Comparison of one-stage anaerobic digestion and two-stage fermentation process of food waste

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Keywords: Anaerobic digestion, Dark fermentation, Food waste, Two-stage, Hydrogen, Methane

Abstract

Purpose: This study aims at comparing the anaerobic performances of a two-stage process with a traditional one-stage reactor.

Methods: Two experimental set-ups were performed: the first scenario consisted in the traditional one-stage anaerobic digestion process while the second scenario consisted in two reactors connected in series: a first fermentative reactor followed by a methanogenic digester. Scenarios were carried out in semi-continuous mode using food waste as substrate. Performances were compared in terms of gas production and volatile solids removal efficiency.

Results: The two-stage fermentation process increased volatile solids removal efficiency of 6.8% and the total specific gas production of 7.7%. These results were obtained with a reduction of the total hydraulic retention time and a consequent increase of the amount of treated substrate. In addition, the fermentative reactor produced a hydrogen rich (22.9%) biogas that can used either by itself or to improve the combustion performance of methane, making a mixture that simulates the composition of hythane.

Conclusions: The physical separation of the two anaerobic phases with the presence of a preliminary step of dark fermentation was demonstrated to be beneficial for the methanogenic phase. The two-stage fermentation process was found to be a suitable technology for increasing biofuel production from organic substrates.

1. Introduction

Anaerobic digestion (AD) of biodegradable substrates is a proven biological-based technology that has gained interest during the last years as it recovers energy in the form of biogas for use in combined heat and power plants [1]. The increasing need for renewable energy generation and the requirement to divert biodegradable waste from landfill have recently increased the interest in further developing the process.

Under this perspective, the scientific community has focus attention on hydrogen production during the fermentative phase of AD. Hydrogen production is considered one of the new frontier of AD owing to its high-energy content and environmentally friendly production [2, 3]. In order to highlight a hydrogen flow in AD, the traditional one-stage technology is separated in a two-stage process equipped with a fermentative reactor and a methanogenic reactor connected in series. While the first stage produces H_2 and CO_2 as gaseous products and releases volatile fatty acids (VFAs) in the liquid solution, the second one converts VFAs and the residual organic biodegradable matter into CH_4 and CO_2 [4, 5]. The advantages of this technology include an energy efficiency increase [6] due to the high calorific value per unit of weight of H_2 and the enhancement of biogas yield in the second stage. Nonetheless, the two-stagefermentation process using bio-waste remains in the earlystages of development and few studies are available providing answers and data about the advantages of the two-stage system compared to the traditional AD technology.

Based on the above background, this study aims at comparing the performances of a two-stage process with a traditional one-stage AD reactor. Two experimental set-ups were performed: the first scenario (Run1) consisted in the traditional one-stage AD process while the second scenario consisted in two reactors connected in series (Run2) evaluating the two-stage process (DF+AD). Scenarios were carried out in semi-continuous mode using food waste (FW) as substrate. Performances were compared in terms of gas production and quality and volatile solids removal efficiency.

2. Material and methods

2.1 Substrate and inocula

Activated sludge collected from the aerobic unit of a municipal wastewater treatment plant was used as inoculum for the fermentative reactor (IN1). Activated sludge were heat treated at 80°C for 30 minutes prior to set-up with the aim of selecting only hydrogen producing bacteria while inhibiting hydrogenotrophic methanogens [7, 8]. The treatment was performed in 250 ml beakers placed in a static oven (UM200, Memmert

GmbH, Germany). The temperature of the medium was continuously measured with a digital tip thermometer (T1, Testo S.p.A., Italy). Treatment time started when the temperature of the medium reached 80°C. After 30 minutes, the inocula were removed from the oven and cooled down to ambient air temperature. Tests were carried out when the inoculum temperature reached mesophilic conditions.

The seed sludge used in the methanogenic reactor used as inoculum for the methanogenic reactor was collected from an anaerobic reactor treating the organic fraction of municipal solid waste (OFMSW) and cattle manure (IN2).

FW was used as the substrate as it has been proven to be a highly desirable feedstock for anaerobic fermentation due to its high biodegradability, availability and well balanced carbon and nutrient contents [9 - 11]. FW was manually sorted from the organic fraction of municipal solid waste collected in a Tuscan municipality (Italy) by means of a kerbside collection system. In order to obtain a slurry with a total solid (TS) content suitable to wet fermentation, the sample was treated in a food processor, sifted with a strainer (3 mm diameter) and mixed with tap water [1].

The characteristics of inocula and substrate in terms of TS, total volatile solids (TVS) and pH are shown in table 1.

Tab. 1 Substrate and inocula characterization.Values are expressed by averages and standard deviations

	TS (% w/w)	TVS (% w/w)	pH
IN1	2.1 ± 0.2	1.5 ± 0.1	7.1 ± 0.0
IN2	2.9 ± 0.1	1.8 ± 0.1	8.2 ± 0.1
FW	5.7 ± 0.1	4.3 ± 0.1	3.8 ± 0.0

2.2 Experimental set-up

Two stainless steel reactors (AISI 316) were employed for hydrogen (R1-H_2) and methane (R2-CH_4) production. The first reactor, dedicated to the fermentative step, had a total volume of 6 l and a working volume of 3 l. The second reactor, dedicated to the methanogenic step, had had a total volume of 20 l and a working volume of 12 l. Temperature was constantly kept at mesophilic conditions (37.0 ± 0.1 °C) by a jacket where warm water heated up by a thermostat (FA90, Falc Instruments s.r.l., Italy) was continuously recycled.Continuous mixing was ensured by mixing blades. Both reactors were equipped with pH probes (Metter Toledo, Italy) and connected to an automatic data acquisition system (LabView, National Instruments Corporation, Italy). Data were recorded every 5 minutes. pH in the fermentative reactor was controlled through NaOH 2M solution addition dosed using peristaltic pumps. In particular, 3 ml of solution were automatically added when a pH decrease under 5.5 was detected. This configuration enabled to constantly keep the pH value in the range 5.5-5.6 all through the test. The reactors were connected to volumetric counters for gas measurement. The produced gas was collected in 10 l multilayer foil bags (Supel TM, Merck KGaA, Germany). After set-up, the reactors were flushed with N_2 gas to ensure anaerobic conditions and to drive off air from the reactor headspace.

The experimental test was divided in two periods (runs).In the first period (Run1), R2-$CH_4$was fed with FW with the aim of evaluating the traditional one-stage AD. Simultaneously R1-H2 was also fed with FW slurry in order to reach steady state conditions. Hydraulic Retention Time (HRT) in R1-H_2 was set to 3.0 days [10] while HRT in R2-CH_4 was set to 17.0 days (APAT, 2005). This configuration determined Organic Loading Rates (OLR) of 14.2 kgTVS/m^3d and 2.5 kgTVS/m^3d for R1-H_2 and R2-CH_4 respectively.In the second period (Run2), the two reactors were connected in series aiming at evaluating the two-stage process. R1-H_2 maintained the same conditions of Run1 while R2-CH_4 maintained the same OLR of Run1 leading to a shorter HRT (12.8 d) comparable to those reported by previous studies [9 – 12].

Table 2 shows the operational conditions applied to the reactors during the experimentation.

Tab. 2Operational conditions applied during the experimental test

	Run1	Run2
HRT R1-H_2 (d)	-	3.0
HRT R2-CH_4 (d)	17.0	12.8
OLR R1-H_2 (kgTVS/m^3d)	-	14.2
OLR R2-CH_4 (kgTVS/m^3d)	2.5	2.5

2.3 Analytical methods

The effluent of both the reactors was monitored daily in terms of TS,TVS, pH, alkalinityand VFAs.

TS, TVS and pH were determined according to standard methods [13]. TS determination was performed at 90°C instead of 105°C until constant weight in order to avoid the volatilization of VFA.Based on the volatile

solids content of the effluent (TVS_{OUT}) and the volatile solids content of the incoming substrate (TVS_{IN}), the daily volatile solids removal efficiency (η_{TVS}) was calculated as follows (Eq. (1)):

$$\eta_{TVS} = \frac{TVS_{IN} - TVS_{OUT}}{TVS_{IN}} \times 100 \quad (1)$$

Alkalinity was measured according to Martín-González et al. [14]. This methodology is a two-end point titration methodology to monitor volatile fatty acids VFAs/alkalinity ratio leading to obtain total alkalinity (TA) and partial alkalinity (PA). The former include both VFAs and bicarbonate alkalinity and the latter is roughly related only to bicarbonate alkalinity. The difference, defined as intermediate alkalinity (IA) is related only to VFAs alkalinity. Several studies include alkalinity ratios as monitoring parameters. For instance the pilot scale digester is daily monitored through the ratios intermediate/partial alkalinity (IA/PA).

Hydrogen, methane, carbon dioxide, nitrogen, oxygen and hydrogen sulphide contents in biogas were analysed usinga gas chromatograph (3000 Micro GC, INFICON, Switzerland)equipped with a thermal conductivity detector. Carbon dioxide and hydrogen sulphidepassed through a PLOTQ column (10 μm /320 μm / 8 m) using helium as gas carrier at temperature of 55°C. The other gas passed through a Molsieve column (30 μm /320 μm / 10 m) using argon as gas carrier at a temperature of 50°C.

VFAs, including acetic, propionic, butyric, isobutyric, valeric, isovalericand caproicacidswere measured using a gas chromatograph (7890B, Agilent Technology, US) with hydrogen as gas carrier, equipped with a CPFFAP column (0.25 mm / 0.5 μm / 30 m) and with a flame ionization detector (250°C). The temperature during the analysis started from 60°C and reaches 250°C with a rate of 20 °C/min.Samples were centrifuged (30 minutes, 13,500 rpm) and filtrated on a 0.45 μm membrane. 500 μl of filtrate were mixed with isoamyl alcohol (1.00179, Merck KGaA, Germany) in a volumetric ratio of 1:1, 200 μl of phosphate buffer solution (pH 2.1), sodium chloride and 10 μl of hexanoic-D11 acid solution (10.000 ppm) used as internal standard. The blend was mixed with a Mortexer™ Multi-Head vortexer (Z755613-1EA, Merck KGaA, Germany) for 10 minutes. The liquid suspension of the sample was then inserted in the gas chromatograph by means of an auto-sampler.

3. Results

During Run1 FW was fed to R1-H_2 and to R2-CH_4 simultaneously. These conditions were maintained for 42 days, the time necessary to guarantee stable conditions in R1-H_2 and R2-CH_4. In the matter of the methanogenic reactor, process stability was monitored through the IA/PA ratio. Indeed, according to Martín-González et al. [14], an IA/PA ratio of below 0.3 is recommended to achieve stable reactor performance. During Run1, IA/PA ratio below 0.3 was reached after 25 days. Other 17 days, corresponding to a whole HRT, were run in order to have steady data to compare. Concerning Run2, it was performed for 26 days, equal to two R2-CH_4 HRTs. The first 13 days were considered state of transition between Run1 and Run2 while from day 13 to day 26 conditions were considered steady and used for comparison. As for R1-H_2, the whole Run1 was considered to be a trial stage while Run2 was entirely considered steady.

Table 3 reports Run1 and Run2 results recorded during their steady phases. Figure 1-4 represent the trends over time of the main parameters of the process such as pH (Fig.1), total VFAs and alkalinity (Fig.2), η_{TVS} (Fig.3) and SGP (Fig. 4) in the two reactors.

Tab. 3 Characterization of reactors effluents and yields of the process. Results are expressed in terms of averages and standard deviations of data recorded during the steady phases. Run1: 25-42 d; Run2: 42-68 d for R1-H_2 and 55-68 for R1-CH_4

	Run1	Run2	
	R2-CH_4	R1-H_2	R2-CH_4
pH	7.33 ± 0.02	5.52 ± 0.02	7.43 ± 0.02
TA ($mgCaCO_3$/l)	10,557 ± 424	6,459 ± 694	11,155 ± 437
IA ($mgCaCO_3$/l)	1,976 ± 307	-	1,840 ± 303
Total VFAs (mg/l)	1,022 ± 273	8,193 ± 711	1,033 ± 340
η_{TVS}(%)	67.0 ± 2.0	23.5 ± 4.0	62.5 ± 2.7
SGP (Nl/kgTVS d)	694.4 ± 24.6	43.1 ± 12.8	704.6 ± 28.5
GPR (Nl/l d)	1.74 ± 0.06	0.61 ± 0.18	1.77 ± 0.05
H_2 (%)	-	22.9 ± 5.5	-
CH_4 (%)	65.2 ± 1.9	-	68.4 ± 1.1
SHP (NlH_2/kgTVS d)	-	12.6 ± 5.0	-
SMP ($NlCH_4$/kgTVS d)	453.1 ± 28.2	-	482.1 ± 24.0

Regarding pH, it was monitored steady in the range 5.5 - 5.6 in the fermentative reactor thanks to the addition of NaOH. The external control of pH was necessary to avoid the drop to values below 4 which could significantly suppress hydrogen production [12]. As for the methanogenic reactor, pH highlighted more neutral values, typical of the methanogenic phase. Indeed, pH in R2-CH_4 was in the range 7.05-7.45.

In the matter of alkalinity, no significant differences were found between Run1 and Run2 in the methanogenic reactor. TA and IA were respectively 10,557 mg$CaCO_3$/l and 1,976 mg/l in Run1 and 11,155 mg$CaCO_3$/l and 1,840 mg/l in Run2. Concerning IA/PA ratio, after 25 days it was found to be steadily below 0.3 highlighting stable reactor performances (Martín-González et al., 2013). In the fermentative reactor TA was totally related to VFAs alkalinity. In this case, PA, related to bicarbonate alkalinity was null and TA coincided with IA. More specifically, Fig. 2 shows a good correlation between TA and Total VFAs in R1-H_2 and between IA and Total VFAs in R2-CH_4. The average VFAs concentration in R1-H_2 was 8,193 mg/l, approximately eight times higher than the concentration found in R2-CH_4. Organic acids are accumulated in the fermentative reactor and are subsequently degraded in the methanogenic digester [15].

Fig. 1pH trend in R1-H_2 (■) and R2-CH_4 (●)

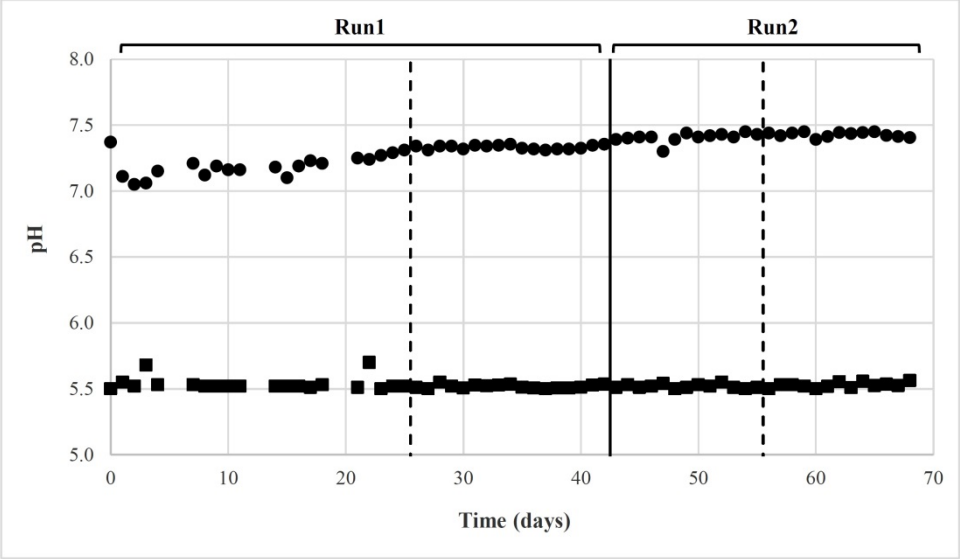
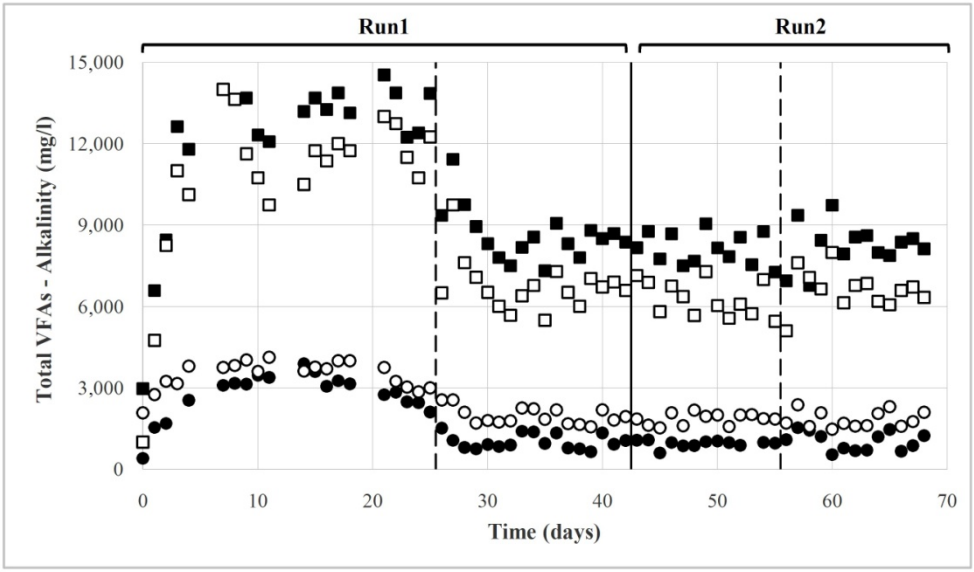


Fig. 2 Total Volatile fatty acids content in R1-H_2 (■) and R1-CH_4 (●) compared with total alkalinity of R1-H_2 (□) and intermediate alkalinity of R2-CH_4 (○) respectively



Concerning volatile solids removal efficiency Fig.3 shows a decrease of η_{TVS} in R2-CH_4. In particular, the average value decreased from 67.0% to 62.5%. This was due to the volatile solids content of the incoming substrate of the methanogenic reactor. Indeed while in Run1 R2-CH_4 was fed with FW, in Run2 it was fed with the outcoming digestate of R1-H_2 that was already partially degraded. Taking into account the whole two-stage

process, where TVS_{IN} is the incoming FW of the fermentative reactor and TVS_{OUT} is the outcoming digestate of the methanogenic reactor, the total η_{TVS} of Run2 was calculated to be 71.5%, 6.8% higher than Run1.

Regarding biogas production and quality, Run2 highlighted a higher methane content, SGP and GPR in the methanogenic stage. CH_4 content increased from 65.2% to 68.4%, GPR from 1.74 Nl/l d to 1.77 Nl/l d and SGP from 694.4 Nl/kgTVS d to 704.6 Nl/kgTVS d. Moreover, the fermentative stage provided a further gasification of the biodegradable matter. R1-H_2 SGP was 43.1 Nl/kgTVS d while the produced biogas was formed by carbon dioxide and hydrogen (22.9%). Adding the SGP of R1-H_2 to the SGP of R2-CH_4, the total SGP of Run2 was found to be 747.7 Nl/kgTVS d, 7.7% higher than Run1.

Fig. 3 Volatile solids removal efficiency (η_{TVS}) in R1-H_2 (■) and R2-CH_4 (●)

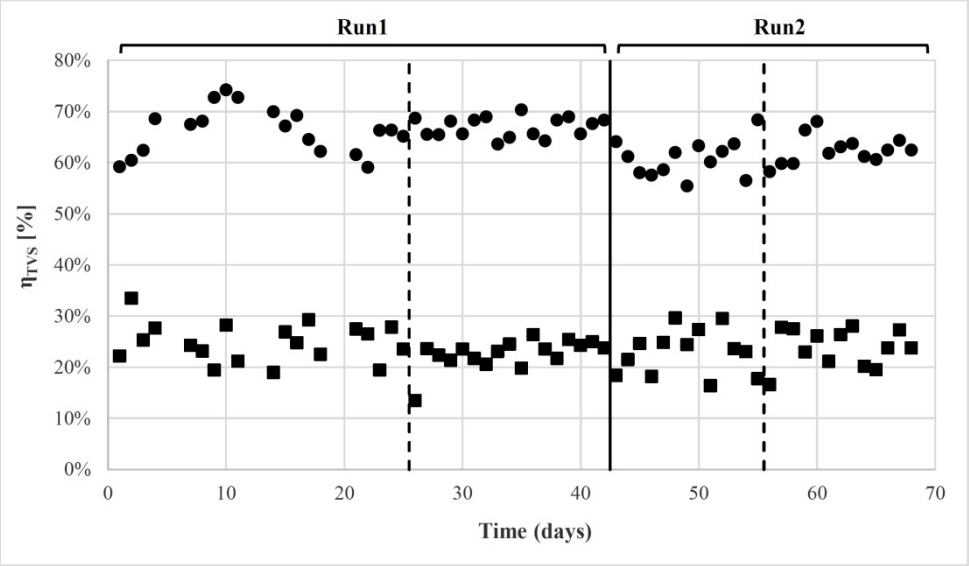
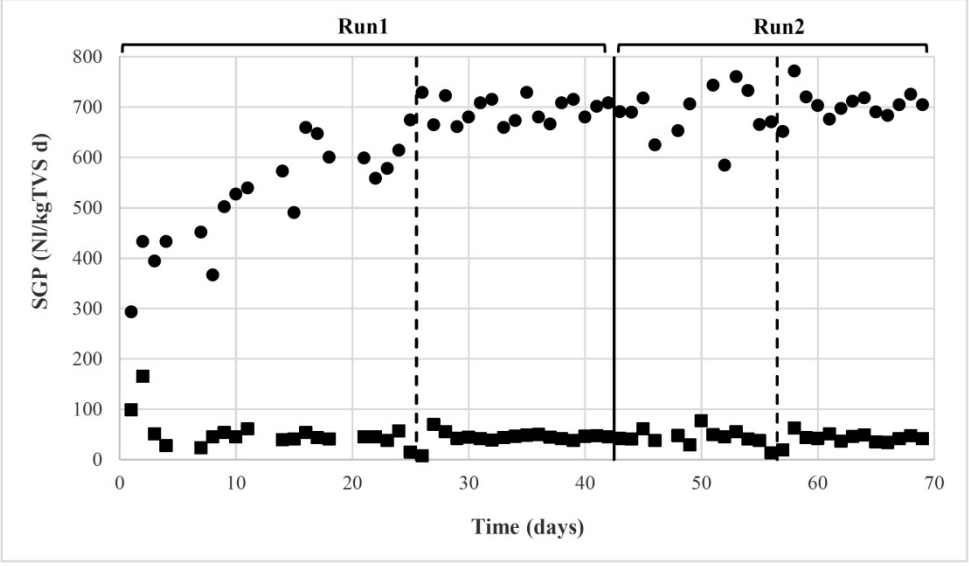


Fig. 4 Specific Gas Production (SGP) in R1-H_2 (■) and R2-CH_4 (●)



4. Conclusions

The physical separation of the two anaerobic phases with the presence of a preliminary step of dark fermentation was demonstrated to be beneficial for the methanogenic phase. More specifically, the higher level of FW hydrolysis achieved during the fermentative phase improved methane production in the second stage. This was due to the production of organic acids in the fermentative reactor that were an optimal readily biodegradable substrate for the methanogenic phase. The total volatile solids removal efficiency increased of 6.8% while the total specific gas production increased of 7.7%. These results were obtained with a reduction of the total hydraulic retention time and a consequent increase of the amount of treated substrate. Indeed while the one-stage process was characterized by an HRT of 17 d, the whole HRT of the two-stage process was approximately 16 d. In addition, the fermentative reactor produced a hydrogen rich (22.9%) biogas that can used

either by itself or to improve the combustion performance of methane, making a mixture that simulates the composition of hythane.

Although no industrial-scale plants are currently available for the fermentative production of hydrogen from biodegradable residues or resources, this research contributed to demonstrate that simple biorefinery process schemes, such as the combined production of hydrogen and methane, would be suitable for increasing biofuel production from organic substrates.

Acknowledgements

The research was supported by the MIUR-Regione Toscana DGRT 1208/2012 and MIUR-MISE-Regione Toscana DGRT 758/2013 PAR FAS 2007-2013 in sub-programme FAR-FAS 2014 (Linea d'Azione 1.1).

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