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Energy recovery from fermentative biohydrogen production of biowaste: a case study based analysis

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Abstract

Anaerobic Digestion of biodegradable substrates could be considered a promising process in terms of both bio-fuels and bio-products production. In this respect, biohydrogen production during the acidogenic phase and polyhydroxyalkanoate generation through the metabolites circulation, can be considered the new borders of process optimization. The results of the assessment presented in this work shows that anaerobic co-digestion of sludge and food waste is an effective process to achieve energy self-sufficiency of wastewater treatment plants. Through batch tests it was possible to estimate the production of hydrogen and methane in the specific case of sludge and food waste and calculate the primary energy produced by different users of biogas.

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Keywords: food waste; wastewater sludge; biohydrogen; biomethane; anaerobic digestion; fuel cells; microturbine; ICE

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1. Introduction

Transitioning to a more circular economy, where the value of product, material and resource is maintained for as long as possible and the generation of waste is minimised, is an essential contribution to the EU's long-term efforts to develop a competitive, sustainable, low-carbon and resource-efficient economy [1]. Anaerobic Digestion (AD) of biodegradable substrates could be considered a promising process in terms of both bio-fuels and bio-products production. In this respect, biohydrogen production during the acidogenic phase and polyhydroxyalkanoate generation through the metabolites circulation, can be considered the new borders of AD process optimization [2, 3, 4].

A significant capacity of anaerobic digestion lays in the wastewater-servicing sector. Most of the conventional wastewater treatment plants (WWTPs) use AD for the treatment of the produced sludge by using digesters with spare capacity to face variation in wastewater flow and future population growth [5]. Due to low organic loading and low biogas yields of sludge, energy recovery via anaerobic digestion in WWTPs is typically not sufficient to cover its energy consumption. Co-digestion of bio-waste with municipal sewage sludge is nowadays consider one of the most strategic approach in waste and wastewater management thus increasing the energy production, reduce costs and facilitating nutrient recycling [5, 6, 7, 8]. Among the available substrates that have been tested for co-digestion, Food Waste (FW) is an optimum co-substrate in order to improve digestion efficiency of sewage sludge because of its readily biodegradability nature [9]. Furthermore, the co-digestion of these two substrates could be potentially suitable for biohydrogen production from dark-fermentation. Indeed, due to their considerable alkalinity, sludge could be used to control pH in the optimal range for biohydrogen production avoiding drops that can bring to the failure of the process when using only FW [10, 11].

In this study, the production of methane and hydrogen of FW and wastewater sludge (WS) were experimentally determined in order to compare possible upgrading solutions for a WWTP in Tuscany. Four possible layouts of FW and WS co-digestion were compared with the current WWTP (reference scenario). In two co-digestion scenarios it was considered to increase methane production by adding FW to WS in the anaerobic digester currently in use at the plant; in other two scenarios, the possibility to produce hydrogen by adding a new digester to perform dark-fermentation was evaluated. For each scenario the mass balance, the energy budget and the greenhouse gas account were estimated.

The data used in the inventory were collected from several sources. The production of methane and hydrogen were determined by performing Biochemical Methane Potential (BMP) and Biochemical Hydrogen Potential (BHP) assays. BHP and BMP tests are well recognized among the scientific community as valuable, simply and low cost tools to assess the potential, adequacy and viability of the fermentative and methanogenic process [12, 13, 14, 15]. Other data were obtained by direct management data of the WWTP, calculations and esteems.

Nomenclature

AD	anaerobic digestion
BHP	biochemical hydrogen potential
BMP	biochemical methane potential
DF	dark-fermentation
FW	food waste
ICE	internal combustion engine
MCFC	melted carbonate fuel cell
OFMSW	organic fraction of municipal solid waste
OLR	organic loading rate
SRT	sludge retention time
TS	total solids
TVS	total volatile solids
VFA	volatile fatty acids
WS	wastewater sludge
WWTP	wastewater treatment plant

2. Materials and methods

2.1. Food waste and wastewater sludge characterization

The WS and the FW used in the BMP and BHP assays were sampled at two treatment facilities in Tuscany. The WS was collected from the aerobic unit of the municipal wastewater treatment plant of Viareggio (LU, Italy) while the FW were sampled form the Organic Fraction of Municipal Solid Waste (OFMSW) delivered to a mechanical-biological treatment facility in the province of Florence. In particular, to obtain the FW samples, approximately 10 tons OFMSW were investigated by means of a picking analysis [16]. This sample was manually sorted in the following fractions: FW (45.8% w/w), garden waste (44.7% w/w), textiles (0.5% w/w), paper and cardboard (2.2% w/w), metals (0.1% w/w), wood (1.1% w/w), plastics (1.7% w/w), glass (1.2% w/w) and other (2.6% w/w). The sorted FW was then used for biohydrogen and biomethane production owing to its recognized potential [14, 17]. In order to homogenize the sample and to make it suitable for a wet fermentation technology, FW was grinded by blender and diluted with tap water until it reached a total solids (TS) content of approximately 15% w/w.

In both BMP and BHP tests, sludge from an anaerobic reactor treating OFMSW was used as inoculum.

FW, WS and the inoculum were characterized through physical, chemical and bromatological analyses (Table 1). TS, Total Volatile Solids (TVS) and pH were determined according to standard methods [18]. According to Angelidaki et al. [14], TS determination was performed at 90°C instead of 105°C until constant weight in order to avoid the volatilization of volatile fatty acids. Proteins, lipids, cellulose, Total Kjeldhal Nitrogen contents were measured in accordance with the European Commission Regulation 2009/152/EC of 27 January 2009 [19]. Carbohydrates were then calculated by subtracting to the total amount, the contents of humidity, ashes, proteins, lipids and fibers. Lignin was measured according to [20]. Concerning the elementary composition C, H, N were obtained following [21] while S and P where measured using [22] and [23] respectively. The oxygen content was estimated by subtracting the sum of C, H, N, S and P from the total. Ammonia was measured according to [24] while Total Organic Carbon (TOC) was measured thanks to [25].Volatile Fatty Acids (VFAs: acetic and propionic acids) were measured according to [26].

Table 1. Food waste (FW), wastewater sludge (WS) and inoculum characterization.

	FW	WS	Inoculum
TS (% w/w)	17.5 ± 0.8	1.9 ± 0.0	2.7 ± 0.1
TVS/TS (% w/w)	73.0 ± 1.5	79.9 ± 0.5	48.7 ± 0.5
pH	4.0 ± 0.2	4.4 ± 0.0	7.4 ± 0.3
TKN (%N w/w)	5.4 ± 0.4	0.2 ± 0.0	0.2 ± 0.0
TOC (%C w/w)	10.6 ± 1.9	1.2 ± 0.2	1.3 ± 0.2
Ammonia (mgN/kg)	856 ± 72	341 ± 47	1,040 ± 82
Acetic acid (mg/l)	5,200 ± 1,050	830 ± 120	< 40
Propionic acid (mg/l)	85 ± 26	390 ± 71	< 40
C (% TS)	53.8 ± 4.0	58.9 ± 4.3	50.8 ± 3.7
H (% TS)	5.7 ± 0.5	6.4 ± 0.5	3.9 ± 0.3
N (% TS)	3.4 ± 0.5	7.5 ± 0.8	8.0 ± 0.9
S (% TS)	0.2 ± 0.0	0.2 ± 0.0	0.2 ± 0.0
P (% TS)	0.6 ± 0.1	0.4 ± 0.1	0.4 ± 0.1
O (% TS)	36.3	26.6	36.7
Proteins (% w/w)	3.8 ± 0.2	0.9 ± 0.1	1.2 ± 0.1
Lipids (% w/w)	2.2 ± 0.2	< 0.3	< 0.3
Carbohydrates (% w/w)	6.9	0.1	0.1
Cellulose (% w/w)	3.5 ± 0.4	0.3 ± 0.3	0.4 ± 0.3
Lignin (% w/w)	1.3 ± 0.2	0.3 ± 0.0	0.3 ± 0.0

2.2. Hydrogen and methane production tests

2.2.1 Biochemical Hydrogen Potential (BHP) tests

The production of hydrogen from FW e SW was experimentally determined by performing biochemical hydrogen potential (BHP) assays. The analyses were conducted based upon the method described by Alibardi and Cossu [27]. The test was performed in triplicate using 1-l stainless steel batch reactors [13]. The vessels were incubated in a water bath at 37°C for 7 days. After set-up the bottles were flushed with N_2 for few minutes to ensure anaerobic conditions in the headspace of the batches. The bottles were daily shaken to guarantee homogeneous conditions in the assay vessels. Each vessel was loaded with a Food/Microorganism ratio of 1/4 (w/w). The working volume of the bottle was approximately 0.5-l and consisted of inoculum, substrate, MES (2-N-Morpholino-EthaneSulfonic acid, VWR, Italy) buffer solution and HCl 2.5M to set initial pH at a value of 5.5. After set-up, the vessels were flushed with N_2 for few minutes to ensure anaerobic conditions. The inoculum, was previously heat-treated at 105°C for 30 minutes with the aim to select only hydrogen producing bacteria and inhibit hydrogenotrophic methanogens [11, 27, 28].

Biogas production was daily estimated by measuring the pressure in the headspace of each reactor and then converting to volume by the application of the ideal gas law. Pressure was measured using a membrane pressure gauge (Model HD2304.0, Delta Ohm S.r.L., Italy). The measured values of pressure were converted into biogas volume as following Eq. (1):

$$V_{\mathrm{biogas}} = \frac{P_{\mathrm{measured}} \cdot T_{\mathrm{NTP}}}{P_{\mathrm{NTP}} \cdot T_{\mathrm{r}}} \cdot V_{\mathrm{r}} \tag{1}$$

where:

- V_{biogas}: volume of daily biogas production, expressed in Normal liter (Nl);
- $P_{measured}$: headspace pressure before the gas sampling (atm);
- T_r and V_r: temperature (K) and volume (l) of the reactor's headspace;
- T_{NTP} and P_{NTP}: normal temperature and pressure, (273.15 K and 1 atm respectively).

The BHP was determined as the cumulated hydrogen production divided by the TVS content contained in each batch. In order to determine the hydrogen production, the hydrogen content of the gas was measured by using gas cromatography (3000 Micro GC, INFICON, Switzerland).

2.2.2 Biochemical Methane Potential (BMP) tests

Biochemical Methane Potential (BMP) assays were performed for 21 days in order to determine the methane production of FW and WS. The analysis were conducted in triplicate based upon previous researches [13] and following the basic guidelines and advices included in Holliger et al. [14].

Each reactor was loaded with different amounts of substrate to achieve a concentration of substrate of about 2 gTVS/100 ml solution in each batch. This concentration is a compromise of, one hand, the need to use a large sample to have a good representativeness and to get a high easy-to-measure gas production, and, on the other hand, to avoid too large and impractical volumes of reactors and gas production and keep the solution dilute to avoid inhibition from accumulation of VFA and ammonia [29]. The inoculum to sample ratio was about 1.5:1 TVS basis and kept under 10:1 weight basis according to Pecorini et al. [13] for fresh feed-in substrate (the amount of inoculum should be enough to prevent the accumulation of VFA and acid conditions). To determine the background methane production a blank assay with only the inoculum was done in triplicate. The inoculum was degassed for 5 days in order to deplete the residual biodegradable organic matter until the achievement of an endogenous metabolism phase.

The test was performed at mesophilic conditions using the same equipment previously presented for BHP tests.

2.3. Co-digestion scenarios, inventory analysis

Four possible layouts of FW and WS co-digestion were compared with the current WWTP (reference scenario). In two co-digestion scenarios, with reference to Figure 1 *Scenario CH_4 (1) and Scenario CH_4 (2)*, it was considered to increase methane production by adding FW to WS in the anaerobic digester currently in use at the WWTP. In other two scenarios, so-called *Scenario H_2 (1) and Scenario H_2 (2)*, the possibility to produce hydrogen by adding a new digester for the dark-fermentation to the current plant was evaluated. For each scenario the mass balance, the energy budget and the greenhouse gas account were estimated. Beside the experimental data that will be presented in the next paragraph, the data reported in Table 2 were assumed in the inventory analysis.

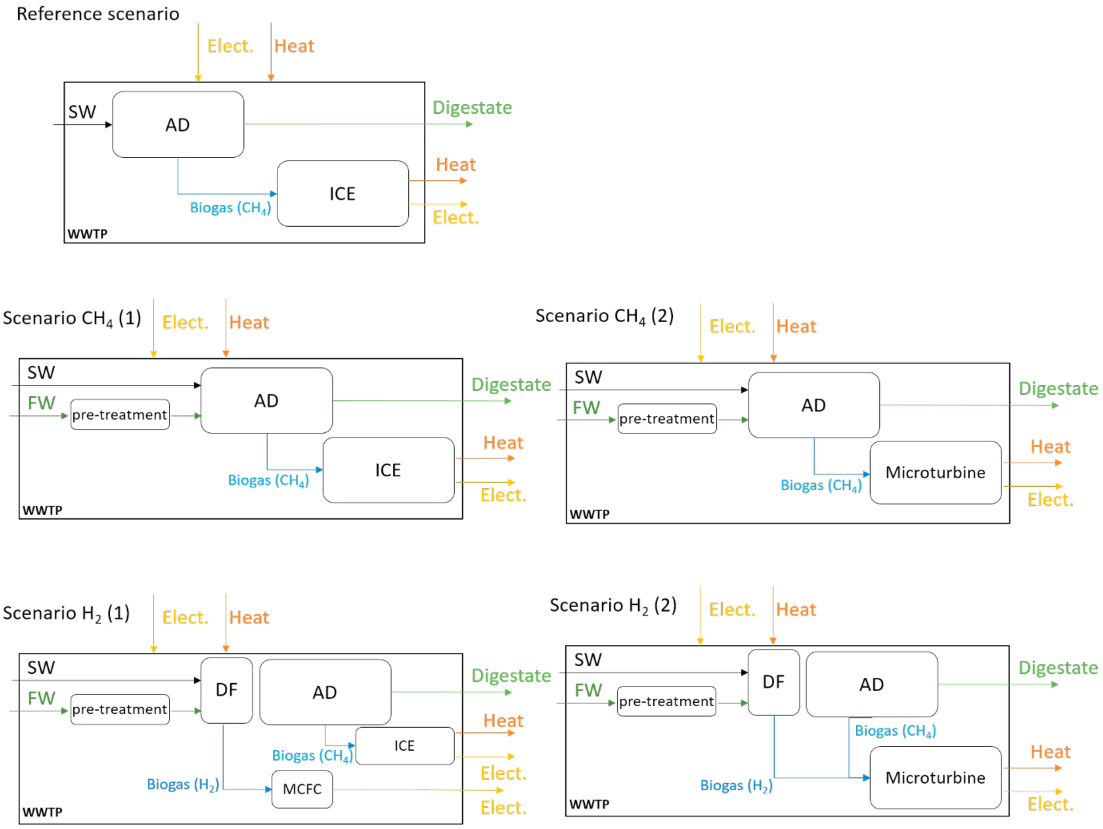

Fig. 1. Co-digestion scenarios layout

Table 2. Mass balance data inventory

	Reference Scenario	Scenario CH_4 (1)	Scenario CH_4 (2)	Scenario H_2 (1)	Scenario H_2 (2)
FW in (t/d)	0	50	50	54	54
TS (%)	-	28	28	28	28
TVS/TS (%)	-	73	73	73	73
WS in (t/d)	160	160	160	214	214
TS (% w/w)	0.7	0.7	0.7	0.7	0.7
TVS (% w/dw)	70	70	70	70	70
Digester volume	4500	4500	4500	818 (H_2) 4500 (CH_4)	818 (H_2) 4500 (CH_4)
SRT (d)	28	23	23	3 (H_2) 17 (CH_4)	3 (H_2) 17 (CH_4)
OLR (kgTVS/m^{3}d)	0.17	1.99	1.99	14.7 (H_2) 2.3 (CH_4)	14.7 (H_2) 2.3 (CH_4)

Table 3 reports the main inventory data concerning energy flows. In particular, the electricity consumptions of the reference scenario were provided by the owner of the WWTP while, for the co-digestion scenario the use of a screw-press to pre-treat the OFMSW prior to AD was considered. In all the scenarios, thermal energy consumptions were calculated accounting the heat needed to warm the digesters (working at mesophilic conditions) and the heat losses.

Concerning the energy production, different choices were done. In the *reference scenario* and in *scenario CH_4 (1)* it was consider to recover the biogas produced by an ICE while, *in scenario CH_4 (2),* the same amount of biogas is used in a micro turbine. The use of a micro turbine was also considered in *scenario H_2 (2)* in which, beside CH_4, also the H_2 is produced. In *scenario H_2 (1)* the ICE that recover biogas from AD was integrated by a MCFC for electricity production by the H_2 from DF.

Table 3. Energy data inventory

	Reference Scenario	Scenario CH_4 (1)	Scenario CH_4 (2)	Scenario H_2 (1)	Scenario H_2 (2)
Electricity consumption (MWh/y)	730	1361	1600	1824	2145
Heat consumption (MWh/y)	1959	2337	2337	3755	3755
Bio-fuel utilization	ICE $\mu_{el} = 0.391$ $\mu_t = 0.445$ Functioning = 7500 h/y	ICE $\mu_{el} = 0.391$ $\mu_t = 0.445$ Functioning = 7500 h/y	Micro turbine $\mu_{el} = 0.33$ Exhaust gas flow = 4 kg/s Exhaust gas temp. = 280°C Functioning = 8000 h/y	MCFC (H_2) $\mu_{el} = 0.45$ Functioning = 7000 h/y ICE (CH_4) $\mu_{el} = 0.391$ $\mu_t = 0.445$ Functioning = 7500 h/y	Micro turbine $\mu_{el} = 0.33$ Exhaust gas flow = 4 kg/s Exhaust gas temp. = 280°C Functioning = 8000 h/y

3. Results

3.1. Hydrogen and methane productions

BMP results for FW were in agreement with previous researches. In particular, the review work of Campuzano and González-Martínez [30] highlighted an average value for methane production of 415 ± 138 $NlCH_4/kgTVS_{sub}$. as biogas production was found lower than FW due to its lower content of readily biodegradable component such as carbohydrates [31].

Concerning hydrogen production the average value of 55.0 $NlH2/kgTVS_{sub}$ is in the range of 25-85 $NlH_2/kgTVS_{sub}$ found by Alibardi and Cossu [27] for FW mixtures. Table 4 reports BMP and BHP tests outcomes in terms of averages and standard deviations.

Table 4. BMP and BHP tests results. Values are expressed as averages and standard deviations.

	FW	WS
BMP ($NlCH_4/kgTVS_{sub}$, $\%CH_4$)	440.5 ± 8.7, 65.0 ± 2.3	159.3 ± 11.3, 55.0 ± 1.9
BHP ($NlH_2/kgTVS_{sub}$, $\%H_2$)	55.0 ± 3.6, 45.0 ± 2.4	0.1 ± 0.0, 0.30 ± 0.02

3.2. Co-digestion scenarios performance

Table 5 shows the results of the mass balance, energy budget and greenhouse gas account estimated for each scenarios.

In Figure 2 the scenarios are compare in terms of energy and environmental performance. In order to assess the benefit gained with co-digestion in terms of energy savings, the net primary energy was calculated according to Eq. 2:

$$Primary\ Energy = \frac{E_{el}}{\mu_{el,rif} \cdot p_g} + \frac{Q_{th}}{\mu_{el,rif} \cdot p_g} \qquad (2)$$

Where:

- E_{el} is the net electricity produced in each scenario;
- Q_{th} is the net thermal energy recovered in each scenario;
- $\mu_{el,rif}$ is the reference efficiency for electricity, assumed equal to 0.525;
- p_g is the coefficient of distribution losses, assumed equal to 0.936
- $\mu_{el,rif}$ is the reference efficiency for thermal energy, assumed equal to 0.90;

Concerning the calculation of CO_2 equivalent saved the conversion factor of 0.551 $kgCO_2/kWh_{el}$.

Table 5. Co-digestion scenarios mass balance, energy budget and GHG emissions comparison

	Reference Scenario	Scenario CH_4 (1)	Scenario CH_4 (2)	Scenario H_2 (1)	Scenario H_2 (2)
Biofuel produced					
Biogas (Nm^3/y)	82,000	2,105,202	2,105,202	535,619 (H_2) 2,662,206 (CH_4)	535,619 (H_2) 2,662,206 (CH_4)
CH_4 (Nm^3/y)	53,827	1,368,381	1,368,381	1,730,434	1,730,434
H_2 (Nm^3/y)	-	-	-	241,028	241,028
Heat (MWh/y)					
In	1,959	2,337	2,337	3,755	3,755
Out	219	5,574	5,069	7,049	6,716
Net	-1,740	3,238	2,732	3,295	2,962
Electricity (MWh/y)					
In	730	1,361	1,600	1,824	2,145
Out	193	4,898	4,409	6,501	5,833
Net	-537	3,537	2,809	4,677	3,689
GHG emissions (t CO_{2eq})					
Produced	163	4,133	4,133	5,226	5,226
Saved	296	-1,949	-1,548	-2,577	-2,032
Net	459	2,184	2,585	2,649	3,194

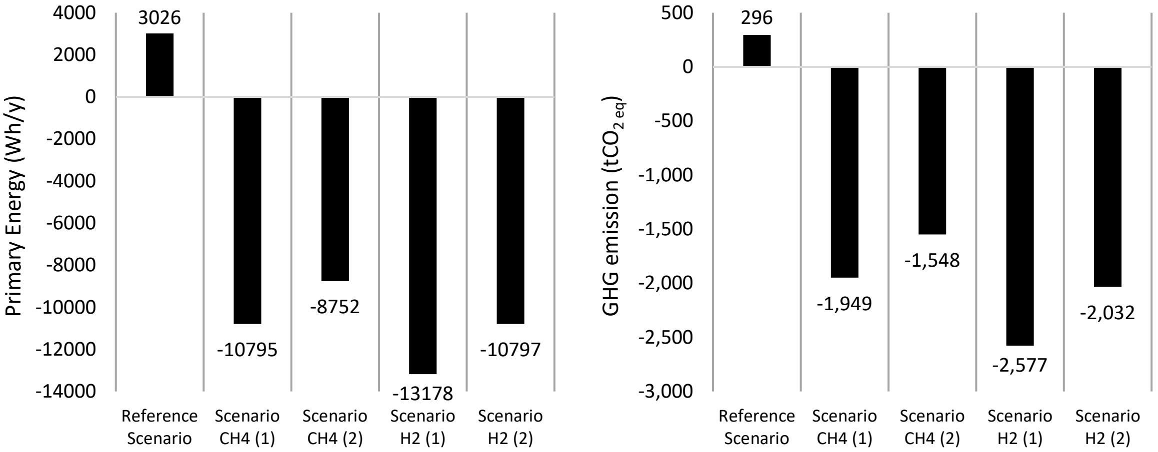

Fig. 2. Co-digestion scenarios performance comparison

4. Conclusions

The results of the assessment presented in this work shows that anaerobic co-digestion of sludge and food waste is an effective process to achieve energy self-sufficiency of wastewater treatment plants.

Moreover, the obtained results demonstrated that dark-fermentation, performed in a dedicated reactor prior to co-digestion, increases the treatment capacity and the biofuel production (both in terms of hydrogen and methane). Through the BHP and BMP tests it was possible to estimate the production of hydrogen and methane in the specific case of sludge and FW and calculate the primary energy produced by different users of biogas.

From experimental assays a specific production of 55.0 $NlH2/kgTVS_{sub}$ and 440 $NlCH_4/kgTVS_{sub}$ in case of FW substrate was obtained, values used to improve the reference scenario. In all the scenarios (with and without dark fermentation), the savings achieved by energy recovery from biogas produced were estimated by comparing the use of a ICE, a microturbine and a ICE integrated by a MCFC. The assessment shows that the scenario in which fuel cells and ICE were considered for energy production is the most virtuous in terms of both primary energy saved and avoided emissions of carbon dioxide.

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