Scale-up evaluation of the anaerobic digestion of food-processing industrial wastes

SCALE-UP EVALUATION OF THE ANAEROBIC DIGESTION OF FOOD-PROCESSING INDUSTRIAL WASTES

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ABSTRACT

This work proposes a semi-pilot scale procedure for the evaluation of biogas production potential and the employment of its results for the scale-up of the process. AD tests were performed at 35°C in 6 L reactors, feeding 3-6% w/w TS in a *fed-batch* mode. Several substrates, generated by food-processing industries, were considered in the study. Assuming solubilization as the limiting step, a theoretical model was proposed and the values of the disintegration kinetic constant (k_{dis}) were calculated from the experimental data. The obtained model was employed as a control tool during tests afterward performed on pilot scale in a 300 L digester fed in a semi-continuous mode. Biogas yields between 0.5 and 0.9 Nm^3/kg_{VS}, and methane contents of 55-63% v/v were obtained on both scales. The model derived from the results of the proposed procedure appeared adequate for a consistent evaluation of the scale-up of the AD process.

KEYWORDS: biogas, anaerobic digestion, food, waste, model

ABBREVIATIONS

AD: Anaerobic Digestion; B_{exp}: experimental biogas yield; B_{th}: theorethical biogas yield; ANOVA: Analysis of Variance; BMP: Bio-Methane Potential; C_{CH4}, C_{CO2}, C_{sub}: Carbon amount in methane, carbon dioxide and substrate; CH_4^{exp}: experimental methane yield; CH_4^{th}: % v/v methane calculated from stoichiometric equation; CHP: Combined Heat and Power; COD: Chemical Oxygen Demand; CSTR: Completely Stirred Tank Reactor; FOS/TAC: ratio between Organic Acids Concentration (Flüchitge Organische Säuren, FOS) and Total Alkalinity (Totales Anorganisches Carbonat, TAC); HRT: Hydraulic Retention Time; k_{dis}: disgregation kinetic constant; NVS: non volatile solids; OFMSW: Organic Fraction of Municipal Solid Waste; OLR: Organic Loading Rate; PMMA: Poly Methyl Methacrylate; SS: Suspended Solids; TOC: Total Organic Carbon; TS: Total Solids; VFA: Volatile Fatty Acid; VS: Volatile Solids; WWTP: Wastewater Treatment Plant.

1. INTRODUCTION

Food-processing industrial wastes correspond to an interesting substrate for the implementation of AD [1], being organic matrices characterized by properties that lay between the high lignin and cellulose contents of crops and the high acidity and relevant content of high soluble organics typical of food wastes. A summarized literature review of biogas and methane yields obtained from agricultural and food wastes is reported in Table 1. Wastes coming from rice, coffee, fruit and vegetables and food appear as the most promising substrates, with biogas yields comparable to WWTP sludge and OFMSW [2, 3]. Nevertheless AD of fruit and vegetable wastes is conventionally affected by a lack of stability [4], therefore two-stage reactors [5], pre-treatments [6-8] or co-digestion processes [9-13] are often adopted.

Substrate	Yield	% solids/mode/scale/T	k_{dis}	Reference
rape	$0.25\ m^3_{methane}/kg_{VS}$	$0.5\ VS_{sub}$,/VS_{in},w.w BMP/0.25 L/35°C	0.24	[14]
sunflower	$0.20\ m^3_{methane}/kg_{VS}$		0.23	
glycerol	$0.30\ m^3_{methane}/kg_{VS}$		0.50	
orange pulp	$0.25\ m^3_{methane}/kg_{VS}$		0.29	
pear pulp	$0.15\ m^3_{methane}/kg_{VS}$		0.18	
apple pulp	$0.18\ m^3_{methane}/kg_{VS}$		0.15	
trilicate	$0.76\ m^3_{biogas}/kg_{VS}$	n.s./BMP/1 L/37°C	0.21	[15]
maize silage	$0.73\ m^3_{biogas}/kg_{VS}$		0.21	
onion	$0.92\ m^3_{biogas}/kg_{VS}$		0.34	
potato	$0.83\ m3_{biogas}/kg_{VS}$		0.26	
rice husk and straw	$0.22\ m^3_{biogas}/kg_{VS}$	n.s./batch/190 L/35°C	n.a.	[16]
rice straw	$0.24\ m^3_{biogas}/kg_{VS}$	7.5% TS/batch/2.5 L/35°C	n.a.	[17]
rice chaff	$0.67\ m^3_{biogas}/kg_{VS}$	BMP/2 L/40.0 °C	n.a.	[18]
wheat straw	$0.57\ m^3_{biogas}/kg_{VS}$		n.a.	
dry bread	$0.65\ m^3_{biogas}/kg_{VS}$		n.a.	
rice straw	$0.42\ m^3_{biogas}/kg_{VS}$	n.s./batch/2 L/40°C	n.a.	[19]
tomato skins and seeds	$0.42\ m^3_{biogas}/kg_{VS}$			
grape stalk	$0.22\ m^3_{biogas}/kg_{VS}$			
pomace	$0.25\ m^3_{biogas}/kg_{VS}$			
coffee pulp and husk	0.65-0.73 $m^3_{methane}/kg_{VS}$	n.s.	n.a.	[20]
fruit and vegetable wastes	$0.32\text{-}0.63\ m^3_{biogas}/kg_{VS}$	n.s./batch/n.d/35-40°C	n.a.	[21]
olive mill and winery residues	0.18-0.21 m^3_{CH4}/kg_{COD}	n.s./batch/1 L/35°C	n.a.	[22]
brewery waste	$0.51\ m^3_{biogas}/kg_{VS}$	BMP/1-2 L/36.5°C	n.a.	[23]
bread waste	$0.58\ m^3_{biogas}/kg_{VS}$		n.a.	
vegetable wastes	$0.36\ m^3_{methane}/kg_{COD}$	BMP/0.12 L/35°C	n.a.	[24]
vegetable fats and oils	$0.23\ m^3_{methane}/kg_{COD}$		n.a. n.a.	
slaughterhouse wastes	0.13-0.26 $m^3_{methane}/kg_{COD}$		n.a.	
plain pasta	$0.33\ m^3_{methane}/kg_{VS}$	BMP/0.25 L/35°C	n.a.	[25]
cabbage	$0.26\ m^3_{methane}/kg_{VS}$		n.a.	
used vegetable oil	$0.65\ m^3_{methane}/kg_{VS}$		n.a.	
potatoes	$0.33\ m^3_{methane}/kg_{VS}$		n.a.	
cheese whey	$0.42\ m^3_{methane}/kg_{VS}$		n.a.	
food waste	$0.4\text{-}1.4\ m^3_{methane}/kg_{VS}$	BMP/0.2 L/35°C	n.a.	[26]
tomato processing waste	$0.33\ m^3_{methane}/kg_{VS}$	BMP/1.1 L/35°C	n.a.	[27]

n.s.: not specified; n.a.: not available

Table 1. Biogas and methane yields and k_{dis} values obtained from AD of some agricultural and food wastes considering batch/fed-batch feeding, BMP/laboratory scale, mesophilic conditions.

This research is focused on the evaluation of the feasibility of the AD of food-processing industrial wastes (coffee, rice, hazelnut, wine, sweets/snacks) in mono-digestion processes. The aim of this work is the assessment of a semi-pilot scale procedure for a reliable and easy to manage evaluation of biogas production potential of complex substrates with a high SS/COD ratio in mono-digestion processes. Several substrates were taken into account as homogeneous mixtures of wastes generated by different food-processing industries. Assuming solubilization as the limiting step for AD of the considered wastes, a theoretical model was proposed and the values of the disintegration kinetic constant (k_{dis}) were calculated from the experimental data gathered for each of the mixtures. AD tests were then repeated on pilot scale, and the previously obtained model was employed as a control tool during the digestion process.

The proposed semi-pilot scale procedure and the model derived from its results have the purpose to overcome the frequent limitations of conventional BMP tests about heterogeneous substrates. The here-presented data descend from tests performed on a higher scale than of traditional BMP/batch tests (see Table 1) and employing a different feeding mode (*fed-batch*), which is more oriented to the scale-up of the process.

2. MATERIALS AND METHODS

2.1. Substrates origin and characterization

The following materials, gathered from producers of Piedmont region within Ecofood project, were considered as substrates in semi-pilot scale tests:

- *coffee husk* (CH, removed with coffee bean shell) and *coffee dus*t (CD, grinded after roasting process);
- *raw hazelnut skin* (RHS, removed with hazelnut shell), *fine hazelnut skin* (FHS,

removed after roasting process), *large hazelnut skin* (LHS, removed after roasting process);

- *rice husk* (RH, removed in de-husking process), *rice bran* (RB, removed in whitening process):

- *cookie by-products* (C, from cookies production), *tea leaves* (TL, from tea beverage production), *snack-cake without cocoa* (SC, from snack cakes production), *cocoa cream by-products* (CC, from cocoa cream production), *cocoa husk* (CH, removed during cocoa beans de-husking);

- *pomace* (P, removed after grapes pressing), *lees* (L, removed after each fermentation step in wine production).

Two different *lees* samples (L1 and L2), showing different physic-chemical features, underwent the tests: L1, collected in October at the end of harvest period, was employed for semi-pilot scale tests; L2, collected in April, was employed for the pilot scale test. L2 sample exhibited detectable sulfur content, due to the use of sulfur dioxide, which produces sulfites, as anti-oxidant in intermediate phases of wine production

Pilot scale tests involved the following substrates:

- *lees* (L_2 sample): fed at an average of 4.3% TS, taking into account a HRT equal to 30 days and a resulting average OLR equal to 1.45 g_{TS}/L*d;

- *rice mixture* (same composition as in the semi-pilot scale tests) was considered in two tests, performed in sequence (a complete degassing was executed after each test):

- in *test 1* the substrate was fed at an average of 3% TS, considering a HRT equal to 20 days and a resulting average OLR equal to 1.50 g_{TS}/L*d;

- in *test 2* the amount of the substrate was enhanced at 6% TS, considering a HRT equal to 20 days and a resulting average OLR equal to 3.00 g_{TS}/L*d.

The considered substrates underwent the analysis of pH, TS and VS according to standard methods [28]. An Orion 420A pH-meter and a Kern MLS-N thermo-balance were employed to analyze pH and TS content. The elemental analysis was performed through a CHNS-O Thermo Fisher Flash 2000 Analyzer EA 1112.

(A)

(B)

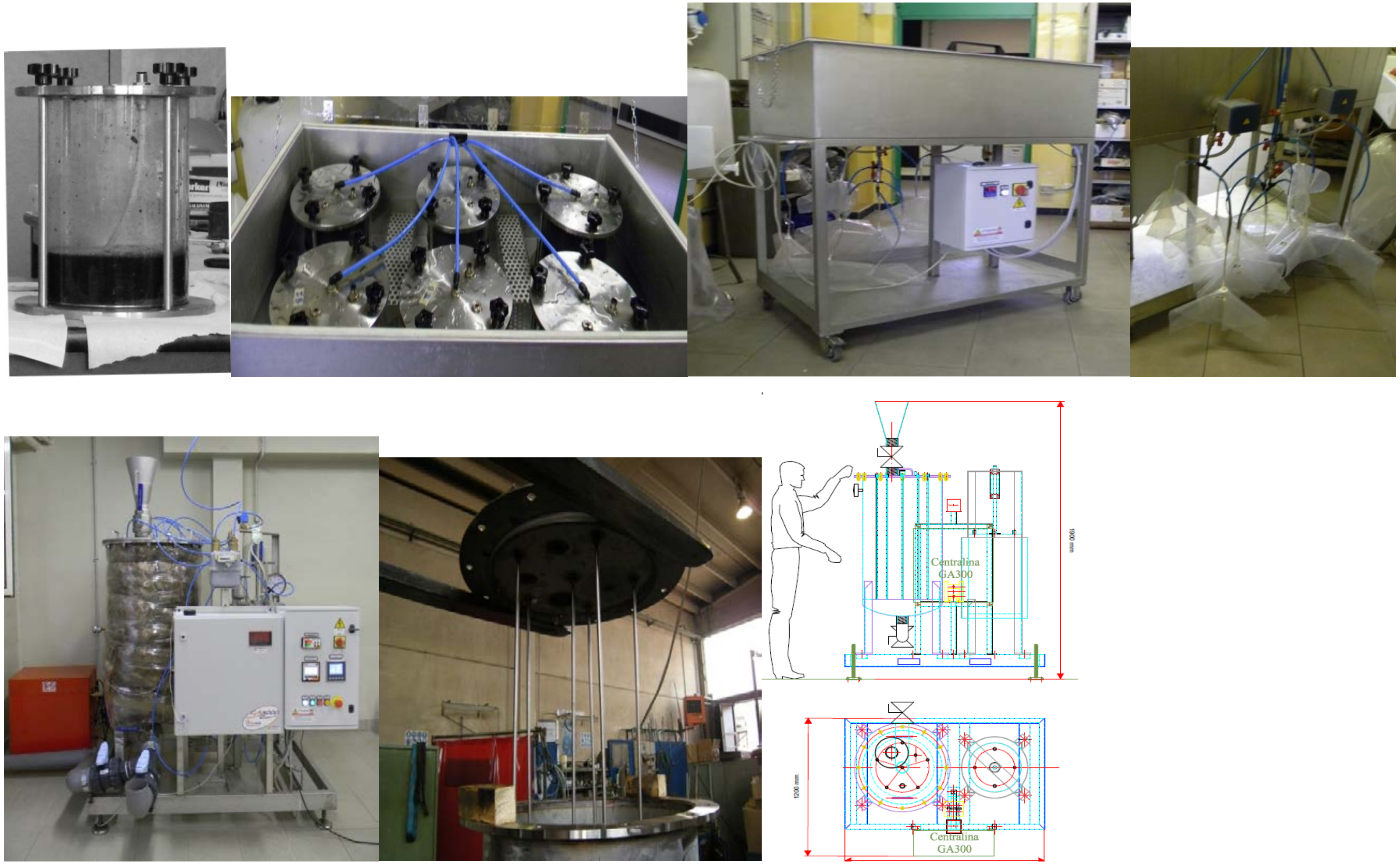


Figure 1. Experimental apparatus employed for (A) semi-pilot scale tests and (B) pilot scale tests

assuming Oxygen content as the complementary fraction towards C, H, N, S amounts. COD was analyzed according to Raposo method [29]. All the analyses were conducted in five replicates.

2.2. AD tests (semi-pilot scale)

The tests were performed in mesophilic conditions (35°C) employing six reactors (6 L PMMA digesters, 3 L working volume) for each mixture, made of unaltered samples (see Figure 1A). The inoculum was prepared employing fresh digestate provided by local WWTP, performing a complete degassing procedure [30]. The same inoculum was employed for all the semi-pilot scale tests that were executed consecutively. Between the digestion of two consequent substrates a transition protocol was established: 150 mL of fresh primary sludge from local WWTP was fed to the digesters as a single addition and a complete degassing procedure was performed.

The feeding was performed in a *fed-batch* mode: 3% TS, content was reached after six 0.5% TS supplements (one every two days) during 11 days; these percentage are referred to the total mass of solids present inside each digester. 6% TS content (only considering CC and CH materials) was achieved after six 1% TS additions. The substrates were added as unaltered materials. The reactors were manually mixed once a day. The tests were considered concluded when the observed variation in the cumulative production was below 1%. TS and VS were analyzed in the digestate before and after each cycle of digestion. Biogas volume (by water displacement) and components (through a Biogas Check analyzer, Geotechnical Instruments Ltd) were determined daily in each digester, as well as pH. Biogas was characterized in terms of CH_4, CO_2, O_2 and “balance” (i.e. all the gases that are different from the first three).

The identification of the single reactors was randomized in each test to avoid any memory effect of previous digestions. Furthermore, with the aim to evaluate the influence of the sequence of the feedstocks in the AD tests, the first substrate (a mix of CH and CD) was again digested at the end of the sequence.

2.3. AD tests (pilot scale)

The tests were performed at 35°C in a 300 L reactor (240 L working volume), equipped with an 80 L gasometer and a system for on-line monitoring of biogas volume and composition (see Figure 1B). Mixing inside the reactor was achieved through biogas re-circulating for 15 minutes at every hour. Digestate was daily analyzed for pH, TS, VS. The inoculum was prepared from digestate provided by local WWTP and properly degassed [30]. The start-up procedure was performed before the pilot-scale tests on the different considered substrates. FOS/TAC, that is the ratio between Organic Acids Concentration (FOS, expressed as mg/L of equivalents of acetic acid) and Total Alkalinity (TAC, expressed as mg/L of $CaCO_3$), was monitored daily in the digestate according to a reference procedure [31].

The feeding was performed in a *semi-continuous* mode. The unaltered substrates were fed to the digester after a pre-mixing phase, in which a proper volume of water, necessary to achieve the desired TS content, was added. When a whole HRT passed the feeding was stopped and the tests were declared concluded when no significant biogas production was detected. Biogas was continuous characterized in terms of CH_4, CO_2, O_2 and "balance" (i.e. all the gases that are different from the first three) through a GA3000 Range Gas Analyzer, Geotechnical Instruments Ltd.

3. MODELLING APPROACH

Solubilization (made of disintegration and hydrolysis*)* is generally assumed as the rate-limiting step during AD of complex substrates with a high SS/COD ratio [32]. It can be proven that the hydrolysis is the rate-limiting step during the uninhibited anaerobic digestion of complex particulate substrate [33]. Moreover, disintegration has the slowest kinetic in the solubilization step [14, 34] and it may be considered as a bottleneck. Disintegration may be considered a surface phenomenon, which is heavily affected by the structure of the particulate matter and by the availability of free accessible surface area.

Assuming a first order kinetic model, the disintegration rate may be achieved through the first part of the cumulative biogas curve obtained from BMP tests [30], according to Eq. (1).

$$B(t) = B)_{exp}(1 - e^{-k_{dis}t}) \quad (1)$$

where:

$B(t)$ represents the cumulative biogas/methane production at a given time

B_{exp} is the ultimate biogas/methane potential yield of the substrate

k_{dis} is the first order disintegration rate [day^{-1}]

t is the time [day]

However the drawback of this approach is that k_{dis} value changes depending on the time used to estimate it [35]. In this framework appears licit to consider if it may be possible, in the analysis of AD of a complex substrate, to derive robust values of a first order k_{dis} from biogas cumulative curves obtained from fed-batch tests. With the aim to assess the robustness of the experimental parameters (k_{dis} and B_{exp}) gathered from semi-pilot scale tests, a model predicting daily biogas production in a semi-continuous CSTR reactor, was designed. The daily biogas production at *t-th* day of experimentation was calculated by means of Eq. (2).

$$B(t) = k_{dis} \times S_e(t) \times B_{exp} \times V_w \quad (2)$$

where the parameters represent:

k_{dis}: first order disintegration rate [day^{-1}]

V_w : working volume of the digester (CSTR) [m^3]

B_{exp} : ultimate biogas/methane potential yield of the substrate [Nm^3/kg_{VS}]

$S_e(t)$: apparent concentration of Volatile Solids into the digester [kg_{VS}/m^3]. This parameter represents the amount of biodegradable VS. If B_{exp} was identical to the theoretical value it means that not biodegradable VS content in the substrate is negligible.

The $S_e(t)$ was calculated by the resolution of the following differential equation (3):

$$\begin{cases} \frac{dS_e(t)}{dt} = \frac{q(t) \times S_o(t)}{V_w} - \frac{q(t) \times S_e(t)}{V_w} - k_{dis} \times S_e(t) \\ S_e(0) = 0 \end{cases} \quad (3)$$

The parameters, not identified before, represent:

$S_o(t)$: VS input concentration

$q(t)$: input and output volumetric flow rate of the anaerobic reactor

All calculations described in this section were performed by means of Matlab/Simulink..

4. RESULTS AND DISCUSSION

4.1. Characterization of the substrates

The results of the characterization of the studied substrates are schematically represented in Table 2: the single materials exhibited acidic pH values (apart from rice processing substrates, cookies by-products and tea leaves, which are neutral), high

VS/TS values, and carbon contents above 40-50%. Considering C/N, single materials' values were sometimes quite high (particularly considering the substrates deriving from hazelnuts and rice processing). Moisture content, pH value, C/N ratio and VS content are the most important parameters to consider in planning an AD process. Typical values of these parameters commonly reported for a correct anaerobic digestion are pH values between 6.5 and 7.5 and C/N between 25 and 30 [1], while moisture content influences the choice of the digester's technology (wet, semi-wet or dry) and the need of a mechanical mixing equipment. VS amount is related to the organic substance content available for biological degradation.

The semi-pilot scale tests considered six mixtures, which were designed gathering substrates generated by single food-industry macro-categories and with the main purpose to obtain an optimal C/N value (see Table 2). The molecular formula of the single substrates, derived from elemental analysis, according to stoichiometric assumptions enabled to calculate the theoretical production of biogas (see B_{th} and CH_4^{th} values in Table 3).

4.2. AD tests (semi-pilot scale)

On the grounds of the results of semi-pilot scale tests performed feeding a 3% TS (see Table 3), the substrates characterized by the highest biogas specific production are the mixtures of wine wastes (0.89 m^3/kg_{VS}) and of sweets without cocoa (0.80 m^3/kg_{VS}). The other substrates exhibit a rather homogenous trend (0.48-0.72 m^3/kg_{VS}), with coffee wastes placed at the bottom end. Methane content exceeded 55% in all cases, with hazelnut and wine mixtures reaching 62-63%. The significance of differences in average biogas yields and methane contents were determined by single factor analysis

Substrate	pH	TS (%)	VS/TS	C	H	N	S	formula	mixture	Mixture formula	relative abundance (%)	TS (%)	VS/TS	C/N
CH	5.8	92.9	91.4	45.9	5.9	2.8	0.2	$C_{23}H_{34}O_{12}N$	coffee mix	$C_{21}H_{31}O_{11}N$	60	95.0	93.7	18
CD	5.1	96.4	95.3	51.7	6.7	2.7	0.1	$C_{19}H_{27}O_{13}N$			40			
RHS	5.7	89.3	96.5	45.7	5.4	1.1	<0.1	$C_{49}H_{53}O_{31}N$	hazelnut mix	$C_{29}H_{42}O_{11}N$	10	94.1	97.6	29
FHS	5.2	95.7	97.5	56.8	6.8	1.2	0.1	$C_{57}H_{76}O_{24}N$			10			
LHS	5.5	94.5	97.7	54.6	7.2	2.2	0.1	$C_{29}H_{42}O_{12}N$			80			
RH	7.2	92.0	83.2	38.5	5.1	0.5	<0.1	$C_{100}H_{125}O_{93}N$	rice mix	$C_{22}H_{34}O_{10}N$	15	92.0	87.8	28
RB	6.9	92.0	88.7	44.9	6.9	2.4	0.1	$C_{22}H_{34}O_{14}N$			85			
C	7.3	92.1	98,4	47.2	7.1	2.0	<0.1	$C_{28}H_{45}O_{20}N$	sweets no cocoa mix	$C_{30}H_{46}O_{17}N$	50	83.6	98.5	25
TL	7.0	24.9	95.8	55.0	38.3	4.7	<0.1	$C_{14}H_{14}O_{7}N$			5			
SC	6.1	80.5	98.7	54.7	9.6	1.9	<0.1	$C_{33}H_{50}O_{16}N$			45			
CC	6.7	99.7	98.2	56.6	8.6	1.3	<0.1	$C_{51}H_{93}O_{22}N$	sweets cocoa mix	$C_{36}H_{61}O_{19}N$	50	95.3	94.5	31
CH	4.8	92.6	91.1	48.3	6.6	2.6	0.2	$C_{22}H_{36}O_{14}N$			50			
P	3.2	16.3	91.5	42.6	2.5	2.8	<0.1	$C_{18}H_{13}O_{16}N$	wine mix	$C_{26}H_{27}O_{19}N$	60	15.4	98.0	33
L_1*	3.4	14.3	80.5	52.4	5.7	1.6	<0.1	$C_{38}H_{50}O_{22}N_1$			40			
L_2**	4.2	12.3	85.4	45.4	5.6	3.7	0.2	$C_{32}H_{54}O_{24}N$	lees**	$C_{32}H_{54}O_{24}N$	100	12.3	85.4	20

*fed in semi-pilot scale tests

** fed in pilot scale tests

Table 2. Characterization of the considered substrates and mixture design.

of variance (ANOVA), choosing a level of significance equal to 0.05. ANOVA results showed that the 6 substrates are different from a statistical point of view (F (22.84) > F_{crit} (2.30)).

The comparison between the results of the first and the second test concerning coffee mix shows no significant difference about biogas and methane production (respectively equal to 0.48 and 0.47 Nm^3 biogas/kg_{VS} and 55.1-55.7 CH_4%). The analysis of the results of the two tests on coffee mix by means of the statistic inference of variance and average values (test F and test t, both with 0.05 significance level), showed no significant differences, hence the sequence of digestion of the different substrates may be considered negligible from the point of view of the properties of the inoculum (F (3.01) < F_{crit}(7.15)).

These results in overall demonstrated that disintegration was the limiting step of the process. Moreover the particulate nature of the tested substrates was a crucial factor, as proven by other studies [18] and even if the microbial community could change over the time, this phenomenon did not influence the results. The pH values measured during the performed tests (see Supplementary Material, Figure I), as well as biogas composition (see Figure 2), reflected the evolution of the different phases of the AD process, which is influenced by the adopted feeding procedure. In all tests the feeding phase lasted 11 days, although the biogas production continued until 19-29 days depending on the relative content of carbohydrates and lipids in the substrates. Comparing the cumulative biogas production curves of the six tested mixtures (see Figure 3), the mixtures may be divided in two groups characterized by analogous production speed in the starting phase of the tests. The error bars in Figure 3 represent the standard deviation of cumulative biogas production calculated on 6 replicates for

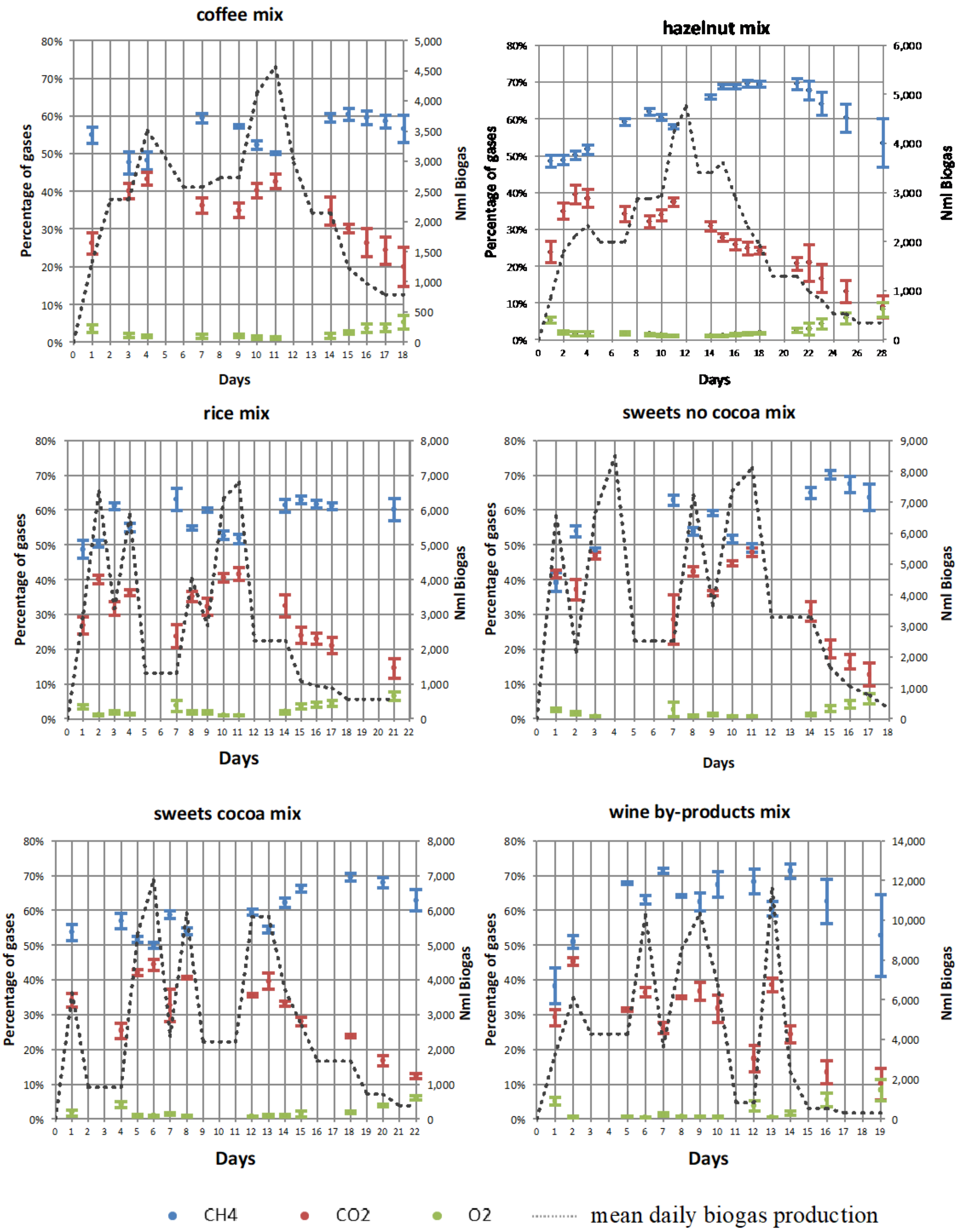


Figure 2. Mean Biogas composition during the semi-pilot scale tests (average values of 6 replicates) performed at 3% TS

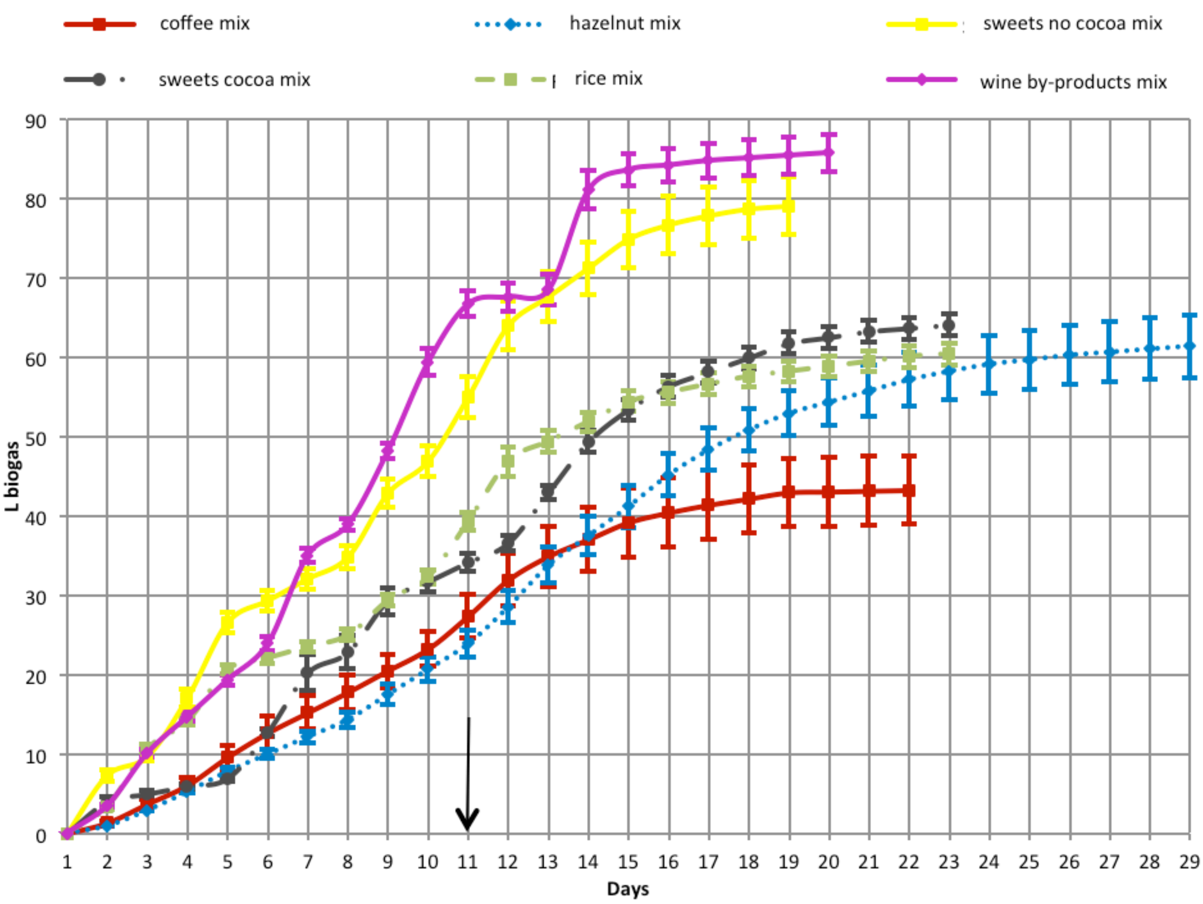


Figure 3. Cumulative curves obtained from semi-pilot scale tests performed at 3%TS (the arrow indicates the stop of the feeding phase).

each substrate. A higher-speed group, made of sweets without cocoa and wine mixtures (having a higher amount of highly biodegradable carbohydrates), and a lower-speed group made of hazelnut, coffee and sweets with cocoa mixtures (rich in less readily degradable substances). Rice mixture exhibited a behavior analogous to the first group in the first 6 days, and then switched to the second group, witnessing its complex nature. Considering the experimental biogas and methane yields (see Table 3), all values were lower than theoretical ones. Experimental yields were considerably higher if compared with literature values referred to BMP tests (see Table 1), with the exception of rice mix that shows a behavior similar to what reported by Menardo and Balsari [18] (0.67 m^3_{biogas}/kg_{VS} - 0.56 % CH_4). All mixtures exhibited a removal of VS above 80% (with the exception of Coffee mixture), and methanation grade values are consistent with carbon balance. Considering carbon balance (see Table 3) the difference between the amount fed and the amount transferred in biogas is due to the carbon content of the digestate, therefore a high transfer of carbon in biogas is connected with an enhanced biodegradation of the substrate and a highly stabilized digestate in the considered experimental conditions. The not complete agreement between the carbon balance and VS balance (see Table 3), is due to the assumption of an equal distribution of the different fractions of the substrates into VS and the digestate; moreover the C content in the mixtures was calculated assuming its equal partitioning between NVS and VS.

The obtained k_{dis} values (see Table 3), slightly higher than the ones found in literature and deriving from BMP tests (see Table 1), revealed that disintegration was a critical phase particularly for hazelnut mixture, while the other substrates exhibited similar values. The comparison of the experimental daily biogas curves with the ones calculated from the gathered k_{dis} values and Eq. (1) (see Figure 4) allowed some general evaluations about the kinetic features of the AD process in the considered operative conditions in the fed-batch system. The peaks in experimental curves didn't happen straight after the feed, but in all cases they occurred about one day after, because of the complex nature of the substrates. See Supplementary materials (Figure II) for details about the model. Generally the deviations of the experimental curves towards the calculated ones, which were higher in correspondence of the two days of the week in which the feeding didn't happen, may be due to a scarce mixing of the systems and to the obvious variability of a biological process performed in six replicates on heterogeneous substrates. Taking into account hazelnut mix, the largest deviations were observed from the twelfth day: the substrate is rich in lipids, which are characterized by a slower kinetic if compared to carbohydrates and proteins, and the determined k_{dis} may be different from the one that could be achieved in absence of limiting factors (i.e. scarceness of lipid degrading bacteria, that needed 12 days to be overtaken). It was not possible to obtain a k_{dis} value for wine mixture: the involved materials were rich of sugars and contained a certain amount of alcohols, therefore hydrolysis was probably not a limiting step of their AD.

The stability of the system about the substrate amount was evaluated on a mixture of CC and CH substrates, performing a semi-pilot scale test feeding 6% TS. The gathered results (see Table 3) showed analogous biogas yields and methane contents if compared with the results obtained feeding 3% TS, therefore the possibility to enhance the amount of fed wastes may be positively evaluated (although a possible stress of the system may be supposed considering the lower k_{dis} and that pH values were placed in a wider range if compared with 3% TS) (see Supplementary Material).

Mixture	$CH_{4_{th}} \left[\frac{m^3}{kg_{VS}}\right]$	CH_4^{th} [%]	$B_{exp} \left[\frac{Nm^3}{kg_{VS}}\right]$	$CH_{4_{exp}}$ [%]	$CH_{4_{exp}}/CH_{4_{th}}$ [%]	$removed\ VS$ [%]	$C_{(CH_4+CO_2)}/C_{sub}$ [%]	$k_{dis\ exp}\ [d^{-1}]$
coffee mix (3% TS)	0.54	54	0.48 ±0.05	55 ±0.65	49	57	53	0.31
hazelnut mix (3% TS)	0.63	57	0.64 ±0.01	63 ±0.58	64	79	65	0.15
rice mix (3% TS)	0.57	56	0.69 ±0.02	56 ±0.61	67	79	82	0.38
sweets no cocoa mix (3% TS)	0.51	53	0.82 ±0.03	56 ±0.41	88	94	85	0.56
sweets cocoa mix (3% TS)	0.54	57	0.72 ±0.01	57 ±0.87	75	80	73	0.34
sweets cocoa mix (6% TS)	0.54	57	0.72 ±0.02	58 ±0.83	76	73	75	0.29
wine mix (3% TS)	0.48	48	0.89 ±0.02	62 ±1.61	1.16	81	[c]	[c]

[a] referred only to LHS
[b] referred only to RB
[c] data not available

Table 3. Biogas and methane production: theoretical and experimental values gathered from semi-pilot scale tests, mass balance referred to VS and carbon, disintegration kinetic constant values (k_{dis})

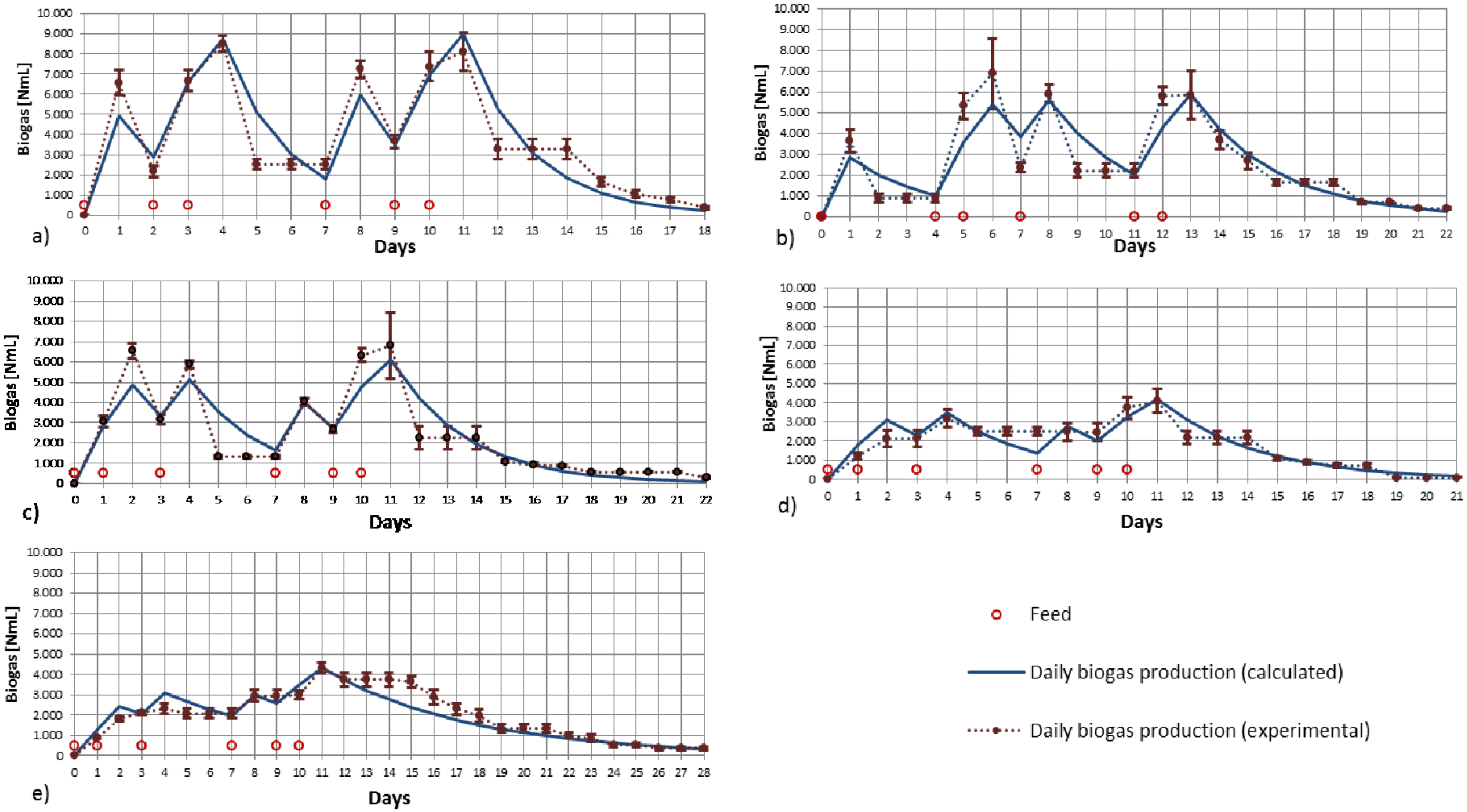


Figure 4. Daily biogas curves (calculated and experimental) gathered from semi-pilot scale tests: a) sweets no cocoa mix; b) sweets cocoa mix; c) rice mix; d) coffee mix; e) hazelnut mix

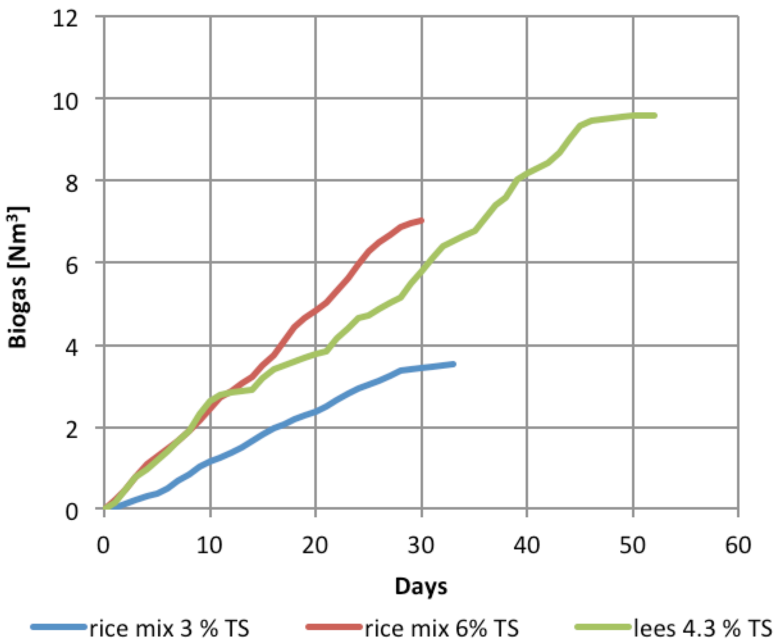


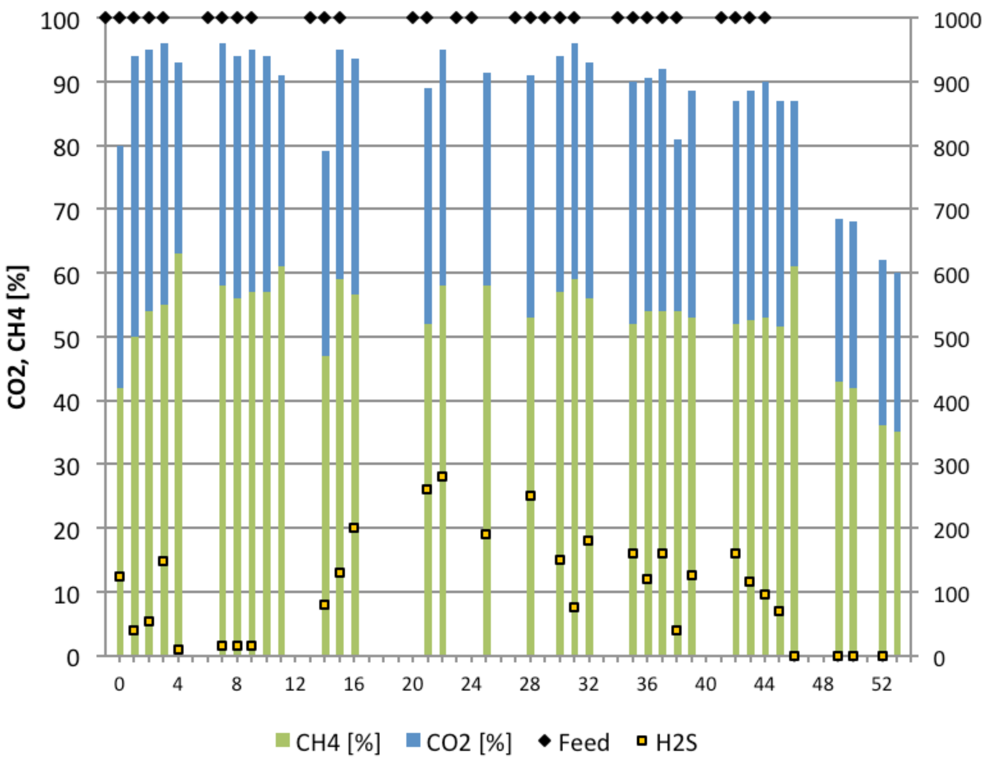
Figure 5. Cumulative curves obtained from pilot-scale tests on rice mixture 3% TS (*test 1*) and 6% TS (*test 2*)

4.3. AD tests (pilot scale)

The results of pilot scale tests showed that, feeding a 3-4% TS, lees produced a higher biogas yield (1.13 Nm^3/kg_{VS}, with an average CH_4 content above 55%), if compared with rice mixture, which generated 0.69 Nm^3/kg_{VS} of biogas (average CH_4 content 47%). Probably the high content of sugars and alcohols of lees was a crucial factor.

Taking into account rice mixture, Tests 1 and 2 had the aim to explore the stability of the system towards the doubling of the amount of the fed substrate. Moreover Test 1 was employed to evaluate the implementation of the proposed model to the scale-up of the process from semi-pilot to pilot scale. The test performed feeding 6%TS of rice mixture (Test 2) produced a biogas yield (0.58 Nm^3/kg_{VS}, with an average CH_4 content around 54%) which was analogous to the one registered with 3% TS (Tests 1). The cumulative biogas production curves are reported in Figure 5.

(A)



(B)

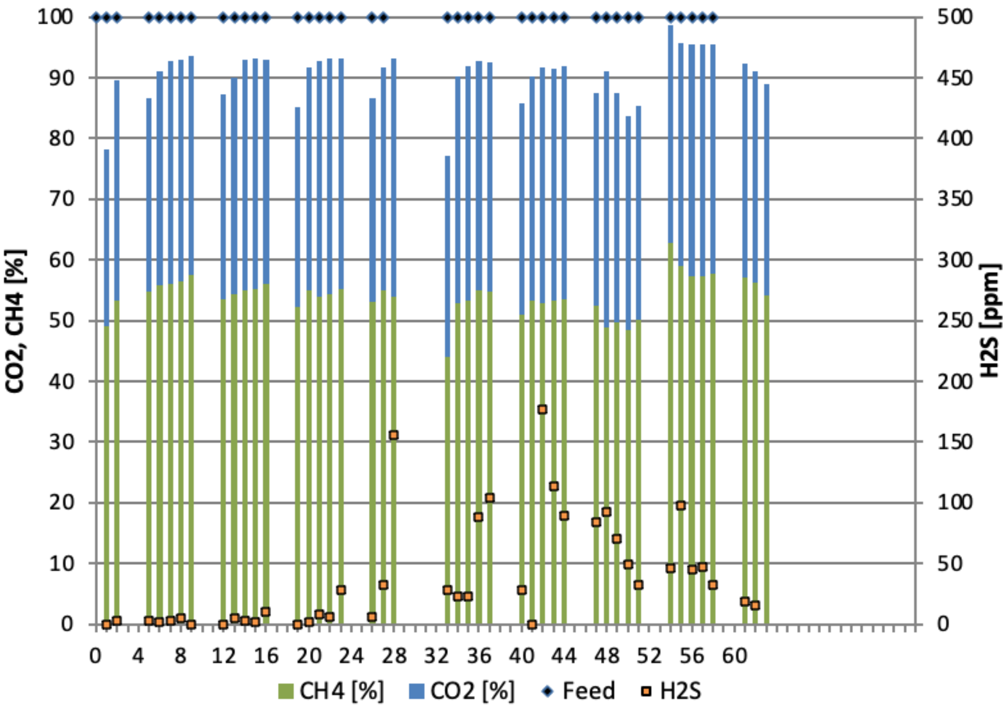


Figure 6. Biogas composition during the pilot scale tests: (A) lees (4.3%TS), (B) rice mixture (3%TS, *Test 1*)

Biogas composition (see Figure 6) reflected the periodical trend of the feed, which happened 5 days/week: the registered minimum values correspond to the two days in which the feed didn't happen. Hydrogen sulfide could be potentially a critical issue during the pilot scale tests: an average concentration of 150 ppm, with a maximum of 280 ppm around the middle of the digestion period, was measured for lees although methane production was not inhibited. Hydrogen sulfide content remained generally below 100 ppm within rice mixture digestion, with a maximum around 180 ppm.

During the pilot scale tests FOS/TAC value was monitored daily in the digestate: it is one of the most significant operative parameters in continuous/semi-continuous fed AD processes [28], allowing a well-timed intervention in case of stress of the system due to an accumulation of organic acids when a high organic load is applied. In general, it is assumed that total alkalinity should be above 2000-3000 mg/L $CaCO_3$ to buffer pH decreasing and to prevent the consequent inhibition of methanogenesis, and that the FOS/TAC value should be around 0.3 to have a stable process [37, 38]. Considering the FOS/TAC trend at the beginning of the test on lees (see Figure 7), sodium bicarbonate was added to the substrate since the fourth day of digestion (a stoichiometric amount of 0.42 g $NaHCO_3/g_{TS}$ was calculated to achieve a TAC equal to 3000 mg/L of $CaCO_3$) in order to increase the buffer capacity of the system. The evolution of pH and FOS/TAC trends outlined the efficacy of the correction. The addition of sodium bicarbonate probably had a positive effect also in preventing hydrogen sulfide over-production.

During test 1 (rice mixture fed at 3% TS), the experimental daily biogas production values were plotted together with the curves calculated as specified in section 3 (the losses of substrate connected to semi-continuous feeding mode were taken into account) (see Figure 8 and Figure 9). See Supplementary materials for the values of the parameters employed in the model. A good agreement between experimental and expected data was observed, although some differences in their trends may be noticed. First of all, the deviations in correspondence of the two days of the week in which the feeding didn't happen (already observed at a semi-pilot scale), which may be due to a scarce mixing of the reactor. As the test proceeded, after about 16 days, the variance of the two trends became consistent: it may be hypothesized that the semi-continuous feeding mode of the tested mixture determined a loss of substrate, that couldn't be digested in the considered experimental conditions. Nevertheless, at a semi-pilot scale the maximum difference between the biogas cumulative production given by the model and the experimental value (recorded at 25th day) is equal to 8.5 %, instead at the end of the pilot-scale test this difference drop down at the 7.1 %. The comparison between the experimental and calculated cumulated biogas curves didn't take into account test 2 (rice mix 6% TS) because the parameters considered in the proposed model were derived for a lower OLR.

A comparison of the results obtained from rice mixture fed at 3% TS at the two different scales may be performed on the grounds of methane production. Pilot scale supplied a value (0.312 methane Nm^3/kg_{VS}) that is equal to 81% of the one obtained on semi-pilot scale (0.386 methane Nm^3/kg_{VS}, see Table 3). A study performed in the same apparatus and operating conditions, on a mix of vegetable wastes, returned a ratio of approximately 0.76 between the methane specific production obtained on a semi-continuous mode (0.223 Nm^3/kg_{VS} added) and the methane specific production obtained on a fed-batch mode (0.294 Nm^3/kg_{VS} added) [39].

Hypothesizing the valorization of biogas generated by AD fed with 3% TS in a CHP unit, the potential specific energy production of the single mixtures was broadly calculated (see Table 4). On the grounds of the evaluated scale effect, a precautionary conversion factor equal to 0.75 was applied to the results gathered from the semi-pilot scale tests (see Table 3). CHP electric and thermal efficiency values were considered as in Ruffino et al. [39].

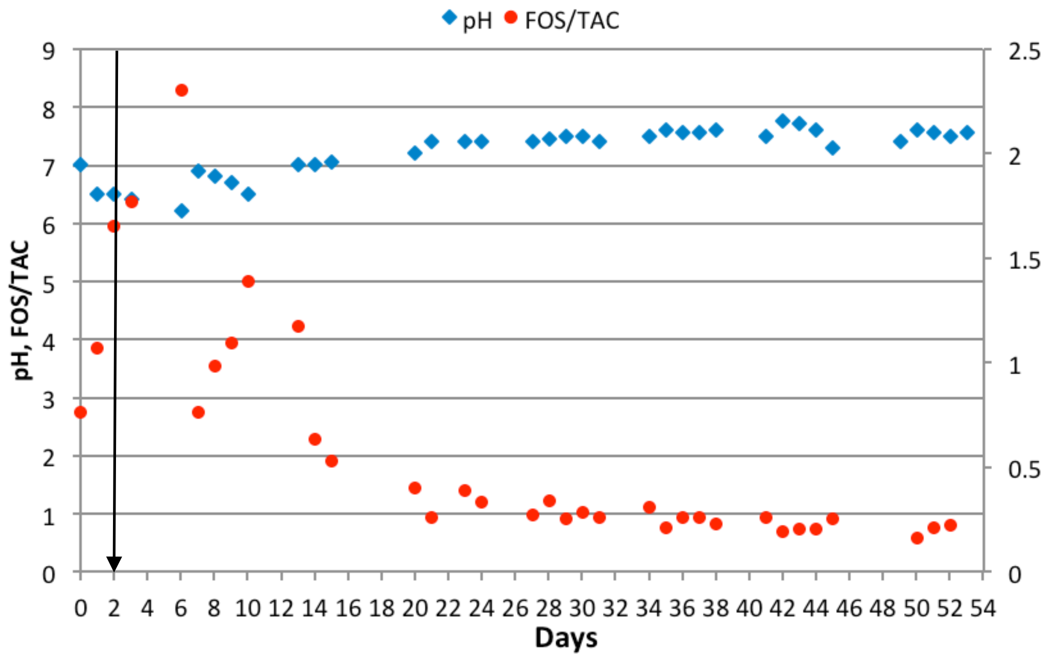


Figure 7. pH and FOS/TAC trends measured during the pilot scale test performed on lees (4.3%TS) (the arrow shows the starting of sodium bicarbonate addition to the feed)

waste	primary energy production	gross electric energy production	gross thermal energy production
coffee mix	1.98	0.69	0.83
hazelnut mix	3.02	1.06	1.27
rice mix	2.90	1.01	1.22
sweets no cocoa mix	3.44	1.21	1.45
sweets cocoa mix	3.08	1.08	1.29
wine mix	4.14	1.45	1.74

Table 4. Preliminary evaluation of the potential energetic valorization of the biogas generated by the considered wastes (AD fed with 3% TS). Data are expressed in kWh/kg_{VS}.

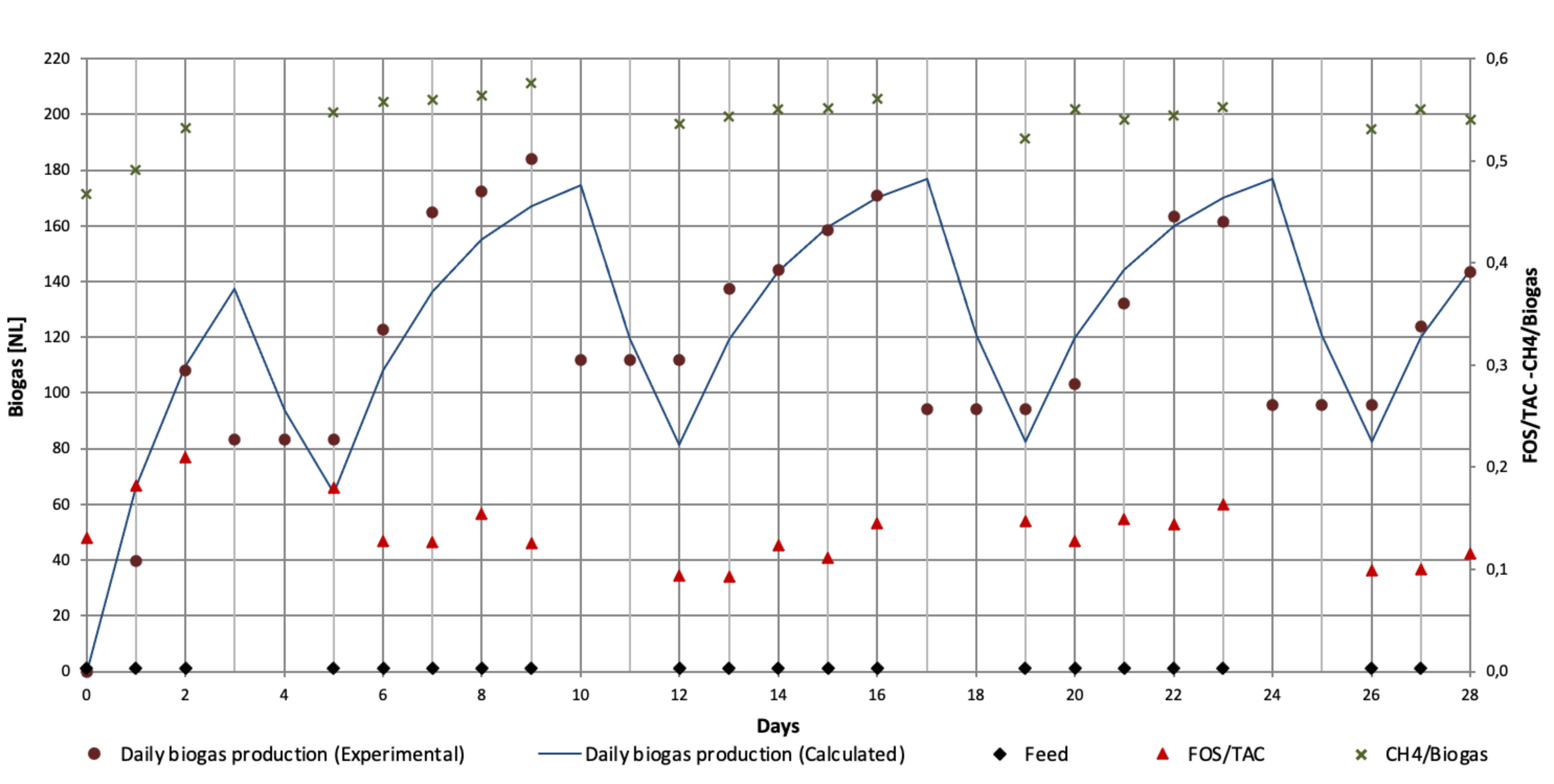


Figure 8. Daily biogas production gathered from pilot scale tests (test 1, 3% TS) on rice mixture Vs expected daily biogas production

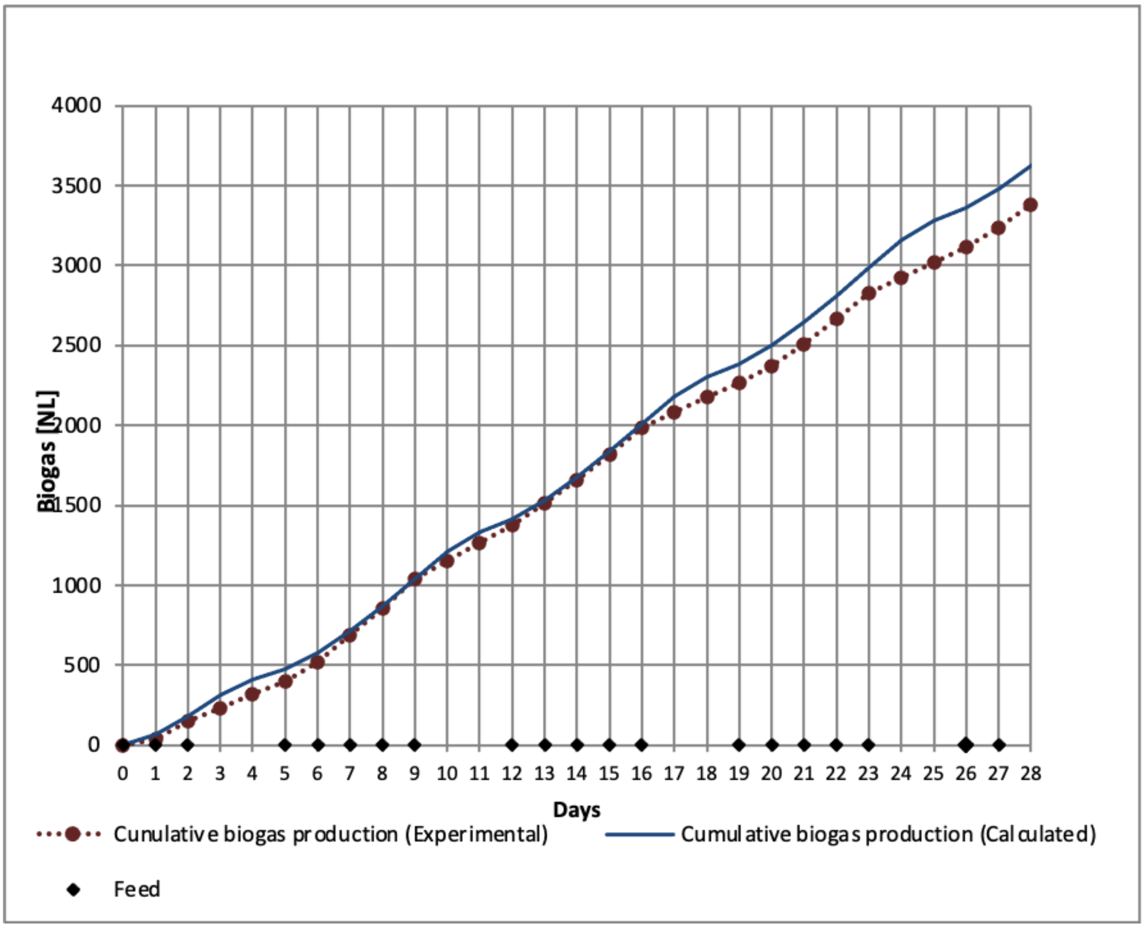


Figure 9. Cumulative biogas production gathered from pilot scale tests (test 1, 3% TS) on rice mixture Vs expected daily biogas production

5. CONCLUSIONS

The employed test procedure allowed the comparison of the implementation of AD on different homogeneous mixtures of industrial food wastes without any pre-treatment. The proposed semi-pilot scale procedure was easy to manage, reliable with heterogeneous substrates, likely to prevent inhibition of methanogenesis. Fed-batch mode revealed itself as a valuable tool to avoid an overload of the system, and to achieve biogas yields higher than literature values obtained from BMP tests. Despite the differences about the scale of the reactors and the feeding mode, the results gathered from semi-pilot and pilot scale tests exhibited a good consistency (0.81 coefficient about methane production). The proposed model, based on the values of k_{dis}, was employed as a control tool during the pilot scale tests and it appeared adequate for the evaluation of the scale-up of the AD process. The observed differences between experimental and calculated values at the two scales were around 7-8%.

The obtained results in terms of biogas production and VS/TS consumption are the consequence of a preliminary investigation towards mixtures of homogeneous wastes, however the performed tests demonstrated that the studied substrates may be considered interesting matrices to be degraded in mono-digestion processes.

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