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Bio-hythane production from food waste by dark fermentation coupled with anaerobic digestion process: a long-term pilot scale experience

C. Cavinato[1*], Giuliano A.[1], D. Bolzonella[2], P. Pavan[1], F. Cecchi[2]

[1] University Ca' Foscari of Venice, Department of Environmental Sciences, Informatics and Statistics, Dorsoduro 2137, 30123 Venice, Italy.

[2] University of Verona, Department of Biotechnology, Strada Le Grazie, 15, 37134 Verona, Italy.

Abstract

In this paper are presented the results of the investigation on optimal process operational conditions of thermophilic dark fermentation and anaerobic digestion of food waste, testing a long term run, applying an organic loading rate of 16.3 kgTVS/m^{3}d in the first phase and 4.8 kgTVS/m^{3}d in the second phase. The hydraulic retention times were maintained at 3.3 days and 12.6 days, respectively, for the first and second phase. Recirculation of anaerobic digested sludge, after a mild solid separation, was applied to the dark fermentation reactor in order to control the pH in the optimal hydrogen production range of 5-6. It was confirmed the possibility to obtain a stable hydrogen production, without using external chemicals for pH control, in a long term test, with a specific hydrogen production of 66.7 l per kg of total volatile solid (TVS) fed and a specific biogas production in the second phase of 0.72 m^3 per kgTVS fed; the produced biogas presented a typical composition with a stable presence of hydrogen and methane in the biogas mixture around 6 and 58%, respectively, carbon dioxide being the rest.

Keywords: hydrogen, bio-hythane, dark fermentation, anaerobic digestion, two-phase system.

AD:Anaerobic Digestion, BHy: Biohythane, COD: Chemical Oxygen Demand, CSTR: Continuos Stirred Tank Reactor, DF: Dark Fermentation, DW: Dry Weight, GP:Gas Production, GPR:Gas Production Rate, H-Ac:Acetic Acid, H-Bu: Butyric Acid, H-Pr: Propionic Acid, HRT:Hydraulic Retention Time, HC: Hydrocarbons, HPR: Hydrogen Production Rate, MPR: Methane Production Rate, OFMSW: Organic Fraction of Municipal Solid Waste, OLR: Organic Loading Rate, PTOT:Total Phosphorus, SGP:Specific Gas Production SHP:Specific Hydrogen Production, SSC:Steady State Condition, TKN:Total Kjiendhal Nitrogen, TS:Total Solids, TVS:Total Volatile Solids, VFAs:Volatile Fatty Acids, WW:Wet Weight, WWTP:Waste Water Treatment Plant

1. Introduction

There are several biological ways to produce hydrogen from organic substrates, among them the dark fermentation is the most promising one, thanks to its simply reactor configuration and continuous hydrogen production capacity coupled with high yield per unit of reactor. Even so hydrogen yields of dark fermentation process vary significantly due to inoculum and substrate characteristics and pre-treatments, especially when the substrate is heterogeneous as in the case of food waste. In recent literature, complex substrates were often used in dark fermentation process for hydrogen production, such as wheat straws, beer lees, sewage sludge, sugar beets, and cornstalk, usually mixed with different inoculum such cow manure, sewage sludge or digested sludge. These inoculums were mostly pre-treated with alkali, acid or heat in order to inhibit the hydrogen-consuming bacteria [1, 2]. In batch processes the hydrogen yields ranged from 16.26 $lH_2/kgTVS_{added}$ for sewage sludge [3], to 257 $lH_2/kgTVS_{added}$ of OMSW [4] even if at extreme thermophilic temperature. In this context it was demonstrated that, in general, the carbohydrate-rich feedstock presents higher hydrogen yields. Shifting the process from a batch to a continuous one, with pH control and using a continuous stirred tank reactor (CSTR), the yields obtained treating the same substrate ranged from a minimum of 22.4 $lH_2/kgTVS_{added}$ at 35°C with an OLR of 26 $kgCOD/m^3d$ [5], to a maximum of 125 $lH_2/kgTVS_{added}$ at 55°C with an OLR of 8 $kgTVS/m^3d$ [6]. Considering that dark fermentation (DF) could convert only one third of the theoretic amount of chemical energy contained in the feedstock [7] and the remaining was stored as soluble volatile fatty acids (VFAs), it is obvious that the effluent obtained must be further treated. There are different technologies available such as Photo-fermentation, Microbial Electrolysis Cells and Anaerobic Digestion (AD) [8]; among them the anaerobic digestion process has been well developed and for example could be easier implemented as DF-AD in existent full scale plant, compared with the other younger technologies.

Therefore an environmentally and economically sustainable approach for hydrogen production, could be the thermophilic two-phase anaerobic digestion process based on following guide lines: no necessity to use an inoculum i.e. from anaerobic digestion; start-up could be done directly feeding the organic substrate without chemical/thermal pre treatment; to exploit the buffer capacity of liquid phase from the anaerobic digestion effluent to control pH. This approach follows the ‘mixed culture biotechnology’ concept expressed by Kleerebezem and Van Loosdrecht [9]; they support the use of undefined mixed cultures, basing the process development on natural/ecological selection by manipulating the operation of the bioprocess or by varying the source of the natural inoculum. In that way it is possible to recover relevant products (such as energy carriers, solvents by fermentation, bio plastics) enriching the microbial population from a natural environment and using waste streams.

Some authors verified the feasibility of phased process, applying the sludge recirculation ad avoiding the use of external pH control. The best yields were achieved by Chu et al. [10]: they used two CSTR reactors, with recirculation rate of 2 and obtained the 42% of H_2 content in the biogas and 205 $lH_2/kgTVS_{added}$, applying an OLR of 38.4 $kgVS/m^3d$. The AD sludge was before settled and recirculated only the thick matter. The pH was maintained at 5.5 and no methane was detected.

Our previous studies at pilot scale [11, 12], demonstrated that it was possible to produce hydrogen in a two-phase approach without inoculum and reagent addiction, using directly the organic waste itself, and controlling the pH using the recirculation of the liquid fraction of anaerobic digestion effluent. The highest yield of about 51 $lH_2/kgTVS_{added}$ was achieved at 16 $kgTVS/m^3d$ of organic loading rate, a hydraulic retention time of 3.3 and 12.6 days for dark fermentation and anaerobic digestion reactors respectively. Applying these conditions it was possible to obtain a gas mixture with an optimal composition to improve combustion engine performances (6.7 $\%H_2$, 53.2 $\%CH_4$, 40.1 $\%CO_2$) that was named bio-hythane. Co-combustion of this mixed gas could reduce nitrogen oxide emission as compared to CH_4 combustion [13] and enhance the engine performance [14].

Following these results, a long-term validation (90 days) of the two-phase approach was carried out, applying an organic loading rate (OLR) in the range of 16-18 $kgTVS/m^3d$ in the first phase and between 4 and 6 $kgTVS/m^3d$ in the second phase. The HRT were maintained at 3.3 days and 12.6 days respectively for first and second phases. All the process parameters were monitored in order to evaluate the long-term sustainability of the system.

This long term run has been planned after the preliminary studies in order to define the reliability of the process for a future industrial scale-up: in fact, the constant production, both in terms of quantity and characteristics of bio-hythane, is still to be demonstrated.

2. Material and methods

The reactors used in this experiment and the analytical procedures, were exhaustively described by Cavinato et al. [11, 12]. It must be highlight the use of pilot scale reactors instead of lab scale ones: two reactors were a continuous stirred tank reactors (CSTR) with a working volume of 0.2 m^3 and 0.76 m^3 for first and second phase respectively. This could be considered as a real full-scale simulation, due both to substrate characteristics (collected directly in the full scale WWTP of Treviso Municipality, northern Italy) and to similar fluid dynamic condition. The flow scheme of the experiment is reported in Figure 1.

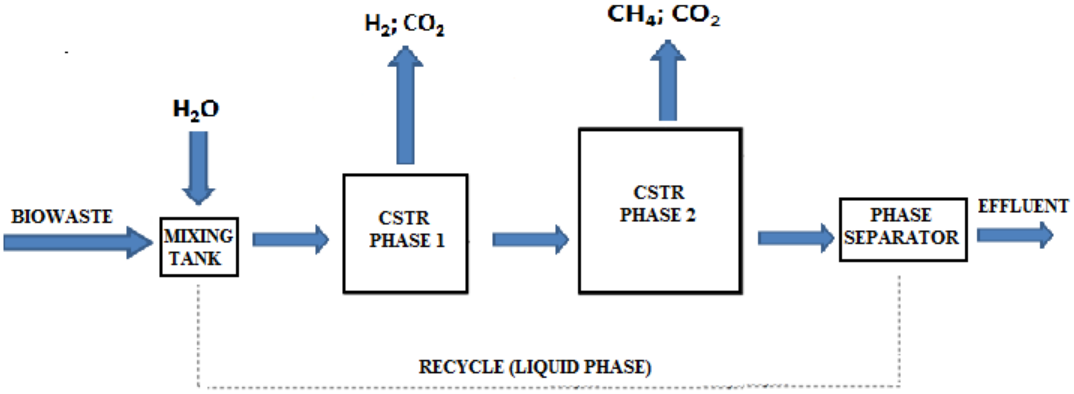


Figure 1. Two phase flow scheme used in the experiment.

Moreover in the Figure 1 was shown the water inlet between first and second reactor, used when total solids content must be adjusted. Both reactors were maintained at 55°C. Substrate characterization is shown in Table 1; the upper part of the table is related to the composition of the food waste collected in the full scale, before mechanical pretreatment adopted to increase the biodegradable fraction which is sent into full scale AD plant. About 30% of total waste is usually removed in the selection line (data not showed). The lower part of the table shown the physical-chemical characterization of the substrate fed to the dark fermentation reactor. As shown in Table 1, the food waste collected has a relevant content of fruit and vegetables (38-46% on wet weight basis), and a content of other food waste (such as meat, pasta, etc.) of 13-16% on wet weight. Biodegradable matter mainly composed the unclassified material, with a TVS on TS content of 65.1%. The amount of total solids of food waste used in this experiment was 26-27%, with the 82% of TVS on TS basis; the COD/TS ratio was about 1 that means a partial substrate oxidation.

Table 1. Composition of collected waste in the WWTP and characterization of the food waste after pretreatment step (WW: wet weight, DW: dry weight)

Composition of incoming waste in the WWTP		
Waste Class	% WW	% DW
Fruit/vegetable	38-46	30-38
Other food waste	13-16	12-19
Paper/ cardboard	13-18	15-19
Plastics	5-10	7-14
Inerts	3-9	14-19
Unclassified materials	10-20	13-25

Characterization of the food waste after pretreatment step					
Parameters	Units	Average	SD	Min	Max
TS	g/kg	266	54	226	316
TVS	g/kg	219	46	189	246
TVS/TS	%TS	82.7	3.0	76.2	85.4
COD	g/kg	257	44	181	320
TKN	g/kg	6.7	1.0	5.2	7.1
P_{TOT}	g/kg	0.5	0.1	0.3	0.7

The first phase reactor, dedicated to hydrogen production, was not inoculated with an active biomass but it was filled up with a mixture of minced organic waste (30% of total working volume) and tap water (70% of total working volume), in order to obtain a total solids content of about 8%. The average OLR applied was 16.8 kgTVS/m^{3}d in the first phase for whole run time, whereas in the second phase during the start up the OLR was increase in stepwise way from 1.3kgTVS/m^{3}d to 4.8 kgTVS/m^{3}d. The HRTs were maintained at 3.3 days and 12.6 days respectively for first and second phases. In Table 2 the characterization of both inoculum is shown. The characteristics of anaerobic digestion inoculum were in the range of the typical AD process values: pH was 7.6, the ammonia content was 1.05 g/l, low VFA concentration (349 mgCOD/l) and the alkalinity shown a high buffering capacity (at pH 4, 5,184 mg CaCO$_3$/l).

Table 2. first and second phase inoculum characterization.

Parameters	Units	First Phase	Second Phase
TS	g/kg	95.0	22.3
TVS	g/kg	86.6	11.9
TVS/TS	%	91.1	53
pH	-	4.7	7.6
VFA	mgCOD/l	3,452	349
N-NH4+	mg/l	745	1,050
Alkalinity @pH 6	mgCaCO$_3$/l		3,840
Alkalinity @pH 4	mgCaCO$_3$/l		5,184
COD	g/kg	95.7	15.5
TKN	g/kg	2.0	0.4
P_{TOT}	g/kg	0.6	0.1

The feedstock was prepared with about 15 kg (depending of volatile solid content) of fresh OFMSW plus tap water and an amount of recirculated digested sludge, in order to obtain 3.3 days of hydraulic retention time. No chemical reagents, thermal treatment or pH control were used.

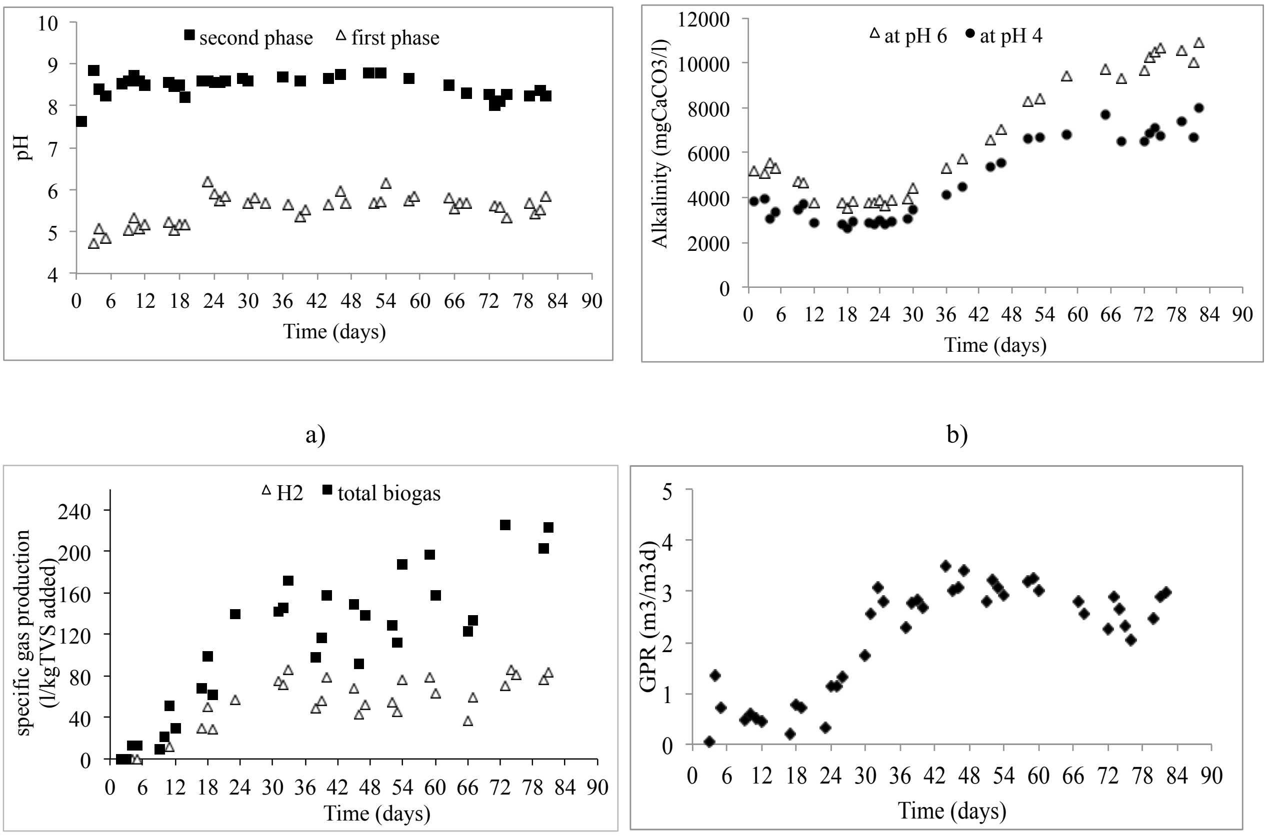
3.Results and discussion

3.1 Long-term process evaluation

The long-term test, carried out at pilot scale, was performed for about 90 days: the start-up phase was identified from day 0 to 49, while the steady state condition (SSC) run for about 40 days that means 13 HRTs for the dark fermentation and 3 HRTs for the anaerobic digestion process.

The first phase was inoculated with food waste and tap water, and this allowed for an initial solubilization of the organic material followed by a pH drop at about 4, with a consequent inhibition of hydrogen-producing bacteria. The strategy used to avoid this pH drop during the experiment was to recycle the liquid phase of the anaerobic digestion sludge, after a mild solid/liquid separation (about 25 gTS/l, so mainly inerts were removed) supporting the fermentative step with alkalinity and keeping the pH at about 5.5-6.0. The pH, the high OLR and low HRT applied, allowed for the selection of the hydrogen producing bacteria: after the first ten days, the hydrogen content reach the 20% of biogas produced in the first reactor, increasing till 50% after about twenty days.

In Figure 2 are illustrated some parameters profile such as, pH, partial and total alkalinity, gas production, both for dark fermentation and anaerobic digestion process.



a) b)

c) d)

Figure 2. a) pH profile of both reactors; b) alkalinity concentration in anaerobic digestion reactor; b) total gas and hydrogen specific gas production in the first phase; c) gas production rate in second phase reactor.

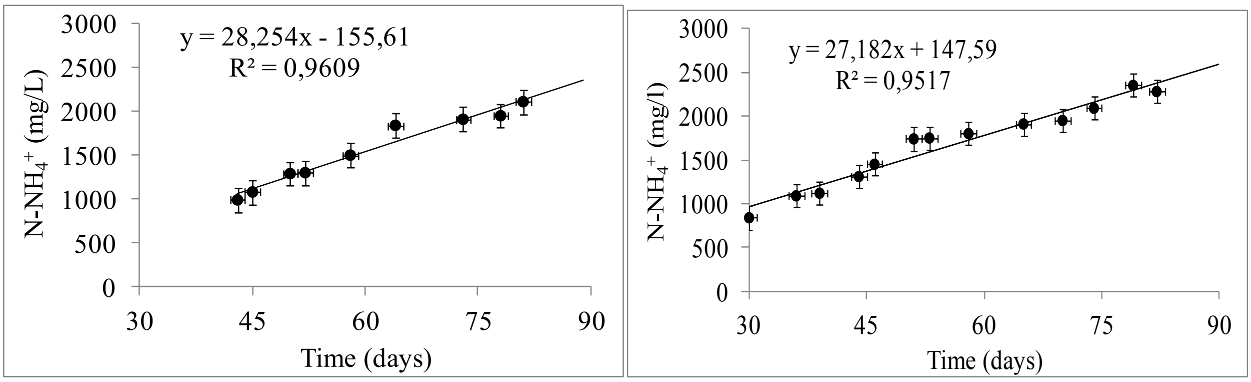
Observing the pH profile along the experiment, it was confirmed the stability of the process, even if this parameter was considered as a delayed detection method of process failure. Thanks to sludge recirculation, dark fermentation pH was always in the optimal range of hydrogenase enzyme with an average value of 5.7±0.3. The anaerobic digestion phase reached the steady state condition after about 50 days, showing an average total alkalinity of 9,806 mg$CaCO_3$/l, an average pH of 8.4 and a total VFA content of 1,107 mgCOD/l. The gas yields were comparable with those find in literature: the biogas produced were 0.17 m^3/KgVS and 0.72 m^3/KgVS for the first and second phase respectively, while the average H_2 and CH_4 percentage were 39% in dark fermentation and 67% in anaerobic digestion. In Table 3 are reported the average values and standard deviation for each parameters monitored, during the SSC conditions.

Table 3. characterization of first and second phase effluent and gas yields.

Parameters	Units	first phase	second phase
TS	g/Kg	53.6±7.5	26.0±0.4
TVS	g/Kg	42.2±6.9	17.8±0.6
COD	gO_2/kg	52.4±10.2	22.2±1.2
TKN	g/kg	1.8±0.5	1.1±0.1
P_{TOT}	g/kg	0.48±0.08	0.2±0.01
pH	-	5.7±0.3	8.4±0.2
VFA	mgCOD/l	11,701±3,164	1,107±1,118
H-Ac	mgCOD/l	3,294±1,643	-
H-Bu	mgCOD/l	4,315±1,477	-
Alkalinity (pH=4)	$mgCaCO_3/l$	-	9,806±1,114
Alkalinity (pH=6)	$mgCaCO_3/l$	-	6,957±600
Gas yields			
SGP	$m^3/KgVS$	0.17±0.1	0.72±0.1
H_2	%	38.5±9.7	-
CH_4	%	4.5±7.1	67±3.7
SHP	l/KgVS	66.7±14.66	-
GPR	m^3/m^3d	2.6±0.5	2.7±0.5

3.2 Ammonia inhibition

One of the main aspects that compromise the stability of the two-phase approach with sludge recirculation, was the ammonia accumulation in the system. In fact, the sludge recirculation permits a continuous ammonia flow back to the first phase, with a consequent increasing of this compound along time. It is well known that high ammonia concentration restrain the good performance of anaerobic microflora specialized for both hydrogen and methane production: this was due to the decompositions of proteins contained in food waste during the anaerobic digestion [15]. In this experiment it was possible to quantify the degradation considering total nitrogen to ammonia conversion: 7% and 39% of total nitrogen was converted into ammonia nitrogen in the first and second phase, respectively. At the steady state the ammonia accumulation rate was about 28 mg/l per day for both reactors, as illustrated in Figure 3a and 3b.

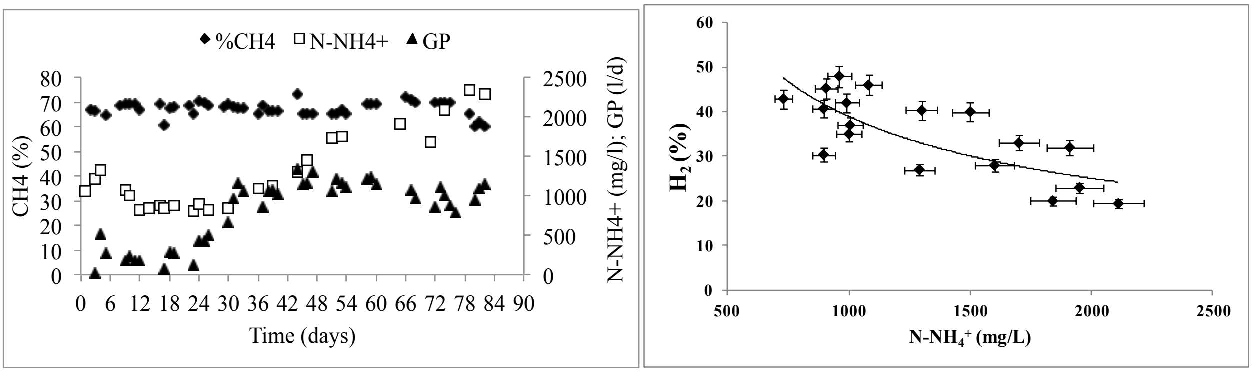


a) b)

Figure 3. a) Ammonia accumulation rate in dark fermentation reactor; b) Ammonia accumulation in anaerobic digestion reactor.

After about 70 days of operation the ammonia concentration reached a level of 2 gN/L with a free ammonia concentration of 916 mg/l (calculation on the basis of the equation given in Angelidaki et al., 1994 [16]); the same authors showed that in thermophilic conditions the free ammonia was responsible of inhibition for methane production and it could be already toxic at 700 mg/l. Moreover, not only methane but also biohydrogen production rate was reported to be highly dependent on pH and ammonia concentration above 2 gN/l [17]. In this paper the authors showed that the hydrogen production rate decreased in correspondence with an ammonia concentration increasing: high ammonia can in fact cause a shift of the metabolic pathway of a mixed culture [17, 18]. For example, these authors showed that testing different ammonia concentrations, the amount of total metabolites remained constant while butyrate and acetate concentrations decreased together with H_2 production.

The same effects were detected in this experiment as illustrated in Figure 4a and 4b, where it's possible to observe how ammonia could influence the methane and hydrogen productions.



a) b)

Figure 4. a) effect of ammonia concentration in the anaerobic digestion reactor; b) effect of ammonia on biohydrogen production in dark fermentation reactor.

Moreover, it is possible to observe that in the second phase reactor the high ammonia concentration (about 2g/l) lead to a decrease of methane production rate from 2.0 $m^3/m^3_r d$ to 1.6 $m^3/m^3_r d$ with a concomitant propionate accumulation (Table 4). Plotting the hydrogen content as percentage (Figure 4b), versus the ammonia concentration in the first reactor, it was possible to observe a relation between this two parameters; that means that the inhibition of hydrogen producing bacteria was caused by ammonia, with simultaneous decrease of acetate and butyrate content (Table 4).

In this table is shown the distribution of volatile fatty acids in acetic, propionic and butirric acid, at different concentration of ammonia, in both reactors. In dark fermentation reactor, increasing the ammonia content from 970 to 1976 mg/l, the acetic and butirric acid decreased (from 3,749 to 1,043 mgCOD/l for H-Ac, and from 5,257 to 1,428 mgCOD/l for H-BU), while propionic acid increased (from 696 to 1,904 mgCOD/l); at the same time hydrogen composition decreased from 43% to 29%. In methanogenic reactor the methane content slightly decreased (from 66% to 61%) with an accumulation o propionic acid.

Table 4. hydrogen and methane yields and volatile fatty acids content at different ammonia concentrations.

		First Phase Reactor			
N-NH4+	HPR	H_2	H-Ac	H-Pr	H-Bu
(mg/l)	(m^3H_2/m^3d)	(%)	(mgCOD/l)	(mgCOD/l)	(mgCOD/l)
970	1.1	43	3,749	696	5,257
1295	0.8	37	1,492	937	3,863
1976	0.7	29	1,043	1,904	1,428
		Second Phase Reactor			
N-NH4+	MPR	CH_4	H-Ac	H-Pr	H-Bu
(mg/l)	($m^3CH_4/m^3_r d$)	(%)	(mgCOD/l)	(mgCOD/l)	(mgCOD/l)
1005	2.0	66	26	-	77
1745	2.1	65	-	-	-
2240	1.6	61	395	1,498	68

In order to solve this problem, the approach we used in our previous studies [11, 12] was to daily remove part of the recycling stream from the second to the first reactor to maintain the ammonia concentration at a constant level in the system so to prevent inhibition problems. Some preliminary tests were carried out in order to remove ammonia on recirculation flow, using an evaporation unit (data not shown): preliminary results shown the possibility to treat part of the second phase effluent in order to concentrate ammonia in the solid fraction (after acidification), with a removal percentage > 99%. The liquid fraction could be reused to dilute de feedstock.

3.3 Hydrogen enriched methane production

Following the data published by some authors on the advantage of hydrogen enriched biogas application [14, 19, 20], it was evaluated the whole biogas composition produced during this long-tem test. In Figure 5 is reported the daily gas composition: the percentage of methane, hydrogen and carbon dioxide were 58%, 6.9% and 36% respectively. Hydrogen content was never below 5% and this met the best characteristics for biohythane mixture.

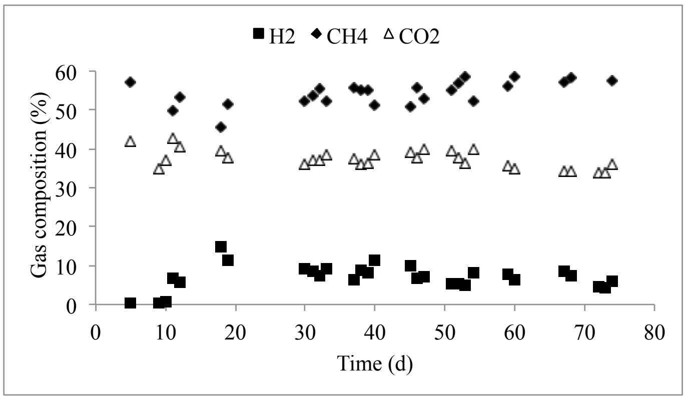


Figure 5. total biohythane composition

The advantages of this mixture were referred to the enhanced combustion performance and the reduction in HC emission. The total specific gas production obtained was 0.80 m^3/kgTVSadded, and a gas production rate of 2.75 m^3/m^3d (Table 5). Calculation considers also the small amount of methane produced in the first phase, due to a not complete inhibition of methanogenic microorganisms.

Table 5. biohythane yields

	First Phase			Second Phase		GP	H_2	CH_4	CO_2	GPR	SGP
	m^3H_2/d	m^3CO_2/d	m^3CH_4/d	m^3CH_4/d	m^3CO_2/d	m^3/d	%	%	%	m^3/m^3_rd	m^3/kgTVS
Average	0.19	0.27	0.015	1.48	0.687	2.645	6.9	58	36	2.75	0.80
SD	0.06	0.05	0.006	0.12	0.10	0.28	1.9	3.0	2.0	0.25	0.11
Min	0.09	0.19	0	1.18	0.53	2.01	5.4	51	33.9	2.16	0.63
Max	0.3	0.37	0.02	1.70	0.9	3.18	11.4	61.3	40.1	3.25	0.95

Considering the total specific gas production and composition and the solids content of OFMSW (Table 1), it was calculated the specific energy production per ton of waste. The calculation was also based on the lower heating value (LHV) of the gas mixture as obtained in the experimental tests. The specific energy production obtained was 404 kWh per ton of waste pre-treated. This value could be compared with the energy consumption for waste pretreatment. For example, taking into account the pretreatment system installed inside the WWPT of Treviso Council (OFMSW coming from a "door by door" collection approach), the specific energy requirement resulted in 20-40 kWh per ton of waste treated [21].

4. Conclusions

A long-term two-phase anaerobic digestion process for hydrogen and methane production was carried out at pilot scale without any inoculum treatment or pH control. The substrate used as feedstock was the food waste, a substrate rich in carbohydrates, apt for biohydrogen production by dark fermentation. It was adopted the anaerobic sludge recirculation, supporting the dark fermentation with alkalinity, keeping the pH in the hydrogenase working range.

The results shown a stable long term run, without any particular parameters variation that could be associated with process failure. The only evidence was the ammonia accumulation that results in small hydrogen production decreasing, but without stability problem. Hydrogen production was 66.7 l/kgTVS added and the specific biogas production in the second phase was 0.72 m^3/kgTVS added. The bio-hythane obtained met the composition characteristics requested (CH_4 58%, H_2 6.9% and CO_2 36%). It was observed an initial ammonia inhibition in the first phase that caused a hydrogen content decreasing; this aspect will be further studied

Acknowledgements

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