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Optimization of two-phase thermophilic anaerobic digestion of biowaste for bio-hythane production through reject water recirculation

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Abstract

The optimization of a two-phase thermophilic anaerobic process treating biowaste for hydrogen and methane production was carried out at pilot scale using two stirred reactors (CSTRs) and without any physical/chemical pretreatment of inoculum. During the experiment the hydrogen production at low hydraulic retention time (3d) was tested, both with and without reject water recirculation and at two organic loading rate (16 and 21 kgTVS/m3d). The better yields were obtained with recirculation where the pH reached an optimal value (5.5) thanks to the buffering capacity of the system. The specific gas production of the first reactor was 51 l/kgVSfed and H2 content in biogas 37%. The mixture of gas obtained from the two reactors met the standards for the biohythane mix only when lower loading rate were applied to the first reactor, with a composition of 6.7% H2, 40.1% CO2 and 52.3% CH4, and with an overall SGP of 0.78 m3/kgVSfed.

Keywords
Biohydrogen; biohythane; thermophilic anaerobic digestion; biowaste; two-phase. .

1 Introduction

In Italy the average biodegradable waste production in 2007 was 6.3 million tons on a total urban waste production of 32.5 million tons, that was e 19.3% of the total production (ISPRA 2009). Among the biodegradable matter collected separately, the organic fraction and garden waste was only 9% on the total amount; most of this was treated in composting systems, while only 1.2% was sent to anaerobic digestion. Considering also the actual renewable energy scenario, it is important to optimize the separate collection and improve the anaerobic digestion in order to obtain energy power through biogas, and a fertilizer as a product.

A step forward of the common anaerobic digestion process, is the separate phase approach finalized to the production of hydrogen in the first phase reactor and methane in the second phase reactor (Martinez-Perez et al., 2007). This approach met two goals: to produce hydrogen by dark fermentation and treat the effluent in anaerobic digestion with the aim to use this gas separately, or to mix this two gas to obtain the bio-hythane. Bio-hythane is the biological production of a gas with an average percentage composition of 10% H_2, 30% CO_2 and 60% of CH_4. The advantage of this mix is that hydrogen and methane are complementary vehicle fuels in many ways: methane has a relatively narrow flammability range that limits the fuel efficiency and oxides of nitrogen (NO_x) emissions improvements that are possible at lean air/fuel ratios; the addition of even a small amount of hydrogen, however, extends the lean flammability range significantly; methane has a slow flame speed, especially in lean air/fuel mixtures, while hydrogen has a flame speed about eight times faster; methane is a fairly stable molecule that can be difficult to ignite, but hydrogen has an ignition energy requirement about 25 times lower than methane; finally, methane can be difficult to completely combust in the engine or catalyze in exhaust after treatment converters, in contrast, hydrogen is a powerful combustion stimulant for accelerating the methane combustion within an engine, and hydrogen is also a powerful reducing agent for efficient catalysis at lower exhaust temperatures. The possibility to use this advantage with biogas produced from renewable resources was studied by Porpatham et al. (2007). They found that adding the 10% of hydrogen in biogas, the combustion rate was enhanced, there was an improvement in thermal efficiency and power output. Moreover a drastic reduction of hydrocarbons (HC) emissions was observed (HC level drops from 1530 ppm with neat biogas to 660 ppm) and there is no significant increase in NO level.

Among the available technologies, biological techniques are a promising option in fact they offers the possibility of generating H_2 that is a renewable and carbon neutral source. Biohydrogen can be achieved in three main ways (Balat et al. 2010): bio photolysis of water by algae; photo-fermentation; dark-fermentation.

Thanks to the higher yield and lower costs, the dark fermentation is gaining importance during last ten years. In fact the reactor configuration is simply and the production of gas is independent from external factors as light sources (Valdez-Vazquez et al. 2009; Hawkes et al 2007).

The biological process allow to treat a wide range of substrate thanks to the microorganisms already present in a mixed culture coming from anaerobic digestion process. In industrial applications the use of mixed cultures for hydrogen production from organic wastes might be more advantageous because pure cultures can easily become contaminated with H_2 consuming bacteria but it is necessary to keep the process stable in terms of hydrogen yields in economically feasible conditions.

On the other hand the microflora in mixed culture often contain unwanted bacteria such as methanogens which consume the produced hydrogen and convert it to methane. Enrichment cultures of the H_2 microflora are prepared by heat/acid/basic treatment which inhibits the activity of the hydrogen consumers while the spore forming anaerobic bacteria survive (Hellenbeck 2009; Mathews and Wang 2009).

During last ten years, most of the study on bio hydrogen production optimization using dark fermentation, were focused on the inhibition of hydrogen consuming bacteria already present in a mixed microflora inoculum, in order to optimize the gas yields. 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. This process has several advantages over the conventional single-stage process, since it permits in specific condition, the selection and enrichment of hydrogen producing bacteria in one reactor, and biogas production in a second reactor. In fact hydrogen is an intermediary product in a single phase AD that is, however, not available because it is rapidly taken up and converted into methane by methane-producing microorganisms.

2 Materials and methods

2.1 Substrate and inoculum

The seed sludge used as inoculum for the methanogenic reactor was collected in the WWTP located in Treviso (northern Italy) where a 2000 m^3 anaerobic digester treats the source collected biowaste at a working temperature of 35ºC.

The characteristics of inoculum and substrate in terms of total solids, volatile solids, macro pollutants, pH and alkalinity are shown in tables 1 and 2.

Table 1 Substrate characterization

parameter	unit	RUN I	RUN II	RUN III
TS	g/kg	241	253	267
TVS	g/kg	203	214	213
TVS/TS	%	84	85	80
COD	gCOD/kg	206	249	207
TKN	gN/kg	7.2	5.6	7.3
TP	gPtot/kg	0.78	0.54	0.32

Table 2 Inoculum characterization

parameter	unit	AV	min	max	SD
TS	g/kg	22.9	22.3	23.4	0.5
TVS	g/kg	13.4	13.0	13.7	0.3
TVS/TS	%	58.5	57.7	59.2	0.6
TKN	mgN/kg	0.50	0.48	22.40	0.02
TP	mgP/kg	0.06	0.06	0.07	0.01
pH		7.51	7.31	7.69	0.16
Alkalinity tot	mg$CaCO_3$/l	2,074	2,060	2,087	111

The inoculum 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.

In order to avoid problems of pipe clogging, the substrate was previously reduced using a grinder.

2.2 Analytical methods

The effluent of both reactors was monitored 2/3 times per week in terms of solid content, chemical oxygen demand, total K 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 NUKOLTM, 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 25um film, using a thermal conductivity detector and argon as gas carrier.

2.3 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 760 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 organic waste was reduced in size using a grinder, than mixed with tap water and anaerobic sludge (in Run III) and fed to the first phase reactor.

The experimental test was divided in three periods (runs); during the first two working periods the OLR of the first reactor was maintained at 21 kgVS/m^3d while HRT was decreased from 6.6d to 3.3d changing the reactor's volume. In the third working period part of the digestate coming from the methanogenic reactor was recirculate in order to give alkalinity buffer to keep the pH around 5.5 (Kataoka et al 2005, Chu et al. 2008, Lee et al. 2010), with a recirculation ratio of 1. Table 3**Error! Reference source not found.** shows the operative conditions applied to the reactors during the experimentation.

Table 3 operative conditions applied during the experimental test

	Run I	Run II	Run III-a	Run-III-b
HRT 1phase (d)	6.6	3.3	3.3	3.3
HRT 2 phase (d)	12.6	12.6	12.6	12.6
OLR 1 phase (kgVS/m^3d)	21	21	16	21
OLR 2 phase (kgVS/m^3d)	10	5	4	5

In all the Runs the second phase hydraulic retention time was fixed at 12.6 days, in order to permit to the anaerobic digestion process to degrade almost all the biodegradable matter. Chu et al (2008) and Lee et al. (2010) applied lower HRT (7.7 and 5 days) as consequence of the high loading rate applied to the first phase and the solubilization of the particulate organic matter in that reactor. Also in this conditions they obtain a good substrate conversion to biogas.

Run III was divided into two sub-period: first sub-period was called Run III-a and an OLR of 16 kgVS/m^3d was applied in order to adapt the whole process to a lower organic load, while in second sub-period called Run III-b the OLR was increased to 21 kgVS/m^3 d as the previous two runs.

The whole experiment length was 185 days (Run I 0-85; Run II 86-117; Run IIIa 118-148; Run IIIb 149-185). For each period was defined a period of start up and a period of stationary state conditions.

3. Results and discussion

In Run I, about 20 kg of organic waste was diluted in 10 l of water and fed once a day, in order to obtain in the first phase an organic loading rate (OLR) of 21.4 kgTVS/m^3d and an hydraulic retention time (HRT) of 6.6. As a consequence the OLR of the second phase was 10.8 kgTVS/m^3d with an HRT of 12.6 days. No inoculum was used but only organic waste without any pretreatment was fed to the reactor. This conditions were applied for 85 days and the steady state (SSC) was reached from day 64. As mentioned above pH is an important parameter involved in the biohydrogen generation process. Applying this conditions, without any inoculum or pre treatment, the system was not able to maintain the pH in the best range for hydrogenase enzyme, in fact it drop at 3.7 during the start up and reached 4.3 during SSC (fig. 2) This low pH value could be explained by the high VFA production that reach a

maximum of about 15 gCOD/l than stabilized at 8.3 gCOD/l, and composed mainly by acetic acid (6,473 mgCOD/l) and small amount of propionic and butyric acids (600 and 778 mgCOD/l respectively). Considering the pKa (3.8) of lactic acid and the pH, it is possible to consider a shift of the system in a solventogenic reactions with a consequent inhibition of the biohydrogen production. In fact, it was already demonstrated by the authors that in a CSTR fed with vegetable waste applying an HRT of 6 days and an OLR of some 35 kgVS/m^3 per day, 43% of total COD was converted into soluble organic compounds, 41% of which was lactate (Traverso et al. 2000, Bolzonella et al., 2005). Soluble VFA content and ammonia (sCOD 75.4 gCOD/l and 528 mgN/l), suggested a shift from acidonenic to solventogenic conditions. Despite of the high content of VFA, the anaerobic reactor was able to convert the acetic acid into methane and CO_2, without any problem of stability. In table 4 are shown the average values of effluents characteristics and yields. As confirmed also by the graphs displayed in fig. 1, the pH reach a constant values of 7.6, while the average total alkalinity was 10.6 g$CaCO_3$/l with a slightly crescent trend. The VFA content (211 mgCOD/l) shown the efficiency of VFA conversion into biogas, that is also not affected by the ammonia content that reach 2,016 mgN/l.

In terms of yields, biohydrogen was produced during the process with 20% of content; this value didn't met the average value found in literature of about 35-40% (Liu et al 2006; Zhu et al 2007; Valdez-Vazquez et al 2005; Li et al 2008). This low value together with the low specific gas production of 13.8 l/kgTVS gives a specific hydrogen production (SHP) of 2.7 lH_2/kg TVS and an gas production rate (GRP) of 0.3 m^3/m^3d . A similar value (< 5 lH_2/kgTVS) was found by Kataoka et al (2005) in a bench scale test, using similar condition applied in the Run I. The SGP of anaerobic digestion process was 0.58 m^3/kgTVS, with a GPR of 6.0 m^3/m^3d and a methane content of 65%.

During Run II it was maintained the same organic loading rate of the previous Run in the first reactor (21 kgTVS/m^3d) feeding 10 kg of organic waste diluted in 20 l of tap water, but the HRT was decreased from 6.6 to 3.3 days using half of the reactor volume (100 l).

The whole period length was of 32 days, and the system reached a steady state condition after 20 days of operation.

The low yields in Run I suggested a shift from acidogenic to solventogenic reaction due to the high HRT applied, with accumulation of by-products as VFA, lactic acid and ethanol, with a consequent inhibition of hydrogen production. As mentioned in the introduction, lower HRT are suggested to avoid the shift of the system and permit to the hydrogen producing bacteria to convert the organic matter into hydrogen and acetic and butyric acids (Valdez-Vazquez et al. 2009; Shin et al 2005; Gomez et al 2006).

The pH value during this second Run dropped from 4.0 to a constant value of 3.5, that is still too low for the normal activity of the hydrogenase enzyme. Compared with the previous Run, the VFA production was reduced as due, in fact it decrease from 8,830 mgCOD/l of Run I to about 3,000 mgCOD/l in Run II (Table 4). In this condition also the ammonia value decreased to 152 mgN/l.

Compared with the Run I in methanogenic reactor the OLR was lower, caused by the lower amount of waste fed in the first reactor.

The HRT was maintained at the same value (12.6 days). Despite the low pH of first reactor

also in this case the anaerobic digestion process confirm the stability of the system. Halving the organic loading rate in the second reactor compared to the Run I, the stability parameters values decrease for about the half of previous period values. Ammonia content was about 1,079 mgN/l.; total alkalinity reach 5,324 mg$CaCO_3$/l. Only the VFA increased to 642 mgCOD/l.

Table 4 Characterization of reactors effluents and yields of the process

parameter	unit	I	II	III a	III b
Characterization of the first phase reactor					
TS	g/kg	168±15	78±5	60±5	73±1
TVS	g/kg	138±11	67±4	48±5	59±2
TVS,TS	%	82±1	86±1	81±3	80±2
COD	gCOD/kg	146±18	67±2	40±8	50±1
TKN	gN/kg	5.0±0.2	2.1±0.4	2.0±0.1	2.3±0.1
PTOT	gP/kg	0.72±0.03	0.25±0.04	2.62±0.77	4.04±0.41
PH		4.3±0.2	3.5±0.1	5.4±0.1	5.4±0.1
NH_3	mgN/l	528±50	152±14	706±169	948±145
VFA	mgCOD/l	8,330±861	2,923±550	13,877±1,673	7,053±338
Characterization of the second phase reactor					
TS	g/kg	77±4	29±4	24±1	30±3
TVS	g/kg	58±4	21±4	16±1	19±2
TVS,TS	%	75±2	69±4	66±1	64±1
COD	gCOD/kg	49±1	23±4	12±3	16±1
TKN	gN/kg	2.4±0.1	1.0±0.1	0.8±0.1	0.8±0.2
PTOT	gP/kg	0.47±0.12	0.20±0.06	0.13±0.06	0.20±0.04
PH		7.6±0.1	8.1±0.1	8,25±0,12	8,24±0,19
NH_3	mgN/l	2,016±175	1,079±57	997±188	1,470±166
VFA	mgCOD/l	211±95	642±142	90±109	604±122
ALKALINITY pH4	mg$CaCO_3$/l	10,582±842	5,324±154	5,173±674	7,100±416
ALKALINITY pH6	mg$CaCO_3$/l	5,066±489	2,737±159	3,160±374	4,024±366
First phase reactor yields					
GP	l/d	53±9	15±3	452±110	244±35
GPR	m^3/m^3d	0.27±0.03	0.16±0.03	2.26±11.81	1.22±0.17
SGP	l/kgTVS	13.8±2.4	7.4±1.8	136.8±35.3	59.9±6.7
H_2	%	19±1	34±3	37±8	34±3
SHP	l/kgTVS	2.7±0.5	2.6±0.6	51.2±11.8	20.4±3.4
Second phase reactor yields					
GP	m^3/d	2.3±0.1	1.3±0.2	1.0±0.1	1.3±0.2
GPR	m^3/m^3d	6.0±0.2	3.4±0.4	2.7±0.3	3.3±0.6
SGP	m^3/kgTVS	0.58±0.07	0.62±0.11	0.64±0.09	0.63±0.12
CH4	%	65±3	60±,1	65±2	65±2

Changing the HRT the biohydrogen yields didn't change in terms of SHP in fact same value was observed (2.6 lH_2/kgTVS), but it increase the H_2 content in the biogas, moved from 20 to 35 %. This means an overall decreased gas production in the first phase, with an SGP changed from 13.8 to 7.4 lH_2/kgTVS, and a GPR from 0.3 to 0.16 m^3/m^3d.

Fig 1

Third period was characterized by the recirculation of the liquid phase (after screw press) coming from the second phase reactor. The characteristic of this effluent allow a buffer control of first phase reactor, thanks to the alkalinity content. The recirculation ratio was set to 1, as suggested by Lee et al. (2010). The quantity of organic waste in Run III-a was 16 kg, while in Run III-b the quantity was increased to 19 kg, and in both case mixed with tap water till a total volume of 30 liters. The OLR applied during Runs III-a and III-b were 16 kgTVS/m^3d and 21 kgTVS/m^3d respectively for first phase reactor, and 4.2 and 5.6 kgTVS/m^3d for second phase reactor. The HRT were the same of previous period (3.3 d and 12.6 d). The stability parameters and macronutrient of both reactors during Run III-a and Run III-b are shown in Table 4.

In both OLR conditions the pH was kept in the optimal range for hydrogen production, that was about 5.4 (fig. 1). The pH of the second phase was about 8.2 in both periods, while the VFA content in the Run III-a was 90 mgCOD/l and in the Run III-b 604 mgCOD/l; this means a reduction of VFA of >95%.

Comparing the two loading conditions in terms of hydrogen yields, it was clear that with the lower OLR the first phase gas yields were better than the high load. Appling the OLR of 16 kgTVS/m^3d the specific gas production obtained was 136 l/kgTVS, with a H_2% of 35 and a specific hydrogen production of 51 lH_2/kgTVS. Changing the OLR to 21 kgTVS/m^3d the SGP decrease to 59.8 l/kgTVS, the H_2% was the same and the SHP decrease to 20.4 lH_2/kgTVS.

Considering the second phase reactor, the GPR, SGP and CH_4% in Run III-a were respectively 2.7 m^3/m^3d, 0.64 m^3/kgTVS and 65%. With the higher OLR (5.6 kgTVS/m^3d) the GPR, SGP and gas composition were respectively 3.3 m^3/m^3d, 0.63 m^3/kgTVS and 65% of methane. This decreased yields in biohydrogen production increasing the OLR was confirmed also by Wang et al. (2009). They study the exploitation of unsterilized food waste as a source for hydrogen and subsequent methane production, where the indigenous food waste microflora was used as inoculum. At lower OLR (15 kg VS/m^3d), acetic acid and butyric acid producing pathway were the dominant hydrogen fermentation pathway, the hydrogen yield was not significantly fluctuated. At higher OLR (37 kgTVS/m^3d), a decrease in hydrolysis rate of substrate and an increase of propionic and lactic acids were observed, which were considered as the main causes for the decrease in hydrogen yield when the system was operated at high OLR.

This behaviour was observed also in this experiment. In `Fig` fig. 2 are shown the short chain VFA concentrations during the two periods (Run III-a and Run III-b). It confirm the better conversion of VFA in acetic and butyric acids in the first period, while at higher OLR the acetic and butyric acids decreased.

Fig 2

Fig 3

This correspondence met the higher hydrogen yields with higher VFA concentration as it's shown in fig. 3, during Run III. At higher SHP values, the VFA concentration was ranging between 5 to 6 gCOD/l, with a small predominance of butyric acid.

It is not clear what is the better ratio HAc/HBu, because of the discordant values reported in literature, but this predominance of butyric acid could be associated to the combination of metabolic reaction, as shown in Eq.1:

$$4C_6H_{12}O_6 + 2H_2O \rightarrow 3CH_3CH_2CH_2COOH + 2CH_3COOH + 8CO_2 + 10H_2 \quad \textbf{Eq. 1}$$

In fig. 4 is plot the relation between the specific hydrogen production and the organic loading rate. The general trend of the experimental results shown a better performance at OLR < 18 kgTVS/m^3d, with a maximum yields at the lower loading applied.

Fig 4

The mass balance of Run III-a is reported in fig.5. The conversion of biogas on COD basis was done considering the rate COD/TVS of inlet organic waste for each Run and ranged between 1.01 and 1.16. The inlet mass content was calculated considering the characteristics of the organic waste, while the two outlet flows rate take into account were the biogas produced by both reactors, and the effluent of the anaerobic digestion reactor (second phase). Biogas is composed by methane, carbon dioxide, water vapour and traces of other gases which, however, are not considered in terms of volume. To quantify the amount of TVS removed with biogas, was considered only the "dry" part and assumed as an ideal gas made up solely of CH_4 and CO_2. The mass was calculated using the molecular weights of methane and carbon dioxide, the molar volume of an ideal gas at 1 atm and 20°C (24.056 l/mol) and the volume fraction of the components taken according to average experimental data. All the mass balance on TS-TVS and COD basis have an error lower than 10%. This minimal error could be associated to wrong sampling or analytical procedures.

Fig 5

The mass balance highlights a missing of nitrogen in the outlet flow. This could be explained by the recirculation of the sludge; it causes an increasing of ammonia concentration as shown in table 4 both in first (from 200 to 1,200 mgN/l) and second phase (from 800 to 1,600 mgN/l). To avoid this accumulation, a regression of ammonia value was made in order to quantify the velocity of ammonia increasing (fig. 6).

Fig 6

Nitrogen accumulation was 16.04 mgN/ld, so it was adopted a daily reduction of the first phase effluent, fed in the anaerobic digestion.

In terms of energy, during the first two Runs the hydrogen production was really low, for this motive the energetic considerations are based only on Run III-a yields, where the recirculation of the sludge was able to keep the pH in the right range, with a consequent significant hydrogen production.

The flow of hydrogen, carbon dioxide and methane were mixed in order to obtain the bio hythane gas, as shown in table 5.

Table 5 Biohythane gas composition (Run IIIa)

	First phase		Second phase		GP	H_2	CH_4	CO_2	GPRtot	SGPtot
	m^3H_2/d	m^3CO_2/d	m^3CH_4/d	m^3CO_2/d	m^3gas/d	%	%	%	m^3gas/m^3d	$m^3/kgVS$
average	0.17	0.28	1.33	0.72	2.51	6.7	53.2	40.1	2.61	0.78
sd	0.04	0.07	0.13	0.07	0.31	-	-	-	0.33	0.09
min	0.09	0.16	1.05	0.57	1.88	5.2	55.9	38.9	1.96	0.58
max	0.22	0.38	1.47	0.79	2.87	7.8	51.2	40.9	2.99	0.89

The biohythane gas mixture in the Run III-a met the gas composition required for an enhanced combustion. As suggested by some authors (Porpatham et al. 2007 Rakopoulos et al. 2009, Reith et al. 2003) the amount of hydrogen must be above 5% with an optimal value at 10%. Major quantity couldn't assure the best performance of engine and of emissions.
Considering the energy density and specific energy of methane and hydrogen and considering the ideal biohythane composition, was calculated and compared the energy content of biogas and bio-hythane. In terms of energy density biohythane is 5,697 vs 5,407 kcal/m^3 of biogas, while considering the amount of energy based on mass, the biohythane is 5849 instead of 4,693 kcal/kg of biogas. Furthermore it was demonstrate (Porpatham et al. 2007 Rakopoulos et al. 2009) that the use of 10% of hydrogen enhance the combustion characteristics of biogas and a drastic reduction in HC emissions was seen (HC level drops from 1,530 ppm with neat biogas to 660 ppm).

4 Conclusions

Two-phase anaerobic digestion process for biohydrogen and methane production, was optimized without chemical-heat shock treatment of inoculum or pH control. The best yield was obtained in Run III-a at lower OLR (16 kgTVS/m^3d), thanks to liquid phase recirculation from the anaerobic digestion. Was obtained an SHP of 51 lH_2/kgTVS and the 37% of H_2 content. The final gas composition met the biohythane characteristic with 6.7% H_2, 40.1% CO_2, 52.3% CH_4. and a whole system SGP of 0.78 $m^3/kgTVS_{fed}$ In next experimental test will be verified lower organic loading rate and changed the recirculation ratio in order to maximize the hydrogen yields.

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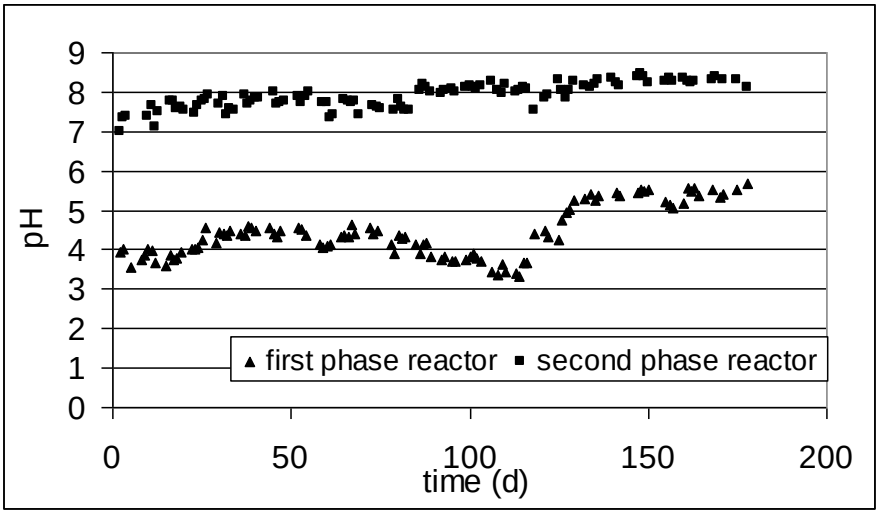
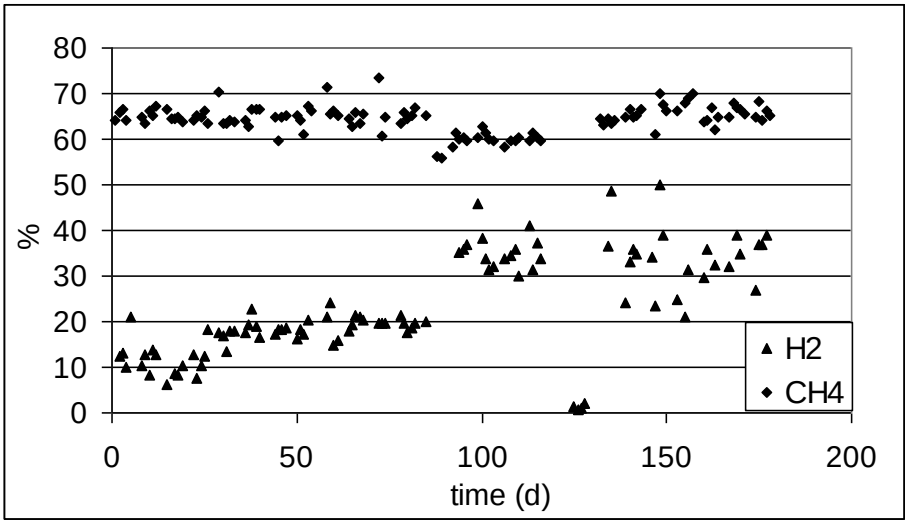


a)



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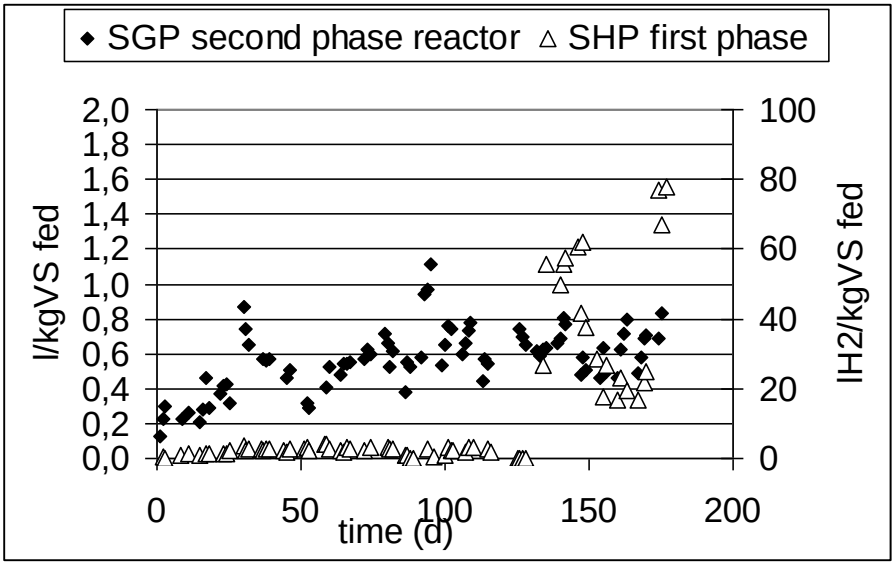

c)

Figure 1 a) pH in first and second phase reactors; b) gas composition; c) specific hydrogen production in first phase reactor and speci

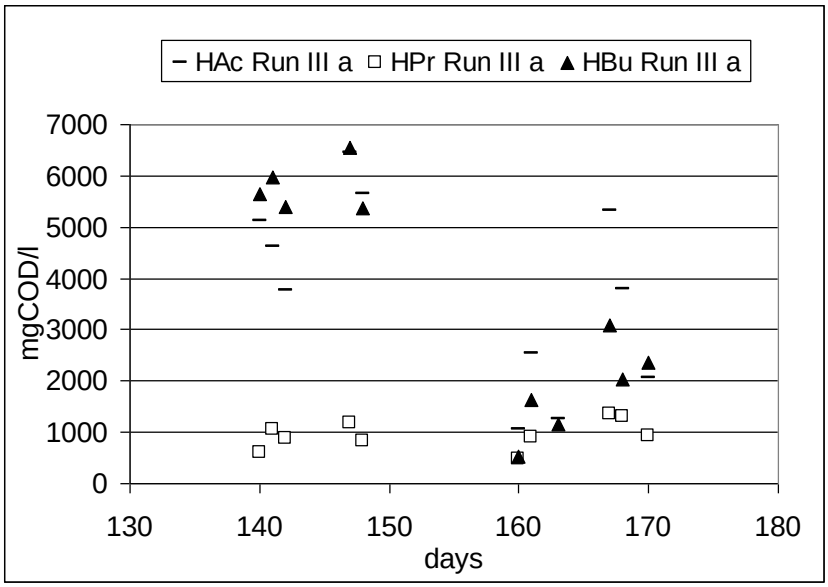

Figure 2 Short chain VFA comparison during Run III.

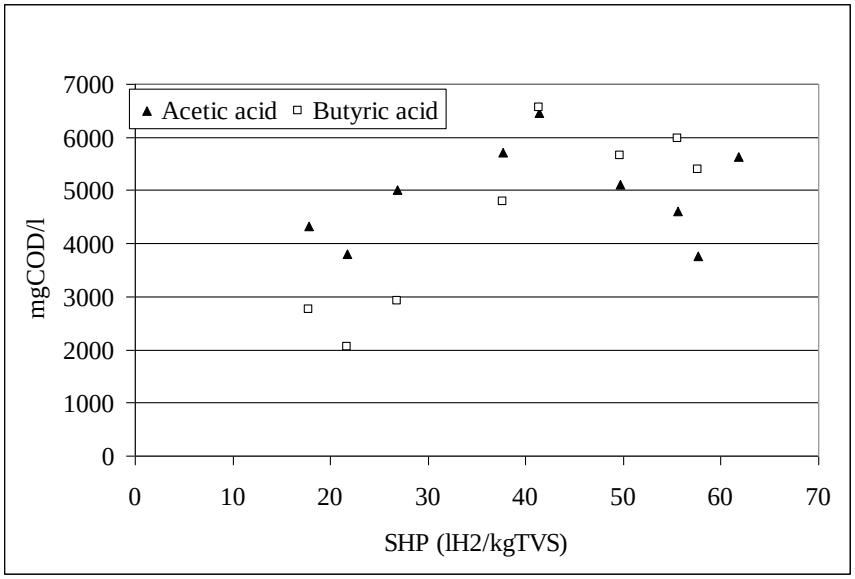

Figure 3 Relation between VFA and SHP during Run III.

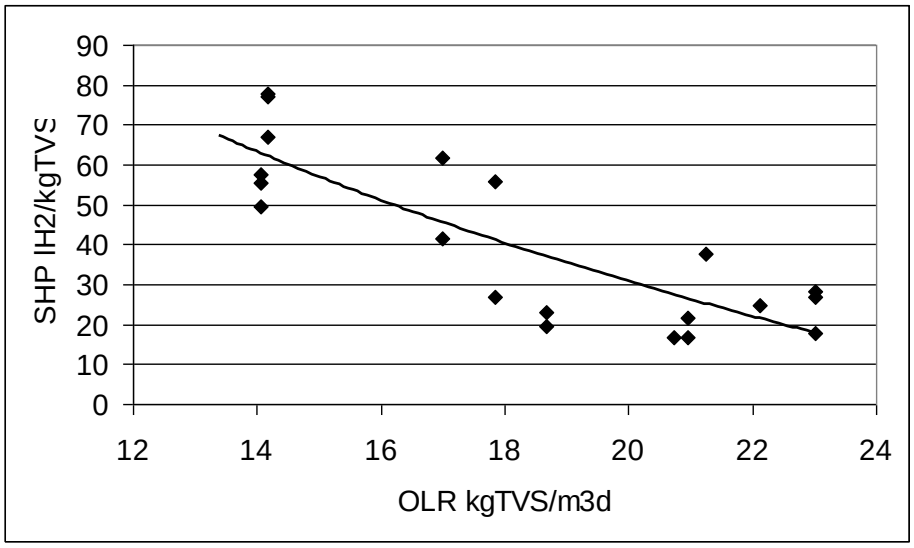

Figure 4 SHP related to the OLR.

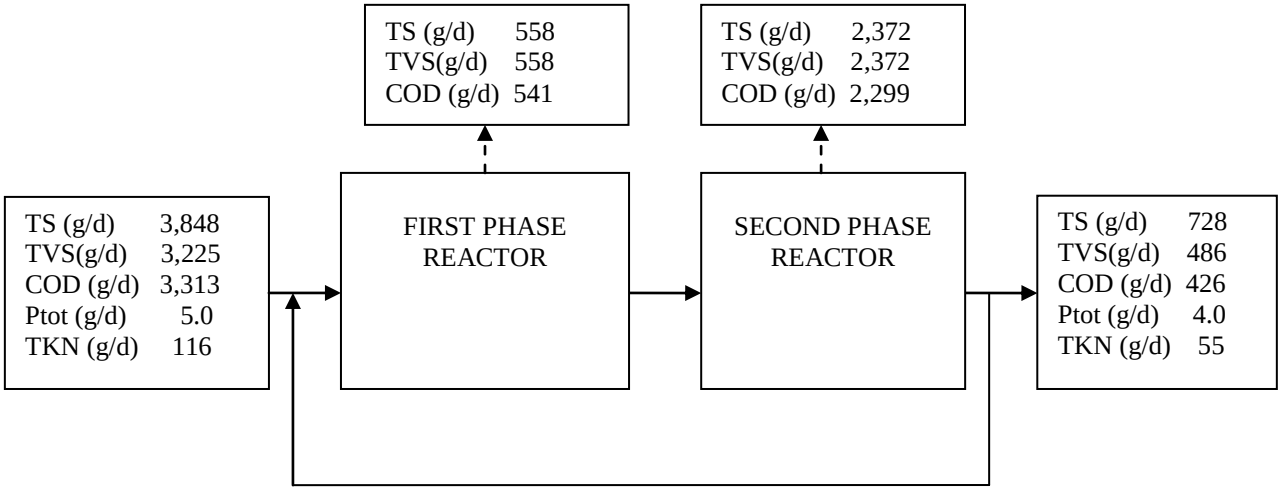

Figure 5 Mass balance of Run IIIa

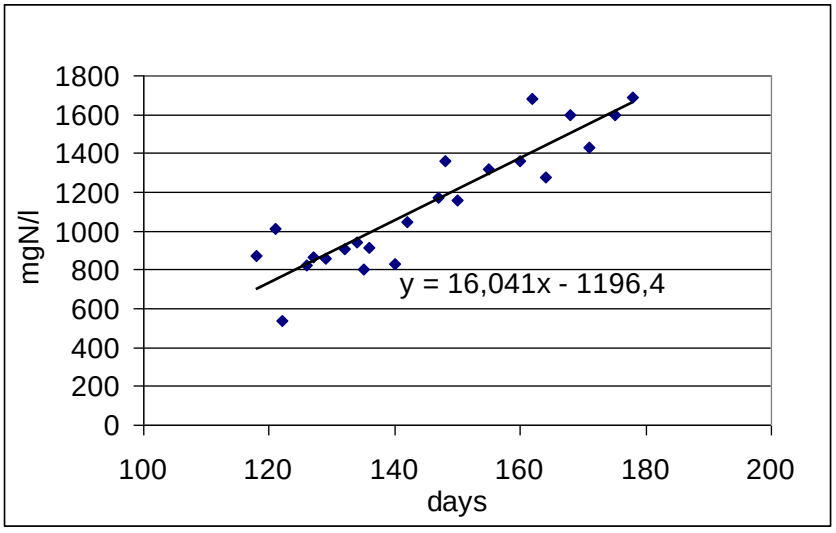

Figure 6 Ammonia accumulation velocity in second phase reactor Run III