Fuel Processing Technology 137 (2015) 359–365

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Comparison of various post-treatments for recovering methane from agricultural digestate

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ARTICLE INFO

Article history:
Received 27 January 2015
Received in revised form 14 April 2015
Accepted 15 April 2015
Available online 12 May 2015

Keywords:
Anaerobic digestion
Digestate
Energy gain
Methane
Post-treatment

ABSTRACT

At full scale biogas plants, a large amount of digestate, which still contains a residual methane potential, is produced daily. Problems related to digestate storage and its use (i.e., biogas losses, the high cost of digestate transportation and limitations imposed by the European Nitrate Directive on its use as soil amendment) have attracted great attention among researcher to find solutions to take advantage of its residual methane potential. Thus, the aim of this study was to evaluate the methane production from digestate (DIG) and solid separated digestate (SS-DIG) and the feasibility of applying different kinds of post-treatments (i.e., thermal, thermo-chemical and enzymatic) in order to enhance their methane recovery. Results revealed that the methane recovery from digestate and solid separated digestate is feasible, considering their residual methane yields (70 NmL CH_4/g VS and 90 NmL CH_4/g VS, respectively). Thermal and alkaline post-treatments did not have a beneficial effect in enhancing methane potentials, while enzymatic post-treatment resulted in an increase of methane yield of 13% and 51% for SS-DIG and DIG samples, respectively. Finally, digestate recirculation permitted to obtain an extra electrical production (up to 4818 kWh_{el}/day), which could represent an extra economical income to farmers.

1. Introduction

Nowadays, biogas production through anaerobic digestion (AD) is regarded as a possible interesting energy carrier for replacing fossil fuels and reducing greenhouse gas (GHG) emissions.

Anaerobic digestion is an old and well-established biological process that involves the anaerobic degradation of organic materials into biogas, a mixture of CH_4 (50–75%) and CO_2 (25–50%), and digestate. The latter mainly constituted of water (over 90%), residual undegraded substrate, and inorganic compounds (i.e., ash). At farm scale, digestate is generally mechanically separated into liquid and solid fractions that are stored and handled separately. The liquid fraction is rich in nitrogen (N) and potassium (K), whereas the solid fraction retains great amount of phosphorus (P) and organic matter (mainly fibres) [1].

To date, the main use of anaerobic digestate has focused on land disposal [2,3]. Nevertheless, digestate, produced throughout the year, has to be stored, as it cannot be used directly on agricultural lands, due to limitations imposed by its stabilization level, crop growth stage and soil type [4]. Furthermore, the increasing number of biogas plants and their concentration in certain regions might lead to an oversupply of digestate, needing the surplus of digestate to be transported to regions with nutrients deficits [5]. Indeed, farms receive back only the amount of digestate which they are allowed to use in their fields, according to the nitrate directive [6,7].

Digestate storage, mainly performed in uncovered tanks, could cause potential emission of biogas into the atmosphere, resulting in a loss of energetic efficiency and in an increased environmental impact of AD plants [8,3].

Solutions to take advantage of the residual methane potential of digestate have been firstly investigated by Balsari et al. [9] who proposed a recirculation of digestate in the digester. Such option could reduce GHG emissions and it could permit to reduce the number of outdoor areas for its storage, while improving the energetic and environmental exploitation of the anaerobic digester [9].

The residual biodegradability of digestate depends on its compositional and structural characteristics, which vary according to the type of substrates fed to the digester and the AD plant configuration

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http://dx.doi.org/10.1016/j.fuproc.2015.04.028
0378-3820/

(i.e., with the presence or not of post-fermenters). The residual methane yields were also found to be closely correlated to other reactor parameters, such as the Hydraulitic Retention Time (HRT) and Organic Loading Rate (OLR) [10,11].

Some studies demonstrated that during anaerobic digestion hemicelluloses are degraded at a faster rate than cellulose, resulting in an accumulation of cellulose and lignin in the solid digestate [12–14]. Thus, treatment methods (i.e., physical, thermo-chemical, chemical, biological or various combinations of them) became fundamentals in order to break the resistant layer of residual lignin and to reduce the crystallinity of cellulose, thus increasing the availability of cellulose to anaerobic microorganisms [15–20]. Generally called as "pre-treatments" when applied on lignocellulosic fibres, the term "post-treatments" is used when they are applied on digested fibres. More recently, some authors have tested mechanical, thermal and chemical post-treatments on digestate and solid separated digestate [21–25]. However, the high-energy consumption for mechanical post-treatments, the high cost of chemicals and the possible formation of inhibiting by-products (i.e., furfural, HMF and phenol compounds) during thermo-chemical post-treatments are limiting barriers for their future industrial development [13,26].

Thus, due to the high cellulose content in agricultural digestate, a promising option is to carry out biological post-treatments, with the use of enzymes (i.e., endo-glucanase, exo-glucanase and β-glucosidase). For this purpose, different enzymatic commercial cocktails were developed at industrial scale in order to promote AD of complex solid substrates. However, according to our knowledge, the use of commercial enzymatic cocktails to enhance the methane production from digestate has not been investigated yet.

In this context, the aim of this study was to evaluate the methane production from digestate (DIG) and solid separated digestate (SS-DIG) and the feasibility of applying different kind of post-treatments (i.e., thermal, thermo-chemical and enzymatic) in order to enhance their methane recovery. Finally, preliminary energetic balances were also performed, by considering different scenarios of digestate recirculation.

2. Materials and methods

2.1. Origin of digestates

DIG and SS-DIG samples were collected from a mesophilic full-scale AD plant in the Lombardy region of Northern Italy. The plant was fed on a mixture (on the overall VS fed) of maize silage (25%), sorghum silage (11%), olive waste (11%), cow manure (8%), pig manure (18%), and turkey poultry manure on coconut chips (26%). The operational characteristics of the anaerobic plant are presented in Table 1. DIG sample was collected at the exit of the post-fermenter and before its inlet into the solid-liquid separator, while SS-DIG was recovered from the separator (helical screw press). Both DIG and SS-DIG were stored in gas-tight containers at 4 °C before their use.

Table 1
Main characteristics of the anaerobic digester plant.

Anaerobic digester parameters	
Number of reactors	2 digesters, 1 post-fermenter, 1 storage tank
Reactors volume (m^3)	Digesters: 2 × 2100 Post-fermenter: 2700 Storage tank: 2700
OLR (kg VS/m^3/day)[a]	3.4
HRT (day)[a]	36
pH[a]	7.5–7.8
Temperature (°C)[a]	43
Biogas	
Biogas (Nm^3/day)	12,000
Methane (%)	52
Total energy (MW)	0.98

[a] Referred to digesters and post-fermenter only.

2.2. Post-treatments

Thermal, alkaline and enzymatic post-treatments were performed on both DIG and SS-DIG samples. They were performed in 500 mL glass bottles closed with rubber septa. Thermal post-treatment was performed at 80 °C for 1 h under stationary conditions. Alkaline post-treatment was conducted by soaking samples in a NaOH solution at a dosage of 1 g NaOH/100 g TS, at 40 °C, for 24 h, without stirring. Alkaline dosage, post-treatment temperatures, and contact times were chosen according to our previous results [18]. Enzymatic post-treatment was conducted by using a commercial enzymatic cocktail, especially developed to enhance biogas production of agricultural substrates (MethaPlus® L 100, DSM Biogas, The Netherlands). The commercial preparation, analysed for its enzymatic activities content, was found to contain 221 IU/mL xylanase, 1740 IU/mL endo-glucanase, 7.62 IU/mL exo-glucanase and 31,900 IU/mL β-glucosidase. To perform the post-treatment, the enzymatic preparation was added to each substrate at a dosage of 0.15 mL/g TS and pH was corrected at appropriate enzyme-specific value (pH = 5) with HCl. Samples were then incubated at 40 °C for 24 h in a thermostatic incubator under stationary condition.

2.3. Analytical determinations

Total solids (TS), volatile solids (VS), ash content and chemical oxygen demand (COD) were analysed according to APHA methods [27]. TKN was determined according to Kjeldahl method [28], by using a mineraliser (BUCHI digestion unit K 438) and a BUCHI 370-K distillator/titrator. $N–NH_4^+$ concentrations were determined by using a commercial photochemical Spectroquant® test kit (Merck, Darmstadt, Germany; Hach Lange GmbH, Dusseldorf, Germany; LCK314 for COD and LCK303 for $N–NH_4$) and a spectrophotometer (HACH Lange DR6000 Hach Company, Loveland, CO., USA). Total phenols were measured according to Velioglu et al. [42] using Folin-Ciocalteu reagent. 200 μL of diluted sample was firstly filtered with a syringe filter 0.22 μm and then mixed with 1.5 ml of Folin-Ciocalteu reagent (previously diluted 10-fold with distilled water) and allowed to stand for 5 min before the addition of 1.5 ml of 20% sodium carbonate. After 90 min, absorbance was measured at 750 nm using a UV-Vis Spectrophotometer. The blank contains only water and the reagents. Total phenols were quantified from a calibration curve obtained by measuring the absorbance of known concentrations of gallic acid.

Structural-carbohydrates (i.e., glucose, xylose and arabinose) from cellulose and hemicelluloses were measured using a strong acid hydrolysis method adapted from Effland [29]. Samples (100 mg) were first hydrolyzed with 12 M H_2SO_4 acid for 2 h at room temperature and then diluted to reach a final acid concentration of 1.5 M and kept at 100 °C for 3 h. The insoluble residue was separated from the supernatant by filtration on fibreglass paper (GFF, WHATMAN®), washed with 50 mL of deionized water and then placed in a crucible. The crucible and the fibreglass paper were dried at 105 °C during 24 h to determine by weighing the amount of Klason lignin. The supernatant was further filtered with nylon filters (20 μm) and analysed for the quantification of monomeric carbohydrates. All monosaccharides (i.e., glucose, xylose, arabinose) were analysed by high pressure liquid chromatography (HPLC) coupled to a refractometric detector. The analysis was carried out with a combined Water/Dionex system (Ultimate 3000), using a Biorad HPX-87H column at 50 °C. The eluent corresponded to 5 mM H_2SO_4 under a flow rate of 0.3 mL/min. A refractive index detector