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Experimental Study of CO_2 Absorption in a Hollow Fiber Membrane Contactor

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A new experimental setup achieved by the CEP-Paris is presented. A hollow fiber membrane (Poly-3-OP) was used as gas-liquid contactors for CO_2 removal from CO_2-N_2 feed gas stream. CO_2 is transferred from gas phase through the hollow fiber membrane contactor into a liquid phase under condition of high or low pressure. CO_2 concentration is measured inlet and outlet the module by gas chromatograph. CO_2 removal efficiency was given for chemical solvents monoethanolamine (MEA), N-methyldiethanolamine (MDEA) and promising blend of methyldiethanolamine and triethylene tetramine (MDEA+TETA) will be tested.
The results show that an increase of solvent's flow lead to an increase of CO_2 removal efficiency which is appreciably the same as well in the case of MEA as in that of MDEA+TETA when gas flow is lower than 20L/h. Effect of CO_2 inlet mass percentage on removal efficiency depends on the solvents used. An important increase of CO_2 removal efficiency is reached by using MDEA+TETA solutions as solvents, as well as MEA under specific operating parameters.

Introduction

This study focuses on the evaluation of an innovative gas-liquid membrane contactor based on hollow fiber having a dense outer skin. The innovative system will promote a fast and selective CO_2 gas transfer and simultaneously avoid the liquid phase transfer through the membrane barrier for a large range of pressure and temperature. This is dense skin's role which allows having non-wetted conditions and so the best transfer (Wang and al., 2005). Moreover the contactor design will be able to operate both for CO_2 precombustion capture and CO_2 postcombustion capture, using either physical solvents or chemicals one.
Experimental setup allows working in continuous absorption-desorption circuit to minimize solvent's cost (Kosaraju and al., 2005; Lu and al., 2007).
MEA, which is a primary alkanolamine, is used currently to remove CO_2. However, MEA solvent has a low absorption capacity for CO_2; and the CO2 absorption capacity of MEA solvent is easily degraded by the presence of SO and O in the flue gas. Oxygen is capable of oxidizing MEA solvent, and SO may react with MEA solvent to form

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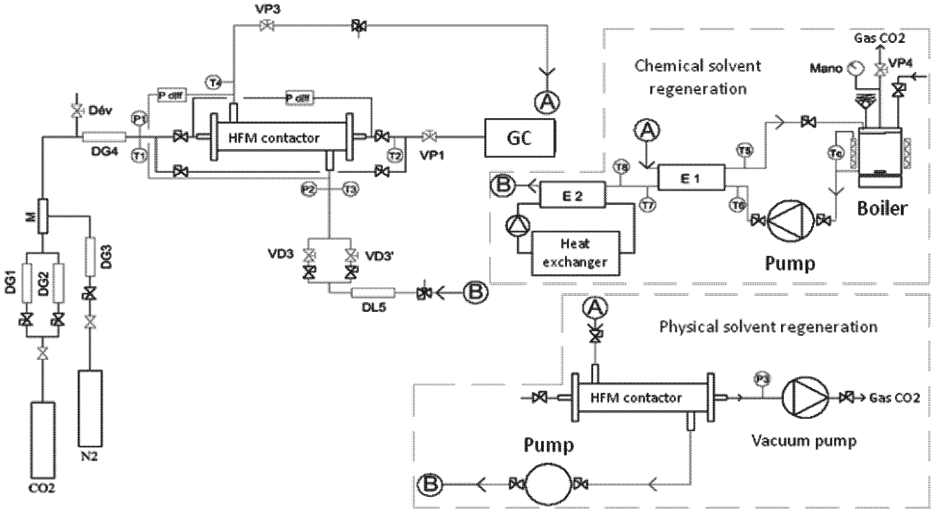
irreversible by products thus reducing the reaction rate of the absorption process as well as the MEA solvent CO absorption capacity. Besides, it also makes the solvent more difficult to be recovered. The problems associated with MEA solvent suggested that future research efforts should be directed toward developing better solvents for removal of CO_2.

Recently, in our laboratory, we focused on the development of a new solvent based on a blend of N-methyldiethanolamine (MDEA) and triethylene tetramine (TETA). The addition of small amounts of TETA leads to a high increase in the CO_2 absorption rates (Amann and Bouallou, 2008). An activator allows an improvement of CO_2 removal efficiency (Lu and al., 2006; Van Loo and al., 2006) and reduced regeneration's costs.

1. Experimental Section

1.1 Experimental setup

A schematic diagram of the experimental setup for performance evaluation of gas-liquid membrane contactor is provided in Figure 1. A gas stream of CO_2-N_2 is used in order to simulate stack effluents. N_2 doesn't react with alkanolamines used so only CO_2 removal efficiency by alkanolamine is measured.



CPG (gas chromatograph) ; DG (thermal mass flow controller) ; DL (coriolis liquid flow controller) ; Dév (pressure's plug) ; E (heat exchanger) ; HFM contactor (hollow fiber membrane contactor); M (CO_2-N_2 mixture) ; P (pressure controller) ; T (temperature) ; VD3 et VD3' (liquid flow control valves) ; VP1 (gas pressure control valve) ; VP3 (liquid pressure control valve) ; VP4 (boiler pressure control valve).

Figure 1: Schematic diagram of the experimental setup.

Membrane module is composed of 210 hollow fibers which are covered with a dense outer skin. This dense skin allows keeping the non-wetted condition necessary to have the best removal efficiency (Wang and al., 2005). Gas stream is introduced in the lumen side of fibers (Lu and al., 2005 and 2006) in counterflow mode in order to have the best removal efficiency (DeMontigny and al., 2006; Wang and al., 2005).

CO_2 transfers from gas mixture in the lumen side through the membranes pores into liquid in the shell side where it is absorbed by alkanolamine aqueous solution. CO_2 concentration is measured outlet of the module by gas chromatograph. A by-pass system allows also knowing exactly CO_2 concentration inlet of the module.
Then loaded solvent is regenerated. In a first stage, loaded solvent is steered in a heat exchanger where it is heated. In the second stage, it entered in a boiler and is hot-regenerated. Then solvent is cooled by two heats exchangers. In the first exchanger, the heat is used to heat loaded solvent outlet of the module. In the second exchanger, water is used to cool regenerated solvent. Finally, solvent enters in the module for a new absorption-desorption cycle.

1.2 Preparation of alkanolamine aqueous solutions

Water and amines are degassed independently and aqueous solutions are prepared under a vacuum. Accurate weightings of the flask before and after the transfer yield the mass of solution. The liquid phase volume was calculated using the density for the aqueous solutions of amines.

1.3 Operating procedure

Five steps are necessary to achieve each experiment:

- At the beginning, the circuit is evacuated before the transfer through a vacuum pump. This is necessary to avoid any tracks of air bubbles which could negatively influence CO_2 removal.
- Then alkanolamine solution is introduced in the boiler (which is not initially heated) before being sent in the circuit for given flow.
- Gas is injected and thanks to a by-pass system, CO_2 concentration inlet in the module is measured every 10 minutes by gas chromatograph. Steady state is reached at the end of 30-45minutes (Lu and al., 2006).
- Then, by-pass system tips up in order to allow the measure of CO_2 concentration outlet the module by gas chromatograph. Temperature in the setup must be equal to ambient temperature for solvent inlet in the module and around 383 K at the boiler.
- At the end of experiment, gas mixture and liquid solvent are emptied of the setup which is cleaned with ethanol solution.

2. Results and discussion

In order to study CO_2 removal for post-combustion application, aqueous chemical solvents solution MEA, MDEA and a promising blend of alkanolamine MDEA+TETA were investigated. We have conducted a series of experiments. Experiments are achieved with Poly-3-OP membranes and results obtained related to the influence of various parameters on CO_2 removal efficiency. This removal efficiency is evaluated by measuring CO_2 concentrations inlet and outlet the module using gas chromatography and it is given by:

$$\eta = \frac{\left(C_{CO_2}^{in} - C_{CO_2}^{out}\right)}{C_{CO_2}^{in}} \text{ x } 100$$

Where $C_{CO_2}^{in}$ and $C_{CO_2}^{out}$ are the CO_2 concentration in the gas stream inlet and outlet of hollow fiber membrane contactor.

2.1 Liquid flow influence on removal efficiency

For experiments, the CO_2 concentration used is of 5 mass percent.

Figure 2 represents comparison between removal efficiency for two liquids flows (2.29 and 6.89L/h) and for different mass concentration (MEA=20%wt., MDEA=50%wt. and MDEA+TETA=(18+6)%wt.).

It shows that the more solvent flow rises, the more CO_2 removal efficiency rises at the same gas flow. Thus, CO_2 removal is more effective.

However, Figure 2 shows also that for the values of gas flow higher than 30L/h, the removal efficiency decreases when blend of MDEA+TETA is used. This decreased is noted for values of gas flow higher than 40L/h when MEA is used.

So for high gas flow, mass transfer in the liquid solvent becomes limiting factor of CO_2 absorption.

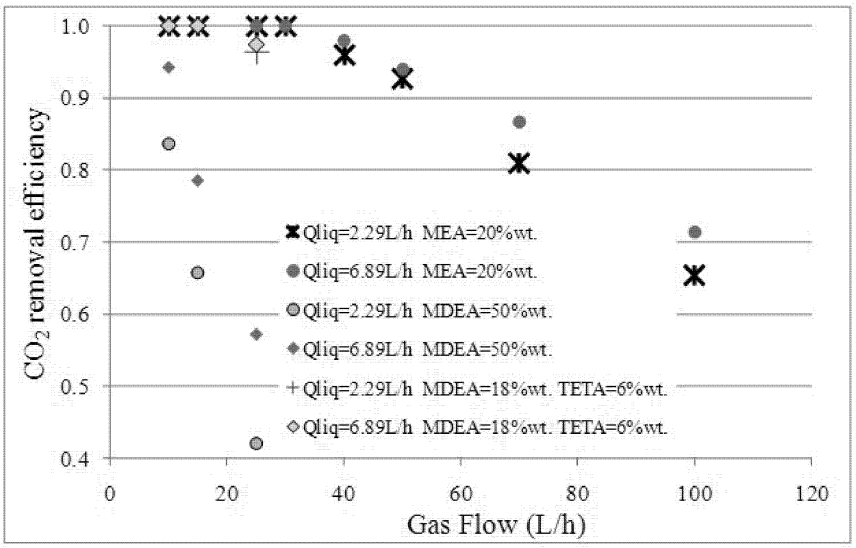


Figure 2: Liquid flow influence on CO_2 removal efficiency; CO_2=5 %wt.

2.2 Influence of CO_2 and alkanolamines mass fractions on CO_2 removal efficiency

Experiments have been achieved in the range of 5 - 15%wt for CO_2 mass fraction. And for 2.29L/h as liquid flow.

Figure 3 shows that removal efficiency is the same order of magnitude for the two CO_2 fractions tested (5%wt. and 15%wt.) for well defined values of the flows. Thus, for MDEA+TETA and MEA, CO_2 removal efficiency is equal for gas flow lower than 15L/h; moreover removal efficiency decreases for high CO_2 mass fraction.

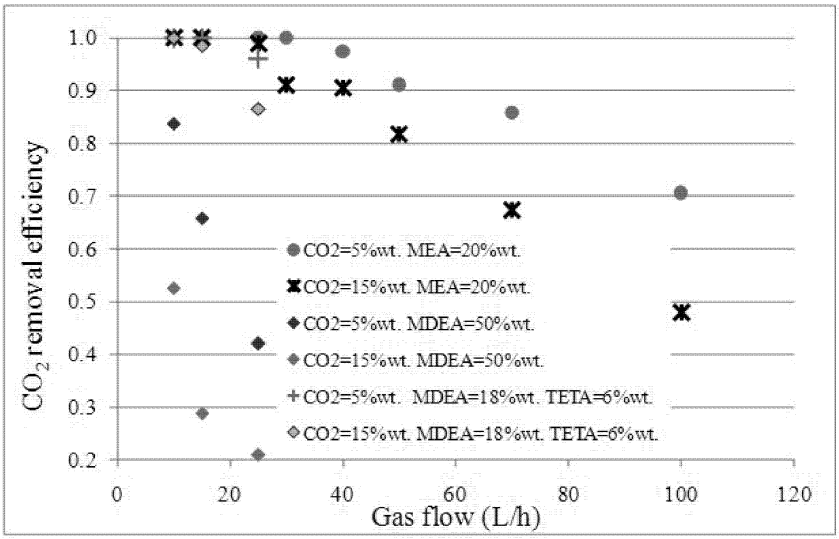


Figure 3: CO_2 and alkanolamine mass percentages on CO_2 removal efficiency; Qliq=2.29 L/h.

Figure 4 shows the influence of MDEA mass fraction on MDEA+TETA mixture. It shows also CO_2 removal efficiency with this alkanolamines blends compared to reference solvent which is MEA. The same removal efficiency is observed when we use MEA or MDEA+TETA (18+6) %wt. and for gas flows lower than 20L/h. The addition of small amounts of TETA leads to a high increase of CO_2 removal efficiency, at given gas flow. So it would be necessary to respect a ratio between MDEA and TETA.

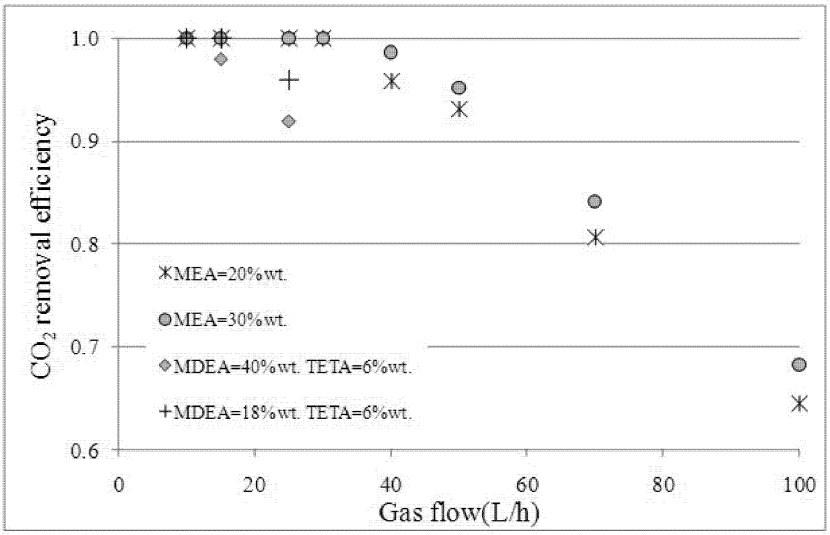


Figure 4: Influence of alkanolamine mass percentage on CO_2 removal efficiency

Conclusion

The new experimental setup achieved by the CEP-Paris allows conducting series of fundamental experiments on hollow fiber gas-liquid contactors in the CO_2 – MEA and CO_2 – MDEA-TETA systems. Fibers have a dense outer skin and our experiments validate that contactor is used under non-wetting condition.

Results confirm that TETA allows rising chemical reaction kinetics of CO_2 absorption in MDEA+TETA blends against MDEA. But, CO_2 removal efficiency is equivalent for MEA and MDEA+TETA for low gas flow condition (lower than 20L/h).

Experiments confirmed that flow characteristics of liquid in hollow-fibers are responsible of low mass transfer in the liquid phase which is one of limiting factor for CO_2 absorption.

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