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## Anaerobic co-digestion of olive-mill solid waste with cattle manure and cattle slurry: analysis of bio-methane potential

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### Abstract

In the present work, the bio-methane potential from anaerobic digestion of OMSW with inoculum and co-digestion of OMSW with cattle manure (CM) and cattle slurry (CS) has been analysed. The OMSW used for the analysis was a pollutant waste came from olive oil processing through three-phase centrifugation systems.

A batch stirred tank reactor has been used, under mesophilic conditions (38°C), in order to study the biogas yield. The whole process has been carried out under wet conditions, and with a Hydraulic Retention Time (HRT) of 55 days. Several tests have been carried out to achieve the best biogas yield.

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*Keywords:* olive mill solid waste; anaerobic digestion; biomethane

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**Nomenclature**

OMW	Olive Mill Wastes
OMSW	Olive Mill Solid Waste
CM	Cattle Manure
CS	Cattle Slurry
OMWW	Olive Mill WasteWater
HHV	Higher Heating Value
LHV	Lower Heating Value
BMP	Bio-Methane Potential
HRT	Hydraulic retention Time
COD	Chemical Oxygen Demand
VS	Volatile Solids
DM	Dry Matter
OM	Organic Matter
TS	Total Solids

**1. Introduction**

In Mediterranean regions the olive tree cultivation and the olive oil extraction are widespread since thousands of years. Nowadays about 10 million hectares of land in all the world are cultivated with 900 million of olive trees, of which about 98% are in the Mediterranean area [1]. The European Union, from 2007 to 2013, have contributed on average of about 72% of the olive oil world total production. Italy has contributed of about 22% of the European production with about 6600 olive mills which produce an average of 455 thousands of tons of olive oil per year. Italy represents, in this way, the second European producer after Spain, and it is followed by Greece, Turkey, Syria and Tunisia [2]. The olive oil industry produces huge quantities of wastes which represent a significant environmental problem in Mediterranean area. This waste are produced in high quantity in a short time, furthermore they are not biodegradable due to the high concentration in organic and phenolic compounds [3,4]. The waste derived by olive mills can be divided in olive mill wastewater (OMWW) and olive mill solid waste (OMSW). The composition and quantity of this waste depends from the olive oil extraction technology used [3]. In general the OMWW is composed of vegetation water and suspended solid, whereas OMSW is made up by olive pulp, peel, pieces of pit and an oil content [5].

Olive oil extraction can be done through discontinuous (traditional pressing system) or continuous (centrifugation system) processes. The discontinuous pressing system is the oldest and more widespread squeezing method, and it is used in the traditional olive mills. This is a low cost and technically simple method. It produces as by-product OMSW and low quantity of OMWW (40-60 l per 100 kg of olives) [6]. The disadvantages of this system are especially the discontinuity of the process and the high costs of manpower. The OMWW of these kinds of olive mills has however a high COD compared to the others methods. In many countries the traditional pressing system is still used even if it is quite expensive [7]. Continuous extraction processes separate the different phases by centrifugation. They are based on the density difference of the diverse components of the olive paste, and can operate at two or three phases. In the three-phase system hot water at the centrifugation step is added, and this produces a greater quantity of OMWW [8]. The three-phase systems generate three fractions: OMSW, OMWW and oil with a low quantity of water. The advantages of these systems are the full automation, a better oil quality, and the necessity of smaller spaces; instead the disadvantages are a greater water and energy consumption, a greater OMWW fraction at the output and high installation costs [3]. The three-phase systems are the most widely used, especially in countries that produce high olive quantities. During the last years they became popular also in Italy. To minimize the OMWW volume and to reduce the washing of phenols, two-phase continuous extraction processes have been developed. Using this system the olive paste is divided in two phases: oil and wet OMSW. The wet OMSW is a semi-solid by-product, a combination of OMSW and OMWW. The two-phase systems are defined ecological because of their high reduction of water consumption, but the resulting residue, which consists of liquid

and solid phase, is difficult to manage because the pollutant load is highly concentrated. In the last 10 years this system is become the main system in Spain, where it represents about 90% of the total installation [8].

In Italy there are 6.600 olive mills, the three phase system is still the most used with about 46% of the total installation. The pressing system represent 42% of the installation, instead the two-phase continuous system only 2%. However in Puglia, the most important Italian Region for the olives cultivation, 55% of olive mills are continuous cycle [9]. Italy is, therefore, characterized by the presence of many little olive mills that work with traditional process.

In this study the OMSW, obtained by three-phase system, is examined in order to use it for energy production. It is composed of olive pulp, peel and pieces of pit. This OMSW is characterized by a high C/N ratio (>34%) due to the presence of pieces of pit, a Lower Heating Value (LHV) of about 23 MJ/kg and a high moisture content (>46%). OMSW can be used both in thermochemical conversion processes and in anaerobic digestion to produce biogas [10–13]. Due to the high moisture content it is not totally convenient to use it in thermochemical processes because it needs to be dried. OMSW can be used, in a very interesting way, in the anaerobic digestion plants, in particular use in small size biogas production plants, up to 100 kW, is very interesting (D.M. 6 July 2012).

Among the countries that produce primary energy from biogas, first of all there are Germany, United Kingdom and Italy [14]. In Germany the biogas used for the primary energy production is almost totally deriving from digestion plants (87.15% of the total product energy), followed by biogas from sewage sludge (9.95%) and biogas from landfill (2.94%). The situation is totally opposite in United Kingdom and Italy. In the first one the main contribution is given by landfill biogas (84%). In Italy most of the primary energy come from landfill biogas (68.97%) and then from “other biogas” (29.56%).

In Italy the number and the power of bioenergy plants are increasing [15,16], in particular in 2012 has been registered an increase of 81.3% in number, and of 34.6% in power compared to 2011. The greater contribute, in terms of number, is given by the biogas plants, in particular those come from agricultural and forestry activities, an increase of 156% in number and 142% in power has been registered. Instead the dominant contribute in terms of installed power is represented by biomass plants, in particular those of urban wastes. In general bioenergy sector contributes at 8% of the total power of the renewable sector [17].

In the present work, the Bio-Methane Potential (BMP) from anaerobic digestion of OMSW with inoculum and co-digestion of OMSW, Cattle Manure (CM) and Cattle Slurry (CS) has been analysed. The OMSW used for the analysis was a pollutant waste come from olive oil processing through three-phase system, method most used in Italy for oil extraction. Biomass energy characterization has been done and a batch stirred tank reactor has been used, under mesophilic conditions (38°C), in order to study the biogas yield. The whole process has been carried out under wet conditions, and with a Hydraulic Retention Time (HRT) of 55 days.

## 2. Materials and methods

In order to evaluate which biomass are more suitable for a specific energy conversion process and to optimize the process, biomass characterisation have to be done, identifying the main energy properties.

The first phase of this study has been the energetic analysis of the biomass selected that is OMSW, CM and CS.

The sampling has been done according to “EN 14778:2011. *Solid biofuels: sampling*” [18]. To prepare the sample “EN 14780:2011. *Solid biofuels: sample preparation*” [19] standard technique has been followed.

The following analysis have been carried out:

- Ultimate analysis (C, H, N contents);
- Moisture content;
- Ash content;
- High and Low Heating Value (HHV and LHV);
- Volatile Solid (VS);

For the ultimate analysis, an analyzer of carbon, hydrogen and nitrogen contents (Leco CHN-2000) has been used. All the tests have been carried out according to the “EN 15104:2011. *Solid biofuels: determination of total content of carbon, hydrogen and nitrogen. Instrumental methods*” [20] standard.

The oxygen content has been calculated using some empirical relationships and subtracting all other compounds from 100% [21,22]:

$$O = 100 - (C + N + H + S) \quad (1)$$

Sulphur content data in OMSW, CM and CS have been taken from the literature [23].

In order to determine the moisture content, the procedures provided by the following technical standards have been taken into account:

- EN 14774-1:2009. *Solid biofuel. Determination of moisture content, oven dry method. Part 1: total moisture, reference method* [24].
- EN 14774-2:2009. *Solid biofuel. Determination of moisture content, oven dry method. Part 2: total moisture, simplified method* [25]
- EN 14774-3:2009. *Solid biofuel. Determination of moisture content, oven dry method. Part 3: moisture in general analysis sample* [26].

For ash content determination, the procedure described in the “EN 14775:2009. *Solid biofuel: Determination of Ash content*” [27] technical standard has been used.

High Heating Value (HHV) of OMSW has been determined using a Parr 6200 calorimeter and according to “EN 14918:2009. *Solid biofuels: determination of calorific value*” [28].

The Volatile Solids (VS) of OMSW have been determined according to “EN 15148 – *Solid biofuels – Determination of the content of volatile matter*” [29].

An experimental determination is useful in order to provide the amount of biogas production resulting from anaerobic degradation of organic substance. The BMP is an essential parameter for assessing design, economic and managing issues for the implementation of the anaerobic digestion process [30]. The BMP is defined as the gas production that would be observed during an infinity time of anaerobic degradation. Actually the experimental time is finite and the BMP can be estimated from the trend of the methane production depending on time.

## 2.1 Experimental setup

In this work a mini-digester has been used (Fig. 1 and Fig. 2). It is composed of:

- BATCH reactor with a volume of 5 l stainless steel
- Mixing system
- Water column which permits the entrance of the product biogas; in this way, as a consequence of the water movement, is possible to evaluate the gas volume
- pH sensor
- Temperature sensor
- Vacuum pump
- Warmed-up resistance
- Pressure gauge
- Air valve
- Valve and pipe for the gas sample taking. This valve can be manually operated, and it is automatically activated when the pressure into the reactor reaches 0.1 bar.



Fig. 1. Anaerobic digestion mini-plant

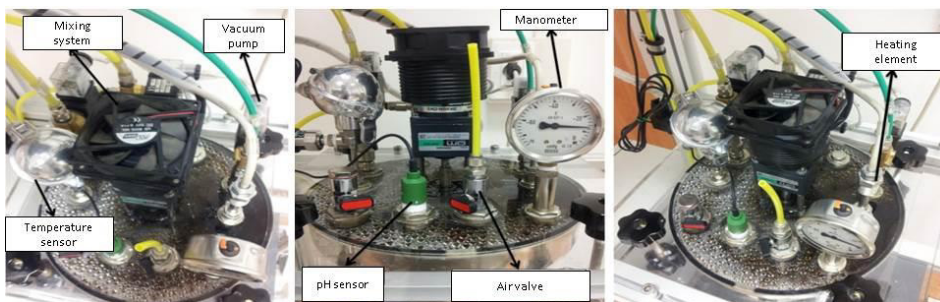


Fig. 2. Reactor elements

The gas is then extracted through tedlar bags and sent to gas chromatograph AGILENT TECHNOLOGY.

### 3. Results and discussion

In a previous work [25] a study on OMSW without olive pit and with a moisture of 69.38% (wet basis) has been done. The maximum quantity of produced biogas had been 25.14 l after 60 days. A cumulative methane production of 9.58 l and a BMP of 0.00147 l/g<sub>VS</sub> had been reached.

In this study OMSW with pit has been considered to verify the biogas production in a wet anaerobic digestion process. The tests concerned two kind of feed:

- OMSW with pit and inoculum,
- OMSW with pit in co-digestion with CM and CS.

The inoculum is composed of digested coming from a real plant for biogas production from cattle sewage, taken in a farm. In Table 1 and Table 2 inoculum and OMSW properties are reported respectively.

OMSW to digested ratio was 2:1 on weight. In this way the initial content of Dry Matter (DM) was 24%, therefore this value has been modified to obtain wet conditions.

Table 1. Inoculum properties

Inoculum – Digested from cattle sewage		
pH	8.26±0.3	-
Dry matter	12.2±0.13	[%]
Ashes	3.1±0.08	[% dry matter]
Volatile Solids	94.96±0.08	[% dry matter]

Table 2. OMSW properties

OMSW		
C	51.157±0.041	[%]
H	7.292±0.038	[%]
N	1.478±0.060	[%]
S	0.10	[%]
O	39.973	[%]
C/N ratio	34.61	-
Moisture (wet basis)	45.89±0.83	[%]
Moisture(dry basis)	84.80	[%]
Dry matter	54.12±0.83	[%]
Ashes	4.381±0.183	[% dry matter]
Volatile Solids	93.11±0.183	[% dry matter]
High Heating Value (HHV)	23.110±0.094	[%]
HHV (dry basis)	24.885	[MJ/kg]
Low Heating Value (LHV)	23.382	[MJ/kg]
pH	5.4±0.2	-

In Table 3 mixture properties are reported.

Table 3. Mixture properties

Biomass properties				
	Dry matter [%]	Weight [kg]	Ashes [% DM]	Volatile Solids [%DM]
Digested	5.15	1	1.5	5.07
OMSW	54.12	1.867	2.1	51.4
Water	0	1		
Mixture properties				
	Dry matter [%]	Weight [kg]	Initial pH	Volatile Solids [%DM]
Mixture	11.88%	3.867	6.51	11.64%

VS determination of the mixture, biogas samples taking and analysis of the gas to the gas-chromatograph have been done every 4 days.

In Fig. 3 trend of VS is reported. As it is shown there is a decreasing trend due to the use of the VS by the microorganism during the digestion reaction.

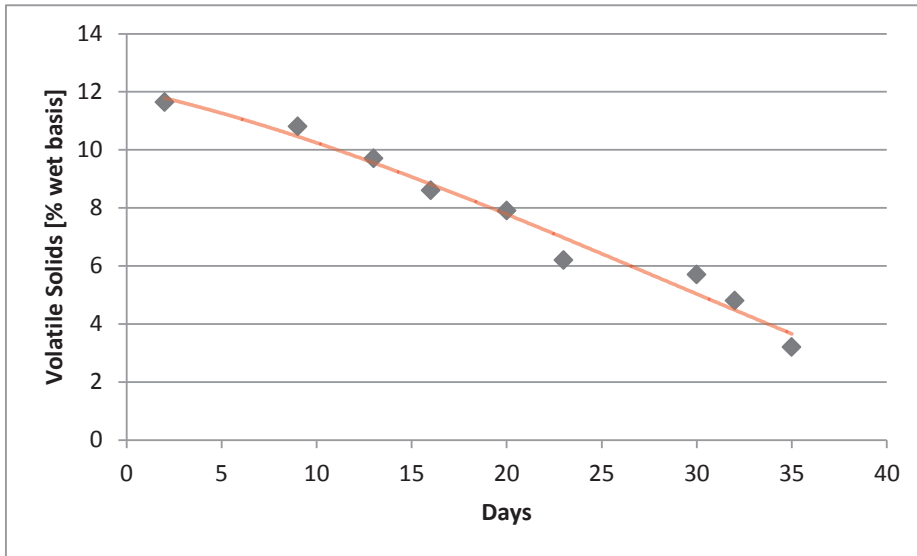


Fig. 3. Volatile Solids trend (% wet basis)

The trend of the VS can be compared with cumulative production of biogas during the reaction (Fig.4). The biogas production increases with decreasing of the VS content in the digestion matrix.

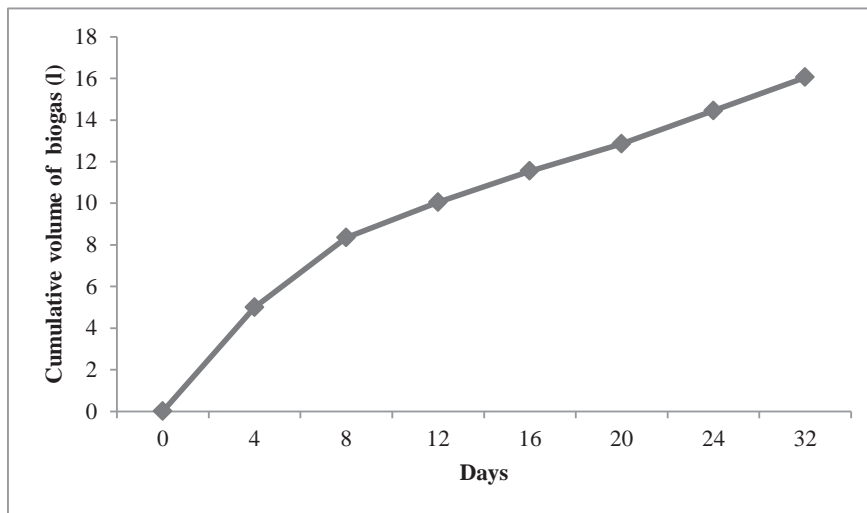


Fig. 4. Cumulative volume of biogas

The digestion reaction has been interrupted at Day 32 when the total biogas production had reached 16.05 l.

Further the comparison with the cumulative volume of methane into the biogas is congruent with the trend of the VS (Fig. 5).

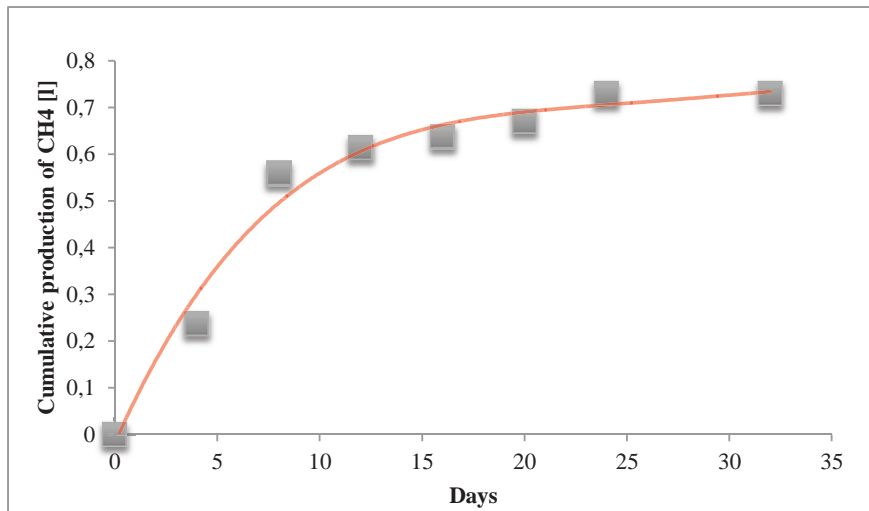


Fig. 5. Cumulative volume of methane

When VS tend to a constant value also the methane production tends to stop.

Furthermore, as it is possible to see in Fig. Fig. 6, the production percentage of CH<sub>4</sub> has had a very alternating trend and the percentages were very low. For this reason the test has been stopped.

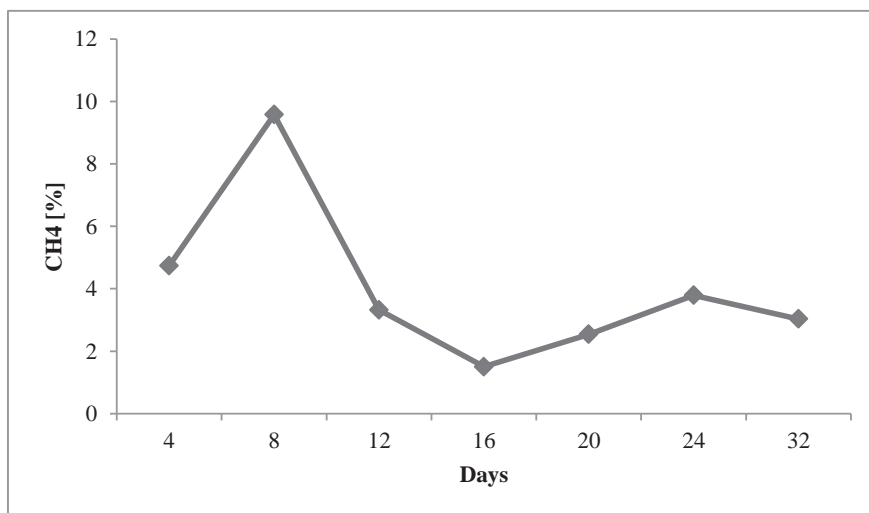


Fig. 6. Production percentage of methane

The cumulative volume of methane has reached 0.73 l after 32 days. This percentage is quite low compared to the total biogas production. The BMP is 0.0023 l/g<sub>VS</sub>.

In Fig. 7 pH trend is reported. At the beginning of the digestion reaction pH was 6.51; however the trend was very fluctuating, showing that had not occurred a good anaerobic digestion reaction.



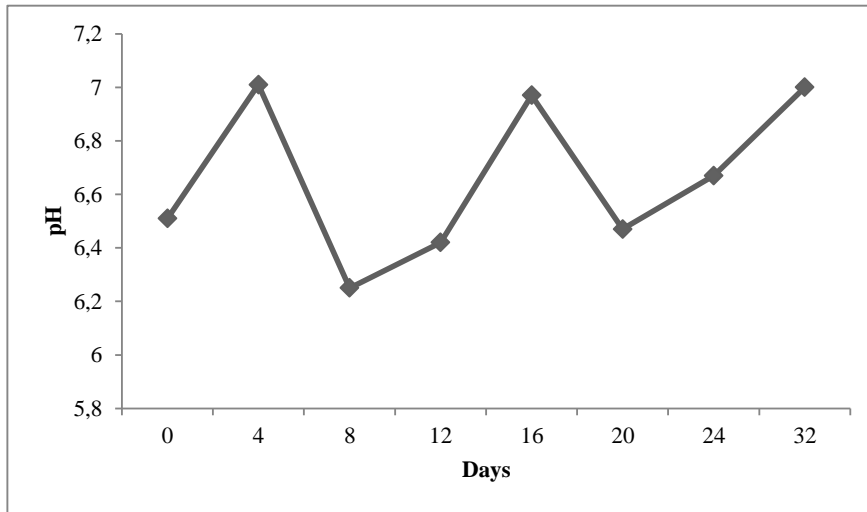


Fig. 7. Trend of pH

For all these reasons the test has been interrupted and co-digestion test with OMSW and other substrates have been done.

Co-digestion test of OMSW with pit, CM and CS has been done (Table 4).

Table 4. Biomass properties

Biomass Properties					
	Dry matter [%]	Moisture (wet basis) [%]	Ashes (dry basis) [%]	Organic matter (dry basis) [%]	Weight [kg]
Cattle slurry	1.04	98.96	35.02	61.73	3.1
Cattle manure	18.46	81.54	15.96	75.63	0.2
OMSW	54.12	45.89	4.75	94.07	1
Total					4.3
Mixture properties					
Total dry matter	14 %				
Initial pH	7.07				
Total organic matter on dry basis	93.6 %				
Total organic matter on wet basis	13.03 %				

HRT was 55 days in which the digester has been maintained in mesophilic conditions with a temperature of 38°C.

Initial pH, thanks to manure and cattle slurry, was 7.07 and the total organic matter on dry basis was 93.6%.

In Fig. 8 and Fig. 9 substrate pH trend is reported. In this case pH remains stable during the process, because the process is stable.

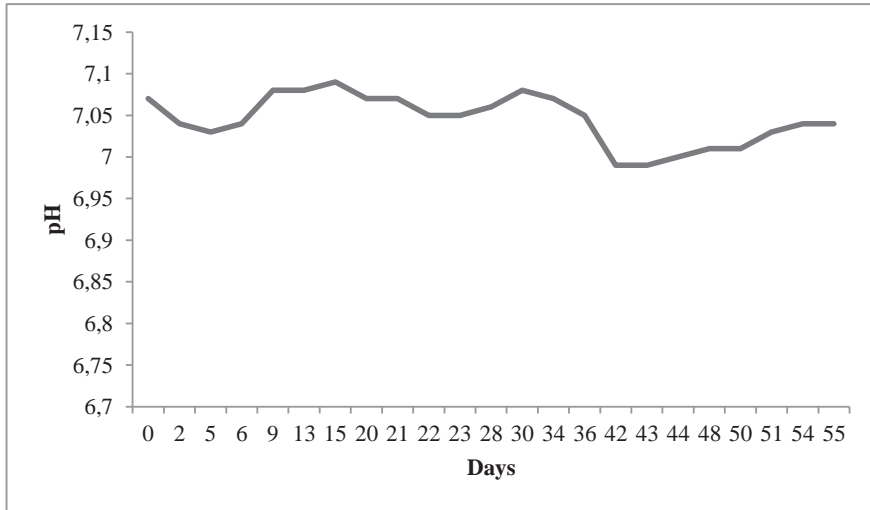


Fig. 8. pH trend

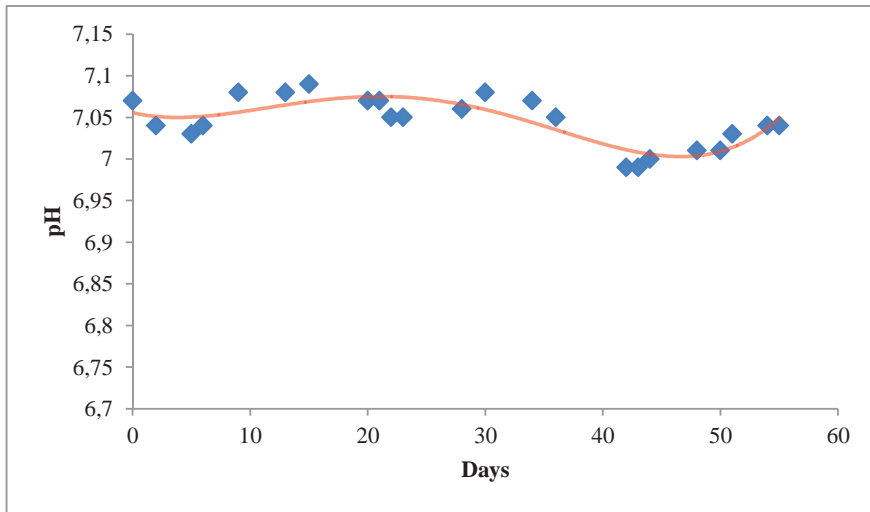


Fig. 9. Representative points of pH and trend line

There is an initial decrease followed by an increase, which corresponds to the beginning of the phase of the higher methane production.

Below the methane percentage into the product biogas is showed (Fig. 10).

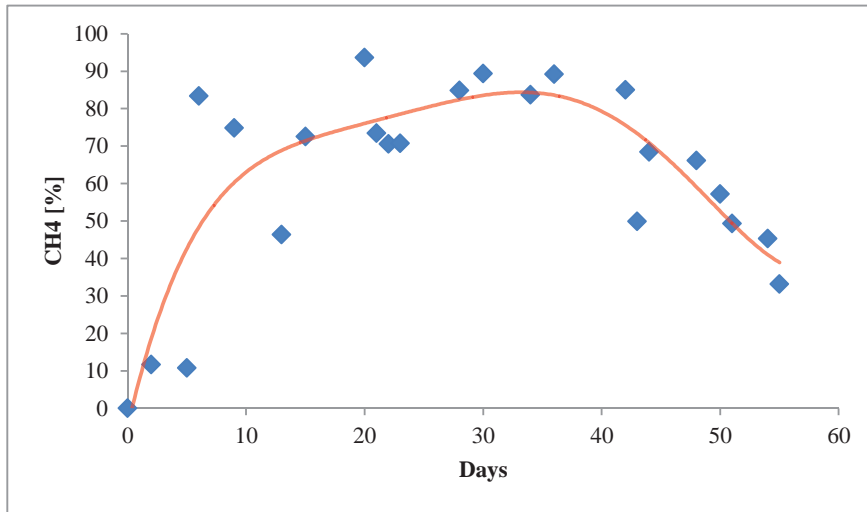


Fig. 10. Percentage of methane in the biogas

The percentage of methane increases initially, keeping constant from Day 7 to Day 40, and after that it decreases. In Fig. 11 the cumulative methane production is presented. The production has reached 40.5 l at the Day 55.

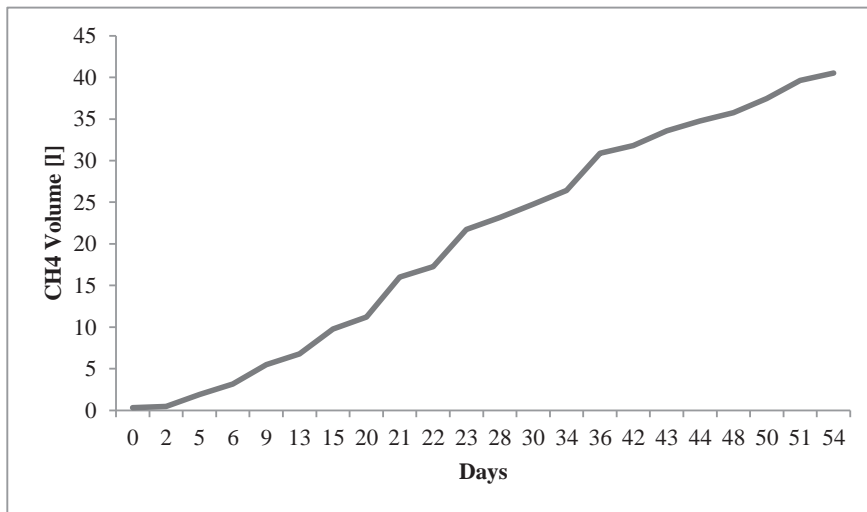


Fig. 11. Cumulative volume of methane

The cumulative production of biogas has reached 63 l at the end of the test (Fig. 12). Therefore the presence of methane into the biogas was 64%.

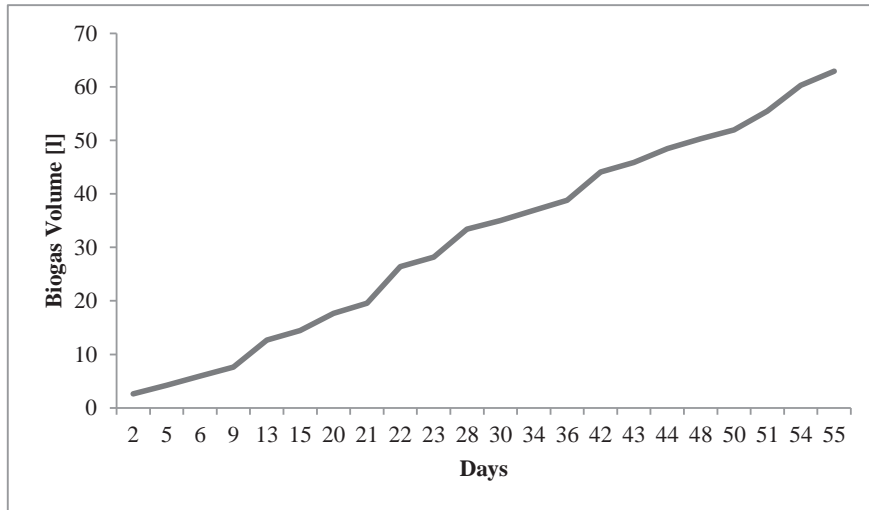


Fig. 12. Cumulate volume of biogas

In Fig. 13 the trend of the VS into the mixture is showed. The time trend of the VS shows behaviour consistent with that expected: the reduction of the VS increases with test time.

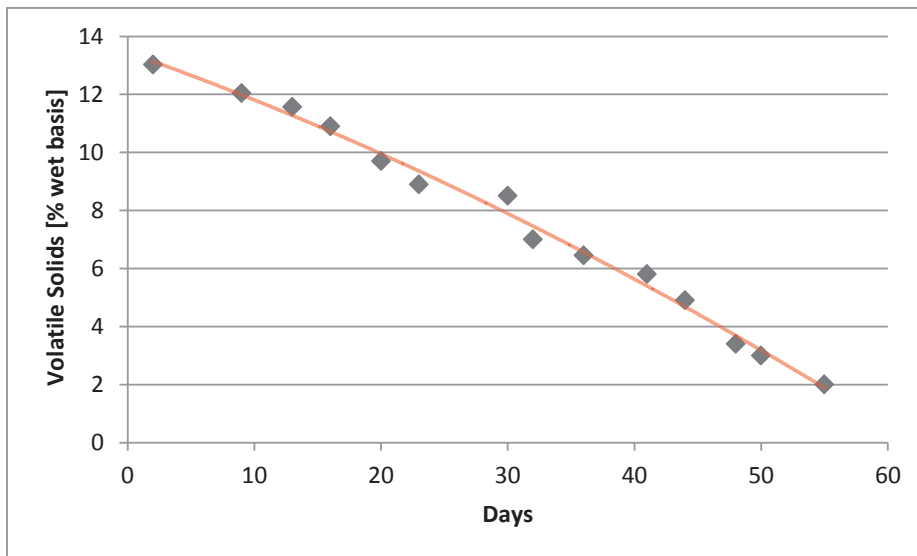


Fig. 13. VS on wet basis and trend line

BMP has reached in this case a value of  $0,103 \text{ l/g}_{\text{VS}}$ .

Therefore comparing the BMP and the methane average percentage of the two tests (Table 5) can be observe as the co-digestion test of OMSW with pit and manure and cattle slurry has produced better results ( $0.1034 \text{ l/g}_{\text{VS}}$  and 64% respectively).

Table 5. BMP and methane average percentage in biogas of the two tests

Test	BMP [l/gvs]	Methane average percentage in biogas [%]
Digestion of OMSW without pit and inoculum	0,0023	4,55
Co-digestion of OMSW with pit and manure and cattle slurry	0,1034	64

### 3.1 Conclusions

Olive-mill wastes represent a significant environmental problem in Mediterranean area where they are produced in huge quantity and seasonally, thus in short periods of time. One of the most promising processes to exploit OMWs for energy production is anaerobic digestion. Especially OMSWs can be used in co-digestion processes with other biomass.

Anaerobic co-digestion technology is increasingly used to simultaneously treat several solid and liquid organic wastes in order to balance the nutrients content, to reduce negative effects of toxic compounds on the process, and, therefore, to increase the biogas yield. Moreover, co-digestion technology contributes to a more efficient use of anaerobic digestion, because multiple streams of wastes can be processed together in a single plant at the same time.

The use of OMSW with pit represents economically a very attractive possibility, in particular for the small olive mills. From the tests carried out with a batch stirred tank reactor results OMSW with pit has better performance if used in co-digestion with other substrates.

The optimal mixture has been found using 4.65% of CM, 72.10% of CS and 23.25% of OMSW with a Total Solid (TS) content of 14%.

### References

- [1] Sesli M, Yegenoglu D. RAPD-PCR analysis of cultured type olives in Turkey. *Afr J Biotechnol* 2009;8.
- [2] International Olive Oil Council. <http://www.internationaloliveoil.org/> n.d. <http://www.internationaloliveoil.org/>.
- [3] Roig A, Cayuela ML, Sánchez-Monedero MA. An overview on olive mill wastes and their valorisation methods. *Waste Manag* 2006;26:960–9. doi:10.1016/j.wasman.2005.07.024.
- [4] Fountoulakis MS, Dokianakis SN, Kornaros ME, Aggelis GG, Lyberatos G. Removal of phenolics in olive mill wastewaters using the white-rot fungus *Pleurotus ostreatus*. *Water Res* 2002;36:4735–44. doi:10.1016/S0043-1354(02)00184-7.
- [5] Doymaz I, Gorel O, Akgun NA. Drying Characteristics of the Solid By-product of Olive Oil Extraction. *Biosyst Eng* 2004;88:213–9. doi:10.1016/j.biosystemseng.2004.03.003.
- [6] Niaounakis M, Halvadakis CP. *Olive Processing Waste Management: Literature Review and Patent Survey* 2nd Edition. Elsevier; 2006.
- [7] Azbar N, Yonar T. Comparative evaluation of a laboratory and full-scale treatment alternatives for the vegetable oil refining industry wastewater (VORW). *Process Biochem* 2004;39:869–75. doi:10.1016/S0032-9592(03)00193-6.
- [8] Dermeche S, Nadour M, Larroche C, Moulti-Mati F, Michaud P. Olive mill wastes: Biochemical characterizations and valorization strategies. *Process Biochem* 2013;48:1532–52. doi:10.1016/j.procbio.2013.07.010.
- [9] ISMEA. Istituto dei Servizi per il Mercato Agricolo e Alimentare (ISMEA). <http://www.ismea.it> n.d. <http://www.ismea.it>.
- [10] Bocci E, Sisinni M, Moneti M, Vecchione L, Di Carlo A, Villarini M. State of Art of Small Scale Biomass Gasification Power Systems: A Review of the Different Typologies. *Energy Procedia* 2014;45:247–56. doi:10.1016/j.egypro.2014.01.027.
- [11] Di Carlo A, Borello D, Bocci E. Process simulation of a hybrid SOFC/mGT and enriched air/steam fluidized bed gasifier power plant. *Int J Hydrog Energy* 2013.

- [12] Bocci E, Di Carlo A, McPhail SJ, Gallucci K, Foscolo PU, Moneti M, et al. Biomass to fuel cells state of the art: A review of the most innovative technology solutions. *Int J Hydrog Energy* 2014;39:21876–95.
- [13] Vecchione L, Moneti M, Di Carlo A, Bocci E. Biomass waste shells analysis and advanced gasification tests. *Green Build Mater Civ Eng* 2014:55.
- [14] Eurobserv'er. *Biogas Barometer* 2012.
- [15] Villarini M, Bocci E, Moneti M, Di Carlo A, Micangeli A. State of Art of Small Scale Solar Powered ORC Systems: A Review of the Different Typologies and Technology Perspectives. *Energy Procedia* 2014;45:257–67. doi:10.1016/j.egypro.2014.01.028.
- [16] Bocci E, Di Carlo A, Vecchione L, Villarini M, De Falco M, Dell'Era A. Technical-Economic Analysis of an Innovative Cogenerative Small Scale Biomass Gasification Power Plant. *Comput. Sci. Its Appl.* 2013, Springer; 2013, p. 256–70.
- [17] GSE. *Rapporto Statistico 2012- Impianti a FER* 2012.
- [18] European Standard EN 14778:2011, Solid biofuels. Sampling. n.d.
- [19] European Standard EN 14780:2011, Solid biofuels: sample preparation. n.d.
- [20] European Standard EN 15104:2011, Solid biofuels: determination of total content of carbon, hydrogen and nitrogen. Instrumental methods. n.d.
- [21] García-Pérez M, Chaala A, Pakdel H, Kretschmer D, Roy C. Vacuum pyrolysis of softwood and hardwood biomass: Comparison between product yields and bio-oil properties. *J Anal Appl Pyrolysis* 2007;78:104–16. doi:10.1016/j.jaap.2006.05.003.
- [22] Naik S, Goud VV, Rout PK, Jacobson K, Dalai AK. Characterization of Canadian biomass for alternative renewable biofuel. *Renew Energy* 2010;35:1624–31. doi:10.1016/j.renene.2009.08.033.
- [23] Manyà JJ, Roca FX, Perales JF. TGA study examining the effect of pressure and peak temperature on biochar yield during pyrolysis of two-phase olive mill waste. *J Anal Appl Pyrolysis* 2013;103:86–95. doi:10.1016/j.jaap.2012.10.006.
- [24] European Standard EN 14774-1:2009, Solid biofuel. Determination of moisture content, oven dry method. Part 1: total moisture, reference method. n.d.
- [25] European Standard EN 14774-2:2009, Solid biofuel. Determination of moisture content, oven dry method. Part 2: total moisture, simplified method. n.d.
- [26] European Standard EN 14774-3:2009, Solid biofuel. Determination of moisture content, oven dry method. Part 3: moisture in general analysis sample. n.d.
- [27] European Standard EN 14775:2009, Solid biofuel: Determination of Ash content. n.d.
- [28] European Standard EN 14918:2009, Solid biofuels: determination of calorific value. n.d.
- [29] European Standard EN 15148 – Solid biofuels – Determination of the content of volatile matter. n.d.
- [30] Eiroa M, Costa JC, Alves MM, Kennes C, Veiga MC. Evaluation of the biomethane potential of solid fish waste. *Waste Manag* 2012;32:1347–52. doi:10.1016/j.wasman.2012.03.020.
- [31] Carlini M, Castellucci S, Cocchi S. Mesophilic Fermentation of SOMW in a Micro Pilot-Scale Anaerobic Digester. *Adv Mater Res* 2014;827:84–90.