8.5% losses in CO_2 have been attributed to biomass growth in various biomethanation studies (Burkhardt & Busch, 2013; Lecker et al., 2017; Luo et al., 2012; Rachbauer et al., 2016). As such, the lower than expected levels of CO_2 in the test suggest that methanogenesis was enhanced in all three experiments via the hydrogenotrophic route (Okoro-Shekwaga et al., 2019). Exp1 yielded the highest biomethane enrichment, followed by Exp3, suggesting that periods before VFA accumulation and depleted VFA intermediates would support higher conversions.

3.2 | Process stability: VFA and pH profiles

3.2.1 | Volatile fatty acids profile

During hydrolysis, whereby, CO_2 is the principal inorganic electron acceptor available, the only possible route for H_2

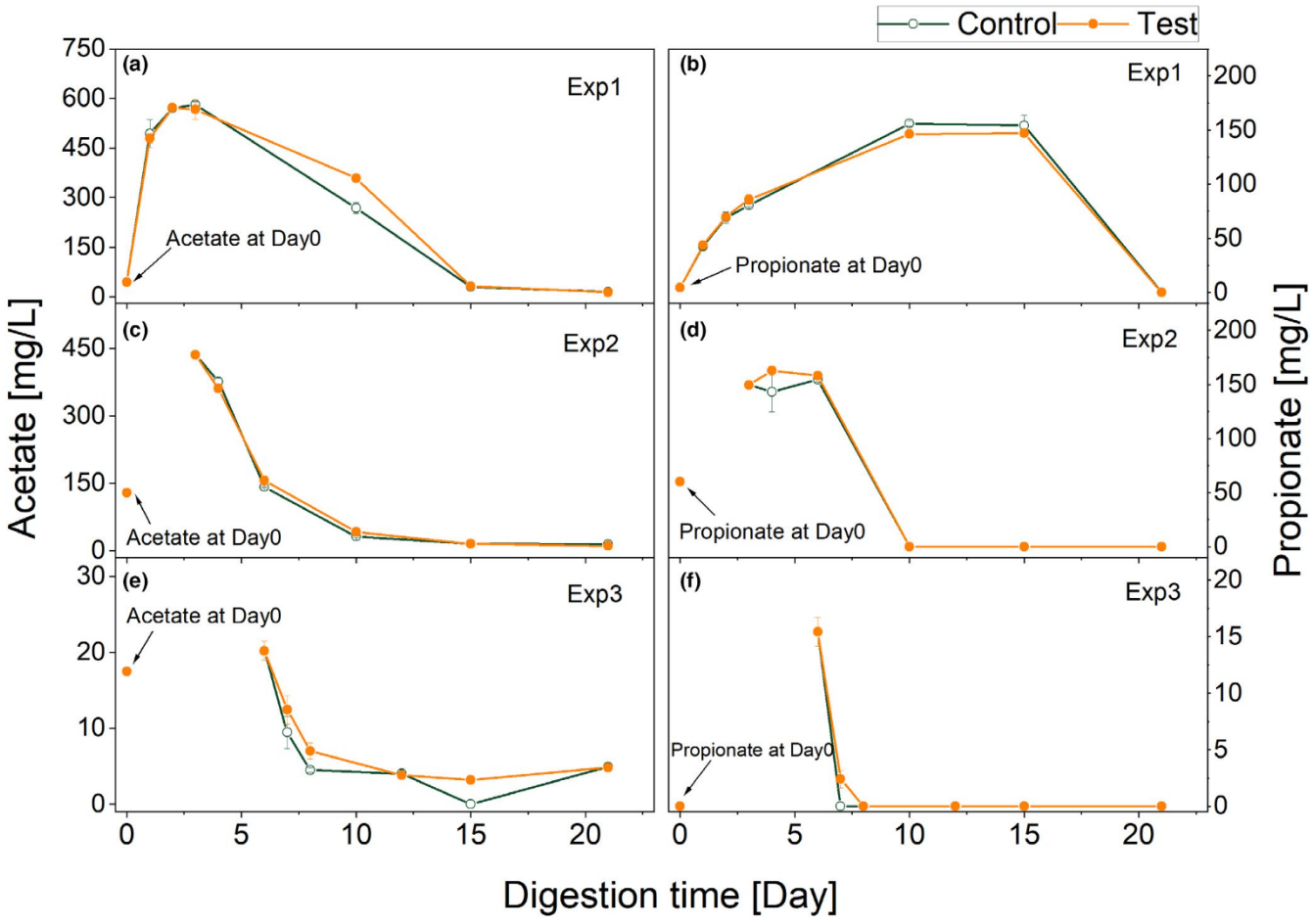

FIGURE 1 Acetate and propionate levels of the liquid content in Exp1, Exp2 and Exp3: acetate (a, c, e) and propionate (b, d, f). Error bars indicate the standard deviation from the mean

consumption would be by hydrogenotrophic methanogenesis or homoacetogenesis, considering the SRB does not pose a competition at this stage (Chen et al., 2008). Similar acetate levels measured in the control and test for the periods H_2 was measured in the head-space of Exp1 (up to 48 h after the addition—Figure 1a) suggests that the H_2 added to the test was not utilised for homoacetogenesis. The same was observed with propionate profiles of the control and test in Figure 1b. Therefore, Exp1 showed no indication of inhibited VFA degradation for the periods H_2 was measured in the head-space as shown in Figure 1a,b.

In Exp2, whereby complete H_2 uptake was observed within 24 h in the test, acetate level in the test was similar to the control (Figure 1c), while propionate was observed to be 6.9% higher in the test (Figure 1d), suggesting possible inhibition on propionate degradation. This was only to a small extent because of the low levels of H_2 used in this study as well as a concomitant rapid H_2 uptake observed with Exp2. This means if H_2 was added during fermentation at higher concentrations than was used in this study, higher levels of propionate accumulation might occur, consequently, inhibiting acetate and methane production rates (Meng et al., 2013).

In Exp3, acetate degradation was slower in the test, for the period immediately following H_2 addition, with acetate levels being 31% and 56% higher in the test after 24 and 48 h, respectively (Figure 1e). Perhaps, this was due to an inhibited acetoclastic methanogenesis (Weiland, 2010) or the added H_2 was converted to acetate through homoacetogenesis as a result of the rise in pH (Modestra et al., 2015; see Section 3.2.2). However, acetate may not over-accumulate at this stage of digestion since only a negligible amount of propionate was available (Figure 1f) and other VFA intermediates were completely depleted.

From all three experiments (Exp1, Exp2 and Exp3), only Exp2 showed signs of VFA (propionate) inhibition, which might be expected to increase in magnitude at higher H_2 loading. Notwithstanding, a rapid utilisation of the added H_2 as observed in Section 3.1 might favour a forward push in propionate degradation, hence, disallowing excessive increases in propionate levels (Meng et al., 2013; Yang et al., 2017). In agreement, when H_2 was added to the co-digestion of manure and acidic whey, Luo and Angelidaki (2013b) reported that acetogenesis was not inhibited. But inhibition to VFA degradation during maize leaf in situ biomethanation was recorded when H_2 was supplied over the stoichiometric H_2:CO_2 ratio (Mulat et al., 2017). During the in situ biomethanation of FW, excessive accumulation of VFA was reported 15 days following the injection of syngas (CO/H_2—at a ratio of 5/4), which the authors suggested was due to inhibitory effects of CO on the methanogens (Yang et al., 2020). However, with a phased increase in the volume of syngas injected, no VFA accumulation was not observed.

3.2.2 | pH profiles

The pH profiles for all three experiments are presented in Figure 2, which shows that the H_2 addition point influenced the extent of pH change of the overall process. The pH of biomethanation systems is often influenced by the CO_2 content of the gaseous phase and the buffering capacity of the liquid phase (Tao et al., 2020). Excessive removal of CO_2 from the AD system causes a rise in pH, which is recommended to be

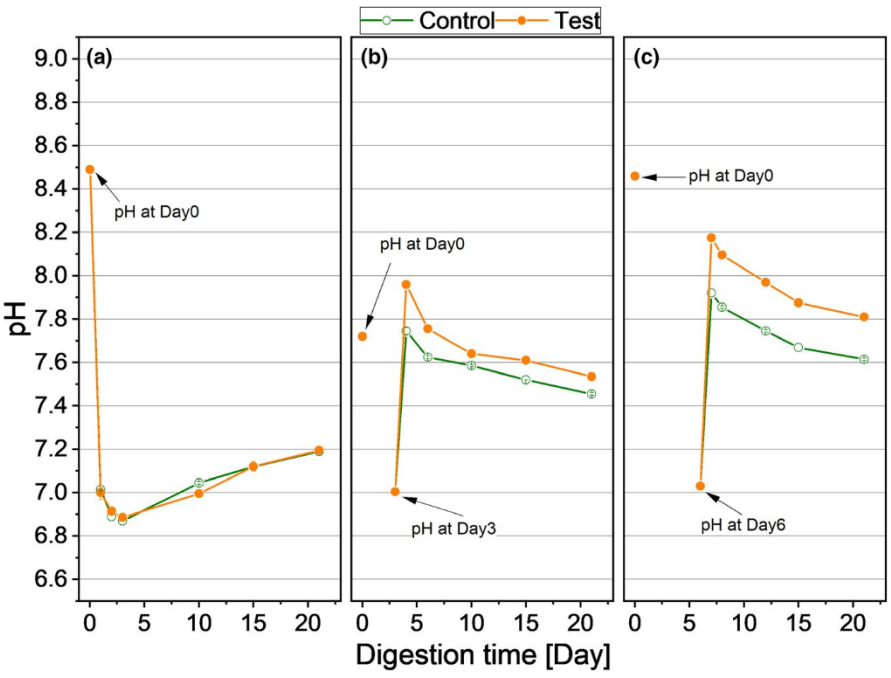

FIGURE 2 pH profiles of the liquid content after H2 addition: (a) Exp1, (b) Exp2 and (c) Exp3. Error bars indicate the standard deviation from the mean

maintained within a range of 6.7 to 7.4 to support optimum methanogenic activities in mesophilic reactors (Wahid et al., 2019). However, the use of acidic substrates helps to buffer down the pH (Luo & Angelidaki, 2013b; Okoro-Shekwaga et al., 2019).

VFA production during primary fermentation caused a decline in the pH of all three experiments immediately after set-up (Kumaran et al., 2016). This high concentration of VFA, which becomes available after H_2 was injected in the test of Exp1, helped to buffer the pH within optimal limits, despite a progressive biomethanation (Okoro-Shekwaga et al., 2019). Thus, the pH of the test in Exp1 remained similar to the control (Figure 2a).

The increase in the pH of the control in Exp2 and Exp3 (Figure 2b,c) was because of the removal of the biogas generated (consequently, CO_2) from the system before H_2 addition. As such, higher pH levels were observed in Exp3 whereby, the biogas contained higher amounts of CO_2 before extraction. Similarly, when H_2 was injected on Day 9 of in situ biomethanation with glucose, complete removal of CO_2 caused pH to rise above 8.5 and up to 9.4, which was buffered with HCl (Wahid et al., 2019).

Higher pH levels measured in the test reactors of Exp2 and Exp3 compared to the corresponding controls demonstrate further CO_2 removal from H_2/CO_2 consumption further on from the H_2 injection point. This effect was higher in the test of Exp3 than Exp2, thus, asserting a higher H_2/CO_2 consumption in Exp3 than in Exp2. The change in pH between the test and control of Exp2 and Exp3 was between 0.1 and 0.3, which is similar to the 0.3 pH (8.0 to 8.3) increase reported during in situ biomethanation using manure (Luo et al., 2012). With further investigations, the addition of acidic whey to manure helped to buffer the system to maintain the pH below 8.0 (Luo & Angelidaki, 2013b). This agrees especially with Exp1, whereby, the pH was maintained below 8.0 throughout the AD period in the test due to a VFA-induced pH buffer.

Although FW is an acidic substrate, the pH buffering capacity of the liquid content reduced as the AD progressed because of the level of VFA available at the time of H_2 addition.

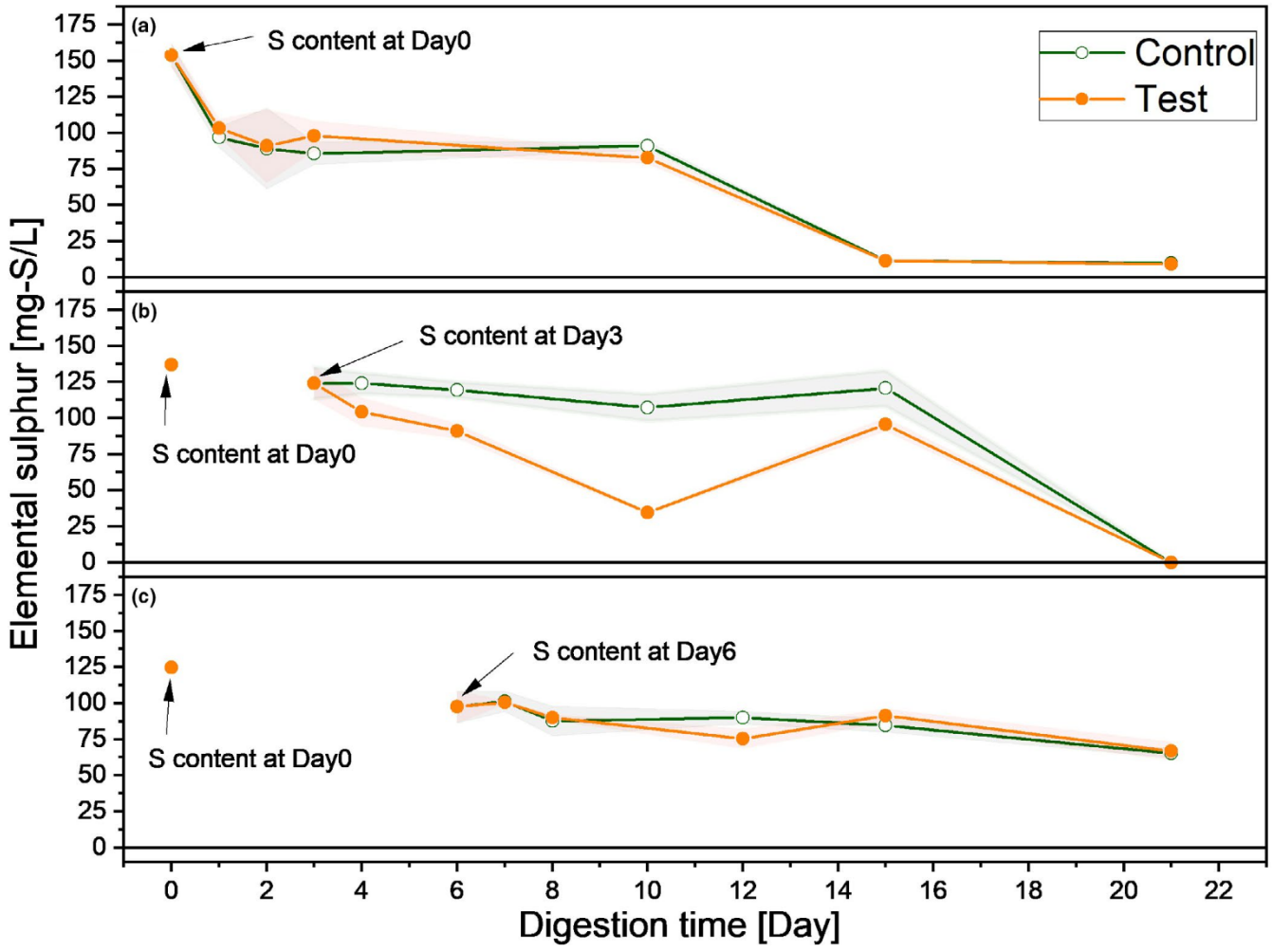

FIGURE 3 Sulphur profiles of the liquid content (dry basis) after H2 addition: (a) Exp1, (b) Exp2 and (c) Exp3. Shaded portion indicates the standard deviation from the mean

Therefore, asides from the feedstock, pH during in situ biomethanation can also be impacted by the digestion stage before the addition of H_2 as observed here.

3.3 | Competitive H_2 utilisation: sulphur degradation

In the absence of oxygen, organic and inorganic sulphur can either be fermented or reduced to dissolved sulphides, which can be translated to the biogas as hydrogen sulphide and is principally progressed by the SRB (Peu et al., 2012). Moreover, sulphur can be distributed in different forms in a thermodynamic equilibrium during AD (Hao et al., 2014). This means its availability in any form will be dependent on the thermodynamic reaction and conditions of the system, such that an increase in one form will imply a decrease in the other. Hence, the potential for sulphide production becomes a function of sulphur biodegradation (Peu et al., 2012).

As presented in Figure 3a, regardless of the H_2 added to the test, sulphur degradation profiles in the control and test followed a similar pattern in Exp1. Because SRB would mainly metabolise intermediates from anaerobic fermentation/hydrolysis (Hao et al., 2014), they do not pose any competition during hydrolysis (Chen et al., 2008). As such, the early-stage reduction in the sulphur for both the control and test (up to Day 3) would follow the initial substrate solubilisation. Furthermore, a similar sulphur degradation trend observed in the test and control of Exp1 means that sulphur degradation was not particularly enhanced by the H_2 added, but followed a typical route as in the control without H_2 addition. This buttresses the assertion given in Section 3.1 that the H_2 added in the test of Exp1 was primarily utilised for CH_4 production.

The highest rate of sulphur degradation after H_2 addition was observed in the test of Exp2 (Figure 3b). Having already gone through initial solubilisation, the system at this stage was enriched with solubilised substrates, such as VFA, CO_2 and hydrolysed sulphur, thus, allowing competition for common substrates. Like Exp1, sulphur levels remained relatively unchanged in the control until Day15, while sulphur levels declined progressively in the test of Exp2 immediately after H_2 addition. Recall from Section 3.1 that H_2 added into the test of Exp2 was completely removed within 24 h. While this was not ultimately converted to biomethane, the decline in sulphur levels in the test for the same period suggests that the added H_2 was co-utilised for sulphur degradation.

Sulphur contents in the test of Exp2 continued to reduce even after the complete uptake of the added H_2, indicating a progressive utilisation of other common substrates. The kinetics and thermodynamics during secondary fermentation are in favour of SRB outcompeting the acetogens for common substrates (Chen et al., 2008) and the SRB-induced secondary fermentation reactions result in lower H_2 yields compared to the same progressed by acetogens. For instance, propionate degradation by SRB and typical acetogens (obligate hydrogen producers—OBHP) goes according to the reactions in Equations 1 and 2, respectively (Meng et al., 2013);

$$4CH_3CH_2COO^- + 3SO_4^{2-} \rightarrow 4CH_3COO^- + 4HCO_3^- + H^+ + 3HS^- \quad \Delta G = -151.3 \tag{1}$$

$$CH_3CH_2COO^- + 2H_2O \rightarrow CH_3COO^- + CO_2 + 3H_2 \quad \Delta G^\circ = +76.1 \tag{2}$$

According to the above equations, SRB-induced propionate degradation (Equation 1) is more thermodynamically favourable but produces lower H_2 than OBHP-induced degradation (Equation 2). Therefore, VFA intermediates degradation by SRB could also have had an impact on the CH_4 yield by reducing the amount of H_2 released from such reactions, which would have been further utilised for CH_4 production. This supports the relatively lower CO_2 removal of 25.4% obtained in the test of Exp2, compared to 38.8% from the test of Exp1. As such, competition for common substrates including H_2 and VFA intermediates could have reduced the overall CO_2 removal potential for H_2 added in Exp2.

As there was a limited amount of solubilised substrate available at the time of adding H_2 to Exp3, competitive H_2 uptake was presumably limited. As a result, regardless of H_2 addition in the test, the sulphur levels of both the control and test in Exp3 remained relatively unchanged throughout the AD period (Figure 3c).

Overall, the percentage of sulphur degraded in both the control and test within each experiment was about the same. In Exp1, 93.5% and 94.1% sulphur removal was recorded from the control and test, respectively. Meanwhile, 100% sulphur removal was recorded in both control and test of Exp2 and Exp3 recorded the least sulphur degradation at 32.9% and 31.3% removal in the control and test, respectively. These results, showing similar levels of sulphur degradation in both the control and test, suggest that the addition of H_2 did not enhance the overall potential for sulphides production from FW. However, the competition for available substrates could potentially reduce H_2/CO_2 conversion efficiencies to biomethane.

3.4 | Overall biogas upgrade

The biomethane and CO_2 yields from Exp1, Exp2 and Exp3 are presented in Figure 4. The addition of H_2 before VFA accumulation in the test of Exp1 enhanced biogas upgrade throughout the experiment (Figure 4a), thus, yielding lower

levels of CO_2 throughout the experiment (Figure 4b). This would indicate that H_2 produced from further VFA degradation was also utilised for biomethane production. In Exp2, AD progressed conventionally until Day 3 before H_2 was added, higher competition for common substrates at this stage was believed to have reduced the potential increase in biomethane attainable from the H_2 added. However, with the depletion of common solubilised substrates such as VFA within the system in Exp3, competition for H_2 at this stage was probably limited, thus, allowing higher biomethanation than Exp2 for the H_2 added.

In all three experiments, the addition of H_2 improved the quality of the biogas, resulting in 12%, 4% and 10% biomethane increases in Exp1, Exp2 and Exp3, respectively. The ratio of CO_2 reduction to biomethane increase in Exp1, Exp2 and Exp3 was 1.7, 0.8 and 1.5, respectively. This supports the foregoing discussions that H_2 added in Exp2 was competed for and hence, not optimally utilised for biomethane production.

Figure 4c presents biogas composition from the entire process, such that, the data charts for Exp2 and Exp3 is inclusive of the biogas extracted before H_2 addition. Therefore, although Exp3 had a higher H_2/CO_2 conversion to biomethane than Exp2 when the initial CH_4 and CO_2 yields generated before the addition of H_2 in these experiments were added to the final yields, the biogas quality from Exp3 was the poorest (Figure 4c). This was due to a higher amount of CO_2 accumulated by Day 6 compared to Day 3, at 386.8 and 193.4 ml, respectively. However, considering a higher biomethanation in Exp3, perhaps, biogas recirculation and continuous H_2 addition might help to improve the overall quality of the biogas produced from such biomethanation set-up (Bassani et al., 2016, 2017; Burkhardt et al., 2015).

3.5 | The implication of the current study

Different H_2 addition rates ranging from 0.3 to 40.2 L-H_2/(L.day) have been used in in situ biomethanation studies at varying hydraulic retention times, achieving about 43.3%–100% CO_2 removal (Agneessens et al., 2017; Alfaro et al., 2019; Bassani et al., 2016; Díaz et al., 2015; Luo & Angelidaki, 2012, 2013b; Mulat et al., 2017; Voelklein et al., 2019; Wahid et al., 2019; Wang et al., 2013). Most of these studies were conducted by injecting H_2 some days after the AD had progressed; typically at a

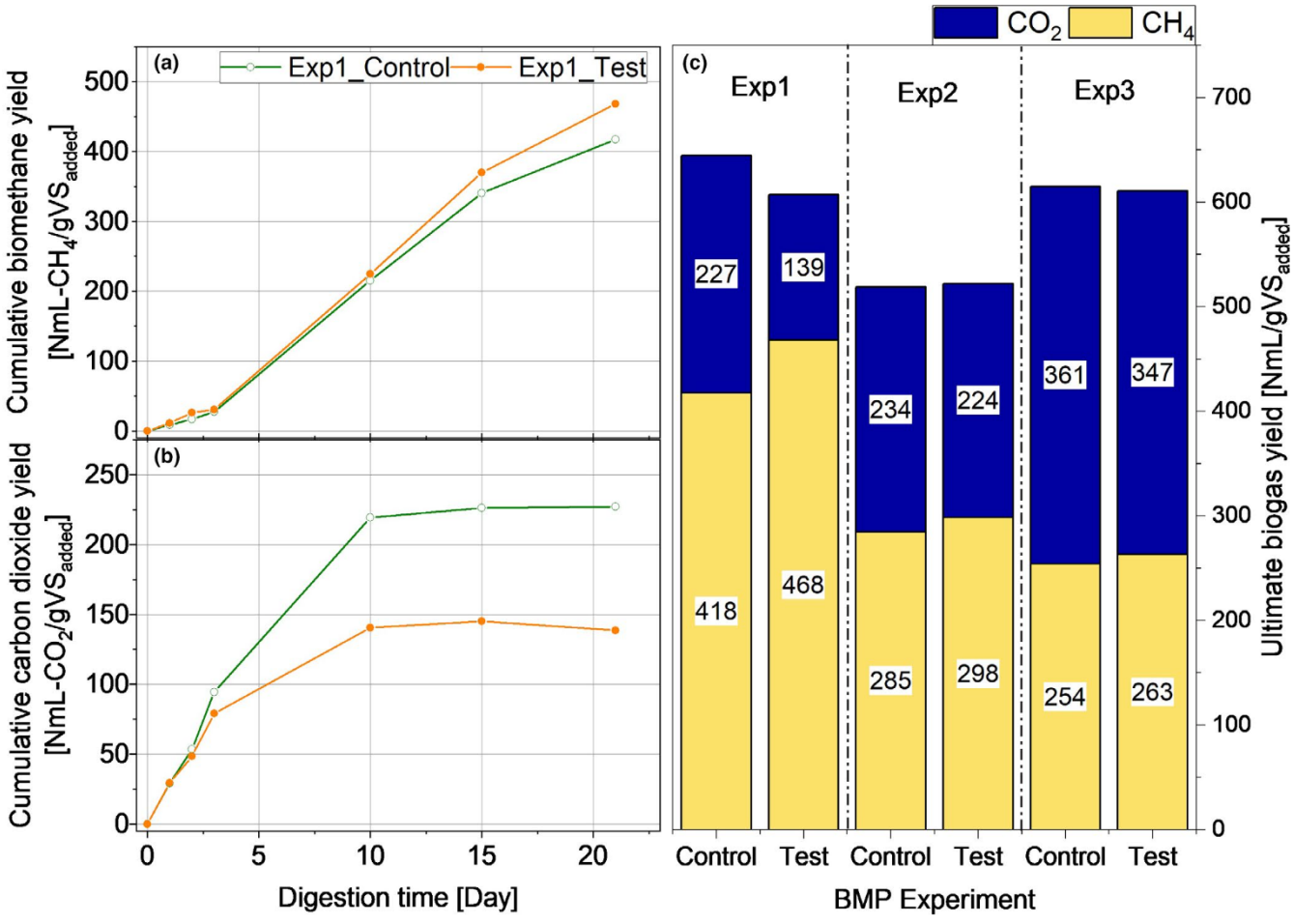

FIGURE 4 Cumulative methane (a) and carbon dioxide yield (b) from Exp1 and ultimate biogas yields (c) from Exp1, Exp2 and Exp3

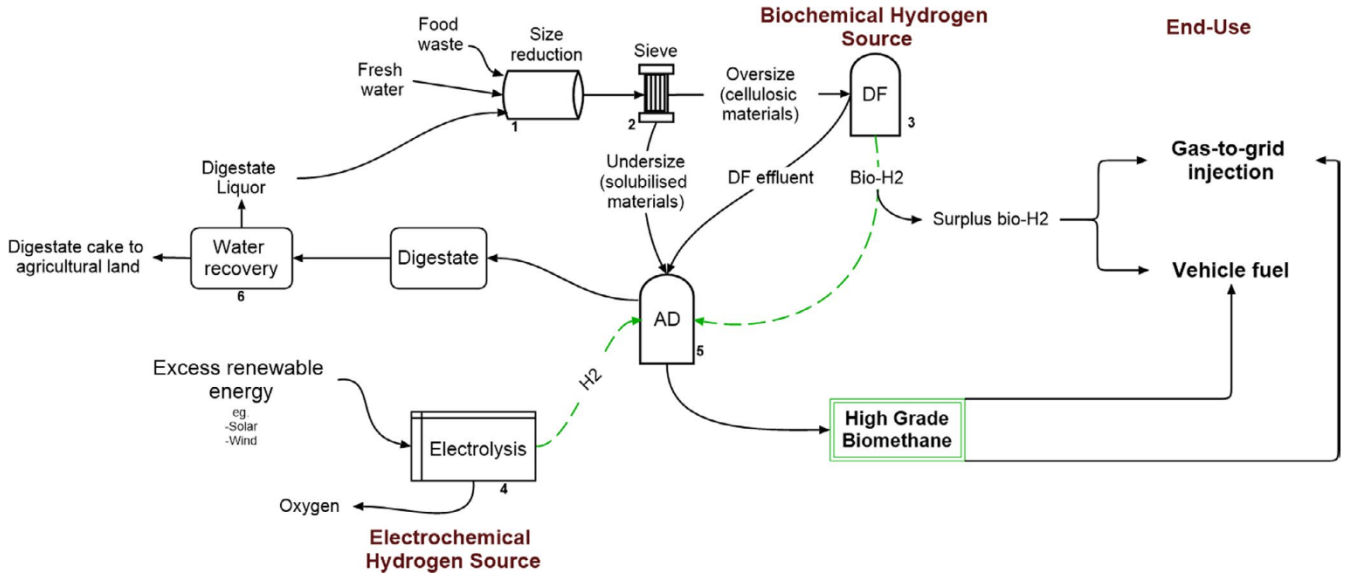

FIGURE 5 Schematic representation of the potential for integrating hydrogen production with anaerobic digestion of food waste for in-situ biomethanation: (1) Food waste grinding to reduce particle size; (2) Particle size fractionation to enhance solubility; (3) Biohydrogen production from oversize fractions characterised by cellulosic materials through dark fermentation (DF); (4) Hydrogen production by electrolysis using excess renewable energy; (5) Anaerobic digestion (AD) of solubilised food waste with the addition of hydrogen (insitu biomethanation) for high-grade biomethane production that could be injected into the gas grid or used as a vehicle fuel and (6) Opportunity for water recovery from the digestate to reduce system water demand and enhance a circular economy. The dash lines from steps 3 and 4 indicate alternative options for hydrogen production

steady state. However, the present study posits that the efficiency of H_2/CO_2 conversion to biomethane is highest when H_2 is added before the production/accumulation of VFA. Moreover, up to 8.1% of the potential biomethane yield was lost, when H_2 was added during/after fermentation instead of at the start of the experiment. CO_2 removal of up to 39% was achieved in the present study using H_2 equivalent to 5% of the head-space at a 21-day hydraulic retention time. Therefore, for a 1 L reactor with an assumed 20% head-space, an equivalent of 10 ml-H_2/L will be required, which is lower than the amounts used in previous studies.

In the UK, as of 31st January 2017, about 10 operational AD plants upgrade biogas to biomethane (by physicochemical methods) for injection into the gas grid; two of which are FW AD plants (WRAP, 2019). According to the present study, FW has huge potential as a sustainable resource for AD in the future, and in situ biomethanation could help to enhance its valorisation through GtG applications. However, before up-scaling for large (commercial) scale applications, it is important to optimise the added H_2 ultimately for CO_2 conversion to biomethane. This can be maximised by injecting H_2 at the start of the AD set-up; in which case, start-up FW ADs would benefit the most.

Previous biomethanation studies suggest that H_2 addition promotes the evolution of a more specialised microbial population of hydrogenotrophic methanogens (Bassani et al., 2017; Luo & Angelidaki, 2013b) and acclimatisation to H_2 by a continuous addition improved hydrogenotrophic methanogenesis (Treu et al., 2018). Therefore, it is proposed that for continuous in situ biomethanation, H_2 addition should be done at the start-up phase of the reactor (where possible) and simultaneously with the FW loading. This should be followed by a stepwise increment in H_2 loading at steady states, with the incorporation of digestate recycling to proliferate acclimatisation. This might allow for a lesser amount of H_2 that can be obtained biologically by dark fermentation (Figure 5). A synergistic approach among renewable energy sources would be the best option for H_2 production where possible.

That being the case, water electrolysis using excess renewable electricity, such as from solar (Figure 5), would give the purest and most consistent quantity of H_2 for in situ biomethanation and have been proposed as an ideal H_2 source for biomethanation (Angelidaki et al., 2018). However, these systems are not yet fully developed, therefore, for current (short term) practice, renewable biological H_2 production by dark fermentation could be a more adaptable alternative. This can be easily incorporated since it requires similar technical knowhow as in the AD system.

To advance this study, future works will include a study of the microbial population during FW in situ biomethanation, as well as gradual increases in H_2 loading to aid acclimatisation and efficient CO_2 conversion to biomethane. Thus, producing a gas that can be fit for injection into the gas grid or for use as a transport fuel.

4 | CONCLUSIONS

The biological treatment of FW for renewable energy generation by AD can be coupled with H_2 injection. However, the injection point could impact the extent of H_2/CO_2 conversion to biomethane and hence, should be carefully selected before setting up such systems. The addition of H_2 before the accumulation of VFA enhanced biomethanation throughout the AD period, resulting in the highest CO_2 conversion to biomethane. The addition of H_2 at the peak of VFA accumulation showed signs of possible propionate inhibition, especially if higher H_2 loads were applied. Also, increases in pH were observed when H_2 was added during and after fermentation. This study posits that different CO_2 conversion rates and biomethane yields can be achieved for the same amount of H_2 added during in situ biomethanation with FW. When H_2 was added before VFA accumulation, at the peak of VFA accumulation and depleted VFA intermediates, 39%, 25% and 34% of CO_2 were respectively removed. Correspondingly, 12%, 4% and 10% increases in biomethane yield were achieved. An enhanced competition for H_2 when added during fermentation is believed to have limited H_2/CO_2 conversion to biomethanation. Hence, periods before accumulation and after degradation of VFA intermediates should be optimised for in situ biomethanation processes with FW. In general, biomethanation has a great potential to become the game-changer modification aimed at enhancing biological CO_2 capture and valorisation for the production of bio-based renewable energy from organic waste like FW.

ACKNOWLEDGEMENT

The authors acknowledge the financial support of Dr Cynthia Kusin Okoro-Shekwaga provided by the University of Leeds through the Leeds International Research Scholarship (LIRS) and the Living Lab Sustainability Program.

ORCID

Cynthia Kusin Okoro-Shekwaga https://orcid.org/0000-0003-2198-2034
Miller Alonso Camargo-Valero https://orcid.org/0000-0003-2962-1698

REFERENCES

Agneessens, L. M., Ottosen, L. D. M., Voigt, N. V., Nielsen, J. L., de Jonge, N., Fischer, C. H., & Kofoed, M. V. W. (2017). In-situ biogas upgrading with pulse H2additions: The relevance of methanogen adaption and inorganic carbon level. *Bioresource Technology*, *233*, 256–263. https://doi.org/10.1016/j.biortech.2017.02.016

Alfaro, N., Fdz-Polanco, M., Fdz-Polanco, F., & Díaz, I. (2019). H2 addition through a submerged membrane for in-situ biogas upgrading in the anaerobic digestion of sewage sludge. *Bioresource Technology*, *280*, 1–8. https://doi.org/10.1016/j.biortech.2019.01.135

Angelidaki, I., Treu, L., Tsapekos, P., Luo, G., Campanaro, S., Wenzel, H., & Kougias, P. G. (2018). Biogas upgrading and utilization: Current status and perspectives. *Biotechnology Advances*, *36*, 452–466. https://doi.org/10.1016/j.biotechadv.2018.01.011

APHA. (2005). *Standard methods for the examination of water and wastewater*, 21st ed. American Public Health Association, American Water Works Association, Water Environment Federation.

Aryal, N., Kvist, T., Ammam, F., Pant, D., & Ottosen, L. D. M. (2018). An overview of microbial biogas enrichment. *Bioresource Technology*, *264*, 359–369. https://doi.org/10.1016/j.biortech.2018.06.013

Bassani, I., Kougias, P. G., & Angelidaki, I. (2016). In-situ biogas upgrading in thermophilic granular UASB reactor: Key factors affecting the hydrogen mass transfer rate. *Bioresource Technology*, *221*, 485–491. https://doi.org/10.1016/j.biortech.2016.09.083

Bassani, I., Kougias, P. G., Treu, L., Porté, H., Campanaro, S., & Angelidaki, I. (2017). Optimization of hydrogen dispersion in thermophilic up-flow reactors for ex situ biogas upgrading. *Bioresource Technology*, *234*, 310–319. https://doi.org/10.1016/j.biortech.2017.03.055

Bright, A., Bulson, H., Henderson, A., Sharpe, N., Dorstewitz, H., & Pickering, J. (2011). *An Introduction to the Production of Biomethane Gas and Injection to the National Grid* [WWW Document]. Advant. West Midlands Waste Resour. Action Program. http://www.wrap.org.uk/sites/files/wrap/AWMBiomethanetoGrid050711.pdf

Burkhardt, M., & Busch, G. (2013). Methanation of hydrogen and carbon dioxide. *Applied Energy*, *111*, 74–79. https://doi.org/10.1016/j.apenergy.2013.04.080

Burkhardt, M., Koschack, T., & Busch, G. (2015). Biocatalytic methanation of hydrogen and carbon dioxide in an anaerobic three-phase system. *Bioresource Technology*, *178*, 330–333. https://doi.org/10.1016/j.biortech.2014.08.023

Chen, J. L., Ortiz, R., Steele, T. W. J., & Stuckey, D. C. (2014). Toxicants inhibiting anaerobic digestion: A review. *Biotechnology Advances*, *32*, 1523–1534. https://doi.org/10.1016/j.biotechadv.2014.10.005

Chen, Y., Cheng, J. J., & Creamer, K. S. (2008). Inhibition of anaerobic digestion process: A review. *Bioresource Technology*, *99*, 4044–4064. https://doi.org/10.1016/j.biortech.2007.01.057

Díaz, I., Pérez, C., Alfaro, N., & Fdz-Polanco, F. (2015). A feasibility study on the bioconversion of CO2and H2to biomethane by gas sparging through polymeric membranes. *Bioresource Technology*, *185*, 246–253. https://doi.org/10.1016/j.biortech.2015.02.114

FAO (Food and Agricultural Organization of the United Nations). (2011). *Global food losses and food waste*. Germany. doi: https://doi.org/10.1098/rstb.2010.0126

Hao, T.-W., Xiang, P.-Y., Mackey, H. R., Chi, K., Lu, H., Chui, H.-K., van Loosdrecht, M. C. M., & Chen, G.-H. (2014). A review of biological sulfate conversions in wastewater treatment. *Water Research*, *65*, 1–21. https://doi.org/10.1016/j.watres.2014.06.043

Izumi, K., Okishio, Y.-K., Nagao, N., Niwa, C., Yamamoto, S., & Toda, T. (2010). Effects of particle size on anaerobic digestion of food waste. *International Biodeterioration & Biodegradation*, *64*, 601–608. https://doi.org/10.1016/j.ibiod.2010.06.013

Kaza, S., Yao, L., Bhada-Tata, P., & Van Woerden, F. (2018). *What a Waste 2.0. A Global Snapshot of Solid Waste Management to 2050*. Washington DC: The World Bank. https://doi.org/10.1596/978-1-4648-1329-0

Kumaran, P., Hephzibah, D., Sivasankari, R., Saifuddin, N., & Shamsuddin, A. H. (2016). A review on industrial scale anaerobic digestion systems deployment in Malaysia: Opportunities and

challenges. *Renewable and Sustainable Energy Reviews*, *56*, 929–940. https://doi.org/10.1016/j.rser.2015.11.069

Lecker, B., Illi, L., Lemmer, A., & Oechsner, H. (2017). Biological hydrogen methanation—A review. *Bioresource Technology*, *245*, 1220–1228. https://doi.org/10.1016/j.biortech.2017.08.176

Linville, J. L., Shen, Y., Urgun-Demirtas, M., & Snyder, S. W. (2016). Effect of particle size and doses of olivine addition on carbon dioxide sequestration during anaerobic digestion of sewage sludge at ambient and mesophilic temperatures. *Process Biochemistry*, *51*, 59–72. https://doi.org/10.1016/j.procbio.2015.10.015

Luo, G., & Angelidaki, I. (2012). Integrated biogas upgrading and hydrogen utilization in an anaerobic reactor containing enriched hydrogenotrophic methanogenic culture. *Biotechnology and Bioengineering*, *109*, 2729–2736. https://doi.org/10.1002/bit.24557

Luo, G., & Angelidaki, I. (2013a). Hollow fiber membrane based H2 diffusion for efficient in situ biogas upgrading in an anaerobic reactor. *Applied Microbiology and Biotechnology*, *97*, 3739–3744. https://doi.org/10.1007/s00253-013-4811-3

Luo, G., & Angelidaki, I. (2013b). Co-digestion of manure and whey for in situ biogas upgrading by the addition of H2: Process performance and microbial insights. *Applied Microbiology and Biotechnology*, *97*, 1373–1381. https://doi.org/10.1007/s00253-012-4547-5

Luo, G., Johansson, S., Boe, K., Xie, L., Zhou, Q., & Angelidaki, I. (2012). Simultaneous hydrogen utilization and in situ biogas upgrading in an anaerobic reactor. *Biotechnology and Bioengineering*, *109*, 1088–1094. https://doi.org/10.1002/bit.24360

Meng, X., Zhang, Y., Li, Q., & Quan, X. (2013). Adding Fe0 powder to enhance the anaerobic conversion of propionate to acetate. *Biochemical Engineering Journal*, *73*, 80–85. https://doi.org/10.1016/j.bej.2013.02.004

Modestra, A. J., Navaneeth, B., & Mohan, V. S. (2015). Bioelectrocatalytic reduction of CO_2: Enrichment of homoacetogens and pH optimization towards enhancement of carboxylic acids biosynthesis. *Journal of CO2 Utilization*, *10*, 78–87. https://doi.org/10.1016/j.jcou.2015.04.001

Mulat, D. G., Mosbæk, F., Ward, A. J., Polag, D., Greule, M., Keppler, F., Nielsen, J. L., & Feilberg, A. (2017). Exogenous addition of H2for an in situ biogas upgrading through biological reduction of carbon dioxide into methane. *Waste Management*, *68*, 146–156. https://doi.org/10.1016/j.wasman.2017.05.054

Muñoz, R., Meier, L., Diaz, I., & Jeison, D. (2015). A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading. *Reviews in Environmental Science & Biotechnology*, *14*, 727–759. https://doi.org/10.1007/s11157-015-9379-1

Okoro-Shekwaga, C. K., Ross, A. B., & Camargo-Valero, M. A. (2019). Improving the biomethane yield from food waste by boosting hydrogenotrophic methanogenesis. *Applied Energy*, *254*, 113629. https://doi.org/10.1016/j.apenergy.2019.113629

Okoro-Shekwaga, C. K., Turnell Suruagy, M. V., Ross, A., & Camargo-Valero, M. A. (2020). Particle size, inoculum-to-substrate ratio and nutrient media effects on biomethane yield from food waste. *Renewable Energy*, *151*, 311–321. https://doi.org/10.1016/j.renene.2019.11.028

Peu, P., Picard, S., Diara, A., Girault, R., Béline, F., Bridoux, G., & Dabert, P. (2012). Prediction of hydrogen sulphide production during anaerobic digestion of organic substrates. *Bioresource Technology*, *121*, 419–424. https://doi.org/10.1016/j.biortech.2012.06.112

Rachbauer, L., Voitl, G., Bochmann, G., & Fuchs, W. (2016). Biological biogas upgrading capacity of a hydrogenotrophic community in a trickle-bed reactor. *Applied Energy*, *180*, 483–490. https://doi.org/10.1016/j.apenergy.2016.07.109

Ryckebosch, E., Drouillon, M., & Vervaeren, H. (2011). Techniques for transformation of biogas to biomethane. *Biomass and Bioenergy*, *35*, 1633–1645. https://doi.org/10.1016/j.biombioe.2011.02.033

Schink, B., Montag, D., Keller, A., & Müller, N. (2017). Hydrogen or formate: Alternative key players in methanogenic degradation. *Environmental Microbiology Reports*, *9*, 189–202. https://doi.org/10.1111/1758-2229.12524

Tao, B., Zhang, Y., Heaven, S., & Banks, C. J. (2020). Predicting pH rise as a control measure for integration of CO2 biomethanisation with anaerobic digestion. *Applied Energy*, *277*, 115535. https://doi.org/10.1016/j.apenergy.2020.115535

Treu, L., Kougias, P. G. G., de Diego-Díaz, B., Campanaro, S., Bassani, I., Fernández-Rodríguez, J., & Angelidaki, I. (2018). Two-year microbial adaptation during hydrogen-mediated biogas upgrading process in a serial reactor configuration. *Bioresource Technology*, *264*, 140–147. https://doi.org/10.1016/j.biortech.2018.05.070

Ullah Khan, I., Hafiz Dzarfan Othman, M., Hashim, H., Matsuura, T., Ismail, A. F., Rezaei-DashtArzhandi, M., & Wan Azelee, I. (2017). Biogas as a renewable energy fuel—A review of biogas upgrading, utilisation and storage. *Energy Conversion and Management*, *150*, 277–294. https://doi.org/10.1016/j.enconman.2017.08.035

Voelklein, M. A., Rusmanis, D., & Murphy, J. D. (2019). Biological methanation: Strategies for in-situ and ex-situ upgrading in anaerobic digestion. *Applied Energy*, *235*, 1061–1071. https://doi.org/10.1016/j.apenergy.2018.11.006

Wahid, R., Mulat, D. G., Gaby, J. C., & Horn, S. J. (2019). Effects of H2:CO2 ratio and H2 supply fluctuation on methane content and microbial community composition during in-situ biological biogas upgrading. *Biotechnology for Biofuels*, *12*(104), 1–15. https://doi.org/10.1186/s13068-019-1443-6

Wang, W., Xie, L., Luo, G., Zhou, Q., & Angelidaki, I. (2013). Performance and microbial community analysis of the anaerobic reactor with coke oven gas biomethanation and in situ biogas upgrading. *Bioresource Technology*, *146*, 234–239. https://doi.org/10.1016/j.biortech.2013.07.049

Weiland, P. (2010). Biogas production: Current state and perspectives. *Applied Microbiology and Biotechnology*, *85*, 849–860. https://doi.org/10.1007/s00253-009-2246-7

WRAP. (2015). *Optimising the value of digestate and digestion systems* [WWW Document]. Waste Resource Action Program. http://www.wrap.org.uk/sites/files/wrap/Optimisingthevalueofdigestateanddigestionsystems_0.pdf

WRAP. (2019). *Operational AD sites | WRAP UK* [WWW Document]. http://www.wrap.org.uk/content/operational-ad-sites. Accessed 2.15.19.

Yang, Y., Zhang, Y., Li, Z., Zhao, Z., Quan, X., & Zhao, Z. (2017). Adding granular activated carbon into anaerobic sludge digestion to promote methane production and sludge decomposition. *Journal of Cleaner Production*, *149*, 1101–1108. https://doi.org/10.1016/j.jclepro.2017.02.156

Yang, Z., Liu, Y., Zhang, J., Mao, K., Kurbonova, M., Liu, G., Zhang, R., & Wang, W. (2020). Improvement of biofuel recovery from food waste by integration of anaerobic digestion, digestate pyrolysis and syngas biomethanation under mesophilic and thermophilic

conditions. *Journal of Cleaner Production*, *256*, 120594. https://doi.org/10.1016/j.jclepro.2020.120594

Yun, Y. M., Sung, S., Kang, S., Kim, M. S., & Kim, D. H. (2017). Enrichment of hydrogenotrophic methanogens by means of gas recycle and its application in biogas upgrading. *Energy*, *135*, 294–302. https://doi.org/10.1016/j.energy.2017.06.133

Zabranska, J., & Pokorna, D. (2018). Bioconversion of carbon dioxide to methane using hydrogen and hydrogenotrophic methanogens. *Biotechnology Advances*, *36*, 707–720. https://doi.org/10.1016/j.biotechadv.2017.12.003

How to cite this article: Okoro-Shekwaga CK, Ross A, Camargo-Valero MA. Enhancing bioenergy production from food waste by in situ biomethanation: Effect of the hydrogen injection point. *Food Energy Secur*. 2021;00:e288. https://doi.org/10.1002/fes3.288