

Hydrogen and Methane Production from Biowaste and Sewage Sludge by Two Phases Anaerobic Codigestion

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The two phases anaerobic codigestion of biowaste and sewage sludge is the key to implementing the integrated treatment approach of municipal wastewater and organic fraction of municipal solid waste. In addition to increasing the production of biogas, the joint treatment of biowaste and wastewater allows to obtain readily biodegradable carbon source, an additive promoter of the denitrification stages and biological phosphorous removal. In order to develop a two-phase anaerobic codigestion process optimized for hydrogen and methane production, implementable in a wastewater treatment plant (WWTP), in the present study a pilot-scale experimental apparatus was used to verify the feasibility and performance of the process. The addition of small amounts (5 – 10 %) of H₂ to rich CH₄ biogas improves the quality of gas combustion while reducing CO₂ emissions. The experimental test was carried out at pilot scale using two stirred reactors both maintained at thermophilic temperature and semi-continuously fed. No chemicals neither recirculation were used to control the pH in first phase. The study lasted 50 days in which there were no evidences of any instability in the process. It was confirmed the possibility to obtain a stable hydrogen production with a specific hydrogen production of 40 L per kgTVS fed and a specific methane production in the second phase of 320 L per kgTVS fed. The biogas produced has a composition characterized by a stable presence of hydrogen over 5 %.

1. Introduction

Codigestion is the simultaneous anaerobic decomposition of mixture of two or more organic substrates (Sosnowsky et al., 2008). Several studies showed benefits of the codigestion, e.g. dilution of potential toxic compounds, improved balance of nutrients, synergistic effects of microorganisms, increased load of biodegradable organic matter and better biogas yield. Today, the anaerobic co-digestion of sewage and organic waste is a standard practice in Europe.

Between the different organic substrates studied, the anaerobic codigestion of sewage sludge (SS) and organic fraction of municipal solid waste (OFMSW – biowaste) is the most popular codigestion research subject (Mata – Alvarez et al., 2011). These studies showed the N content of sewage sludge can supplement a possible deficit of nutrients in the other co – substrate (e.g. biowaste), whereas the higher biodegradability of the biowaste allows an increase in biogas production potential. Therefore, the anaerobic codigestion of biowaste and sewage sludge is the key to implementation of the integrated treatment approach of municipal wastewater and biowaste. In addition to the advantages mentioned, the joint treatment of biowaste and wastewater allows to obtain improvements in the wastewater treatment: by two phases anaerobic codigestion (fermentation and methanogenesis), readily biodegradable Chemical Oxygen Demand (rbCOD) is produced. The rbCOD is an additive promoter of the stages of denitrification and biological phosphorous removal.

Recently, several studies showed the hydrogen can be produced by dark fermentation of biowaste, with recirculation of digestate to control pH (Gottardo et al., 2013). Moreover the two-phase anaerobic digestion of carbohydrate-rich substrates (e.g. biowaste) has been studied for the production of bio-hythane, a mixed gas

comprising hydrogen, methane and carbon dioxide. Hydrogen (10% addition was found to be the most suitable) significantly enhances the combustion rate of biogas (Porpatham et al. 2007).

In order to develop a two-phase anaerobic codigestion process optimized for the production of Bio-hythane (Biological Hydrogen and meTHANE), implementable in a wastewater treatment plant, in the present study, a pilot-scale experimental apparatus was designed and constructed to examine the feasibility and performance of the two-stage anaerobic codigestion process using biowaste and sewage sludge. Thermophilic temperature was applied to one phase (Shin et al., 2004) and also two phases (Ueno et al., 2007) as the better temperature for hydrogen and methane production (Cecchi et al., 1993).

To simulate the implementation of this process in a waste water treatment plant (WWTP), the biowaste / sewage sludge (SS) ratio has been chosen considering the production of the two substrates for people equivalent.

2. Material and Method

2.1 Experimental set – up

Two stirred reactors (CSTR) with 230 L of working volume each were used for the experiment. The reactors were heated by 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 biowaste was reduced in size using a grinder, mixed with sewage sludge and then fed to the first stage reactor. During the whole experiment (50 d), the Organic Loading Rate (OLR) and Hydraulic Retention Time (HRT) were maintained at about 18 kgTVS/m³d and 3.3 d, respectively, for the first stage and about 3.5 kgTVS/m³d and 15 d for the second stage. The biowaste / SS ratio has been chosen considering the production of 250 gWET/d Person Equivalent (PE) for biowaste and 60 gTS/d PE for SS. Thus the biowaste / SS ratio adopted in this study was 50/50 on VS basis.

2.2 Substrate and Inoculum

The anaerobic digested sludge used as inoculum for the methanogenic reactor was collected in the WWTP located in Treviso (northern Italy) where a 2000 m³ anaerobic digester treats the source collected biowaste at 35 °C. The sludge was acclimatized for one week to thermophilic temperature (Bolzonella et al., 2003).

The fermentative reactor was inoculated with separately collected biowaste, coming from the municipality of Treviso, and SS, coming from the WWTP above mentioned, and then regularly fed.

2.3 Analytical methods

The effluents of the reactors were monitored 2/3 times per week in terms of total and volatile solids content, chemical oxygen demand, Total Kjidehal Nitrogen (TKN) and Total Phosphorus (TP). The process stability parameters, namely pH, volatile fatty acid content and speciation, total and partial alkalinity and ammonia, were checked daily. All the analyses, except for Volatile Fatty Acids (VFAs), were carried out in accordance with the Standard Methods (APHA–AWWA–WEF 2012). 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, 15 x 0.53 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 and 160 °C, with a rate of 10 °C/min. The analysed samples were centrifuged and filtrated on a 0.45 µm membrane. Gas productions were monitored continuously by a gas flow meter (Ritter Company, drum-type wet-test volumetric gas meters), while the hydrogen content was measured by a gas-chromatograph (GC Agilent Technology 6890 N) equipped with the column HP-PLOT MOLESIEVE, 30 x 0.53 mm ID x 25 µm film, using a thermal conductivity detector and argon as gas carrier.

3. Results and discussion

The main chemical – physical characteristics of the biowaste and SS used as fed in this experiment are reported in Table 1 and 2.

Table 1: Characterization of OFMSW

Parameters	Units	Average	SD	Max	Min
TS	g/Kg _{WW}	249.2	40.9	303.2	171.5
TVS	g/Kg _{WW}	225.8	38.1	275	153.8
COD	g/Kg _{DW}	967.9	86.5	1,078.5	874.4
TKN	g/Kg _{DW}	25.58	3.5	29.4	18.8
P _{TOT}	g/Kg _{DW}	6.7	4.4	15.2	3

Table 2: Characterization of SS

Parameters	Units	Average	SD	Max	Min
TS	g/Kg	52.6	14.5	96.3	26.7
TVS	g/Kg	36.9	10.1	63.4	17.8
COD	g/Kg _{DW}	780.7	59.2	910.2	737.4
TKN	g/Kg _{DW}	51.3	5.9	62.3	45.2
P _{TOT}	g/Kg _{DW}	14.9	4.3	21.7	8.5
pH		6.4	0.1	6.7	6
Alkalinity (pH = 6)	mgCaCO ₃ /L	186.3	93.2	360	64.6
Alkalinity (pH = 4)	mgCaCO ₃ /L	803.2	209.4	1,098.2	510
NH ₄ ⁺	mgN-NH ₄ ⁺ /L	133.3	45.9	196.9	71.4

To optimize the hydrogen production by fermentation is necessary to optimize the activity of enzyme hydrogenase: recent studies have shown that to maximize the yield of hydrogen production the pH should be maintained in the range 5 - 6.5, with an optimum value at 5.5 (Valdez – Vazquez et al., 2009). In the works reported in literature, to buffer the pH in the first phase reactor, some authors (e.g. Antonopoulou et al., 2008) have used chemicals like sodium hydroxide and potassium hydroxide, while other authors (e.g. Lee et al., 2010) recirculated the second phase sludge to support the fermentation with buffering agents.

In order to verify if the alkalinity present in the SS can buffer the pH in the first phase, neither chemicals nor second phase sludge were added in the first reactor. As shown in Figure 1, except the first week, the pH in the first reactor was maintained greater than or equal to 5.

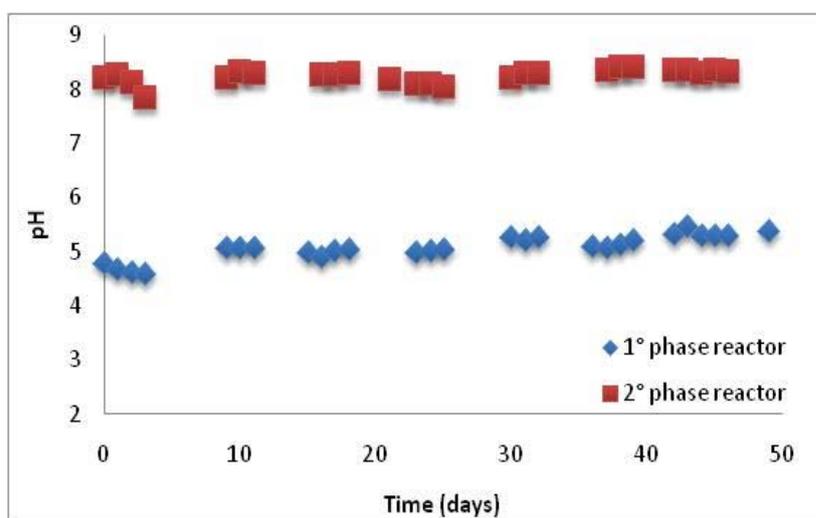


Figure 1: pH range in first & second phase reactors.

The pH of first reactor was always in the functional range of hydrogenase enzymes with an average value of 5.09 ± 0.2 , due to alkalinity of the SS.

The proof of the good functionality of the enzymes above mentioned was showed in hydrogen production in the first stage.

As shown in Figure 2, after around twenty days the hydrogen production of the fermenter, expressed as specific hydrogen production (SHP), is maintained around 40 L/kgTVS fed.

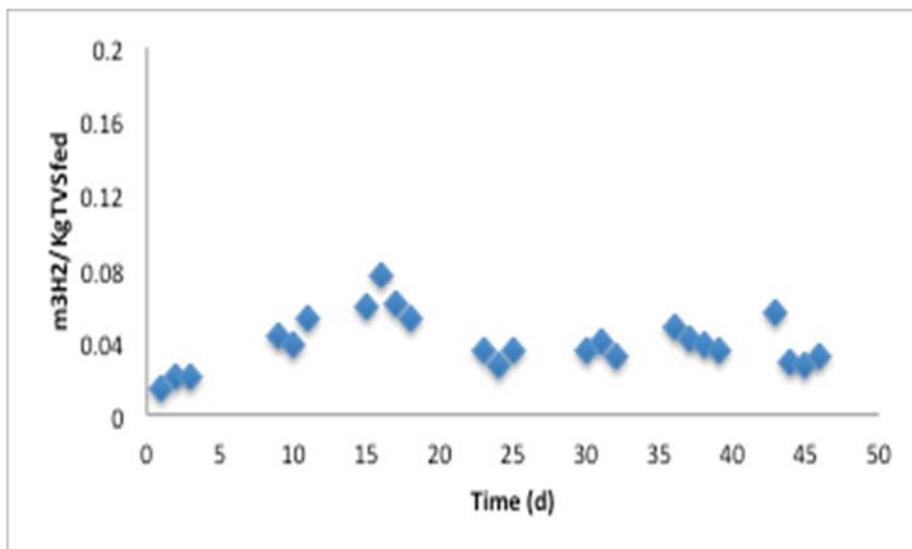


Figure 2: SHP range in the fermenter.

This value is about 60 % lower than the average value of SHP observed in our previous work (Cavinato et al., 2012) in which, however, only biowaste was fed. Moreover, around 51 % on TVS basis of the organic load is formed by biowaste, this result can be considered congruent with (or even higher than) the expected value. In table 3, the characterization of effluents and the corresponding gas yields, during SSC condition, are shown; in this table are also reported the total volatile fatty acid concentrations (VFA) and particularly acetic and butyric acid concentration, since they are the predominant by – products generated.

Table 3: Characterization of first and second phase effluent and gas yields.

Parameters	Units	1° Reactor	2° Reactor
Characterization of effluent			
TS	g/Kg	70.6 ± 20.6	23.9 ± 5.3
TVS	g/Kg	52.8 ± 17.1	15.8 ± 3.2
COD	g/Kg _{ww}	811.8 ± 116	791.3 ± 47.1
sCOD	mg/l	17,789 ± 2,391	905 ± 223
TKN	g/Kg _{DW}	37.8 ± 3.1	38 ± 2.2
P _{TOT}	g/Kg _{DW}	13.9 ± 3.9	15.7 ± 5.2
pH		5.1 ± 0.1	8.2 ± 0.1
VFA	mgCOD/L	8,131 ± 2,803	239 ± 115
Acetic Acid	mgCOD/L	2,992 ± 726	3,344 ± 696
Butyric Acid	mgCOD/L	3,472 ± 771	5,747 ± 996
Alkalinity (pH = 6)	mgCaCO ₃ /L		3,596 ± 434
Alkalinity (pH = 4)	mgCaCO ₃ /L	3,111 ± 519	5,755 ± 549
VFA/ALK	mgAC/mgCaCO ₃		0.18 ± 0.04
NH ₄ ⁺	mgN-NH ₄ ⁺ /L	677 ± 126	1,328 ± 190
Gas yields			
Specific Gas Production (SGP)	m ³ _{biogas} /KgTVS _{fed}	0.1 ± 0.02	0.5 ± 0.09
Gas Production Rate (GPR)	m ³ _{biogas} /m ³ _{reactor} d	1.7 ± 0.25	1.6 ± 0.29
H ₂	%	40 ± 10	
CH ₄	%		67 ± 0.01
Specific Hydrogen Production (SHP)	m ³ _{Hydrogen} /KgTVS _{fed}	0.04 ± 0.01	
Specific Methane Production (SMP)	m ³ _{Methane} /KgTVS _{fed}		0.32 ± 0.1

In terms of BioHythane produced, in the Figure 3 is shown the daily gas composition: the percentage of methane, hydrogen and carbon dioxide were 58.6 %, 7.5 % and 33.9 % respectively. Calculation considers also the small amount of methane produced in the first phase, due to a not complete inhibition of methanogenic microorganisms.

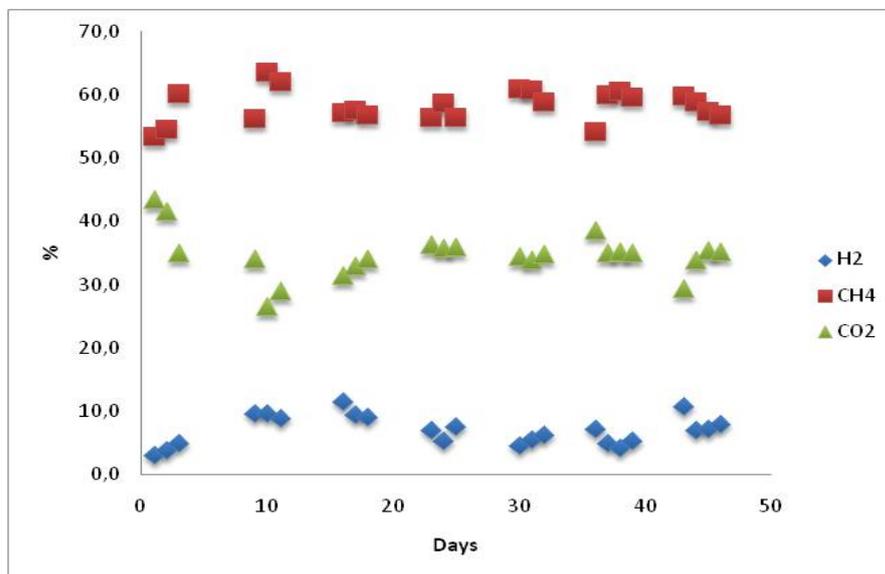


Figure 3: Gas percentage per day produced through this system.

Hydrogen content was never below 5 % and this met the best characteristics for biohythane mixture. The total specific gas production obtained was 0.58 m³/kgTVS added, and a gas production rate of 1.65 m³/m³d.

4. Conclusion

A two-phase anaerobic codigestion process of biowaste and SS for the hydrogen and methane production, was carried out at pilot scale. The following conclusions are drawn:

- During the 50 d of observation of the process, instability phenomena (eg proliferation of methanogenic, metabolic shift, etc.) were not detected.
- The alkalinity of the SS was sufficient to buffer the pH of the first phase, therefore it was not necessary to add chemicals or second phase sludge in the first reactor.
- If one considers the contribution, in term of TVS, of the biowaste on total load, the hydrogen production, expressed as SHP, was congruent with the expect value.
- The biohythane obtained met the composition characteristics requested (CH₄ 58.6 %, H₂ 7.5 % and CO₂ 33.9 %).

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