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# Olive Oil Mill Waste Treatment: Improving the Sustainability of the Olive Oil Industry with Anaerobic Digestion Technology

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## 1. Introduction

The processes used to treat waste streams are chosen according to technical feasibility, simplicity, economics, societal needs and political priorities. However, the needs and priorities of a sustainable society undergo pressure which means a shift in the focus of wastewater treatment from pollution control to resource exploitation (Angenent et al., 2004). The organic fraction of agro-wastes (e.g. olive oil wastes, sugar beet pulp, potato pulp, potato thick stillage or brewer's grains) has been recognized as a valuable resource that can be converted into useful products via microbially mediated transformations. Organic waste can be treated in various ways, of which bio-processing strategies resulting in the production of bioenergy (methane, hydrogen, electricity) are promising (Khalid et al., 2011). The aim of the present chapter is to discuss: firstly the quantities, characteristics and current treatments of the solid wastes and wastewaters from the continuous olive oil extraction industry for their exploitation and recovery; secondly, anaerobic digestion processes as an alternative for waste treatment and valuable energy recovery

## 2. Olive mill extraction wastes

### 2.1 Olive oil extraction technology

The olive mill elaboration system has evolved over time for economic and environmental reasons. The traditional system or "pressing system" was replaced in the 70s by the three-phase continuous centrifugation system. The centrifugation of the milled and beaten olives to obtain olive oil by the three-phase system produces 20% oil, 50% three-phase olive mill wastewaters (3POMWW) and 30% three-phase olive mill solid wastes (3POMSW). This three-phase system led to an increase in the processing capacity and consequently to an increase in the yield of the mills and the growth of the average mill size. However, large quantities of water needed for carrying out the three-phase process generate a high volume of olive mill wastewaters. The uncontrolled discharge of 3POMWW brought environmental problems. In some countries, technology manufacturers developed the "ecological" two-phase process. This system enables

reduced fresh water consumption in the centrifugation phase. The two-phase process has attracted special interest in countries where water supplies are restricted. The quantity of water required to carry out the two-phase process is much lower than in the three-phase process and a considerable reduction in generated two-phase olive mill wastewaters (2POMWW) is achieved. However, the two-phase process led to a slight increase in solid wastes. The quantities of two-phase olive mill solid wastes (2POMSW) are 60% higher than those generated in the three-phase system (3POMSW).

Over 2.9 million tonnes of virgin olive oil are produced annually worldwide, of which 2.4-2.6 million tonnes are produced in the European Union (IOOC, 2009). Currently, both elaboration systems, three- and two-phase, coexist in the Mediterranean area (Niaounakis & Halvadakis, 2004). Spain, the largest producer of olive oil in the world, currently uses the two-phase system in 98% of its olive mills. 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). Croatia uses the two-phase system in 55% of its mills and produces 4,500 tonnes of olive oil (2008/2009 season). In olive oil producing countries such as Cyprus, Portugal and Italy, only around 5% of the mills use the two-phase system (Roig et al., 2006). Other large producers such as Greece or Malta have continued using mainly the three-phase system although the two-phase system is being introduced slowly. The high quantities of wastes produced in both systems makes sustainable treatments necessary.

## 2.2 Waste quantities and characteristics

3POMSW are produced in a proportion of 500 kg per ton of olives and are basically made up of dry pulp and stones.

3POMWW are the main wastes generated in the three-phase olive mill system (1,200 L ton<sup>-1</sup> milled olives). The annual 3POMWW production of Mediterranean olive-growing countries is estimated between 7-30 million m<sup>3</sup>. The chemical composition of 3POMWW is complex due to the water from the milled olives (vegetation water) and the soft tissues from the olive fruit. Typical composition of three-phase olive mill wastewaters is: pH 5.04, COD 43.0 g L<sup>-1</sup> (COD: Chemical Oxygen Demand), total sugars 17.4 g L<sup>-1</sup>, total phenols 2.5 g L<sup>-1</sup> and lipids 0.75 g L<sup>-1</sup> (D'Annibale et al., 2006).

The change from the three-phase to the two-phase elaboration system reduces the high generation of wastewaters produced in the three-phase process. The two-phase elaboration process generates 800 kg of 2POMSW per ton of olives processed. 2POMSW have a 60%-70% humidity content, 13%-15% lignin, 18%-20% cellulose and hemicellulose and 2.5%-3% oil (Borja et al., 2002). In a similar way to 3POMWW, the composition of 2POMSW is complex due to the vegetation water. Consequently, 2POMSW and 3POMWW are the main problematic streams.

2POMWW are a mixture between the water used for olive washing before the milling process and the water coming from washing the oil in a vertical centrifuge. Initial studies gave volumes of 2POMWW of around 250 L ton<sup>-1</sup> of olives in total. However, current studies have suggested a significant reduction in the amount of water to be added to the vertical centrifuge.

### **3. Olive oil mill wastes - Current treatments**

#### **3.1 Three-phase olive mill wastes**

##### **3.1.1 Three-phase olive mill solid waste (3POMSW)**

The traditional use of 3POMSW is to extract the residual olive oil. 3POMSW have around 4% residual oil on wet basis, which can be extracted by mechanical and/or chemical treatments. There are several extraction methods, the most usual being a first centrifugation where 40%-50% of the residual oil is extracted (Sánchez & Ruiz, 2006), followed by a drying process from 60-70% to 8% moisture (400°C-800°C) and extraction with solvents (hexane). Finally, the oil extracted 3POMSW is used for co-generation of heat and electricity in combustion-turbine cycles or a gas-turbine cycle. Oil extraction factories usually use this energy for their own drying process before extraction.

##### **3.1.2 Three-phase olive mill wastewater (3POMWW)**

Due to their high organic load and problematic disposal, the depuration of 3POMWW has been the subject of a great number of studies over the years. Initial treatments in the 60s focused on the use of 3POMWW as a soil conditioner if previously neutralized with lime (Albi Romero & Fiestas Ros de Ursinos, 1960). The addition of 3POMWW to the soil seems beneficial, as it produces an increase in nitrogen-fixing organisms (Garcia-Barrionuevo et al., 1992).

3POMWW are a potential source of biophenols, some being studied for potential industrial exploitation (Cardoso et al., 2011). The extraction of polyphenols provides a double opportunity to obtain high added value biomolecules and to reduce the phytotoxicity of the effluent (Bertín et al., 2011). López and Ramos-Cormenzana (1996) showed the possibility of obtaining 4.4 g L<sup>-1</sup> of Xanthan with 3POMWW diluted to 30%-40%. The 3POMWW have also been studied as a source of natural pigments (anthocyanins) and different exopolysaccharides, and as a growth medium for algae (Ramos-Cormenzana et al., 1995). 3POMWW have been used as a growth media for the microbial production of extra-cellular lipase (D'Annibale et al., 2006) and for composting with olive leaves (Michailides et al., 2011).

Most of these studies, although very interesting, do not solve the problem because the quantities required for these studies are very small in contrast to the high quantity generated annually. The final destination of these wastewaters is mainly evaporation ponds. In the Mediterranean countries the summers are very hot, the evaporation ponds are large pools built with waterproof materials where the wastewaters can be stored for their evaporation in the summer period. After solar drying, the remaining solids can be used as fertilizer (Rozzi & Malpei, 1996). Although the evaporation ponds are very simple constructions, failure in the insulation of the basin can contaminate the ground water. Another disadvantage of these ponds is the production of putrid odors and insects during the decomposition processes (Khoufi et al., 2006).

#### **3.2 Two-phase olive mill wastes**

##### **3.2.1 Two-phase olive mill solid wastes (2POMSW)**

2POMSW have around 3.5% residual oil in wet basis. Like 3POMSW, this waste is also used for residual olive oil extraction. However, the humidity of 2POMSW is higher than

3POMSW. In order to obtain 8% humidity before extraction, the intensity and the length of the drying process are higher for 2POMSW than for 3POMSW. Furthermore, the vegetation water fraction of the olives gives 2POMSW a complex composition generating a high number of problems during the drying process. The high concentration in reducing sugars gives 2POMSW a doughy consistency in the continuous rotary dryer. This consistency creates dead areas which cannot be dried properly in the drying place, making residual oil extraction more difficult. Although the extraction process is more expensive and less profitable for 2POMSW than 3POMSW, this residual oil extraction is still applied. The extracted 2POMSW have 30%-45% stones, 15%-30% olive skin and 30%-50% pulp (Cruz et al., 2006). They are used for the co-generation of heat and electricity in combustion-turbine cycles or a gas-turbine cycle in the same way as 3POMSW. The oil extraction factory usually uses this type of energy for its own drying process before extraction.

Composts of 2POMSW is another alternative. The initial 2POMSW is phytotoxic, but Alburquerque et al. (2006) found the mixture with grape stalk and olive leaves as bulking agents free of phytotoxicity and suitable as soil conditioners.

Currently there are several experimental treatments for 2POMSW using it as a source of pharmaceutical compounds. A new process based on the hydrothermal treatment of 2POMSW led to a final solid enriched in minor components with functional activities (Lama-Muñoz et al., 2011). Other studies have been carried out using the bacteria *Penibacillus Jamila* for the production of exo-polysaccharides with 2POMSW as growth media (Ramos-Cormenzana & Monteoliva-Sánchez, 2000). There are two patented products extracted from 2POMSW: oleoic acid and maslinic acid. Maslinic acid is being used for a treatment against the human immunodeficiency virus (HIV-1) (Parra et al., 2009). The walls of the olives are rich in polysaccharides such as L-arabinose. These polysaccharides are part of 2POMSW and can also be extracted and exploited (Cardoso et al., 2003).

2POMSW have also been used as feeding for animals. There are several studies about the digestibility of the protein content in 2POMSW used as sheep and goat feed (Martín et al., 2003; Molina Alcaide et al., 2003). Maslinic acid obtained from 2POMSW added to the diet of rainbow trout increased growth and protein-turnover rates (Fernández-Navarro et al., 2008).

The application of 2POMSW as a fertilizer has also been considered. Although the vegetation water gives a phytotoxic effect similar to 3POMWW, it has been observed that the fertilizer effect prevails over the phytotoxic effect when the dosage is not very high (Sierra et al., 2000).

An extremely low quantity of 2POMSW is used in these treatments, so none could be used as an integral treatment for this problematic waste.

### 3.2.2 Two-phase olive mill wastewaters (2POMWW)

Different options have been studied for the treatment of the wastewaters generated during the purification of olive oil. The use of oxidative methods for the treatment of 2POMWW has been reported in literature (Martínez-Nieto et al., 2011). These methods are based on the use of chemical oxidants such as permanganate, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) or Fenton-like reaction. Aerobic treatment using a completely mixed activated sludge reactor was also reported (Borja et al., 1995a). The results obtained with the aerobic treatment indicated that more than 93% of the input COD concentration can be removed. The most commonly used treatment of both 2POMWW and 3POMWW is storage in evaporation ponds (section 3.1.2).

## 4. Anaerobic treatments

Anaerobic wastewater treatment has evolved into a competitive treatment technology in the past few decades. Many different types of organically polluted wastewaters, even those that were previously believed not to be suitable for anaerobic wastewater treatment, are now treated by anaerobic high-rate conversion processes (Van Lier, 2008).

Similar to anaerobic wastewater treatment, since the introduction of anaerobic digestion of solid waste in the beginning of the 1990s, adoption of the technology has been increasing (De Baere & Mattheeuws, 2010). European energy output from solid waste digestion plants rose to 5.3 Mtoe in 2009, which is 236 ktoe more than in 2008 (EurObserv'ER, 2010).

This section focuses on the principles of bioenergy production through anaerobic processes. Methanogenic anaerobic digestion (methane), biological hydrogen production (hydrogen) and microbial fuel cell technology (electricity) will be explained and discussed.

### 4.1 Methanogenic anaerobic digestion

The anaerobic digestion process is a biological process carried out by three different groups of microorganisms (hydrolytics, acetogenics and methanogenics) (Gujer & Zehnder, 1983)) which transform organic matter to obtain 90% biogas [a mixture  $\text{CH}_4/\text{CO}_2$  ( $\approx 65\%$ - $35\%$ )] and only 10% excess sludge. Biogas has a high calorific value (5000-6000 kcal  $\text{m}^{-3}$ ) and can be used for electricity or heat.

The main advantages of the anaerobic process compared with other types of treatment are (Van Lier, 2007):

- High applicable chemical oxygen demand (COD).
- No use of fossil fuels for treatment
- No use of or very little use of chemicals; simple technology (Figure 1) with high treatment efficiencies.
- Anaerobic sludge can be stored unfed, so the reactors can be operated during the harvesting seasons only (e.g. 4 months per year in the olive oil mill industry).
- Effective pathogen removal.
- High degree of compliance with many national waste strategies implemented to reduce the amount of biodegradable waste entering landfills.
- The slurry produced (digestate) is an improved fertiliser.

Methanogenic anaerobic digestion of organic material has been performed for about a century. Therefore, the food web of anaerobic digestion is reasonably well understood (Figure 2).

Anaerobic digestion of biodegradable wastes involves a large spectrum of bacteria of which three main groups can be distinguished. The first group comprises fermenting bacteria which perform **hydrolysis and acidogenesis** (e.g. *Clostridium butyricum*, *Propionibacterium*). This involves the action of exo-enzymes to hydrolyze matter such as proteins, fats and carbohydrates into smaller units which can then enter the cells to undergo an oxidation-reduction process resulting in the formation of volatile fatty acids (VFA) and some carbon dioxide and hydrogen. The fermenting bacteria are usually designated as an acidifying or acidogenic population because they produce VFA.

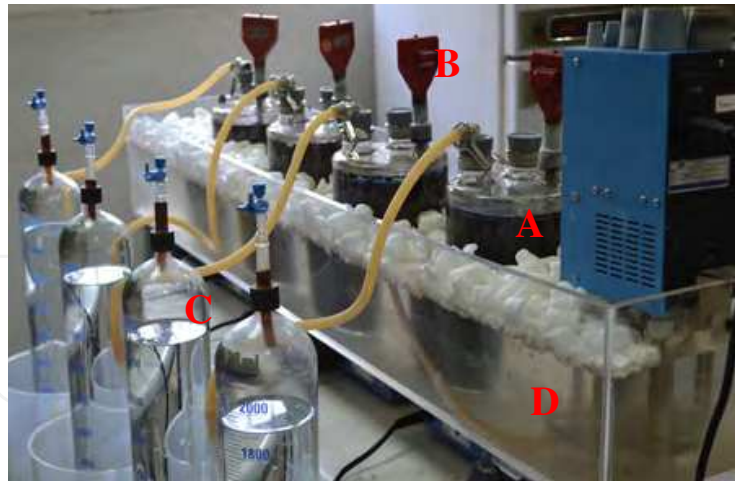


Fig. 1. Experimental laboratory scale anaerobic reactors (A: reactor, B: pH-meter, C: gasometer with NaOH for methane measurement, D: water bath for temperature control).

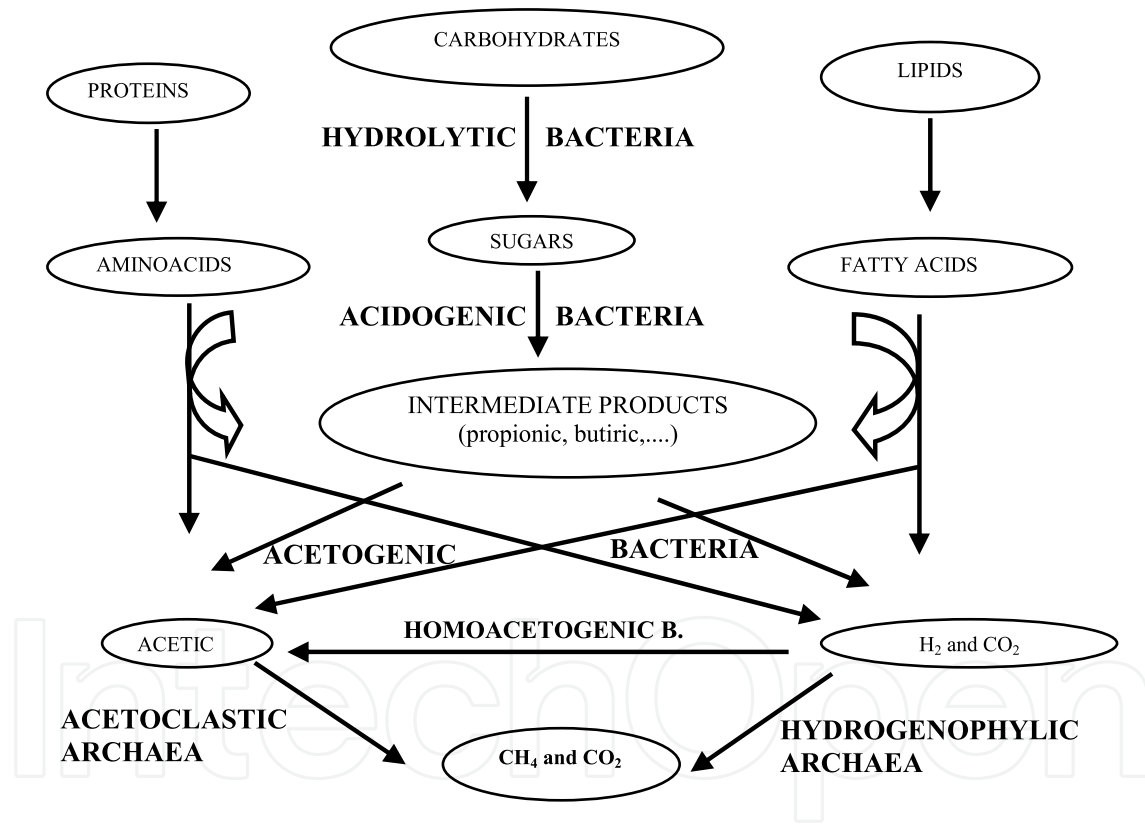


Fig. 2. Diagram of the different steps of anaerobic digestion

**Acetogenic bacteria** (e.g. *Clostridium aceticum*, *Acetobacterium woodii*) constitute the second group and are responsible for breaking down the products of the acidification step to acetic acid. In addition, hydrogen and carbon dioxide are also produced during acetogenesis.

The third group involves methanogenic Archaea (e.g. *Methanobrevibacter smithii*, *Methanobacterium thermoautotrophicum*, *Methanosarcina barkerii*, *Methanotrix soebugenii*) convert acetic acid or carbon dioxide and hydrogen into methane. Other possible methanogenic substrates such as formic acid, methanol, carbon monoxide, and

methyamines are of minor importance in most anaerobic digestion processes. In addition to these three main groups, hydrogen consuming acetogenic bacteria are always present in small numbers in an anaerobic digester. They produce acetic acid from carbon dioxide and hydrogen and, therefore, compete for hydrogen with the methanogenic archaea.

The synthesis of propionic acid from acetic acid, as well as the production of longer chain VFA, occur to a limited extent in anaerobic digestion. Competition for hydrogen can also be expected from **sulfate reducing bacteria**.

In conventional applications, the acid- and methane-forming microorganisms are kept together inside the reactor system with a delicate balance between these two groups of organisms, because they differ greatly in terms of physiology, nutritional needs, growth kinetics and their sensitivity to environmental conditions. Problems encountered with stability and control in conventional design applications have led researchers to new solutions such as the physical separation of acid-formers and methane-formers in two separate reactors. Optimum environmental conditions for each group of organism is provided separately to enhance the overall process stability and control (Cha & Noike, 1997).

#### 4.2 Biological hydrogen production

Hydrogen is a clean, recyclable, and efficient energy carrier. The possibility of converting hydrogen into electricity via fuel cells makes the application of hydrogen energy very promising (Chang et al., 2002).

Hydrogen production via dark fermentation is a special type of anaerobic digestion consisting of only hydrolysis and acidogenesis. It leads to the production of hydrogen, carbon dioxide and some simple organic compounds [VFA and alcohols]. These readily degradable organic compounds can be used for further methane production. (Bartacek et al., 2007)

Much interest has recently been expressed in the biological production of hydrogen from waste streams by dark fermentation. Biological hydrogen production shares many common features with methanogenic anaerobic digestion, especially the relative ease with which the two gaseous products can be separated from the treated waste.

From hydrogen-producing mixed cultures, a wide range of species have been isolated, more specifically from the genera *Clostridium* (*Clostridium pasteurianum*, *Clostridium saccharobutylicum*, *C. butyricum*), *Enterobacter* (*E. aerogenes*) and *Bacillus* under mesophilic conditions; and from the genera *Thermoanaerobacterium* (*Thermoanaerobacterium thermosaccharolyticum*), and *Caldicellulosiruptor* (*Caldicellulosiruptor saccharolyticus*, *C. thermocellum*, *Bacillus thermozeamaize*) under thermophilic or extremophilic conditions.

However, the low efficiency of the hydrogen production process remains the main limiting factor. Much research will be needed to be carried out to reach hydrogen yields comparable with the theoretical efficiency maximum. Although a relatively high efficiency has been reached using pure substrates, the low hydrogen yield with complex (real) substrates remains a great challenge.



### 4.3 Microbial fuel cell technology

The microbial fuel cell (MFC) is a new energy technology in which microorganisms produce electricity directly from renewable biodegradable materials (Logan et al., 2006). During microbial oxidation of biodegradable matter, not only are protons and oxidized products formed but electrons are remarkably transferred from the bacteria towards a solid electrode. The electrons flow through an electrical circuit towards the cathode where a final electron acceptor is reduced resulting in generation of electrical power (Figure 3).

Although interest in microbial fuel cells was relatively high in the 1960s, research has been limited as the cost of other energy sources remained low and the available microbial fuel cells lacked efficiency and long term stability. However, in the past seven to eight years there has been a resurgence in microbial fuel cell research. In fact, the efficiency of this energy conversion is potentially higher than the actual waste treatment technology for energy recovery, such as anaerobic digestion or incineration (Logan et al., 2006).

Microbial fuel cells have been validated at lab-scale with simple organic substrates, pure culture and highly controlled experimental conditions. Organic substrates as volatile fatty acids and more recently wastewater have generated high energy production (Catal et al., 2008; Clauwaert et al., 2007; Clauwaert et al., 2008; Rabaey et al., 2003; Rabaey & Verstraete, 2005). Over the last 10 years, the improvement in the design of microbial fuel cells has increased electrical generation 10,000 times (Debabov, 2008). However, full scale application has not yet been developed.

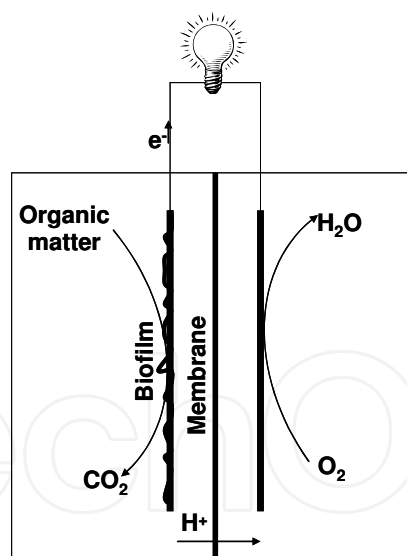


Fig. 3. Microbial Fuel Cell (MFC) set up

## 5. Anaerobic treatment of olive oil mill wastes

### 5.1 Three-phase olive mill wastes

#### 5.1.1 Three-phase olive mill solid wastes (3POMSW)

The heterogeneous cellulosic and lignocellulosic structures of the husk make the anaerobic digestion of this waste impossible because the microorganisms are unable to attack these

complex structures. Therefore, anaerobic digestion is not a suitable technology for the treatment of 3POMSW.

### 5.1.2 Three-phase olive mill wastewaters (3POMWW)

Anaerobic digestion is a promising alternative for the treatment of 3POMWW. It allows for the disposal of these wastewaters achieving considerable organic material removals and producing renewable energy in the form of biogas, which could be used as an energy source in the olive oil mill itself.

Certain components of 3POMWW such as poly-phenols, pH, oil, etc. may inhibit the AD process. Martín et al., (1991) obtained methane yields of 260 mL CH<sub>4</sub> g<sup>-1</sup> COD for 3POMWW. Borja et al. (1995b) improved the methane production using a pre-treatment stage with *Geotrichum candidum*, *Azotobacter Chroococcum* and *Aspergillus terreus*. The latest study reported methane yield coefficients of 300 (*Geotrichum*-pretreated 3POMWW), 315 (*Azotobacter*-pretreated 3POMWW) and 350 (*Aspergillus*-pretreated 3POMWW) mL CH<sub>4</sub> g<sup>-1</sup> COD against the 260 mL CH<sub>4</sub> g<sup>-1</sup> COD obtained for the untreated 3POMWW.

3POMWW have a low nitrogen content which limits the AD process due to the fact that the microorganisms need this element for their metabolism. In this way, co-digestion with rich nitrogen substrates may improve the biodegradability of the mixture. Azbar et al., (2008) studied the co-digestion of 3POMWW with laying hen litter obtaining a significant improvement in the biodegradability of 3POMWW. Co-digestion with liquid cow manure [20% 3POMWW, 80% liquid cow manure (v:v)] also showed good results in terms of COD and volatile solids removal (Dareioti et al., 2010).

Another option is the combination of catalytically oxidized olive mill wastewaters (by Fenton's reagent) plus anaerobic digestion. El-Gohary et al. (2009) found that the digestion of catalytically oxidized 3POMWW followed by a classical upflow anaerobic sludge blanket reactor (UASB) and a hybrid UASB as a post-treatment step is a promising alternative.

Other treatments envisage the combination of an initial liquid-liquid extraction with ethyl acetate for exploitation of the phenol content, followed by aerobic or anaerobic digestion of the phenolic extracted 3POMWW (Khoufi et al., 2006).

The use of sand filtration and subsequent treatment with powered activated carbon in batch systems has also been studied as a pre-treatment. This pre-treatment allowed COD removal efficiencies of 80%-85% for an HRT of 5 days and at an OLR of 8 g COD L<sup>-1</sup> d<sup>-1</sup>. A methane yield of 300 mL biogas g<sup>-1</sup> COD removed was achieved (Sabbah et al., 2004).

The separation of the digestion phases, hydrolytic-acidogenic reactor and methanogenic reactor, in two completely independent reactors can also be considered as a way to improve the AD digestion of these wastes. Bertín et al. (2010) studied different acidogenic configurations of biofilm reactors using ceramic filters or granular activated carbon with good results.

The latest research studies report AD as a promising technology for the treatment of 3POMWW, leading to sustainable waste treatment and an environmentally friendly solution.

## 5.2 Two-phase olive mill wastes

### 5.2.1 Two-phase olive mill solid wastes (2POMSW)

Borja et al. (2002) carried out an initial anaerobic digestibility study with four different dilutions of 2POMSW (20%, 40%, 60% and 80 %). The main findings showed that the performance of the reactor [in terms of COD removal (%)] is practically independent of the feed COD concentration. Studies with no-diluted 2POMSW were carried out by the same authors with similar results (Rincón et al., 2007). The methane yields obtained in these studies ranged between 200-300 mL CH<sub>4</sub> g<sup>-1</sup> COD removed. The 2POMSW is easily biodegradable by mesophilic anaerobic digestion and COD removal efficiencies up to 97 % may be achieved (Rincón et al., 2007).

Rincón et al. (2006, 2008a) studied the different microorganisms participating in the 2POMSW anaerobic digestion. For the determination of the microorganism population polymerase chain reaction (PCR), denaturing gradient gel electrophoresis (DGGE), cloning and sequencing techniques were employed. The results showed differences in the microbial communities, both bacterial and archaeal, with varying OLRs. Analysis of the microbial communities may be decisive in understanding the microbial processes taking place during 2POMSW decomposition in anaerobic reactors and optimizing their performance. During this experimental study the most frequently encountered microbial group were the Firmicutes (53.3% of analyzed sequences), represented mostly by members of the Clostridiales (Figure 4). Chloroflexi also represented an important bacterial group in the study (23.4% of sequences) and has been reported as a major constituent in anaerobic systems (Rincón, 2006). The Gamma-Proteobacteria (8.5% sequences, represented mainly by the genus *Pseudomonas*), Actinobacteria (6.4%) and Bacteroidetes (4.3%) are also significant components of the microbial communities during the anaerobic decomposition of 2POMSW (Figure 4). The major archaeal component detected for the 2POMSW anaerobic digestion was *Methanosaeta concilii* (formerly *Methanothrix soehngenii*) (Figure 5). Furthermore, results showed the existence of molecular diversity within the genus *Methanosaeta* in the anaerobic process under study (Rincón et al., 2006).

As has been explained in section 4.1, the anaerobic digestion process could be more stable if the hydrolytic-acidogenic and the methanogenic stages were physically separated. The microorganisms participating in this kind of biological treatment (bacteria and methanogenic archaea) have different requirements in terms of growing kinetic, optimal working conditions and sensitivity to environmental conditions. Studies in two stages allow for the enrichment of the different populations of microorganisms (Cha & Noike, 1997). The separation in the hydrolytic-acidogenic and the methanogenic steps showed improved results as compared to one simple AD stage. The acidification of the 2POMSW in an initial hydrolytic-acidogenic step achieved a high concentration of total volatile fatty acids 14.5 g L<sup>-1</sup> (expressed as acetic acid) at an OLR as high as 12.9 g COD L<sup>-1</sup> d<sup>-1</sup> (Rincón et al., 2008b). After this initial acidification, the OLRs achieved in the methanogenic reactor were in the order of 22.0 g COD L<sup>-1</sup> d<sup>-1</sup> with COD and volatile solid removals of 94.3%-61.3% and 92.8%-56.1%, respectively, for OLRs between 0.8 and 20.0 g COD L<sup>-1</sup>d<sup>-1</sup>. Methane yields of 268 mL CH<sub>4</sub> g<sup>-1</sup> COD removed were achieved (Rincón et al., 2009, 2010).

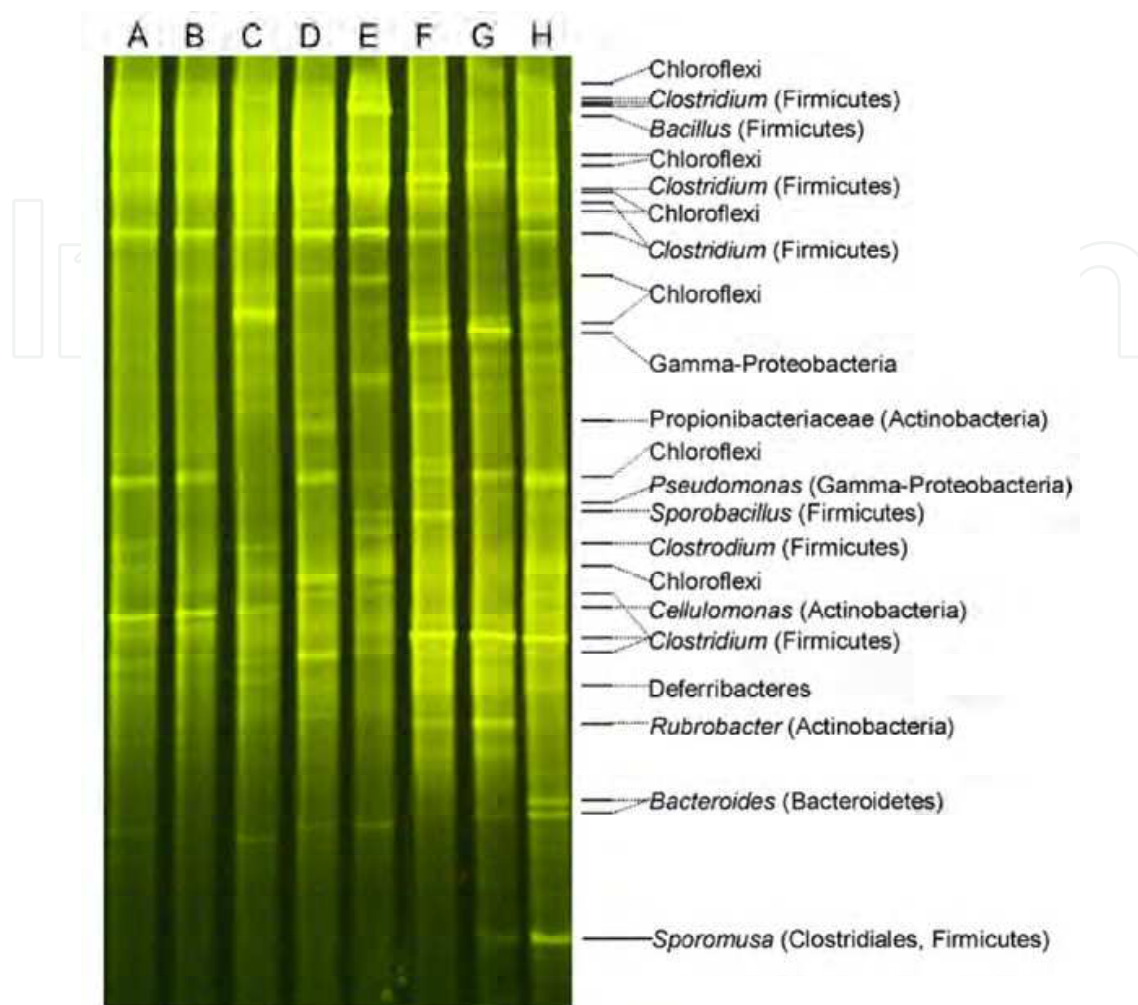


Fig. 4. DGGE analysis of the diversity of bacterial communities at different OLRs studied in one stage anaerobic digestion of 2POMSW (Rincón et al., 2008a). The position of the major electrophoretic bands corresponding to the 16S rRNA gene of the identified bacteria are indicated. A, B, C, D, E, F, G and H are the increasing OLRs studied in g COD L<sup>-1</sup> d<sup>-1</sup>: 2.3 (A), 3.0 (B), 4.5 (C), 5.8 (D), 6.8 (E), 8.3 (F), 9.2 (G) and 11.0 (H).

Other studies in two-stages at thermophilic scale reported 2POMSW as an ideal substrate for biohydrogen and methane production. These studies used diluted 2POMSW (1:4) with tap water achieving  $18.5 \pm 0.4$  mmol CH<sub>4</sub> g<sup>-1</sup> total solid added (TS). Experiments for biohydrogen production followed by methane production, generated 1.6 mmol H<sub>2</sub> g<sup>-1</sup> TS added and 19.0 mmol CH<sub>4</sub> g<sup>-1</sup> TS in the methanogenic stage (Gavala et al., 2005). Mesophilic bio-hydrogen production from 3POMSW has shown to be feasible at mesophilic temperature resulting in 2.8-4.5 mmol H<sub>2</sub> per gram of carbohydrates consumed in the reactor (Koutrouli et al., 2006). Methane production in these assays achieved a maximum value of 1.13 L CH<sub>4</sub> L<sup>-1</sup> d<sup>-1</sup> at 10 days of HRT. Hydrogen is a renewable energy source and one of the most attractive applications is the conversion of hydrogen to electricity via fuel cells (Koutrouli et al., 2006)

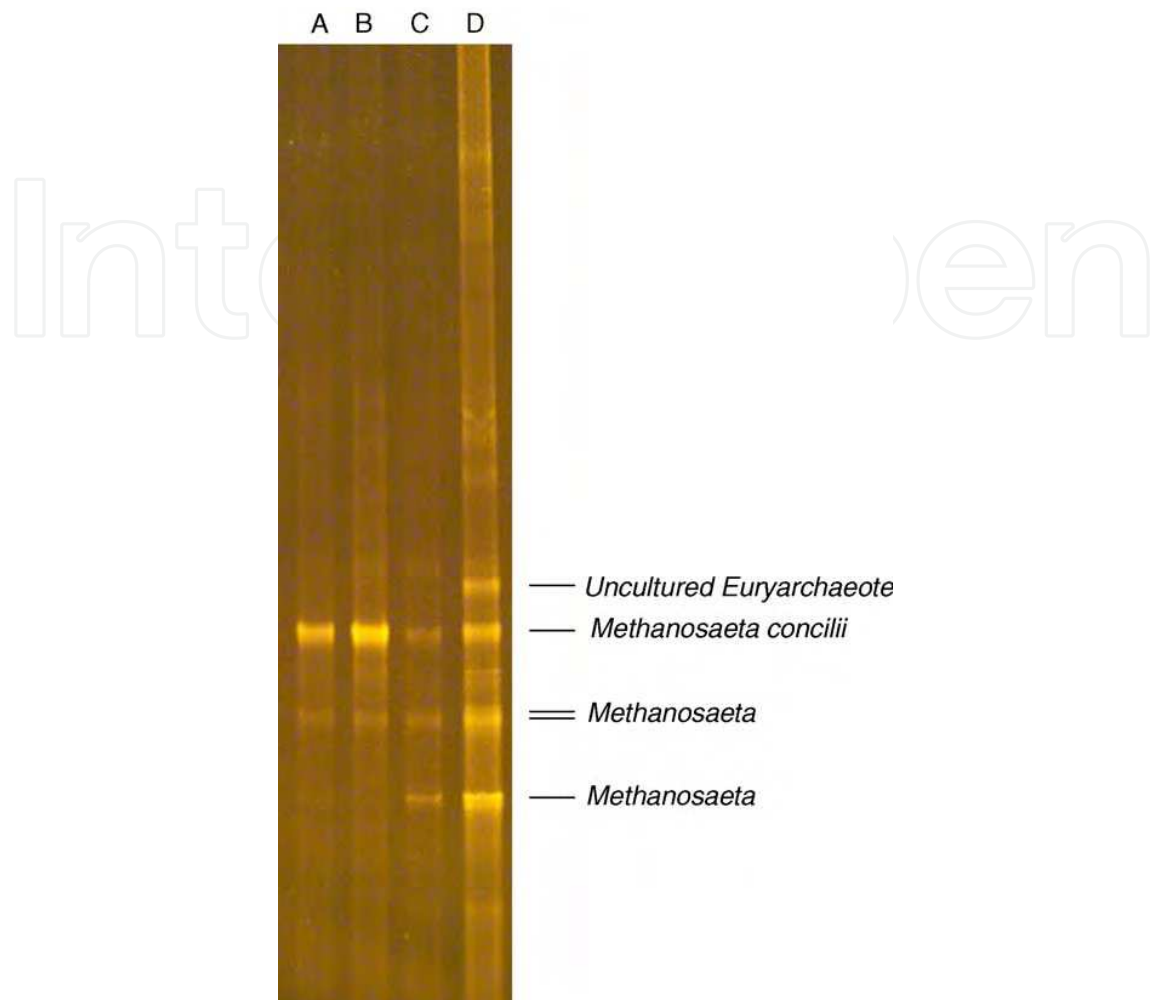


Fig. 5. DGGE analysis of the diversity of archaeal communities at different OLRs studied in one stage anaerobic digestion of 2POMSW (Rincón et al., 2006). The position of the major electrophoretic bands corresponding to the 16S rRNA gene of the identified archaea are indicated. A, B, C and D are the increasing OLRs studied in  $\text{g COD L}^{-1} \text{d}^{-1}$ : 0.75 (A), 1.5 (B), 2.25 (C) and 3.0 (D).

### 5.2.2 Two-phase olive mill wastewaters

Anaerobic treatment of this wastewater is very promising and beneficial. The production of biogas enables the process to generate or recover energy instead of just saving energy. This reduces operational costs as compared with other processes such as the physical, physicochemical or biological aerobic treatments previously mentioned (Wheatley, 1990). A kinetic study of the anaerobic digestion of wastewaters derived from the washing of virgin olive oil was previously reported (Borja et al., 1993). The study was carried out in a completely mixed reactor with biomass immobilized on sepiolite at a concentration of  $10.8 \text{ g VSS L}^{-1}$  operating at  $35^\circ\text{C}$ . COD removal efficiencies of more than 89% were achieved. Olive oil mills are usually small enterprises. Therefore, complex waste treatment systems are usually difficult to implement. Energy recovery from the generated wastewater with a

single unit like the previously explained MFC (section 4.3) is very promising. Preliminary studies of the treatment of 2POMWW have been reported by Feroso et al. (2011).

## 6. Conclusion

Three-phase olive mill wastewaters (3POMWW) and two-phase olive mill solid wastes (2POMSW) are the main wastes generated in the olive mill industry (1,200 L of 3POMWW per ton of milled olives and 800 kg of 2POMSW per ton of milled olives, respectively). The composition of 3POMWW and 2POMSW is very complex due to the vegetation water. Currently, the final destination of 3POMWW is mainly evaporation ponds and the final destination of 2POMSW is evaporation ponds and co-generation. Although the evaporation ponds are very simple constructions, failure in the insulation of the basin can contaminate the ground water and they generate putrid odors and insects during the decomposition processes. The co-generation processes have a high number of environmental disadvantages: nitrogen oxides production, emission of suspended ashes, etc.

Anaerobic digestion is already successfully used for many agro-industrial residues, such as sugar beet pulp, potato pulp, potato thick stillage or brewer's grains. This technology allows an efficient solids stabilisation and energy recovery. Both 2POMSW and 3POMWW have been shown to be promising substrates for anaerobic digestion, however full scale application is not a reality yet.

## 7. Acknowledgment

The authors wish to express their gratitude to the Spanish "Ministerio de Educación y Ciencia" (Project REN 2001-0472/TECNO) and to the contracts JAE-Doc from "Junta para la Ampliación de Estudios del CSIC" co-financed by the European Social Funds.

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Edited by Dr. Dimitrios Boskou

ISBN 978-953-307-921-9

Hard cover, 510 pages

**Publisher** InTech

**Published online** 01, February, 2012

**Published in print edition** February, 2012

The health-promoting effects attributed to olive oil, and the development of the olive oil industry have intensified the quest for new information, stimulating wide areas of research. This book is a source of recently accumulated information. It covers a broad range of topics from chemistry, technology, and quality assessment, to bioavailability and function of important molecules, recovery of bioactive compounds, preparation of olive oil-based functional products, and identification of novel pharmacological targets for the prevention and treatment of certain diseases.

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Bárbara Rincón, Fernando G. Feroso and Rafael Borja (2012). Olive Oil Mill Waste Treatment: Improving the Sustainability of the Olive Oil Industry with Anaerobic Digestion Technology, Olive Oil - Constituents, Quality, Health Properties and Bioconversions, Dr. Dimitrios Boskou (Ed.), ISBN: 978-953-307-921-9, InTech, Available from: <http://www.intechopen.com/books/olive-oil-constituents-quality-health-properties-and-bioconversions/anaerobic-treatment-of-olive-oil-mill-wastes-improving-the-sustainability-of-the-olive-oil-industry>

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