Applied Mathematical Sciences Vol. 8, 2014, no. 132, 6665 - 6678
HIKARI Ltd, www.m-hikari.com
http://dx.doi.org/10.12988/ams.2014.474551

Methane Potentials from Grape Marc by a Laboratory Scale Plant

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Abstract

The choice of grape marc as biomass to produce energy has a double purpose. It provides a valid alternative to the handing over to distilleries, which represents a considerable cost for the community and also gives value to a form of agricultural-industrial waste. In this paper, the results of an experiment performed at ERSAF (Lombardy) in their laboratories in Mantova are assessed. A laboratory scale plant was used in order to evaluate the biogas and the methane produced by the anaerobic digestion (AD) of fresh grape marc and to evaluate the role of seeds in the production of methane. The results indicate there have get yields of up to 110 Nm^3/t sv of methane, with a much faster production rate than with other bio-masses. The inclusion of grape seeds has a positive effect on the production of biogas and methane. With crushed grape marc a higher percentage of CH_4 could be reach than to the other tests, suggesting that the grape seeds crushed favours the methanogenesis. Nevertheless the differences between this matrix and that with as such grape marc are not statistically significant.

Keywords: Anaerobic digestion, Biogas, Wine production residues, By-products valorization, bio-waste management

1 Introduction and aim of the work

From the point of view of the environmental sustainability, energy production from agro-industrial by-product is a strategic opportunity to fight against climate change and to reduce emissions of greenhouse gases. These have reached 31.6 $GtCO_2eq$ in 2012, the highest level in history as documented by the International

Energy Agency - IEA (FAO, 2014), while the Italian quota amounted to about 0.5 $GtCO_2eq$ (INEA, 2013). The need to reduce the use of energy sources from fossil fuels and increase the use of renewable energy has been further reaffirmed in an international context (IPCC, 2014) and is a target of the policy on climate and energy promoted by the European Union (Dir 2009/28/EC).

In this regard, the wine industry residues are an opportunity for significant interest in countries where the spread of grapevine is consolidated or by growing (Krzywoszynska, 2013). In Italy, such by-product correspond to an average of about 1.5-1.7 Mg of grape marc generated from about 10 Mg of wine grapes (Ribéreau-Gayon et al., 2007). If we consider a national production of 6000 Gg of wine grapes (ISTAT, 2013), it is possible to reach about 900-1020 Gg of grape marc from wine industry.

In the EU, the use of the wine industry residues for agronomic purposes or for energy purposes is permitted only from few years (Reg. EC no. 479/2008 and 702/2009 and for Italy the Ministerial Decree no. 7407 of 4 August 2010) because in the past there was the constraint of the compulsory distillation.

Now, the alternative uses of these residues allow to include energy production via anaerobic digestion or incineration, the spreading on agricultural land (raw or composted), and the use as a raw material for the production of cosmetics and pharmaceuticals goods.

The use of wine industry residues in agriculture and on the beneficial effects of the composts as organic fertilisers and in soil amendments has been widely studied over ten years by many researchers (Bertran et al., 2004; Bustamante et al., 2009; Carmona et al., 2012; Díaz et al., 2002; Moldes et al., 2007; Reis et al., 2003; Ruggieri et al., 2009).

The use of the untreated grape marc for the production of energy from biogas, in co-digestion with other biomass, allows to obtain environmental and economic benefits (Amon et al., 2009; Balsari et al., 2009; Celma et al., 2007; Dinuccio et al., 2010; Fountoulakis et al., 2008; Moletta, 2005; Schievano et al., 2009).

However, the availability of such biomass is only partially exploited, especially in Sicily, which contributes to the national wine production with 17% of cultivated area, 15% of grape production and 12% of wine production (ISTAT, 2013). In this context, the use of the grape marc would help to extend the range of useful biomass to power plants continuously and at the same time to exploit a local resource, bringing benefits to the wine sector and contributing to the development of renewable energy sector.

To this end, to consider the possibility and convenience of use of grape marc for biogas production has a dual purpose: to reduce the cost of their management and to increase the value of a waste or by-product, by disengaging energy supply from dedicated crops grown solely for that purpose.

In this context, the aim of the work is the evaluation of biogas yields from anaerobic digestion (AD) of fresh grape marc and the effects of the seeds presence and of their integrity status on yields in biogas and methane. The paper describes the results of batch tests on untreated grape marc, without seeds and pressed.

2 Methods

2.1 The laboratory scale plant

The experiment was carried out in a preassembled laboratory-scale biogas plant placed at Mantova (Italy) E.R.S.A.F. (Ente Regionale per i Servizi all'Agricoltura e alle Foreste della Regione Lombardia), the Lombardy regional board responsible for regional agriculture extension services. This plant was designed by Prof. Pierluigi Navarotto of the University of Milan and created by Italian companies both for the mechanical part and for the data management software (Marchesi et al., 2010). An agreement between the Department of the University of Catania (DiGeSA) and the ERSAF of Mantova made possible the plant use for the experimentation.

The plant is composed of 4 modules: the first one functions as the main control and analysis unit while the others, all of which are the same, have 12 polyethylene mini-reactors in bacth of four litres each, positioned in a case with a ventilated hot-plate. Each mini-reactor is equipped with a screw cap with airtight and a pickup point for the sampling of the biomass during fermentation.

Inside the first module are housed the system for the drying of biogas, the counter drum for the direct measurement of the quantity produced and the analysis system for the measurement of biogas quality in terms of percentage of oxygen, carbon dioxide and methane.

For the collection of the biogas each reactor is connected to a polyamide gasometer of two litres capacity. Among the reactors and gasholders are installed the dehumidifiers. They have the purpose of breaking down the excess water vapor which is formed during the process.

The gasometers are contained in appropriate cases, with a confined space that forces them to dilate in the vertical position. On top of the cases there is a micro–switch that starts the sampling and later the emptying, once it send the signal to the dedicated software that the gasholders are full.

First of all, the "dryer" is activated by lowering the temperature of the gas in order to favor the condensation of the residual water vapor, which will subsequently be removed by the peristaltic pump. The biogas is sucked by the sampling pump, passing first through the dryer, then the analyzer of hydrogen sulfide (H_2S) which detects the amount of the same gas (in ppm).

Before the biogas reaches the analyzer of the other gases for the measurement of methane (CH_4), carbon dioxide (CO_2) and oxygen (O_2), H_2S is trapped in the active carbon filter.

The precision volumetric meter is positioned at the end of the circuit and measures the amount of biogas produced with an error of 0.2% at a flow rate of 1 liter/minute. When the analysis is complete, the biogas is ejected from the system and the machine closes the circuit connecting the measuring system to the gasometers. For safety, after each analysis, the analyzers are "washed" with nitrogen to avoid any pools of H_2S that may damage the system.

Each component of the main control unit is directly connected to a computer that, thanks to special dedicated software, continuously and automatically monitors the sampling and the data registration for the 36 reactors. These can be managed independently in order to control loading, sampling, analysis of data and disposal.

2.2 Experimental conditions

The experiment was carried out according to standard procedure (Ficara et al., 2011) by evaluating four different matrixes: three represent theses test and one “blank” test. The thesis 1 was made up of inoculum and grape marc as such (UGM – Untreated Grape Marc), the thesis 2 of inoculum and grape marc without seeds (WSGM – Without Seeds Grape Marc), the thesis 3 of inoculum and pressed grape marc (PGM – Pressed Grape Marc) , the “blank” test of inoculum only (Inoculum). Three repetitions were carried out for each thesis test.
The grape marc were taken at a winery in Mantova province and derived from grape cultivar "Ancellotta", vinified in red and subjected to racking and light pressing after ten days of maceration. The use of the grape marc of red wine is recommended because this is typically subjected to fermentation process along with the wine and then contain a fair amount of alcohol (about 5-6%) useful for biogas production process. The inoculum consists of digestate taken from an real-scale anaerobic digestion plant of Mantova province and made by cattle slurry supplemented with corn silage.
The principal chemical characterization of these biomass is showed in Table 1.
Each reactor was fed with a total of 2000 g of inoculum and 177.36 g of grape marc as well as to respect the ratio 2:1 that means two parts of volatile solids (sv) inoculum and a part of volatile solids (sv) grape marc (Koppar and Pullammanappallil, 2008; Vismara et al., 2011).
Process temperature in each reactor was maintained in mesophilic conditions (40°C ± 2°C).

Table 1. Chemical characterization of biomass (*)

Chemical properties	Unit	Grape marc	Inoculum
Moisture	[wt%]	73.5	95.3
Total Solids (ts)	[wt%]	26.5	4.7
Volatile Solids (vs)	[wt%]	24.7	3.2
“ “	[ts%]	93.2	68.1
Total Nitrogen	[wt%]	1.8	0.3
“ “	[ts%]	6.9	6.4
Organic Carbon	[wt%]	5.6	1.6
“ “	[ts%]	21.3	35.1

(*) The values were determined by ERSAF laboratory (Mantova-Lombardy) by using standard methodologies.

2.3 Analysis of parameters during the AD test

Before starting the AD process the following parameters were evaluated on matrices: pH, FOS/TAC ratio (FOS stands for Flüchtige Organische Säuren, i.e. volatile organic acids, and is measured in mg HAceq/l, while TAC stands for

Totales Anorganisches Carbonat, i.e. total inorganic carbonate and is measured in mg $CaCO_3$/l), COD (Chemical Oxygen Demand) and N-NH_4^+ in order to assess the trend until the digestate (Vismara et al., 2011).
After 15 days of the process starting and at the conclusion of the same, FOS/TAC and pH were measured in order to determine the quotient of the acid concentration and the buffer capacity in the fermentation substrate.
The other two parameters (COD, N-NH_4^+) were verified at the end of the process in order to compare them final values with those initials.
The pH was measured by a high-precision pH-meter (CRISON BASIC 20). The FOS/TAC ratio was calculated using a two step end point potentiometric titration (Hach Lange TIM 840). The COD was measured by a thermostat (Hach Lange LT200) and N-NH_4^+ by a spectrophotometer (Hach Lange DR2800).
Finally, a chemical characterization was made on the digestates by the ERSAF laboratory.
The daily data of the biogas volume were normalized to normal cubic meters (Nm^3) (dry gas, T = 0 °C, P = 1013 hPa) according to the following equation:

$$\text{1 Normal cubic metre} = 1.054915 \text{ Standard cubic metre} \quad (1)$$

Methane concentration of recorded biogas was provided from analysis system of the laboratory scale plant.
Net biogas and methane yield of the tested biomasses were obtained by deducting the biogas and methane volume of the “blank” test.
Data were analysed by analysis of variance procedure (ANOVA) followed by Tukey’s means grouping tests by means of JMP 11.1 (sas) software.

3 Results and discussion

The test were carried out until exhaustion of the biogas production. The biogas produced during the AD was collected within of the gasometers for the time necessary to reach a volume such as to activate the micro-switch that is able to start the qualitative and quantitative sampling of biogas. After receiving the signal, the system has performed the sampling and recorded the results in a completely automated way. Only the “blank” test (Inoculum) did not produce an amount of biogas that automatically started sampling. So this was done manually. Similarly, manual sampling was performed at the end of the test, after about 21 days, in order to evaluate the amount of biogas produced in the interval of time between the last automatic sampling and the cessation of the AD when no automatic sampling was possible.
In all tests regarding to the grape marc (Figure 1), the daily production of raw biogas increases exponentially during the initial phase until the 5-6th day after loading, even if with varying velocities and volumes for each test. During the successive phase, the production suffered a major decrease until the end of the process, after about 21 days. The mean values of biogas cumulated production start from 0.67 L d^{-1} for getting 5.31 L d^{-1} of the third week of work. The total production of biogas from the “Inoculum” (blank test) was on average more than 10 times lower (about 0.38 L) than that net obtained from the "grape marc" (about

5.15 L on average), demonstrating the high biogas production capacity of grape marc. The tests on the grape marc gave different total volumes of net biogas, passing from 3.86 L for the WSGM test to 5.15 L for the PGM test and 5.79 L for UGM test. In particular, there are no statistically significant differences, for $p = 0.05$, between the mean biogas production of UGM test and PGM test.

Even the production of methane per ton of grape marc under standard conditions follow the same trend of raw biogas production (Figure 2). The UGM was the strongest thesis with about 28 $Nm^3\ t^{-1}$ of as received (ar) grape marc, 104 $Nm^3\ t^{-1}$ of total solids and 112 $Nm^3\ t^{-1}$ of volatile solids. While the WSGM test produced a smaller quantity of methane with 19 $Nm^3\ t^{-1}$ of as received (ar) grape marc, 71 $Nm^3\ t^{-1}$ of total solids and 76 $Nm^3\ t^{-1}$ of volatile solids, demonstrating that the inclusion of grape seeds has a positive effect on the production of biogas and methane. The PGM test gave no statically different values on methane production with respect to the UGM test. Nevertheless these values are lower than those gained by other biomass and organic wastes usable in AD (Dinuccio et al., 2010; Labatut et al., 2011; Roati et al., 2012; Ward et al., 2008; Weiland, 2010).

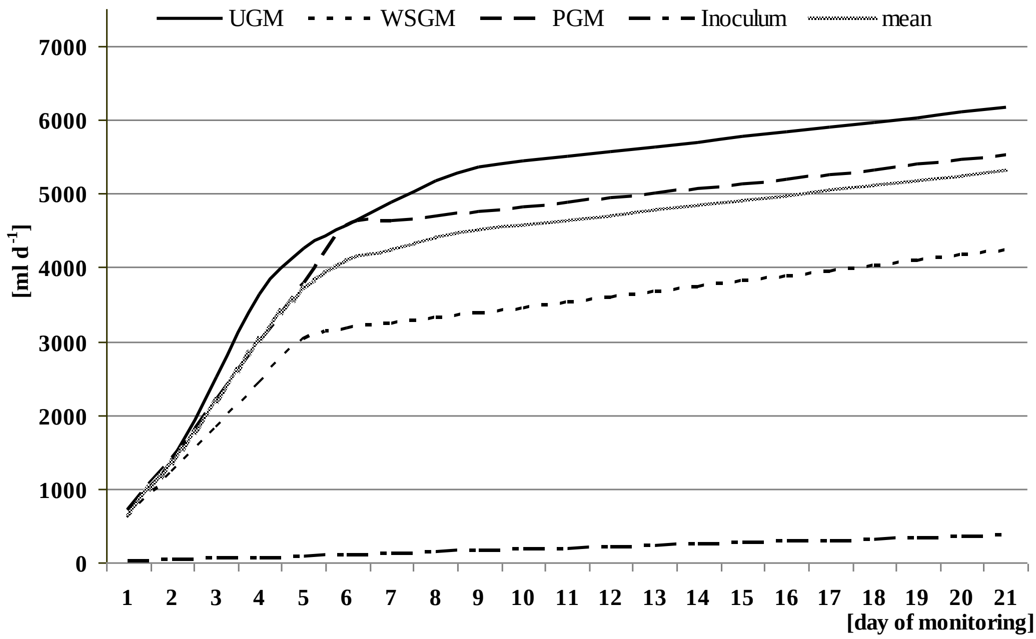
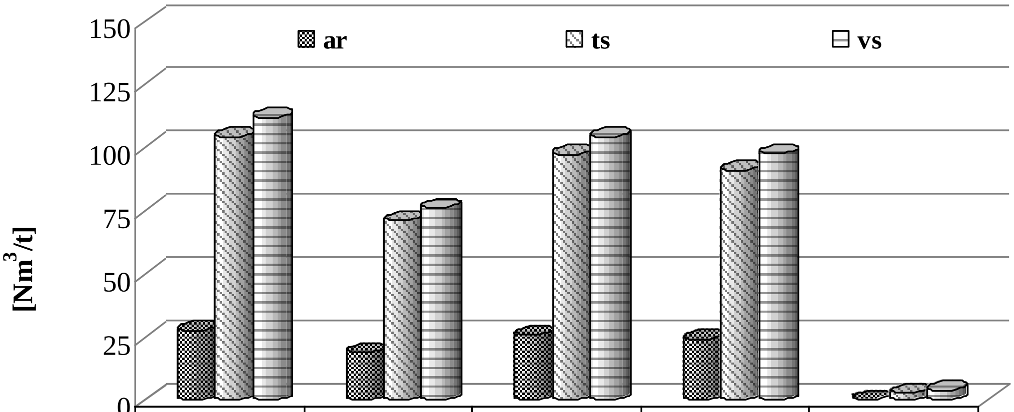


Figure 1. Daily Biogas production (ml d^{-1}) in the four different test thesis. Data are referred at 0 °C and 1 atm conditions.



	UGM	*WSGM*	*PGM*	*mean*	*Inoculum*
ar	*27.68* a	*18.82* b	*25.78* a	*24.09*	*0.13* c
ts	*104.44* a	*71.01* b	*97.27* a	*90.91*	*2.78* c
vs	*112.05* a	*76.19* b	*104.36* a	*97.53*	*4.08* c

Means followed in the same row by the same letter are not statistically different (p = 0.05) according to Tukey's test.

Figure 2. Methane production per tonne of grape marc (Nm^3/t), as received (ar), as total solids (ts) and volatile solids (vs) in the three different test thesis and per tonne of inoculum in the "control" test.

Although the production of methane (CH_4) per tonne of inoculum is much lower than that of the grape marc, the average percentage obtained of the total volume of biogas was equal to 64%. This value is in line with other data reported in literature on AD of bovine slurry and corn silage (CRPA, 2008).

As concerns the grape marc, the tests gave, on average, percentages of CH_4 between 80% in UGM test and 84% in PGM test (Figure 3). These values are higher than those reported by other authors, whose percentages of methane amounted to approximately 50% of the total biogas volume (Dinuccio et al., 2010; Roati et al., 2012). The PGM test show a higher percentage of CH_4 than to the other tests, probably because the crushed grape seeds promote microbiological activity in the digesters. But, the differences between the tests are not statistically significant and these are of only few percentage points. This could mean that the yield in methane of untreated grape marc is similar to the other considered matrixes.

Analyzing the production of biogas together at the varying of the FOS/TAC value of each test (Figure 4) it is evident that the AD process is closely linked to the degradation of the organic substance. The value of the FOS/TAC decreases as the biogas production proceeds, passing from values higher than 0.6 to values between 0.1 and 0.2. During the maximum production of biogas this parameter reaches values ranging from 0.4 to 0.5 which are correspond to the optimal range.

Lastly, after about 21 days, that is the end of the test, the FOS/TAC was reduced by 75% on average, while after 15 days of the start of the tests, it was already reduced by 70% on average, showing that the process was now being conclusive.

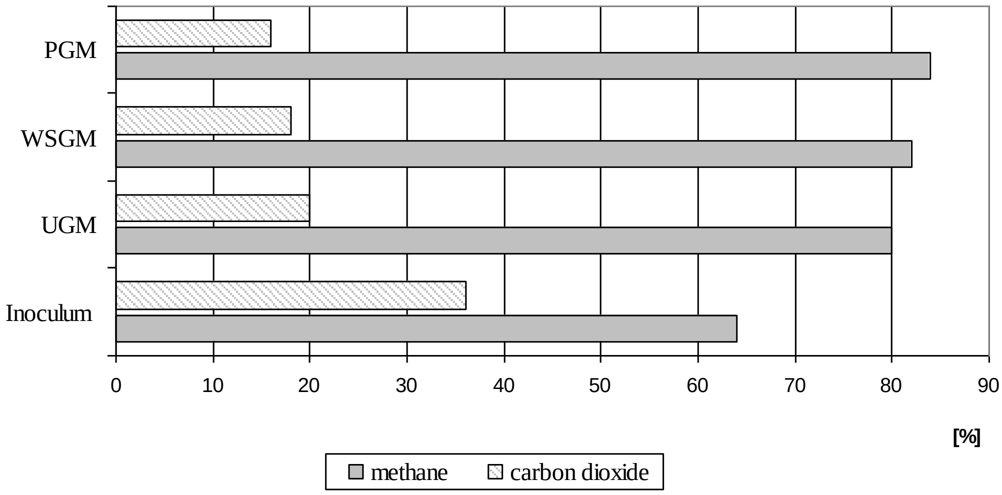


Figure 3. Average percentage of methane and carbon dioxide during AD in the four different thesis test.

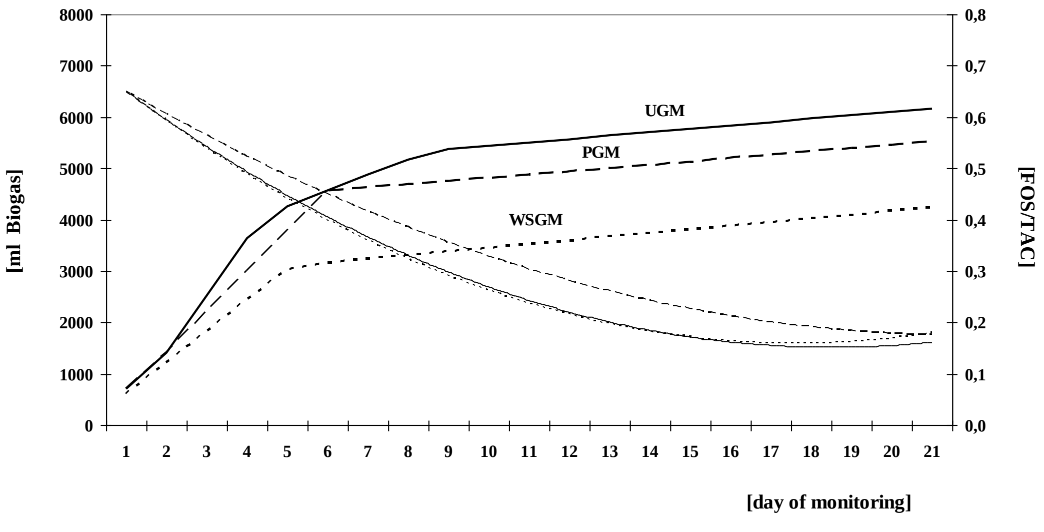


Figure 4. Representation of biogas production together with the monitoring of the FOS/TAC value (mg/L acetic acid and mg/L calcium carbonate ratio) along the monitoring period in the three different test thesis.

Before the fermentation process the pH of inoculum was equal to 8.1 while that of the grape marc was distinctly acid and it stood on average to 3.8. At the beginning of the fermentation (t_0), putting together the inoculum and the grape marc, the pH value was on average equal to 8.8 for the three different test thesis (Figure 5). After 15 days (t_{15}), thank to the buffering capacity of the inoculum, the pH of the thesis with the grape marc (UGM and WSGM) was stabilized to about 8, which represents an good value for the AD (Weiland, 2010). The PGM test maintains the pH higher compared to the other tests probably for the presence of oleic and linolenic acids of the pressed seeds. After 21 days (t_{21}) the pH values were for all tests between 7.9 and 8.1 thank to the buffering capacity of the environment of the digester. However, on average, there are no statistically significant differences between values of t_{15} and those of t_{21} no ever between the four tests.

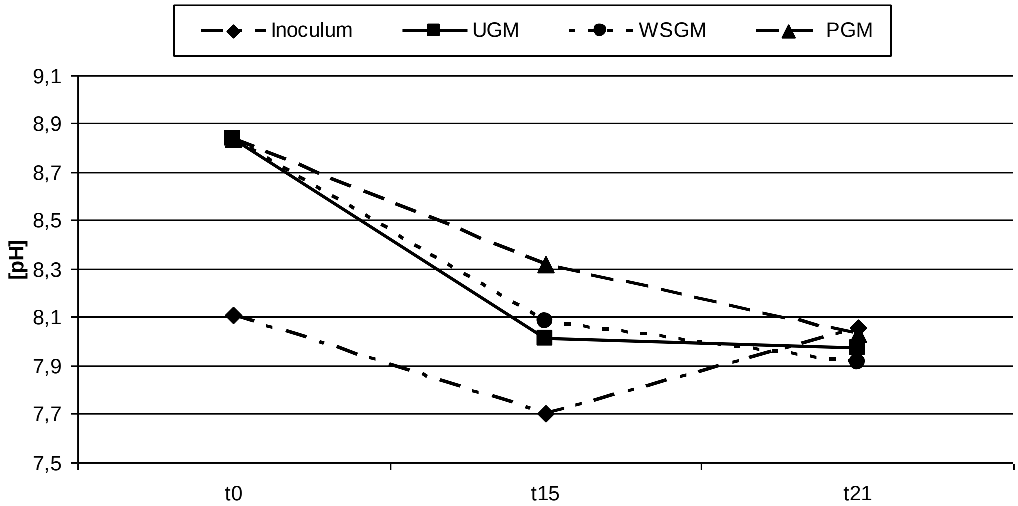


Figure 5. Values of pH before the AD (t0), after fifteen days (t15) and twenty-one days (t21) after the beginning of the fermentation.

The mean COD_{t0} was reduced of its initial amount from mean values of about 85 g/L to 60 g/L (COD_{t21}) after 21 days from loading. (Table 2). The lowest values of COD_{t21} were recorded for the UGM thesis, followed by the WSGM thesis and PGM thesis. This result indicates as the production of biogas is closely related to the chemically oxidisable organic fraction; infact the net volume of biogas was greater in UGM thesis. Nevertheless, from the statistical point of view, the mean values of the three thesis are not different.

As to be expected, the ammonia nitrogen ($N\text{-}NH_4^+$) is increased, reaching average values of 1.67 g/L ($N\text{-}NH_4^+{}_{t21}$), which represents about the 60% of total nitrogen, in line with that reported by other authors (Vismara et al., 2011). The production of ammonia nitrogen was lower in the WSGM thesis, increasing by only 20%, while in the PGM thesis and UGM thesis increased respectively by 39% and 52% compared to the initial values.

Finally, the results of chemical analyzes on digestate offer additional insights (Table 3). On average, the total solids is decreased by about 20% compared to the initial mean values (26.5%) while volatile solids decreased by the 26% compared

to the initial mean values (93.2%). However, between the test UGM and WSGM there are no statistically significant differences and the values are in line with those reported by other authors (Vismara et al., 2011). Instead, between the PGM test and the other two tests, the differences are significant and the lower values diverge from the average reported by other authors. In this test, a higher percentage of total solids and a lower percentage of volatile solids was remained. This is due to the fact that the crushed grape marc have favoured the degradation of the organic substance during the AD which corresponds to a higher percentage of methane (Figure 3).
Similarly, the percentage of total nitrogen are the same in UGM and WSGM, while there is a significant difference between these and the PGM test where the values are lower.

Table 2. Variations of COD (g/l) and $N\text{-}NH_4^+$ (g/l) between the beginning and end of the test

THESIS	$COD t_0$	$COD t_{21}$	$\Delta t_0\text{-}t_{21}$ COD	$N\text{-}NH_4^+\ t_0$	$N\text{-}NH_4^+\ t_{21}$	$\Delta t_{21}\text{-}t_0\ N\text{-}NH_4^+$
UGM	85.4 a	53.7 b	*31.7*	1.22 c	1.85 a	*0.63*
WSGM	85.4 a	60.4 b	*25.0*	1.22 c	1.47 bc	*0.25*
PGM	85.4 a	65.6 ab	*19.8*	1.22 c	1.69 ab	*0.47*
mean	*85.4 a*	*59.9b*	*25.5*	*1.22 b*	*1.67 a*	*0.45*

Means followed in the same column by the same letter are not statistically different (p = 0.05) according to Tukey's test.

Table 3. Variations of chemical properties in digestate at the end of the test (*)

Chemical properties	Unit	Mean grape marc	UGM digestate	WSGM digestate	PGM digestate	Inoculum	Inoculum digestate
Moisture	[wt%]	73.5 d	95.3 b	95.3 b	92.1 c	95.3 b	96.1 a
Total Solids (ts)	[wt%]	26.5 a	4.7 c	4.7 c	7.9 b	4.7 c	3.9 d
Volatile Solids (vs)	[ts%]	93.2 a	70.9 c	76.6 b	53.7 e	68.1 d	71.8 c
Total Nitrogen	[ts%]	6.9 b	6.4 c	6.2 c	4.2 d	6.4 c	7.4 a

Means followed in the same row by the same letter are not statistically different (p = 0.05) according to Tukey's test.
(*) The values were determined by ERSAF laboratory (Mantova-Lombardy) by using standard methodologies.

4 Conclusions

The results of the tests confirm the energetic potential of the grape marc in biogas and methane production, supplying most of the biogas as early as the 5-6th day from the loading of the digesters.
The results seem to suggest that crushed grape marc could favoured the degradation of the organic substance during the AD with a higher percentage of

methane. But in fact, the yield in methane of untreated grape marc was no statistically different from the other considered matrixes, that is grape marc without seed and crushed grape marc, suggesting in this way to avoid the extra costs to crush or remove the seeds of the grape marc. Moreover, the presence of the grape seeds is to favour the production of biogas and methane, being the data of the thesis test without seeds provided always statistically lower values.
The fermentation of fresh grape marc could represent a possible solution for its disposal as a by-product and at the same time a source of income: from the transformation of CH_4 into electric energy corresponds about 300 kWh per tonne of fresh grape marc. Considering the availability of this biomass in Sicily, that is about 132,500 t year^{-1}, the total energetic potential is close to a value of about 40 MWhel year^{-1}.

Acknowledgements. The authors thank Drs Fabio Araldi, Matteo Zagni, Barbara Bertazzoni of ERSAF Lombardy (Mantova) and Eng. Erica Massi for their precious support during the experimental tests and laboratory analyzes.

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Received: June 1, 2014