Process Safety and Environmental Protection 102 (2016) 361–369

Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.elsevier.com/locate/psep

Influence of a steam-explosion pre-treatment on the methane yield and kinetics of anaerobic digestion of two-phase olive mil solid waste or alperujo

Bárbara Rincón, Guillermo Rodríguez-Gutiérrez, Lucía Bujalance, Juan Fernández-Bolaños, Rafael Borja*

Instituto de la Grasa (CSIC), Campus Universidad Pablo de Olavide, Edificio 46 Ctra. de Utrera, km. 1, 41013 Sevilla, Spain

ARTICLE INFO

Article history:
Received 23 February 2016
Received in revised form 4 April 2016
Accepted 7 April 2016
Available online 1 June 2016

Keywords:
Olive mill solid waste
Anaerobic processes
Batch processing
Steam-explosion pre-treatment
Kinetics parameters
Cellulose

ABSTRACT

This study investigated the effect of a steam-explosion pre-treatment on the anaerobic digestion of the two-phase olive mill solid waste (OMSW) or alperujo. The OMSW was subjected to a steam explosion pre-treatment at 200 °C and 1.57 MPa during 5 min. After this pre-treatment a solid fraction (SF) and a liquid fraction (LF) were generated. These two fractions were used to obtain methane through anaerobic digestion with the aim of evaluating the effect of the pre-treatment on the methane yields obtained. Biochemical methane potential (BMP) tests of both untreated OMSW and steam-explosion pre-treated OMSW, i.e. SF and LF, as described above, revealed that the maximum methane yield (589 ± 42 mL CH_4/g VS_{added}) was achieved for the LF generated after the pre-treatment. From a kinetic point of view the BMP tests of untreated OMSW and the SF obtained after the pre-treatment showed a first exponential stage followed by a second sigmoidal stage after a lag period. By contrast for the LF, only a single exponential stage was observed.

1. Introduction

The olive oil industry is one of the more important industrial sectors in Spain, in which the 90% of the olive oil is produced by the two-phase olive oil extraction system. In the two-phase system the water consumed during the elaboration process is very low and the volume of liquid wastes generated are also lower (0.25 L of liquid effluents/kg olives processed *vs.* 1.24 L of liquid effluents/kg olives processed in the three-phase system), these volumes make the two-phase extraction system more environmental friendly than the previous three-phase olive oil extraction system (Alba, 1997). In the two-phase extraction system oil and a solid waste with a high percentage of humidity (65–70%) called olive mill solid waste (OMSW) or alperujo are generated. Spain is the largest producer of olive oil in the world, hence, it is also the biggest producer of olive oil mill wastes with 4–5 million tons of OMSW or alperujo per year (SMAFE, 2016). The two-phase OMSW is usually composed by water, with an organic fraction containing fats, proteins, sugars, organic acids, lignin, cellulose, hemicellulose, pectins, gums, tannins and polyphenols. It is acidic, almost black in color, and has a smooth doughlike structure. It is also rich in inorganic constituents, especially potassium. The toxic character of this waste is due to its concentration of phenolics (Borja et al., 2002). The high pollution potential and large volumes of these solid wastes generate serious environmental problems for Spain and in particular for Andalucía, the region where most of the mills are located.

* *Corresponding author*. Tel.: +34 95 4611550X223; fax: +34 95 4616790.
E-mail address: brlloren@cica.es (B. Rincón).
http://dx.doi.org/10.1016/j.psep.2016.04.010

Currently, the pomace olive oil industries use the alperujo as biomass for energy generation, after drying and extracting the pomace olive oil. The high humidity and organic content of alperujo makes the drying process the more expensive step in the industry (García-Ibañez et al., 2004). At present, the electricity generation is being funding by the Spanish Government, but the reduction of this help makes necessary to find new alternatives to get the total utilization of the waste through its valuable components. To treat successfully lignocellulosic materials special pre-treatments, like physical, biological or chemicals, must be applied. The utilization of this olive waste must be also focused on the recovery of bioactive components (Fernández-Bolaños et al., 2002) simultaneously diminishing the bio-toxicity of alperujo for further bioprocesses application like methane generation by anaerobic digestion.

Anaerobic digestion is a highly efficient process which produces methane as a final product, which can be used as an energy source for electricity and on-site heating due to its high heating value (35,793 kJ/m^3 at STP – standard temperature and pressure: 273 K, 101,325 Pa conditions) (Chanakya and Khuntia, 2014; Nielfa et al., 2015; Xue et al., 2015). Anaerobic degradation of particulate materials and complex compounds occurs in four steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis. Hydrolysis is generally the rate-limiting step when bacteria release extracellular enzymes that break down and further solubilize organic particulate matter to be used as substrate in subsequent reactions (Jackowiak et al., 2011). Therefore, to improve digestion efficiency, the most productive approach is to disrupt the chemical bonds in the material to be subjected to hydrolysis. In fact, the structure and composition of lignocellulosic compounds makes its anaerobic digestion especially difficult (Jeihanipour et al., 2011). In addition, the presence of lignin in this structure acts as a physical barrier that induces a non-productive adsorption of the enzyme. Thus, with a view to disrupting the lignocellulose structure of the wastes in order to increase its anaerobic digestibility, pre-treatments would appear to be not only ideal but also necessary in some cases.

The "Steam Explosion" (SE) process is commonly used for lignocellulosic material pre-treatment. In this method, biomass particles are heated with high-pressure saturated steam for a short period of time and the pressure is swiftly reduced to terminate the reactions, which causes the biomass to undergo an explosive decompression. Typical pre-treatment temperature, pressure and time fall within the ranges of 160–260 °C, 0.69–4.83 MPa, and several seconds to a few minutes, respectively. Under these conditions, hemicellulose is hydrolysed into its component sugars and lignin is transformed to a certain degree, thus making pre-treated biomass more degradable (Zheng et al., 2014). The use of these technologies for alperujo revalorization has studied successfully obtaining two phases, a liquid rich in phenols and sugars, and a solid phase partially detoxified rich in oil and cellulose (Rodríguez et al., 2007a). The SE treatment leads to break a part of the lignocellulosic structure also making the cellulose more accessible to enzymatic processes than untreated cellulose (Rodríguez et al., 2007b). In this way the hydrolysis is easier for the hydrolytic-acidogenic bacteria and the results could be better than when the lignocellulosic structure is intact. The use of the Steam-thermal pre-treatment could improve the results of a biological treatment of these wastes.

Some authors have found that a SE pre-treatment affected the methane yield obtained from different substrates compared to the results obtained without pre-treatment. In this way, biochemical methane potential (BMP) tests were conducted recently at laboratory scale to determine the specific methane yields of un-/pre-treated barley straw (thermal pressure hydrolysis). A methane potential of 228 mL CH_4/g VS was measured for untreated barley straw; and of 251 mL CH_4/g VS for thermal pressure hydrolysis-straw (190 °C, 30 min) (Schumacher et al., 2014). Thermal hydrolysis has led to an increase of the methane productions (up to 50%) and kinetics parameters (even double) in the anaerobic digestion processes of six different solid wastes, among them municipal solid wastes (MSW), organic fraction of municipal solid wastes, grease wastes, spent grains, etc. (Cano et al., 2014). The assessment of the biodegradability of thermal steam-exploded pig manure was performed compared to untreated samples. The pre-treatment was performed under different combinations of temperature and time, ranging 150–180 °C and 5–60 min, and used as substrate in a series of batch BMP tests. Results were analyzed in terms of methane yield, kinetic parameters and severity factor. For all the pre-treatment conditions, methane yield and degradation rates increased when compared to untreated pig slurry. An ANOVA study determined that temperature was the main factor, and the optimum combination of temperature-time of pre-treatment was 170 °C – 30 min, doubling methane production from 159 to 329 mL CH_4/gVS_{fed}. These operation conditions correspond to a severity factor of 3.54, which was considered an upper limit for the pre-treatment due to the possible formation of inhibitory compounds, hindering the process if this limit is exceeded (Ferreira et al., 2014). In this sense, the BMP of steam exploded wheat straw was evaluated in a pilot plant under different temperature-time combinations. The optimum was obtained for 1 min and 220 °C thermal pre-treatment, resulting in a 20% increase in methane production respect non-treated straw. For more severe treatments the biodegradability decreased due to a possible formation of inhibitory compounds (Ferreira et al., 2013). SE was also used to improve methane production of bulrush showing a higher methane yield than the simple raw. Specifically, a maximum methane yield of 205.3 mL per degradable volatile solid was obtained at 11.0% moisture, 1.72 MPa steam pressure, and 8.14 min residence time. The breakage and disruption of rigid lignin structure by SE was confirmed by thermo-gravimetric analysis (Wang et al., 2010).

The aim of this study was to evaluate the influence of a SE pre-treatment on the characteristics of two-phase OMSW and methane yield in BMP tests compared to an untreated OMSW. A kinetic study of the different stages involved in the methane production of the solid and liquid fractions generated after the pre-treatment was also carried out. There are not previous studies in the literature about the influence of SE pre-treatment of this substrate on its anaerobic digestion process.

2. Materials and methods

2.1. *Two-phase OMSW*

The two-phase OMSW used in the experiments was collected from an olive oil mill located in the Instituto de la Grasa (CSIC) of Seville (Spain). The olive variety was *Lechín*. OMSW was sieved through a 2 mm mesh to remove olive stone pieces. The sample was immediately treated in the SE reactor and anaerobically digested through a BMP test assay. The characteristics of the sieved two-phase OMSW are given in Table 1.