AIDIC *Conference Series*, Vol. 9, 2009
Editor Sauro Pierucci
DOI: 10.3303/ACOS0909008

ISBN 978-88-95608-10-5 ISSN 2036-5969

BIO-HYTHANE PRODUCTION BY THERMOPHILIC TWO-PHASE ANAEROBIC DIGESTION OF ORGANIC FRACTION OF MUNICIPAL SOLID WASTE: PRELIMINARY RESULTS

Cristina Cavinato[a], David Bolzonella [b], Anna Laura Eusebi[c], Paolo Pavan[a]

[a] Department of Environmental Science, University of Venice, Dorsoduro, 2137, I-30123,Venice, Italy. cavinato@unive.it
[b] University of Verona – Department of Science, Technology and Markets of Wine, via della Piave, San Floriano, Verona-Italy.
[c]Institute of Hydraulics and Transportation Infrastructures, Marche Polytechnic University, Ancona.

The increasing interest on hythane, a highly efficient and ultra clean burning alternative fuel (a mixture of hydrogen and methane) led many researchers to attempt hydrogen production by anaerobic fermentation of biomass. Biomass with a high carbohydrate content can be converted to hydrogen and organic acids through the action of fermentative bacteria. Then, the treated organic waste can be further treated in anaerobic conditions to produce methane.
The aim of this experimental work is to evaluate the hydrogen and methane production efficiency of the organic fraction of municipal solid waste (OFMSW) treatment through the two-phases anaerobic digestion process. The work was carried out at pilot scale, using two CSTRs (200 l and 380 l of working volume respectively) both maintained at thermophilic temperature (55°C) and fed semi-continuously with organic waste diluted with tap water. The experiment was divided in four period where different organic loading rate to the first phase were tested (20, 30 and 40 kgTVS/m^{3}d).
This paper deals with the results coming from the first two experimental runs while the other two will be performed in next months. A complete set of parameter, including the gas yields, hydrogen from the fermentative reactor and methane from the anaerobic digestor, were monitored. An hydrogen rich biogas production of 7,4 and 15,9 lgas/kgTVSf was reached respectively in the first and second period, in the fermentative reactor, showing CO_2 content of 65%(period 1) and 85% (period 2). The methanogenic phase shown constant stability parameters and a specific gas production of 0,64 m^3/kgTVSf.

1. INTRODUCTION

Considering the energy production scenario of next years, three are the main points to consider to develop sustainable systems according to environmental concerns: the CO_2 emissions reduction when fossil fuels are used, the energy saving by optimisation of the actual industrial processes and the energy production from renewable sources. These three directions define the new paradigm in the energy sector. In particular, the energy production processes from renewable sources have to be deeply investigated to define their optimisation and to obtain a real alternative to traditional systems.
In this field, a specific interest is growing about the possibility to obtain H_2-enriched biogas, using a separate controlled fermentative step before methanogenesys. In fact, this two-phase approach lead to the production of bio-hythane, a mix of methane, carbon dioxide and hydrogen according to the following ranges of concentration: 50-60%, 35-45% and 5-10%.
Recently, the idea of producing hydrogen from a controlled fermentative step, which operates at low pH, short HRT and high loading rate, has gained interest among the researchers. Considering studies carried out with real substrates, Angelidaki and co-workers (Liu et al., 2006) showed that the two-phase process treating the organic

Please cite this article as: Cavinato C., Bolzonella D., Eusebi A.L. and Pavan P., (2009), Bio-hythane production by thermophilic two-phase anaerobic digestion of organic fraction of municipal solid waste: preliminary results, AIDIC Conference Series, 09, 61-66 DOI: 10.3303/ACOS0909008

fraction of municipal solid waste produced 43 mL of H_2 per gram of VS fed in the first reactor, operating with short HRT (some 2 days) and without pH control, which was stable in the range 5-5.5. Methane production was some 500 mL CH_4 in the second reactor. The process gave a 21% increase in yields compared to a single phase process. Also in this case the production of hydrogen was related to the presence of acetate and butyrate in the first reactor. In the field of two-phase anaerobic digestion processes, other studies were carried out on the treatment of wastes at different biodegradability as biowaste differently sorted (Pavan et al., 2000) or waste activated sludge (Bolzonella et al., 2007).
Starting from these previous evidences, the aim of this work is to optimize a two phase thermophilic anaerobic digestion process for bio-hythane production treating source collected organic fraction of municipal solid waste.

2. MATERIAL AND METHODS

2.1 Substrate characterization

The substrate used was the organic fraction of municipal solid waste of Treviso's municipality (north Italy). This material is suitable for anaerobic digestion process thanks to its high biomethanisation potential. 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.
TS	(g/L)	242,9	145,3	304,7	71,3
TVS	(g/L)	179,5	150,0	220,9	40,13
TVS/TS	(%TS)	73,8	61,5	88,4	10,6
TKN	(mgN/L)	5738	2178	8436	2280
Ptot	(mgP/L)	198,7	140,7	250,0	39,6
COD	(gCOD/L)	217,2	151,9	273,6	41,02

2.2 Experimental set-up

The tests were carried out using two stainless steel CSTR reactors (AISI 304). The first reactor, dedicated to the fermentative step, has 200 l of working volume, while the second reactor dedicated to the methanogenic step has 380 l of 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 methanogenic reactor was inoculated with the anaerobic digested sludge coming from the full scale digestor of Treviso WWTP and maintained at thermophilic temperature for one week. The operative conditions adopted during the tests are shown in table 2.

Table 2 Operatinal conditions of whole experimental work.

Working period:	1	2	3	4
HRT fermentative step, d	3,3	6,7	3,3	3,3
HRT methanogenic step, d	12,6	12,6	12,6	12,6
OLR fermentative step, kgTVS/m^3 d	20	20	30	40
OLR methanogenic step, kgTVS/m^3 d	5	10	15	20

The experiment was divided in four periods: during the first two periods the HRT tested was 3,3 d and 6,7 d maintaining the same OLR in the first phase (20 kgTVS/m^3 d) and changing the OLR of the second reactor from 5 to 10 kgTVS/m^3 d, while during the last two periods the OLR on the first reactor was increased to 30 and 40 kgTVS/m^3 d. The results presented were obtained from the first two working periods, the other two will be performed in next months. The increasing of HRT was tested in order to optimize the gas production coming from the first reactor.

2.3 Analytical methods

The effluent of both reactors was monitored daily in terms of solid content, chemical oxygen demand, total Kjieldhal nitrogen, total phosphorus, and, for the methanogenic phase, also the stability parameters (pH, alkalinity, ammonia and volatile fatty acid content), all in accordance with the Standard Methods (APHA-AWWA-WEF).

Volatile fatty acids (VFA) content was monitored using a gas chromatograph (Carlo Erba instruments) with hydrogen as gas carrier, equipped with a Fused Silica Capillary Column (Supelco NUKOL™, 15m x 0,53mm x 0,5 µm film thickness) and with a flame ionization detector (200°C). The temperature during the analysis starts 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) equiped with the column HP-PLOT MOLESIEVE, 30m x 0.53mm ID x 25um film, using a thermal conductivity detector and helium as gas carrier.

3. RESULTS AND DISCUSSION

After the inoculum with full scale anaerobic digestion sludge, during the first week the 2nd phase reactor was fed only with waste activated sludge. In the same week the fermentative reactor was filled with 100 l of tap water and fed once a day using diluted OFMSW, in order to obtain 3,3 days of HRT and an organic loading rate of about 20 kgTVS/m^3d. After this week the methanogenic reactor was fed daily with the fermentative reactor effluent. The system took 2 hydraulic retention times to reach a steady state condition, showing the capacity of the microorganisms to adapt to these new conditions.

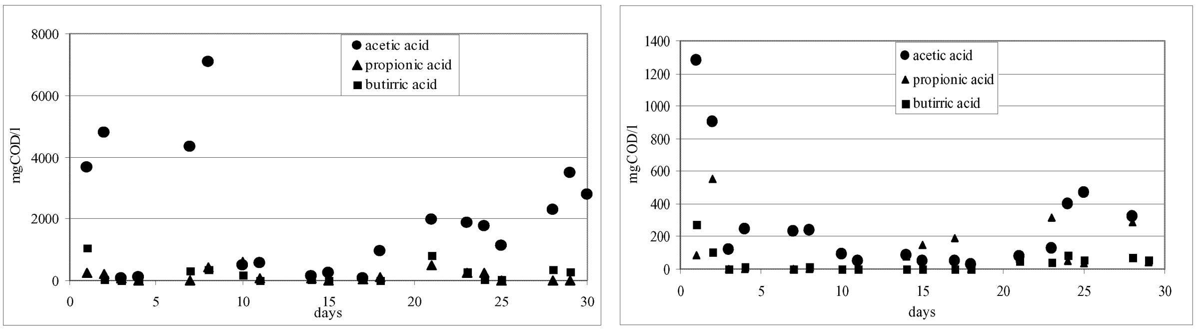

Figure 3. Evolution of VFA during the first period: fermentative a) and methanogenic b) reactor.

The VFA production trend is shown in figure 3, where the concentration of acids in the first phase shows the high activity of acid producing bacteria (more than 3000 mg/l). This high concentration of low-chain compounds

fed to methanogenic microorganisms led to a high biogas production, without any stability problem. In fact the concentration of VFA in the second reactor was less than 500 mgCOD/l when steady state conditions were reached.
Considering the other typical stability parameters, such as alkalinity, ammonia and pH, no problem in process behaviour can be observed in the 2nd phase reactor. In fact, the addition of waste during the test allowed an alkalinity improvement, as shown by the average data reported in table 3; concerning the ammonia content, that reached an average value of 1050 mgN/l (fig. 4).

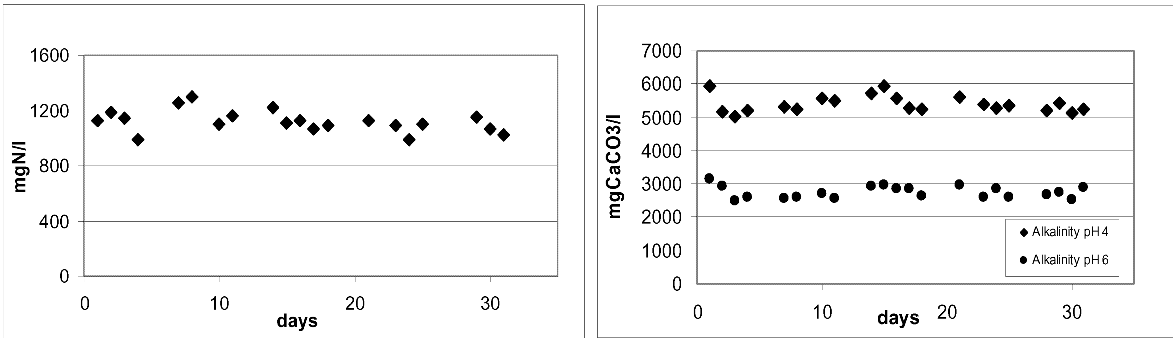

Figure 4 Evolution of ammonia and alkalinity in the anaerobic digestor during the first period.

In terms of process yields, the anaerobic digestion of treated OFMSW shows a high gas production, with an SGP of 0,64 m^3/kgTVSf, a typical value for this substrate (REF NOSTRA !!). The gas production was monitored also in the first phase in order to quantify the hydrogen production.
The SGP in this phase was 7,4 l/kgTVSf, while specific hydrogen production (SHP) was 2,6 l/kgTVSf (fig 5). This value is lower than those find in literature in similar conditions, so we considered the necessity to change the HRT in order enhance the first phase gas production.

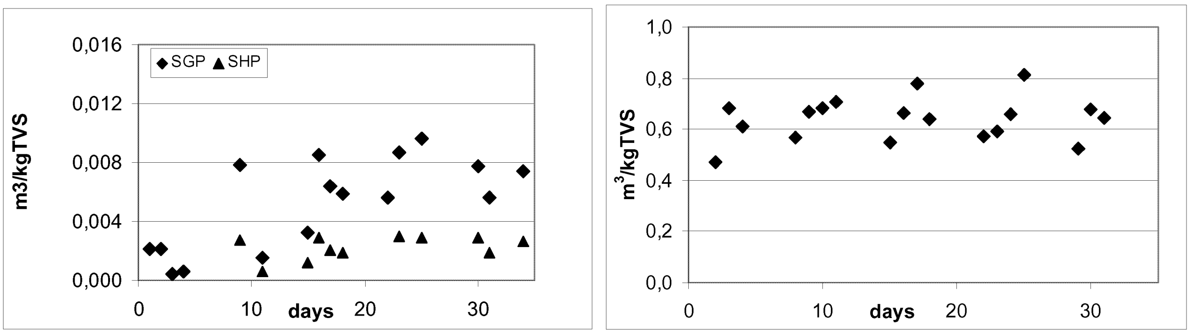

Figure 5. Specific gas production in the first and second phase during the first working period.

In this second period the system took about 3 HRTs to reach the steady state condition. The pH increased to 4,3 in spite of the large amount of acid produced (about 7500 mgCOD/l) and the ammonia concentration reached 530 mgN/l. The second reactor shown an improvement of alkalinity and ammonia that reached 10000 $mgCaCO_3$/l and about 2000 mgN/l respectively; also the VFA concentration (less than 300 mgCOD/l) showed the stability of the system (fig.6).

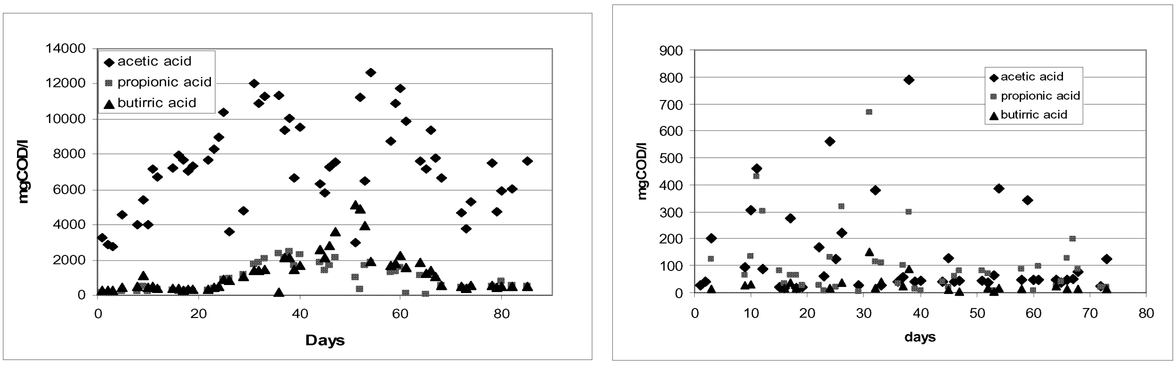

Figure 6. Evolution of VFA during the second period: fermentative a) and methanogenic b) reactor.

In terms of yield the second reactor maintain the SGP 0,63 m^3/kgTVSf but increased the GPR from 3,43 (previous period) to 7,01 $m^3/m^3_r d$. The SGP of first reactor shows a small increase of SGP that rose up to 15,9 l/kgTVSf, but the average value of SHP was 2,4 l/kgTVSf.
This value is lower than those find in literature in similar conditions (Cooney et al., 2007; Liu et al., 2006), but it has to be underlined that these are the lower loaded conditions foreseen to study in this experimental set up. Increasing OLR to 30 and 40 kgTVS/m^3 d, could improve significatively the production.
The table 3 shows all the parameters monitored during the first period.

Table 3. Characterisation of the reactors effluents and biogas yields.

	units	period 1	period 2
First phase reactor			
pH		3,51	4,32
NH_3	(mgN/L)	152	530
TKN	(mgN/L)	2009	4720
Ptot	(mgP/L)	291	758
COD	(gCOD/L)	67	158
TS	(g/L)	78	172
TVS	(g/L)	67	142
TVS	(%TS)	86	83
VFA	(mgCOD/L)	2641	7605
Second phase reactor			
pH		8,09	7,68
Alkalinity (pH6)	($mgCaCO_3$/L)	2726	4823
Alkalinity (pH4)	($mgCaCO_3$/L)	5316	10085
NH_3	(mgN/L)	1048	1955
TKN	(mgN/L)	1016	2388
Ptot	(mgP/L)	216	486
COD	(gCOD/L)	24	61
TS	(g/L)	29,3	75,6
TVS	(g/L)	21	56,8
TVS	(%TS)	71,1	75,2
VFA	(mgCOD/L)	611	223

	Yiels- first phase		
$OLR_{1° phase}$	($kgTVS/m^3d$)	21,01	20,6
$GPR_{1° phase}$	(m^3/m^3_r d)	0,15	0,32
$SGP_{1° phase}$	($l/kgTVS_f$)	7,4	15,9
SHP	($lH_2/kgTVS_f$)	2,6	2,4
CO_2	(%)	65,51	84,93
	Yiels-second phase		
$OLR\ 2_{° phase}$	($kgTVS/m^3d$)	5,36	11,25
$GPR_{2° phase}$	(m^3/m^3_r d)	3,43	7,01
$SGP_{2° phase}$	($m^3/kgTVS_f$)	0,64	0,63
CH_4	(%)	59,81	65,38
CO_2	(%)	33,71	33,85

4. CONCLUSIONS

The two phase approach confirm the possibility to use high OFMSW load condition in the first phase, without any stability problem in the second phase when high VFA content is loaded to methanogenic reactor. The biogas production was about 7,01 m^3/m^3_r d in the methanogenic reactor, reaching a SGP value of 0,63 $m^3/kgTVS_f$. During the conditions studied, the biogas production obtained in the fermentative reactor was quite low (total SGP 15,9 l/kgTVSf, hydrogen SHP 2,4 l/kgTVSf). At this stage, hydrogen production is still under expected values probably because of the drop of pH in the first reactor under values of 4,5 a condition favorable for fermentative lactic bacteria rather than hydrogen forming ones. In the next experimental trials pH in the first step will be controlled and maintained in the range > 5 so to improve the hydrogen formation.

5. REFERENCES

Bolzonella D., Zanette M., Pavan P., Cecchi F. (2007). Two-phase anaerobic digestion of waste activated sludge: effect of a extreme thermophilic (70°C) pre-fermentation step. Industrial and Engineering Chemistry Research, 46(20), 6655

Cooney M., Maynard N., Cannizzaro C., Benemann J. (2007). Two phase anaerobic digestion for production of hydrogen-methane mixture. Bioresource technology, 98, pp. 2641-2651.

Gavala HN, Skiadas LV, Ahring BK (2006). Biological hydrogen production in suspended and attached growth anaerobic reactor systems. International Journal of Hydrogen energy, 31 (9), pp. 1164-1175.

Liu DW, Zeng RJ, Angelidaki I. (2008). Effects of pH and hydraulic retention time on hydrogen production versus methanogenesis during anaerobic fermentation of organic household solid waste under extreme-thermophilic temperature (70 degrees C). Biotechnology and Bioengineering, 100 (6), pp. 1108-1114.

Liu DW, Liu DP, Zeng RJ, Angelidaki I. (2006). Hydrogen and methane production from household solid waste in the two-stage fermentation process. WATER RESEARCH 40(11), pp. 2230-2236

Pavan, P, Traverso, P.G., Battistoni, P., Cecchi, F. and Mata- Alvarez, J. (2000). Two-phase anaerobic digestion of source sorted OFMSW: performance and kinetic study. Water Science & Technology, 41, 3, 111-118.

Valdez-Vazquez I., Ríos-Leal E., Esparza-García F., Cecchi F. and Poggi-Varaldo H. M. (2005). Semi-continuous solid substrate anaerobic reactors for H2 production from organic waste: Mesophilic versus thermophilic regime. International Journal of Hydrogen energy, 30, (13-14), pp. 1383-11391.