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Study of an innovative gas-liquid contactor for CO_2 absorption

E. Chabanon[a], C. Bouallou[a], J.C Remigy[b], E. Lasseuguette[b], Y. Medina[b]
E. Favre[c], P.T. Nguyen[c], D. Roizard[c]

[a]*Centre Energétique et Procédés (CEP) MINES ParisTech, 60 boulevard Saint Michel 75006 Paris, France*
[b]*Laboratoire de Génie Chimique (LGC) Université Paul Sabatier, 118 route de Narbonne 31062 Toulouse, France*
[c]*Laboratoire Réactions et Génie des Procédés (LRGP UPR 3349-Nancy Université), ENSIC-BP 451, 1 rue Grandville, 54001 Nancy Cédex, France*

Abstract

The absorption of CO_2 from a CO_2/N_2 mixture is investigated using a membrane gas absorption process. In order to avoid any wetting problem and maintain optimal the removal efficiency, composite membranes, with a porous support coated by a dense layer, are used. Two composite membranes are studied: Oxyplus® and a polypropylene (PP) porous fiber coated by poly(1-trimethylsilyl-1-propyne) (PTMSP). The influence of some parameters on the CO_2 removal efficiency is explored.
A lower removal efficiencies is obtained with a PP-PTMSP fiber compared with Oxyplus® because of a PTMSP layer thickness four times larger than the dense layer of Oxyplus® fibers. Indeed, this dense layer is the key parameter which controls the membrane resistance. Experiments achieved validate the resistance of the membrane to the wettability. Increasing the liquid flow raises the removal efficiency of at least 5 %. This one is higher than 90 %. In the Oxyplus® module case, similar removal efficiencies are obtained, around 99 %, with the blend of methyldiethanolamine and triethylene tetramine (MDEA+TETA) and with monoethanolamine (MEA) for gas velocities lower than 0.84 $m.s^{-1}$. A 363 K regeneration temperature of liquid phase and 2 bar is sufficient to maintain a 90 % CO_2 removal efficiency.
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Keywords: Composite membrane, PTMSP dense layer, continuous CO_2 absorption-desorption cycles

1. Introduction

Reduction of greenhouse gas concentration in atmosphere, especially CO_2, is one of the great aims of the XXIth century. The capture is the most expensive step of the capture storage chain (CCS). And it has been the object of many projects developed during the last two decades. Thus, hollow fiber membrane contactors (HFMC) have been investigated as an alternative processes to

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packed columns [1, 5]. Indeed, the HFMC interfacial area is easily known and remains constant. Thus, the process is easier to scale-up because it does not depend on the operating conditions such as the temperature or the flow rate. The HFMC is a compact process which should help to reduce both absorber and stripper units size by 65 % [11, 16]. The gas and the liquid phases are controlled independently. Thus, the operational flexibility is higher for the HFMC than the packed columns. Nevertheless, HFMC is not a selective process by itself [1-5], that is why it is combined with a chemical absorption in case of the postcombustion capture.
The liquid phase is generally an aqueous solution of alkanolamine, mainly MEA solutions. Thus, it is the liquid phase and especially reaction with CO_2 which is the driving force of the mass transfer. Moreover, the conventional microporous fibers are very sensitive to pores wetting by the liquid phase. The membrane wetting leads to a decrease of the removal efficiency [6-10]. This is why composite dense membranes have been investigated. They avoid the pore wetting by using a porous support coated by a dense layer which is totally impermeable to the liquid phase and does not react with it.

2. Experimental section

A commercial composite membrane, commercialized by Membrana (Oxyplus®), is used as reference. A dense outer layer in polymethylpentene (PMP) coats a support of polypropylene (PP). Results obtained are compared with a composite membrane developed by LGC and LRGP. A support of PP is coated by a dense outer layer of poly(1-trimethylsilyl-1-propyne) (PTMSP), (PP-PTMSP). The support is a microporous hollow fiber also commercialized by Membrana (Oxyphan®). Hollow fiber modules have been prepared at the LGC at a laboratory scale. Table 1 presents the geometrical characteristics of membrane modules which are studied.

Table 1: Data on hollow fiber modules

	Oxyplus® 210	Oxyplus® 290	Oxyplus® 463	Oxyplus® 579	PP-PTSMP
Number of fibers	210	290	463	579	210
Shell i.d. (m)	0.013	0.013	0.013	0.013	0.013
Fiber o.d (μm)	380	380	380	380	385
Fiber thickness (μm)	90	90	90	90	52.5
Layer thickness (μm)	~0.5	~0.5	~0.5	~0.5	2.5
Support thickness (μm)	~86.5	~86.5	~86.5	~86.5	50
Fiber Length (m)	0.240	0.205	0.143	0.120	0.286
Interfacial area (m^2/m^3)	0.75	1.21	2.77	4.12	0.64
Packing fraction, ϕ	0.18	0.25	0.40	0.50	0.18

The experimental set-up is shown in Fig. 1 [14]. The dense layer keeps the non-wetted condition necessary to have the optimal removal efficiency [11]. The gas stream is introduced in the lumen side of fibers [12, 13] in counter-current flow to have the optimal removal efficiency [6, 11]. CO_2 transfers from CO_2/N_2 mixture through the membrane into the liquid in the shell side where it is absorbed. The CO_2 concentration is measured at the outlet of the module by gas chromatography (GC). A by-pass system is used to measure the CO_2 concentration inlet of the module. The loaded solvent is regenerated in a boiler and used for a new absorption-desorption cycle. 30 min are required to reach the steady state of the liquid phase before absorption starts. The CO_2 absorption follows during 50 min. Three types of liquid solvents are considered: an aqueous solution of a primary alkanolamine: MEA (20 and 30 %wt.), an aqueous solution of a tertiary alkanolamine:

MDEA (25 and 50 %wt.) and an aqueous blend developed by CEP: MDEA (18 and 25 %wt.) with a primary alkanolamine: TETA (6 %wt.) (Fig. 2).

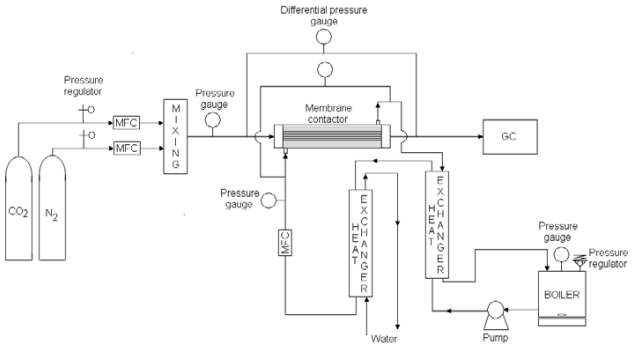

Fig. 1: Experimental set-up

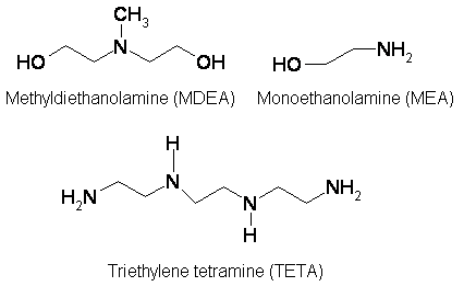

Fig. 2: Chemical solvents structures

3. Results and discussions

A series of experiments are conducted to study CO_2 removal for postcombustion capture. The influence of some parameters is investigated: gas and liquid velocities, solvent concentration, module packing fraction, layer type or the regeneration temperature. The removal efficiency is expressed as:

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

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

3.1. Influence of velocities

The influence of the velocity and the amine mass fraction are presented in Figs. 3 and 4. A 5% CO_2 volume fraction in feed gas is applied.

Results obtained with a 20 %wt. MEA (Fig. 3.) solution show a significant decrease of the removal efficiency at a low liquid velocity (0.006 $m.s^{-1}$) and a gas velocity higher than 0.50 $m.s^{-1}$. But the removal efficiency is higher than 90 %. In fact, the liquid mass transfer resistance is low for the high liquid velocity (0.017 $m.s^{-1}$) because of a lowest limit liquid layer thickness. The high liquid velocity can also lead to a better distribution of the liquid phase in the shell side.

Nevertheless, rising gas velocity reduces the removal efficiency because of a lower contact time between the two phases. This effect is more significant with MDEA solution. This is due to a lower kinetic reaction with CO_2 than the MEA.

It can be clearly seen on Fig. 4 that the higher removal efficiencies are obtained with the blend than with MDEA solutions. The TETA activator action on the CO_2 removal efficiency is demonstrated.

Regarding the alkanolamine, increasing the MDEA mass fraction in blend has no significant effect on the removal efficiency because the CO_2 mass transfer is governed by the reaction CO_2-TETA. Furthermore, the CO_2 removal efficiency measured with the blend is equivalent to the efficiency measured with MEA aqueous solutions. No significant effect is observed with increase the MEA mass fraction. But, in case of MDEA aqueous solution, increased the alkanolamine mass fraction allows rising the removal efficiency. This is because a higher MDEA quantity is

free to react with CO_2. A raise by two of the MDEA mass fraction raises the CO_2 removal efficiency by a factor of 1.5.

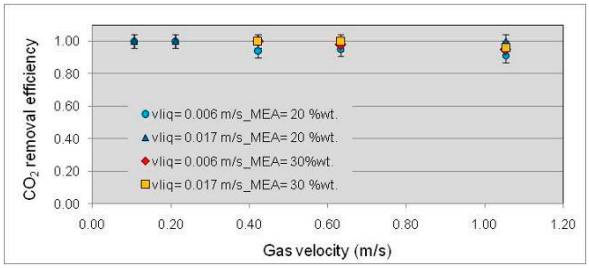

Fig 3: Influence of the gas and liquid velocities on the CO_2 removal efficiency with MEA, Oxyplus® 210 module, CO_2= 5 %, T = 295 K, P = 200 kPa.

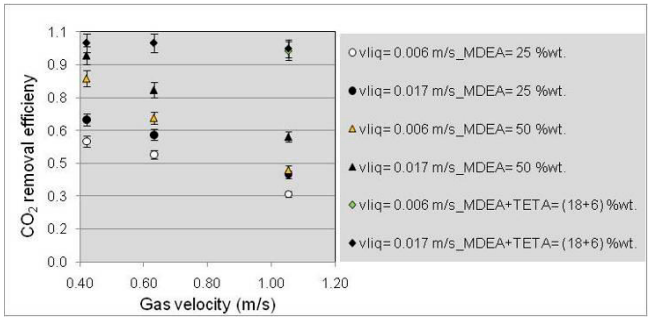

Fig 4: Influence of the phase velocities on the CO_2 removal efficiency with MDEA and MDEA + TETA, Oxyplus® 210 module, CO_2= 5 %, T = 295 K, P = 200 kPa.

3.2. Influence of packing fraction

The same liquid cross section for all modules is required to study influence of the packing fraction on the CO_2 removal efficiency. Experiments are conducted with a 5% CO_2 volume fraction in the gas phase and a 1.05 $m.s^{-1}$ gas velocity. Two liquid phases (a 30%wt MEA solution and a (18+6) %wt MDEA+TETA solution) and two liquid velocities (0.006 and 0.017 $m.s^{-1}$) are investigated. The modules characteristics are presented in Table 1.

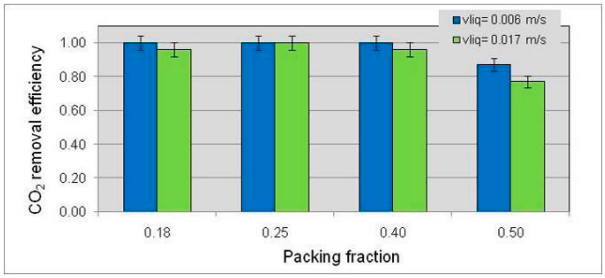

Fig.5: Influence of the module packing fraction on the CO_2 removal efficiency, Oxyplus® modules, liquid phase: MEA= 30%wt., T = 295K, P = 200 kPa

Results obtained (Fig. 5) for a packing fraction between 18 and 40 % allows having CO_2 removal efficiency higher than 90 %. But, if the packing fraction is higher than 40 % then the removal efficiency decreases. This can be explained by the creation of preferential channels around fibers bundles which decrease the overall mass transfer coefficient and the removal efficiency. These results are confirmed by results obtained with the blend of alkanolamines presented in Fig.6.

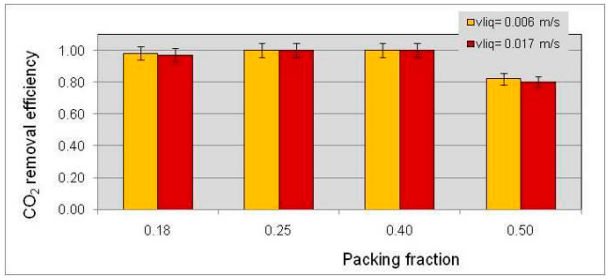

Fig.6: Influence of the packing fraction on the CO_2 removal efficiency with blend , Oxyplus® modules, liquid phase: MDEA+TETA= (18+6) %wt., T = 295K, P = 200 kPa

3.3. Influence of CO_2 fraction in the gas phase

Two CO_2 volume fractions (5 and 15 %), a 0.006 $m.s^{-1}$ liquid velocity and three liquid phases (MEA, MDEA and MDEA+TETA) are considered.

The CO_2 removal efficiency is equivalent for a gas velocity range from 0.40 to 0.9 $m.s^{-1}$ for both MEA and MDEA+TETA liquid phase (Fig. 9) and whatever the CO_2 volume fraction. A gas velocity higher than 0.9 $m.s^{-1}$ leads to a reduce of the CO_2 removal efficiency which is more significant for a 15 % CO_2 volume fraction. But the results are still equivalent for MEA and MDEA+TETA solutions; the CO_2 removal efficiencies are higher than 80 %.

Regarding MDEA aqueous solution, the removal efficiency is higher for the lower CO_2 volume fraction due to a lower kinetic reaction between CO_2 and MDEA. But for both CO_2 volume fraction used, the removal efficiency decreases with the raise of the gas velocity (Fig. 7).

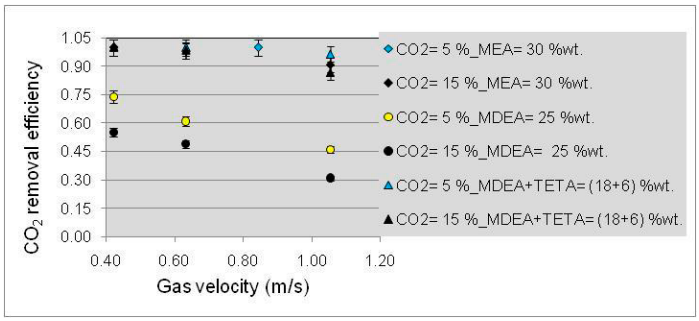

Fig.7: Influence of the feed CO_2 volume fraction on the removal efficiency, Oxyplus® 210 module, T = 295 K, P = 200 kPa, v_{liq}= 0.006$m.s^{-1}$.

3.4. Influence of regeneration temperature

Experimental set-up allows measuring continuous absorption-desorption of CO_2 cycle. Influence of the regeneration temperature on the removal efficiency is investigated. A 30%wt. MEA solution beforehand loaded with CO_2 is used as liquid phase. For 7 hours, CO_2 absorption-desorption is measured by determination of carbonatation ratio, which is the amine fraction reacting with CO_2, using a correlation presented by [15]:

$$\alpha = 0.28315\,pH - 0.005663\,(T - 273.15) - 0.021375\,(w_{MEA} - 12.1046) - 3.33843 \quad (1)$$

Where α is the carbonatation ratio (-), pH is the pH of liquid phase (-), T is the liquid temperature (K), and w_{MEA} is the MEA mass fraction in liquid phase (%w/w).

A 15 % CO_2 volume fraction in the gas phase, a 1.05 $m.s^{-1}$gas velocity and a 0.017 $m.s^{-1}$ liquid velocity are considered. Three regeneration temperatures are studied: 363, 373 and 383 K.

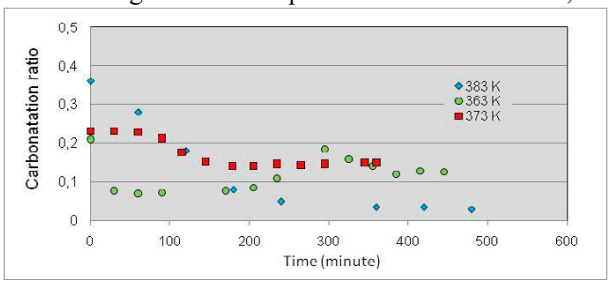

Fig. 8: Influence of the loaded liquid regeneration on the carbonatation ratio, P = 200 kPa. Oxyplus® 210 module ,MEA = 30 %wt. CO_2 = 15 %, v_{gas}= 1.05 $m.s^{-1}$, v_{liq}= 0.017 $m.s^{-1}$

Fig.8. shows the influence of temperature on the loaded liquid regeneration. A 383 K temperature allowed a complete regeneration of the liquid phase with a 0.4 initial carbonatation ratio. The removal efficiency was 89 %. A similar value is obtained for non-loaded conditions.
But a 363 or 373 K temperature leads to a decrease of the carbonation ratio up to a limit value which corresponds to the residual carbonatation ratio. In both cases, a 90 % removal efficiency is measured which is equivalent to results obtained in non-loaded conditions.
So, a 363 K regeneration temperature is enough to maintain a residual carbonation ratio and the CO_2 removal efficiency obtained in non-loaded conditions.

3.5. Nature of dense outer layer.

Two dense layers are investigated: a PTMSP layer and a PMP layer. Both have been coated on a PP support. The PTMSP is a polymer which is highly permeable to CO_2 (around 20 000 Barrer against 500 Barrer for PMP).
Fig. 9 shows a high removal efficiency for the lowest CO_2 fraction in the gas phase, similarly to Oxyplus® modules. Results obtained show that for the high gas velocities, the decrease of the CO_2 removal efficiency is more significant compared to Oxyplus® modules. This is probably due to the fact that thickness of PTMPS is around four times larger than thickness of PMP on the same support. The membrane resistance is thus governed by the layer thickness. As this is a dense material, the most important parameter is its permeability coefficient to CO_2.

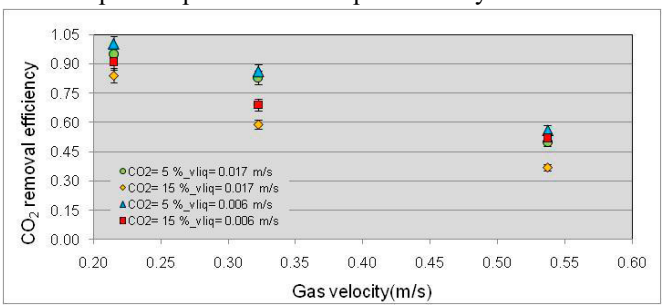

Fig.9: Influence of the CO_2 volume fraction and phases velocities on the CO_2 removal efficiency, PP-PTMSP module, MEA = 30 %wt., T = 295 K, P = 200 kPa

4. Conclusion

These preliminary results show that composite membranes can achieve promising performance for CO_2 postcombustion capture. These fibers are composed of a porous support coated by a

dense outer layer. The influence of several parameters on CO_2 removal efficiency has been studied: phase compositions, phase velocities, packing fraction and nature of layer. Three liquid phases has been used: MEA, MDEA and MDEA+TETA.
The influence of each parameter on the CO_2 removal efficiency obtained is in accordance with the results expected: higher removal efficiency for a high liquid velocity, a high alkanolamine mass fraction in the liquid phase, a low CO_2 volume fraction in the gas phase. Furthermore, CO_2 removal efficiencies obtained are equivalent for MEA aqueous solution and blend solution.
Influence of regeneration temperature is studied and has shown that 263 K is sufficient to have similar removal efficiency with fresh alkanolamine and a good regeneration of loaded liquid phase.
The resistance to wettability of composites membranes used has been validated. In fact, no wetting problem has occurred and CO_2 removal efficiency is maintained higher than 90 %.
Moreover, experiments have shown that dense layers governed the CO_2 mass transfer in the membrane. Thus, a particular attention must be brought to select the polymer which will be the dense layer and to coat porous support in order to maintain its physical-chemical properties.

5. Nomenclature

C	Concentration ($mol.m^{-3}$)
P	Pressure (kPa)
T	Temperature (K)
v	Velocity ($m.s^{-1}$)
w	Mass fraction (%w/w)

Subscripts

CO_2	Carbon dioxide
in	Inner
liq	Liquid
out	Outer

Greek letter

η	Removal efficiency (-)

Abbreviations

MEA	Monoethanolamine
MDEA	Methyldiethanolamine
TETA	Triethylene Tetramine
PP	Polypropylene
PMP	Polymethylpentene
PTMSP	Polytrimethylsilylpropyne

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