Influence of thermal pre-treatment on the anaerobic digestion of olive mill solid waste

L. Bujalance, B. Rincón, F.G. Fermoso and R. Borja

Instituto de la Grasa (CSIC). Avenida Padre García Tejero, 4, 41012, Sevilla, Spain.
(E-mail: luciabujama@gmail.com; brlloren@cica.es; fgfermoso@ig.csic.es; rborja@cica.es)

Abstract
Olive mill solid waste (OMSW) is the main waste produced by the two-phase centrifugation olive oil extraction system. 98 % of Spanish olive oil factories use this extraction system producing from 2 to 4 million tonnes of this waste annually. The high quantity of organic matter contained in the OMSW makes of it a substrate susceptible to be treated with anaerobic digestion. OMSWs contain a high concentration of cellulose, hemicellulose and lignin, a previous thermal pre-treatment for degradation of these compounds before anaerobic digestion was studied. Four different temperatures were assessed (100ºC, 120ºC, 160ºC y 180ºC) for each of them four different times were also studied (60, 120 y 180 minutes) and based in the best solubilization of the organic matter a biochemical methane potential test was carried out. The methane yields obtained: 391.5±14 mL CH_4/g SV for 120ºC (180 min), 379.6±0.0ml CH_4/g SV for 180ºC (180min) and 373.3±3.7 mL CH_4/g SV for OMSW without pre-treatment showed how the thermal pre-treatment helped in all the cases to obtain a better yield than in the case of the non-pretreated OMSW. After 5 days of similar behavior in the BMP test, the pre-treated OMSW at 120ºC showed the slower kinetic for methane production and the pre-treatment at 180ºC the fastest one compared with the others. This might indicate that, even with the presence of possible inhibitors in the pretreated OMSW at 120 ºC, the amount of total bioavailable organic matter increased by the thermal pre-treatment and the methane yields increased with it.

Keywords
Olive mill solid waste; thermal pre-treatment; cellulose; hemicellulose; biochemical methane production.

INTRODUCTION

Over the past few years, Spain has produced between 1.412.000 tonnes (2003/2004 season) and 1.028.000 tonnes (2008/2009 season) of olive oil, which meant 57.7% and 53% of European production (IOOC 2009). The main waste produced in the two-phase centrifugation system for olive oil extraction is the olive mill solid waste (OMSW). Currently 98 % of Spanish olive oil factories use this extraction system and OMSW is produced in a proportion of 800 kg ton^{-1} of olives milled (Alba, 2001). The high quantities of wastes produced in the olive oil mills makes sustainable treatments necessary. The high content of organic matter contained in the OMSW makes of it a substrate susceptible to be treated with anaerobic digestion (Borja et al., 2002; Rincón *et al.* 2007). Anaerobic digestion enhances the treatment of this problematic waste reducing its environmental impact and obtaining biomethane of high energetic value as final product. OMSWs contain a high concentration of cellulose, hemicellulose and lignin and a pre-treatment to break part of these structures might improve the methane yields obtained by anaerobic digestion. In this work a thermal pre-treatment was studied. Four different temperatures of pre-treatment were assessed (100ºC, 120ºC, 160ºC y 180ºC), for each of them four different times were also studied (60, 120 y 180 minutes) and based in the best solubilization of the organic matter biological methane potential (BMP) tests were carried out.

MATERIAL AND METHODS

The two-phase OMSW used in the experiments was collected from the experimental olive oil factory located at 'Instituto de la Grasa (CSIC)', Seville (Spain). Before to be used, the OMSW was sieved through a 2 mm mesh removing olive stone pieces. Some of the characteristics of the OMSW used in the experiments are detailed in Table 1. Anaerobic sludge was obtained from an

industrial upflow anaerobic sludge blanket (UASB) reactor treating brewery wastewater. The solid content for this sludge was total solids (TS): 69 g/kg and volatile solids (VS): 25 g/kg.
The biochemical methane potential test after the pre-treatment was ran at 35±2 ºC and stirred at 500 rpm. Methane was measured by liquid displacement using sodium hydroxide 3 N to retain the CO_2 produced in the biogas. All analyses were performed according to the Standard Methods of APHA recommendations (APHA, 1989).

Table 1. Main characteristics of the OMSW used in the experiments. Where TS: total solids, VS: volatile solids, COD: total chemical oxygen demand, SCOD: soluble chemical oxygen demand, TKN: total Kjeldahl nitrogen, AN: ammoniacal nitrogen, and TA: total alkalinity.

PARAMETERS	VALUES
TS ($g\ Kg^{-1}$)	265.0±2.6
VS ($g\ Kg^{-1}$)	228.4±2.3
COD ($gO_2\ Kg^{-1}$)	331.1±0.7
SCOD ($gO_2\ Kg^{-1}$)	143.4±3.2
pH	4.98±0.2
TA ($g\ CaCO_3\ Kg^{-1}$)	2.5±0.0
Hemicellulose (%)	11.3± 0.2
Cellulose (%)	5.2±0.1
Lignin (%)	19.7±0.4
Fats (%)	3.8±0.3

RESULTS AND DISCUSSION

Table 2 shows the best values of COD and SCOD obtained after the thermal pre-treatment under different conditions (temperatures and times). The best solubilization or increase of SCOD was obtained for the thermal pre-treatment at 120ºC (180 min) and at 180ºC (180 min).

Table 2. Best solubilization achieved with the temperature and time used in the thermal pre-treatments.

	COD ($gO_2\ Kg^{-1}$)	**SCOD ($gO_2\ Kg^{-1}$)**
120ºC		
60min	335.2±2.4	126.1±0.0
120min	326.2±0.0	128.5±0.0
180 min	360.8±0.3	**150.6±0.1**
180ºC		
60min	313.7±0.0	97.7±0.5
120min	348.6±0.0	153.1±1.1
180 min	377.5±0.0	**157.2±0.0**

Pre-treatments at 120ºC (180 min) and at 180ºC (180 min) were used to carry out the BMP test and to compare them with the control, which was OMSW without pre-treatment. Figure 1 shows the methane yields obtained for the BMP test.

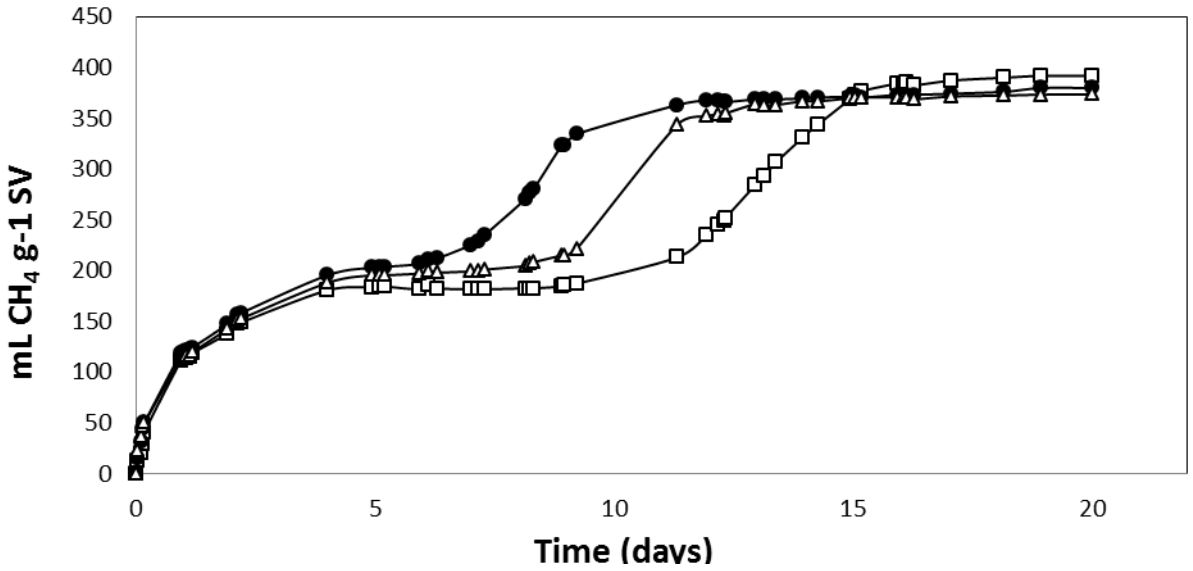

Figure 1. Methane yields obtained through BMP test for OMSW without pre-treatment (Δ) and OMSW pre-treated at 120ºC (180 min) (□) and at 180ºC (180min) (●).

The methane yields obtained: 391.5±14 mL CH_4/g SV (120ºC-180 min), 379.6±0.0ml CH_4/g SV (180ºC -180min) and 373.3 ± 3.7 mL CH_4/g SV showed how the thermal pre-treatment helped in all the cases to obtain a better yield and specially in the case of 120ºC and 180 min as a 4.9 % more of methane than in the OMSW without thermal treatment was produced.

Different kinetics were found in the BMP tests. In a first stage, up to day 5, the three BMP tests were similar, indicating the same kind of easily biodegradable organic matter. The pre-treatment most likely did not improve the availability of this easily organic matter already available. From day 5 a clear difference could be observed. The pre-treated OMSW at 120ºC was the one with slower kinetic at the BMP test compared with the pre-treated OMSW at 180 ºC and with the OMSW without pre-treatment. The pre-treated OMSW at 180ºC showed the fastest one compared with the others. This might indicate that at 120ºC there was a release of possible inhibitors for the anaerobic consortia; these inhibitors most likely could be phenolic compounds, known by its antimicrobial activity (Borja *et al.* 1997). At 180ºC, most likely these inhibitors were not present anymore or much less active as can be observed in Fig. 1. The pre-treatment at 180ºC helped to release easily biodegradable organic compounds in this second stage. Both BMP tests, at 120ºC and 180ºC, achieved higher methane yields than the no-pretreated OMSW, this might indicate that, even with the presence of possible inhibitors at 120ºC, the amount of total bioavailable organic matter increased by the action of thermal pre-treatments.

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