

Direct upgrading of biogas produced by anaerobic digestion: preliminary results at laboratory scale

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Abstract The present study investigated, at laboratory scale, the possibility of achieving biogas upgrading with a single step of treatment, namely without involving any pre- or post-treatment or multiple stage recirculation. In this respect, three commercial molecular sieves (i.e., Honeywell 13X, 4A, and 5A) have been tested according two different configurations in series (4A/13X and 4A/5A) in 25/75 v/v relative amounts. A control trap containing only the 4A molecular sieve using the same amount of the in series configurations has also been used. Real biogas feed directly from the production reactors at atmosphere pressure has been used in the experiments. 4A sample resulted highly efficient in biogas upgrading (CO₂ retention rate of 42.4 gCO₂/kg, equivalent to 0.96 mmolCO₂/g) but its activity was limited to 18 days while by increasing the material amount and combining different types of molecular sieves in series, performance increased. The possibility to regenerate and reuse the sieves was also proven although preliminary.

Keywords: anaerobic digestion, biogas upgrading, biomethane, CO₂ adsorption, molecular sieves.

1. Introduction

The conversion of biogas produced by anaerobic digestion (AD) to biomethane is an important tool in the framework of the EU Green Deal (European Commission, 2021). Water scrubbing, membrane separation and pressure swing adsorption are the most widespread upgrading technologies but they require complex plants and specialized personnel (Angelidaki et al., 2018; Ardolino et al., 2021).

The present study investigated, at laboratory scale, the possibility of achieving biogas upgrading with a single step of treatment, namely without involving any pre- or post-treatment or multiple stage recirculation. Such result would allow small-scale AD plants to perform convenient in-situ biomethane production entirely in accordance with REPowerEU objective. In this respect, three commercial molecular sieves (i.e., Honeywell 13X, 4A, and 5A) have been tested according two different

configurations in series (4A/13X and 4A/5A) in 25/75 v/v relative amounts. A control trap containing only the 4A molecular sieve using the same amount of the in series configurations has also been used. Another peculiarity of the experiment is that real biogas feed directly from the production reactors at atmospheric pressure has been used. Semi-continuous AD reactors fed with thickened sludge (TSL) and organic fraction of municipal solid waste (OFMSW) at laboratory scale have been directly connected to the traps filled with molecular sieves. Being TSL and OFMSW very common waste streams, their recycling to biomethane and digestate is essential in an encouraged context of sustainable waste management.

2. Materials and Methods

Adsorbing supports were supplied by a plant of the UOP Honeywell company located in Reggio Calabria (Italy). In particular, due to the ability to separate humidity and different gases from biogas, zeolites labelled as 13X, 5A and 4A were considered. Those kinds of molecular sieves are aluminosilicate inorganic compounds generally used as solid adsorbents in industrial applications and are commercialized in different sizes in the form of beads (13X and 5A) and pellets (4A). Basically, the chemical formulas of these molecular sieves include Na, Al and Si for 13X and 4A, differing for the Si/Al molar ratio and Ca, Na, Al and Si for 5A. According to the different pore size, nominally 1.0 nm, 0.5 nm and 0.4 nm respectively for 13X, 5A and 4A, zeolite can adsorb different kind of molecules, such as water and CO₂, as in the case of the present study. In addition, after drying, purification, separation and recovery of gases and liquids, the adsorbed substances can be desorbed, and the molecular sieves regenerated.

Semi-continuous AD test was performed at laboratory scale by using the Bioprocess Control Bioreactor System (BPC Instruments). The system involved five 2 L glass reactors (designed as A, B, C, D, and E) internally equipped with a stirrer necessary to ensure continuous

mixing. The reactors were immersed in a thermostatic bath set at 35°C (i.e., mesophilic conditions).

Each reactor was fed with the same mix of thickened sludge (TSL) and dried organic fraction of municipal solid waste (OFMSW), 50/50 on volatile solids (VS) basis. As operational parameters, organic loading rate (OLR) and hydraulic retention time (HRT) were set at 1 gVS/L·d and 21 days, respectively. TSL was periodically collected from the gravity thickener of a wastewater treatment plant (population equivalent of 30,000) located in Reggio Calabria (Italy). Samples were stored at 4°C before their use. OFMSW was prepared in laboratory according to (Calabrò and Pangallo, 2020), it was subsequently dried at 35°C for 7 days and then grounded by a cutting mill PULVERISETTE 15. Lastly, inoculum used in the test came from previous AD experiments fed with similar substrates. Materials' characterisation (in terms of pH, total solids, TS, VS, and volatile fatty acids, VFA) is reported in Table 1. Parameters were determined according to standard methods (APHA et al., 2012; Liebetrau et al., 2016).

Table 1. Materials' characterisation

Material	TS [%]	VS [%TS]	pH	VFA [mg/L]
Inoculum	2.2 ± 0.23	68.2 ± 0.41	7.5	-
OFMSW*	21.7 ± 0.56	96.2 ± 0.13	6.1	-
TSL	1.7 ± 0.04	74.8 ± 0.28	6.5	226.4
	1.7 ± 0.22	76.7 ± 1.09	6.7	292.8
	2.4 ± 0.37	77.4 ± 0.10	6.7	218.7

*Referred to wet sample before drying

Each semi-continuous AD reactor was connected through a Tygon® tube to a hermetically sealed glass beaker. Each beaker was labelled as the respective connected reactor (i.e., A, B, C, D, and E).

Three distinct test phases were carried out:

- traps were filled exclusively with distilled water for 11 days in order to verify regular and uniform biogas production in all reactors (start-up phase).
- Traps were respectively filled with 400 mL of distilled water (trap A), 400 mL of 3 M NaOH solution (trap B), 115 g (25% of beaker total volume) of 4A molecular sieve (trap C), 115 g and 272 g (25/75 v/v) respectively of 4A and 13X molecular sieves placed in series (trap D), 115 g and 310 g (25/75 v/v) of 4A and 5A molecular sieves placed in series (trap E). During this phase, gas exiting each trap was periodically captured with a 100 mL syringe in order to measure possible residual CO₂ content through a water displacement apparatus connected to an external 3 M NaOH trap. The

second phase was interrupted when CH₄ content in gas leaving trap C (i.e., filled with 4A sieve) was lower than 90%. This occurrence was observed after 43 days and it was related to adsorbent progressive exhaustion.

- Molecular sieves in traps C, D, and E were all replaced with 400 mL of 3 M NaOH solution in order to verify that CH₄ productions from all processes at regime phase were still regular and uniform.

3. Results and discussions

In the start-up phase, biogas productions from all reactors were recorded as all respective traps were exclusively filled with distilled water. Being experimental conditions set equal for all reactors, expectedly, all processes run regularly and uniformly (Figure 1a). Nevertheless, process B was slightly the least biologically active (average daily biogas yields of 178.8 NmL/gVS, 178.1 NmL/gVS, 190.5 NmL/gVS, 194.6 NmL/gVS, and 199.7 NmL/gVS of reactors A, B, C, D, and E, respectively). This evidence was also observed during the third (and last) phase of the AD test in which CH₄ productions from reactors B, C, D, and E were compared (average daily CH₄ yields of 189.2 NmL/gVS, 207.3 NmL/gVS, 206.1 NmL/gVS, and 211.7 NmL/gVS of reactors B, C, D, and E, respectively, Figure 1a). The implications of such evidence will be further discussed. It is worthy noticing that the circumstance that average daily CH₄ yields of the last phase of the test were larger than biogas ones of start-up phase is not contradictory since AD performances are often better during the steady state due to the adaptation of the microbial consortium (see behaviour of process A for which only biogas production was monitored throughout the test).

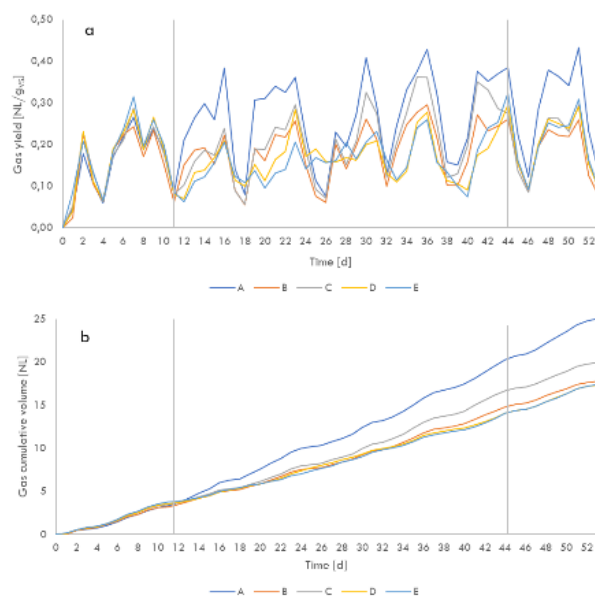


Figure 1. a) Gas yields of each reactor-trap series and b) cumulative volume of gas produced by each reactor-trap series

From day 11 onwards (i.e., beginning of the second phase), differences among processes were recorded. Reactor A obviously showed the highest daily gas yield as respective trap was still filled with distilled water so that determining total biogas production (adsorption of CO₂ in water at room temperature is negligible). Conversely, daily gas yields of reactors B, C, D, and E were affected by CO₂ retention by traps. Specifically, gas exiting from trap B was basically the CH₄ produced by the respective reactor as trap B contained the ordinary 3 M NaOH solution. On the other hand, gas leaving traps C, D, and E was the result of the tested biogas upgrading being those traps filled with molecular sieves (25% 4A, 25/75 4A/13X, and 25/75 4A/5A, respectively), moreover it has already been demonstrated that these reactors behaved very similarly in terms of CH₄/biogas production. What emerges from Figure 1a, and more clearly from Figure 1b, is that volumes of gas exiting from traps follow the sequence C > B > D ≈ E. Regarding the process in the reactor B as a control (thus CH₄ production reference), on the basis of that sequence it can be stated that traps D and E necessarily retained a higher quantity of CO₂ due to the further activity of 5A and 13X molecular sieves present in those traps which were able to adsorb a bigger quantity of CO₂ with respect to 4A, as demonstrated by the adsorption experiment reported above.

Table 2. CH₄ contents in gas exiting from molecular sieves traps

Trap	Time [d]*			
	8	18	28	30
C	100%	98%	91%	87%
D	98%	99%	95%	95%
E	98%	98%	100%	97%

*from the beginning of the second phase

It emerges that basically the entire volume of gas from trap C was CH₄ until day 18 of trap operation with 4A sieve. Accordingly, it can be stated that 4A sieve performed biogas upgrading quite well and consistently with values of CH₄ purity after pressure swing adsorption treatment found in literature (i.e., 96-98% (Lombardi and Francini, 2020)). The 4A sieve was considered exhausted after about 30 days of usage, namely when CH₄ content in treated gas was lower than the still satisfactory value of 90%. A 4A CO₂ retention rate of 42.4 gCO₂/kg (equivalent to 0.96 mmolCO₂/g) was calculated by dividing the mass of retained CO₂ during the 18 days of trap C operations (i.e., 6.6 gCO₂, namely the difference between total biogas cumulative volume of reactor A and total gas cumulative volume of reactor C, Figure 1b) by the mass of 4A sieve used to fill the 25% of the trap bottle (i.e., 115 g). As already mentioned, the regularity of production in reactors A and C makes this calculation sufficiently reliable. Previously, CO₂ retention capacity of 4A sieve employed in PSA process was estimated to

be 0.81 mmolCO₂/g in the pressure range of 1-5 bar (Palomino et al., 2010). Moreover, the value of 1.16 mmolCO₂/g was estimated considering the application of 4A sieve under vacuum conditions (0.1-1 bar) (Bacsik et al., 2016).

In addition, results reported for reactor D and E proved that the coupling of molecular sieves, respectively 4A/13X and 4A/5A, further increased the biogas upgrading with respect to reactor C. Indeed, in both cases the lower gas cumulative volume reported in Figure 1b was due to a higher quantity of CO₂ retained not only in the 25% volume filled with of 4A sieve but also adsorbed in the remaining volume (75%) filled with 13X and 5A sieves, respectively. Accordingly, higher level of CH₄, equal to 95% and 97% for reactor D and E were revealed (Table 2) even after 30 days of usage. In turn, the longer operation time proved the absence of saturation, as registered instead for reactor C. The higher quantity of molecular sieves (25/75 mixed type), as well as the typology, 5A and 13X, characterized by a higher CO₂ adsorption ability, could explain the obtained results, both in term of higher CO₂ adsorption and CH₄ yield.

4. Conclusions

The potentiality of different kind of molecular sieves for the upgrading of biogas was clearly evidenced. The ability of those sieves to adsorb CO₂ in the proposed operational conditions was tested and proved. In particular, 4A sample resulted highly efficient in biogas upgrading (CO₂ retention rate of 42.4 gCO₂/kg, equivalent to 0.96 mmolCO₂/g) but its activity was limited in the run time experiment (18 days). A further improvement was reached by increasing the material amount in the traps (from 25% to 100% of total trap volume) and combining different types of molecular sieves, namely 4A/13X and 4A/5A (both 25/75 v/v), able to obtain higher and constant biogas upgrading for the whole testing time (30 days), without causing significative changes in the zeolite structures. The possibility to regenerate and reuse this kind of materials was also proven.

The features of the proposed upgrading solutions (i.e., use of common commercial materials, application of low pressure, and absence of preliminary treatments) coupled with satisfactory processes' performances, make biogas upgrading potentially economically viable particularly for small-scale digesters.

Nevertheless, future research is needed to both investigate the most appropriate modality of regeneration of the exhausted sieves and evaluate the effects on the sieves (in terms of adsorption efficiency) of multiple regeneration cycles in the long term.

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