Feasibility of separated-phase anaerobic digestion for biogas production from olive mill waste water

A. Koumara, E. Kiatipis, A. Eftaxias, V. Diamantis, A. Aivasidis

Laboratory of Wastewater Management and Treatment Technologies, Department of Environmental Engineering, Democritus University of Thrace, 12, Vas. Sofias str, 67100 Xanthi, Greece
Presenting author email: alexandra.koumara@gmail.com, bdiamant@env.duth.gr

Abstract

In this study we evaluated the process of OMW acidification as a pre-treatment to anaerobic digestion. The acidified OMW was digested in anaerobic batch and continuous stirred tank reactors (CSTR). OMW acidification was performed under mesophilic conditions using an acidogenic CSTR with biomass recirculation. The acidogenic CSTR was operated at an average hydraulic residence time (HRT) = 1.2 d and organic loading rate (OLR) = 31 kgCOD m^{-3} d^{-1}. The methanogenic reactor was operated with gradually decreasing the HRT from 16 to 4 d corresponding to an OLR increase from 1 to 7 kgCOD m^{-3} d^{-1}. From the batch anaerobic experiments, it was demonstrated that the acidified OMW displayed a biogas yield between 0.35-0.40 m^3 $kgCOD^{-1}$ significantly higher compared to the non-acidified OMW which was maintained between 0.20-0.30 m^3 $kgCOD^{-1}$. The maximum biogas production rate was in the range of 2.5-3 m^3 biogas m^{-3} d^{-1}. The biogas methane content was constant at 71%. For OLR less than 4 kgCOD $m^{-3}d^{-1}$ the percentage of COD removal was up to 90% while decreased to 76% with increasing OLR to 7 kgCOD m^{-3} d^{-1}. The conversion of soluble phenolic compounds by the acidification process was 18% and by the proceeding methanization additional 48% (57% in total). Under steady-state conditions, the biogas yield coefficient was equal to 0.48 m^3 biogas $kgCODin^{-1}$ and the methane yield 0.36 NL m^3CH_4 $kgCOD^{-1}rem$. The proposed technology is of interest for the anaerobic digestion of OMW and further implementation under field conditions is necessary.

Keywords: Olive mill wastewater, anaerobic treatment, biogas, phenolics

1. Introduction

Olive oil production is an important branch of the Mediterranean economy, as 75.8% of the world's production according to FAOSTAT originates from Europe, with the largest producer countries being Spain (1.219.074 tn / y), Italy (584,658 tn / y) and Greece (335.800 t / y) [1]. Wastes generated from olive mills are characterized by a high organic load and consist mainly of carbohydrates, lipids and phenolics. There are three types of technologies (pressure systems, two-phase or three-phase centrifugation). In particular, three-phase mills generate approximately 1-1.6 m^3 of olive mill waste water (OMW) and 800 kg of solid waste, while from the two-phase systems 0.2 m^3 of OMW and 500 kg of solid waste per ton of olive fruit processed [2,3]. Management is a significant problem for producer countries because it is a phytotoxic waste, and its disposal on the ground, at sea or streams is prohibited.

OMW is of great interest for biogas production through anaerobic digestion technologies. The latter are considered efficient and economically viable for stabilizing olive mill wastes, due to the reduced energy requirements, the concurrent biogas production and the low biomass yield. Previous studies, however, demonstrated that biogas production from OMW was relatively low, due to the presence to phenolic compounds and lipids [3-5]. Two-stage anaerobic digestion systems have been studied for the treatment of olive mill wastes and co-substrates such as cheese whey and sewage sludge [4, 6-8]. The main advantages they display in comparison to single-stage anaerobic bioreactors are: shorter retention times, higher methane yields, reduced risk of accumulation of toxic materials and protection of methanogenic microorganisms from low pH.

The purpose of this paper was to investigate the performance of batch and continuous anaerobic bioreactors treating pre-acidified olive mill waste water. The study emphasized on COD, carbohydrates

and phenolic removal under both acidification and methanization phase. The anaerobic digestion process was also evaluated based on biogas production and methane yield.

2. Materials and methods

2.1 Origin of waste

The olive mill waste water (OMW) was obtained from a three-phase olive mill (in Xanthi, Greece) and the solids > 1mm were separated using a screen. During the experiment the screened OMW was kept inside a refrigerator at 5 ± 1 ° C.

2.2 Continuous anaerobic digestion studies

The pilot-scale facility consisted of an acidogenic (7 L) and a methanogenic CSTR (42 L) both operated under mesophilic conditions. (Figure 1). Both reactor's temperature was maintained at (37 - 39 °C) using a water bath (MGW LAUDA), they were continuously mechanically agitated and their pH was monitored by electronic pH-meters (Endress Hauser). The methanogenic reactor (SCHOTT Duran 6076-11) was additionally equipped with a biogas meter (Ritter Kunstoffwerk KWU B). The biogas composition in methane and carbon dioxide was determined by infrared spectrometer (BINOS).

2.3 Batch anaerobic digestion studies

In total 10 batch experiments (6 with non-acidified and 4 with acidified OMW) were performed under mesophilic conditions, and each reactor had a working volume of 2 L. Biogas production was measured using a wet gas meter. All batch reactors were mixed using a magnetic stirrer and the operational temperature was maintained at 37 °C using a water bath.

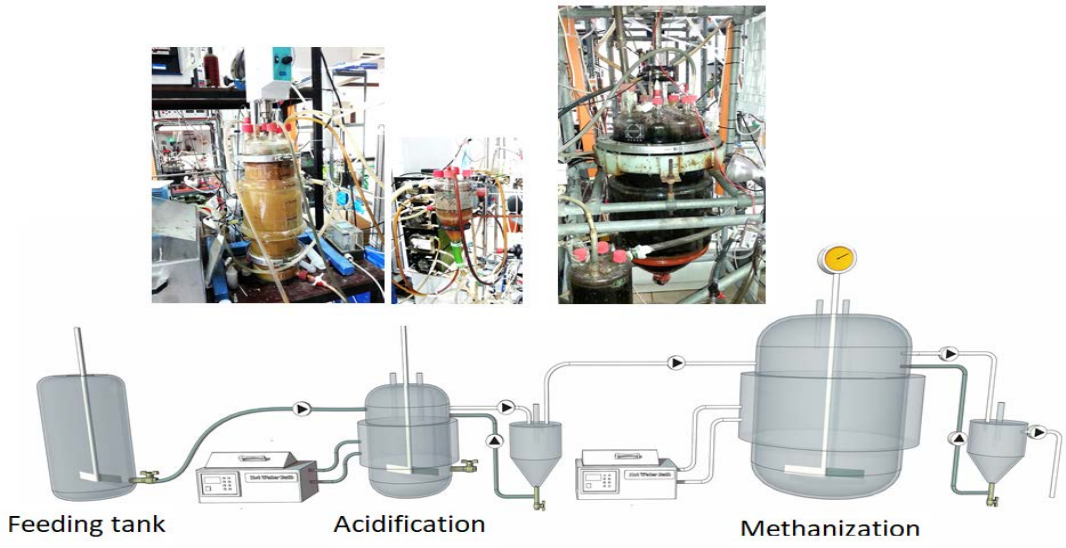

Figure 1. Schematic and photographic representation of the separated-phase anaerobic digestion facility for continuous anaerobic treatment of olive mill waste.

2.4 Analytical methods

Laboratory analyses were performed according to the Standard Methods for the Examination of Water and Wastewater [9]. The physical and chemical parameters determined are: Total COD and Soluble COD, TSS, TS, VSS, VS, pH, EC, VFAs, phenolic compounds (Folin-Ciocalteu method), carbohydrates (anthrone method), orthophosphates (PO_4^{3}-P) and ammoniacal nitrogen (NH_4^{+}-N). The above measurements were performed on samples from Raw Wastewater, Feed Input (F), Intermediate Sedimentation (IMS), CSTR (AD) Anaerobic Reactor, and Final Clarification (FC), with sampling

frequency twice a week. The soluble fraction of COD, Phenolic compounds, Carbohydrates, PO_4^{3} -P, NH_4^{+} -N was carried out by filtering with a pore diameter of 45 μm. Finally, the measurement of volatile fatty acids (VFAs) (acetic, propionic, butyric, isobutyric and valeric acid) was done using a gas chromatograph (Perkin Elmer Auto System XL) as described by Diamantis et al. [10].

3. Results and discussion

3.1 Performance of batch anaerobic reactors

The acidified OMW was digested in batch anaerobic reactors (Figure 2). The data from the batch studies demonstrated that the acidified OMW displayed a biogas yield between 0.35-0.40 m^3 $kgCOD^{-1}$, significantly higher compared to the non-acidified OMW which was maintained between 0.20-0.30 m^3 $kgCOD^{-1}$. The increase in biogas yield was attributed to the (partial) removal of phenolic compounds during the acidification process (18%).

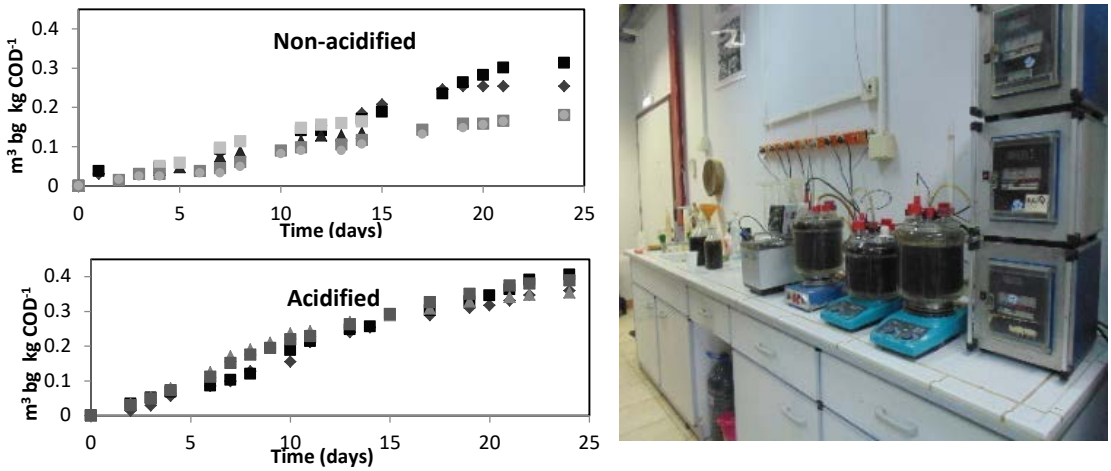

Figure 2. Cummulative biogas yield during batch anaerobic digestion of acidified and non-acidified OMW. The results correspond to two (2) different OMW samples and two (2) replicates each.

3.2 Performance of continuous separated phase system

The acidification CSTR was operated at an average hydraulic retention time (HRT) and organic loading rate (OLR) equal to 1.15 ± 0.7 days and 31.3 ± 17 kgCOD m^{-3} d^{-1} respectively. Under these conditions the reactor pH was maintained at 4.81 ± 0.2. The removal of CODt and CODs during the acidification process was 20 ± 0.1% and 17 ± 0.1% respectively similar to the conversion of OMW phenolic compounds (18 ± 0.2%). On the contrary, the bioconversion of soluble carbohydrates during the acidification process was 61 ± 0.1% (Table 1).

The methanogenic reactor was operated at a hydraulic retention time (HRT) from 3.7 to 16 days. Correspondingly, the OLR ranged from 1.4 to 9.5 kgCOD m^{-3} d^{-1}. Under these conditions the bioreactor pH was maintained on average at 7.0, which is within the optimal range for the growth of methanogenic bacteria and biogas production. No accumulation of VFAs was observed nor a requirement to use chemicals to regulate it (Figure 3). However, a decrease of the pH from 7.4 to 6.6 was recorded with increasing the OLR from 3 to 8 kgCOD m^{-3} d^{-1}.

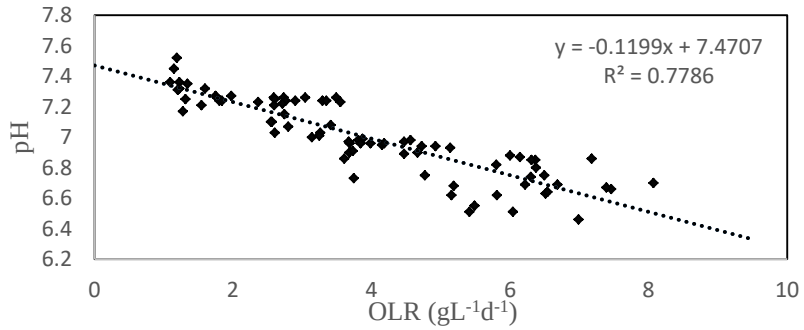

Figure 3. Effect of the volumetric organic load rate on the pH value during the operation of the methanogenesis reactor.

The proper functioning of the acidification step was confirmed by the production of VFAs and the fermentation of carbohydrates (Table 1). The volatile fatty acids produced in the acidification step were composed of: 37% acetic acid, 15% propionic acid, 1% isobutyrate, 46% butyric acid and 1% valeric acid. In the anaerobic digester the respective percentages of VFAs were 47, 25, 3, and 25%. Phenolic compounds of OMW, which have been the focus of attention of many researchers due to their difficult conversion [3, 5, 11], were converted in the entire assembly at percentage of 57%. The majority of the phenolic compounds (48%) were removed in the methanization stage.

In the assembly carbohydrate removal was 93 ± 0.03%, which is explained by the easily biodegradable nature of these compounds and indicates the efficacy of the microbial population in their degradation.

Table 1. Parameter variation throughout the assembly during experimental process.

Parameter	Unit	ACS influent	ACS ef / AD in	AD effluent
CODt	g L^{-1}	53.6 ± 8.9	42.4 ± 5.5	9.04 ± 1.6
CODs	g L^{-1}	26.2 ± 4.7	21.6 ± 3.1	5.7 ± 0.7
TSS	g L^{-1}	10.1 ± 4.3	7.8 ± 2.1	2.3 ± 0.7
VSS	g L^{-1}	9.5 ± 4.2	7.3 ± 2.1	1.9 ± 1
pH		4.78 ± 0.1	4.68 ± 0.1	7.01 ± 0.3
EC	mS cm^{-1}	6.81 ± 0.5	7.21 ± 0.6	7.04 ± 0.5
VFAs	g L^{-1}	0.89 ± 0.21	2.48 ± 0.967	0.65 ± 0.38
Acetate	g L^{-1}	0.54 ± 0.21	1.05 ± 0.21	0.31 ± 0.21
Propionate	g L^{-1}	0.13 ± 0.038	0.37 ± 0.114	0.16 ± 0.06
Isobutyrate	g L^{-1}	0.043 ± 0.02	0.047 ± 0.017	< 0.002
Butyrate	g L^{-1}	0.18 ± 0.079	1.14 ± 0.59	0.17 ± 0.13
Valerate	g L^{-1}	0.027 ± 0.014	0.34 ± 0.027	-
Phenolics	g L^{-1}	1.85 ± 0.62	1.52 ± 0.59	0.79 ± 0.25
Carbohydrates	gL^{-1}	3.00 ± 0.82	1.16 ± 0.317	0.22 ± 0.53
PO_4^{3-}-P	mg L^{-1}	183.4 ± 110	183.2 ± 103	125.4 ± 73
NH_4^+- N	mg L^{-1}	117.3 ± 92	100.3 ± 38	22.5 ± 11

The biogas production rate (BPR) and the organic load rate (OLR) during methanogenic reactor operation are shown in Figure 4. The maximum BPR was determined between 2.5-3.0 m^3 biogas m^{-3} d^{-1}, corresponding to an OLR between 6-8 kgCOD m^{-3} d^{-1} (Figure 4). The biogas methane content was equal to 71 ± 2%. Under (semi) steady-state conditions the biogas yield was determined equal to 0.48 m^3 biogas $kgCODin^{-1}$, and the methane yield 0.36 m^3CH_4 $kgCODrem^{-1}$ which is relatively high compared to previous studies: 0.30 m^3CH_4 $kgCODrem^{-1}$ [12], 0.135 m^3CH_4 $kgCODrem^{-1}$ [13] and 0.225 m^3CH_4 $kgCODrem^{-1}$ [14]. (Figure 5).

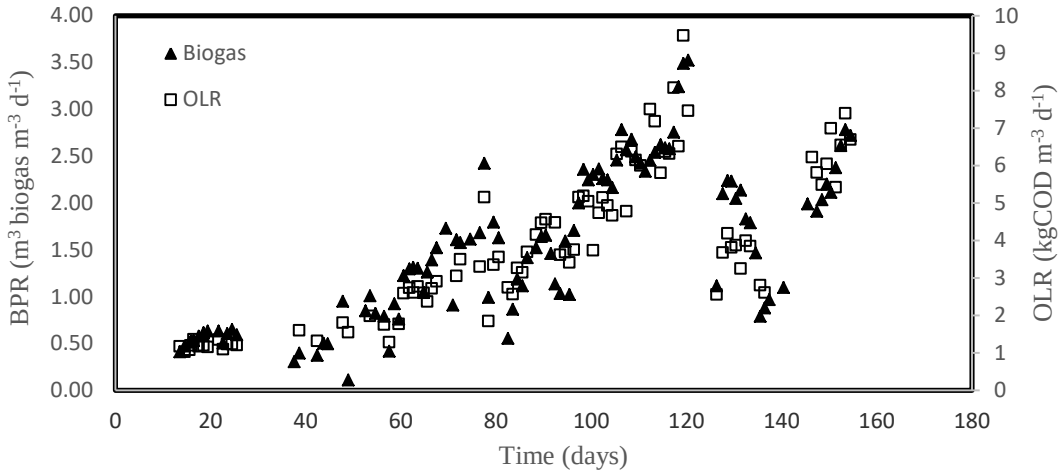

Figure 5. Variation in the volumetric biogas production rate in the anaerobic reactor in relation to the organic loading rate and the time of the experiment.

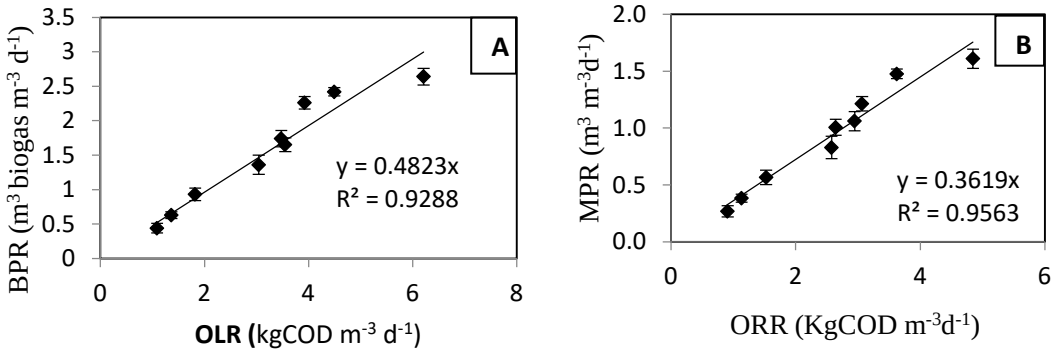

Figure 4. (A) Effect of the volumetric rate of organic loading on the volumetric biogas production rate. (B) Effect of the COD removal rate on the volumetric methane production rate.

The effect of the OLR on the COD removal efficiency is shown in Figure 6. At high OLR (> 6 kgCOD m^{-3} d^{-1}) COD removal efficiency was relatively low (70-80%). At low OLR (<4 kgCODin m^{-3} d^{-1}), the COD removal efficiency was between 85-90%. The CODt and CODs removal obtained in the assembly was on average equal to 83 ± 0.01% and 78 ± 0.07% respectively.

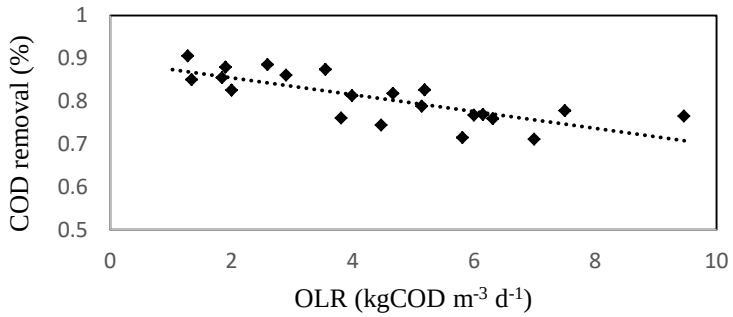

Figure 6. Effect of OLR on COD removal (%) during the experiment.

The results of this study demonstrate that the anaerobic treatment of OMW in a separated-phase (two-stage) system is an effective solution that produces better results regarding methane production than the one-stage technologies studied (Table 2).

Table 2. Performance of methanization reactors in one and two-stage systems treating OME.

Reference	**HRT** (d)	**OLR** (kgCOD $m^{-3}d^{-1}$)	**CODt removal** (%)	**Biogas Productivity** (m^3bg $m^{-3}d^{-1}$)	**CH_4** (%)	**Methane Productinity** ($m^3CH_4m^{-3}day^{-1}$)	**Methane Yield** (m^3 $kgCODin^{-1}$)
[4] 2-stage process	36	4.59	77	1.5	83	1.67	0.35
	36	2.28	70	1.16	84	1.32	0.53
	24	6.87	72	2.05	80	2.23	0.31
	24	3.42	67	1.61	82	1.7	0.47
[6] 2-stage process	20	3.95	-	0.96	66	0.64	0.16
	15	5.26	-	1.22	65	0.79	0.15
	10	7.9	-	1.69	67	1.13	0.14
[14] 1-stage process	215	0.75	97	-	-	0.16	0.21
	108	1.5	96.6	-	-	0.33	0.22
	71.9	2.25	96	-	-	0.48	0.21
	54	3.00	95.6	-	-	0.66	0.22
[13] 1-stage process	10	-	-	0.53	79.5	0.38	0.03
	20	-	-	0.69	81.9	0.55	0.08
	30	-	-	0.47	84	0.39	0.08
	40	-	-	0.39	82.6	0.32	0.09
This work	11	3.9	78	2.26	69	1.21	0.31
	10.4	1.8	84	0.93	70	0.57	0.32
	9.4	4.5	81	2.42	71	1.48	0.33
	7.1	6.2	78	2.64	72	1.61	0.26
	5.5	3.5	85	1.74	70	1.06	0.31

4. Conclusions

- Acidification of olive mill wastes can lead to high methane yield, and makes their valorization for biogas production feasible.
- Phenolic compounds were removed by 57%, of which the majority (48%) was removed in the methanogenic reactor.

- The COD removal efficiency in the whole system was 70-90% and it is consistent with previous studies [4, 12].
- For OLR greater than 6 kgCOD m^{-3} d^{-1}, the COD removal efficiency of the system was reduced between 70-80%.

LITERATURE

[1] Food and Agriculture Organization of the United Nations Statistics Division http://faostat.fao.org

[2] Alburquerque J, Gonzalves J, Garcia D, and Cegarra J.: Agrochemical characterisation of 'alperujo', a solid by-product of the two-phase centrifugation method for olive oil extraction. Bioresource Technology, 91(2):195–200 (2004).

[3] Roig A., Cayuela M.L. and Sánchez-Monedero M.A.: An overview on olive mill wastes and their valorisation methods. Waste Management, 26(9), pp. 960–969 (2006). doi: 10.1016/j.wasman.2005.07.024.

[4] Fezzani B. and Ben Cheikh R.: Extension of the anaerobic digestion model no. 1 (ADM1) to include phenol compounds biodegradation processes for simulating the anaerobic co-digestion of olive mill wastes at mesophilic temperature. Journal of Hazardous Materials, 172(2-3), pp. 1430–1438 (2010).

[5] Borja R., Alba J., Banks C. J.: Impact of the main phenolic compounds in olive mill waste water (OMW) on the kinetics of acetoclastic methanogenesis. Process Biochemistry, Vol. 32, No. 2, pp. 121-132 (1997).

[6] Koutrouli, E.C., Kalfas, H., Gavala, H.N., Skiadas, I.V., Stamatelatou, K. and Lyberatos, G.: Hydrogen and methane production through two-stage mesophilic anaerobic digestion of olive pulp. Bioresource Technology, 100(15), pp. 3718–3723 (2009).

[7] Daminer G.N, Chen S.: Two-phase anaerobic digestion of unscreened dairy manure. Process Biochemistry 40 (2005) 3542–3549 (2005).

[8] Jingquan Lu, Hariklia N. Gavala, Ioannis V. Skiadas, Zuzana Mladenovska, Birgitte K. Ahring.: Improving anaerobic sewage sludge digestion by implementation of a hyper-thermophilic prehydrolysis step. Journal of Environmental Management 88, 881–889 (2008).

[9] APHA, AWWA, WPCF : ″Standard Methods for the examination of water and wastewater″. Franson MA, editors. Washington, DC: American Public Health Association (1995).

[10] Diamantis V., Melidis P., Aivasidis A.: Continuous determination of volatile products in anaerobic fermenters by on-line capillary gas chromatography. Analytica Chimica Acta 573-574, 189-194 (2006).

[11] Cara F., Ionataa E., Monacoa G., Marcolongoa L., Gonçalves M. R., Marquesb I. P.: Olive Mill Wastewater Anaerobically Digested: Phenolic Compounds with Antiradical Activity. Chemical Engineering Transactions, Vol. 27, (2012).

[12] Bojra R., Rincon B. Raposo F., Alba J., Martin A.: A study of anaerobic digestibility of two-phases olive mill solid waste (OMSW) at mesophilic temperature. Process Biochemistry 38, pp. 733-742 (2002).

[13] Tekin Ali R, Coskun A. Dalgic.: Biogas production from olive pomace. Resources, Conservation and Recycling 30, pp. 301–313 (2000).

[14] Rincón B., Raposo F, Borja R, Gonzalez J.M., Portillo M.C. and Saiz-Jimenez C.: Performance and microbial communities of a continuous stirred tank anaerobic reactor treating two-phases olive mill solid wastes at low organic loading rates. Journal of Biotechnology 121, pp. 534–543 (2006).