Biogas Upgrading by Physical Water Washing in a Micro-Pilot Absorption Column Conducted at Low Temperature and Pressure

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The European Energy Policy has currently two main goals to reach: to minimize exposure to volatility of fossil fuel prices and to reduce of greenhouse gas (GHG) emissions. To reach these targets a practical way, among the others is represented by the biogas production by anaerobic digestion (Bonoli et al., 2014) (AD) and its upgrading to biomethane.

In this work the absorption of CO_2 is studied using a column working at atmospheric pressure and low temperature (5<T<20 °C) to investigate the feasibility of the process and analyze from an economical point of view the advantage of avoiding the use a pressurized system. A glass laboratory-pilot absorption column was used for gathering the experimental data. It is a column 1 meter high, thermostated using water and filled with 40 cm of structured packing (Sulzer CX), adapted to operate continuously. A synthetic biogas was prepared mixing a stream of CO_2 (>99%) and a stream of methane (>99.9 %) in order to reproduce a typical raw biogas composition, i.e. molar fraction of methane of about 0.6. The internal temperature was monitored by a thermocouple and the inlet and outlet flow of biogas (G) was measured using a mass flowmeter while the water flow rate (L) was monitored using a magnetic induction flowmeter. The compositions were determined using a 3000A micro-Gas Chromatograph Agilent, previously calibrated. The temperature was varied between 6.5 and 20 °C and the water flow rate between about 0.5 and 5 L/h. The composition of the gas exiting the micro-pilot plant was monitored every 5 minutes until the stationary condition.

1. Introduction

The European Energy Policy has currently two main goals to reach: to minimize exposure to volatility of fossil fuel prices and to reduce the greenhouse gas (GHG) emissions (Pöschl et al., 2010). To reach these targets the biogas production by anaerobic digestion (AD) and its upgrading to biomethane is an attractive method. Biogas is a more versatile renewable energy source (compared to wind and solar energy), once the starting feedstock is well-known, characterized and standardized. Moreover, it has a determinate energy value at a fixed composition, and thus its potential utilization is mainly independent of factors like geographical location and seasons and moreover it is easy to store. In addition biomethane can be used directly for heating and electricity generation or as a substitute for fossil fuel applications, transport fuel and power generation (Ryckebosch et al., 2011). Raw biogas, as shown in Table 1, contains a certain amount of impurities like water, dust, H_2S, CO_2, siloxanes, hydrocarbons, NH_3, oxygen and several other compounds (Rasi et al., 2007), that are generated as by-products from the active sludge in the fermentation processes and their concentration in the final product is dependent on the feedstock used for its production. These must be removed to reach the required standards of quality.

Table 1: typical composition for three different raw biogas

Biogas type	CH$_4$ (%)	CO$_2$ (%)	O$_2$	(%)N$_2$	(%)H$_2$S (ppm)	Benzene (ppb)	Toluene (ppb)
Landfill	47–57	37–41	<1	<1–17	36–115	0.6–2.3	1.7–5.1
Sewage	61–65	36–38	<1	<2	Trace	0.1–0.3	2.8–11.8
Agricolture	55–58	37–38	<1	<1–2	32–169	0.7–1.3	0.2–0.7

The more the CO$_2$ is removed the less the impurities will be in the mixture because carbon dioxide is order of magnitude more concentrated that these latter compounds, obtaining a product rich in methane and suitable for all the application already described. Different processes were developed for the effective removal of CO$_2$ from biogas (Wellinger et al., 2005). These are mainly based on the absorption using water or an amine solution as solvent. CO$_2$ removal by absorption and stripping with aqueous amine is a well-understood and widely used technology. The basic process, patented in 1930 (Bottoms, 1930), is one in which CO$_2$ is absorbed from a fuel gas or combustion gas near ambient temperature into an aqueous solution of amine with low volatility. The amine is regenerated by stripping with water vapor at 100 to 120 °C, and the water is condensed from the stripper vapor, leaving pure CO$_2$ that can be compressed to 100 to 150 bar for geologic sequestration. Hundreds of plants currently remove CO$_2$ from natural gas, hydrogen, and other gases with low oxygen. Four coal-fired plants with power outputs of 6 to 30 MW separate CO$_2$ from flue gas using 20 % monoethanolamine (MEA) (Rochelle, 2009). Other non-common separations are performed by cryogenic technology that can vary from simple straight or once through compression (Krich et al., 2005) to more complex processes involving some form of recycle and/or auto-refrigerationor (Zanganeh, 2009) or by membrane technology (Strevett et al., 1995). For what concern the physical methods, the removal of CO$_2$ with water represents the most important upgrading step to reach the specified Wobbe index (Klimstra, 1986), i.e. to have a gas with a high calorific value. Tipically, for enhancing the CO$_2$ absorption, the operative pressure of the absorber is set between 10 (Tynell, 2005) and 20 bar (Budzianowski, 2012), in order to increase its partial pressure and thus its solubility in the solvent. To release the carbon dioxide captured from the water, and thus for regenerating the washing liquid, a second column at low pressure is used. This process is generally called Pressure Swing Absorption (PSA) and it is characterized by high energy cost, due to the use of a compressor for having the first column pressurized.

In this work the absorption of CO$_2$ is studied using a single column system, working at 1 bar and low temperature (lower than 15 °C) to investigate the feasibility of the process avoiding the expensive pressurized equipments. As far as the author know, data performed at these operative conditions are not reported in literature, showing that this particular way to perform this technology is not studied yet. This low-pressure column should perform a major removal of the fed carbon dioxide in a double columns system, where the second columns, of reduced dimension and costs, should work at higher pressure for the final purification of bio-methane. In this paper the feasibility study concerning the first absorprion column is presented.

2. Experimental

2.1 Materials and methods

A synthetic biogas was prepared mixing a stream of CO$_2$ (>99.99 %) and a stream of methane (>99.99 %) in order to reproduce a typical raw biogas composition. The composition of the gas entering and exiting the column was measured using a 3000A micro-Gas Chromatograph Agilent equipped with a PLOTQ column, set to 35° C. The instrument was calibrated properly mixing the pure components.

2.2 Absorption column

The bench scale plant used for the experimental determinations is schematically represented in Figure 1.
The molar fraction concerning the gas phase are presented with the letter y while the one of the liquid phase with the letter x. If the compositions are referred to the bottom of the column, the subscript 1 is used while for the top of the column the subscript 2 is used.
A cylindrical glass column, jacketed in order to be thermostated, was used with internal diameter of 43 mm. The column was filled with Sulzer DX structured packing for a height of 390 mm.
The gas line is provided by the two cylinders of methane and carbon dioxide. Two mass flowmeters are used to control and measure the flowrates of each gas. CO$_2$ and CH$_4$ are then mixed and fed at the column bottom. The measurement of the composition was performed by sending either the inlet or the outlet gas to the micro-GC by automatic sampling. For every sampling, the gas was pumped in the sampling loop of the micro-GC for 2 min, allowing to have the same composition of the biogas that is flowing in the plant. The micro-gas chromatograph

was equipped with a PLOTQ column and the analysis of the biogas was performed at an oven temperature of 45 °C.
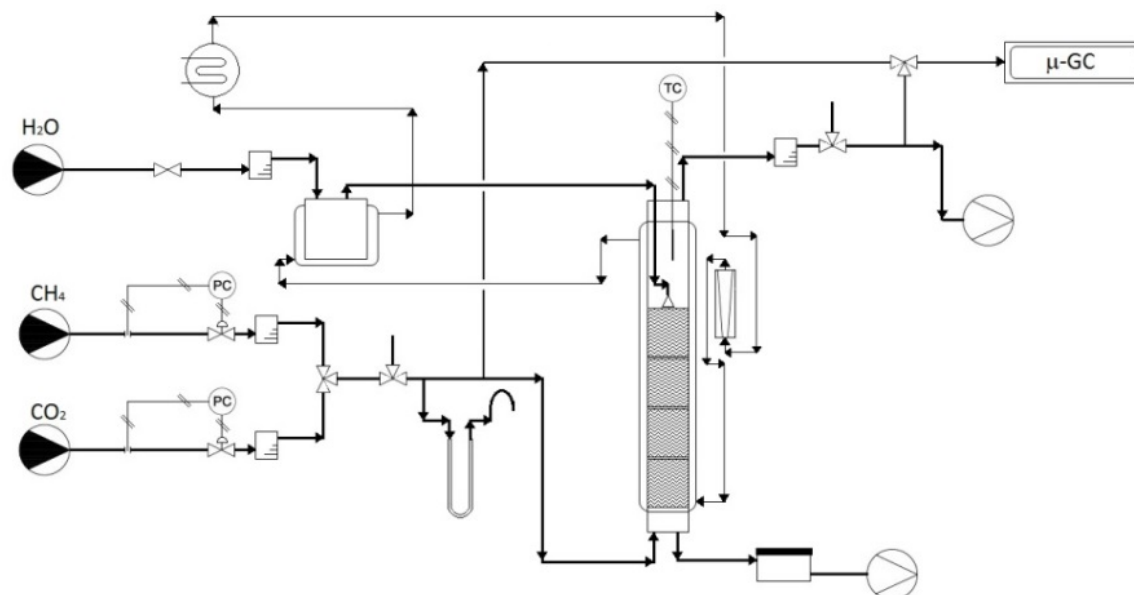

Figure 1: laboratory bench scale absorption column scheme

A manometer filled with silicone oil, with an end connected to the tube in which the gas flows and the other end open is used for the measurement of the pressure drop, using the equivalence 1 mm Hg= 13 mm oil. The use of silicone oil allows to measure very low pressure drop in the columns. As seen from Figure 1 the column is jacketed to maintain a constant temperature, which is measured by a thermocouple inserted in the column, and placed at the top of the packaging (Tc in Figure 1).

Municipal water, coming from the city network, is pre-treated in a softener to remove the calcium. Subsequently it is sent to a valve and a magnetic induction flowmeter to carefully set and measure the flow of liquid entering the column. The temperature of the flow of water was set equal to the temperature of the column by the liquid thermostatic vessel.

2.3 Experimental procedure

Once the column temperature is reached, the inlet biogas composition was regulated by modifying the CO_2 and CH_4 flow by acting on the mass flowmeters. The gas flowrate (G) is measured before and after the column to verify the absence of losses. After this check, the water flow (L) is set to the desired value. This latter action corresponds to the start of the experiment. The biogas composition entering and exiting form the column was monitored every 5 minutes until steady state conditions were reached. The global molar balance was verified considering all the flows involved, with an average error in the experiments not greater than 3%. This experimental protocol was repeated for all the tests that were carried out, varying the column temperature and either the gas or the liquid flow. Seven experiments were run changing the operative parameters above mentioned: in RUN 1-2 the biogas to liquid flowrate ratio was varied at a constant temperature (10 °C), while in RUN 3-4 the parameter changed was the column temperature, which was set to 6.5 and 20 °C at a fixed L/G' ratio (G' is the methane flow). RUN 5-7 were performed changing the column temperature and the L/G' ratio in order to compare them with the simulations to assess their reliability. All the operative parameters for each run are summarized in Table 2:

Table 2: operative parameters used for the experiments: G_1: total flow (CH_4+CO_2) entering in the column; G'_1: CH_4 flow; L_1= water flow

RUN	G_1 [L h^{-1}]	[LG'$_1$ h^{-1}]	[molL$_1$ h^{-1}]	[LT	[°C]y$_{1CO2}$	[-L/G']	[-
1	6.82	0.227	1.6	10.0	0.20	380	
2	6.82	0.227	3.0	10.0	0.20	734	
3	13.19	0.374	4.9	9.3	0.32	728	
4	13.24	0.326	4.0	20.0	0.41	681	
5	9.21	0.208	4.0	6.5	0.46	1,070	
6	13.20	0.276	4.0	15.0	0.50	806	
7	14.15	0.395	2.0	13.5	0.33	281	

The experiments were repeated at least two times and the numbers reported are an average of the results obtained.

2.4 Simulations

The experimental runs were simulated using PRO/II software version 9.1 by Simulation Science (Sim-Sci-Esscor, Schneider Electric). The computer algorithm used for the micropilot simulation was the PRO/II SURE VLE. The fluid phase equilibria of the system CO_2/CH_4/water was taken into account using UNIQUAC model for the calculation of activity coefficient in liquid phase and RKS Equation of State for the fugacity in vapor phase as suggested by Cozma et al. (2013). The Henry coefficient of CO_2 in water was calculated from Eq(1):

$$lnH = C_1 + \frac{C_2}{T} + C_3 lnT \tag{1}$$

where H is the Henry coefficient in MPa and T the temperature in K. The parameters C1=-47.166, C2=0 and C3=9.1768 were regressed from the experimental data reported in the paper of Carrol et al. (1991). The column was designed as a trays column with 10 theoretical trays. This value has been calculated considering the HETP (Height Equivalent Theoretical Plates) resulting from 30 cm of DX sulzer body.

3. Results and discussion

The results gathered show that the plant can reach the steady state after about 40 min after the start. Coherently, the higher the L/G' ratio, the better CO_2 absorption is obtained. In particular in RUN 2, using a L/G' of 734 the absorption reached is about 40 %. Also comparing RUN 3 and 4, that as previously mentioned were operated for comparing the effect on temperature showed that the higher absorption of carbon dioxide is obtained at lower temperature. The results are shown in Figure 2:
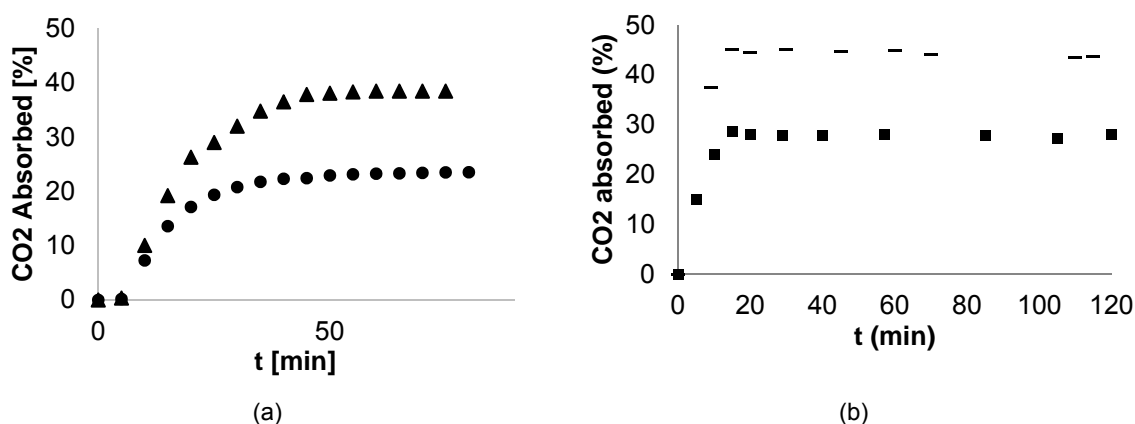

(a)   (b)

Figure 2: (a) absorption of CO_2 versus time at 10°C and different L/G': (•) 380; (▲) 734.(b) absorption of CO_2 versus time at L/G'=700 and different temperatures: (■) 20.0 °C; (-) 9.3 °C

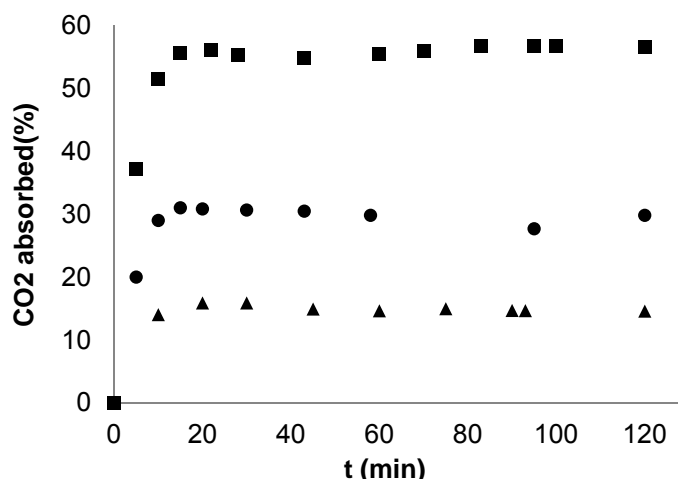The results of RUN 5-7 are summarized in Figure 3:

Figure 3: experimental results of RUN 5 (■), 6 (●) and 7 (▲)

The results show that the higher the L/G ratio and the lower the temperature, the higher the CO_2 absorption is. For all the RUNS a pressure drop in the range 0.10-0.20 mmHg was measured, which is consistent with the use of a structured packing and the mass balances confirmed all the measured biogas outlet compositions. The simulation performed showed a satisfactory fitting to the experimental data, as showed in Figure 4:
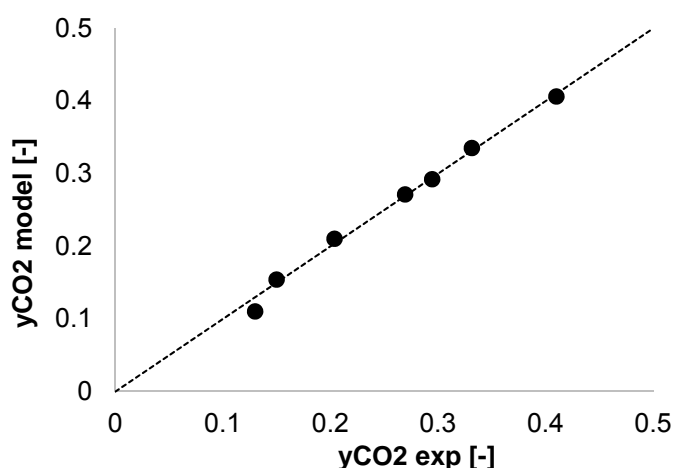

Figure 4: parity plot between experimental and simulated data

As shown in the results a high amount of CO_2 is removed using an atmospheric column. An economical assessment can be drawn to verify the feasibility of the process. Nowadays, as already stated in the introduction section, to upgrade biogas to biomethane a high pressure column is used. The atmospheric column technology proposed in this article can be used for the removal of a high amount of CO_2 and a smaller high-pressure column can follow it to reach high pureness methane. Using this process scheme the CAPEX and OPEX term related to the high pressure column and to the biogas compressor are reduced because of the smaller gas flow due to the lower CO_2 content.

4. Conclusion

A study on the biogas upgrading by physical CO_2 absorption at low pressure and temperature was carried out using water in a bench scale absorption column. The best result in terms of CO_2 absorbed was 70 % and was obtained using a L/G' ratio of 660 and a temperature of 6.5 °C. All the data collected varying the main operative parameters permit to conclude that the proposed technology can be suitable for the biogas upgrading. The study of the whole double columns system and its relative economic feasibility will be the object of a further work.

Acknowledgements

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