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Energy recovery from one- and two-stage anaerobic digestion of food waste

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ABSTRACT

One- and two-stage anaerobic digestion of food waste aimed at recovering methane (CH_4) and hydrogen and methane ($H_2 + CH_4$), respectively, were compared in order to assess the potential benefits from the two-stage process in terms of overall energy recovery. Results suggest that a two-stage process where the first reactor is properly operated in order to achieve a significant net hydrogen production, may display a 20% comparatively higher energy recovery yield as a result, mainly, of enhanced methane production as well as of the associated hydrogen production. The highest methane production of the two-stage process was due to improved hydrolysis and fermentation of food waste, with increased amounts of volatile fatty acids being readily available to methanogenesis.

1. Introduction

In current applications of anaerobic digestion (AD) systems, organic matter is converted into a mixture of gaseous compounds, mainly methane (CH_4) and carbon dioxide (CO_2), via acid fermentation and volatile fatty acids (VFAs) degradation, and through the activity of two groups of microorganisms: acid-forming and methane-forming bacterial biomass, respectively (Zhang et al., 2016). In a single-reactor system, namely one-stage anaerobic digestion (1S-AD), those microorganisms are kept together in a balance, which is delicate, because both groups differ widely in terms of physiology, nutritional needs, growth kinetics, and sensitivity towards environmental conditions (Demirel and Yenigün, 2002). By way of example, the pH prevailing in 1S-AD systems (pH between 7 and 8) does not provide optimal growth conditions for acidifying hydrolytic bacteria, leading to inefficient hydrolysis/fermentation rates (especially for slowly degradable lignocellulosic substrates) and, in turn, diminishing biogas production (Giovannini et al., 2016). Considering these aspects, Pohland and Ghosh (1971) proposed the two-stage AD system (2S-AD), where the sub-processes organic matter hydrolysis and its fermentation to organic acids are physically separated from the methane production process.

Since then, the comparison of the performances of 1S-AD and 2S-AD has been debated extensively, and advantages/drawbacks of both systems have been considered and evaluated by several authors (Demirel and Yenigün, 2002; Reith et al., 2003; Han and Shin, 2004; Liu et al., 2006; Gómez et al., 2006, 2009; Ueno et al., 2007; Cooney et al., 2007; Chu et al., 2008; Thompson, 2008; Dong et al., 2011).

In 2S-AD systems, the physical separation of the reactors responsible for the two independent processes enables optimal conditions for the acidogenic and the methanogenic bacterial biomass to be established, thus optimising specific metabolic activities and ultimately maximising methane generation (Schievano et al., 2014). Moreover, the first acidogenic reactor may act as an effective buffer against sudden pH drops caused by accumulation

Abbreviations: 1S-AD, one-stage anaerobic digestion system; 2S-AD, two-stage anaerobic digestion system; AD, anaerobic digestion; AS, activated sludge; CSTR, continuously stirred tank reactor; DOC, dissolved organic carbon; FW, food waste; G_{max}, maximum gas yield; ISR, inoculum-to-substrate ratio; MS, methanogenic sludge; OBS_{H2}, observed H_2 production; R_{max}, maximum gas production rate; SER, specific energy recovery; SHP, specific hydrogen production; SMP, specific methane production; t_{95}, time required to attain 95% of the maximum biogas yield; TAN, total ammonia nitrogen; $THEO_{H2}$, theoretical H_2 production; TOC, total organic carbon; TS, total solids; VFAs, short-chained volatile fatty acids; VS, volatile solids; λ, lag phase duration.

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of VFAs, which may hinder methanogenic microorganisms. As a consequence, higher process reliability, resilience, stability, as well as higher substrate conversion are anticipated for 2S-AD systems.

Nevertheless, 1S-AD is a well-established system for the treatment of organic waste, characterised by a simple set-up and relatively limited investment and operating costs, and as a matter of fact most of the full-scale digestion plants in Europe (90% of the installed AD capacity) are designed and operated as one-stage systems (Rapport et al., 2012). A major drawback with 1S-AD is that the produced biogas is frequently reported to display a poor quality in terms of its calorific value (Zhang et al., 2015; Sunyoto et al., 2016).

The issue of operating AD in the 2S-AD configuration has become again topical in recent years as a result of the interest aroused by the possibility of producing bio-hydrogen from organic substrates through dark fermentation (Lee and Chung, 2010; Dong et al., 2011; De Gioannis et al., 2013; Cappai et al., 2014). Indeed, under appropriate operating conditions, facultative or strict anaerobic microorganisms are able to convert organic substrates into bio-H_2 through fermentation; the H_2 produced is recoverable, provided that a harsh environment for hydrogenophylic methanogens is guaranteed. In addition to H_2 and CO_2, which are the most abundant gaseous products, a mix of volatile fatty acids (VFAs) and reduced end products including alcohols is generated as well, which is suitable for further valorisation. This can be accomplished through a variety of potential alternatives, differing for the type of process applied and/or the characteristics of the resulting product (s). The subsequent treatment phase downstream of fermentation may possibly include: 1) a second anaerobic digestion stage for CH_4 production; 2) a photofermentation stage aimed at H_2 production; 3) a microbial electrolysis cell devoted to H_2 production; 4) a microbial fuel cell for direct electricity generation; 5) a biochemical stage for biopolymer production. Hydrogen has the highest energy content per unit weight (142 MJ/kg) of any known gaseous fuel, and sequential H_2 and CH_4 production is, from a theoretical point of view, energetically more favourable than 1S-AD (Dong et al., 2009); from a practical point of view, the two gas streams may be valued individually, or mixed to form a hydrogen-enriched biogas (namely bio-hythane) characterised by an improved quality for gas engines applications (Porpatham et al., 2007). However, H_2 recovery through dark fermentation of organic substrates is not yet considered neither technically reliable nor commercially attractive. Assessing the increased overall energy recovery and, in particular, also higher CH_4 yields of 2S-AD systems could greatly contribute to the affirmation of fermentative hydrogen production as a viable process.

Few studies are available that provide ultimate answers about the advantages of AD operated in two distinct phases (Aslanzadeh et al., 2014); even fewer, in particular, provide a comparison between 1S- and 2S-AD where the latter is contextualised and focused on the possibility of combining the recovery of both H_2 and CH_4 from a complex substrate such as food waste (FW). Voelklein et al. (2016) operated a two-stage anaerobic CSTR observing a methane yield from FW ranging between 371 and 419 NL CH_4/kg VS, 23% higher than from the one-stage process; no data on H_2 production were observed because, as reported by the authors, the goal was to optimise the acidification process and maximise methane yield rather than to produce H_2. Grimberg et al. (2015) achieved a methane production yield from FW of 446 NL CH_4/kg $VS_{removed}$ in a two-stage CSTR-based process, fairly higher than the yield of 380 NL CH_4/kg $VS_{removed}$ observed in a one-stage process (no available data about H_2 production were provided). Aslanzadeh et al. (2014) evaluated the effects of organic loading rate and hydraulic retention time on CH_4 production in one- and two-stage systems treating municipal FW: a maximum methane production of 380 NL CH_4/kg VS was obtained in the two-stage process versus a maximum of 330 NL CH_4/kg VS observed in the one-stage. Nathao et al. (2013) compared the performance of one- and two-stage mesophilic AD of FW in batch reactors at varying ratios of feedstock to microbial inoculum (F/M), observing yields of 55 NL H_2/kg VS and 94 NL CH_4/kg VS at food to microorganisms ratio of 7.5 in the two-stage process, to be compared with a CH_4 yield of 82 NL/kg VS attained in the one-stage system. Interesting economic considerations were derived by Lee and Chung (2010) who managed a two-stage pilot-scale process treating FW, connected to a PEM (Proton Exchange Membrane) fuel cell. When single CH_4 and combined $H_2 + CH_4$ production were compared, negligible differences in the production costs were estimated, whilst a gain by 12–25% in terms of overall energy production was observed for the two-stage system.

The objective of the present study was to compare 1S- and 2S-AD of a complex substrate (FW) aimed at recovering CH_4 and $H_2 + CH_4$, respectively. Batch tests were performed under mesophilic conditions, the performances in terms of H_2 and CH_4 yields and volatile solids removal efficiency were evaluated, and the overall energy recoverable from the two AD systems was estimated.

2. Materials and methods

2.1. Substrate and inocula

Due to the inherent heterogeneity of municipal FW, a standardised FW was used in the present study to allow repeatable and directly comparable experiments. FW was prepared by mixing (on a wet weight basis) 10% of meat, 65% of fruit and vegetables, 10% of bread and 15% of cooked pasta. Due to their tendency to rapid degradation, FW samples were purposely prepared for each experiment by mixing the individual components and shredding the obtained mixture with a blender (RETSCH Knife Mill Grindomix GM200) to a final particle size below 2 cm. This particle size range was adopted in order to be compatible with the pumping and mixing systems of the bench-scale reactors. The adopted shredding conditions were capable of producing a homogeneous mixture while keeping energy consumption to a minimum, in accordance with a typical AD process layout.

Activated sludge (AS) from the aerobic unit of a municipal wastewater treatment plant was used to inoculate the first phase of the 2S-AD test, without performing any specific treatment to inhibit methanogens, as suggested by the results presented in Cappai et al. (2014).

Methanogenic sludge (MS), collected from the anaerobic digester of a municipal solid waste treatment plant operated under mesophilic conditions at an HRT of 14–16 days, was used as the inoculum in both the 1S-AD test and in the second phase of the 2S-AD test. The MS inoculum was preliminarily maintained under anaerobic conditions in the reactor at 39 ± 1 °C until biogas production stopped in order to deplete the residual biodegradable organic material, as also suggested by Raposo et al. (2011).

The main characteristics of the FW, of the inocula and of the feeds are shown in Table 1. As the feeds were analysed before each experiment, the values in Table 1 are reported as mean and standard deviations of 4 replicates, while FW and inocula were analysed in triplicate.

2.2. Experimental set-up

The methanogenic test (1S-AD) was conducted in a batch mode at 39 ± 1 °C using a 2-L glass reactor (BIOFLO 110 - New Brunswick Scientific; BioCommand Lite software; 1.8 L working volume). An inoculum-to-substrate ratio (ISR) of 2 g $VS_{inoculum}$/g $VS_{substrate}$ was adopted in order to limit inhibition effects associated with

Table 1
Main characteristics of concern for FW, inocula and feeds for the 1S-AD and 2S-AD tests (average value ± standard deviation).

Parameter	Unit of measure	FW	AS	MS	Test		
					1S-AD	2S-AD	
						1st stage	2nd stage
Initial pH	–	5.5 ± 0.2	7.1 ± 0.1	7.8 ± 0.1	7.6 ± 0.1	6.9 ± 0.1	7.3 ± 0.1
TS	% wt	22.6 ± 1.3	0.9 ± 0.1	5.2 ± 0.3	6.4 ± 0.2	4.1 ± 0.3	4.2 ± 0.2
VS	% wt	22.0 ± 1.2	0.6 ± 0.1	3.0 ± 0.2	4.3 ± 0.3	3.8 ± 0.4	2.4 ± 0.5
TOC	% TS	46.2 ± 0.4	36.4 ± 0.3	24.3 ± 0.6	29.2 ± 1.4	44.5 ± 2.7	30.1 ± 2.3

accumulation of intermediate compounds, such as VFAs, during substrate degradation (Raposo et al., 2011).

The hydrogenogenic + methanogenic test (2S-AD) was conducted in a batch mode at 39 ± 1 °C using a 2-L glass reactor (1.8 L working volume) for the first stage and a 5-L glass reactor (DIAFERM - Diachrom SA; Dia-Net software; 4.5 L working volume) for the second stage. The effluent from the fermentative-hydrogenogenic reactor was fed to the methanogenic stage after mixing with MS according to the same ISR adopted for the 1S-AD test (2 g $VS_{inoculum}$/g $VS_{substrate}$). All the reactors were equipped with mechanical stirring (150 rpm) and automatic pH control through NaOH addition. An operating pH set-point value of 6.5 and an ISR of 0.14 g $VS_{inoculum}$/g $VS_{substrate}$ were adopted for the first stage of the 2S-AD test, as suggested by Cappai et al. (2014). On the basis of preliminary tests, control of operating pH was not deemed necessary in the 1S-AD test and in the methanogenic stage of the 2S-AD test. This assumption proved to be correct on the basis of the periodic pH measurements taken during the experiments.

Biogas production was assessed by the volume displacement principle. The measured gas volume was converted to standard temperature and pressure conditions (T = 0 °C, p = 1 atm).

All reactors were flushed with N_2 gas to drive off air from the headspace before starting the experiments.

2.3. Analytical methods

All analyses were conducted in triplicate (N = 3) and results are presented as average value of the replicates with associated standard deviation.

The contents of total solids (TS) and volatile solids (VS) were measured according to the APHA Standard Methods (APHA, Awwa, 1998). The total organic carbon concentration (TOC) and its soluble fraction (dissolved organic carbon (DOC), on 0.45 μm filtered samples) were measured using a Shimadzu TOC analyser equipped with modules for the analysis of both liquid and solid samples (TOC-VCSN and SSM-5000 module, Shimadzu, Japan). Total ammonia-nitrogen (TAN) was determined on 0.45 μm filtered samples according to the APHA Standard Methods (APHA, Awwa, 1998) using a Hitachi U-2000 spectrophotometer operated at a wavelength of 420 nm. The biogas was sampled periodically from the reactors with a 1-mL gastight syringe and injected through a valve in a gas chromatograph (Model 7890B, Agilent Technology) equipped with a thermal conductivity detector and two stainless columns packed with HayeSep N (80/100 mesh) and Shincarbon ST (50/80 mesh) connected in series. The operating temperatures of the valve and the TCD were 90 °C and 200 °C, respectively, and He was the carrier gas at a constant pressure of 8 psi in the HayeSep N column and 25 psi in the Shincarbon ST column (at 70 °C). The oven temperature was set initially at 70 °C (3-min holding time), followed by a ramp of 10 °C/min up to 160 °C (3-min holding time).

The concentrations of VFAs (acetic [HAc], propionic [HPr], butyric + iso-butyric [HBu], valeric + iso-valeric [HVa], hexanoic + iso-hexanoic [HHEx], heptanoic [HHep]) were determined using a gas chromatograph with Flame-Ionization Detection (Model 7890B, Agilent Technology) equipped with an HP-FFAP capillary column (30 m, inner diameter 0.53 mm, Agilent Technology). The samples were filtered using a 0.45 μm cellulose acetate filter and then acidified with concentrated H_3PO_4 (pH < 3). The injection volume was 0.6 μl. The temperatures of the injector and the detector were 250 °C and 300 °C, respectively. The oven temperature was initially set at 70 °C (3-min holding time), followed by a ramp of 20 °C/min up to 180 °C (3-min holding time). He (1.6 mL/min, split ratio 20:1) was used as carrier gas.

2.4. Kinetic model

The sigmoid-type modified Gompertz function was used to analyse and describe the H_2 and CH_4 production during each test. In the Gompertz model, the evolution of gas production G(t) over time is expressed as follows (Eq. (1)) (Zwietering et al., 1990; Lay et al., 1999):

$$G(t) = G_{max} \exp\left\{-\exp\left[\frac{R_{max} \cdot e}{G_{max}}(\lambda - t) + 1\right]\right\} \quad (1)$$

where G_{max} is the maximum gas yield, R_{max} is the maximum gas production rate, λ is the lag phase duration, and the value of "e" is 2.71828. The time required to attain 95% of the maximum biogas yield, namely t_{95}, was derived from the Gompertz equation as follows (Eq. (2)):

$$t_{95} = \frac{G_{max}}{R_{max} \cdot e}(1 - \ln(-\ln 0.95)) + \lambda \quad (2)$$

The experimental data were fitted with the Gompertz equation and G_{max}, R_{max}, λ, and t_{95} were estimated using the software TableCurve 2D (v. 5.01, Systat Software Inc.). Dedicated statistical parameters including the coefficient of determination, the fit standard error and the F statistics were adopted to judge the goodness of fit for each experimental data set.

2.5. Calculations

The hydrolysis and the acidification yields (%) were calculated for the first stage of the 2S-AD test as expressed in Eqs. (3) and (4) (Graunke and Wilkie, 2014; Voelklein et al., 2016):

$$\textit{hydrolysis yield}\ (\%) = 100 \times DOC/TOC_i \quad (3)$$

$$\textit{acidification yield}\ (\%) = 100 \times VFAs/DOC \quad (4)$$

where TOC_i is the initial total organic carbon concentration and VFAs is the concentration of net VFAs (final-initial) expressed as g C/L.

In order to provide information on the accuracy of the measurement of the amount of biogas produced, the following calculation was performed for each test:

$$\textit{gasified portion of TOC removed}\ (\%) = \frac{100 \times C_{gas}}{TOC_{initial} - TOC_{final}} \quad (5)$$

where C_{gas}, $TOC_{initial}$, and TOC_{final} are the organic carbon mass in the produced gas, in the influent at the beginning of the test and in the effluent at the end of the test, respectively.

The specific methane production (SMP) for the 1S-AD test was expressed as the methane produced per unit mass of initial VS added to the methanogenic reactor. As for the 2S-AD test, the specific hydrogen production (SHP) was calculated per unit mass of initial VS added to the first reactor and, in order to consider the performance of the whole system, the SMP for the second reactor was calculated as the methane produced per unit mass of initial VS added to the first reactor, as indicated also by Schievano et al. (2014).

The specific gas production, either SHP or SMP, was converted to a specific energy recovery (SER) per unit mass of VS added to the two systems (1S-AD and 2S-AD). The SER was calculated by considering the lower heating value of H_2 and CH_4, equal to 12.74 MJ/Nm^3 and 35.16 MJ/Nm^3, respectively (Schievano et al., 2014).

3. Results and discussion

3.1. One-stage process (1S-AD test)

3.1.1. Methane production

Although the operating pH was not controlled during the 1S-AD test, the observed pH values (7.3–7.8, data not shown) were found to lie within the recommended range for methanogenesis (6.5–8) (Mtz.-Viturtia et al., 1995) for the entire duration of the experiments.

Fig. 1(a) shows the specific CH_4 production (SMP) cumulative curve and the evolution over time of the CH_4 content in the gas produced. The methane content increased up to about 66% vol. after the first 50 h, then remained fairly constant until the test was stopped. The overall SMP (328.6 NL CH_4/kg VS) is within the range of values reported by other authors for 1S-AD of FW performed under similar operating conditions, though significant differences may be found in the literature which reflect the influence of a number of factors, mainly the FW composition in terms of carbohydrates, proteins, and lipids (which in turn depends on the geographic origin and seasonal variability of food and the specific eating habits (Zhang et al., 2014)). Browne and Murphy (2013) observed a SMP of 358 NL CH_4/kg VS in AD batch test on FW. Cabbai et al. (2013) reported a SMP of 364 NL CH_4/kg VS from household waste. El-Mashad and Zhang (2010) attained a SMP of 353 NL CH_4/kg VS from FW.

A rapid accumulation of acetate, up to 1380 mg/L, was detected during the first 24 h and almost completely degraded afterwards up to roughly 70 h from the beginning of the test (Fig. 1(b)). Additionally, a significant accumulation of propionate, with a concentration of around 1600 mg/L, was detected during the first 50 h, followed likely by transformation to acetate and syntrophic conversion to methane. The overall residual VFAs concentration was found to be almost negligible after around 150 h. As for substrate conversion, the final VS removal efficiency was 53.3% and the amount of gasified carbon was found to account for 97.4% of the TOC removed (Eq. (5)).

The Total Ammonia Nitrogen (TAN) concentration at the end of the 1S-AD test was 1300 mg/L, lower than the level of 3000 mg/L commonly reported to exert toxic effects (Wu et al., 2016), and no evidence of hindering of biomass activity by an ammonia excess was gained from the experimental results.

3.1.2. Reaction kinetics

The kinetic parameters derived from fitting of the experimental data with the Gompertz equation (Eq. (1)) are shown in Table 2. The model fitting was high, with an R^2 of 0.990. The estimated maximum methane production rate was 3.89 NL CH_4/(kg VS_*h) (Table 2), similar to that obtained by Yin et al. (2016) for batch AD tests performed on FW. The calculated lag phase duration resulted to be fairly short (4.5 h), as observed also by Elbeshbishy et al. (2012), who performed methanogenic tests on FW, and the t_{95} was equal to 125 h, confirming the high rate of biodegradation of the substrate.

3.2. Two-stage process (2S-AD test)

3.2.1. First stage – hydrogen production

Fig. 2(a) shows the specific H_2 production (SHP) cumulative curve and the evolution over time of the H_2 content in the gas produced during the first stage of the 2S-AD test. The hydrogen content peaked at 66% vol. during the first 12 h, then decreased continuously until the test was stopped, presumably due to biological H_2 consumption. To this regard, the fact that methane was never detected during the first stage of the 2S-AD test may imply that H_2 consumption was caused by the onset of either propionic fermentation (Dong et al., 2010) or homoacetogenesis (Siriwongrungson et al., 2007; Saady, 2013).

The total SHP attained (56.5 NL H_2/kg VS) falls within the range of values reported by other authors for fermentative hydrogen production from FW under similar operating conditions, though it is again worth mentioning that wide ranges of values have been reported (De Gioannis et al., 2013; Cappai et al., 2014). Hydrogen production lasted about 26 h and a final VS removal efficiency of 34.1% was estimated; the amount of gasified carbon was found

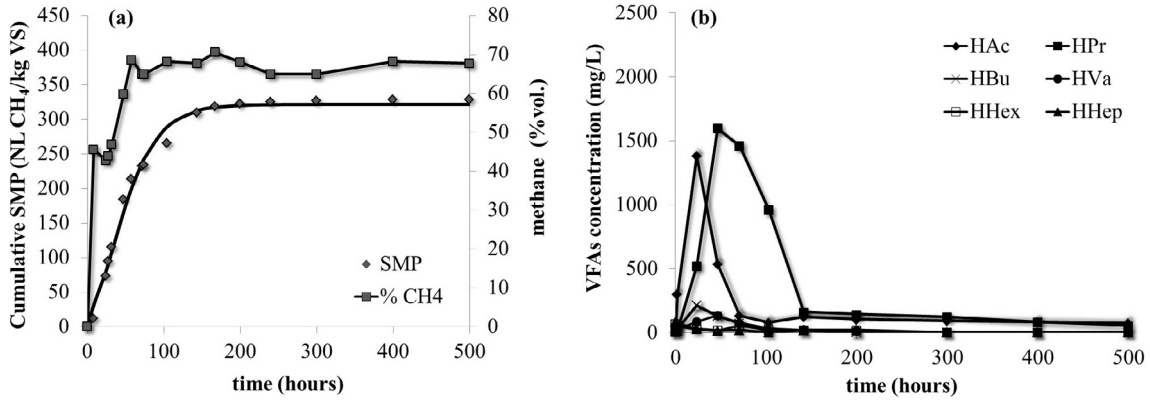

Fig. 1. 1S-AD test: evolution over time of (a) specific CH_4 production (SMP; solid line indicates Gompertz-model curve) and CH_4 content in the gas produced, (b) VFAs concentration.

Table 2
Kinetic parameters calculated for the 1S-AD and 2S-AD tests.

Mathematic model	Estimated parameter	Unit	1S-AD (CH_4)	2S-AD	
				1st stage (H_2)	2nd stage (CH_4)
Gompertz model	G_{max}	NL (CH_4 or H_2)/kg VS	321.7	58.6	380.1
	R_{max}	NL (CH_4 or H_2)/kg VS h	3.89	3.84	2.37
	λ	h	4.47	4.15	20.4
	t_{95}	h	125.1	26.4	250.6
	R^2	–	0.990	0.988	0.996

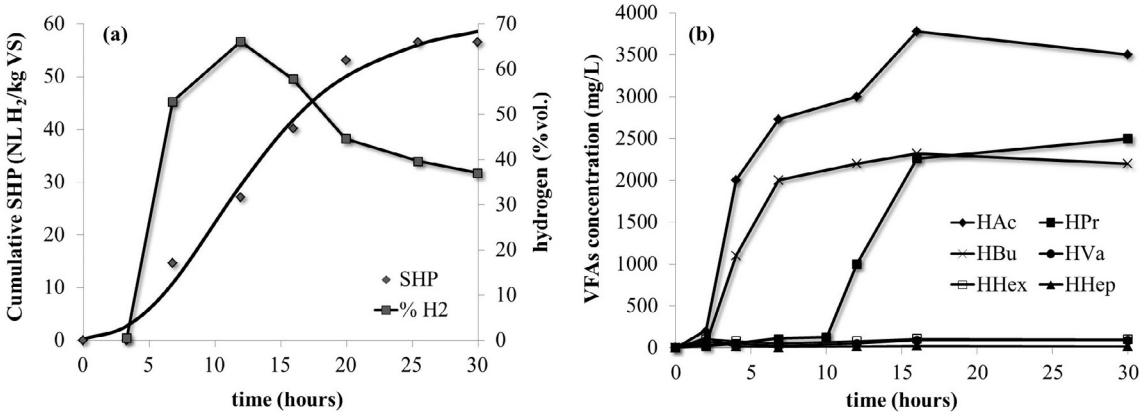

Fig. 2. 2S-AD test, first stage: evolution over time of (a) specific H_2 production (SHP; solid line indicates Gompertz-model curve) and H_2 content in the gas produced, (b) VFAs concentration.

to account for 97% of the TOC removed (Eq. (5)). The losses due to CO_2 production accounted for about 4% of the carbon fed to the system. Therefore, most of the carbon was still in the liquid phase at the end of the first stage and available for further conversion in the second stage, as reported also by Alibardi and Cossu (2016).

Fermentable sugars generated from carbohydrates by hydrolytic bacteria enable the rapid growth of acidogens, which generate hydrogen via the acetic and butyric pathways (Eqs. (6) and (7)):

$$C_6H_{12}O_6 + 2\,H_2O \rightarrow 2\,CH_3COOH + 2\,CO_2 + 4\,H_2 \quad (6)$$

$$C_6H_{12}O_6 \rightarrow CH_3(CH_2)_2COOH + 2\,H_2 + 2\,CO_2 \quad (7)$$

The analysis of VFAs generation over time indicated the main presence of acetate (55% of total VFAs, 2730 mg/L) and butyrate (41% of total VFAs, 2000 mg/L) during the first 7 h of fermentation, while propionate was found to be produced at later stages (Fig. 2 (b)). At the end of the test, the total VFAs concentration was 8410 mg/L, with acetate (42%), propionate (30%) and butyrate (26%) as the major soluble products. According to Vavilin et al. (2008) and Graunke and Wilkie (2014), hydrolysis of particulate matter into soluble species is assumed to be the rate-limiting step in AD and, in this sense, essential in order to obtain an adequate biogas generation. The hydrolysis and acidification yields at the end of the hydrogenogenic stage were calculated to be 42.4% and 48.9%, respectively. The latter is higher than the values reported by Voelklein et al. (2016) (34%–41%) and Chen et al. (2015) (29%–36%).

It is interesting to note that Voelklein et al. (2016) also observed lower specific H_2 yields (1.7–11.8 L/kg VS) as compared with the present study, with H_2 concentrations in the range of 5.6–16.2% vol., pointing out that the process was arguably not optimised for H_2 production, while no data on the observed H_2 production were provided by Chen et al. (2015).

As shown by Eqs. (6) and (7), the formation of acetate and butyrate is associated with a net production of H_2, whereas ethanol and propionate production are associated to H_2-neutral and H_2-consuming pathways, respectively. In order to derive information about the metabolic pathways taking place during the fermentation stage, the theoretical H_2 production ($THEO_{H2}$) was calculated assuming the generation of 2 mol H_2/mole acetate and butyrate produced and the consumption of 1 mol H_2/mole propionate produced (Jungermann et al., 1973; Li and Fang, 2007; Antonopoulou et al., 2008), and compared with the observed H_2 production (OBS_{H2}). The similarity between OBS_{H2} and $THEO_{H2}$, though fair (77.1%), indicates that processes other than acetic/butyric fermentation and propionic production took place, which may include homoacetogenic fermentation, a non-syntrophic reaction, where hydrogen and carbon dioxide are used to produce acetate; the onset of homoacetogenesis is also corroborated by the decrease in the H_2 content of the gas observed after about 10–12 h of fermentation (Fig. 2(a)). Although the effects of homoacetogenesis on dark fermentation may be relevant, it is still unclear whether homoacetogenic H_2 consumption acts during the entire fermentation process along with concomitant hydrogenogenic pathways, or it only occurs at some point during the process when the substrate gets depleted and the biomass is then forced to switch to different metabolic pathways (Saady, 2013). This and other aspects confirm how complex and intricate the hydrogenogenic fermentation process is. Therefore, the identification of operating conditions that optimise substrate hydrolysis and H_2 production and lead to a suitable outflow for methanogenesis in the second stage, is crucial to the overall energy balance of the 2S-AD system.

3.2.2. Second stage – methane production

Fig. 3(a) shows the SMP cumulative curve and the evolution over time of the CH_4 content in the gas produced during the second stage of the 2S-AD test.

The methane content in the gas produced was higher than that observed in the 1S-AD test, increasing gradually with time and peaking at 77% vol. (Fig. 3(a)). Therefore, the 2S-AD configuration allowed an enrichment of the methane content by 16.7% as

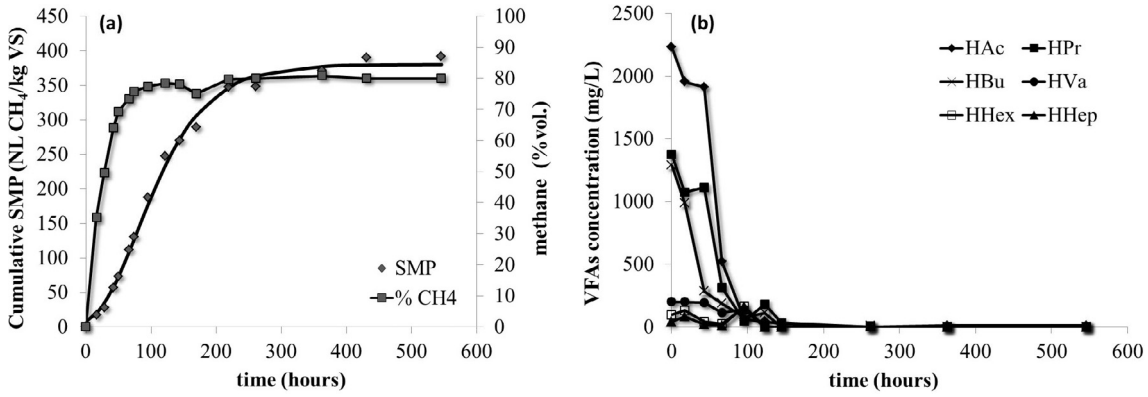

Fig. 3. 2S-AD test, second stage: evolution over time of (a) specific CH_4 production (SMP; solid line indicates Gompertz-model curve) and CH_4 content in the gas produced, (b) VFAs concentration.

compared to the 1S-AD. This is consistent with Voelklein et al. (2016), who stated that a hydrolysis/fermentative reactor may serve as a carbon dioxide stripping step, reducing the potential costs for upgrading the biogas to biomethane.

The total SMP attained (392 NL CH_4/kg VS) was 19% higher than that observed for the 1S-AD test, a result similar to that reported by Voelklein et al. (2016). The VS removal in the methanogenic stage was 46.9%, which led to a 66.7% overall removal for the entire process. The amount of gasified carbon was found to account for 97.5% of the TOC removed in the methanogenic stage (Eq. (5)).

A gradual decrease in the VFAs concentration over time was observed (Fig. 3(b)), which resulted in a total removal of 97%, and control of the operating pH was not necessary as the pH values were always within the recommended range for methanogenesis (pH span 7.4–7.8, data not shown). Finally, the TAN concentration at the end of the 2S-AD test was 985 mg/L, lower than the reported inhibition level of 3000 mg/L.

3.2.3. Reaction kinetics

The experimental biogas production data for each stage of the 2S-AD test were fitted with the Gompertz equation (Eq. (1)) and the derived kinetic parameters are reported in Table 2.

Concerning the first stage, the Gompertz model fitted well the experimental data (R^2 = 0.988). The estimated kinetic parameters were as follows: maximum hydrogen production rate = 3.84 NL H_2/(kg VS_*h), lag phase duration = 4.2 h and t_{95} = 26.4 h.

A good fitting was also observed for biogas production data in the second stage (R^2 = 0.996). The maximum rate of methane production was 2.37 NL CH_4/(kg VS_*h), lower than that calculated for the 1S-AD test (Table 2). This issue could be explained by a slight inhibition effect exerted by the significant VFAs concentration which characterised the inflow to the second stage in the 2S-AD test, and is also mirrored by the much longer, as compared with the 1S-AD test, lag phase duration (20.4 h vs 4.5 h) and t_{95} (250 h vs 125 h). However, despite the lower methane production rate estimated for the 2S-AD, the longer production period (about 430 h versus 200 h) allowed for a higher SMP as compared to the 1S-AD test.

3.3. Specific energy recovery calculation

A comparison of the specific energy recovery (SER) values was conducted for the 1S-AD and 2S-AD process configurations. Such a comparison was made on the basis of the observed biogas production in the two cases as explained in Section 2.5.

The global SER from the 2S-AD was calculated to be 14.5 MJ/kg VS; in particular, H_2 production in the first stage accounts for 5% (0.7 MJ/kg VS) of the total energy generated, while the contribution of CH_4 production during the second stage is as high as 13.8 MJ/kg VS. Both values are within the range reported by Schievano et al. (2014) for 2S-AD of fruit/vegetable waste.

As for the 1S-AD test, the methane production corresponded to a SER of 11.6 MJ/kg VS, 20% less than the overall SER attained with 2S-AD test, as expected, and also even lower than that associated to the second stage of the 2S-AD test.

These results clearly show that adopting the two-stage configuration for the AD process results in a 20% comparatively higher energy recovery yield, which is mainly ascribed to the improved digestion conditions induced in the methanogenic stage.

4. Conclusions

One- and two-stage anaerobic digestion of food waste aimed at recovering methane and hydrogen plus methane, respectively, were compared in order to assess the benefits associated with the two-stage approach in terms of overall energy recovery. The results obtained suggest that a two-stage process where the first reactor is properly operated in order to achieve a significant net hydrogen production, may display a 20% comparatively higher energy recovery yield as a result, mainly, of enhanced methane generation, as well as of the associated hydrogen production.

The highest methane production of the two-stage process, observed despite the hydrogen recovered is a potential substrate for methanogenesis, was due to improved hydrolysis and fermentation of food waste with increased amounts of volatile fatty acids being readily available to methanogenesis. This figure, if on one hand resulted in a slight inhibition effect on the methanogens, as revealed by the slower methanogenic kinetics and the longer lag-phase duration compared to the one-stage anaerobic digestion, nevertheless allowed to achieve a higher specific methane potential over a hydraulic retention time of manageable duration.

Although not directly assessed in the present study and thus requiring further specific quantification, additional advantages of the two-stage configuration in terms of the overall environmental profile of the investigated process may also be anticipated. In particular, the 25% increase in volatile solids removal achieved in the two-stage anaerobic digestion system (66.7% VS removal vs. 53.3%) also implies a higher degree of digestate stabilisation, which may represent a relevant indirect effect when the subsequent treatment requirements and the final destination of digestate are concerned. Potential indirect outcomes on the carbon footprint of the two-stage process are also expected. These are mainly related to the avoided CO_2 emissions deriving from biogas energy use, to the absence of CO_2 in the emissions generated by hydrogen

combustion, to the reduced energy demand of the digestate treatment units as well as to the reduced use of synthetic soil amending agents (if digestate is to be used for agronomic purposes). As mentioned above, a specific quantification of all such effects requires a dedicate study to account the positive and negative, direct and indirect CO_2 burdens of the investigated process, which was beyond the scopes of the present work.

At the moment, there are no industrial-scale plants for the fermentative production of hydrogen from biodegradable residues or resources. It is the opinion of the authors that a combined process which, besides allowing the recovery of hydrogen, also produces more methane than a one-stage one may boost the interest of technicians and companies in the fermentative production of hydrogen.

Moreover, the production of methane from biodegradable waste, and even more that of hydrogen, are processes naturally included in the biorefinery concept, which is currently regarded as a means to thoroughly apply the principles of circular economy in the management of organic residues. However, one of the major concerns that cast shadows on a possible implementation of the waste biorefinery concept is linked to the required plant size, considered by many to be very high and not compatible, for acceptable waste transport distances, with the European scenario. In Europe, therefore, simple biorefinery process schemes, such as the combined production of hydrogen and methane, would be more suitable, at least in the short-medium term.

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