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Two-phase thermophilic anaerobic digestion process for biohythane production treating biowaste: preliminary results.

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Abstract

This paper deals with the optimisation of a two-phase anaerobic process treating biowaste for hydrogen and methane production. Nor physical neither chemical pre treatments were used to optimise the process. The work was carried out at pilot scale, using two CSTRs (200 l and 380 l working volume respectively) both maintained at thermophilic temperature (55°C) and fed semi-continuously with biowaste. The experiment was divided in three periods; during the first two periods the organic loading rate was maintained at 20 kgTVS/m^{3}d and the hydraulic retention time was changed from 6.6 to 3.3 days, while in the last period the digestate of the second reactor was recirculated to the first reactor in order to buffer the system and control pH at levels around 5. The HRT was maintained at 3.3 days and the OLR was decreased at 16.5 kgTVS/m^{3}d. The best yield was obtained in the last period where a specific hydrogen production of 50.9 l/kgVS$_{fed}$ was reached, with a H_2 content in biogas from the first reactor of 36%. The methanogenic stage after the hydrogen conversion reached a specific biogas production of 0.62 m^3/kgVS$_{fed}$ and an overall organic removal above 70%, without any stability problem. The overall biogas production was some 1.5 m^3 per day with a gas composition of 10% H_2 and 50% CH_4.

Keywords
Biohydogen; biohythane; anaerobic digestion; food waste; two-phase; thermophilic temperature.

INTRODUCTION

Among all the technologies dealt with H_2 production, dark fermentation is becoming the most interesting application thanks to its accomplishment of the dual goals of waste reduction and energy production, especially if considering the two-stage configuration. In fact, because of the insignificant reduction of the organic content, a stage after the fermentative hydrogen-production process is required to convert the fermentation end products to other forms of energy or to further amounts of hydrogen. At present the most near-market alternative for this second stage is anaerobic digestion to methane (Hawkes et al. 2007). The two-stage process has several advantages over the conventional single-stage process, since it permits the selection and enrichment of different bacteria in each reactor and increase the stability of the whole process by controlling the acidification phase in first reactor and hence preventing the overloading and/or the inhibition of the methanogenic population in the second reactor (Koutrouli et al. 2009).

This approach makes biological hydrogen production a promising alternative to meet increasing energy needs as substitute for fossil fuels, because suitable for the production of bio-hythane, a mixed gas comprising hydrogen, methane and carbon dioxide. Hydrogen presence in biogas (10% addition was found to be the most suitable) significantly enhances the combustion rate and extends the lean limit of combustion of biogas, moreover the CO_2 emissions during combustion are reduced (Porpatham et al. 2007).

While the anaerobic digestion for methane production is a well established technology at industrial scale (De Baere, 2006, Bolzonella et al., 2006), the dark fermentation of complex substrates, as biowaste, need to be optimize in order to obtain a stable and continuous hydrogen conversion with low costs added.

Most of the research carried out on hydrogen production from biowaste, considered to improve the hydrogen yields through chemical or thermal pre-treatments of the inoculum and/or the substrate in order to inhibit the formation of hydrogen consuming bacteria, or to maintain the pH between 5 and 6 (Oh et al. 2003, Valdez-Vazquez et al. 2005, Gomez et al. 2006, Ueno et al. 2007b, Kim et al. 2009, Lin et al. 2010).

According to this scenario and in order to develop a two stage process easily scalable at industrial level, in this work was evaluated the possibility to run all the operating conditions without any chemical or thermal treatment. Only the process operational parameters like hydraulic retention time (HRT), organic loading rate (OLR) and the recirculation of digestate for pH control were considered. Thermophilic temperature was applied to both phases as the better temperature for hydrogen and methane production (Shin et al. 2004, Ueno et al. 2007a, Cecchi et al. 1993). The inoculum of the first phase was prepared using indigenous microbial cultures contained in biowaste as suggested by Wang et al. (2009). It was also evaluated the behaviour of anaerobic digestion changing the first stage parameters.

MATERIAL AND METHODS

Inoculum and substrate

The seed sludge used as inoculum for the methanogenic reactor was collected in the WWTP located in Treviso (northern Italy) where a 2,000 m^3 anaerobic digester treats the source collected biowaste at 35ºC. Sludge pH, total solids, total volatile solids and total alkalinity were 7.41, 26.7 g/l, 16.6 g/l, 2,450 $mgCaCO_3/l$ respectively. The sludge was than acclimatized for one week to thermophilic temperature (55ºC) moving through a one-step temperature change (Cecchi et al. 1993, Bolzonella et al 2003). The fermentative reactor was fed with the source collected organic biowaste coming from the same WWTP, mixed with tap water. The feedstock was prepared without adding any chemical reagent and without thermal treatment. This kind of substrate has a high carbohydrate content that can be converted into hydrogen and organic acids through the action of fermentative bacteria. Table 1 shows the main characteristics of this substrate.

Table 1 Characterisation of the organic fraction of municipal solid waste.

	units	average	min	max	S.d.	number of samples
TKN	(mgN/L)	5,738	2,178	8,436	2,280	50
Ptot	(mgP/L)	198.7	140.7	250.0	39.6	50
COD	(gCOD/L)	217.2	151.9	273.6	41.0	50

TS	(g/L)	242.9	145.3	304.7	71.3	50
TVS	(g/L)	179.5	150.0	220.9	40.13	50
TVS	(%TS)	73.8	61.5	88.4	10.6	50

Analytical methods

The effluent of both reactors was monitored three times per week in terms of solid content, chemical oxygen demand, total Kjeldahl nitrogen, total phosphorus, and daily for the stability parameters such as pH, volatile fatty acid content, alkalinity and ammonia, all in accordance with the Standard Methods (APHA-AWWA-WEF). Volatile fatty acids content was monitored using a gas chromatograph (Carlo Erba instruments) with hydrogen as gas carrier, equipped with a Fused Silica Capillary Column (Supelco NUKOL^{TM}, 15m x 0.53mm x 0.5 µm film thickness) and with a flame ionization detector (200°C). The temperature during the analysis started from 80°C and reaches 200°C trough two other steps at 140°C and 160°C, with a rate of 10°C/min. The analyzed samples were centrifuged and filtrated with a 0.45 µm membrane.

Gas production was monitored continuously by two gas flow meters (Ritter Company, drum-type wet-test volumetric gas meters), while the biogas composition (CO_2-CH_4-H_2S) was defined by a portable infrared gas analyser (geotechnical instrument, model. GA2000). Hydrogen content in the fermentative reactor was measured by a gas-chromatograph (GC Agilent Technology 6890N) equipped with the column HP-PLOT MOLESIEVE, 30m x 0.53mm ID x 25µm film, using a thermal conductivity detector and argon as gas carrier.

Experimental set up

Two stainless steel CSTR reactors (AISI 304) were employed for optimized H_2 and CH_4 production, respectively. The first reactor, dedicated to the fermentative step, had a 200 l working volume, while the second reactor dedicated to the methanogenic step had a 380 l working volume. Both the reactors were heated by a hot water recirculation system and maintained at 55°C using electrical heater controlled by a PT100-based thermostatic probe. The feeding system was semi-continuous, arranged once per day.

The experimental test was divided in three periods (runs); during the first two working periods the OLR of the first reactor was maintained at 20 kgVS/m^{3}d and HRT was decreased from 6.6d to 3.3d. The choice to apply this OLR value was evaluated considering literature data and the characteristics of biowaste used. In the third working period part of the digestate coming from the methanogenic reactor was recirculated in order to give alkalinity buffer to keep the pH around 5 (Kataoka et al 2005, Chu et al. 2008, Lee et al. 2010). The HRT was kept at the same conditions of period II, but the OLR was decrease to 16.5 kgVS/m^3 in order to adapt the whole process to a low organic load. Increasing OLRs will be studied in the future. Table 2 shows the operating conditions applied to the reactors during the experimentation.

Table 2 Operating conditions applied during the experimental test

	Run I	Run II	Run III
HRT 1phase (d)	6.6	3.3	3.3
HRT 2 phase (d)	12.67	12.67	12.67
OLR 1 phase (kgVS/m3d)	20.6	21.01	16.50
OLR 2 phase (kgVS/m3d)	11.25	5.36	4.46

RESULTS

The pilot plant was operated for 140 consecutive days. For each run the stationary state conditions were reached after about 20 days. In a bench scale study on hydrogen production, Wang et al. (2009) used the microorganism already present in the food waste as first phase inoculum, without any chemical addiction. Treating this food waste in a mesophilic semi-continuous rotating drum reactor of 0.2 m^3 of volume, applying an OLR of 22.65 $kgVS/m^3d$ and an HRT of 6.6 d, they obtained an hydrogen production of 65 l/kgVS with a pH ranged between 5.2 and 5.8.

During the first period of this study (80 days), the HRT and OLR were set at similar values (6.6 d and 20 $kgVS/m^3d$ respectively) using only biowaste as inoculum of the first reactor and anaerobic digestion sludge for the methanogenic reactor.

The initial pH of the biowaste (mixed with tap water) was 3.70 and reached 4.32 during the first period (Figure 1). This can be probably ascribed to the formation of lactic acid rather than short chain fatty acids (Traverso et al., 2000). Hydrogen production is reported to proceed in the pH range 4.5-6.7 but is even known that the undissociated acetic and butyric acids increases as the pH falls towards the pKas of 4.78 and 4.81 respectively (Hawkes et al. 2007).

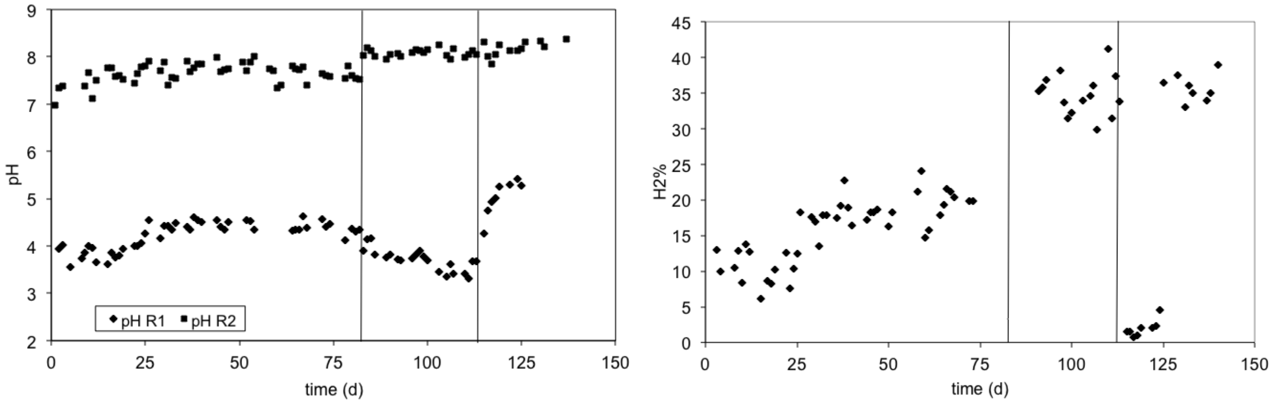

Figure 1. pH variation of two reactors and gas composition (H_2 percentage) in the first phase during the three runs.

The pH obtained did not meet the optimal condition for hydrogen production as obtained by Wang, that is usually between 5 and 6, (Hawkes et al. 2007, Van Ginkel et al. 2001), in fact this pH could shift the reactions to solventogenesis due to the formation of undissociated organic acids (Valdez-Vazquez and Poggi-Varaldo 2009). Kataoka et al. (2005) used food waste as inoculum without treatment, using a thermophilic CSTR and applying HRT between 2.5 and 6d but with this conditions they reached a pH of 4-4.5 and a production of hydrogen lower than 5 l/kgVS. Kim et al (2009) tested non treated food waste in batch tests without treatment nor inoculum and obtained a similar result of 4.4 l/kgVS with high level of lactate (18 gCOD/l). In this work, during the first period the total gas production of the first phase was 15.9 l/kgVS with an hydrogen content of 15%, that means a H_2 yield of 2.4 l/kgVS (Figure 2), result similar to those mentioned.

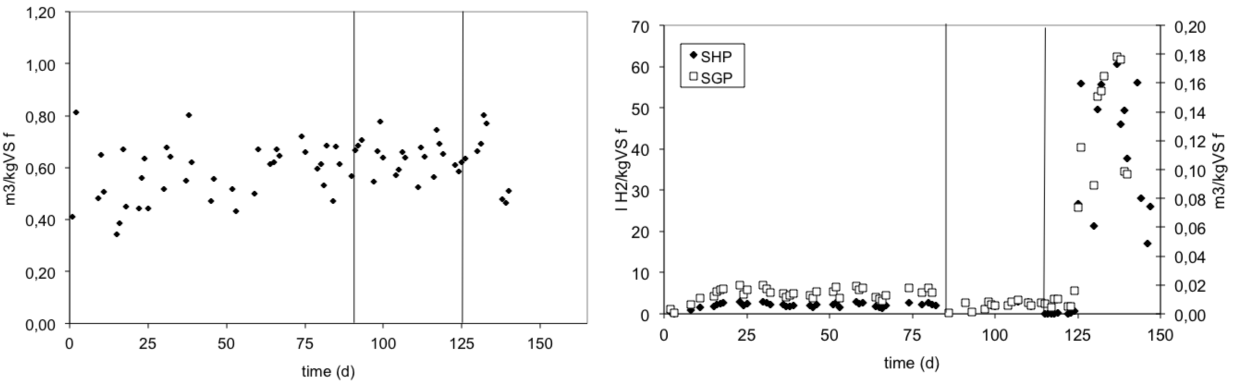

Figure 2. Specific gas production and specific hydrogen production in first reactor, and specific gas production in methanogenic reactor during the whole experimental test.

The VFA content in this run was high and mainly due to acetic acid that reached an average value of 7.73 gCOD/l, and butyric acid (1.22 gCOD/l): that indicated how the hydrogen production pathway was inhibited by acetogens producing acetate through H_2 and CO_2 use. In the methanogenic reactor the average pH was 7.68 and the specific gas production was 0.63 m^3/kgVS (65% CH_4) with a biogas production rate of 7.01 m^3/m^3d. This high biogas production was mainly due to the optimal conversion of the high amount of acetic acid coming from the first phase, that decrease until 223 mgCOD/l in the methanogenic reactor. During the second period, the hydraulic retention time was changed from 6.6 to 3.3 days. Kim et al. (2008a) consider the necessity to use high HRT (> 1d) if treating complex substrate because of the slow biodegradability of some components as confirmed by Hawkes et al (2007) that consider an optimum HRT between a few hours and 3 days, depending on substrate. HRT is one of the key parameters for hydrogen production, in fact short HRT is necessary if an anaerobic inoculum is used because it allows for the washout of the H_2 consuming bacteria. In this case any inoculum was used, but even the retention time was decrease to 3.3 days maintaining the same OLR, in order to observe how the methabolic pathway was changing.

As shown in figure 1, the pH during the second period drop down to 3.51 with an overall gas production of 7.4 l/kgVS and a hydrogen content of 35%.

The VFA production also decreased to 2.71 gCOD/l but the ratio between butyric acid and acetic acid remained the same as in run 1, with a predominance of acetic acid. The reduction of VFA concentration compared to the first period, led to a pH increase in methanogenic reactor that was stable at 8.09. The SGP was the same of the previous period (0.64 m^3/kgVS, 60% CH_4) and the gas production rate decreased to 3.4 m^3/m^3d. This was because the HRT was maintained at 12.6 days in the methanogenic reactor while the dilution rate applied to the first phase was increased.

In the third and last period, the recirculation of the digestate was activated to keep the pH in the range 5-6.

Table 3 Summary of the monitored parameters and process yield during the whole experimental test.

	UM	run 1	run 2	run 3
		First phase		
pH		4.32	3.51	5.47
NH_3	(mgN/L)	530.8	152.2	978.0
COD	(gCOD/L)	157.9	66.9	45.4
TS	(g/L)	172.2	78.0	57.1
TVS	(g/L)	142.4	67.4	45.1
TVS	(%TS)	82.7	86.4	79.2
VFA	(mgCOD/L)	11,550	2,712	13,355
		Second phase		
pH		7.68	8.09	8.33
Alkalinity (pH6)	($mgCaCO_3$/L)	4,823	2,726	5,988
Alkalinity (pH4)	($mgCaCO_3$/L)	10,085	5,316	3,640
NH_3	(mgN/L)	1,955	1,047	1,185
COD	(gCOD/L)	60.7	24.2	14.61
TS	(g/L)	75.6	29.3	24.4
TVS	(g/L)	56.8	21.0	16.2
TVS	(%TS)	75.2	71.1	66.3
VFA	(mgCOD/L)	223.3	611.3	98.0
		Yields first phase		
OLR	($kgTVS/m^3d$)	20.6	21.0	16.5
GPR	($m^3/m^3_r\,d$)	0.32	0.15	2.40
SGP	($l/kgTVS_f$)	15.9	7.4	145.6
SHP	($lH_2/kgTVS_f$)	2.4	2.6	50.9
H2	(%)	15	35	36
		Yiels second phase		

OLR	($kgTVS/m^3d$)	11.25	5.36	4.46
GPR	($m^3/m^3_r\,d$)	7.0	3.4	2.9
SGP	($m^3/kgTVS_f$)	0.63	0.64	0.62
CH_4	(%)	65.4	59.8	67.5
CO_2	(%)	33.8	33.7	32.5

The alkalinity fed into the first phase gave buffer capacity to the system and allowed for keeping the pH around 5.5, a value clearly higher compared to those observed in the first two runs.
As shown in figure 1, after 1 week the pH rose up till 5.47 with an average hydrogen production of 50.9 l/kgVS add and an average percentage of 36%. The total VFA content was 13.3 gCOD/l, but in this case the molar ratio between butyric acid and acetic acid increased. Considering the following reaction:

$$4C_6H_{12}O_6 + 2H_2O \rightarrow 3CH_3CH_2CH_2COOH + 2CH_3COOH + 8CO_2 + 10H_2 \qquad (1)$$

a theoretical hydrogen yield of 2.5 $molH_2$/mol hexose should be obtained in ideal conditions. In this study the experimental data do not reach this value, but a modest 0.41 $molH_2$/mol hexose calculated considering 1 gVS equivalent to 0.9 g of hexose (Valdez-Vazquez et al. 2006), that is the 16.6% of efficiency. This could be caused by the effect of the hydrogen consuming bacteria present on the recirculation sludge that could limit hydrogen production (Kramer et al. 2005). The yield obtained is otherwise comparable with other works treating biowaste with heat shock treatment/chemicals addictions (Table 4), and with the data of hydrogen yields treating biowaste in a two phase approach using the recirculation of digested sludge (Table 5).

Table 4 Comparison of continuous/semi continuous process treating food waste with thermal or chemical treatment or pH control.

substrate	inoculum treated	substrate treated	pH control	T	pH	HRT	H2	SHP	Ref
				°C		d	%	l/kgVS add	
OFMSW	NO	YES	YES	34	5 - 6	3	25-27	26.5 - 34	*Gomez et al. 2006*
potato waste	NO	NO	YES	35	5.5	0.25	45	28.5	*Zhu et al .2008*
food waste	YES	YES	NO	35	5.3	1.25		24.5	*Kim et al.2008b*
Food waste	YES	NO	NO	37	5.5-7	0.2-0.5	18.7	290	*Han et al. 2005*
solid waste, spent brewery grains	YES	NO	NO	40	6	3		41.6 *	*Chou et al. 2008*
food waste	NO	NO	NO	55	5.4	33	36	50.9	*this study*

*on TS basis

Table 5 Comparison of two-phase processes treating food waste and adopting the recirculation of digested sludge.

First phase					Second phase			
Qr/Qi	pH	HRT	OLR	SHP	HRT	OLR	SGP	Ref.
		d	$kgVS/m^3d$	$l/kgVS_{add}$	d	$kgVS/m^3d$	$l/kgVS_{add}$	
0.25-0.5	5 - 6	2.5-6	20.8 – 8.45	20-30	18-30	2.84 – 1.18	0.49	*Kataoka et al. 2005*
2	5.5	1,3	38.4	205	5	6.6	0.61*	*Chu et al. 2008*
1	5.5 – 5.57	1,9	39*	150*	7.7	8.4*	0.21 (CH4)*	*Lee et al. 2010*
1	5.47	3.3	16.5	50.9	12.6	4.5	0.62	*this study*

* on COD basis

In these references, higher yields were obtained applying higher OLR, lower hydraulic retention time, and higher recirculation ratio. The methanogenic reactor was stable also in this last period, with an average specific biogas production of 0.62 m^3/kgVS and a GPR of 2.9 m^3/m^3d. This confirm the efficiency of separate phase that results in a high biogas production and a TS-TVS and COD removal of more than 70%.

It is interesting to observe that the daily production of H_2 and CH_4 on volume basis results in 20% and 80% respectively, that is the composition of “hythane”. Considering also carbon dioxide as part of the bio-hythane gas, the percentage composition of the whole daily gas production obtained in this work results in a surplus of CO_2. Treating the gas flow from first phase sequestering the CO_2, the composition of the mix became 58.76 % CH_4, 28.29% CO_2 and 12.94% H_2 that could be suitable for modified engine application tests.

Conclusions

Two phase thermophilic anaerobic digestion was tested for biohydrogen production treating complex substrate as the biowaste from separate collection. The test was carried out without any thermal or chemical treatment of the feedstock and without using an anaerobic inoculum. The results shown a low hydrogen production if treating only food waste even changing the HRT, caused by wrong pH and metabolic pathways. The recirculation of digested sludge into the first phase shows the feasibility of the approach, in fact the pH was kept at about 5.5 with a consequent higher hydrogen yield of 50.9 l/kgVSadd. In order to improve the hydrogen yield, further conditions will be investigated for example increasing the recirculation ratio and the organic loading rate.

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