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# Bio-hythane production by thermophilic two-phase anaerobic digestion of organic fraction of municipal solid waste. Preliminary results

Cristina Cavinato[1*], David Bolzonella [2], Anna Laura Eusebi[3], Paolo Pavan[1]
[1] Department of Environmental Science, University of Venice, Dorsoduro, 2137, I-30123,Venice, Italy. cavinato@unive.it
[2] University of Verona – Department of Science, Technology and Markets of Wine, via della Piave, San Floriano, Verona-Italy.
[3]Institute of Hydraulics and Transportation Infrastructures, Marche Polytechnic University, Ancona.

The increasing interest on hythane, a highly efficent and ultra clean burning alternative fuel (a mixture of hydrogen and methane) led many researchers to attempt hydrogen production by anaerobic digestion of biomass. The wet biomass with high carbohydrate content can be converted to hydrogen and organic acids through the action of fermentative bacteria. The aim of this experimental work is to evaluate the hydrogen and methane production efficency 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 (100 l and 380 l of working volume respectively) both maintained at thermophilic temperature (55°C) and fed semicontinuosly with organic waste mixed with tap water. The short HRT applied to the acidogenic phase (3 days) and the high temperature, facilitate the solubilisation of waste and the acidification of medium (pH lower than 4), conditions that aid hydrogen formation. The experiment was divided in three period where different organic loading rate to the first phase were tested (18, 36 and 54 kgTVS/m$^3$d). This paper consider the results coming from the first period, 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 0,06 m$^3$gas/kgTVSf was reached in the fermentative reactor, showing a 65 % $CO_2$ content. The methanogenic phase shown constant stability parameters (pH value 8, VFA 255 mgCOD/l, ammonia 1150 mgN/l) and a specific gas production of 0,73 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

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actual industrial processes and energy production from renewable sources. These three directions must to be followed together and at the same time to reach a synergistic effect. In particular, the energy production processes from renewable sources, both considering dry and wet substrates, have to be deeply investigated about their optimisation 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 with real substrates, Angelidaki and co-workers (Liu et al., 2006) showed that the two-phase process treating the organic 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. On the other hand, $CH_4$ 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 optimise 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 characterisation

The substrate used was the organic fraction of municipal solid waste, obtained by mechanical selection of source collected waste of Treviso's municipality (north Italy). This material is suitable for anaerobic digestion process thanks to its high biomethanisation potential. Table 2.1 shows the main characteristics of this substrate.

*Table 2.1 Characterisation of the organic fraction of municipal solid waste.*

| | units | average | min | max | S.d. |
|---|---|---|---|---|---|
| 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 |
| TS | (g/L) | 242,9 | 145,3 | 304,7 | 71,3 |
| TVS | (g/L) | 179,5 | 150,0 | 220,9 | 40,13 |
| TVS | (%TS) | 73,8 | 61,5 | 88,4 | 10,6 |

**2.2 Experimental set-up**
The test were carried out using two stainless steel CSTR reactors (AISI 304). The first reactor, dedicated to the fermentative step, has 100 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 an 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 2.2.

*Table 2.2 Operative conditions of whole experimental work.*

| Working period: | 1 | 2 | 3 |
|---|---|---|---|
| HRT fermentative step, d | 3,3 | 3,3 | 3,3 |
| HRT methanogenic step, d | 12,6 | 12,6 | 12,6 |
| OLR fermentative step, kgTVS/$m^3$ d | 18 | 36 | 54 |
| OLR methanogenic step, kgTVS/$m^3$ d | 5 | 10 | 15 |

During the whole experimental work the flow rate will be maintained constant (30 l/d) in order to maintain the same HRT in the three periods; the organic loading rate will be increased changing the substrate dilution in the digester feeding.

**2.3 Analytical methods**
The effluent of both reactors was monitored daily in terms of solid content, chemical oxigen demand, total Kjiendhal nitrogen, total phosphorus, and, for the methanogenic phase, also the stability parameters (pH, alkalinity, ammonia and volatil fatty acid content), 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 ionisation detector (200°C). The temperature during the analysis started from 80°C and reach 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 2$^{nd}$ 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 18 kgTVS/$m^3$d. 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.

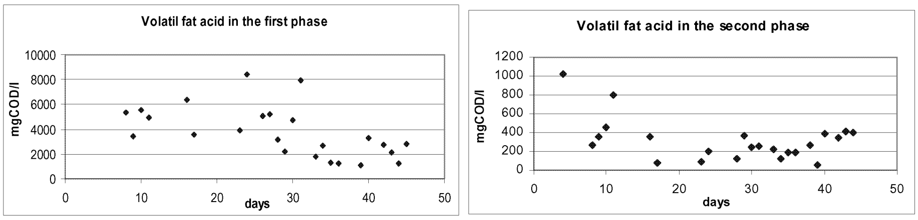


*Figure 3.1 Evolution of VFA during the first period: fermentative a) and methanogenic b) reactor.*

The VFA production trend is shown in figure 3.1 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 an 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 3.1; concerning the ammonia content, it increase constantly, starting from 600 mgN/l and reaching an average value of 1100 mgN/l (fig. 3.2).

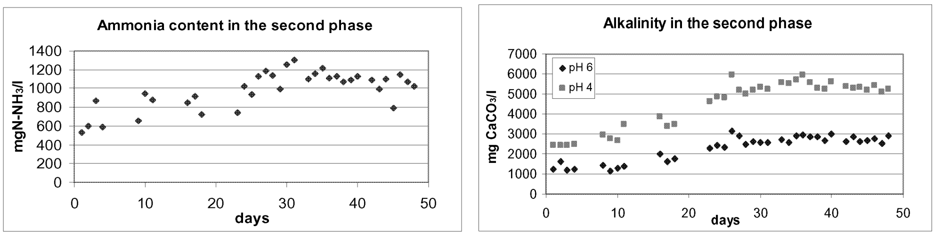


*Figure 3.2 Evolution of ammonia and alkalinity during the first period.*

The table 3.1 shows all the parameters monitored during the first period. In terms of process yields, the anaerobic digestion of treated OFMSW shows an high gas production, with an SGP of 0,73 $m^3$/kgTVSf, a typical value for this substrate. The gas production was monitored also in the first phase in order to quantify the hydrogen production. The SGP in this phase was 0,06 $m^3$/kgTVSf, while specific hydrogen production (SHP) was 0,021 $m^3$/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 36 and 54 kgTVS/$m^3$ d, could improve significatively the production. Furthermore, the low ammonia content (168 mg/l) observed in these conditions suggests that only a light degradation of proteins fraction was achieved. An increase of 1st phase HRT could be considered in order to obtain and higher grade of substrate degradation also in this step, increasing the specific biogas production (SHP).

*Table 3.1 Influent and effluent characterization and process yields.*

| | units | average | min | max | S.d. |
|---|---|---|---|---|---|
| | | ***Digesters feed*** | | | |
| pH | | 4,91 | 4,65 | 5,09 | 0,14 |
| $NH_3$ | (mgN/L) | 33,5 | 32,1 | 34,5 | 0,89 |
| TKN | (mgN/L) | 1921,1 | 726,12 | 2212,2 | 608,3 |
| Ptot | (mgP/L) | 207,7 | 120,3 | 302,7 | 68,3 |
| COD | (gCOD/L) | 74,02 | 50,65 | 91,19 | 13,61 |
| TS | (g/L) | 82,05 | 48,42 | 101,58 | 18,73 |
| TVS | (g/L) | 64,15 | 42,79 | 78,49 | 12,11 |
| TVS | (%TS) | 79,71 | 61,47 | 88,37 | 10,06 |
| | | ***First phase reactor*** | | | |
| pH | | 3,71 | 3,32 | 4,17 | 0,23 |
| $NH_3$ | (mgN/L) | 167,86 | 110,00 | 250,00 | 32,50 |
| TKN | (mgN/L) | 1691,53 | 1405,58 | 2146,81 | 259,15 |
| Ptot | (mgP/L) | 255,44 | 183,76 | 419,20 | 76,17 |
| COD | (gCOD/L) | 72,69 | 64,67 | 85,86 | 5,64 |
| TS | (g/L) | 76,72 | 70,83 | 88,42 | 4,79 |
| TVS | (g/L) | 65,50 | 60,42 | 72,83 | 4,02 |
| TVS | (%TS) | 85,37 | 78,57 | 88,06 | 2,43 |
| VFA | (mgCOD/L) | 3483 | 1068 | 7926 | 1996 |
| | | ***Second phase reactor*** | | | |
| pH | | 8,08 | 7,94 | 8,26 | 0,08 |
| Alkalinity (pH6) | ($mgCaCO_3/L$) | 2746 | 2490 | 3136 | 179,95 |
| Alkalinity (pH4) | ($mgCaCO_3/L$) | 5395 | 5017 | 5938 | 250 |
| $NH_3$ | (mgN/L) | 1106,19 | 790,00 | 1300,00 | 106,42 |
| TKN | (mgN/L) | 901,18 | 726,79 | 1172,09 | 148,79 |
| Ptot | (mgP/L) | 207,18 | 140,70 | 250,02 | 38,29 |
| COD | (gCOD/L) | 22,47 | 11,76 | 26,62 | 4,46 |
| TS | (g/L) | 27,18 | 18,81 | 34,66 | 4,54 |
| TVS | (g/L) | 19,56 | 11,58 | 25,67 | 4,12 |
| TVS | (%TS) | 71,96 | 61,54 | 77,78 | 5,09 |
| VFA | (mgCOD/L) | 255,7 | 54,1 | 412,0 | 113,1 |
| | | ***Yiels- first phase*** | | | |
| $GPR_{1° phase}$ | ($m^3/m^3_r$ d) | 1,10 | 1,00 | 1,31 | 0,10 |
| $SGP_{1° phase}$ | ($m^3/kgTVS_f$) | 0,06 | 0,001 | 0,014 | 0,004 |
| SHP | ($m^3H2/kgTVS_f$) | 0,021 | 0,028 | 0,016 | 0,003 |
| $CO_2$ | (%) | 64,54 | 54,20 | 70,12 | 3,64 |

| | | | | | |
|---|---|---|---|---|---|
| | | ***Yiels-second phase*** | | | |
| GPR $_{2° phase}$ | ($m^3/m^3_r$ d) | 3,48 | 2,63 | 5,35 | 0,69 |
| SGP $_{2° phase}$ | ($m^3$/kgTVS$_f$) | 0,73 | 0,43 | 1,08 | 0,18 |
| $CH_4$ | (%) | 65,78 | 61,10 | 67,3 | 1,62 |
| $CO_2$ | (%) | 33,72 | 31,61 | 35,72 | 1,08 |

## 4. Conclusions

The two phase approach confirm the possibility to use high OFMSW load condition in 1st phase, without any stability problem in 2nd phase when high VFA content is loaded to methanogenic reactor. The biogas production was about 3,48 $m^3/m^3_r$ d in the methanogenic reactor, reaching a SGP value of 0,73 $m^3$/kgTVS$_f$. During the conditions studied, the biogas production obtained in the fermentative reactor was quite low (total SGP 0,06 $m^3$/kgTVSf, hydrogen SGP 0,02 $m^3$/kgTVSf), even if comparable with the values founded in literature. The low substrate degradation, also detectable considering ammonia/TKN ratio in 1st phase effluent, can be linked to the low HRT used. Higher HRT and higher OLR could be suggested to improve the process performances. Future work will be dedicated to deep investigate these aspects.

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