WASTED SARDINE OIL AS A CO-SUBSTRATE FOR BIOGAS PRODUCTION– PILOT EXPERIMENT OF DECENTRALIZED ORGANIC WASTE MANAGEMENT IN A PIG FARM

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1 INTRODUCTION

Sardine fishing and canning is a traditional industry in Portugal and between 50,000 – 80,000 ton/year of sardines are captured by the Portuguese fish fleet. Almost one third of this quantity is processed by the canning industry and 60% exported. One important operation of the sardine canning process, consists of steam cooking once the fish is canned (Pires, 2006). Once the sardines are packed in cans, the next step consists of the meat cooking. Here, the open cans are fed into an automatic steam cookers, through which the cans pass while being held inverted on perforated conveyors to allow simultaneous entry of the steam and drainage of the condensate and oil exuded from the flesh.

The mixture of oils and grease that are collected from the cooking wastewater, will be designated as wasted sardine oil (WSO) (Ockerman *et al.*, 1988). Some companies are recovering it and then selling it to others that produce other by-products, nevertheless there are others that can not do it with a guaranty of minimum quality. Biogas could be an alternative of valorization and help to reduce the final amount of grease and oils entering the final wastewater stream. WSO, according to the Regulation (CE) nº. 1774/2002, of 3rd October, is classified as an animal sub product of category 3 and it can be processed in a biogas plant.

During long time it was reported in the literature, an inhibitory phenomena related with the concentration of long chain fatty acids (LCFA), especially in digesters with a continuous feeding (Angelidaki, *et al.*,1990; Hwu *et al.*, 1998; Pereira *et al.*, 2003). Nevertheless, Fernandez *et al.* (2005) referring to a co-digestion system with simulated organic fraction of municipal solid waste, reported that fats from animal and vegetable origin could be almost completely converted, confirming the possibility of lipids digestion. The studies of Pereira *et al.* (2005) demonstrated the mass transfer limitations caused by LCFA accumulation onto anaerobic sludge and how this problem can be overcome. The most abundant LCFA’s normally found in sardine oil are palmitic acid (16:1), oleic acid (18:1), eicosapentanoic acid (20:5) and docosahexanoic acid (22:6), respectively in a percentage on the total fatty acids of 19,14,20,12 % (Gámez-Mezaa *et al.*, 1999; Shiraia *et al.*, 2002).

In the same region where the canning plant is located, there are several full scale farm biogas plants where it could be interesting to introduce other substrates to co-digest with pig slurry (PS), in order to raise biogas production.

1.1 Research objectives

The purpose of this work was to demonstrate in a commercial pig farm with a biogas plant and in real conditions, the possibilities to co-digest WSO and PS at farm level. Anaerobic digestion is one of the most adequate technologies to manage this type of industrial organic waste streams (Chowdhury *et al.*, 2009), and the decentralized operations of organic waste management for biogas production have many advantages but also a number of uncertainties that must be evaluated (Weiland, 2006; Raven *et al.*, 2007).

Since it was the first time that in Portugal such an experience was done, the production of technical information to the veterinary authorities was a secondary goal.

2 MATERIALS AND METHODS

2.1 Origin of materials

Pig slurry (PS) was obtained in a 1000 sow farrow-to-finish pig farm and it was used the screened slurry fraction that feeds the operating farm digesters. An interception of the feeding circuit was done in order to supply the pilot plant on site. Wasted sardine oil (WSO) was originated from a fish canning factory during the early weeks of

August, within the season of the year when sardine body weight fat content is higher (May to December). The WSO was collected from the exudate rejection stream of the steam cooking process. Inoculum was obtained from a mesophilic (35ºC) sewage sludge digester. Characteristics of PS and WSO are presented in Table 2.

2.1 Lab and pilot set-up

Exploratory lab trials, were performed using glass reactors (CSTR) with V= 2 litre. Although results will not be shown, these trials are mentioned due to their importance in the preliminary work phase of the pilot assay. The main goal of these trials was to make practical tests for the mixing of both streams, hydraulic behaviour, compositions and methane yield.

Pilot scale trials were performed on site, in the farrow-to-finish pig farm in a biogas mobile pilot plant, previously designed in a standard shipping container (Ferreira, 2007; Ferreira *et al.*, 2008). This plant consists of an automatic device, equipped with a heated stainless steel CSTR digester (V_{work} = 1,6 m^3) with a mechanical mixer, a mixing tank and tanks for slurry , pumpable feedstocks and digestate, all equipped with the respective pumping and mixing systems. This set up was operated in real conditions during 4 months.

Dynamic mesophilic (35º - 37º C) continuous pilot trials with a HRT=16 days**,** were performed with pig slurry (PS) as mono-substrate (OLR = 1,6 Kg $COD/m^3.d^{-1}$) and with mixtures of WSO:PS with a volumetric composition (% v/v) of 2:98 (OLR = 3,0 Kg $COD/m^3.d^{-1}$) , 3:97 (OLR = 3,7 Kg $COD/m^3.d^{-1}$) and 5:95 (OLR = 5,2 Kg $COD/m^3.d^{-1}$). The main operational parameters (methane, carbon dioxide, H_2S and COD fractions of the digestate, nitrogen and phosphorous) has also been investigated. Table 1 describes for each of the assay periods, the respective loading compositions.

2.2 Analytical methods

The pH, chemical oxygen demand (COD), total solids (TS), volatile solids (VS), total kjeldahl nitrogen (TKN), ammonical nitrogen (NH_4^+-N), total phosphorous (TP), total volatile fatty acids (T-VFA), Bicarbonate alkalinity were determined according to standards methods (APHA, 1995).

TABLE 1 **Trials description and loading compositions**

Period (day)	PS:WSO (% v/v)	PS (kg SV/day)	WSO (kg SV/day)	PS (kg COD/day)	WSO (kg COD/day)
I : (1 to 25)	100:0	1,54	0	2,57	0
II : (26 to 57)	98:2	1,51	1,66	2,52	2,32
III: (58 to 89)	97:3	1,49	2,49	2,49	3,48
IV: (90 to 122)	95:5	1,46	4,16	2,44	5,80

3 RESULTS

Characterization of WSO (Table 2.) indicates a very high COD content and good complementarities with PS, concerning nutrients balance. Regarding WSO characteristics, there is not much available information in the literature about this particular stream of this industry. The available data is not comparable because the fat content of sardines is not reported neither the steam cooking process described.

TABLE 2 **Characterization of the co-substrates (results are given as means of triplicates with standard deviations)**

Waste	Pig slurry (g/l)	WSO (g/l)
Total solids (TS)	22,6 ± 7,5	876 ± 7
Volatile solids (VS)	15,4 ± 5,8	831 ± 6
Chemical oxygen demand (COD)	25,7 ± 2,9	1159 ± 26
Total Kjeldahl nitrogen (TKN)	2,5 ± 0,7	0,63 ± 0,29
Fat content	-	805 ± 29

The time course of the daily methane production of the dynamic experiment is depicted in Fig.1 for I,II,III and IV periods. Table 3 summarizes the obtained average production for each period. Following the methane production results, it can be seen from the period II (PS:WSO - 98:2) production profile, that biomass needs a period to adapt to the new substrate. Although after a period of about 10 days the production became stable. On the other hand after biomass have already used WSO as co-substrate, first in period III (PS:WSO - 97:3) and after in period IV (PS:WSO - 95:5), the response of the system to an increase on the WSO loading rate was characterised by a rapid conversion. A similar type of response to fish oil waste pulses was obtained in a co-digestion system with a continuous feeding of cow manure with food waste (Neves *et al.*, 2008).

TABLE 3 **Biogas and methane production (results are given as means of observations with standard deviations)**

Period (day)	biogas (l/day)	methane (l/day)	methane (l/kg VS)	methane (kg COD-CH_4 /day)
I : (1 to 25)	961 ± 74	692 ± 53	450 ± 35	1,98 ± 0,15
II : (26 to 57)	1937 ± 255	1356 ± 178	428 ± 56	3,87 ± 0,50
III: (58 to 89)	2863 ± 254	2004 ± 178	503 ± 45	5,73 ± 0,51
IV: (90 to 122)	3691 ± 174	2571 ± 134	458± 24	7,35 ± 0,38

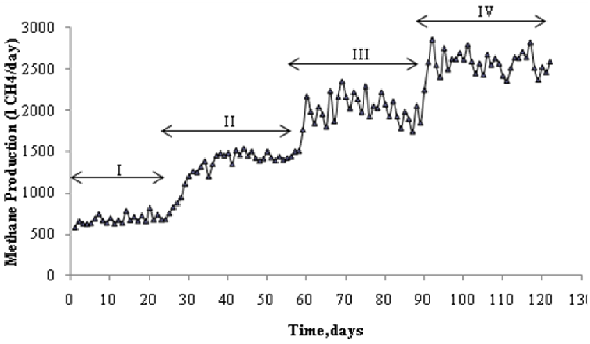

FIGURE 1 **Time course of methane production for the four periods (l CH_4/day)**

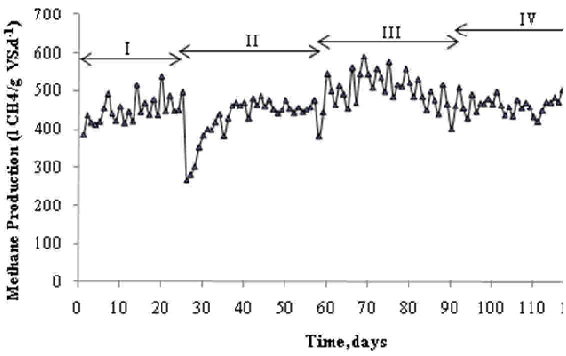

FIGURE 2 **Time course of specific methane production for the four periods (l CH_4/g VS.d^{-1})**

The especific methane production is represented in Fig. 2. For each of the periods where WSO was co-digested with pig slurry, it can be observed the evolution of the substrate conversion by the system and the respective average figures are presented in table 3. The results of the periods II, III and IV show some differences that can be explained in one hand due to in period II, biomass was not acclimatized to WSO. On the other hand the highest methane conversion rate recorded in period III might suggest a complete mineralization of the WSO added.

Although during period IV the average daily methane production kept a stable patern and raised in relation to period III about 28%, nevertheless a reduction on the average specific methane production of 9% was obtained. Taking into account the daily loading of WSO into the digester, it's equivalent to a concentration of 3,63 g $COD_{oil}/l_{reactor}$. Supported in the conclusions of Neves *et al.*, 2008, this figure is almost five times less than the 18 g $COD_{oil}/l_{reactor}$ capable to induce a persistent inhibition of the process. Pereira *et al.* (2005) described this inhibition due to a physical phenomena of adsortion and entrappment in the sludge that become "encapsulated" by a LCFA layer. On the other hand the process stability was monitored measuring the pH and T-VFA/BA ratio. Both indicators, suggests that the co-digestion process was robust. Therefore the most likely explanation for this difference, may have been a loss of efficiency in the mixing operation of the two substrates in the mixing tank, taking in account that a larger amout of SWO had to be mixed. A more detailed monitoring of soluble COD in the effluent could have also been recommended to clarify this issue.

Operational results are summarized in table 4. It can be observed that increasing the percentage of WSO in the composition of feedstock, methane productivity raises from 0,43 to 1,61 m^3 methane/m^3 digester.d^{-1}. This represents an yield gain of the system of almost for times. According to the expectations and taking into account the lipidic fraction of the SWO, the biogas quality didn't suffer substantial changes within the co-digestion experiment.

TABLE 4 **Operating and process performance obtained from pilot plant trials**

Mixture PS:WSO (% v/v)	HRT days	OLR kg COD/m^3.d^{-1}	m^3 methane/ m^3 digester.d^{-1}	Biogas quality % CH_4	Biogas quality ppm H_2S	COD removal %	m^3 methane/ m^3 biomass
100:0	16	1,6	0,43	72	> 1500	77	7
98:2	16	3,0	0,85	70	> 1500	80	14
97:3	16	3,7	1,25	70	> 1500	96	20
95:5	16	5,2	1,61	70	> 1500	90	26

4 CONCLUSIONS

Co-digestion process of pig slurry with wasted sardine oil was performed with a high conversion of the inlet COD. The incremental addition of WSO to a composition (% v:v) of 95:5 enhanced the methane productivity in four times, when compared with the same system digesting pig slurry as the mono-substrate.

The pilot experiment showed that WSO could be a food industry waste stream easily to be co-digested at farm scale biogas plants. In the particular case of this canning plant, a regional waste management solution could be envisaged and the awareness of the competent authorities about this waste management technology alternative was improved.

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