Anaerobic digestion of olive mill effluents in an automatized baffled reactor and biomethane production by vacuum swing adsorption on natural zeolites from tuffs

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Abstract

Olive mill effluents management by anaerobic digestion might be a successful approach, by reducing the environmental impact and exploiting the energetic potential of these byproducts. The main technical barrier for the production of biogas from olive mill effluents is related to polyphenolic compounds, able to inhibit the metanogenic bacteria. A prototype vacuum swing adsorption reactor (VSA) was developed and used for the upgrading of the biogas produced in the ABR. The reactor is based on the adsorption of carbon dioxide on natural zeolites, at atmospheric pressure. Biogas is upgraded to biomethane on a tuff column, which can be regenerated by means of a vacuum pump. Using more than one column allows to perform a continuous process. Each column was filled with 12 Kg of tuff (65 ± 5 % Chabazite), and the prototype worked with a flow rate of 1800 Lbiogas day-1. A very high purity biomethane (95.4 - 99.2 %) was obtained from the prototype. The concentration of carbon dioxide in biomethane produced was always lower than 0.3 %, and methane lost in the waste was lower than 0.1%. The materials were demonstrated to be able to work for more than 30 days without losing efficiency.

Keywords:

Biogas, biomethane, pressure swing adsorption, anaerobic baffled reactor, olive mill effluents, zeolites.

1. INTRODUCTION

The management of olive mill effluents is still a critical point in the olive oil production chain: the high nitrogen content of these by-products does not allow to dispose them in lands, according to European Directive 676/91/CEE. Moreover, the energetic potential of these resources cannot be neglected, in order to reduce the consumption of fossil fuels and achieve the objectives of Europe 2020. In this framework, energy production from this kind of biomass needs to be improved: while combustion is inefficient for the high water content, anaerobic digestion is hampered by the presence of polyphenolic substances able to kill methanogenic bacteria. The management of olive pomace and olive mill wastewaters is linked to several energetic and environmental issues. The combustion of olive pomace leads to emissions of air pollutants and has a low energy efficiency. Olive mill wastewaters management is a critical point due to the high carbon and nitrogen content. Nevertheless, polyphenolic compounds enhance the ecotoxicity of these kinds of biomasses (Sampaio 2011).

In this framework, olive mill effluents management by anaerobic digestion might be a versatile solution, by reducing the environmental impact and exploiting the energetic potential of these byproducts. The main technical barrier for the production of biogas from olive mill effluents is related to polyphenolic compounds, able to inhibit the metanogenic bacteria. Several solutions have been proposed, including selective polyphenols removal, dedicated inocula, aerobic pretreatments and codigestion. Anaerobic baffled reactors (ABR) are also known for their suitability for hardly fermentable kinds of biomass: while in the first tanks hydrolysis takes place and polyphenolic compounds are removed, in the last tanks methanogenic bacteria are protected from these compounds (Bachman

1985).

Biogas obtained with this approach can be upgraded to biomethane only if a small scale upgrading system can be developed. Among many upgrading technologies available, vacuum swing adsorption (VSA) offers several advantages in terms of efficiency, biomethane purity and scalability. Synthetic zeolites have been extensively used in VSA technology, but they have some limitations in terms of costs. As an alternative to these materials, natural zeolites from tuffs are available at low price as a waste of building industry. In previous studies, natural zeolites were demonstrated to be able to simultaneously remove carbon dioxide and hydrogen sulfide (Alonso Vicario 2011, Paolini 2014).

Hence, the aim of this paper is to demonstrate the feasibility of biomethane production from olive mill effluents using, using an anaerobic baffled reactor followed by a vacuum swing adsorption system based on natural zeolites from tuffs.

2. MATERIALS AND METHODS

2.1 Biogas production from OME in ABR

A polypropylene anaerobic baffled reactor composed of 5 digestion tanks for a total volume of 1 m^3 was used. The ABR was fed (rate 0.35 m^3 per week) with a 50:50 mixture of olive cake and bovine manure. A daily monitoring of biogas flow rate and composition was performed.

2.2. Biomethane production with natural zeolites

The VSA prototype was composed by a biogas inlet, a desulphurization column, a dehydration system, a gas compressor, a set of adsorbing columns for biogas upgrading, a set of pneumatic valves, a vacuum pump, and a biomethane outlet. All components were according 94/9/CE directive. Adsorbing columns of polyethylene, 6 cm diameter per 1 m length were filled with 7 Kg of natural zeolites “Tufo giallo della via tiberina” (TGVT), whose composition and chemical-physical properties were given elsewhere (Paolini 2014). Biogas was pressurized for 1 minute in the column, and subsequently 6 minutes of biogas upgrading were performed. Then, the column was depressurized for 2 minutes and regenerated under vacuum for 5 minutes. Finally, the column was left under vacuum without purge for 1 minute and was ready for a new pressurization cycle. A total cycle lasted 15 minutes. Two columns were used, in order to continuously produce biomethane: while one column was performing biogas upgrading, the other was regenerated. Adsorbing columns were connected with pneumatic valves. An ATEX gas compressor with a maximum flow rate of 100 mL/min was used. A vacuum pump “piINLINE MINI Xi”, produced by PIAB, was integrated to the system.

In a previous work (Paolini 2014), the possibility to simultaneously remove water, hydrogen sulphide and carbon dioxide from a real biogas stream using natural zeolites has been demonstrated to be possible. Anyway, in this application, it was necessary to remove the two former compounds before the VSA unit, in order to avoid damages to valves and pumps. Hence, water was removed by cooling, and desulfurization was performed on iron oxide pellets. Hydrogen sulfide concentration was always kept below 8 ppm.

2.3. Biogas and biomethane monitoring

The composition of biogas and biomethane was analyzed with a Gasmet Biogas analyzer, equiped with specific infrared sensors for carbon dioxide and methane, and electrochemical sensors for oxygen and hydrogen sulfide. The production of biogas from the ABR was monitored for 6 months. The VSA upgrading system was coupled to the ABR for 3 months and biomethane was analyzed each day. In order to observe the effect of VSA cycles, biomethane composistion was monitored each minute for 1 hour (representative of almost 4 complete cycles). Emissions from the vacuum pump were also monitored.

3. RESULTS AND DISCUSSION

3.1. Biogas production

In the experimental conditions described in paragraph 2.1, ABR prototype produced 75 L/h of biogas, whose composition is reported in Table 1 (paragraph 3.2). A methane concentration ranging from 45.3 to 51.5 % was obtained. No significant variations in biogas rate and compositions were observed during the experimentation time. Such a biogas source is an ideal stream for the validation of an upgrading system, since it is possible to monitor its performances in constant feeding conditions.

3.2. Biogas upgrading

The performance of the VSA upgrading system is given in Table. Biomethane purity can be higher than 99%, and was never lower than 95%. Furthermore, carbon dioxide concentration was always lower than 0.3%.

Table 1. Biogas upgrading performances

	Biogas		**Biomethane**	
	Average	*min and max*	*Average*	*min and max*
Methane	**47.7 %**	45.3 - 51.5 %	**98.4 %**	95.4% - 99.2 %
Carbon dioxide	**48.6 %**	46.7 - 53.2 %	**0.06 %**	<0.1 - 0.3 %
Oxygen	**2.0 %**	1.2 - 3.1 %	**0.5 %**	0.2 - 1.5 %
Nitrogen and hydrogen	**1.7 %**	0.9 - 3.5 %	**0.9 %**	0.5 - 2.8 %

3.3. Daily monitoring of biomethane

Temporal variations were also investigated, by measuring the performances of the VSA each day. No statistically significant variations were observed for all the experimentations. This stability is due not only to the adsorbing material, but also to the stability of the entering biogas itself.

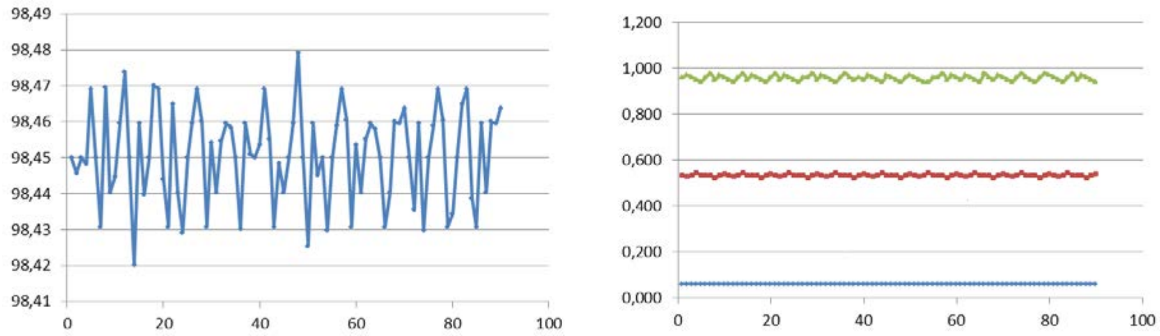

Figure 1. Biomethane composition (daily variations). Left: methane. Right: carbon dioxide (red), oxygen (green), nitrogen and hydrogen (blue). Note that a different scale was used.

3.4. Effects of VSA cycles

The biomethane composition through VSA phases was also investigated. Methane is the main component of biogas during all the process. Anyway, a strong concentration reduction is observed during the pressurization. The same phenomenon is observed for the secondary biomethane components, including carbon dioxide. Anyway, a CO2 concentration always remains lower than 0.2%.

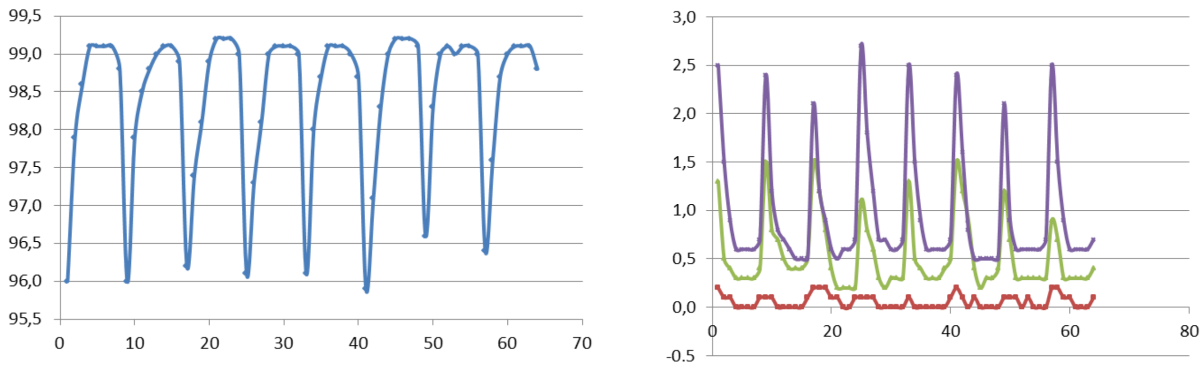

Figure 2. Biomethane composition (minute variations). Left: methane. Right: carbon dioxide (red), oxygen (green), nitrogen and hydrogen (purple). Note that a different scale was used.

3.3. Emissions from VSA waste

During the regeneration, a 4 L/min air flow passes through the column and reaches the vacuum pump. The pump dilutes the flow with 30 L/min of air. The emissions of the vacuum pump were monitored, and the average composition is given in Table. The emission is comparable with atmospheric air, since only the concentration of carbon dioxide is slowly higher. No significant losses of methane were observed, and hydrogen sulfide was not detected.

Table 2. VSA waste composition

Flow rate	**34.5 - 36.0 L/min**
Methane	**< 0.1 %**
Carbon dioxide	**1.5 - 3.0 %**
Hydrogen sulfide	**< 1 ppm**
Oxygen	**19.5 - 20.5 %**
Nitrogen	**75.5 - 77.5 %**

4. CONCLUSIONS

The feasibility of biomethane production from olive mill effluents was demonstrated. Biogas production from olive pomace was performed by codigestion with bovine manure, in an anaerobic baffled reactor. Results obtained confirmed that the energetic exploitation of this byproduct can be efficiently be performed with this approach. Carbon dioxide downstream the upgrading system was always lower than 0.2 - 0.3%, resulting in a high purity biomethane. This promising result was obtained using a vacuum swing adsorption on natural zeolites from tuffs. Hence, two wastes (olive mill effluents and tuffs) were exploited risulting in a high quality fuel.

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