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Biohydrogen production from food waste in batch and semi-continuous conditions: evaluation of a two-phase approach with digestate recirculation for pH control

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Abstract

The research investigated the production of Biohythane in a two-phase anaerobic digestion process treating food waste as substrate. Preliminary batch assays were carried out at initial organic loadings of 15, 20, 25 and 30 kg TVS m^{-3}, in stirred 1.5-l reactors at 55 °C. The results showed all hydrogen was produced within the first 24 hours after feeding and the highest load tested gave the maximum hydrogen production (0.047 m^3 H_2 kg^{-1}VS, H_2 30%). Similar loadings were then tested in a two-phase system. Hydraulic retention times of 3 and 12 days were applied to the first and second reactor respectively. In order to keep the pH at ~5.5, either supernatant or whole digestate from the methanogenic reactor was recirculated to the first phase. Results showed that hydrogen was produced (0.117 Nm^3 kg^{-1} VS, 47.7%) when recirculating whole digestate with an organic loading rate of 20 kg TVS m^{-3} day^{-1}.

Keywords: Biohydrogen, Biohythane, Two-phase, pH control, Anaerobic Digestion

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Abbreviation

AD: anaerobic digestion, FW: food waste, HRT: hydraulic retention time, SHP: specific hydrogen production, BHO: bio-hydrogen production, OLR: organic loading rate, PTOT: total phosphorus, SGP: specific gas production, SSC: steady state condition, TKN: total Kjeldahl nitrogen, TS: total solids, TVS: total volatile solids, VFAs: volatile fatty acids, IOL: initial organic loads, CSTR: continuous stirred tank reactor, GC: gas chromatography, OFMSW: organic fraction of municipal solid waste.

1. Introduction

Anaerobic digestion (AD) is a strong and well-established technique for renewable energy production. When applied to waste management, in addition to the production of carbon-neutral energy, it gives the extra benefit of treating organic wastes that would otherwise have to be processed in another way. The technique is even more attractive as it has also been demonstrated to be capable of producing hydrogen: this is already considered an important carrier for next-generation technologies, and much research is now focused on the best way to produce it in a clean and cost-effective way. Biological hydrogen production from organic biomass fermentation is widely considered as one of the best options with the greatest future potential [1]. Hydrogen is produced during fermentation and acetogenesis in the anaerobic digestion process, and a two-phase AD system can be exploited to produce both hydrogen and methane [2, 3]. With such a scenario, the hydrogen could be used either by itself or to improve the combustion performance of methane, making a mixture that simulates the composition of Hythane. Such a mixture, often described as BioHythane, has a typical composition of 5-10% H_2, 30-40% CO_2, 50-65% CH_4, and has been shown to give better efficiency and emissions performance than natural gas when used in a conventional internal combustion engine [4, 5, 6].

One of the most important challenges for sustaining hydrogen production in a reactor optimised for dark fermentation is to avoid the growth of H_2-consuming bacteria [7]. Due to the daily addition of mixed culture contained in food waste (FW), there is always a risk that unwanted archaea such as H_2-consuming methanogens could grow and deplete the hydrogen produced. There are many ways to select H_2-producing bacteria in a mixed culture approach, such as physical-chemical treatment (heat-shock or chemical treatment of inoculum or substrate) or process parameter optimisation (low retention time, selection of organic loading). Many of these have already been discussed by other authors [8, 9, 10, 11].

Several reviews have been published on optimisation of conditions for biohydrogen production though dark fermentation, but there is still some confusion due to the wide range of conditions applied [12, 13]. The type of substrate makes a big difference in terms of yield, and most studies have used simple synthetic substrates (e.g. glucose) that only require a short hydraulic retention time (HRT) in a single-stage reactor for effective conversion. FW is a combination of components some of which require more complex metabolic pathways to break them down. This affects the HRT, which typically ranges from 2 to 5 days in a continuous or semi-continuous fed system. Two-phase approaches using FW as substrate without recirculation have been tested over a wide range of organic loadings [14, 15, 16, 17, 18, 19], and in general showed a specific hydrogen production (SHP) below 71 m^3 H_2 kg^{-1} VS. Only a few studies have used a two phase approach with recirculation of the AD effluent [11, 14, 16, 20].

The present research used a two-phased approach with the objective of maximising hydrogen production in the first phase, while maintaining an acceptable methane conversion in the second phase. The purpose was to determine the best conditions for producing hydrogen in such a system using FW as substrate. The particular emphasis of the work was to develop a self-sustaining process that could be scaled up, using digestate recirculation as a means of controlling pH without external chemical additions. First, preliminary batch tests were carried out to test inoculum activity and determine the initial organic loading for a semi-continuous study. This type of test could be described as a Biohydrogen Production (BHP) test, since the reactors were fed only once at the start of the test and gas production and composition were monitored until no net production was achieved. In the semi-continuous experiments, four organic loading rates (OLR) were tested with recirculation of either whole digestate from the second phase or liquid obtained after centrifugation of the digestate, to determine which was most effective for pH control.

2. MATERIALS AND METHODS

2.1 Substrate and inoculum characteristics

The substrate used was source segregated domestic food waste collected from the South Shropshire Biowaste Digester in Ludlow, UK [21]. The material was first taken out of biodegradable plastic bags and any non-biodegradable contaminants (including large bones and fruit stones) were removed. It was then homogenised using a macerating grinder (S52/010 Waste Disposer, IMC Ltd, UK), packed into 4-litre plastic storage containers, and frozen at -18 ^oC. Before use the feedstock was thawed and stored at 4 ^oC. The inoculum used was from Millbrook Wastewater Treatment Works,

Southampton, UK, an anaerobic digestion plant treating municipal wastewater biosolids at an operating temperature of 37 °C. Table 1 presents the substrate and inoculum characteristics.

Table 1. Characteristics of substrate and inoculum

Parameter	Unit	Value ± SD	
		Substrate	Inoculum
TS	g/kg WW	248 ± 19	35.2 ± 0.5
TVS	g/kg WW	236 ± 22	23.1 ± 0.4
pH		nd	7.5
TKN	mgN/kg WW	5983 ± 497	nd
NH_3	mgN/kg WW	nd	1911 ± 43
COD	mgO_2/kg TS	998 ± 71	nd
Total VFA	mgCOD/l	nd	509 ± 64
Total alkalinity	$mgCaCO_3$/l	nd	8500 ± 248

Nd: not determined

2.2 Reactor configuration

The continuously-stirred tank reactors (CSTR) used in this experimentation had volumes of either 2 or 5 L and were fitted with a flanged top plate through which a stirrer was inserted via a draught tube: this allowed the digester contents to be stirred continuously at 30 rpm by an off-set bar stirrer, as shown in Figure 1. The digesters were maintained at 52 °C by circulation of hot water from a thermostatically controlled reservoir. Feeding was carried out via a hole in the top flange and digestate was removed via a wide-bore tube in the base. Gas production was measured with a gas flow meter (gas counter) constructed and calibrated as described by Walker and co-workers [22] and connected to gas sampling bags (SKC Ltd, Blandford Forum, UK). The device works by means of an inverted tipping bucket immersed in liquid. As the gas bubbles fill the bucket it tips and a magnet activates a reed switch connected to a counting device. Gas production is reported at STP of 0 °C and 101.325 kPa.

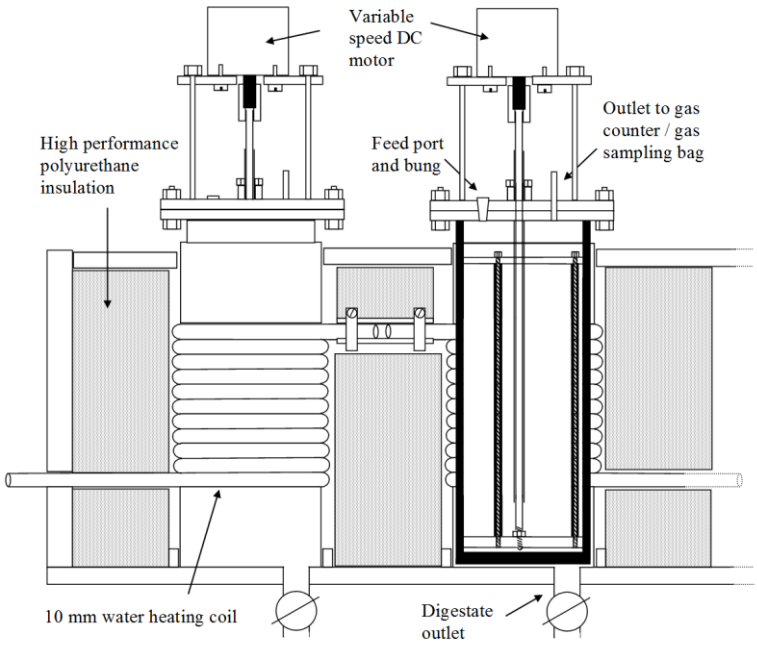


Figure 1: Cross-section diagram of CSTR digesters showing heating coils (left) and stirrer (right) [37].

2.3 Analytical methods

Total solids (TS), total volatile solids (TVS), total Kjeldahl nitrogen (TKN), chemical oxygen demand (COD) and ammonia were measured according to Standard Methods 2540 G, 4500 PJ, 5220 B, and 4500-NH_3 G, respectively [23]. pH was measured using a Jenway 3010 pH meter (Jenway, London, UK) with temperature compensation and combination electrodes, calibrated daily with standard buffer solutions (Fisher Scientific UK Ltd, Loughborough, UK). Alkalinity was determined by titration with 0.25 N H_2SO_4 to endpoint pH 4.0 and the results expressed as total alkalinity. VFA concentrations were quantified in a Shimazdu GC-2010 gas chromatograph (Shimadzu, Milton Keynes, UK), using a flame ionisation detector and a capillary column type SGE BP-21 with helium as carrier gas. The GC oven temperature was programmed to increase from 60 to 210 °C in 15 min, with a final hold time of 5 min. The temperatures of injector and detector were 200 and 250 °C, respectively. Standard solutions containing 50, 250 and 500 mg/L of acetic, propionic, iso-butyric, n-butyric, iso-valeric, valeric, hexanoic and heptanoic acids were used for VFA calibration. Samples for VFA determination were acidified by addition of formic acid to give a 10% concentration. Gas composition was measured using a Varian CP 3800 gas chromatograph (Varian, UK) with a gas sampling loop using argon as the carrier gas at a flow of 50 ml min^{-1}. The GC was fitted with a Hayesep C column and a molecular sieve 13 x (80–100 mesh) operating at a

temperature of 50 ^{o}C. The GC was calibrated using standard gases containing 35% CO_2 and 65% CH_4, and 20% H_2 with 80% N_2.

2.4 Experimental set-up

For the batch tests, 12 reactors with a 2 L volume were initially filled in with 1.5 L of inoculum without any nutrient supplement, and held at 52 ^{o}C for 5 days. Tests were carried out in triplicate at initial organic loads (IOL) of 15, 20, 25, and 30 kg TVS m^{-3} corresponding to wet weight feed additions of 94.1, 138.2, 156.9 and 207.4 g of FW. The surplus of inoculum was hence removed in order to keep a total volume of 1.5 L; substrate/inoculum TVS ratio was respectively 0.68, 1.04, 1.19 and 1.64. Gas production, gas composition and VFA concentration were measured every hour for the first 8 hours, then at longer intervals.

The semi-continuous trial was carried out in eight pairs of CSTR digesters, each pair comprising a hydrolytic reactor with a working volume of 1 L, and a methanogenic digester with a working volume of 4 L. Feeding of the reactors was carried out as shown in Table 2. Four pairs of reactors were operated with recirculation of whole digestate, and four with recirculation of digestate supernatant after centrifugation. To achieve this, 333 mL of digestate was removed every day from each phase before feeding. For the four systems with supernatant-only recirculation, the digestate from the methanogenic reactor was centrifuged at 3000 rpm for 30 minutes in a refrigerated centrifuge (Centra-8R Model 2478, IEC Co., USA) and the supernatant was separated from the solids which were then disposed of. The amount of FW required in each case to give the desired OLR was then made up to 333 mL by adding either whole digestate or supernatant from the second phase, and the mixture was fed to the hydrolytic reactor. The digestate removed from the hydrolytic reactor was fed to the second phase. This gave internal HRT of 3 and 12 days in the hydrolytic and methanogenic reactors respectively, but the total HRT of the system was much longer (Table 2).

Gas production was monitored daily; gas composition, VFA and pH every two days; ammonia and alkalinity every three days; TS, TVS, COD, TKN once per week.

Table 2. Experimental conditions in semi-continuous trial

Reactor pair	Feed	I Phase		II Phase	Whole system			
		OLR	Internal HRT	Internal HRT	OLR	Total HRT	Recirculation	Qr/Qin*
	g WW day^{-1}	kg TVS m^{-3} day^{-1}	days	days	kg TVS m^{-3} day^{-1}	days		
1	63	15	3	12	3	79	Digestate	4,29
2	85	20	3	12	4	59	Digestate	2,92
3	106	25	3	12	5	43	Digestate	2,14
4	127	30	3	12	6	39	Digestate	1,62
5	63	15	3	12	3	79	Supernatant	4,29
6	85	20	3	12	4	59	Supernatant	2,92
7	106	25	3	12	5	43	Supernatant	2,14
8	127	30	3	12	6	39	Supernatant	1,62

* Ratio of volume of recycled digestate to new feed

3. Results and discussion

3.1 Batch tests

The results of the batch tests (Table 3) showed that increasing the initial organic load led to a progressive increase in hydrogen production, with IOL of 15, 20, 25 and 30 kg TVS m^{-3} giving SHP of 0.012, 0.021, 0.035 and 0.047 Nm^3 kg^{-1} TVS respectively. These values were reached after 24 h in fact the maximum hydrogen content was reached before 24 h in all tests. In contrast the specific biogas production decreased with increasing IOL from 0.782 at IOL 15 to 0.239 Nm^3 kg^{-1} TVS at IOL 30. The methane content also fell, and at 30 kg TVS m^{-3} only accounted for about 10% of the gas volume. In terms of cumulative yield, the highest hydrogen production was at 30 kg TVS m^{-3} (2116 mL of H_2 in 327 hours); methane and total biogas production were both maximised at 25 kg TVS m^{-3} with 12.58 L of CH_4 and 24.80 L of biogas in 327 hours.

Table 3. Batch test results at four initial organic loadings

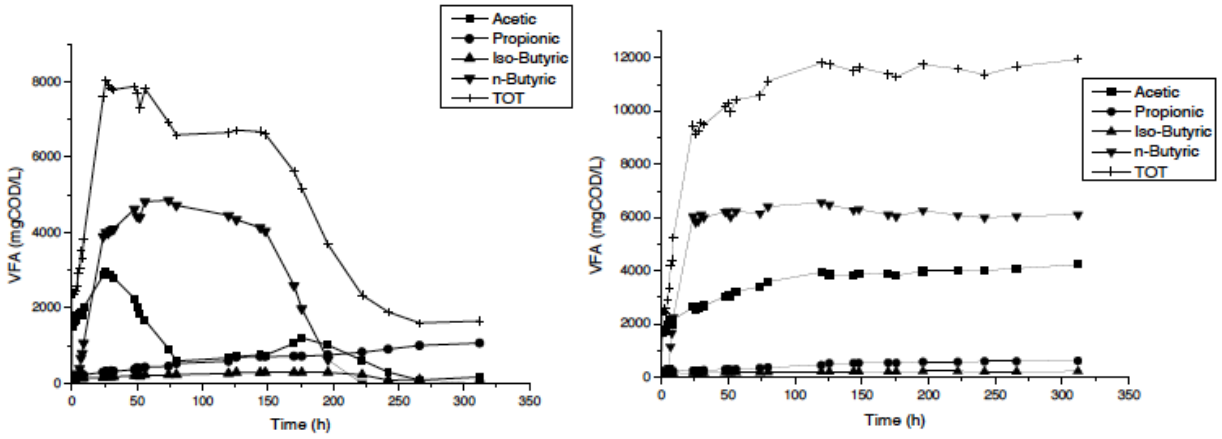
Parameter		Unit	IOL (kg TVS m^{-3})			
			15	20	25	30
Gas Production	H_2	Nm^3 kg^{-1} TVS	0.012	0.021	0.035	0.047
	CH_4		0.042	0.360	0.335	0.021
	Biogas		0.782	0.709	0.661	0.239
H_2	min	%	0.0	0.0	0.0	3.2
	max		17.7	19.4	31.6	27.9
	stability		0.0	0.0	0.0	6.4 ± 2.2
CH_4	min	%	9.3	7.3	2.8	2.1
	max		72.8	71.4	68.9	40.9
	stability		69.9 ± 2.1	70.0 ± 2.4	73.9 ± 1.0	9.5 ± 4.5
Cumulative Production (320 hours)	H_2	mL	263	623	1322	2116
	CH_4		9,534	10,799	12,581	942
	Biogas		17,594	21,271	24,805	10,758

Table 4. Reference results for batch tests carried out using Food Waste as substrate

Reference	Nature of FW	Inoculum/substrate pre-treatment	pH control	T range	pH	SHP l $kgVS^{-1}$
[31]	OFMSW	Y	Y	M	5.5	46-118
[24]	FW from household	N	N	T	6	57
[24]	FW from household	N	N	M	<4.8	39
[32]	OFMSW	N	Y	M	5-6	121.6
[33]	OFMSW, Primary Sludge and Waste Activated Sludge mixture	N	Y	M	7	112
[34]	Household solid waste	N	Y	Extr-T	7	257
[35]	Rice + carrots organic waste	N	-	M	-	19-96
[36]	Selected OFMSW	N	-	T	7	195

As shown in Table 4, the results obtained in the present research are very close to those of Jinming and co-workers [24], who carried out batch tests on a similar type of FW without any pre-treatment or pH control, and found SHP of 0.057 and 0.039 Nm^3 kg^{-1} TVS in the thermophilic and mesophilic ranges respectively. The batch tests in this research demonstrated that in a single reactor dark fermentation can be isolated by applying an IOL of 30 kg TVS m^{-3} or above, as at this load methanogenesis was completely inhibited while hydrogen production was constant and continuous with an average H_2 concentration of 6.4% throughout the 327 hours of the test (Table 3). These results confirmed that high organic loadings enhance hydrogen production whilst as the same time inhibiting methanogenesis, probably as a result of the accumulation of intermediate products

leading to a fall in pH. Figures 2a and 2b show the profiles of total VFA and some individual acids (acetic, propionic and butyric) at two of the applied IOL (20 and 30 kg TVS m^{-3} respectively).



a) **b)**

Figure 2: a) VFA production during IOL 20; b) VFA production during IOL 30.

At IOL 20 there was an accumulation of acetic and butyric acids during the first 150 h, almost all of which was then converted into methane and carbon dioxide after 300 h. This showed that methanogenic activity was not inhibited and the microorganisms were able to use and convert the VFA into CH_4 and CO_2. In contrast, IOL 30 showed accumulation of VFA with no subsequent conversion to methane, indicating that methanogenesis was inhibited; this condition gave the best hydrogen yields compared to the other IOL tested.

3.2 Semi-continuous trials

The trials carried out with supernatant recirculation showed no positive results in term of hydrogen production. At the higher OLRs of 25 and 30 kg TVS m^{-3} day^{-1}, the first phase immediately fell into acidic conditions, leading quickly to failure in the methanogenic phase. The two lower OLRs of 15 and 20 kg TVS m^{-3} day^{-1} showed the ability to sustain methanogenesis in the second phase. In the conditions applied, however, the pH in the first phase was always below 4.5, far from the optimal range for hydrogenase enzyme of 5.5-6.5 [25]. The conditions at OLR of 15 and 20 kg TVS m^{-3} day^{-1} instead gave a good example of two-phase AD for methane production, where the first phase provides optimal conditions for hydrolysis and the second phase for methanogenesis. The OLR of 20 kg TVS m^{-3} day^{-1} in particular could be considered as an optimal loading for a two-phase system, as it gave the highest SGP of over above 0.8 Nm^3 kg^{-1} VS, although steady state conditions had not yet been reached.

The tests carried out with recirculation of the whole digestate gave much more interesting results. Table 5 summarises all of the parameters monitored for all four reactor pairs, together with the yield

from the process. As can be seen, the loading of 20 kg TVS m^{-3} day^{-1} on the hydrolytic reactor gave the best performance with a stable hydrogen concentration of 47.7% in the first phase (Figure 3a) and 60% methane in the second phase (Figure 3b).

Table 5. Steady state condition average values of process parameters for loadings of 15, 20, 25 and 30 kg TVS m^{-3} day^{-1} applied to the hydrolytic reactor of a two-phase system treating FW with digestate recirculation

Parameter	Unit	15	20	25	30
		kg TVS m^{-3} day^{-1}			
Characterisation of the first phase reactor					
TS	g kg^{-1} WW	47.06 ± 1.38	56.59± 18	104.88± 0.44	114.39± 0.26
TVS	g kg^{-1} WW	36.94 ± 1.30	45.26± 19	92.31± 0.48	101.19± 0.21
COD	mg O_2 g^{-1} TS	987 ± 33	1034 ± 30	920± 51	929± 50
TKN	mg N g^{-1} TS	68 ± 9	92 ± 7	57 ± 2	55± 5
pH		5.82 ± 0.24	5.22± 0.16	4.63± 0.1	5.03± 0.1
NH_3	mg NH_4^+-N L^{-1}	2910 ± 87	2666± 81	1893± 51	1708± 96
VFA	mg COD L^{-1}	10468 ± 197	13756± 1318	6664± 304	12847± 1268
Alkalinity	mg $CaCO_3$ L^{-1}	10500 ± 404	8547± 523	3554± 312	6150± 1075
Characterisation of the second phase reactor					
TS	g kg^{-1} WW	39.64 ± 0.40	43.38± 1.0	49.20± 0.17	62.79± 0.31
TVS	g kg^{-1} WW	28.91 ± 0.18	32.08± 0.9	36.88± 0.22	49.79± 0.34
COD	mg O_2 g^{-1} TS	937 ± 28	936 ± 28	722± 23	793± 21
TKN	mg N g^{-1} TS	59 ± 5	46.9 ± 2	89.8 ± 5	86.1± 2
pH		7.80 ± 0.01	7.69± 0.07	7.55± 0.03	5.72± 0.1
NH_3	mg NH_4^+-N L^{-1}	2975 ± 93	3295± 151	2471± 204	2524± 284
VFA	mg COD L^{-1}	3850 ± 336	7064± 979	6034± 678	17494± 2133
Alkalinity	mg $CaCO_3$ L^{-1}	10500 ± 404	14090± 437	11803± 518	10897± 860
First phase reactor yields					
SGP	Nm^3 kg^{-1} TVS	0.201 ± 0.028	0.240± 0.032	0.009± 0.002	0.053± 0.018
H_2	%	0.5 ± 0.1	47.7± 1.1	0.4± 0.3	42.8± 3.5
CH_4	%	24.6 ± 2.3	0.3± 0.1	0.6±0.1	0.3±0.1
SHP	Nm^3 kg^{-1} TVS	0.001	0.117± 0.014	0.000	0.022± 0.09
Second phase reactor yields					
SGP	Nm^3 kg^{-1} TVS	0.728 ± 0.060	0.512± 0.031	0.619± 0.033	0.210± 0.071
H_2	%	-	-	-	-
CH_4	%	65.6 ± 2.2	61.2± 2.4	65.1± 0.1	37.3± 3.9
SMP	Nm^3 kg^{-1} TVS	0.484 ± 0.035	0.311± 0.035	0.422± 0.059	0.077± 0.036

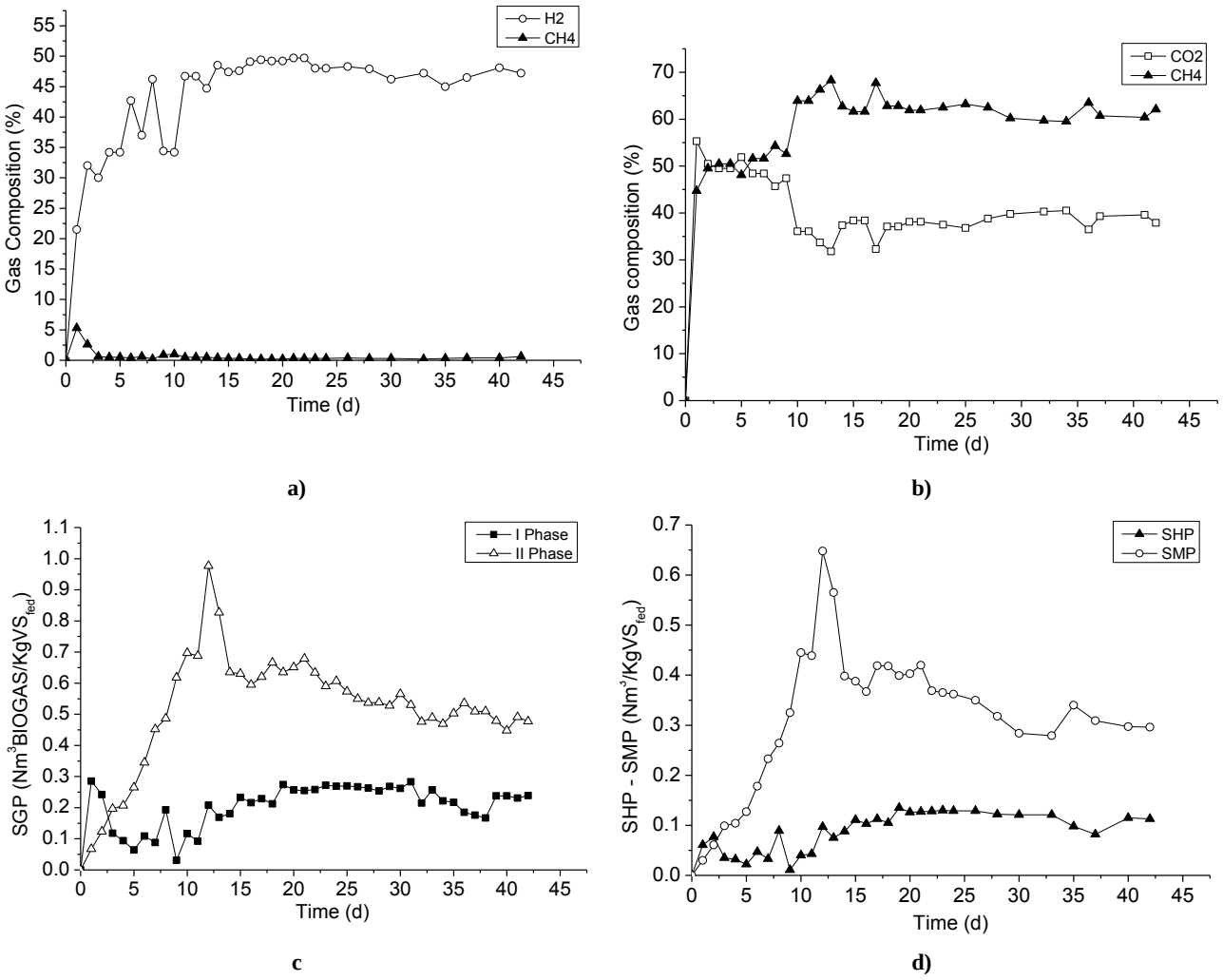


Figure 3. Gas production parameters at OLR 20 kg TVS m^{-3} day^{-1} with whole digestate recirculation: a) Gas composition of the first phase; b) Gas composition of the second phase; c) SGP; d) SHP and SMP

In Figure 3c it can be seen that the SGP with a loading of 20 kg TVS m^{-3} day^{-1} on the first phase showed a small decrease after day 32 for several days, but then regained a stable value of around 0.240 Nm^3 kg^{-1} TVS. The SHP (Figure 3d) showed a similar trend, with an average production of 0.117 Nm^3 kg^{-1} TVS. pH and total alkalinity in first phase were stable at 5.22 and 8.5 g $CaCO_3$ L^{-1} respectively after day 15. Total VFA in the first phase was quite high as expected, stabilising at around 13.8 g COD L^{-1}, but with no signs of further accumulation. Ammonia on the other hand showed an upward trend, reaching around 2.7 g NH_4^+-N L^{-1} in the final week.

Table 6 shows results from other studies in which hydrogen has been produced under similar conditions and where external pH control was not used. The H_2 concentration and SHP found in the

present work are far higher than that measured by other authors; a better performance is reported only by Chu and co-workers [16], who found an SHP of 0.205 Nm^3 kg^{-1} TVS with an H_2 concentration of 52-56%.

Table 6. Experimental conditions and hydrogen yields in CSTR-type reactors treating FW only without external pH control

Reference	I Phase	II Phase	OLR	T range**	pH	HRT	H_2	SHP
	Reactor type	Reactor type	I Phase kgVS $m^{-3}d^{-1}$			days	%	l kg-1 TVS
[14]	CSTR	CSTR	-	T	5 - 6	2.5 – 6	25 – 63	20 – 30
[14]	CSTR	CSTR	4.7 – 5.6	T	5	7.07	44	-
[15]	CSTR	CSTR	37.5	M	5.2	2	42	43
[16]	CSTR	CSTR	38.4	T	5.5	1.3	52 – 56	205
[17]	SCRD*	CSTR	15.1	M	5.2 – 5.8	10		71
[17]	SCRD*	CSTR	22.65	M	5.2 – 5.8	6.6	30	65
[18]	CSTR	CSTR	170	M	4.9	0.31	29	2.7
[18]	CSTR	CSTR	49	T	4.8	1.20	34	7.6
[19]	CSTR	CSTR	3 – 4.5	T	5.3	3	-	48
[19]	CSTR	CSTR	3 – 4.5	T	5.3	1	-	40

*Semi Continuous Rotating Drum

** T - thermophilic, M - mesophilic

At the loading of 20 kg TVS m^{-3} day^{-1} on the hydrolytic reactor, a stable methane concentration of 61.2% was established in the second phase after about 15 days (Figure 3c) and the SGP was 0.512 Nm^3 kg^{-1} VS. pH was stable at 7.69 throughout the trial. With respect to VFA, acetic and butyric acids were detected at fairly low and stable concentrations throughout the experimental run, while propionic acid accumulated sharply during the first 15 days. Total VFA were still accumulating slightly at the end of the run, with an average value in the final two weeks of 7.1 g COD L^{-1}. Ammonia also accumulated, with the average for the last week equal to 3.3 g NH_4^+-N L^{-1}. The total SGP for the whole two-phase system was 0.752 Nm^3 kg^{-1} TVS.

Two phase approaches with conditions similar to those applied in this experiment have been tested by others, as shown in Table 7. The performance of the second phase was similar in terms of SGP to that in the present study.

Table 7. Experimental condition applied and hydrogen yields without pre-treatment and external pH control in a two-phase system

Reference	Substrate	First Phase					Second Phase			
		T range	pH	HRT	OLR	SHP	T range	HRT	OLR	SGP
				days	kgVS $m^{-3}d^{-1}$	l kg^{-1} TVS		days	kgVS $m^{-3}d^{-1}$	Nm^3 kg^{-1} TVS
[14]	FW	T	5-6	2.5-6	20.8-8.45	20-30	T	18-30	2.84-1.18	0.49
[16]	FW	T	5.5	1.3	38.4	205	M	5	6.6	0.61
[38]	FW	T	5.5-5.7	1.9	39*	83	T	7.7	8.4*	0.21**
[30]	FW	T	5.4	3.3	16	51	T	12.6	4	0.64

* On a COD basis

** CH_4

Concerning the other three load conditions, some observations can be made based on the results in Table 5. The loading of 15 kg TVS m^{-3} day^{-1} on the hydrolytic reactor was insufficient to reduce the pH to the optimum of 5.5 for dark fermentation, so that on recirculation of whole digestate the H_2-consuming and CH_4-producing archaea were no longer inhibited, with consequent methane production. The loading of 25 kg TVS m^{-3} day^{-1} on the hydrolytic reactor was too high for the system tested as the alkalinity recirculated was insufficient, resulting in a reduction of pH to the point where hydrogen production was not possible in the first phase. As happened with supernatant recirculation, the system behaved like a two-phase system for methane production. As result, in the first phase only solubilisation of organic compounds occurred, while in the second phase methanogenesis showed good performance as the COD arrived already solubilised and ready to use. The results obtained during the working period at 30 kg TVS m^{-3} day^{-1} showed that raising the organic load gave a general inhibition of both the phases. The SHP, SMP and SGP are shown in Figure 4.

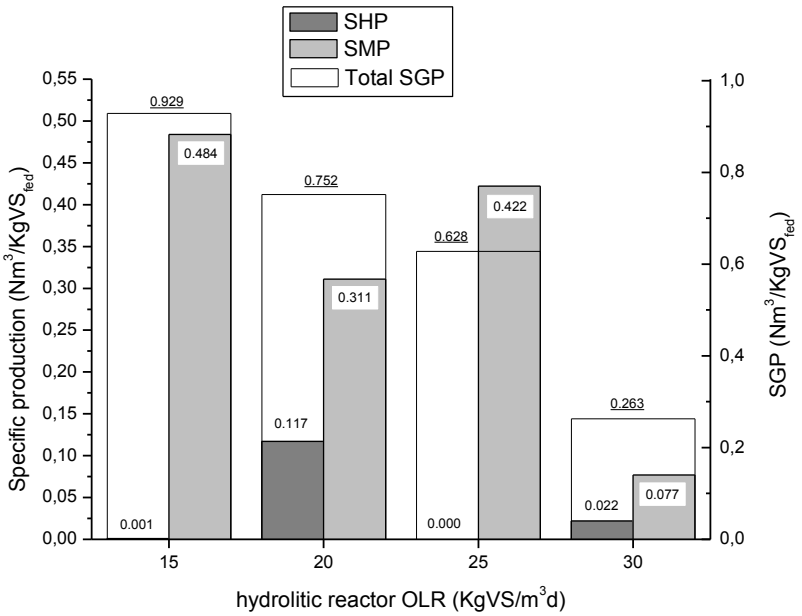


Figure 4. Specific gas productions for all loadings tested with whole digestate recirculation

The results clearly showed that not all of the conditions tested were suitable for combined hydrogen and methane production. At all of the loadings tested, recirculation of supernatant alone from the second phase did not lead to adequate pH control and was not sufficient to sustain dark fermentation for hydrogen production in the first phase. Recirculation of whole digestate returned not only alkalinity but also biomass, providing a continual inoculum of fermentative organisms to the first phase. At the two lower loadings this also allowed the recycled methanogenic organisms to take advantage of the acids and hydrogen produced, preventing the necessary drop in pH. At the highest loading where over-acidification occurred, it is possible that a greater volume of digestate could be recirculated from the second stage to improve the alkalinity in the first stage reactor. This would however reduce the internal HRT in both phases. It is clear that a suitable balance has to be achieved between OLR, total HRT and internal HRT in the two phases, and for this substrate the balance appears to be at a loading of around 20 kg TVS m^{-3} day^{-1} on the hydrolytic reactor, corresponding to an OLR on the whole system of 4 kg TVS m^{-3} day^{-1}. This loading rate gave a final gas composition of 18% H_2, 39% CH_4 and 43% CO_2 which does not match the ideal biohythane profile as the percentage of hydrogen is too high. There are a number of possible solutions for this, such as splitting the food waste load so that a proportion is added directly to the second phase reactor; or alternatively dosing some of the hydrogen-rich gas from the first into the second phase reactor as a substrate for hydrogentrophic methanogenesis. The main problem seen in the operation of this system was the accumulation of ammonia: this in turn may be associated with population changes in the anaerobic consortium and with VFA accumulation [26, 27]. This is likely to lead to deterioration in system performance, although it is unclear whether this would first affect the

hydrolytic or methanogenic phase. Although trace element addition has been shown to prevent propionic acid accumulation in mesophilic FW digestion [28] this solution has so far not proved effective in thermophilic conditions with the same food waste [29]. For future scale-up of the process, measures to control ammonia accumulation may have to be applied: an example of a possible solution is given by Cavinato and co-workers [30].

4. Conclusions

Batch tests were effective in showing the suitability of the selected inoculum/substrate ratios for testing for hydrogen production in the thermophilic range. During batch tests, the highest initial load gave the greatest hydrogen yield, while methanogenesis was completely inhibited at an IOL of 30 kg TVS m^{-3}.

Semi-continuous trials with supernatant recirculation did not show any significant hydrogen production. The supernatant recirculated about 90% of the digestate alkalinity but this was not enough to control the pH in the first phase, where acidic conditions established within the first week. At OLR of 25 and 30 kg TVS m^{-3} day^{-1} on the hydrolytic reactor both phases were completely inhibited, while at 15 and 20 kg TVS m^{-3} day^{-1} the system acted as a two-stage AD system for methane production.

Tests with whole digestate recirculation demonstrated that a high hydrogen yield could be achieved with an OLR of 20 kg TVS m^{-3} day^{-1} on the hydrolytic reactor. With the recirculation conditions applied, the load of 15 kg TVS m^{-3} day^{-1} was too low and led to a methanogenic shift within the first month, while 25 and 30 kg TVS m^{-3} day^{-1} were too high and led to acidic conditions in the first phase.

For hydrogen production the best yield was obtained at an OLR of 20 kg TVS m^{-3} day^{-1} on the hydrolytic reactor and recirculating whole digestate with a Qr/Qin ratio of 2.9. In the first phase pH was self-controlled over the experimental period at a value of 5.22 and a SHP of 0.117 Nm^3 kg^{-1} VS was observed. Hydrogen concentration in the biogas was 47.7%. SGP in the second phase was 0.512 Nm^3 kg^{-1} VS while the total SGP was 0.752 Nm^3 kg^{-1} VS. These results are better than achieved in most previous studies, but there are issues in relation to long term stability as a result of high ammonia concentrations, possibly associated with volatile fatty acid accumulation. If a solution to this can be found the process appears promising for scale-up.

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