Renewable Energy 215 (2023) 119014

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

Bioeconomy for sustainable development of biomethane sector: Potential and challenges for agro-industrial by-products

Francesca Valenti [a], Roberta Selvaggi [b,*], Biagio Pecorino [b], Simona MC. Porto [c]

[a] Department of Agricultural and Food Sciences, Alma Mater Studiorum-University of Bologna, Viale Giuseppe Fanin 50, 40127, Bologna, Italy
[b] Agricultural Economics Section, Department of Agriculture, Food and Environment, University of Catania, Via S. Sofia 100, 95123, Catania, Italy
[c] Building and Land Engineering Section, Department of Agriculture, Food and Environment, University of Catania, Via S. Sofia 100, 95123, Catania, Italy

ARTICLE INFO

Keywords:
By-products
Feedstocks
Biochemical methane potential test
Waste-to-resource
Biomethane
Advanced biofuels

ABSTRACT

Agro-industrial transformation chains generate huge amounts of by-products which can be used as biomass for anaerobic digestion (AD) process, by avoiding their disposal in landfill and therefore environmental issues. This study has investigated a biomass mix to increase biogas production optimizing AD process parameters with the aim of enhancing AD performance in terms of produced biogas quality. In detail, both Biochemical Methane Potential (BMP) and AD approaches were adopted for investigating the effect of mixing seven Mediterranean feedstocks (i.e., olive pomace, citrus pulp, poultry and cattle manure, whey, tomato peels, and cereal straw) on methane production for bioenergy generation. The BMP test demonstrated that the tested mix had potential to be used for biogas production with 60.9% of methane content in the produced biogas. In detail, the specific production was equal to 343.1 Nm^3CH_4/tVS, confirmed by the results obtained during the AD test, about 333 Nm^3CH_4/tVS. As result, the tested mix demonstrated good net energy outputs and provide a flexible and useful solution to generate bioenergy from by-products. These findings confirm the possibility of using these by-products as energy sources and initiating virtuous bioeconomy processes for the sustainable utilization of renewable natural resources, transforming waste-to-resources.

1. Introduction

The challenges and uncertainties facing the global energy system are at their highest level in nearly 50 years since the era of the last major energy shocks in the 1970s [1].

Industrial society to prosper relied on oil or gas as it was thermodynamic system powered by cheap and abundant energy sources [2], although, the continued rapid growth in the use of non-renewable fossil fuels has affected their future availability [3].

In this context, there is an imminent need for an energy transition related to energy security concerns, but also because of the multiplication of environmental damages.

A shift from conventional to nonconventional sources has begun. The renewable energy sources represent a suitable alternative to conventional fossil fuels due to both the possible advantages in terms of environmental impact reduction (e.g., CO_2 and other GHG emissions), according to the Kyoto protocol, and improvement of living standard of developing countries by producing cost effective energy as well as using bioenergy efficiency [4–6]. The energy and climate policies in the EU and the Green New Deal promote the utilization of renewable resources boosting the development of biogas plants for energy production [7].

Worldwide, biomass is the most widely used renewable energy source [8,9], and its application is constantly increasing [10].

The use of by-products obtained by agro-industrial transformation processes is closely linked to the goals of the bioeconomy strategy. In fact, these biomasses contain undegraded and noble substances (e.g., pectin, limonene, essential oils, etc.) able to become resources for subsequent processes (i.e., anaerobic digestion, nutraceutical extraction, etc.) [11].

In this context, the use of residual biomasses can reduce soil consumption to produce dedicated energy crops and can contribute to soil organic matter increase by recycling the nutrients (e.g., N, P and K) in the digestate [12]. Moreover, this virtuous and sustainable process is able to reduce GHG emissions due to agri-food wastes disposal. In this regard, the disposal of agri-food wastes leads to different problems of both economic and environmental nature such as the high

* Corresponding author.
E-mail addresses: francesca.valenti9@unibo.it (F. Valenti), roberta.selvaggi@unict.it (R. Selvaggi), pecorino@unict.it (B. Pecorino), simona.porto@unict.its (S.MC. Porto).

https://doi.org/10.1016/j.renene.2023.119014
Received 3 September 2022; Received in revised form 30 May 2023; Accepted 8 July 2023
Available online 8 July 2023
0960-1481/© 2023 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

transportation costs of the wastes, the lack of disposal sites and the difficulties to store for long time periods organic wastes due to their fermentation process. Therefore, the goals fixed by the EU are very challenging and encourage to move toward high recycling targets, paving the road from a linear to a circular economy as a real answer for the challenge of globalization [13].

The bioeconomy starts with the valorization of waste as if it were a resource, removing it from the fate of disposal. The valorization of by-products from the agribusiness industry is a goal of sustainable development, which is gaining great interest in solving environmental and energy resource challenges that are increasingly scarce and impactful [14].

The goal of a correct waste management is not only to reduce the disposed waste volumes, but also to reuse or recovery and recycling all suitable materials [15]. As stated by Sagastume Gutierrez et al., [16] several waste-to energy alternatives to produce energy from biomass sources were worldwide investigated. Among available technologies to produce renewable energy, Anaerobic Digestion (AD) has emerged as one of the most promising technologies for waste management [17]. AD can be applied at almost all types of biodegradable source separated organic fraction of agricultural or industrial food waste and food manufacturing residues [18–20]. Sagastume Gutierrez et al., [16] reported that the choice of an adequate technology also depends on the biomass characteristics and properties by highlighting that for biomass sources with more than 50% moisture (e.g., agricultural waste and by-products) the AD processes are more indicated.

AD has been recognized as an environmental-friendly technology to convert organic matter into biogas [21] useable to reduce dependence on fossil fuels. Moreover, the AD process can add significant value to agribusiness supply chains, as waste management is one of the main costs for the companies [22]. Worldwide several research studies demonstrated that AD has the minimal impact on the environment since its global warming, eutrophication and acidification potency as well as carbon footprint in comparison to composting and incineration is very low [23–25].

Recently several research studies have been carried out on analysing biomass mixes and technical solutions to both increase biogas production and optimize AD process parameters in order to enhance the quality of produced biogas [18,26,27]. Usually, the baseline matrix has been livestock manure in co-digestion with different biomasses (e.g., by-products or waste from agro-industrial). As early as 20 years ago, Callaghan et al. [28] studied the possibility of optimizing the simultaneous co-digestion process of a mix consisting of cattle and chicken manure and fruit and vegetable wastes. Approximately a decade later, Muradin and Foltynowicz [29] tested the co-digestion of a mix of nine biomasses from different supply chains, such as municipal sludge, corn silage, soybean oil, fruit and vegetable pomace, potato pulp, vine waste, grain, and plant tissue waste.

Wickham et al. [30] went further with a co-digestion trial between sewage sludge and organic waste. Tasnim et al. [31] evaluated the co-digestion performance of mixed cattle manure, sewage sludge and water hyacinth. Valenti et al. [18] investigated the possibility of blending six feedstocks from agricultural and agro-industrial activities by applying batch and semi-continuous co-digestion methodologies. Furthermore, having demonstrated the success of biogas production from multiple organic residues, Valenti et al. [19] also carried out a comparative study of multiple mixes of the same biomasses, varying within the mix the percentage contents of the biomasses.

All authors agree that the main advantage of AD process is the enhancement of production of biogas and its methane content, by helping the improvement of the process stabilisation [32–37].

The world production of biogas from biomasses has been strongly implemented in the last twenty years with a growing number of biogas plants. In 2019, the total biogas production in EU and Italy were: 18,429 MNm^3 and 2183 MNm^3 [38]. This enhancement in biogas plants makes Italy the third world producer after China and Germany, even though investments have been above all in Northern Italy [39–41].

Unfortunately, nowadays, in some countries the biogas sector is not yet uniformly developed as occur in some regions of the South of Italy [42].

In those territorial areas where there is a large availability of biomass, entrepreneurs intend to maximize its use for biogas purposes and are interested in identifying the most effective and efficient mixes [43]. In this regard, Mediterranean area could represent a suitable case study where the biogas sector has great potential for developing and can rely on huge volumes of available biomass, not yet used for noble purposes and often destined for landfill [19]. In this context, the application of bioeconomy principles would be practical and would benefit everyone [44].

In fact, at the basis of the proper functioning of AD processes is the knowledge of the organic mixture for feeding the digester. On its composition depends, not only the production of biogas, but also the maintenance of the system's qualitative-quantitative efficiency parameters.

The optimum of the full-scale system can be simulated on a laboratory scale in order to predetermine the technical feasibility of the mixtures that are intended to be adopted in the energy production process. Therefore, investigating new biomass mixes and evaluating the performance of tested mixtures is urgent and imperative for the development of the biogas sector in Mediterranean area [45].

So, considering the advancement of knowledge, by overcoming the results obtained by Valenti et al., [18], and with the aim of facilitating the development of planning future biogas plans, this study focused on the application of both batch and semi-continuous co-digestion approaches to analyse the effect of mixing seven feedstocks, highly available in Mediterranean area (i.e., olive pomace, citrus pulp, poultry and cattle manure, whey, cereal straw and tomato peels), on biogas and methane production for bioenergy generation.

To the best of our knowledge, in this study, for the first time, the effect of mixing the selected specific feedstocks on methane production for bioenergy generation was investigated. In detail, the tested feedstock-mixture (FM) was defined for research purposes since it is not routinely in use as a digester feeding diet in the Mediterranean area. Thus, by considering the positive achieved results, this mix is of particular interest to stakeholders who are always looking for new biomass to feed plants that are getting larger and larger.

Since the anaerobic digestion will play an important role in the future by generating energy and adding values to the by-products of the agro-industrial sector, the results of this study could be relevant for sustainable developing the biogas sector, according to bioeconomy perspective.

2. Materials and methods

2.1. Feedstock-mixture composition and characteristics

Several and diverse by-products and agricultural residues are available in Mediterranean area and could be valorised for producing bioenergy through AD process by the biogas plants. Among the available biomasses, based on both their suitability with AD process and their availability within the study area, seven feedstocks were selected as suitable ones for the co-digestion process. The selected feedstocks have been in part provided from the University of Catania, Department of Agriculture, Food and Environment (i.e., citrus pulp and tomato peels), and then collected and shipped in coolers to the Research Center for Animal Production (Centro Ricerche Produzioni Animali - C.R.P.A.). Meanwhile the other ones (i.e., olive pomace (three phase), poultry and cattle manure, whey, and cereal straw), were collected by C.R.P.A. from the nearest farms located in Emilia-Romagna region (Italy).

By considering both the availability of the selected agricultural residues and by-products, and above all the results of the FMs previously analysed by Valenti et al. [18], a new FM of the selected seven biomasses was investigated.

The selected FM was firstly prepared for the Biomethane potential test (BMP) – e.g., batch co-digestion, based on the amount and availability of the agricultural wastes and by-products available in the study area and by taking into account the typical FM actually used in Mediterranean biogas plants is composed of seven Mediterranean feedstocks mainly available in the study area, i.e., 5% of cattle manure, 13% of poultry manure, 6% of tomato peels, 18% of silage, 18% of olive pomace, 20% of whey and 20% of citrus pulp (percentages w/w) (Table 1).

Each considered feedstock prior to be mixed with others was firstly chopped to reduce particle size by means a blender and kept frozen prior to use. As reported in Table 1, each individual feedstock was chemically characterized according to the parameters of total solids (TS) and volatile solids (VS).

2.2. Equipment and procedures of BMP and AD test

2.2.1. BMP test

As worldwide known, the BMP test is adopted for evaluating the maximum amount of methane and/or biogas that can be produced from the analysed feedstocks. It was carried out following both the UNI EN ISO 11734/2004 framework [46], and the UNI/TS 11703:2018 [47], as illustrated by Valenti et al. [19]. Before starting the semi-continuous AD test the BMP static test was carried out by simulating a controlled environment.

The equipment included a glass bottle (i.e., the digester) with a total volume of about 2200 ml, which was filled with the selected FM to about 70% and then placed in a thermostat cabinet, by keeping temperature of about 38 °C for the entire digestion process. The test was run in duplicates.

The mass method was adopted for analysing and monitoring the content of produced biogas [19]. In detail, during the gas analysis, the volume of the produced biogas was computed, as well as the methane content, carbon dioxide, and hydrogen sulphide were monitored to analyse the quality of the produced biogas. The measurements were continuously carried out and the total amount of produced biogas was computed and reported in a cumulative production curve, which was useful for obtaining key information about the degradation rate [46].

A range of parameters was firstly measured for each considered feedstock and then for the selected FM before and during AD test.

In detail, the FM has been chemically characterized, by analysing firstly TS and VS. TS and ash contents were measured by following the standard methods, which consists of drying and incinerating the samples at respectively 105 °C and 550 °C [48]. Total nitrogen (NTK) and total phosphorus (P) of the samples (pre and post digestion) were analysed using the USEPA approved HACH® standard methods. Elemental analysis of carbon and nitrogen was carried out by Atlantic MicroLabs in Norcross, GA.

pH and FOS/TAC ratio of the digestate were measured by using a Hach titrator, (i.e., Nordmann titration method), trough the TIM 840 titrator (HACH-LANGE) [6].

The methane yield was measured accordingly to the standard ISO 11734 [46]. In detail, the BMP test was performed by following the method developed by CRPA Lab, and the obtained results were expressed in normal cubic meters of methane per ton of volatile solids (Nm^3CH_4/tVS).

The amount of methane (CH_4), carbon dioxide (CO_2), hydrogen sulphide (H_2S) contained in the recorded biogas were quantified using a SRI GC Multiple Gas Analyzer with valve injection. The degradability of the organic substance (i.e., VS reduction) was calculated by considering the ratio between the amount of the produced biogas and the amount of VS loaded.

Table 1
Characteristics of feedstocks and percentages of FM composition.

Feedstocks	TS	VS	FM composition
	[%w/w]	[%TS]	[%]
Citrus pulp	17.41	74.20	20
Poultry manure	32.36	89.66	13
Olive pomace	16.53	88.89	18
Cattle manure	12.31	85.72	5
Whey	5.89	65.26	20
Silage	35.24	93.84	18
Tomato peels	27.03	96.22	6
Total	–	–	100

2.2.2. AD test

After BMP test the FM was used as feed to run semi-continuous AD test. It is well known that AD is a multistage process of biological reactions without oxygen. The AD process can be composed of 4 main stages: hydrolysis, acidogenesis, acetogenesis, methanogenesis. Bacteria present in the process mineralize the organic substance introduced into the system in CH_4, CO_2, ammonia (NH_3), H_2S and water (H_2O). In addition to the mineralization of the organic substance, other reactions may cause growth of high molecular weight fatty acids, butyric acid, and propionic acid, but these reactions only occur due to the biological process management problems. Indeed, in "regular" mesophilic conditions (i.e., 37 °C), acetic acid is the primary precursor of methane.

As BMP test also for AD test, the activity was carried out at CRPA Lab by using an AD reactor with continuous feeding to simulate the real-scale conditions and observe the biological process [6]. The experimental system that was developed by CRPA Lab (Fig. 1) consists of continuous-feed steel mini digesters, with a volume of 24L, mixed and heated both in mesophilic or thermophilic conditions [49]. The adopted system provides the continuous recording of the amount of produced biogas by means a manometric system, with the aim of periodically monitoring the quality of biogas in terms of CH_4, CO_2, H_2S percentages. The system allows periodically (e.g., daily, weekly, or even more frequently) the FM loading and digestate discharging.

The reactor showed in Fig. 2 was continuously monitored through a

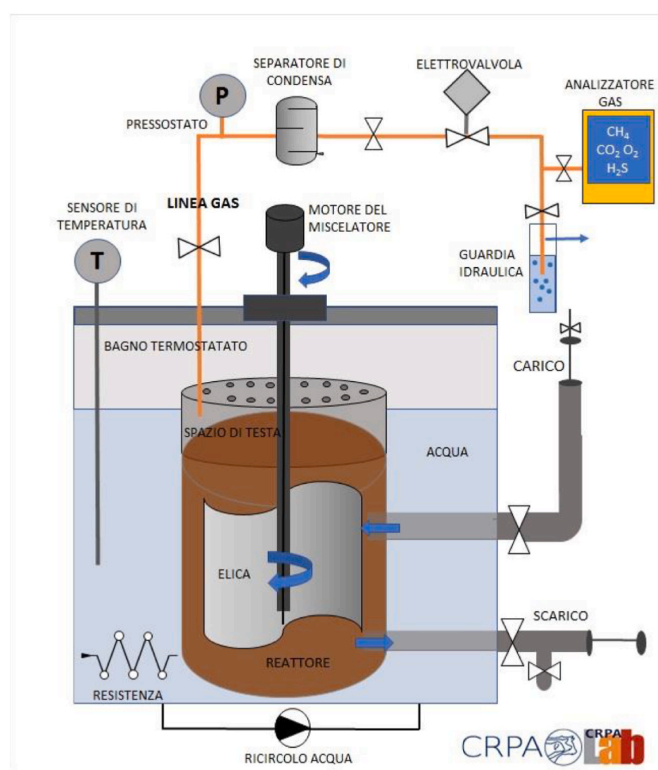

Fig. 1. Scheme of the AD experimental equipment, designed by CRPA Lab.

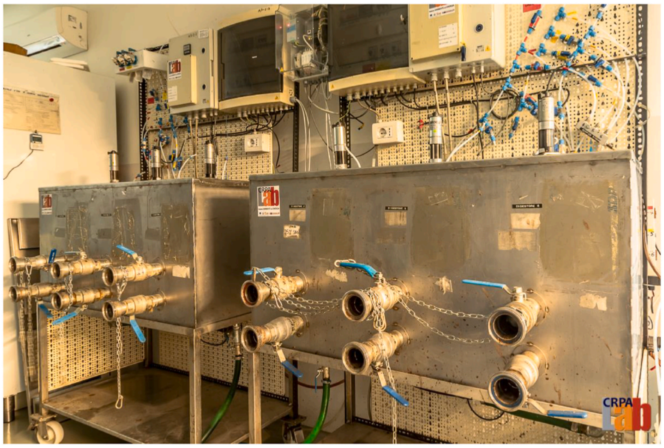

Fig. 2. Reactor used during the carried out AD test, designed by CRPA Lab.

manometer, by measuring the pressure increase within the headspace, due to generated accumulated gas and then released by venting. The overpressure was converted to biogas volume by following the equation proposed by Valero et al. [50], at both standard pressure (i.e., 1013.25 mbar) and standard temperature (i.e., 0 °C).

The quality of biogas, in terms of CH_4, H_2S, and CO_2 content, was recorded by using an infrared gas analyser (Geotech Instrument, Leamington Spa, UK). The reactor was daily fed and the digestate was daily collected and analysed for monitoring the process.

The reactor was provided with a feeding system, with a "syringe" for digestate extraction and a transducer for pressure monitoring during biogas production within the digester head space. The digestate was weekly monitored and was chemically characterized according to the parameters of TS, VS for evaluating the organic matter degradation rate, as well acidity (FOS), alkalinity (TAC), NTK, total organic carbon (TOC), and Ammonia Nitrogen (N–NH_4^+). Furthermore, before starting the test and at the end also P and K were analysed.

The test started by filling the reactor with an inoculum coming from an agricultural biogas plant that operates in same mesophile conditions, useful for making as far as possible suitable the microbial flora for the organic substance degradation and to reduce the start-up phase. The adopted inoculum was sampled the same day when the AD test started and was chemically characterized according to the parameters of TS, VS, FOS, TAC, NTK, N–NH_4^+, P, K, and Volatile Fatty Acids (VFAs), reported in Table 2.

The Stainless-steel digester (CSTR, Completely Stirred Tank Reactor) was set at 41 °C corresponding to mesophilic conditions. The test lasted about 80 days (start-up and the steady state phase included), with a required hydraulic retention time (HRT) of 26 days for reaching the organic loading rate (OLR) of 4.7 kg of volatile solids per day per m^3 of reactor. The digester 23 L (16 L working volume) was daily fed and the produced biogas was daily monitored.

VFAs during the AD test were measured by adopting the gas chromatographic (GC) method. As reported by Valenti et al. [6], 10 mL of the collected AD digestate was firstly centrifuged for 15 min using a centrifuge at 7025 times gravity (xg) to collect the supernatant, which was then washed using 85% (w/w) orthophosphoric acid to remove remaining solids and prepare the liquid sample for the GC analysis by means the GC system (GC-Agilent 7820A), equipped with a capillary column (Colonna Agilent J&W DB) and a flame ionization detector (FID).

3. Results and discussion

3.1. Feedstock-mixture characteristics

Each individual feedstock was analysed prior being mixed. All the primary characteristics were listed in Table 1. By analysing the results, almost all feedstocks showed a good moisture content. Olive pomace, with a TS percentage of about 16% and about its 88% consists of organic substance (VS), demonstrated a good moisture content. Also in tomato peels analysed sample the content was about 27% and 96% of TS, respectively for TS and VS. Analysed sampled of citrus pulp showed TS equal to about 17% with the ash content approximately equal to 74% of TS. The analyses of poultry and cattle manure, coming from laying chicken farm and cattle farm, respectively, demonstrated for poultry sample a dry matter content of 32%, VS content of 69% of TS, indeed a better moisture content, was recorded for cattle manure sample with the TS percentage of about 12% and approximately its 85% consists of organic substance (VS). Instead of, as regard sample of silage, which is characterised by particle size not homogeneous and greater than other feedstocks, the TS content was equal to about 35% and VS content to 93% of TS.

Then, based on different percentages of the analysed biomasses reported in Table 1, the FM was selected for carrying out firstly the BMP test and then the AD test.

The FM was designed by improving the FM analysed by Valenti et al., [19], by considering both the feedstocks availability and the FMs actually adopted within the biogas plants located in the study area.

Before BMP test, also the FM was primary characterised as reported in Table 3. Furthermore, during the BMP test, the FM has been chemically characterized, by analysing both TS and VS. The analysed average TS content was equal to 236.17 g/kg and the average VS content was equal to 206.58 g/kg that corresponds to about 87% of TS.

3.2. BMP and AD test

3.2.1. BMP test

Before starting AD test on the selected FM, a BMP test was carried out in duplicate. As averaged results, the specific production of methane for the FM was equal to 343.1 Nm^3CH_4/tVS (Fig. 3) with a VS reduction of about 68.4%. The peak value of the production, about 69.8 Nm^3CH_4/t (K_{max} value), was observed after 2.4 days (Table 4). BMP test results were listed in Table 4. Both the reactors adopted for the two replicates were cultured at 38 ± 1 °C for 27 days.

As it possible to observe from Fig. 3 the process was prompted quickly, due to the suitability of the adopted inoculum (i.e., suitable

Table 2
Characteristics of adopted inoculum.

TS	VS		pH	NTK		N–NH_4^+		P		K		FOS	TAC
[g/kg]	[g/kg]	[%TS]		[mg/kg]	[%TS]	[mg/kg]	[%NTK]	[mg/kg]	[%TS]	[mg/kg]	[%TS]	[mg/kg]	[mg/kg]
54.92	38.66	70.39	7.75	3053	5.56	1930	63.22	666	1.21	4117	7.50	3462	13659

VFA								
Acetic	Propionic	Iso-butyric	Butyric	Iso-valeric	Valeric	Iso-Caproic	Caproic	Heptane
[mg/kg]								
449	<50	<50	<50	<50	<50	<50	<50	<50

Table 3
Characteristics of FM.

FM sample	TS	VS		pH	NTK		$N–NH_4^+$		TOC	C/N
[date]	[g/kg]	[g/kg]	[%TS]	–	[mg/kg]	[%TS]	[mg/kg]	[%TS]	[%TS]	–
First day	236.39	210.74	89.15	4.62	6766	2.86	893	13.20	49.29	17.22
10th day	234.99	203.36	86.54	–	–	–	–	–	–	–
Last day	237.13	205.65	86.72	–	–	–	–	–	–	–
Average	236.17	206.58	87.47	–	–	–	–	–	–	–
Standard deviation	1.08	3.78	4.46	–	–	–	–	–	–	–

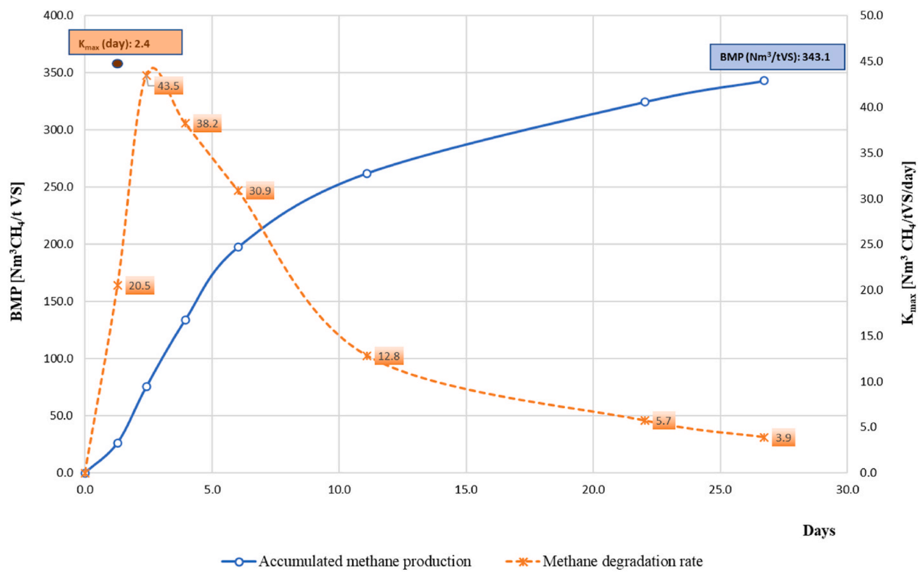

Fig. 3. Accumulated and daily methane production of the BMP test. Data are average of the two replicates.

Table 4
BMP test results of the analysed FM.

FM	BMP	BMP Peak value	K_{max} [a]	VS reduction	CH_4
	[Nm^3CH_4/tVS]	[Nm^3CH_4/t]	[days]	[%]	[%]
Sample 1	335.1	68.2	2.5	67.6	60.4
Sample 2	351.1	71.4	2.3	69.1	61.3
Average	343.1	69.8	2.4	68.4	60.9

[a] K_{max}: maximum degradation rate.

microbial flora). Furthermore, the methane production was immediately started, from the first days of the BMP test. As commonly observed in BMP test results, daily methane production curve (Fig. 3) allowed to identify the two different phases, respectively characterised, the first by an intense growth and the second one by a reduction of the speed production. Within the common practical a third phase could be identified, in which it is possible to observe a horizontal asymptote, which means that the maximum value of production was reached. In detail, the peak value of the production (i.e., K_{max} value) was obtained after about 2 days (Table 4).

3.2.2. AD test

The AD test parameters were set in order to monitor the biological parameters most significant for evaluating the AD process of the selected FM. Basically the test was set both for simulating the conditions of the FMs adopted in the biogas plants already present in the study area (e.g., Mediterranean area) and evaluating the necessary conditions for having and keeping a stable biological process. Therefore, the OLR as daily organic load, express in kgVS/m^3day was defined based on the BMP test results, by considering the expected biogas production, and the chemical characterisation of each single analysed feedstock.

The inoculum adopted for starting the AD test was chemical characterised prior to be used, and the results were listed in Table 2. The test duration was 80 days. Based on the chemical analyses results, the HRT was defined on 26 days, with a daily load of 4.7 kgVS/m^3day. From day 37 day, for a week the organic daily loading rate was increased to 5.5 kgVS/m^3day due to several days off for holiday. Therefore, the expected weekly load rate was spread over the actual weekly loading days with a consequent increase in the daily organic load rate.

During the AD test the specific methane production reached stability with an average value of 333 Nm^3 CH_4/tVS and it is possible to observe for about 50 consecutive days, production kept unchanged while in the last week a drop in methane production, an increase of FOS/TAC in the digestate, and a consequently accumulation of $N–NH_4^+$, were observed. This latter in any case was always below the critical values with the maximum measured ones equal to 3675 mg/kg.

At the beginning of the test the concentration of TS was equal to 5.5%, instead of at the end an increase in the value was observed by reaching 14% (Table 5).

In order to assess the stability of the biological process, analyses for evaluating the concentration of VFAs on digestate samples (Table 6) were carried out. The sample on day "0" refers to the starting inoculum and showed a low concentration of acetic acid, equals to 449 mg/kg, and negligible values of the other considered acids. The acetic acid value highly decreases during the test until the final stage, when after day 60 an increase was recorded (Table 6). Propionic acid remains negligible until the final stage in which the concentration reaches the value of at maximum 130 mg/kg at the end of the test.

The methane production was daily monitored. The accumulated biogas production is shown in Fig. 4. The biogas was daily detected and analysed for quantifying the percentage of methane as shown in Fig. 5.

Table 5
Characteristics of samples recorded during AD test.

FM sample	TS	VS		pH	FOS	TAC	FOS/TAC	N-NH_4^+	NTK	P	K
[day]	[g/kg]	[g/kg]	[%TS]	–	[mg/kg]	[mg/kg]	–	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
0	54.92	38.66	70.39	7.75	3462	13659	0.25	1930	3053	666	4117
5				–	4135	13651	0.3	–	–	–	–
12	57.77	38.68	66.96		2768	14690	0.19	2066	–	–	–
19					3255	15005	0.22	–	–	–	–
26	63.93	44.49	70.06		2526	15812	0.16	2272	–	–	–
33					3600	16224	0.22	–	–	–	–
40	83.01	60.96	73.44		3756	16755	0.22	2528	–	–	–
47					4496	17997	0.25	–	–	–	–
54	98.2	74.19	75.55		4380	18364	0.24	2937	–	–	–
61					4376	19826	0.22	–	–	–	–
68	102.94	78.18	75.95		5298	21304	0.25	3406	–	–	–
75					6300	22011	0.29	–	–	–	–
End	112.85	88.96	78.83	7.84	6964	22466	0.30	3554	6439	1492	5110
Average	81.95	60.63	73.02	–	4255	17520	0.24	–	–	–	–

Table 6
VFAs computed on samples recorded during AD test.

FM sample	Acetic acid	Propionic acid	Iso-butyric acid	Butyric acid	Iso-valeric acid	Valeric acid	Iso-caproic acid	Caproic acid
[day]	[mg/kg]							
0	449	<50	<50	<50	<50	<50	<50	<50
12	<50	<50	<50	<50	<50	<50	<50	<50
26	<50	<50	<50	<50	<50	<50	<50	<50
40	<50	<50	<50	<50	<50	<50	<50	<50
54	<50	129	<50	<50	<50	<50	<50	<50
68	344	<50	<50	<50	<50	<50	<50	<50
End	380	130	<50	<50	<50	<50	<50	<50

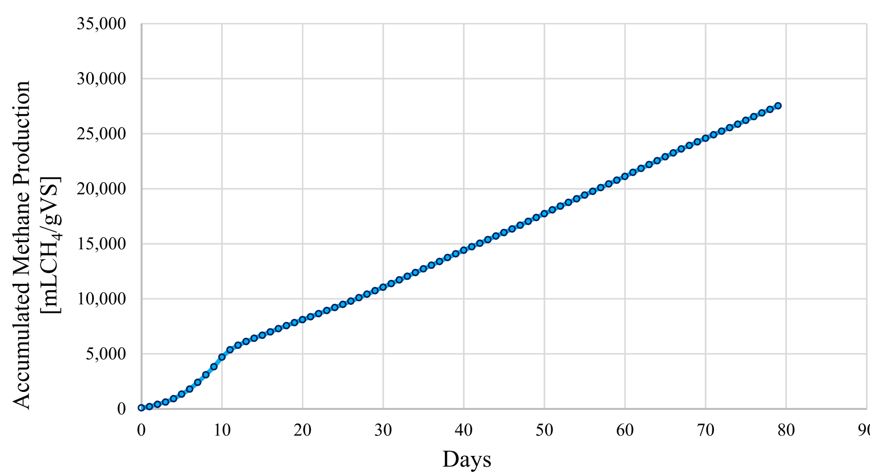

Fig. 4. Accumulated Methane production during AD test.

The average value of methane recorded during the entire test was 60.4%. Furthermore, at the end of the AD test, the analysis of the residual methane potential of the digestate was carried out on the final sample by obtaining a value equal to 121.5 Nm^3CH_4/tVS. The residual methane potential was measured by following both UNI EN ISO 11734:2004 [46] and UNI/TS 11703:2018 [47] standards.

The H_2S content, measured in produced biogas, is shown in Fig. 6. During the digestion process H_2S concentration reached the maximum value of 992 ppm during the final phase. The increment in H_2S content and a consequently lower concentration of CH_4 in the produced biogas was detected firstly after 55 days of the AD test and then after around 75 days of the AD test. CO_2 content in produced biogas was analysed too and its trend was reported in Fig. 7. It is possible to notice that, after the stabilisation process during the first days, in which the CO_2 reached the highest percentage of about 48% at day 5, the content of CO_2 was kept always between 35% and 40%.

The reactor was daily fed, and the same amount of the AD effluent was removed and kept refrigerator. The collected samples were every 12 days chemically characterized for TS and VS, with the aim of evaluating the degradation of the organic matter inside the reactor. Both the trend of monitored TS and VS were reported in Figs. 8 and 9, respectively.

During the test an increase in TS concentration was observed (Fig. 8). In the first 26 days it was affect by a slight decrease, then an increase was recorded. Therefore, the stability of the biological process was evaluated by analysing the stored samples for VFAs concentration. In detail acetic acid, butyric and iso-butyric acid, caproic and iso-caproic acid, valeric

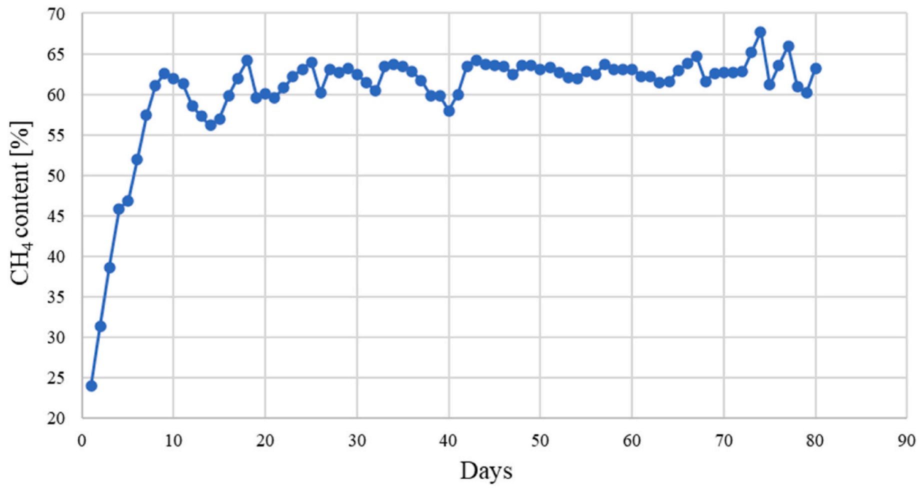

Fig. 5. CH_4 content measured on recorded daily produced biogas.

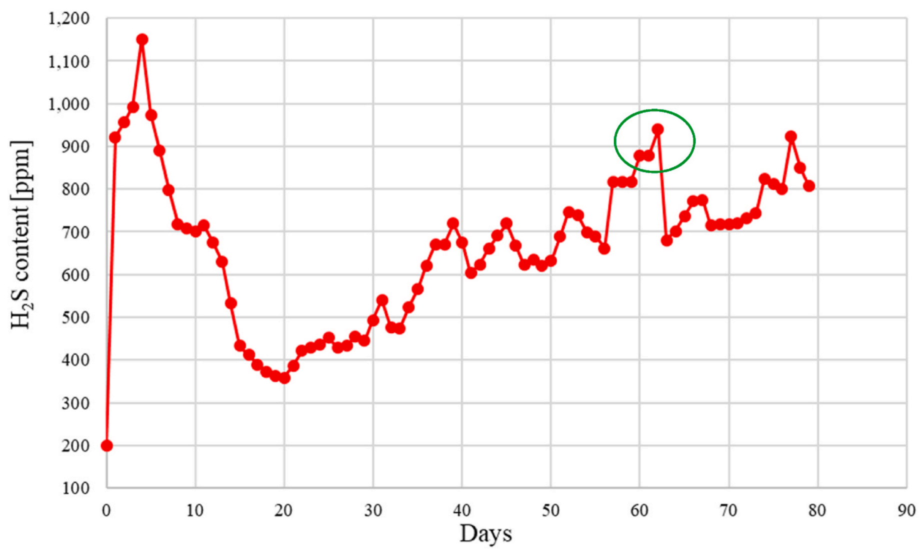

Fig. 6. H_2S content measured on recorded daily produced biogas.

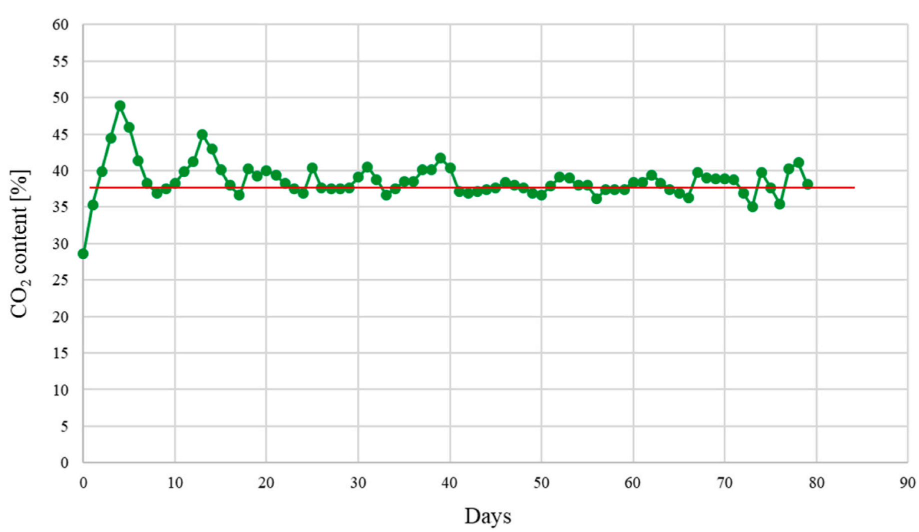

Fig. 7. CO_2 content measured on recorded daily produced biogas.

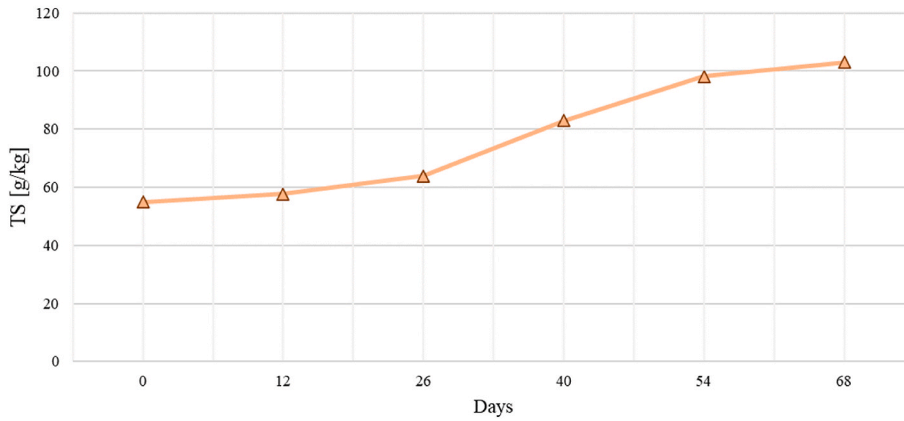

Fig. 8. TS trend monitored every 12 days during the AD test.

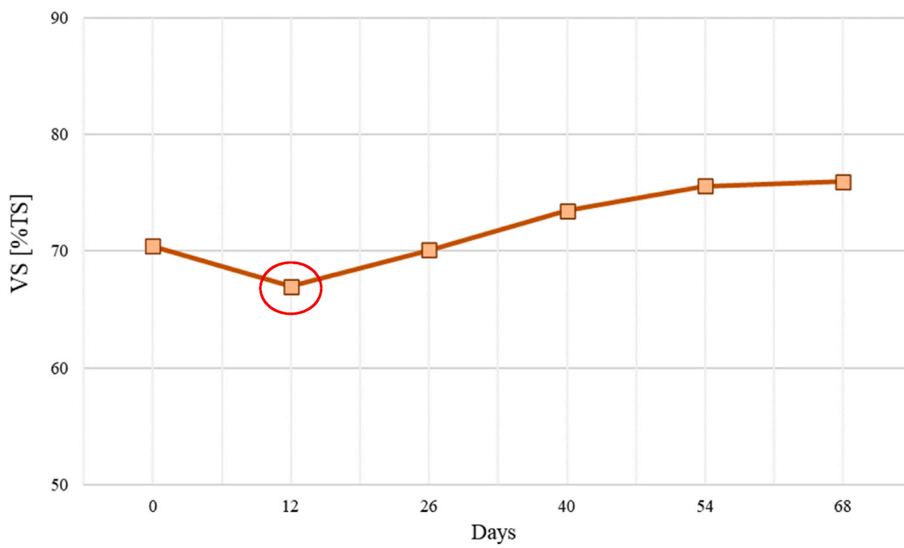

Fig. 9. VS trend monitored every 12 days during the AD test.

and iso-valeric acid, and propionic acid were analysed. In Fig. 9 acetic acid and propionic acid trends were reported.

The sample day "0" refers to the original inoculum; in the next collected samples during the beginning of the test the highest value of acetic acid, 450 mg/kg, was observed, which kept stable with a slight decrease after 50 days until reaching a concentration of 380 mg/kg at the end of the test (Fig. 10). Meanwhile, a propionic acid accumulation was also observed after 50 days of the AD test, by reaching a concentration value of about 150 mg/kg at the end of the test. In detail, during the increase of propionic acid, an increment in H_2S content and a

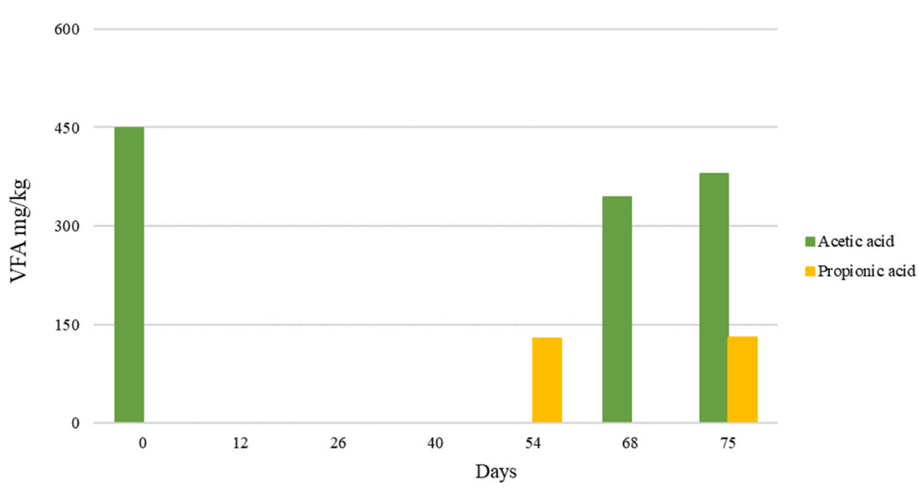

Fig. 10. Acetic and propionic acid concentrations in recorded digestate samples.

consequently decrease of CH_4 in the produced biogas was detected firstly after 55 days of the AD test and then after around 75 days of the AD test, as shown in Figs. 6 and 10, since the methane production is strongly related to the presence of propionic acid. Indeed, where an accumulation of the specific VFAs was observed, immediately increase of H_2S and decrease of CH_4 were presented. Since the propionic acid levels remained below the critical ones, the methane production was not affected because, as stated by Wu et al., [51], only concentrations of VFAs above 3 g/L are considered inhibitory for methanogenic bacteria. The computed values of acetic acid remain below the critical threshold, by slightly exceeding 400 mg/kg. The values of the other VFAs are negligible.

The FOS/TAC ratio (volatile organic acid and buffer capacity ratio) was computed by weekly analysing the digested daily extract. The results showed a constant ratio, as reported in Fig. 11, with a mean value of the entire test of 0.24 by indicating the stability of the process (Table 5). After the stabilisation phase (day 5) the FOS/TAC ratio decrease by reaching the equilibrium conditions until day 61 of the test. After, a slight increase was detected which correspond to a deterioration in the quality of biogas with higher values of H_2S that, at maximum, reached the value of about 940 ppm at day 63 (Fig. 6).

The FOS values fall within the stability range, by ranging from about 2500 to 6300 mg/kg, instead of the TAC values ranged from 13650 to 22000 mg/kg (Table 5). The pH values recorded during the AD test were kept constant during the entire test, just little slightly higher than the neutral value, about 7.8.

The AD obtained results showed that the selected FM could be a win-win solutions for valorising diverse agricultural residues and by-products available in Mediterranean area. As reported by Valenti et al. [18], the best results for enhancing biomethane production were obtained with the FM composed of silage 18%, whey 20%, poultry manure 13%, cattle manure 5%, olive pomace 18% and citrus pulp 26%, but by introducing tomato peels, the achieved results were improved. In detail, the investigated FM demonstrated a methane content of produced biogas higher than that obtained by the FMs previously investigated in literature by Valenti et al. [18]. In this regard, several FMs composed of cattle and poultry manure, silage, olive pomace, whey, and citrus pulp, without taken into account tomato peels, were investigated by the authors. In detail, as result, the FM3 was selected as the best FM with 57% of methane content in produced biogas. So, this study represents a step forward since it allows of valorising a new agro-industrial by-product (tomato peels) by enhancing bioenergy production.

Aravani et al., [52] investigated Mediterranean suitable substrate in Southern Greece (i.e., corn silage, cattle manure, watermelons, and tomato residues) in terms of methane yield maximization during AD test. In their study which is the case closer to our study, a OLR around 5 g and HRT of 20 days, were adopted, like our work. Usually, the adopted OLR in literature were found lower, and more specifically ranging between 1 and 4 g, due to the fact that at high OLR, the high content of non-fiber carbohydrates and fat may increase the rate of propionic acid to a level that the rate of its consumption is exceed by determining an inhibition of methanogens and severe pH decrease. For this reason, high OLR corresponds to short HRT [52].

The obtained results are new with regards the considered feedstocks (i.e., Mediterranean agricultural feedstocks). In this regard, as stated by Pan et al., [53], despite recent advancement in AD processes, the effect of feedstock compositions and operating conditions on the biomethane production processes has not been deeply explored. Therefore, they carried out a review investigating the effects of feedstock characteristics on the performance of an anaerobic digestion process. As result, by confirming the novelty of the FM tested in this study, it is possible to highlight that almost all the carried-out research studies on this topic were focussed only on food waste substrates [53]. However, Di Fraia et al., [54] investigated similar agro-industrial products (e.g., tomato residues, olive pomace) for estimating their energy potential, BMP or AD tests have not been performed. Their energy potential estimation of residual biomass was carried out through an equation-model by adopting the lower heating value of methane [54].

It is well known that energy is the backbone of any society's economic development. Recent estimates reveal that 84% of global primary energy consumption is provided by fossil fuels [3]. However, the current energy condition entails two negative externalities: fossil fuels are cheap but will run out (in fact, they are known as "non-renewable"); the environmental impacts and CO2 emissions brought about by their increasing use threaten the living world [55–57]. Against this backdrop, a rapid and comprehensive transition to renewable, low-carbon, environmentally friendly energy sources is deemed a pressing need, although not without an examination of its feasibility. Starting from this scope, the results obtained in this study, aimed at evaluating the technical feasibility of Mediterranean feedstocks co-digestion by enhancing the use of a mixture of biomass in AD process, demonstrated that the selected FM is viable to carry out the co-digestion, by enhancing the methane content of produced biogas.

4. Conclusions

The study proposed both BMP and semi-continuous AD approaches with the aim of evaluating the technical feasibility of a FM composed of seven Mediterranean feedstocks by improving the valorization of agricultural by-products. Indeed, the FM was tested for estimating its methane production and verifying the possible inhibitory effects on the biological process. As result, the FM was energetically interesting in terms of methane potential as showed by the analysis results.

Firstly, the BMP test demonstrated that the FM had potential to be used for biogas production, with a specific methane production equal to 343.1 Nm^3CH_4/tVS and a degradability of volatile solids (i.e., VS

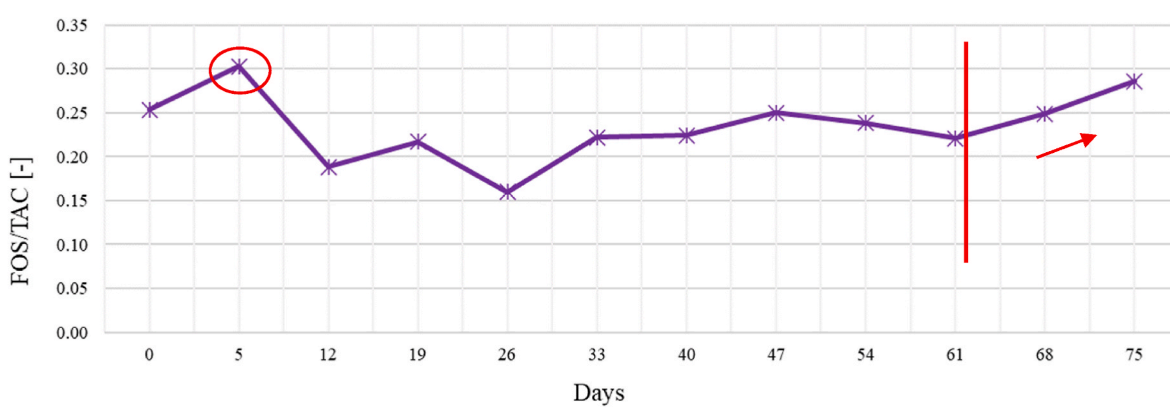

Fig. 11. FOS/TAC ratio computed by weekly samples during the AD test.

reduction) of about on average to 68.4%, with a great methane content recorded in the produced biogas equal to about 60.9%.

After BMP test, the AD test was carried out. The starting phase of the AD process was carried out with a slow loading ramp of about 26 days, it was checked and monitored, for avoiding any critical issues during the test. During the AD test the specific methane production was equal to about 333 Nm^3CH_4/tVS and it was found to be in line with that measured in the BMP tests and with the expected one by considering the production of each single feedstock.

The AD test demonstrated that the selected FM is viable to carry out the co-digestion, by enhancing the methane content of produced biogas. In detail, based on the obtained results, the FM could have positive net energy outputs and provide a flexible and useful solution to generate bioenergy from several agricultural residues and by-products available in Mediterranean area.

The optimal use of biomass to have higher conversion efficiency would suggest the use of cascade biorefinery processes. Studies on biorefineries and their environmental and economic evaluation are few in the literature, so there would be a need for further studies on the economic and technical evaluation of the possibility of the decomposition of materials used as biomass to feed the anaerobic digestion process. Efficient conversion in a cascade biorefinery depends on the spectrum of various end products and cost-effective processing schemes.

CRediT authorship contribution statement

Francesca Valenti: contributes to, Conceptualization, Data curation, Formal analysis, Methodology, Software, Investigation, Writing – original draft, Writing – review & editing. **Roberta Selvaggi:** contributes to, Conceptualization, Data curation, Formal analysis, Investigation, Writing – original draft, and, Writing – review & editing, Supervision. **Biagio Pecorino:** contributes to, Visualization. **Simona MC. Porto:** contributes to, Visualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This research was carried out within the project entitled "*Sostenibilità dell'agricoltura e dell'industria agro-alimentare Mediterranea*"—Programma Operativo Nazionale (PON) FSE–FESR "Research and Innovation 2014–2020, D.D. 407/2018" Attraction and Mobility (AIM)–Proposal: AIM1848200, Line 1, CUP E64I19002440007 supported by Italian Ministry of Education, University and Research (MIUR). Furthermore, it is in line with the aim of the project by the University of Catania: UPB: 5A722192127 (*Piano per la ricercar 2016–2018 – 'Contributo della meccanica agraria e delle costruzioni rurali per il miglioramento della sostenibilità delle produzioni agricole, zootecniche e agro-industriali'*).

The authors gratefully acknowledge support from CRPA Lab at C.R.P. A. SpA (Centro Ricerche Produzioni Animali) of Emilia-Romagna region.

References

[1] Available online (accessed on, Bristish Petroleum Statistical Review of World Energy, 2022. (Accessed 23 July 2022).
[2] V. Smil, Energy and Civilization, MIT Press Ltd., Cambridge, MA, USA, 2018, 2018.
[3] L. Delannoy, P.Y. Longaretti, D.J. Murphy, E. Prados, Assessing global long-term EROI of gas: a net-energy perspective on the energy transition, Energies 14 (2021) 5112.
[4] M. Lanfranchi, C. Giannetto, A. De Pascale, Analysis and models for the reduction of food waste in organized large-scale retail distribution in eastern Sicily, Am J ApplScim 11 (10) (2014) 1860–1874.
[5] D.R. Schneider, N. Duić, Ž. Bogdan, Mapping the potential for decentralized energy generation based on 406 renewable energy sources in the Republic of Croatia, Energy 32 (9) (2007) 1731–1744.
[6] F. Valenti, S.M.C. Porto, R. Selvaggi, B. Pecorino, Co-digestion of By-Products and Agricultural Residues: A Bioeconomy Perspective for a Mediterranean Feedstock Mixture, 700, Science of the Total Environment, 2020, 134440, https://doi.org/10.1016/j.scitotenv.2019.134440.
[7] F. Demichelis, T. Tommasi, F.A. Deorsola, D. Marchisio, D. Fino, Effect of inoculum origin and substrate-inoculum ratio to enhance the anaerobic digestion of organic fraction municipal solid waste (OFMSW), J. Clean. Prod. 351 (2022), 131539.
[8] M. Hiloidhari, D.C. Baruah, M. Kumari, S. Kumari, I.S. Thakur, Prospect and potential of biomass power to mitigate climate change: a case study in India, J. Clean. Prod. 220 (2019) 931–944, https://doi.org/10.1016/j.jclepro.2019.02.194.
[9] A.S. Gutierrez, J.J. Cabello Eras, L. Hens, C. Vandecasteele, The energy potential of agriculture, agroindustrial, livestock, and slaughterhouse biomass wastes through direct combustion and anaerobic digestion. The case of Colombia, J. Clean. Prod. 269 (2020), 122317.
[10] N. Bilandzija, N. Voca, B. Jelcic, V. Jurisic, A. Matin, M. Grubor, T. Kricka, Evaluation of Croatian agricultural solid biomass energy potential, Renew. Sustain. Energy Rev. 93 (2018) 225–230, https://doi.org/10.1016/j.rser.2018.05.040.
[11] A. Castellano, R. Selvaggi, P. Mantovi, D. Spina, M. Hamam, G. Pappalardo, The effect of fertilization with microfiltered liquid digestate on the quality parameters of Citrus fruits, Front. Sustain. Food Syst. 7 (2023) 2023, https://doi.org/10.3389/fsufs.2023.1128103.
[12] G. Pappalardo, E. Trimarchi, R. Selvaggi, Assessment of economic viability and production costs for the innovative microfiltered digestate, J. Environ. Manag. 332 (2023), 117360, https://doi.org/10.1016/j.jenvman.2023.117360.
[13] EU. http://eur-lex.europa.eu/resource.html?uri=cellar:aa88c66d-4553-11e4- a0cb-01aa75ed71a1.0022.03/DOC_1&format=PDF, 2014. November 2021.
[14] A. Zabaniotou, P. Kamaterou, Food waste valorization advocating Circular Bioeconomy-A critical review of potentialities and perspectives of spent coffee grounds biorefinery, J. Clean. Prod. 211 (2019) 1553–1566.
[15] E. Papargyropoulou, R. Lozano, K. Steinberger, J. Wright, N. Ujang, Z. Bin, The food waste hierarchy as a framework for the management of food surplus and food waste, J. Clean. Prod. 76 (2014) 106–115.
[16] A. Sagastume Gutierrez, J.J. Cabello Eras, L. Hens, C. Vandecasteele, The energy potential of agriculture, agroindustrial, livestock, and slaughterhouse biomass wastes through direct combustion and anaerobic digestion. The case of Colombia, J. Clean. Prod. 269 (2020), 122317.
[17] F. Valenti, J.P. Rojas-Sossa, Y. Zhong, S.M.C. Porto, A. Toscano, T. Marsh, B. E. Dale, Y. Liu, W. Liao, Effects of Mediterranean agricultural residues on microbial community and anaerobic digestion performance, Biofuel., Bioproduct. Biorefin. 16 (2) (2022) 523–536, https://doi.org/10.1002/bbb.2321.
[18] F. Valenti, Y. Zhong, M. Sun, S.M.C. Porto, A. Toscano, B.E. Dale, F. Sibilla, W. Liao, Anaerobic co-digestion of multiple agricultural residues to enhance biogas production in southern Italy, Waste Manag. 78 (2018) 151–157.
[19] F. Valenti, S.M.C. Porto, R. Selvaggi, B. Pecorino, Evaluation of biomethane potential from by-products and agricultural residues co-digestion in southern Italy, J. Environ. Manag. 223 (2018) 834–840.
[20] F. Valenti, W. Liao, S.M.C. Porto, Life cycle assessment of agro-industrial by-product reuse: a comparison between anaerobic digestion and conventional disposal treatments, Green Chem. 22 (20) (2020) 7119–7139, https://doi.org/10.1039/d0gc01918f.
[21] O. Kuczman, M.V. Diniz Gueri, S.N. Melegari De Souza, W.N. Schirmer, H.J. Alves, D. Secco, W.G. Buratto, C. Bastos Ribeiro, F. Beltrame Hernandes, Food waste anaerobic digestion of a popular restaurant in Southern Brazil, J. Clean. Prod. 196 (2018) 382–389.
[22] S. Tait, P.W. Harris, B.K. McCabe, Biogas recovery by anaerobic digestion of Australian agro-industry waste: a review, J. Clean. Prod. 299 (2021), 126876.
[23] S. Elkhalifa, T. Al–Ansari, H.R. Mackey, G. McKay, Food waste to biochars through pyrolysis: a review, Resour. Conserv. Recycl. 144 (2019) 310–320, https://doi.org/10.1016/j.resconrec.2019.01.024.
[24] R. Kapoor, P. Ghosh, B. Tyagi, V.K. Vijay, V. Vijay, I.S. Thakur, H. Kamyab, D. D. Nguyen, A. Kumar, Advances in biogas valorization and utilization systems: a comprehensive review, J. Clean. Prod. 273 (2020), 123052, https://doi.org/10.1016/j.jclepro.2020.123052.
[25] S.K. Awasthi, M. Kumar, S. Sarsaiya, V. Ahluwalia, H. Chen, G. Kaur, R. Sirohi, R. Sindhu, P. Binod, A. Pandey, R. Rathour, S. Kumar, L. Singh, Z. Zhang, M. J. Taherzadeh, M.K. Awasthi, Multi-criteria research lines on livestock manure biorefinery development towards a circular economy: from the perspective of a life cycle assessment and business models strategies, J. Clean. Prod. 341 (2022), 130862.
[26] K. Liu, Y.Q. Tang, T. Matsui, S. Morimura, X.L. Wu, K. Kida, Thermophilic anaerobic co-digestion of garbage, screened swine and dairy cattle manure, J. Biosci. Bioeng. 107 (2009) 54–60.
[27] C.L. Gou, Z.H. Yang, J. Huang, H.L. Wang, H.Y. Xu, L.K. Wang, Effects of temperature and organic loading rate on the performance and microbial community of anaerobic co-digestion of waste activated sludge and food waste, Chemosphere 105 (2014) 146–151.
[28] F.J. Callaghan, D.A.J. Wase, K. Thayanithy, C.F. Forster, Continuous co-digestion of cattle slurry with fruit and vegetable wastes and chicken manure, Biomass Bioenergy 22 (2002) 71–77.
[29] M. Muradin, Z. Foltynowicz, Potential for producing biogas from agricultural waste in rural plants in Poland, Sustainability 6 (8) (2014) 5065–5074.

[30] R. Wickham, B. Galway, H. Bustamante, L.D. Nghiem, Biomethane potential evaluation of co-digestion of sewage sludge and organic wastes, Int. Biodeterior. Biodegrad. 113 (2016) 3–8.
[31] F. Tasnim, S.A. Iqbal, A.R. Chowdhury, Biogas production from anaerobic co-digestion of cow manure with kitchen waste and Water Hyacinth, Renew. Energy 109 (2017) 434–439.
[32] J. Mata-Alvarez, S. Mace, P. Llabres, Anaerobic digestion of organic solid wastes, Overv Res Achiev Perspect Bioresour Technol 74 (2000) 3–16.
[33] P.S. Jagadabhi, A. Lehtomaki, J. Rintala, Co-digestion of grass silage and cow manure in a cstr by re-circulation of alkali treated solids of the digestate, Environ. Technol. 29 (2008) 1085–1093.
[34] J.B. Holm-Nielsen, T. Al Seadi, P. Oleskowicz-Popiel, The future of anaerobic digestion and biogas utilization, Bioresour. Technol. 100 (2009) 5478–5484.
[35] J. Mata-Alvarez, J. Dosta, S. Mace, S. Astals, Codigestion of solid wastes: a review of its uses and perspectives including modeling, Crit. Rev. Biotechnol. 31 (2011) 99–111.
[36] S. Astals, D.J. Batstone, J. Mata-Alvarez, P.D. Jensen, Identification of synergistic impacts during anaerobic co-digestion of organic wastes, Bioresour. Technol. 169 (2014) 421–427.
[37] F.A. Shah, Q. Mahmood, N. Rashid, A. Pervez, I.A. Raja, M.M. Shah, Co-digestion, pretreatment and digester design for enhanced methanogenesis, Renew. Sustain. Energy Rev. 42 (2015) 627–642.
[38] Eurostat, 2019. https://ec.europa.eu/eurostat/statisticsexplained/index.php/Renewable_energy_statistics#of_renewable_energy_used_in_transport_activities_in_2018, 09/2020.
[39] F. Valenti, W. Liao, S.M.C. Porto, A GIS-based spatial index of feedstock-mixture availability for anaerobic co-digestion of Mediterranean by-products and agricultural residues, Biofuels, Bioproducts and Biorefining 12 (3) (2018) 362–378.
[40] R. Selvaggi, F. Valenti, G. Pappalardo, L. Rossi, S. Bozzetto, B. Pecorino, B.E. Dale, Sequential crops for food, energy and economic development in rural areas: the case of Sicily, Biofuel., Bioproduct. Biorefin. 12 (2018) 22–28.
[41] R. Selvaggi, G. Pappalardo, G. Chinnici, C.I. Fabbri, Assessing land efficiency of biomethane industry: a case study of Sicily, Energy Pol. 119 (2018) 689–695.
[42] F. Valenti, S.M.C. Porto, B.E. Dale, W. Liao, Spatial analysis of feedstock supply and logistics to establish regional biogas power generation: a case study in the region of Sicily, Renew. Sustain. Energy Rev. 97 (2018) 50–63.
[43] R. Selvaggi, F. Valenti, Assessment of fruit and vegetable residues suitable for renewable energy production: GIS-based model for developing new frontiers within the context of circular economy, Applied System Innovation 4 (1) (2021) 1–15, https://doi.org/10.3390/ASI4010010.
[44] G. Pappalardo, R. Selvaggi, B. Pecorino, Biomethane production potential in Southern Italy: an empirical approach, Renew. Sustain. Energy Rev. 158 (2021), 112190, https://doi.org/10.1016/j.rser.2022.112190.
[45] R. Selvaggi, F. Valenti, B. Pecorino, S.M.C. Porto, Assessment of tomato peels suitable for producing biomethane within the context of circular economy: a GIS-based model analysis, Sustainability 13 (10) (2021) 5559, https://doi.org/10.3390/su13105559.
[46] ISO-11734, Water Quality—Evaluation of the Ultimate Anaerobic Biodegradability of Organic Compounds in Digested Sludge—Method by Measurement of the Biogas Production, 1995.
[47] UNI/TS 11703:204, Method for the Assessment of Potential Production of Methane from Anaerobic Digestion in Wet Conditions – Matrix into Foodstuffs. UNI/CT 284, 22 February 2018.
[48] APHA-AWWA-WPCF, Standard Methods for the Examination of Water and Wastewater, twenty-first ed., American Public Health Association, Washington, DC, 2005.
[49] M. Soldano, N. Labartino, L. Rossi, C. Fabbri, S. Piccinini, Recovery of agro-industrial by-products for anaerobic digestion: olive pomace and citrus pulp, in: Proceedings 22th European Biomass Conference and Exhibition, 2014, pp. 23–26. June 2014 pp. 203–205.
[50] D. Valero, J.A. Montes, J.L. Rico, C. Rico, Influence of headspace pressure on methane production in Biochemical Methane Potential (BMP) tests, Waste Manag. 48 (2015), https://doi.org/10.1016/j.wasman.2015.11.012.
[51] B. Wu, X. Zhang, D. Shang, D. Bao, S. Zhang, T. Zheng, Energetic-environmental-economic assessment of the biogas system with three utilization pathways: combined heat and power, biomethane and fuel cell, Bioresour. Technol. 214 (2016) 722–728.
[52] V.P. Avarani, K. Tsigkou, V.G. Papadakis, Ww Wang, M. Kornaros, Anaerobic co-digestion of agricultural residues produced in Southern Greece during the spring/summer season, Biochem. Eng. J. 192 (2023), 108826.
[53] S. Pan, C. Tsai, C. Liu, S. Wang, H. Kim, C. Fan, iScience 24 (2021), 102704.
[54] S. Di Fraia, S. Fabozzi, A. Macaluso, L. Vanoli, Energy potential of residual biomass from agro-industry in a Mediterranean region of southern Italy (Campania), J. Clean. Prod. 227 (2020), 124085.
[55] T. Napp, D. Bernie, R. Thomas, J. Lowe, A. Hawkes, A. Gambhir, Exploring the feasibility of low-carbon scenarios using Historical energy transitions analysis, Energies 10 (2017) 116.
[56] J. Jewell, A. Cherp, On the political feasibility of climate change mitigation pathways: is it too late to keep warming below 1.5 °C? WIREs Clim. Chang. 11 (2019) 621, 2019.
[57] J. Nieto, O.Ã.Å. Carpintero, L.J. Miguel, I. de Blas, Macroeconomic modelling under energy constraints: global low carbon transition scenarios, Energy Pol. 137 (2020), 111090.