Biohythane production from the organic fraction of municipal solid waste: improving existing anaerobic digestion plants

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Abstract: Anaerobic digestion of biowaste is a widespread technology in Europe either in its classical conception or in a co-digestion approach. In order to improve this process, we studied a two-phase thermophilic process for the production of biogas enriched in hydrogen, the so called bio-hythane, from biowaste. The study, carried out at pilot scale using two thermophilic (55°C) stirred reactors of 0.20 m^3 and 0.76 m^3 working volume, respectively, demonstrated the feasibility of the process. Nor physical neither chemical pre-treatments were used to treat the inoculum or the substrates to optimize the process, but only a partial recycle of digested sludge from the second to the first reactor to maintain pH at an optimal level. The experiment was divided in three runs where the OLR was changed (16, 21, 14 $kgTVS/m^3d$), maintaining the HRT (3d and 12d for the first and second reactor, respectively). The higher specific yields in terms of hydrogen (SHP) and bio-hythane were 74 $l/kgTVS_{fed}$ (40 % of H_2 in first phase biogas) and up to 0.98 $m^3/kgTVS_{fed}$ (SGP) respectively. Finally, considering the results obtained, a full-scale implementation for a 2,000 m^3 mesophilic reactor co-digesting biowaste and waste activated sludge was analysed: preliminary results demonstrate both the technological and economic feasibility of the proposed approach.

Keywords: hydrogen; dark fermentation; anaerobic digestion; biohythane; organic waste; thermophilic range.

Introduction

Anaerobic digestion (AD) is a widespread technology for organic waste treatment and biogas production. At present, some 2.3 million tonnes of biowaste are treated via AD in Europe, but treatment capacity is expected to increase to 6 million tons in the next few years because of economy subsistence of and favourable taxation for renewable energy production (de Baere et al., 2010). An interesting option for this process is the co-digestion of biowaste together with excess sludge in wastewater treatment plants (WWTPs) (Cecchi et al., 1994, Pavan et al., 2000, Bolzonella et al., 2006): in this process wastewaters and biowaste produced in a given area are co-treated in the same treatment facility with considerable economic and environmental advantages. Basically, separately collected biowaste and sewage sludge are co-treated in a typical mesophilc anaerobic reactor producing interesting amounts of biogas and organic material suitable for agronomic uses, while reject water from anaerobic sludge dewatering is treated in the same WWTP.

A further improvement of this approach, or AD of biowaste in general, consists in the application of a two phase thermophilic AD process for the co-production of hydrogen from the first-phase anaerobic reactor and methane from the second-phase reactor. The produced mixture of gas is called bio-hythane. It was demonstrated that using this enriched biogas engine performance could be improved taking into account the complementarity of hydrogen and methane. Porpatham et al (2007) and Rakaopoulos et al (2009) demonstrated that the addiction to biogas of a hydrogen percentage between 5 and 10, improves the combustion performance with a reduction of NOx and hydrocarbons emission.

In order to verify the possibility to implement this approach in a full scale mesophilic AD reactor for the co-treatment of separately collected biowaste and wastewater sludge, we carried out a pilot scale study dealing with the two-phase thermophilic AD of biowaste for bio-hythane generation. The main findings of the study and a preliminary economic feasibility are discussed in the paper.

Material and methods

Pilot scale two phase anaerobic digestion process

Considering the short HRT typical of fermentation phase and the high values of kinetic constants, the inoculum was fed only in the anaerobic reactor, while the first reactor was fed directly with biowaste mixed with water. The seed sludge used 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, and heated at 55°C for one week before feeding. The characteristics of inoculum and substrate in terms of total solids, volatile solids, macro pollutants, pH and alkalinity are shown in Table 1.

Table 1: 2nd phase inoculum and substrate characteristics

parameter	unit	AV	min	max	SD
		Inoculum			
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	mgCaCO$_3$/l	2,074	2,060	2,087	111
		OFMSW			
TS	g/kg	267.1	205.0	303.9	31.6
TVS	g/kg	213.6	175.8	232.8	18.8
TVS,TS	%	80.3	73.8	85.7	4.3
COD	gCOD/l	207.1	174.7	255.3	27.5
TKN	gN/l	7.3	5.9	8.7	1.0
Ptot	gPtot/l	0.32	0.24	0.39	0.06

The feedstock of bio-hydrogen reactor was prepared without any physical or chemical pretreatment, avoiding additional costs for hydrogen producing bacteria selection. In order to avoid problems of pipe clogging, the substrate was previously reduced using a grinder. 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 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 25um film, using a thermal conductivity detector and argon as gas carrier. The reactors used were two stainless steel CSTR reactors (AISI 304). The first reactor had a 200 l working volume and was dedicated to the fermentative step, while the second reactor had a 760 l working volume and was dedicated to the methanogenic phase. Both the reactors were maintained at 55°C and the feeding system was semi-continuous (once per day). The experimental test was divided in three periods (runs) where the OLR was increased and 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 2 shows the operative conditions applied to the reactors during the experimentation.

Table 2: operative conditions applied during the experimental test

	Run I	Run II	Run III
HRT 1phase (d)	3.3	3.3	3.3
HRT 2 phase (d)	12.6	12.6	12.6

OLR 1 phase (kgVS/m^3d)	16	21	14
OLR 2 phase (kgVS/m^3d)	4.2	5.6	3.7

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.

Treviso full scale plant

The biowaste/wastewater treatment plant of Treviso Municipality has been working since 1999. It was planned with a streamline for water treatment (50,000 PE) for C, N and P removal via BNR (Johannesbourg scheme), with the possibility to expand the plant capacity up to 70,000 PE, and streamline for sludge treatment covering the whole plant's capacity, with anaerobic co-digestion treatment of sludge and OFMSW (2,200 m^3 working volume). The OFMSW come from the municipal separate collection, and it was mechanically sorted (iron and ferrous materials were removed and screened) and shredded using a blade hammer, 15 mm cut size. The biomass was then sent to a wet mixer/separator where the TS content was lowered to 7-8 % using the sludge coming from the WWTP, and the floating residual materials and bottom residues are withdrawn.

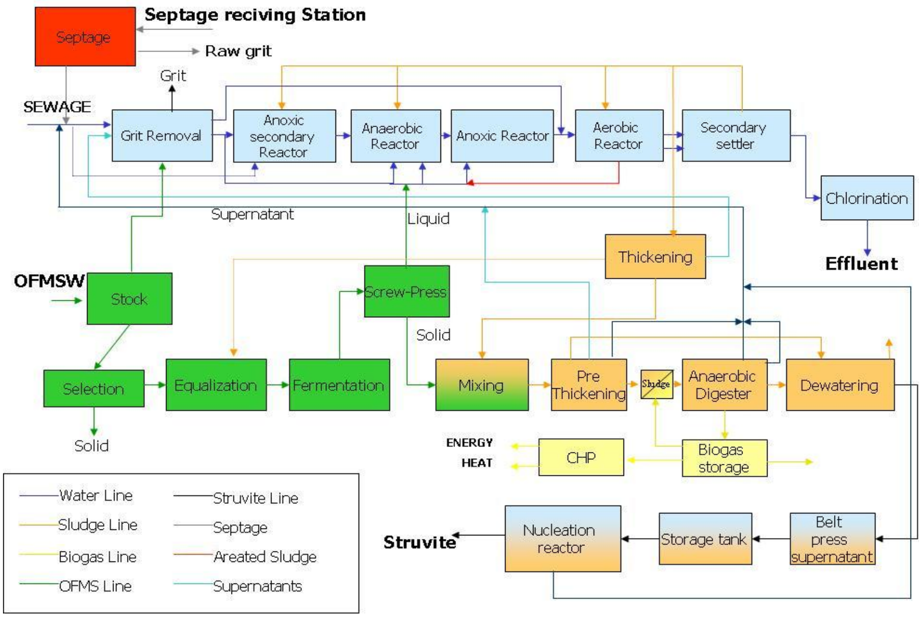

Figure 1: Treviso wastewater treatment plant flow scheme

Then, the mixture is sent to the digester by a shredding pump, together with the rest of the sewage sludge, fed daily on a continuous basis. The digester was a CSTR type, insulated concrete walls, provided with a 190 kWe cogeneration unit for the use of produced biogas.

Results and discussion

Pilot scale: process evaluation and biohythane production

The recirculation of the supernatant water was set with a ratio of 1 to the feed flow rate. Thus, the process was studied considering a light phase separation after the digester, using the liquid supernatant to dilute the feed flow rate to the fermentation unit. In this way, an effective control of alkalinity through ammonia concentration was done. The OLRs applied to the first phase reactor during Runs I and II were 16 kgTVS/m^{3}d and 21 kgTVS/m^{3}d respectively, while the HRT was maintained at 3.3 days. The OLRs applied to the anaerobic digestion reactor were 4.2 and 5.6 kgTVS/m^{3}d, while the hydraulic retention time was set at 12.6 days. In Table 3 are shown the stability parameters and macronutrient of both reactors during first two runs (data reported are the average values of a SSC reached after 1 complete HRT of the reactor). The pH of both runs in the first phase was kept in the optimal range for hydrogen production that was about 5.4. The higher hydrogen production obtained at the lower OLR was in contrast with some literature data that shown an increased hydrogen production at higher organic loading rate.

Table 3 Characterization of reactors effluents and yields of the process

Parameter	Unit	I	II
Characterization of the first phase reactor			
TS	g/kg	60±5	73±1
TVS	g/kg	48±5	59±2
TVS,TS	%	81±3	80±2
COD	gCOD/kg	40±8	50±1
TKN	gN/kg	2.0±0.1	2.3±0.1
PTOT	gP/kg	2.62±0.77	4.04±0.41
pH		5.4±0.1	5.4±0.1
NH_3	mgN/l	706±169	948±145
VFA	mgCOD/l	13,877±1,673	7,053±338
Characterization of the second phase reactor			
TS	g/kg	24±1	30±3
TVS	g/kg	16±1	19±2
TVS,TS	%	66±1	64±1
COD	gCOD/kg	12±3	16±1
TKN	gN/kg	0.8±0.1	0.8±0.2
PTOT	gP/kg	0.13±0.06	0.20±0.04
PH		8,25±0,12	8,24±0,19
NH_3	mgN/l	997±188	1,470±166
VFA	mgCOD/l	90±109	604±122
ALKALINITY pH4	$gCaCO_3/l$	5,173±0,674	7,100±0,416

ALKALINITY pH6	gCaCO$_3$/l	3,160±0,374	4,024±0,366
	First phase reactor yields		
GP	l/d	452±110	244±35
GPR	m^3/m^{3}d	2.26±11.81	1.22±0.17
SGP	l/kgTVS	136.8±35.3	59.9±6.7
H$_2$	%	37±8	34±3
SHP	l/kgTVS	51.2±11.8	20.4±3.4
	Second phase reactor yields		
GP	m^3/d	1.0±0.1	1.3±0.2
GPR	m^3/m^{3}d	2.7±0.3	3.3±0.6
SGP	m^3/kgTVS	0.64±0.09	0.63±0.12
CH4	%	65±2	65±2

Appling the OLR of 16 kgTVS/m^{3}d the specific gas production obtained was 136 l/kgTVS, with a H$_2$ percentage of 35 and a specific hydrogen production of 51 lH$_2$/kgTVS. Changing the OLR to 21 kgTVS/m^{3}d 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 I were respectively 2.7 m^3/m^{3}d, 0.64 m^3/kgTVS and 65%. With the higher OLR (5.6 kgTVS/m^{3}d) the GPR, SGP and gas composition were respectively 3.3 m^3/m^{3}d, 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). The last test at 14 kgTVS/m^{3}d is running now; considering the first yields results it is possible to confirm that decreasing the OLR >16 kgTVS/m^3 d the hydrogen production increase. In fact, at this moment, the total gas production is 221 l/kgTVS, with a H$_2$ % of 35 and a specific hydrogen production of 73.8 lH$_2$/kgTVS$_{fed}$.

Table 4: bio hythane mixture obtained

	m^{3}H$_2$/d DF	m^{3}CO$_2$/d DF	m^{3}CH$_4$/d DA	m^{3}CO$_2$/d DA	m^{3}gas/d	%H$_2$	%CH$_4$	%CO$_2$	GPR [m^{3}gas/m^{3}d]	SGP [lgas/kgVS]
RUN I										
Average	0,168	0,285	1,337	0,722	2,512	6,7	53,2	40,1	2,6	779
S.d.	0,041	0,070	0,134	0,072	0,317	-	-	-	0,3	98
Min	0,097	0,165	1,053	0,569	1,884	5,2	55,9	38,9	2,0	584
Max	0,225	0,381	1,471	0,795	2,872	7,8	51,2	40,9	3.0	890
RUN II										
Average	0,083	0,161	1,665	0,882	2,791	3,0	59,7	37,4	2,9	661
S.d.	0,012	0,023	0,286	0,151	0,472	-	-	-	0,5	111
Min	0,075	0,145	1,257	0,665	2,142	3,5	58,7	37,8	2,2	507

Max	0,107	0,207	2,053	1,087	3,454	3,1	59,4	37,5	3,598	818
RUN III										
Average	0,220	0,408	1,411	0,740	2,779	7,9	50,8	41,3	2,9	980
S.d.	0,055	0,103	0,185	0,097	0,439	-	-	-	0,5	154
Min	0,179	0,333	1,280	0,672	2,464	7,3	51,9	40,8	2,6	869
Max	0,283	0,525	1,541	0,809	3,158	9,0	48,8	42,2	3,3	1113

In terms of energy, it was evaluated and compared the final production and composition in terms of bio-hythane mixture. As shown in Table 4, Runs I and III met the bio-hythane gas composition required for an enhanced combustion. In Run III the total specific gas production was 0,98 $m^3/kgTVS_{fed}$. 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%, where an enhanced combustion characteristic of biogas and a drastic reduction in HC emissions were seen (HC level drops from 1,530 ppm with neat biogas to 660 ppm).

Full scale plant: implementation approach

The full-scale plant of Treviso could be an example of an easy way of implementation for a two phase (dark fermentation and anaerobic digestion) process. Actually, the plant is authorised for the treatment of 6000 t/y of OFMSW, with the characteristics reported in table 5. Using the data obtained during the research, it is simple to make a simulation of the benefits coming from the application of this technique to the existing plant. A synthesis of the data used for the simulation and the results obtained are reported in Table 5.

Table 5. Data used and results obtained for the simulation of the process applied to the full scale plant of Treviso

Parameter	Units	Value
OFMSW flowate	t/d	20
Refuses from sorting line	t/d	5
TS influent	t/d	4
TVS influent	t/d	3
Overall SGP	$m^3/kgTVS$	0.98
overall biogas production	m^3/d	3147
hydrogen production	m^3/d	249
overall energy produced	kWh/d	8341

(*) in this simulation, for simplicity, no benefits coming from sewage sludge digestion are considered, and also the further energy recovery from the surplus of heat coming from CHP is added

These data can be easily compared with the benefits coming from a traditional mesophilic codigestion in the same plant, in which a maximum of 5,300 kWh/d can be produced, showing an increase of 57 % in terms of electrical energy output can be reached. Another consideration has to be considered in terms of the economics of this approach. A quick evaluation of the NPV can be done considering the benefits in terms of energy reached and the additional plant cost needed for the process. The equation and data inputs used for NPV are as follows:

Actualisation index: i = 5,3% - 1,8% = 3,5% (bank index – inflation index)

For a generic year n, the NPV is given by:

$$N.P.V._n = -Co + (bn - cn)\frac{(1{,}035)^n - 1}{(1{,}035)^n * 0{,}0035}$$

where bn and cn are the sums of benefits and management costs on an annual basis, Co the investment costs. In this case the only benefit considered is the price of green certificates in Italy, which actually can be considered some 190 euros/MWh globally, evaluated on the basis of the surplus energy produced (3000 kWh/d). About the investment cost, an overall price of some 250.000 is considered, as sum of the tank, mixing, piping for heating, pumps and some accessory equipment. Management costs are prudentially considered at 3% of the total investment cost. Figure 2 reports the results of the NPV analysis.

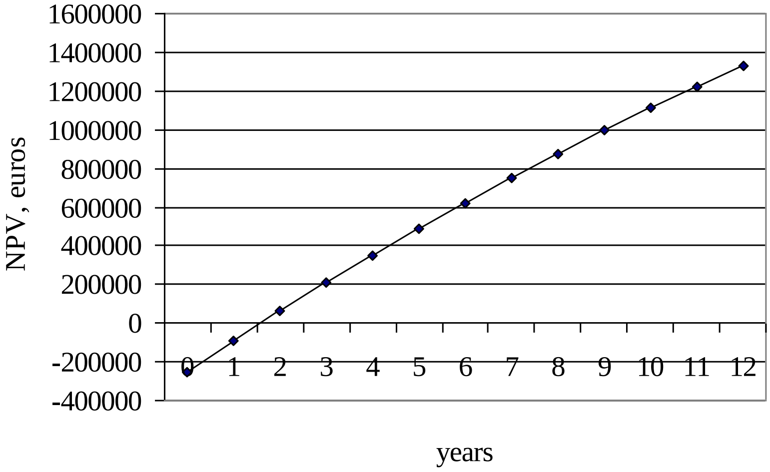

Figure 2. NPV of the approach proposed.

As can be seen, the investment costs are completely recovered within the second year of activity, while at the end of the 12th years some 1.3 million of euro of net income can be achieved by this approach. Other benefits came from the increase of heat recovery and also from the reduction of final mass after digestion, but they are prudentially not considered here.

Another way to use this process can be given by pushing on pure hydrogen recovery. The application of membrane technology on gas separation (Beggella et al. 2010) could assure a constant hydrogen flow rate despite the heterogeneity of inlet organic waste. Considering the energy density and specific energy of methane and hydrogen and considering the biohythane composition, the energy content of biogas and bio-hythane was calculated and compared. As shown in Table 6, in terms of energy density biohythane is 5697 vs 5407 kcal/m^3 of biogas, while considering the amount of energy based on mass, the biohythane is 5849 instead of 4693 kcal/kg of biogas.

Table 6 energetic comparison

	specific energy		energy density	
	Mj/kg	kcal/kg	Mj/m^3	kcal/m^3
Hydrogen	143,0	34210	10,8	2581
Methane	55,6	13301	37,8	9043
Natural gas	53,6	12823	36,4	8708

Hythane	50,2	12017	34,6	8284
Bio-Hythane	24,5	5849	23,8	5697
Biogas	19,6	4694	22,6	5407

Conclusion

The optimisation of two-phase thermophilic anaerobic digestion process for hydrogen and methane production was investigated. Dark fermentation in the first reactor was optimised without any reagent addiction for pH control and without any previous treatment of inoculum. Recirculation of rejected wastewater after anaerobic digestion from the second was sufficient to keep the process at ideal condition for hydrogen production (pH around 5.5). The highest yield in terms of H_2 production was obtained at the lower loading condition, with a maximum specific hydrogen production of 73.8 $lH_2/kgTVS_{fed}$ for an applied OLR of 14 $kgTVS/m^3$ per day On the other hand, the second reactor maintained its typical yield of some 0.7 X m^3/ kgTVS $_{fed}$. The full-scale feasibility for this process implementation was also analysed. The preliminary results show an interesting increase in the electrical energy output of 57% compared with the mesophilic anaerobic digestion. As a consequence, a complete recovery of the investment costs is obtained after 2 years of operation.

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