

CO₂ Removal from Biogas as Product of Waste-Water-Treatments

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Abstract. In order to satisfy the future energy demands, the development of alternative sources of energy is currently object of interest. Among all the possibilities, biogas is a renewable methane-based fuel obtainable by anaerobic digestion of different types of raw materials, including waste-waters. This gas product contains relevant amounts of methane (CH₄), carbon dioxide (CO₂) with traces of other compounds and, to be used, it needs to be purified from the components responsible of a decreasing in the combustion efficiency. On the upgrading process, the CO₂ removal is necessary to respect the Wobbe Index specification and it can be realized by various technologies in different devices. Among all the current techniques, CO₂-absorption into physical or chemical solvents in packed towers is commonly applied, but the use of gas-liquid membrane contactors represents an innovative alternative. In particular the second ones are characterized by various operational advantages, such as independent gas/liquid control, optimal load of the absorbent, no entrainment, flooding or foaming and modular and very compact devices. In this work a polypropylene hollow fiber membrane contactor was used to investigate the CO₂-absorption from a model gas mixture into aqueous solutions of monoethanolamine (MEA), piperazine (PZ), methyl-diethanolamine (MDEA) and their mixtures. The effect of reagent type and concentration was studied as well as the influence of temperature and gas composition. Experimental results show the high reactivity of MEA and PZ, capable of increasing the absorption rate in MDEA-based solvents, characterized by large loading capacity and easiness of regeneration.

Keywords: Biogas · Biomethane · CO₂ absorption · Membrane contactor

1 Introduction

Biogas is a non-petroleum-based fuel composed of methane (CH₄), carbon dioxide (CO₂) and traces of other compounds (H₂O, H₂S, NH₃, CO, O₂, N₂, syloxanes, hydrocarbons), seen as a potential solution in the current energetic-environmental scenario. This gas mixture represents a renewable resource obtainable from different types of organic materials, such as sewage sludges, agricultural and municipal wastes, by the action of various groups of microorganisms in absence of air. Anaerobic digestion is a complex biological process capable of converting an organic substrate to methane through three major steps: hydrolysis, acetogenesis and methanogenesis.

The composition of the final system depends on the nature of the initial substrate. For example, levels of methane are different in the decomposition of fat (about 70%), protein (about 63%) and cellulose (about 50%). Moreover the global process can include pretreatments and co-digestion technologies to enhance the production of methane (Andriani et al. 2014).

The application of biogas from waste-water-treatments are various, but its utilization as an alternative source of energy attracts the main part of the public attention. To be transported and used, the fuel needs to be purified from the components harmful to natural gas grid, appliances or end-users and to be upgraded to enhance the combustion efficiency. In the second case, carbon dioxide is removed to optimize calorific value and relative density, in order to respect the Wobbe Index specification. The final product, the so-called biomethane, is a gaseous fuel typically containing methane (95–97%) and small amounts of carbon dioxide (1–3%). The biogas upgrading can be realized by different techniques, based on CO₂-adsorption on solid substrates, CO₂-absorption into physical or chemical solvents, cryogenic and membrane separation or on CH₄-enrichment by biological processes (Rickebosch et al. 2011; Tippayawong and Thanompongchart 2010).

Among all these technologies, carbon dioxide scrubbing with water or basic solvents is commonly applied. The gas absorption using membrane gas–liquid contactors is regarded as a promising alternative to the conventional technologies for the removal and recovery of CO₂ from various feed streams (Gabelman and Hwang 1999). This process can offer operational and economic advantages over spray towers or packed columns. Operational advantages include independent gas/liquid control, flexible operation, optimal load of the absorption liquid, no entrainment, flooding or foaming and modular and very compact equipment.

In this work a polypropylene hollow fiber membrane contactor was utilized to absorb CO₂ from a model gas mixture into an aqueous solution. Three different reagents were selected and studied to this end: two well-known reagents, monoethanolamine (MEA) and methyldiethanolamine (MDEA), and two less common alternatives, piperazine (PZ) and PZ/MDEA mixtures. Important criteria for the selection of liquid absorbents are high reactivity with CO₂, large loading capacity, easiness of regeneration, nontoxicity, chemical compatibility with the membrane material, low vapor pressure, good thermal stability. For the various options mentioned above, the effect of reagent type and concentration has been investigated as well as the influence of temperature and gas composition.

2 Materials and Methods

Carbon dioxide and methane of more than 99.9% purity (procured by Air Liquid Italia) were used as feed gases. The absorbing reagents employed during the tests are monoethanolamine (MEA) $\geq 99\%$, piperazine (PZ) $\geq 99\%$, methyl-diethanolamine (MDEA) $\geq 99\%$, all obtained from Aldrich.

Figure 1 shows a schematic drawing of the experimental equipment. The system is continuous in the gas phase, with the gas flowing into the lumen of the hollow fibers, and discontinuous in the liquid phase.

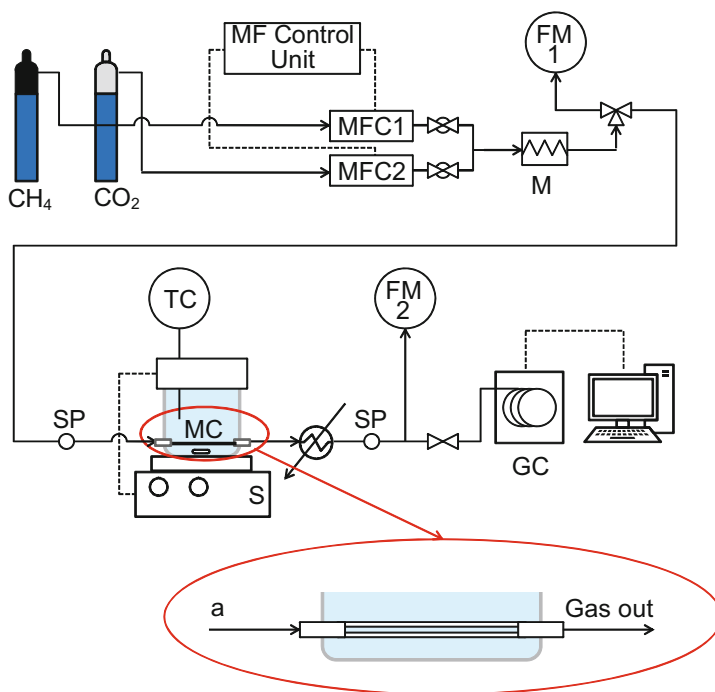


Fig. 1. Experimental setup for absorption of CO₂ in aqueous solutions. MC: membrane contactor; MFC: mass flow controller; M: mixer; SP: sampling point; FM: flow meter; TC: temperature controller; S: magnetic stirrer; GC: gas chromatograph

The absorbent aqueous solution is contained into a glass vessel that can be thermally insulated. A magnetic stirrer ensures the continuous mixing of the liquid. The liquid temperature is monitored and maintained at the desired value (within $\pm 1^\circ\text{C}$) by a temperature controller. Two side openings at the bottom of the vessel, sealed by rubber o-rings, enable the module housing. The membrane modules are built in-house and are composed of four polypropylene hollow fibers (Accurel S6/2 from Membrana, Germany),

In a typical experiment, a liquid solution at known concentration is charged into the stirred vessel, and then the gas stream is fed from compressed gas cylinders to the module at a selected flow rate. The flow rate and the composition are adjusted by means of mass flow controllers (Brooks Instrument MFC SLA 5850) that send the pure gases to a mixer and then to the module. The gas volume flow rates at the inlet and at the outlet of the contactor are measured by digital bubble meters while the compositions are continuously analyzed using an Agilent 490 microGC equipped with a capillary column PoraPLOT U and a thermal conductivity detector. The carbon dioxide absorption flux Q ($\text{mol}/\text{m}^2\text{s}$) is estimated by performing a mass balance over the contactor, based on the measured change in CO₂ flow rate between the inlet and the outlet of the membrane module, at any time:

$$Q_{CO_2} = \frac{v(C_{CO_2,in} - C_{CO_2,out})}{A} \quad (1)$$

where v is the gas flow rate (m^3/s), C_{CO_2} is the CO_2 concentration (mol/m^3) in the gas phase (at the inlet and outlet of the contactor), A is the interfacial area useful for the mass transfer.

3 Results and Discussions

MEA is commonly used as benchmark reagent as abundant literature data are available. PZ has been identified recently as a promising new reagent for CO_2 capture owing to its significant advantages: PZ-based aqueous solutions are resistant to thermal and oxidative degradation, have less volatility than MEA solutions, are not corrosive to stainless steel, are less toxic; moreover, the rate constant for the reaction of PZ with CO_2 is very high. On the contrary, MDEA reaction rate with CO_2 is lower than that of many other alkanolamines; notwithstanding MDEA has found widespread use because of its great loading capacity and its very low heat of reaction.

The mixtures of PZ and MDEA are expected to retain the high rate of the reaction of PZ with CO_2 and the low enthalpy of the reaction of MDEA with CO_2 , leading to high absorption rates and low stripper reboiler duty, a factor that usually constitutes the main cost in CO_2 removal units and is principally dependent on the heat of reaction.

As an example, a selection of the many obtained results is shown here. Figure 2 illustrates the results of the various experimental tests carried out to study the effect of single reagent concentration. CO_2 absorption flux is plotted as a function of MEA, PZ or MDEA concentration in the aqueous solution. In all cases a rise in concentration gradually increases CO_2 transfer rate. PZ behaves qualitatively like MEA, showing however a higher performance. For MDEA solutions the fluxes are one order of magnitude lower.

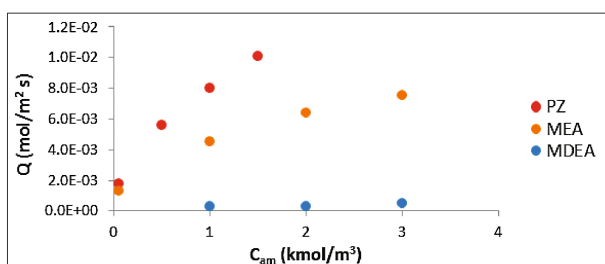


Fig. 2. Effect of single reagent concentration on the absorption flux from a biogas containing 15% v/v of CO_2 with the balance being CH_4 . $T = 25^\circ C$, $P = 1$ atm

The effect of reagent type on CO_2 absorption rate can be appreciated in Fig. 3. The PZ-based absorbents show the best CO_2 uptake efficiency. The solutions containing both MDEA and PZ achieve slightly lower performance, that get worse if the PZ percentage is reduced. These trends can be qualitatively explained if the physico-chemical parameters governing the process are taken into consideration.

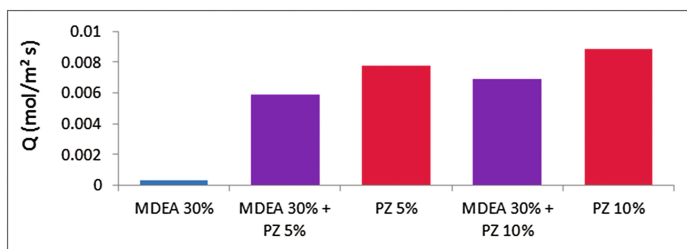


Fig. 3. Effect of liquid composition on the absorption flux from a biogas containing 15% v/v of CO₂ with the balance being CH₄. T = 25° C, P = 1 atm

The reaction rate of CO₂ with PZ may explain the higher removal efficiency of this reagent. From literature data, at $T = 25^\circ \text{C}$ $k_{\text{PZ}} = 58000 \text{ m}^3/(\text{kmol s})$ (Samanta and Bandyopadhyay 2007), whereas $k_{\text{MDEA}} = 4 \text{ m}^3/(\text{kmol s})$ (Versteeg and van Swaaij 1988), 4 orders of magnitude lower. Comparing PZ solutions and MDEA/PZ solutions, an appreciable reduction in the absorption flux can be observed for the latter, also when the two systems retain the same PZ concentration. This fact can be ascribed to the higher viscosity resulting from the MDEA addition in the PZ aqueous solution, which hinders molecular diffusion in the liquid phase. However it is not convenient to enhance overly the PZ content, because the heat of absorption for the mixed absorbent is significantly increased by adding PZ as an activator: for comparison, heats of absorption at 120° C (desorber conditions) and loading 0.4 mol-CO₂/mol-amine are ~55 kJ/mol CO₂ for MDEA and ~100 kJ/mol CO₂ for PZ (Kim and Svendsen 2011).

4 Conclusions

Amine based absorbents are particularly efficient in CO₂ removal from biogas and allow, by suitably varying the ratio between liquid and gas flow rates, to obtain bio-methane of high purity (CO₂ capture efficiency can reach 100%). Nevertheless each reagent has its own advantages and drawbacks, associated with different reaction mechanisms and different physicochemical properties. An aqueous mixture of 30 wt% MDEA and 5 wt% PZ seems a convenient option that maintains acceptable absorption rate, very high loading capacity, low heat of absorption.

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