Optimization of biogas upgrading by absorption of CO_2 into ethanolamine solution

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Abstract

Energy usesof biogas from anaerobic digestion depend on its quality, which is related to its CH_4 and CO_2content and the presence of impurities (SH_2, ammonia, siloxanes). Methane enrichment of biogas makes it suitable for usein the same applications as natural gas. Different technologies have been developed for this purpose, although their costs suppose a major drawback. Process optimization is therefore needed to improve techniques and achieve increased operational efficiency. Methane losses need tobe minimized for economic and environmental reasons.The main objective of this study wasto optimize a continuous absorption process to remove CO_2 from biogas and hence increase its heating value. Four different absorbents were tested in preliminary batch experiments, the best results being obtained with monoethanolamine (MEA). Experiments were subsequently carried out with this absorbent in a packed tower using two types of materials. The L/G ratio had a marked influence as an operational parameter on the efficiency of the absorption process, modifying MEA consumption and the quality of the upgraded biogas. Different L/G ratios were tested in both types of packed material. Despite differing in terms of materials and geometry, no relevant differences were found. In fact, the optimum L/G ratio seemed to fall within the 0.9-1.2rangewhen recirculating a 5% MEA solution. A quadratic correlation fitted the experimental data, giving a theoretical optimum L/G ratio of 1.05-1.11, for which the minimum MEA consumption would be reach 6.1-6.2 g MEA/L removed CO_2.

Keywords: Chemical absorption; L/G ratio; MEA; packed tower

1. Introduction

The energy uses of biogas from anaerobic digestion depend on its quality, which is related to its methane and carbon dioxide content and the presence of impurities such as SH_2, siloxanes andammonia. Different technologies have been developed for upgrading biogas, taking into accountgas production and purity requirements. These factors are extremelyimportant in the dimensioning of the biogas plant as well as in itseconomic evaluation, asthe costs of purification systems are linked to the scale of the process. Process optimization is therefore important in order to improve these systemsand achievegreateroperational efficiency. CH_4 losses should be minimized for economic and ecological reasons, seeing asmethane is a greenhouse gas that is 28 times more harmful than carbon dioxide [1].

The choiceof the mostsuitablemethod to upgrade biogas mainly depends on the chemical nature of the component to remove [2].Methane-enrichedbiogas can be obtained viacarbon dioxide removal, thereby increasing its heating value and hence its efficiency [3]. Methane enrichment of biogas makes it suitable for use in the same applications as natural gas (vehicle fuel, injection into thenatural gas grid, residential uses, etc.).These applications are regulated by national regulatory frameworks such as taxsystems, green energy certifications and tariffs for electricity providers [2].

Different techniques have been developed to remove CO_2 from a gas stream: physical/chemical absorption, adsorption, pressure swing absorption (PSA) andvacuumswing absorption (VSA), membrane separation, cryogenic separation and biological removal [4,5]. The choice depends on economic, ecological or other types of concerns [4].

In absorption processes, the gas stream and the liquid are maintained in contact throughout a columnfilled withrandom or structured packed material to ensure improved contact between the two phases.Water and polyethylene glycol constitute the physical absorbents that may be used.Polyethylene glycol (PEG), commercially known as Selexol^{TM}, is also a common physical absorbent used in CO_2 absorption. Conceptually they comprisethe same technique, although $CO_2$is more solublein PEG than in water [4].

Amines are widely-usedabsorbents with high efficiencyas they react with CO_2[4,5] and so are usually employed in chemical scrubbers. Due to their characteristic selective properties, CH_4 losses are very low (<0.1% [3]).However, corrosion constitutesone of theirmajordrawbacks[4,6], especially in the case of ethanolamine (MEA), theeffects of which are particularly appreciable whenthe concentration exceeds 20% [7]. Several experiments comparing amines have been carried out, always obtaining the bestresults for MEA[8,9,10]. Biernacki et al. [9]conductedan eco-efficiency analysis in an actual biomethane plant, comparing MEA and DEA (diethanolamine). These authorsshowed MEA (30%) to be asustainable alkanolamine for biogas upgrading, taking into considerationeconomic, social and ecological aspects.

The main objective of this studywas to optimize a continuous absorption process to remove CO_2 from biogas and hence increase its heating value. Different absorbents were tested in batch experiments in order to compare their CO_2 absorption capacity when treating synthetic samples of biogas. The best absorbent was used in a packed column to treat biogas obtained from anaerobic codigestion. Two different packed materials were employed, optimizingthe L/G ratio and determiningthe minimum absorbent consumption for both types of materials .

2. Materials and methods

2.1 Biogas

Synthetic biogas

The biogas used in the preliminary batch experiments was made synthetically froma mixture of CO_2 and CH_4. Mixtures were prepared in 25 L Tedlar bags, introducing thesegases in suitableamounts to reach a final composition of approximately 60%CH_4 and 40%CO_2.

Biogas

The CH_4concentration in the biogas used in the continuous absorptionexperimentsvaried (50-70%) as it was obtained from anaerobic codigestion at 55ºC of cattle manure, food waste and glycerin from the biodiesel industry[11,12,13].

2.2 Absorbents

Four different absorbents (Merck quality) weretested:monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and polyethylene glycol dimethyl ether(PEGDME). Table 1shows the density, molecular weight and purity of these chemical substances.

Table 1.Main characteristics of the absorbents used in the absorption experiments

	MEA	DEA	MDEA	PEGDME
Density (g/mL)	1.0164	1.097	1.04	1.08
Molecular weight (g/mol)	61.08	1015.14	119.16	2000
Purity (%)	≥ 99.5	≥ 99.2	≥ 99	99.9

2.3 Equipment

Batchexperiments

The equipment employed in the batch experiments was [14,15]:

- 25 L capacity Tedlar bags to contain the synthetic biogas.
- A system to control the biogas stream,composed ofa vacuum pump and a flow regulator.
- A gas washing bottle (500 mL) to contain the absorbent solution.

Continuousabsorptionexperiments

The main componentsof the experimental equipment employed in the continuousabsorptionexperimentswere the following:

- Solvent container: a glass tank positioned on a magnetic agitator. The tank cover had two openings: one was used to send the absorbent solution to the packed tower and the other to return the solution from the tower to the tankwhen there was recirculation.
- Packed tower: the liquid-gas contact unit was a polycarbonate column (height: 30 cm; diameter: 6.5 cm) with inlet and outlet ports for the gas tubing. The packed tower had a plastic cap, with a stainless steel support at the bottom. The packed material was randomly placed(packed bedheight: 17 cm). A space must be kept between the support and the bottom of the tower to facilitate the entry of gas into the absorption unit. The cap covering the tower had a coil spring and O-ring gasket to ensure a hermetic seal. The top support was held in placeby means ofthe coil spring when the tower cover was closed, thus avoiding displacement of the packed material.The absorbent was introduced through the cover inlet using a flow distributor. This mechanical element ensured that the liquid wet all the packed materialequally.
- Gas control system: the biogas generated in the anaerobic digester was collected in Tedlar bags and subsequently sent to the packed tower using a vacuum pump. A flow regulator controlled the flow rate.
- Liquid control system: the absorbent was regulated by means ofa peristaltic pump.
- Packed material: Two different types of random packed materials were tested.Their main characteristics are givenin Table 2. One of them, helical packed material (“HPM”),was made of plastic and is mainly used for wastewater treatment[16]. The other type, Raschig rings (“RR”), was made of borosilicate glass and is commonly used in packedbedabsorption towers.

Table 2. Main characteristics of the two packed-bed materials used in the absorption packed tower.

Type of packed material	Material	Height (mm)	Diameter (mm)
HPM	PVC	9	7
RR	Borosilicate glass	9	9

Process monitoring

Both batch and continuousabsorption experiments were monitoredby measuring the composition of the biogas before and during the upgrading treatment. The CO_2 concentration was thus known throughout the experiments. Two devices were used forthis purpose:

- An Agilent Technologies gas chromatographer (model: 7890A), equipped with a molecular sieve 13X 80/100 3 fits per 1/8”, a Porapack-N 80/100 column (10 fits per 1/8”) and a thermal conductivity detector.
- A Geotech portable gas analyzer (model: Biogas Check), which had the advantage of providingfaster measurements than the chromatographer, which is especially important in continuousabsorption experiments.

The results obtained from both devices were similar, as verified by measuringthe same biogas samples.

2.4 Experimental procedure

Batchexperiments

The synthetic biogas was pumped from the Tedlar bags to the experimental system. In the gas washing bottle, biogas bubbled into the absorbent (250 mL) transferring CO_2 to the liquid phase. Samples of the upgraded biogas werecollected todetermine its composition. The four types of absorbent were tested using two different concentrations (15% and 30%), in agreement with the literature[10,17]. A total of 12.24 L of biogas were treated in each experimentfor one hour.

Continuousabsorptionexperiments

Based on the results of the batch experiments, the best absorbent was subsequently used in a continuous absorptionprocessin which the gas and the liquid were in counter-current contact. This setupresults in the highest absorption rate [18].

Experiments were carried out with and without recirculation of the absorbent (1L). When recirculating, the liquid exiting the packed tower was returned to the solvent container and mixed with the rest of the solution usingagitation.Tedlar bagswere used to collect the upgraded biogas. Throughout the experiments, the Tedlar bags used to collect the upgraded biogas were substituted every five minutesin order to measure the composition of the gas.

Different ratios between the volumetric flow of the absorbent liquid and the biogas (L/G ratio) were tested.The objective was to find an optimum range for the L/G ratio that involved the lowest consumption of the absorbent. So that the results are not affected by the variability in biogas composition, the experimental data is given as follows in order to compare the experiments thus carried out:

- The data is plotted as C/Co versus the volume of treated CO_2.Co and C refer respectively to the concentration before and after the biogas upgrading process.
- The absorption experiment was considered complete when a C/Co = 0.10 was reached.
- The time until C/Co = 0.10 was reachedis referred to as$t_{0.10}$.

3. Results and discussion

3.1 Batch experiments

Table 3shows the results obtained in the batch experiments for the four absorbents testedat two different concentrations. The composition of the upgraded biogas is also given.

Table 3. Results of the composition of the upgraded biogas and the absorption capacity of MEA, DEA, MDEA and PEGDME obtained in batch experiments

Absorbent	**Concentration**	**mg retained CO_2/g absorbent**	**Upgraded biogas**	
			%CO_2	**%CH_4**
MEA	15%	185.5	5.74	94.26
DEA		146.8	13.83	86.17
MDEA		151.2	14.43	85.57
PEGDME		86.5	29.33	70.67
MEA	30%	84.0	3.28	96.72
DEA		67.3	14.66	85.34
MDEA		77.1	19.16	80.84
PEGDME		42.5	24.52	75.48

These preliminary experiments revealed MEA to be the absorbent with the highest absorption capacity,as it retained more CO_2using the same volume of absorbent.Moreover, ahigher concentration of absorbents in the liquid phase did not seem to imply a higher retention capacity. In fact, the best results in this respect were found using a 15% concentration.

3.2 Continuousabsorption experiments

Based on the results of the batch experiments, the continuous absorptionprocess wastested using MEA as absorbent. Corrosion played an important rolein adjusting its concentration for the experiments. First,a 15% concentration was tested without recirculation, using identical liquid and gas flows (L/G ratio = 1.0). As expected, all the CO_2 was removed from the biogas. However, MEA consumption was very high and corrosion effects were rapidly detected in some parts of the equipment. The experiment was repeated halvingthe MEA concentration, obtaining similar results.

Taking these findings into account, all the continuousabsorptionexperiments weresubsequently carried out recirculating the absorbent and using a lower concentration (5% MEA) to prevent damage to the equipment. Different L/G ratios were tested usingthe two types of packed material. Aroonwilas et al. [17] note that not only the liquid load has an impact on CO_2 absorption efficiency, although it also varies from packing to packing, depending on geometric features.

In order to determine the optimumL/G ratio, the variation in the CO_2 content of the biogas (C/Co) throughout the experimentswasplotted against the volume of CO_2 removed. Figures 1 and 2 show the results for HPM and RR, respectively. Although these two packed materials were very different in terms of material and geometry, no relevant differences were found. In fact, the optimum L/G ratio seemed to fall within the 0.9-1.2 range for both materials.

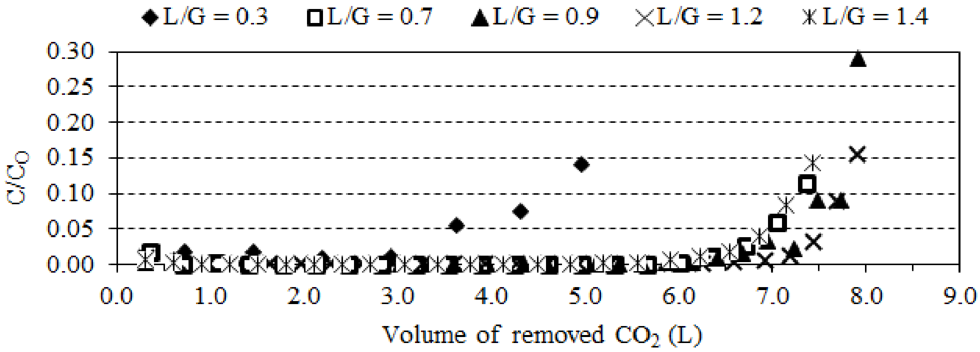

Fig1.Variation in CO_2 concentrationversus the volume of CO_2 removed from biogasin a continuous absorption process using HPM and recirculating a 5% MEA solution

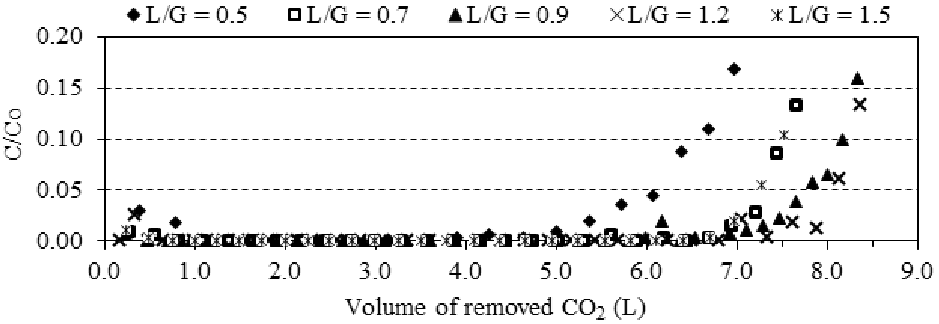

Fig 2.Variation in CO_2 concentration versus the volume of CO_2 removed from biogasin a continuous absorption process using RR and recirculating a 5% MEA solution

Table 4 provides the reductions in CO_2 in the biogas obtained for each L/G ratio and packed material. In general,higherreductions were obtained when using RR, though with minor differences. For each tested L/G ratio, the total volume oftreated gasbefore reaching $t_{0.10}$was known, as well as the composition before and after the upgrading process. Therefore, an average concentration of CO_2 can be estimated for the totalvolume of upgraded biogas (Table 4), falling within the 0.2-1.5% CO_2 range. The minimum concentration was met for the L/G ratio closest to the optimum. One possible application of methane-enriched biogas is injection into thenatural gas grid. Quality requirements in this respect differ between countries and even between single grid sections within one country [19]. In Spain, for instance, the limit value is 3% CO_2[20], whereas in Austria andSweden,it is 2% CO_2[21]. Another possible application is as vehicle fuel, in whichCO_2-N_2specifications are 1.5-4.5% [22].

Figure 3shows the correlation between the L/G ratio and MEAconsumption for both of the packed materials under study. MEA consumption was calculated considering the volume of absorbent employed and the duration of the experiments ($t_{0.10}$). A quadratic correlation fitted the experimental data and gave a theoretical optimum L/G ratio in the 1.05-1.06 and 1.07-1.11 ranges for HPM and RR, respectively. The lowest absorbent consumption was found for the optimum L/G: 6.1-6.2 g MEA/L removed CO_2.

Table 4.Reduction inCO_2 and mean concentration of the upgraded biogas for $t_{0.10}$ obtained in the continuousabsorption experiments

Packed material	**L/G ratio**	**$t_{0.10}$ (min)**	**CO_2 reduction (%)**	**CO_2 in the upgraded biogas up to $t_{0.10}$ (%)**
HPM	0.3	32	96.2	1.51
	0.7	104	98.9	0.41
	0.9	141	98.6	0.42
	1.2	121	99.4	0.22
	1.4	111	97.3	0.97
RR	0.5	88	98.2	0.58
	0.7	136	99.3	0.22
	0.9	180	99.2	0.27
	1.2	182	99.4	0.19
	1.5	140	99.2	0.30

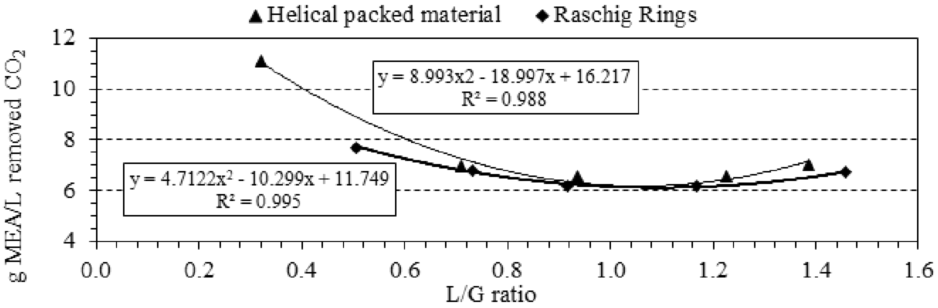

Fig3. Quadratic correlation between MEA consumption andthe L/G ratio in a continuous absorption process using HPM and RR as packed-bed materials

Tippayawong and Thanompongchart [23] also tested different absorbents ($Ca(OH)_2$, NaOH and MEA) in a packed tower to upgrade biogas. Although they reported the best resultswith the amine using a L/G ratio = 1, they did not obtaina 0% CO_2 biogas, probably due to the low MEA concentration employed (0.6%). In fact, the lowest C/Co ratiothey obtained was 0.15. Other authors, Lin and Shyu [10] and Aroonwilas et al. [17],obtained better resultsusing higher concentrations of MEA (10-30%and 18%, respectively).However, the gas streamthese authors used did not contain methane; it was a synthetic mixture of CO_2–N_2 and CO_2– air, respectively. According to their data and graphs, MEA consumption in the experiments carried out by Lin and Shyu [10] using 10%MEA was approximately 12 g MEA/L until reaching $t_{0.10}$.Using 5% MEA, a L/G ratio = 2 and a 1 L/min gas flow with 40% CO_2,Bidart et al. [8] obtained 101.6 g MEA/L treated CO_2. This consumption increased when using MEA concentrations of 10% and 15%. These results show the importance of optimizingthe L/G ratio and the MEA concentration, as a higher concentration does not always imply a reduction in absorbent consumption.

4. Conclusions

Chemical absorption is an effectivemethodfor removing carbon dioxide from a gas stream.In this study, three amines (MEA, DEA and DEA) and PEGDME were tested in batch absorptionexperiments to select the most suitable to retain the CO_2 present in synthetic biogas. Results showed MEA to be the substance with the greater absorption capacity.This substance was thus usedin a continuous absorptionprocess carried out in a packed tower with random packed-bed material.The L/G ratio had a marked influence as an operational parameter on the efficiency of the absorption process, modifying MEA consumption and the quality of the upgraded biogas.

Regardless ofthe differences in geometry and material that characterise the twopacked materialsused in this study,no relevant differences were found in the results.In fact, the optimum L/G ratio for both materialsfell within the 0.9-1.2 range when recirculating a 5% MEA solution as absorbent. MEA consumption and the L/G ratio seemed to have a quadratic correlationthat supported this conclusion. Based on the fitting of the experimental data,the theoretical optimum L/G ratio fell within the 1.5-1.11 range, for which the minimum MEA consumption would be obtained:6.1-6.2 g MEA/L removed CO_2.The upgraded biogas from the experiments met the legal limits forCO_2 content to beinjected in the natural gas grid or to be used as vehicle fuel in countries like Spain, Austria or Sweden.

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