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Co-digestion of by-products and agricultural residues: a bioeconomy perspective for a Mediterranean feedstock mixture

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Abstract

This study focused on applying batch and continuous co-digestion approaches to investigate the effects of a feedstock mixture (FM) constituted by ten Mediterranean feedstocks highly available in the Mediterranean area (i.e., olive pomace, olive mill wastewater, citrus pulp, poultry litter, poultry and cattle manure, whey and cereal straw) on methane production for bioenergy generation. For the same feedstock mixture (FM), two different anaerobic digestion (AD) tests were carried out to evaluate the possible inhibitory effects of some biomasses on the biological process.

The first AD test showed a methane yield equal to 229 Nm^3CH_4/tVS (27% lower than that measured during the batch test). During the second AD test, the specific production was 272 m^3CH_4/tVS. Both tests showed a similar methane content of methane in the biogas, equal to about 57%.

The first AD test showed an inhibition effect of the process: total conversion of the organic matter into biogas was not ended. The second batch test demonstrated that the selected FM could be viable to carry out the co-digestion and could provide a flexible solution to generate advanced biofuels in biogas plants located in the Mediterranean area.

Keywords

Biomethane; Anaerobic Digestion; Bioeconomy; Biomasses; Advanced biofuels.

1. Introduction

Among the greatest challenges human beings face in the 21st century, environmental pollution and energy instability are the most crucial. In detail, air pollution and global warming are the major concerns for the natural environment, which could be attributed to the large amount of greenhouse gases (GHG) from the continuous increasing combustion of fossil fuels (Abdshahian et al., 2010; Bansal et al., 2013; Hosseini et al., 2013). In this regard, it is well known that GHG, with 60% of

CO_2 emissions and about 15% of CH_4 emissions, are the most responsible in global warming (Williams et al., 2012; Hosseini and Wahid, 2014; Rahimnejad et al., 2015).

According to the Kyoto protocol the key factor to both reduce CO_2 and other GHG emissions and improve the living standard of developing countries is to produce cost effective energy as well as use bioenergy efficiency (Changua et al., 1999; Garnier, 2014; Ebner et al., 2015). In this context, renewable bioenergy is a promising alternative to achieve the world energy requirements by avoiding extra economic burden and any significant environmental impacts (Morero et al., 2015; Raimondo et al., 2018; Valenti et al., 2018a). Renewable energy supply chains were documented by Ingrao et al. 2018a as important for transitioning to equitable, sustainable, post fossil-carbon societies. In this context, biomass has become one of the most interesting input for sustainable processes.

The opportunity to disaggregate and re-aggregate the chemical components of biomass improves the value of resources usually considered only a cost, such as waste. The sectors which were born around this opportunity (e.g., bio-materials, specialized micro-organisms, fibers, new foods.) have shown important growth capacities and have developed new processes and products (Birner, 2018). The new knowledge gives multifunctional characteristics to agricultural byproducts. Therefore, a reformulation of the boundaries between sectors is required: a sustainable bioeconomy must prioritize the production of high-quality foods, but also the transformation of waste material into energy, as the last step in a series of use and reuse cycles (Ingrao et al., 2018b). As defined by Food and Agriculture Organization of the United Nations (FAO) the principal aim of the bioeconomy is not only to replace fossil raw materials, but also to develop completely new products and processes (FAO, 2018).

In reports from a few years ago, a systemic approach to the circular economy and to the bioeconomy was applied, but recently these concepts were better defined considering also the aspects of bio-based products and the sustainable use of renewable resources (EFA, 2018). Moreover, both concepts were often used as substitutes but are very different.

The concept of circular economy is based on rethinking industrial processes (Frosch and Gallopoulos, 1989) and draws from the ideas of industrial ecology and industrial metabolism formulated between 1970's and 1980's. The general framework of circular economy contemplates that, in opposition to linear economy, economic actors would exert no net effects on the environment (D'Amato et al., 2017). This involves a system to obtain net reductions at the organizational supply chain and industrial levels (The Ellen MacArthur Foundation, 2012; Murray et al., 2015).

Bioeconomy was defined by Georgescu-Roegenas in 1975, as a biophysical perspective to the economy. This concept is based on the idea that industrial inputs (e.g., material, chemicals, energy) should be derived from renewable biological resources, with research and innovation enabling the transformational process (Kleinschmit et al., 2014; Pfau et al., 2014; Bugge et al., 2016).

More generally, the choice of the adoption of these two concepts as economic and environmental strategy is motivated by the fact that they all propose to adapt to or transform the current economy towards a more sustainable one. In this context forestry and the agriculture and forest industry can play a fundamental role in providing bio-based substitutes for non-renewables ones in different fields (Ollikainen, 2014; Roos and Stendahl, 2015).

In energy field, several type of biomass can be reused as feedstock to produce biogas via the anaerobic digestion (AD) process, which is a biological treatment without oxygen to produce biogas, a mixture formed mainly of methane and carbon dioxide. AD is a well-established technology to treat organic-matter rich biomass and is increasingly gaining ground as one valid route to produce renewable energy in a sustainable manner (Ciriminna et al., 2019). So, it contributes to create the conditions for a closed circular economy to reduce environmental and economic costs resulting from food waste disposal agri-food supply chains (Borrello et al., 2016).

Biogas is an environmentally derived energy source which attracts increasing attention (Esposito et al., 2012) due to its capabilities of both waste treatment and energy recover (Gebrezgabher et al., 2010). A relevant number of research studies was carried out on all aspects of biogas production, processing and utilization.

AD has been applied worldwide as a biological process to reuse by-products and waste materials, by transforming them into energy sources through the treatment of various organic waste such as municipal solid waste, food waste, industrial waste, sewage sludge, animal manure and agricultural residues (Comparetti et al., 2015; Çelik and Demirer, 2015; Huang et al., 2015; Shen et al., 2015; Yong et al., 2015). In detail, AD of organic waste could help to reduce odour release, a decrement of pathogens and a low requirement for organic sludge. Furthermore, the digestate produced at the end of the process can be adopted as an organic fertilizer for arable land instead of mineral and organic fertilizer as well as an organic substrate for greenhouse cultivation (De Vries et al., 2012; Ounnar et al., 2012; Nasir et al., 2013; Hidalgo and Martín-Marroquín, 2015; Selvaggi et al., 2018a;

Katinas et al., 2019). In fact, in the context of a circular economy, the digestate can contribute to improve agronomical value of soils (Pappalardo et al., 2018a) and to reduce fertilizer costs (Amon et al., 2007; Pappalardo et al., 2018b).

However, the AD process from different organic biomasses is a relatively sensitive process which mainly depends on the compounds of substrates that can be converted into biogas: chemical composition and biodegradability of the biomasses are the key factors for the biogas and biomethane productions (Salminen and Rintala, 2002). Many studies have been performed on the AD process using mono-substrates (Schittenhelm, 2008; Khalid et al., 2011; Babaee et al., 2013).

In the last years there were many researches aiming to deepen AD knowledge and to broaden its application (Mata-Alvarez et al., 2000; Cavinato et al., 2010; Kacprzak et al., 2010; Astals et al., 2013; Sahito et al., 2014; Hubenov et al., 2015; Ohemeng-Ntiamoah and Datta, 2019). In most of them, co-digestion of agricultural waste and manure was investigated. In detail, Cavinato et al. (2010) carried out co-digestion of cattle manure, agro-wastes and energy crops; Kacprzak et al. (2010) analysed co-digestion of agricultural and waste; Hubenov et al. (2015) investigated a co-digestion of waste fruit and vegetables and swine manure; Sahito et al. (2014) carried out canola straw and buffalo dung co-digestion. In contrast, Schittenhelm (2008) analysed only maize digestion and Astals et al. (2013) carried out a pig manure co-digestion. As result the co-digestion process was adopted to overcome the difficulty of mixing agro-industrial by-products and livestock manure (Chen et al., 2013; Valenti et al., 2018b).

Anaerobic co-digestion (AcoD) can establish good synergisms in the digestion reactor and it is economically feasible. Therefore, in the last decades, AcoD has been widely used to enhance the biogas production and several publications have dramatically increased becoming AcoD as the most relevant topic within research focused on AD process.

Several researches studied the AcoD of livestock manure with different biomasses (i.e., municipal, industrial and agricultural by-products) to enhance biogas production (Callaghan et al., 2002; Giuliano et al., 2013; Sahito et al., 2014). In particular, Callaghan et al. (2002) focused on optimization of a co-digestion process by using three feedstocks of cattle and chicken manure, and fruit/vegetable wastes. Muradin and Foltynowicz (2014) carried out an economic analysis of a biogas plant which treated nine feedstocks (i.e., corn silage, potato pulp, spent vinessa waste, fruit and vegetable pomace, cereals, plat tissue waste, municipal sludge and soya oil). Wickham et al. (2016) analysed different mixing ratio of sewage sludge and organic waste co-digestion to evaluate their biomethane potential. Tasnim et al. (2017) showed a better gas production from the mixed co-digestion of cow manure, sewage sludge and water hyacinth than the co-digestion of cow manure and kitchen wastes. Valenti et al. (2018c) investigated the effect of mixing six agro-industrial feedstocks (i.e., citrus pulp, olive pomace, whey, corn silage, cattle and poultry manure) on biomethane production, considering different analytical approaches. Valenti et al. (2018b) investigated six different feedstock-mixtures containing five Mediterranean biomasses such as poultry manure, Italian sainfoin silage (Hedysarum Coronarium L.) and opuntia fresh cladodes and, among the main available biomasses, citrus pulp and olive pomace by demonstrating a good biogas production from different organic matrices.

As stated by all these authors, the main advantage of AcoD process is the improvement of biogas production and its methane content. Moreover, AcoD could help to improve the stabilization of the process, the dilution of inhibitory substances, the nutrient balance and the reduction of GHG emissions. Furthermore, AcoD could also contribute to achieve synergetic effect of microorganisms, and increase the load of biodegradable organic matter (Mata-Alvarez et al., 2000; Jagadabhi et al., 2008; Holm-Nielsen et al., 2009; Mata-Alvarez et al., 2011; Astals et al., 2014; Mata-Alvarez et al., 2014; Shah et al., 2015).

Actually, the transport cost of the feedstocks to the biogas plants during the supply phase is the first selection criteria for considering new biomasses or selecting new location for biogas plants (Valenti at al., 2018d). Despite this fact, it is still important to select the best biomasses (i.e., by-products and agricultural waste) and feedstock-mixture with the aim of favouring synergisms and optimizing methane production. Yet, in-depth analyses of parameters, which could affect AcoD, and adjustment of operating parameters and optimisation strategies are still necessary. It is crucial to know the potential biogas production of a feeding organic mixture to achieve the correct approach in operating AD processes. By considering the availability of several agricultural residues and by-products and the absence of a correlation between BMP and single substrate properties (Rodrigues et al., 2019), increasingly digesters aim to adopt mix of different feedstocks to improve their digestion process performance. Lab-scale tests are required to determine the feasibility of such operations. So, in Sicily, the largest island in the Mediterranean basin highly characterised by agricultural activities, the development of the AD sector could be achieved by reusing and valorising the large amount of by-products available (Selvaggi et al., 2017 and 2018b). Therefore, the research of possible anaerobic digestion of multiple feedstocks is urgently needed to reduce disposal costs for companies that produce wastes and by-products and to increase their incomes.

In this context, the study reported in this paper focused on applying batch and continuous co-digestion approaches to investigate the effects of a feedstock mixture (FM) constituted by ten Mediterranean feedstocks highly available in the Mediterranean area (i.e., olive pomace, olive mill wastewater, citrus pulp, poultry litter, poultry and cattle manure, whey and cereal straw) on methane production for bioenergy generation. The novelty of this research is that the chemical tests were performed to put in evidence a new mix of biomasses: new limits for the contents of citrus pulp (most available by-product) were tested.

2. Materials and Methods

2.1 Feedstocks characteristics

Among the agricultural residues and by-product produced in the Mediterranean area, ten biomasses were selected as suitable feedstocks for the co-digestion process, based on their potential availability: citrus pulp, olive mill wastewater, Triticale silage, poultry litter, poultry and cattle manure, whey, tomato peels and cereal straw.

By considering the potential availability of the selected agricultural residues and by-products, a feedstock-mixtures (FM) of the selected ten biomasses was prepared based on the typical Mediterranean feedstock-mixture already used in digesters located in Sicily (Table 1). Citrus pulp was selected as main feedstock since it is highly available in the study areas where there is a relevant production of citrus fruits (Valenti at al., 2016; 2017a; 2017b; 2017c; Chinnici et al., 2018).

The biomasses used to carry out the co-digestion process have been partially provided from the Department of Agriculture, Food and Environment of the University of Catania (Sicily, Italy). In detail, citrus pulp and tomato peels were collected and shipped in coolers to the CRPA Lab (Research Center for Animal Production). The other feedstocks considered for the mixture, i.e. olive pomace (three phase), olive mill wastewater, poultry litter, poultry and cattle manure, whey, and cereal straw were collected by CRPA from farms located in Emilia-Romagna region (Italy).

Each individual sample was firstly chopped to reduce particle size by using a blender, and then were kept frozen prior to use. Every feedstock was chemically characterized according to the parameters of total solids (TS) and volatile solids (VS). The characteristics of individual feedstocks and of the selected feedstock-mixture are listed in Table 1.

Table 1. Characteristics of individual feedstocks and mass ratios of different feedstocks in FM.

2.2 Equipment and protocols of biomethane potential and semi-continuous anaerobic digestion of feedstock-mixture (FM)

2.2.1 Biomethane potential test

The Biomethane Potential (BMP) test, which allows the evaluation of the maximum content of methane and/or biogas that can be produced from biomasses, was modified based on methods reported in the UNI EN ISO 11734/2004 framework, described by Valenti et al. (2018b). Before starting the semi-continuous anaerobic digestion test the BMP static test was performed by simulating what usually could happen in a real-scale anaerobic plant.

The digester, a glass bottle with a total volume of about 2200 ml, was filled with the FM to about 70% and then placed in a thermostat cabinet (temperature of about 38 °C) for the entire digestion process. The BMP test was carried out also for citrus pulp, since it represents the main feedstock within the analysed FM. The content of produced biogas was monitored by adopting the mass method (Valenti et al., 2018b). In detail, during the gas analysis, the volume of the produced biogas was calculated, and the quality of the biogas was analysed.

During the test the biogas was analysed continuously, and the total amount of gas produced was reported in a cumulative production curve in order to provide also information about the degradation rate (Soldano et al., 2014]. Biogas quality, in terms of carbon dioxide (CO_2) and methane (CH_4) content, was determined using an infrared gas analyser (Geotech Instrument, Leamington Spa, UK).

2.2.2 Anaerobic digestion test

As well known, AD is a multistage process of biological reactions in series and in parallel, in absence of oxygen. The process can be traced back to 4 main phases: hydrolysis, acidogenesis, acetogenesis, methanogenesis. Methanogenic bacteria are only operational in the last phase. The families of bacteria mineralize the organic substance mainly in methane (CH_4), dioxide carbon (CO_2), ammonia (NH_3), hydrogen sulphide (H_2S) and water (H_2O). The process involves several families of bacteria: fermentative bacteria, acetogenic bacteria that produce H_2, Acetogenic bacteria using H_2, Archea oxygen-reducing metanigenes, acetyl methanogens (using acetic acid). In addition to the transformations described above, other reactions may also trigger accumulation of high molecular weight fatty acids, alcohols, propionic acid and butyric acid. However, these reactions occur above all in case of management problems of the biological process. In normal mesophilic conditions, acetic acid is the main precursor of methane (about 70% of methane is produced starting from acetic acid).

The activity was carried out at CRPA Lab by using anaerobic digestion reactors with continuous feeding to simulate the real-scale condition and monitor the biological process (Soldano et al., 2014). The experimental system developed by CRPA Lab consists of nine continuous-feed steel mini digesters, with a volume of 23L, mixed and heated (in mesophilic or thermophilic conditions). The system allows both the continuous recording of the amount of biogas produced (manometric system) and the periodic monitoring of the biogas quality (percentage of methane and carbon dioxide). The methodology involves the loading of feedstock-mixtures (FM) and the discharge of digestate (daily or even more frequently). Each reactor has an independent line and there are no common parts between them.

Each reactor was supervised continuously by means of a manometer in order to measure pressure augmentation generated in the headspace, due to the collection of gas produced and then released by venting. The conversion of the overpressure to biogas volume was calculated at standard pressure (1013.25 mbar) and standard temperature (0°C). The feeding of each digester involves the loading of the mixture and the daily discharge of the digestate, which was then analysed for the whole process control.

For the FM, two different AD tests were carried out in two different phases.

Each reactor was provided with a 'syringe' to extract digestate and a transducer to measure the pressure generated in the digester head space during the process. The digestate was weekly monitored and was chemically characterized according to the parameters of TS and VS for evaluating the organic matter degradation rate.

The first test started by filling the reactor with an inoculum taken from a digester that used citrus pulp and olive pomace in order to make the microbial flora suitable for degrading as far as possible the organic substance used during the test and to reduce the start-up phase.

The adopted inoculum was chemically characterized according to the parameters of TS, VS, acidity (FOS) and alkalinity (TAC) (Table 2).

The digesters were set at 38°C (mesophilic conditions); the hydraulic retention time (HRT) was 50 days and the organic loading rate (OLR) was 4.8kg of VS per day per m^3 of reactor. The test was performed for about 4 months including the start-up and the steady state phase. Stainless steel digester (CSTR, Completely Stirred Tank Reactor), 23L each (16L working volume), was fed daily.

The second test started by using a different inoculum, taken from a digester that used similar biomasses. The digesters were set at the same temperature of the first trial (38°C - mesophilic conditions); the HRT was 54 days and the OLR was 3.3kg of VS per day per m^3 of reactor. The test lasted about 54 days. Stainless steel digester (CSTR), 23L each (16L working volume), was fed daily. Biogas production was daily analysed and the obtained digestate was collected weekly and chemically characterised according to the parameters of TS, VS, FOS and TAC (Table 2) for evaluating the organic matter degradation rate.

Table 2. Characteristics of adopted inoculum.

2.3 Analytical methods

Different parameters were measured for each feedstock and then for the considered FM before and during continuous test The FM has been chemically characterized for the content of TS and VS. Total solids and ash contents were determined drying and incinerating the samples at 105 °C and 550°C, respectively, according to the standard methods (APHA-AWWA-WPCF, 2005). Following the Nordmann titration method, pH and FOS/TAC ratio of the digestate were performed using a Hach titrator, by adopting the TIM 840 titrator by HACH-LANGE.

The calculation of the methane yield, as biochemical methane potential (BMP), was carried out in accordance with the standard ISO 11734. FOS/TAC ratio computation consists of weighting about 5.0 grams of fresh sample, added in a plastic container suitable for titration 50 mL of distilled water. The first titration is carried out with H_2SO_4 0.1 N titrator until reaching pH value of 5.0 to complete bicarbonate titration, then to reach pH value of 4.4 by titrating the alkalinity.

Volatile fatty acids (VFAs) are important elements in controlling the anaerobic digestion process. They are important to decompose organics and to generate gasses, methane and carbon dioxide. Oxygen demand decreases when both decomposing and generating occur continuously and completely. The BMP test was performed by following the method set by CRPA Lab and the obtained results were expressed in normal cubic meters of methane per ton of VS (Nm^3CH_4/tVS). The VS reduction, in terms of degradability of the organic matter, was calculated considering the ratio between the amount of the produced biogas and the amount of VS loaded. By using a gas chromatographic (GC) method, VFAs were measured during the semi-continuous process. 10 mL of the collected AD effluent was centrifuged at 7025 times gravity (xg) for 15 min using a centrifuge to obtain the supernatant. Then, the supernatant was washed using 85% (w/w) orthophosphoric acid at a ratio of 1–5 (acid to sample) to remove remaining solids and prepare the sample for the GC analysis. A GC system (GC-Agilent 7820A), which was equipped with a capillary column (Colonna Agilent J&W DB) and a flame ionization detector (FID). The total VFA is the sum of six targeted VFAs (acetic acid, butyric acid, hexanoic acid, heptanoic acid, valeric acid, and propionic acid).

3. Results and discussion

3.1 Feedstock-mixture characteristics

The main characteristics of each analysed biomass were reported in Table 1. In detail, the highest TS content approximately equal to 94% was shown for cereal straw samples, and the analysed sample of tomato peels, reported the highest values of VS content, about 96% of TS. Regarding the lowest analysed TS and VS contents, they were recorded for whey and poultry manure samples, respectively for TS and VS contents. A dry substance of approximately 3% was found for whey samples, and the ash content of about 67% of TS was registered for poultry manure samples, coming from laying chicken farm. From the analyses of TS and VS contents related to the other selected feedstocks, the results showed a TS content range between 5% (olive mill wastewater) and 75% (poultry litter), and VS content range between 69% (olive mill wastewater) and 91% (cereal straw).

Then, based on different percentages of the analysed biomasses a FM was selected for anaerobic digestion test. In detail, the percentage of each adopted feedstock were listed in Table 1. Before starting AD test the FM was analysed by carrying out a BMP test.

The FM was designed by taking into account the feedstocks availability and the diets currently adopted in the biogas plants located in Sicily.

After the FM definition, before starting BMP test, the FM was characterised as reported in Table 3. The FM was chemical analysed several times during the test (Table 3).

Table 3. Characteristics of FM.

3.2 BMP and continuous anaerobic digestion test

3.2.1 BMP test

Before starting anaerobic digestion test on the selected FM, a BMP test was carried out. As reported in Table 1, since citrus pulp represents the highest concentration of the feedstock-mixture, the BMP test was carried out also for citrus pulp (Table 4). In particular, the specific yield of methane for the FM was equal to 312.2 Nm^3CH_4/tVS (Figure 1) with a VS reduction of about 67.8%. Moreover, the peak value of the production, about 62.4 Nm^3CH_4/t, which corresponds to the maximum degradation speed (K_{max}) value, was observed after 2.6 days (Table 4). The specific production of methane obtained from BMP test on citrus pulp was equal to 310 Nm^3CH_4/tVS with a percentage of methane in the analysed produced biogas equal to 63.2%. Batch test results are listed in Table 4. Both the reactors were cultured at 38 ± 1 °C for 27 days. The total quantity of methane produced from both the analysed FM and citrus pulp was reported in Figure1.

Table 4. Batch test results of the analysed feedstock-mixture.

Figure 1. Accumulated methane production during BMP test.

Figure 2. FM and citrus pulp daily methane production.

As shown in Figure 1 no significant differences were reported by trend production of the FM and its main feedstock. The process was triggered quickly, due to the microbial flora contained in the adopted inoculum, and the production of methane immediately started, from the first days of the BMP test. The daily methane production curve allowed the identification of two different phases (Figure 2). The first phase was characterised by an intense growth, meanwhile, during the second phase a reduction of the speed production was recorded. Moreover, the peak value of the production, the K_{max} value, was observed after three days for the analysed FM, and after eight days for citrus pulp (Table 4).

3.2.2 Continuous anaerobic digestion test

The characteristics of the adopted inoculum are listed in Table 2. The HRT was defined on 50 days based on the chemical analyses results, with a daily load of 373 g. In Table 5 the amount in terms of grams, VS and TS of each feedstock is detailed. FM was characterized by high values of acidity; a high pH value of about 8.05 was recorded at the beginning of the test.

Table 5. FM characteristics for daily load.

As reported in Table 5, the citrus pulp (40%) is the main feedstock within the selected FM; in terms of organic matter the citrus pulp contributes as well as triticale silage about 27%, followed by whey and poultry manure with 13% and 12% of VS, respectively.

3.2.2.1 First anaerobic digestion test

The methane specific production recorded during the entire AD test was equal to 229 Nm^3 CH_4 / t VS. In Figure 3 the accumulated biogas production for the first test is shown. The daily percentage of methane recorded in the biogas is shown in Figure 4 with the average value for the entire test of 57.8%. The hydrogen sulphide (H_2S) content, measured in biogas is shown in Figure 5. During the first test, H_2S concentration reached the maximum value of 800 ppm after 40 days.

Figure 3. Accumulated biogas production during the first AD test.

Figure 4. Biogas composition in terms of CH_4 content from the first AD test.

Figure 5. Biogas composition in terms of H_2S content from the first AD test.

Every day 373 g of the FM were fed to the reactor and the same amount of the AD effluent was removed from the reactor and stored in the refrigerator. Weekly, the stored samples were chemically characterized for TS and VS in order to evaluate the degradation of the organic matter inside the reactor. In Figure 6 the trend of the monitored TS and VS parameters was reported.

Figure 6. TS and VS trend during the first AD test.

During the first 60 days of testing, a first increase in TS concentration was observed (Figure 6). Therefore, analyses on the stored samples aiming at determining the concentration of VFA were carried out in order to evaluate the stability of the biological process. Furthermore, acetic acid, butyric acid, hexanoic acid, heptanoic acid, valeric acid, and propionic acid were analysed. In Figure 7 acetic acid and propionic acid trends were reported.

Day 0- sample refers to the original inoculum; in the next recorded samples during the beginning of the test a high value of acetic acid, 5300 mg/kg, was already observed, which increases until reaching a concentration of 11140 mg/kg. This concentration contributes to inhibit the methanogenic microorganisms (Figure 7). At the same time, an accumulation of propionic acid was also observed in the first month of the AD test, whose concentration reached about 4000 mg/kg up to day 103. From day 84 to day 101 an imbalance was also observed in the acetic - propionic ratio, with higher concentration of propionic acid.

Figure 7. Acetic and propionic acids concentrations in digestate samples, monitored during the first AD test.

By analysing the entire process, from 39th day until 54th day the biological process has shown several inhibition signs. The acetic acid was continuously increasing, an increase in the FOS/TAC ratio was also recorded, with consequent lowering of methane production. A deterioration in the quality of biogas was observed with methane content of about 50% and high values of H_2S of about 800 ppm were found.

The inhibition of the process avoided the total conversion of the organic matter into biogas, which has been very low with respect to expectations (Valenti et al., 2018b; 2018c) (about 25-30% less). Furthermore, the process inhibition led to a gradational accumulation of VFA (mostly acetic acid and propionic acid) that could be the main responsible of the high risk-acid processes.

3.2.2.2 Second anaerobic digestion test

Due to the inhibition of the process a second batch test was performed, by considering the same feedstock mixture analysed during the first AD test but using a different inoculum. The adopted inoculum was taken from a biogas plant located in Southern Italy which typically uses the analysed feedstocks (i.e., citrus pulp, olive pomace, triticale silage, cattle and poultry manure and cereal straw). Furthermore, to exclude that the high concentration of citrus pulp and olive mill wastewater lead to the inhibition of the process during the first AD, the second AD test started by adding gradually these two main feedstocks. Firstly, about 1/3 of citrus pulp and olive mill wastewater was replaced by cattle manure. After about 10 days, citrus pulp was gradually increased to replace partially the cattle manure used as feedstock-substitute, and subsequently, once the process became stable the amount of olive mill wastewater was increased. At the day 38^{th}, the FM reached the same composition in terms of feedstock- percentages as that used in the first AD test. Then, for two weeks, until 54^{th} day, the process was monitored with the daily full load. In this way, by introducing one variable at a time, the TS% was kept fix at 21%, and the organic loading rate (OLR) at 3.3 kg VS/m^3 day. The test lasted ad 54^{th} days, only one HRT, just to try in different conditions the same FM analysed during the first AD test. It was decided to set this AD test with a lower organic loading rate (OLR) than the previous AD test.

The methane specific production recorded during the entire test was equal to 297 Nm^3 CH_4 / t VS. The accumulated biogas production is shown in Figure 8. The percentage of methane content recorded in the biogas detected daily is shown in Figure 9 and the average value measured for the entire test was equal to 56.5%. The hydrogen sulphide (H_2S) content, was also measured in produced biogas. During the test H_2S concentration reached the maximum value of 700 ppm at 27^{th} day.

Figure 8. Accumulated biogas production during second AD test.

Figure 9. Biogas composition in terms of CH_4 content during the second AD test.

The FOS-TAC ratio (volatile organic acid and buffer capacity ratio) measured in the digested daily extract was linear and constant, as shown in Figure 10, with a mean value of the entire test of 0.27 indicating process equilibrium. Acidity values (FOS) fall within the stability range, with values ranged from 3100 to 4800 mg/kg and alkalinity (TAC) ranged from 11000 to 17000 mg/kg. The pH values recorded during the AD test were sometimes slightly higher than the neutral value, about 8.00.

Figure 10. FOS/TAC ratio monitoring during the second AD test.

Also in this AD test, analyses on the stored samples aiming at determining the concentration of VFA were carried out in order to evaluate the stability of the biological process. In Figure 11, acetic acid and propionic acid trends were reported.

Figure 11. Acetic and propionic acid concentrations in digestate samples, monitored during the second AD test.

In this second AD test the recorded values of acetic acid remain below the critical threshold, with values that exceed slightly 500 mg kg^{-1}. The values of the other VFAs are negligible.

The results clearly demonstrate the viability of the mixing ratio to carry out the AcoD to generate renewable energy. Under the stabilized culture condition, the FM demonstrates good performance on methane production due to the high citrus pulp content. Anaerobic co-digestion of different organic residues has been widely investigated, but only a few studies regarded multiple feedstocks investigation to demonstrate successful biogas production from multiple organic residues (Muradin et al., 2014; Wickman et al., 2016; Tasnim et al., 2017). In this context, the study described in this paper reports the effect on methane production of a diet obtained by mixing ten feedstocks typically available in the Mediterranean area. Such a diet has not been tested before in literature. Furthermore, the methane content produced from the analysed FM (56.5% and 57.38% for first AD and second AD respectively) is also in line with the results reported by Hobenov et al. (2015) (percentage of methane recorded range 57-62%) which regarded a FM of potatoes, tomatoes, cucumbers, apple wastes and swine manure, and the results reported by Giuliano et al. (2013) (percentage of methane recorded range 54-57%) which regarded a FM of cattle slurry, cow manure, triticale maize silage, onion and potatoes. As reported by Valenti et al. (2018c), which investigate the effect of mixing other Mediterranean feedstocks, the obtained results could be useful for developing biogas production in Mediterranean regions with similar sources of organic residues.

4. Conclusions

In this study, in order to evaluate the technical feasibility of a FM constituted by ten Mediterranean feedstocks co-digestion (citrus pulp, olive pomace, tomato peels, olive mill wastewater, poultry litter, poultry and cattle manure, whey and cereal straw), both batch and semi-continuous anaerobic digestion approaches were applied. The FM was analysed for evaluating its methane production and verifying the possible inhibitory effects on the biological process. The analysed FM is energetically interesting in terms of methane potential. The batch digestion showed that the FM had potential to be used for biogas production, in this regard, the test showed a production of biogas equal to 312 Nm^3CH_4/t VS with a VS reduction of about 68%; methane production of about 62.4 Nm^3CH_4/t and 57.7% of methane in the produced biogas. Two different AD tests were carried out. During the first AD test the specific methane production was equal to 229 Nm^3CH_4/tVS, it was 27% lower than that measured during the batch test, with 56.5% of methane measured in biogas. Instead, during the second batch test, in which a different inoculum was used and the feeding plan was gradually introduced, the specific production of methane was 272 m^3CH_4/tVS; with 57.8% of methane measured in biogas, since the lower organic loading reduced inhibiting effects. On both AD tests, high values of hydrogen sulphide were recorded, therefore, desulfurization systems, in order to keep the biogas concentrations under control, should be considered. However, during the first AD test, the inhibition of the process avoided the total conversion of the organic matter into biogas, the second AD test demonstrated that the selected FM could be viable to carry out the co-digestion. In detail, the FM could be a flexible and suitable solution to generate sustainable bioenergy from diverse agricultural residues in Mediterranean area.

The results of the research study proposed in this paper demonstrate that it is possible to develop a sustainable bioeconomy strategy by integrating the sustainable production of renewable natural resources and by converting these resources and waste streams into value added products such as food, feed, bio-based products and bio-energy.

Moreover, the development of a sustainable bioeconomy for replacing non-renewable resources (i.e. reduction of greenhouses gas emissions), by supplying food to societies and preserving natural resources, will depend not only on innovations in biomass transformation processes, i.e., anaerobic digestion, but also on the organization of biomass feedstock production or biomass-based product consumption. These concepts are fundamental for a social sustainable development and to create a thriving economy based on the respects for the environment (BIT, 2017).

According to the principles contained in the Juncker's Agenda for Jobs, Growth, Fairness and Democratic Change, it is essential to reduce the fossil fuels and finite materials dependence without the over-exploitation of renewable resources, preventing land use change, regenerating the environment and creating new economic growth and jobs and leveraging on local diversities and traditions in the rural areas (including those that are no usually cultivated).

In this regard, to make real the obtained result at lab scale, further improvements of the research study are needed. The assessment of the analysed feedstocks availability could be obtained, by developing GIS-based model, which combine AD and BMP results with spatial analyses. This will be relevant to improve the real reuse of by-products and agricultural residues for bioenergy production. In detail, a GIS-modelling approach could integrate information base suitable for the application of multi-criteria analysis methods that aim to optimize the biogas plant location from an economic and environmental point of view.

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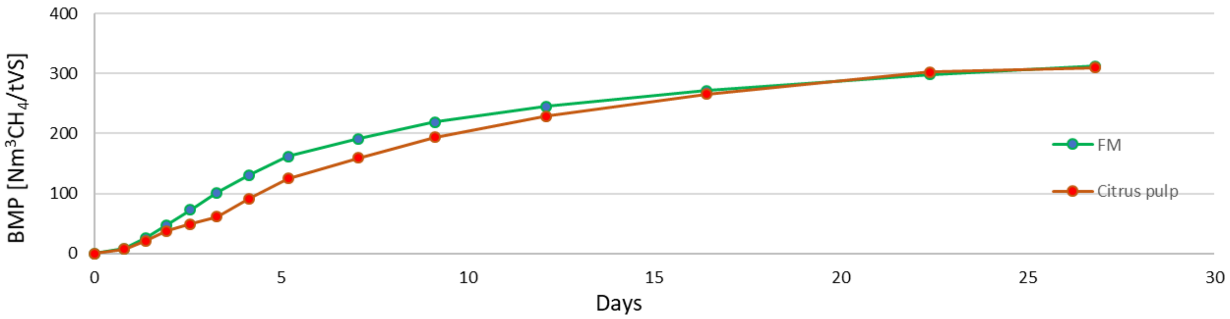


Figure 1. Accumulated methane production during BMP test.

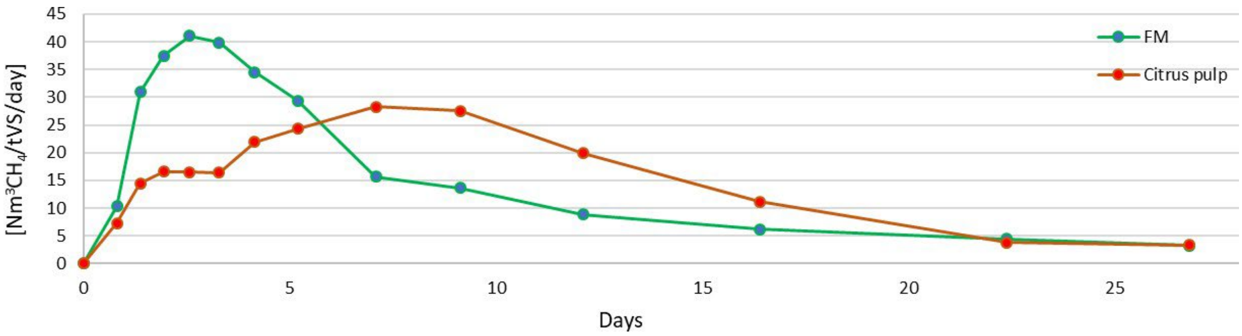


Figure 2. FM and citrus pulp daily methane production.

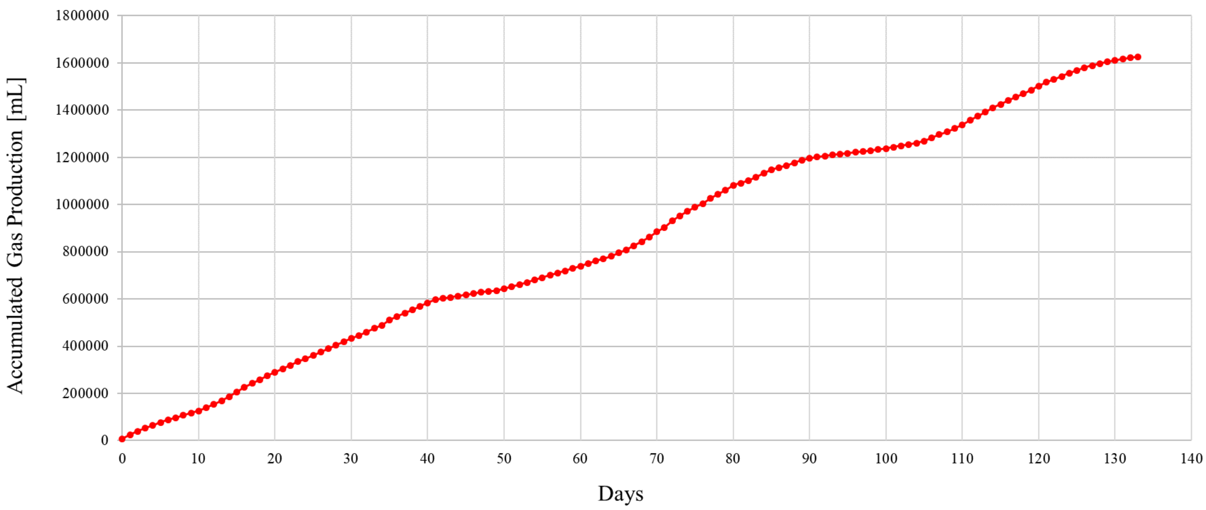


Figure 3. Accumulated biogas production during the first AD test.

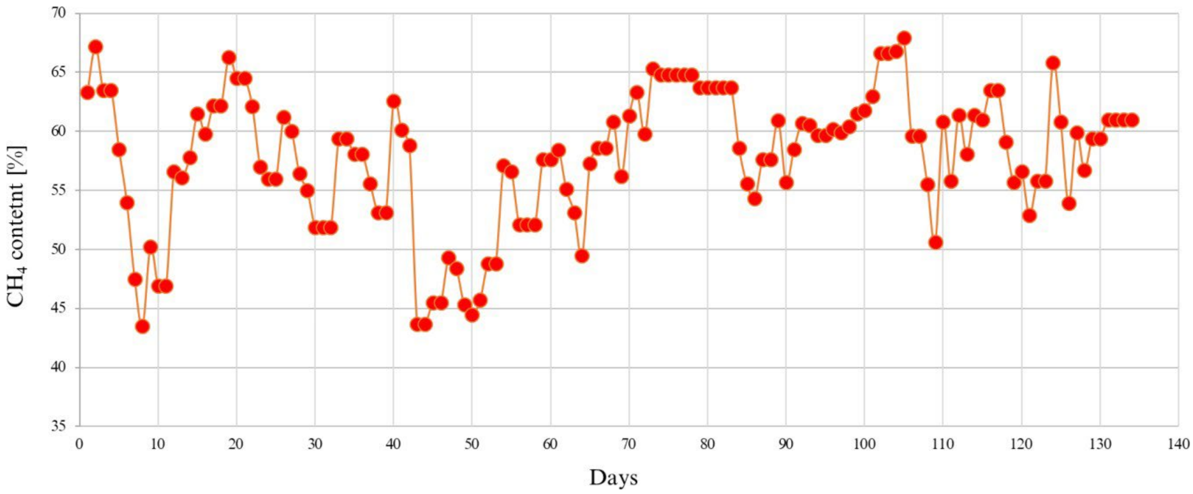


Figure 4. Biogas composition in terms of CH_4 content from the first AD test.

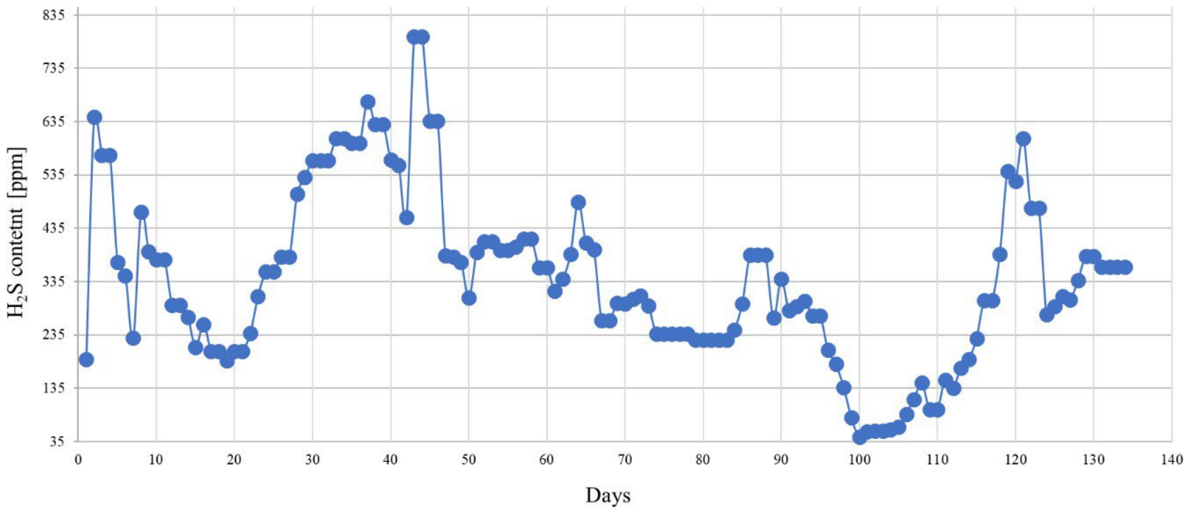


Figure 5. Biogas composition in terms of H_2S content from the first AD test.

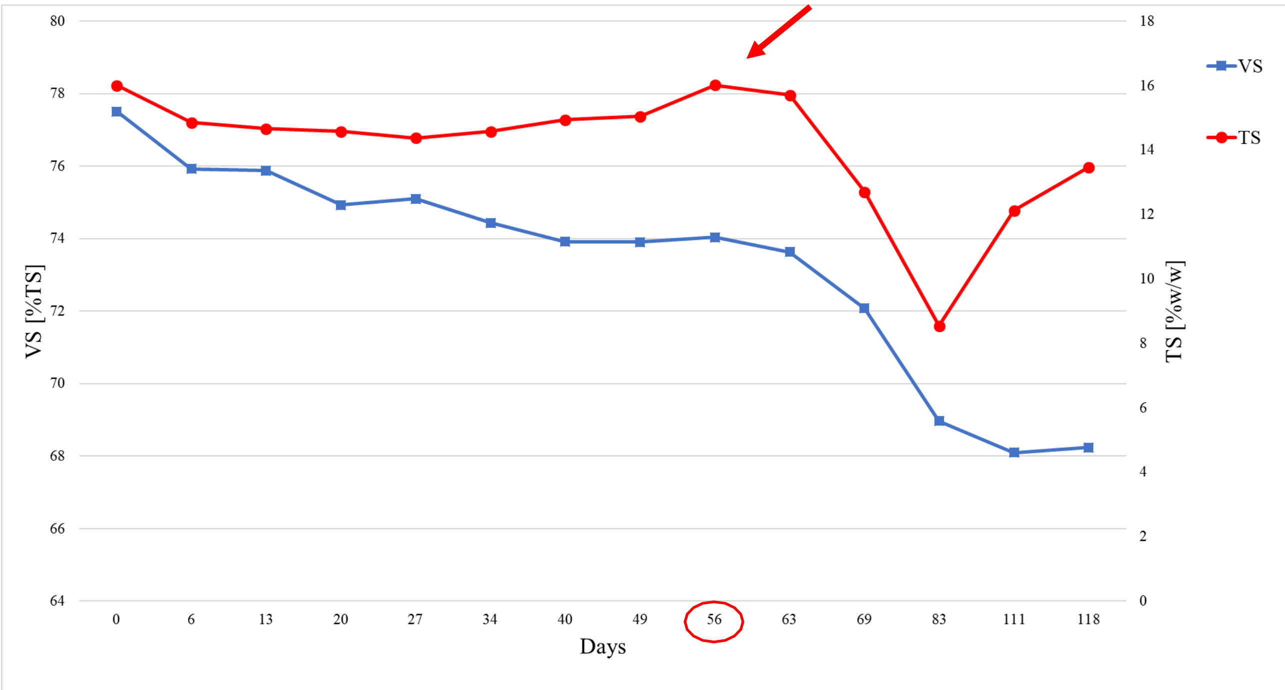


Figure 6. TS and VS trend during the first AD test.

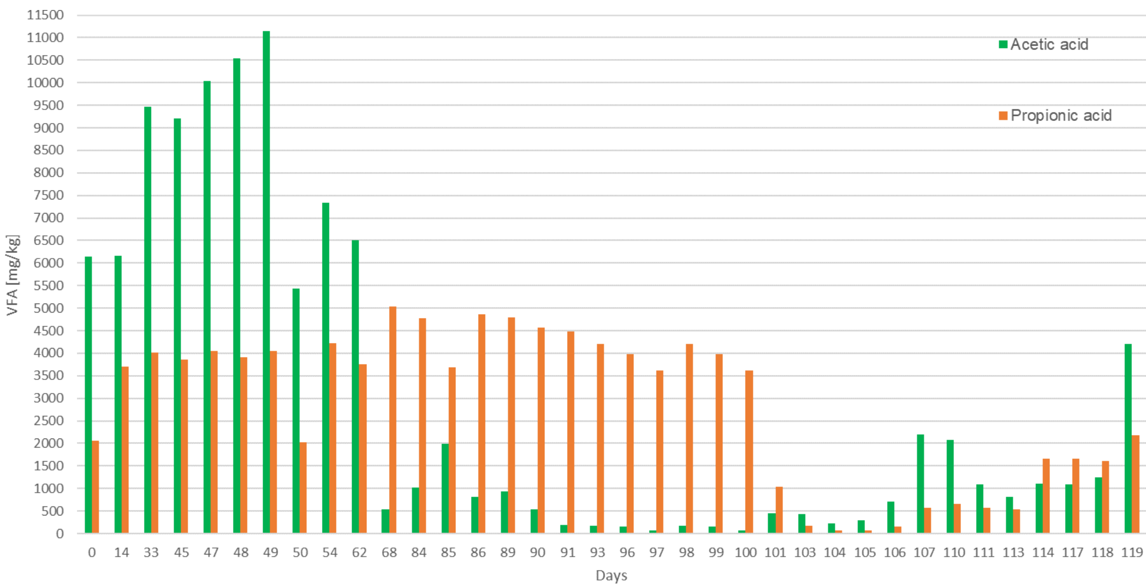


Figure 7. Acetic and propionic acids concentrations in digestate samples, monitored during the first AD test.

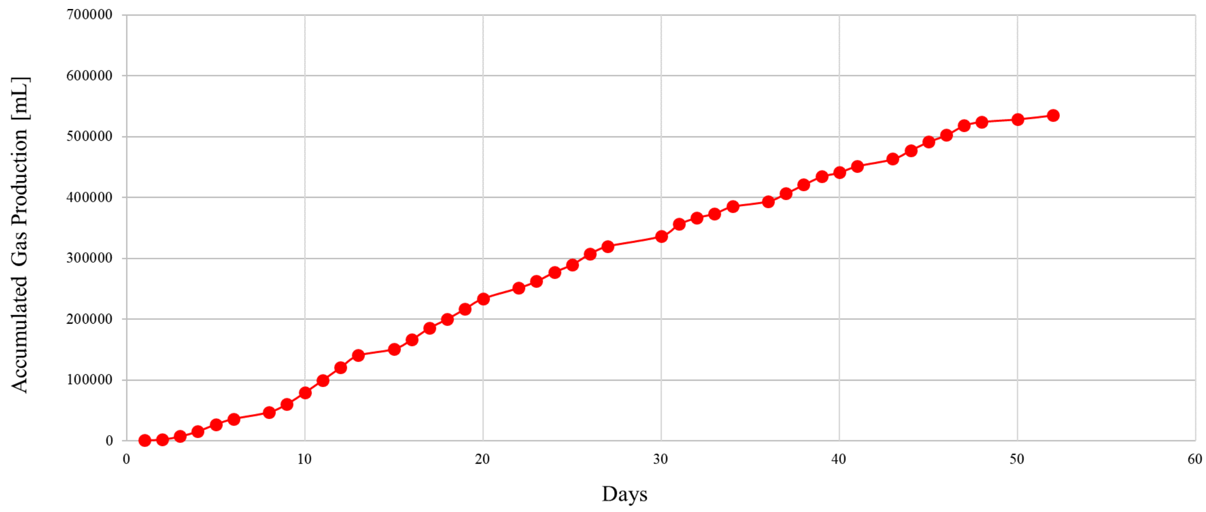


Figure 8. Accumulated biogas production during second AD test.

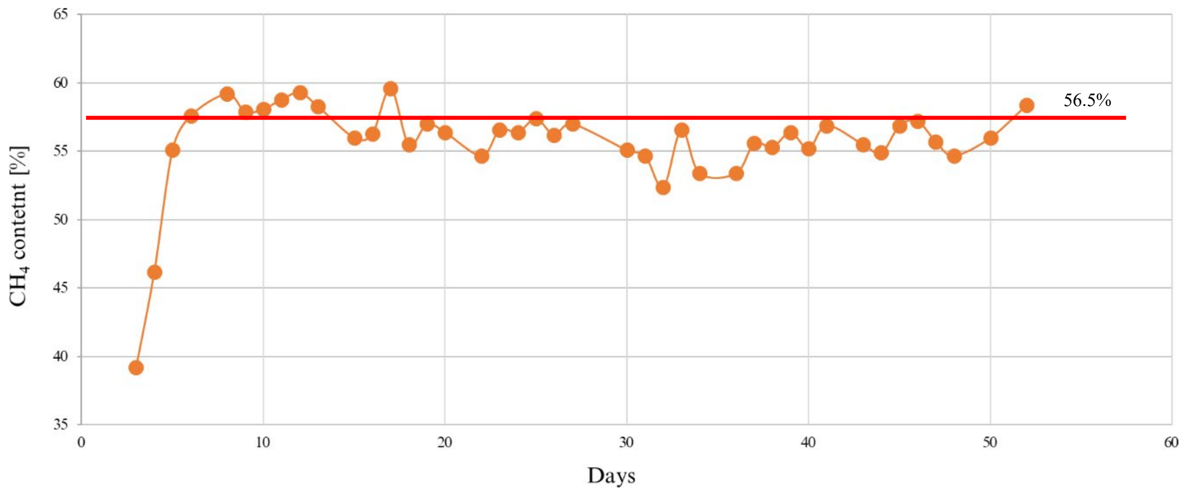


Figure 9. Biogas composition in terms of CH_4 content during the second AD test.

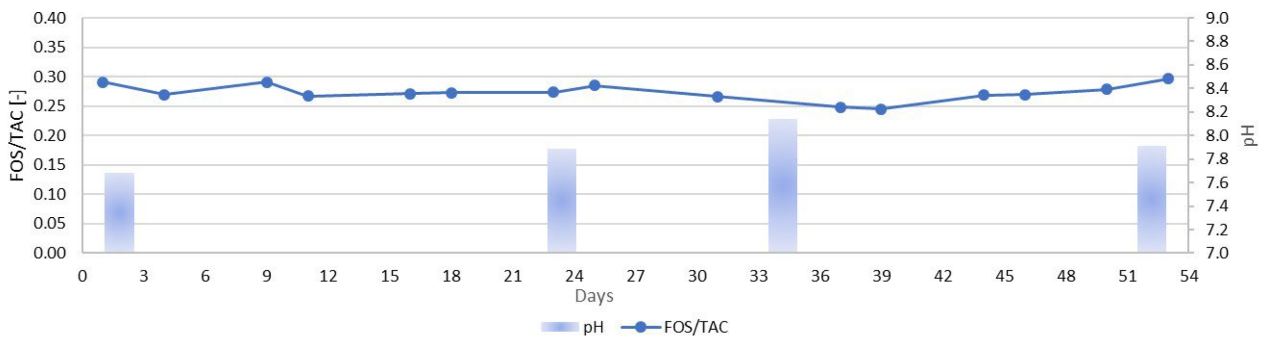


Figure 10. FOS/TAC ratio monitoring during the second AD test.

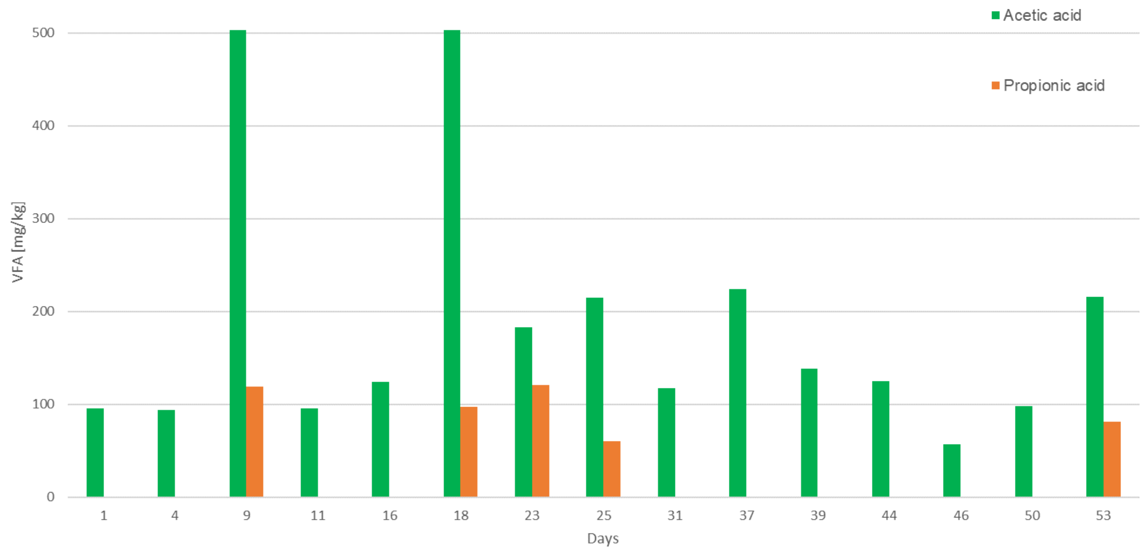


Figure 11. Acetic and propionic acid concentrations in digestate samples, monitored during the second AD test.

Table 1. Characteristics of individual feedstocks and mass ratios of different feedstocks in FM.

Matrices	TS [% w/w[a]]	VS [% TS]	FM composition [%w/w, DM[a]]
Citrus pulp	17	74	40
Olive mill wastewater	5	69	15
Poultry manure	34	67	10
Triticale silage	30	92	9
Poultry litter	75	86	8
Olive pomace	16	90	5
Cattle manure	14	85	5
Whey	3	71	4
Cereal straw	94	91	2
Tomato peels	27	96	2
Total	-	-	100

[a] DM means dry matter.

Table 2. Characteristics of adopted inoculum.

Inoculum	TS [%w/w]	VS [%TS]	FOS [$mgHAc_{eq}/L$]	TAC [$mgCaCO_3/L$]	FOS/TAC [-]
First AD test	16.00	77.50	12184	23721	0.51
Second AD test	5.90	72.28	3195	10990	0.29

Table 3. Characteristics of FM.

FM sample [date]	TS [%]	VS [%TS]
10/10/17	24.30	82.30
10/24/17	23.20	82.80
11/15/17	24.60	82.40
01/02/17	23.00	82.20
02/01/18	23.40	83.30
Average	23.70	82.60
Standard deviation	0.70	0.00

Table 4. Batch test results of the analysed feedstock-mixture.

Matrices	TS	VS	BMP	BMP Peak value	Kmax[1]	VS reduction	CH_4	H_2S
	[g/kg]	[g/kg]	[Nm^3CH_4/t]	[Nm^3CH_4/t]	[days]	[%]	[%]	[ppm]
FM	243	200	312.2	62.4	2.6	67.8	57.7	433
Citrus pulp	174	136	310.2	42.0	8.4	58.0	63.2	268

[1] Kmax: maximum degradation rate of volatile solids.

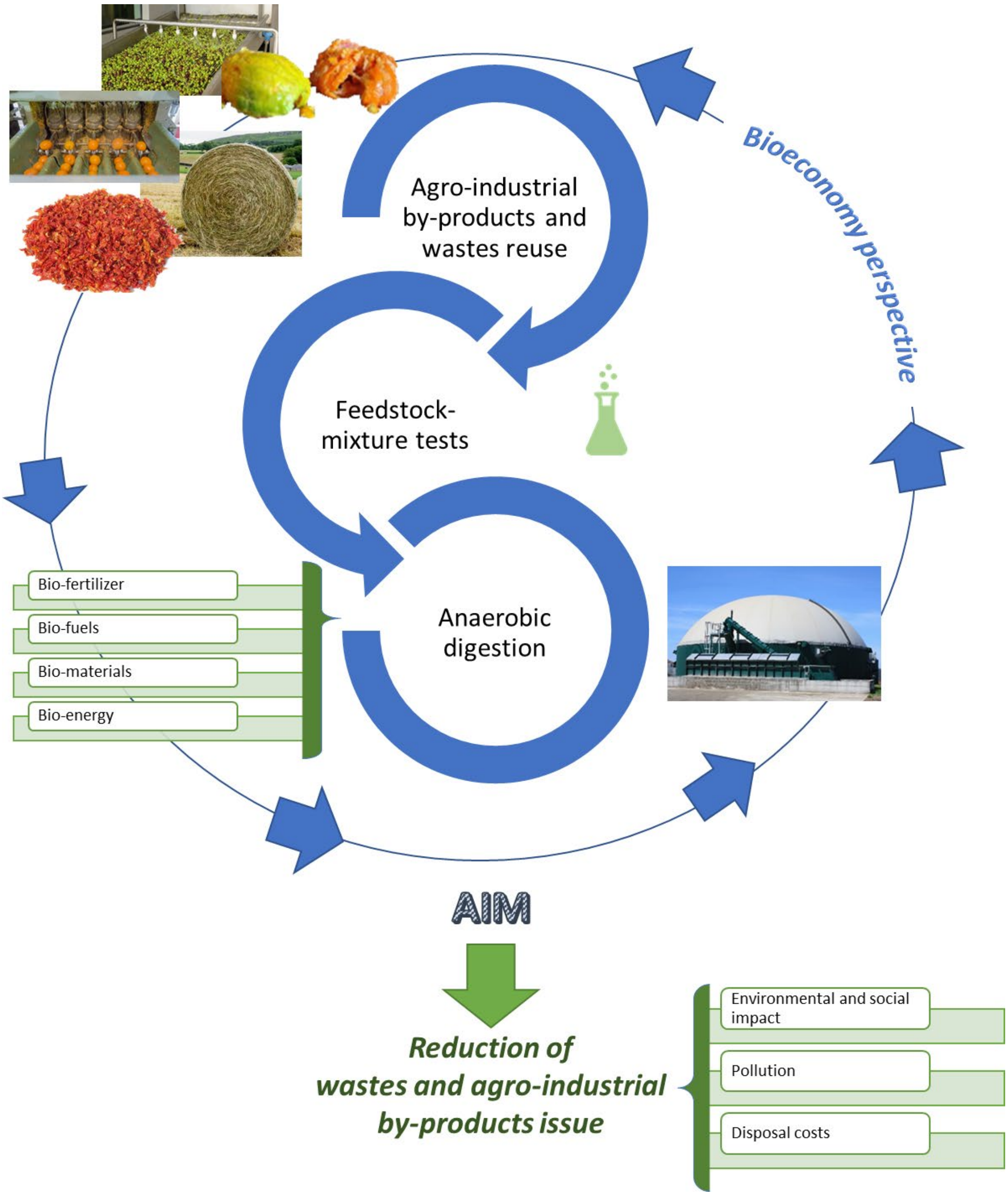
Table 5. FM characteristics for daily load

Feedstock	Amount on FM	Daily amount* loaded	Daily amount* of TS loaded	Daily amount* of VS loaded	VS on FM
	[%]	[g]	[g]	[g]	[%]
Citrus pulp	40	149.20	26.00	19.20	27
Olive mill wastewater	15	18.70	3.00	2.70	4
Poultry manure	10	37.30	12.60	8.50	12
Triticale silage	9	29.80	22.30	19.10	27
Poultry litter	8	14.90	0.50	0.40	0.5
Olive pomace	5	56.00	2.60	1.80	3
Cattle manure	5	18.70	2.60	2.20	3
Whey	4	33.60	10.20	9.40	13
Cereal straw	2	7.50	7.00	6.40	9
Tomato peels	2	7.50	2.00	1.90	3
Total	100	373.00	89.00	72.00	100

* Weekly amount based on six days.

Highlights

- Selected feedstocks mixture (FM) were evaluated by applying BMP and AD tests
- AD on Mediterranean FM was carried out to investigate advanced biofuels production
- Biomethane from agro-waste and by-products improves waste management sustainability
- A sustainable bioeconomy strategy can integrate preservation of natural resources
- ~~Digestate can improve agronomical soil value and reduce fertilizer costs~~
- AD contributes to create the conditions for a closed circular economy


Agro-industrial by-products and wastes reuse
Feedstock-mixture tests
Anaerobic digestion
Bioeconomy perspective
Bio-fertilizer
Bio-fuels
Bio-materials
Bio-energy
AIM
Reduction of wastes and agro-industrial by-products issue
Environmental and social impact
Pollution
Disposal costs

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