Waste Management xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

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

Optimization of the anaerobic co-digestion of pasteurized slaughterhouse waste, pig slurry and glycerine

Ángela Rodríguez-Abalde [a,b], Xavier Flotats [c], Belén Fernández [a,*]

[a] IRTA, GIRO Joint Research Unit IRTA-UPC, Torre Marimon, E-08140, Caldes de Montbui, Barcelona, Spain
[b] EnergyLab, Edificio CITEXVI – Local 1, Fonte das Abelleiras, s/n, Campus Universitario de Vigo, E-36310 Vigo, Spain
[c] GIRO Joint Research Unit IRTA-UPC, Department of Agrifood Engineering and Biotechnology, Universitat Politècnica de Catalunya – BarcelonaTECH, Parc Mediterrani de la Tecnologia, Building D-4, E-08860, Castelldefels, Barcelona, Spain

ARTICLE INFO

Article history:
Received 15 September 2016
Revised 29 November 2016
Accepted 15 December 2016
Available online xxxx

Keywords:
Co-digestion
Slaughterhouse waste
Pig slurry
Glycerin
C/N ratio

ABSTRACT

The feasibility of co-digestion of blends of two different animal by-products (pig manure and pasteurized slaughterhouse waste) and recovered glycerine was studied in mesophilic conditions. Experiments were performed in a lab-scale CSTR along 490 days, with a hydraulic retention time of 21–33 days and with a step-wise increased organic loading rate, by adding and/or changing the wastes ratio, from 0.8 to 3.2 $kg_{COD}\ m^{-3}\ d^{-1}$. The best methane production rate (0.64 $Nm^3_{CH4}\ m^{-3}\ d^{-1}$) represented an increment of 2.9-fold the initial one (0.22 $Nm^3_{CH4}\ m^{-3}\ d^{-1}$ with pig manure solely). It was attained with a ternary mixture composed, in terms of inlet volatile solids, by 35% pig slurry, 47% pasteurized slaughterhouse waste and 18% glycerine. This blend was obtained through a stepwise C/N adjustment: this strategy led to a more balanced biodegradation due to unstressed bacterial populations through the performance, showed by the VFA-related indicators. Besides this, an improved methane yield (+153%) and an organic matter removal efficiency (+83%), regarding the digestion of solely pig slurry, were attained when the C/N ratio was adjusted to 10.3.

1. Introduction

The increasing demand of renewable energy sources and reuse of wastes require good technological solutions, following current European regulations and state member policies. Biogas is a form of renewable energy produced from biomass by the anaerobic digestion (AD) process. The biogas is used to produce electricity, heat or as transport fuel (De Vries et al., 2012). Main substrates for AD include agricultural biomass in the form of animal manures, energy crops (e.g. maize) and organic residues from the processing industry (e.g. glycerine, beet tails, animal wastes, fruit pulp wastes). The use of animal manure and other organic wastes as bioenergy feedstock would allow farmers to take profit of new economic markets for traditional waste products. Livestock waste-to-bioenergy technologies, as AD, have the advantage to convert the treatment of livestock waste from a cost into a profit that can diversify farm incomes.

Nonetheless of the interesting environmental advantages of the livestock waste treatment by AD, as the greenhouse gases emissions reductions, biogas production using only animal manure is not economically sustainable, and addition of biomass from other sources is needed (Møller et al., 2007). The livestock co-digestion with other organic waste sources, combined with good manure management practices, have shown an improvement in the economic feasibility in many individual or centralized agro-biogas installations.

The successful of the co-digestion strategies resides in the selection of co-substrates that must be showing complementary characteristics. Pig manure (PM) is characterized by a high buffer capacity and contains a wide variety of micro and macronutrients necessary for the growth and activity of anaerobic microorganisms, but shows high ammonium concentration and low organic matter content (Hartmann and Ahring, 2006). Several positive experiences have been described about the co-digestion of pig manure with complementary substrates as algae, food wastes or catch crops (Astals et al., 2015; Dennehy et al., 2016; Molinuevo-Salces et al., 2015).

The co-substrates selection depends on their geographic availability in the area where the biogas plant is located, which, at the same time, is related with the kind of agro-food industry economy developed in this area. In the case of Catalonia, the meat sector is of great importance, being also one of the top five industries in Spain (Blancafort, 2009). This sector generates large

* Corresponding author.
E-mail address: belen.fernandez@irta.cat (B. Fernández).

http://dx.doi.org/10.1016/j.wasman.2016.12.022
0956-053X/© 2016 Elsevier Ltd. All rights reserved.

quantities of materials not intended for human consumption, so called animal by-products (ABP). Besides animal food or meat and bone meal production, AD is one of the allowed methods to valorise these products (European Community, 2009, 2011). Due to their composition, mainly composed by proteins and lipids with variable water content (Rodríguez-Abalde et al., 2011), ABP are considered good substrates for the AD process, according to the high methane yield potential. Although inhibitory processes could take place because of the combined release of ammonia due to protein decomposition and long chain fatty acids (LCFA) coming from fat degradation (Wang et al., 2016; Chen et al., 2008). ABP co-digestion strategy could reduce inhibition phenomena, and allows the progressive acclimatization of the bacteria to specific inhibitors such as ammonia (Edström et al., 2003) and/or LCFA (Silvestre et al., 2011), thus facilitating the control of the anaerobic process.

In the last decade, other organic substrate, generated in huge quantities, is the recovered glycerine (RG) generated as by-product of the biodiesel manufacturing industry. The biodiesel production in the European Union has increased from 500,000 tons in 1998 to 9,000,000 tons in 2009 (EBB, 2010). Each tone of biodiesel generates 0.1 tone of RG. The RG contains different components (alcohols, water, inorganic salts, free fatty acids, un-reacted triglycerides and methyl esters) that required removal from the RG before used as a raw material for alimentary, cosmetic or drug industry. The purification step might be economically unfeasible for most biodiesel plants, being their energy valorisation by AD an attractive option (Castrillón et al., 2011; Fountoulakis et al., 2010). Since glycerine is characterized by low nitrogen content and high organic matter concentration, the co-digestion with rich nitrogen organic waste, as the PM or ABP wastes, could be an adequate strategy to limit the risk of organic overloading of their anaerobic mono-digestion (Astals et al., 2012; Robra et al., 2010).

Most studies about co-digestion are based in the use of two substrates, although there are several experiences with ternary mixtures such as tomato residues with corn stover and dairy manure (Li et al., 2016), manure with food waste and sewage sludge in a proportion of 70:20:10 (Marañón et al., 2012) or cattle manure and food waste supplemented with crude glycerine (Castrillón et al., 2013). As an innovation aspect of this study, the results of ternary mixture co-digestion using pig manure, slaughterhouse and recovered glycerine are shown. The tertiary mixtures analysed have been designed based on the C/N ratio.

The aim of this study is to investigate the effect of adding recovered glycerine from biodiesel manufacturing during the continuous co-digestion of pig manure and slaughterhouse waste as strategy to balance the C/N ratio. The study includes the analysis of the effect of binary and tertiary mixtures on the biogas productivity and the stability of the process in terms of intermediary compounds as the volatile fatty acids and ammonia.

2. Material and methods

2.1. Wastes & inocula

PM was collected from a centralized manure treatment facility located in Lleida (Spain). Fourteen fresh manure samples were collected (approximately every 3 months) and characterized, in order to account the temporal variability (seasonal fluctuations, changes in pig slurry management, etc.). The first sample was used for batch tests, while all samples were characterized and used as feedstock for the continuous AD experiment.

Slaughterhouse waste (ABP) came from a pig slaughterhouse facility located in Barcelona (Spain). They consisted of a mixture of internal organs (kidney, lungs, livers and hearts, reproductive organs and fatty fractions), all classified as ABP type 3 (European Community, 2009, 2011). All fractions were minced using an industrial mincer till a particle size of 4 mm, mixed and pasteurized at 70 °C during 60 min, following European ABP regulations (European Community, 2009, 2011). The pasteurization was done in a high pressure and temperature autoclave (Iberfluid Instruments, Spain). Three pasteurized ABP (PP-ABP) were used along the experiments: one for characterization and batch tests (BMP) and other two as feedstock of the digester.

Enough quantity of RG was collected once from the glycerol-containing waste discharge of a biodiesel factory located in Barcelona (Spain) and used for characterization, batch tests and feedstock of the digester. All materials, PP-ABP, PM and RG, were frozen till being used.

The inoculum used in the batch test corresponds with the anaerobic sludge sampled in a wastewater treatment plant (WWTP) located in Barcelona. The inoculum used in the continuous experiment was a mixture (ratio 4:1, expressed as % volume) of digested sewage sludge, collected in the same WWTP as the inoculum for batch experiment, and the effluent of a mesophilic pig manure anaerobic digester (Lleida, Spain).

2.2. Analytical methods

Usual parameters were measured according to Standard Methods (APHA, AWWA, WEF, 1995): total and volatile solids (TS, VS), pH, alkalinity ratio (AR), total Kjeldhal nitrogen (TKN), total ammonium nitrogen (TAN) and sulphate ($SO_4^{2-}S$). Total carbon (TC) and total nitrogen (TN) were determined by elemental analysis (Leco, USA). Total chemical oxygen demand (COD) was determined by a modified Standard Methods procedure (Noguerol-Arias et al., 2012). Free ammonia (FAN) content was calculated using the formula given by Hansen et al. (1998). Proteins were calculated by multiplying the organic nitrogen by 6.25 $g_{protein}\,g_{Norg}^{-1}$ factor (Gelegenis et al., 2007). The fat content was analysed following recommendations of *n*-hexane extractable material for sludge, sediment and solid samples method of EPA (2005). Volatile fatty acids (acetic, propionic, i-butyric, *n*-butyric, i-valeric, *n*-valeric, i-caproic and *n*-caproic acids) were determined by gas chromatography (VARIAN CO-300) with a flame ionisation detector (FID) and a capillary column (TRB-FFAP de 30 m × 0.32 m × 0.25 μm). The carrier gas was helium (2 ml min^{-1}). Biogas composition (CH_4/CO_2) was determined by gas chromatography. The CH_4 and CO_2 were determinate with a packed column (Varian Haysep-Q 80-100 MESH 2 mm × 1/8″ × 2 mm SS). The carrier gas was helium (2 ml min^{-1}). The injector and column temperature were 250 °C and 105 °C respectively.

2.3. Biochemical methane potential tests

The mesophilic anaerobic biodegradability (AB), expressed as a percentage of the total COD and calculated according to Soto et al. (1993), of every waste was determined by triplicate through biochemical methane potential (BMP) tests. Glass vials of 1.2 L were filled with 0.5 kg of a solution composed by the inoculum (5 $g_{VSS}\,l^{-1}$), the substrate (initial concentration of 5 $g_{COD}\,l^{-1}$), macronutrient solutions (NH_4Cl, HPO_4K_2, $MgSO_4$, $MgCl_2$), micronutrient solution (H_3BO_3, $ZnCl_2$, $CuCl_2$, $MnCl_2$, $(NH_4)_6Mo_7O_2$, $CoCl_2$, $NiCl_2$, EDTA, HCl, $NaSeO_3$, resazurine) and bicarbonate (1 $g_{NaHCO3}\,g_{COD}^{-1}$) as a buffer. The vials were kept at 35 °C and were continuously shaken at 100 rpm during 30 days of experimental time. Samples of gas from the headspace were taken periodically and measured by gas chromatography. Net methane volume, or total accumulated methane from vials minus the total accumulated methane from blanks, was used to calculate the maximum methane yields. All the cumulative methane yields were expressed under normal conditions (0 °C, 1 atm). Methane production and

Please cite this article in press as: Rodríguez-Abalde, Á., et al. Optimization of the anaerobic co-digestion of pasteurized slaughterhouse waste, pig slurry and glycerine. Waste Management (2016), http://dx.doi.org/10.1016/j.wasman.2016.12.022