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Hollow fiber membrane contactors for CO_2 capture: from lab-scale screening to pilot-plant module conception

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Abstract

Post combustion Carbon Capture and Storage technology (CCS) is viewed as an efficient solution to reduce CO_2 emissions of coal-fired power stations. In CCS, an aqueous amine solution can be used as a chemical solvent to selectively remove CO_2 from the gas stream. The gas/liquid contact is performed within an absorption tower consisting of a packed column over which the absorption liquid and gas are flowing counter currently. The large active area required for CO_2 mass transfer efficiency from the gas into the liquid induces the use of large absorption tower, which drastically increases the cost of the process. An alternative technology to packed column is using hollow fibers membrane contactors (HFMC) as they offer attractive potentialities for intensified gas absorption processes. This holds especially for post combustion CO_2 capture application, for which a significant decrease of the size of the absorber or stripper unit could be of great interest. The aim of this work is to identify a suitable membrane material through lab-scale measurements to design a pilot-scale hollow fiber membrane contactor module.

1. Introduction

The control of CO_2 emissions to the atmosphere has become a worldwide issue over the last few years as a direct correlation between greenhouse gas emissions and climate change is now commonly accepted. An important source of carbon dioxide emissions comes from coal-fired stations where the flue gas at atmospheric pressure is predominantly composed of N_2 (≈90%) with a small fraction of CO_2 (≈10%). Although some controversy has arisen in recent literature[1], post combustion Carbon Capture and Storage (CCS) technology is one of the solution considered on a short-term schedule as it does not require deep modifications of existing power stations[2]. In CCS,

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the flue gas is usually contacted with an aqueous amine solution within an absorption tower (or absorber) at low temperatures around T≈40 °C. The solvent selectively captures CO_2 molecules to yield a targeted removal (usually ≈90%) of carbon dioxide at the bottom of the absorber. The rich solvent is then directed towards a regeneration column (or stripper) at high temperature around T≈120 °C, where vapor pressure is used to strip the CO_2 from the liquid solution. The lean absorbent is then cycled back to the absorber and the freed carbon dioxide is pressurized prior to its transport and storage. The benchmark solvent of CCS process is a 30 % wt monoethanolamine (MEA) solution where the primary amine displays a high reactivity towards CO_2 absorption. However, this process suffers from high energy requirement, corrosion and degradation[3].

The absorption zone usually consists of a packed column in which the absorption liquid and gas are flowing counter currently. A large active contact area is required for CO_2 mass transfer efficiency from the gas into the liquid thereby inducing the use of large absorption tower. An alternative technology to packed column is using hollow fibers membrane contactors (HFMC) as they offer attractive potentialities for intensified gas absorption processes[4]. This holds especially for post combustion CO_2 capture application, for which a significant decrease in the size of the absorber or stripper unit could be of great interest. The ideal material candidate for a membrane contactor application should combine a high gas permeability, achieve non wetting conditions on a long term basis (i.e. show solvent compatibility properties), be compatible with module design characteristics (i.e. glue compatibility) and show a low cost. Even though a very large number of studies on CO_2 absorption in membrane contactors have been reported, several key issues remain largely unexplored. Among them, the stability in time of the material which is used for membrane contactor application appears to be of primary importance, but poorly documented. Most studies report lab-scale experiments but on a short term basis (i.e. on hours or days scale)[5]. The aim of this work is to identify a suitable membrane material to design a pilot-scale hollow fiber membrane contactor module. We first focus on a series of lab-scale experiments performed over selected samples of different flat sheet membrane materials. These tests lead to a ranking of polymers in term of material stability and resistance to contact with MEA solution. The best material is then selected for gas/liquid absorption experiments in a lab-scale hollow fiber module where mass transfer performance is assessed. The collection of all these experimental data is currently used to design a 10 m^2 module for pilot-plant tests which will allow to capture up to 10 kg of CO_2 per hour. This work was carried out within the FP7 project CESAR.

2. Experimental section

2.1. Amine

MEA was purchased from Sigma Aldrich (Reagent grade, purity > 99%) and aqueous amine solutions were subsequently prepared using deionized water.

2.2. Membrane Materials

Lab-scale tests were operated on 4 different type of polymers, namely Polypropylene (PP), Nylon, Polytetrafluoroethylene (PTFE) and Polyvinyldene fluoride (PVDF). We chose to consider flat sheet membranes due to the largest choice of materials available in this geometry compared to hollow fibers bundle. Different membrane samples prepared from the same polymer have been considered, in order to check that the results are primarily governed by the polymer type and not influenced by the membrane preparation and structure. The set of membrane material samples used in this work is reported in table 1.

Table 1 List of flat sheet membrane materials screened in this work.

Material	Provider	Name / Ref	Pore size (µm)
PTFE	Millipore	Fluoropore	0.22
	Sartorius	Hydrophobic PTFE membrane filters	0.20
	GE Water	Tefsep	0.22
	GE Water	Tefsep	5.00
PVDF	Pall	Fluorotrans W	0.20
	Millipore	Durapore membrane filters	0.22
	Pall Gelman	Biotrace transfer membranes	0.45
	Pall Gelman	Fluorotrans	0.20
PP	GE Water	Polysep	0.10
Nylon	GE Water	Magna Nylon supported	0.10

2.3. Aging protocols

In order to study long-term aging of the membrane material, we perform several experiments where flat sheet membranes are dipped into a 30 % wt MEA aqueous solution. The aging protocols are as follow:

- A: The membranes are contacted with the MEA solution at room temperature for about 2 months.
- B: The membranes are placed into a oven and an extended contact of 1 week with MEA is performed at a temperature of T=40°C.
- C: The same protocol as B is operated at T=80°C.
- D: The same protocol as C is operated but with extended aging length (up to 12 months).

2.4. Gas permeability measurements

Gas permeability measurements have been performed on fresh and liquid exposed samples in order to possibly evaluate the solvent/membrane compatibility. The basic concept is the following: any effect of the solvent on the membrane (chemical, mechanical) should lead to modifications in the structure of the membrane and consequently in the overall gas permeability. If a very sensitive and highly reproducible method is used, significant changes of the gas permeability are observed in link with material ageing phenomena. To our knowledge, gas permeability has never been proposed to assess the membrane stability issues for membrane contactors applications. In order to determine experimentally the gas permeability, a controlled flowrate/variable pressure method was used. The set-up is depicted in figure 1.
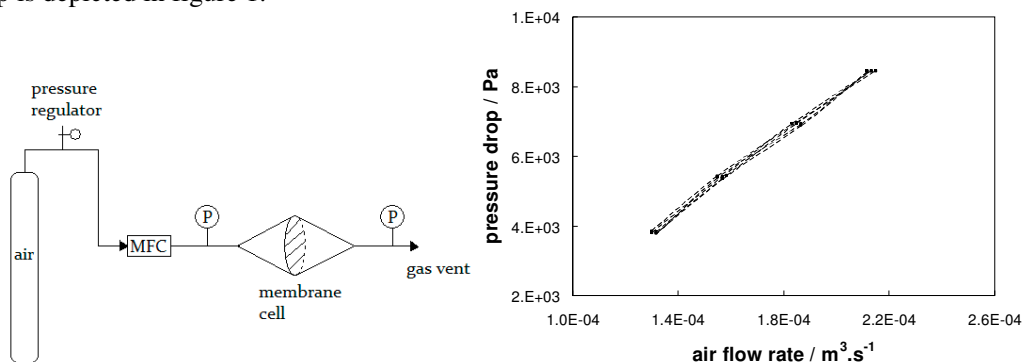

Figure 1 Gas permeability measurement set-up (left) and test of the reproducibility of the gas permeability experiments (membrane sample: PP Polysep, GE Water) (right).

Air is flowing through an open cell under steady state conditions where the membrane (diameter 12 cm) is placed on a filter holder. A pressure regulator and a mass flow controller impose the operating conditions and the pressure drop is measured. Experiments are performed on native materials and membranes in contact with MEA solution following aging protocol A. The reproducibility of the technique is excellent as can be seen on figure 1 where 5 experiments on the same sample are presented.

2.5. Contact angle measurements

In order to characterize the ability of the membrane polymer to sustain solvent-repellent conditions and to avoid penetration of the liquid meniscus into the pores, we perform contact angle measurements of water droplets on top of flat sheet membrane samples. The contact angles were measured using a PG-X goniometer. Water was pumped inside the device and a droplet was put down on top of flat sheet membranes. A built-in camera records the image of the droplet (see figure 2) and a computer software directly computes the contact angle between the surface and the droplet as well as droplet height and volume. Experiments are repeated 10 times on both sides of the membrane.
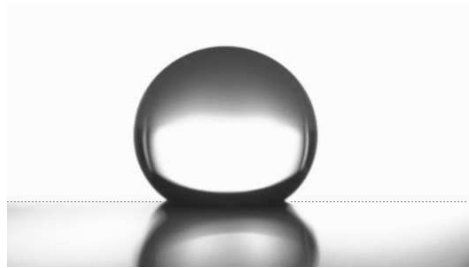

Figure 2 Snapshot of a water droplet sitting on top of a PTFE surface.

2.6.   Analysis

Different analytical methods are used to follow both the physical and chemical modification of the polymer membranes:

- Thermal Gravimetric Analysis (TGA) are performed to collect data about the thermal stability (degradation temperature) of polymers as a function of aging time. Polymer samples are subjected to a temperature rate of 5°C/min under air flow.
- Differential Scanning Calorimetry analysis (DSC) and Thermal Mechanic Analysis (TMA) are used to follow the evolution of the glass transition temperature (T_G) of the polymers. For TMA analysis, samples are subjected to a temperature rate of 5°C/min under air flow and a penetration force of 0.1 N. For DSC analysis, samples are sealed in an aluminum cell and subjected to a temperature rate of 5°C/min under inert gas flow.
- Infra Red and Raman spectroscopy are used to study chemical changes in the polymer structure. Spectra are recorded in transmission with a germanium crystal, 256 scans, for FTIR and with a 785 nm laser with a power of 400mW, 3 accumulations of 5s, for Raman.
- Sterical Exclusion Chromatography (SEC) analysis is achieved in order to study polymer chain length modification. SEC analysis are performed with DMF as solvent at 70°C, with THF as solvent at 30°C, and with TCB as solvent at 150°C. Molecular weights are measured from calibration curve using standard polystyrenes.

2.7. Mini-module measurements

A lab-scale hollow fibers membrane contactor device is used to study the stability over time and to determine mass transfer performances in a real gas absorption situation with MEA. The absorption experiments set-up is depicted in Figure 3. CO_2/N_2 mixtures are prepared using two mass flow meters (model 5800S, Brooks) and flowed on the shell side of the membrane contactor. A 30% wt MEA aqueous solution is flowed inside the fibers counter currently. The liquid flowrate is controlled by a high precision pump (HPLC type 515, Waters) and the pressure can be regulated by a valve located at the liquid outlet. The hollow fiber module is installed in a thermostated oven and an infra-red analyzer (MGA-3000 Multi-gas analyzer ADC) is used in order to measure the gas phase composition at the entrance and at the exit of the module. Care was taken to achieve steady state conditions for each measurement, reflected by a constant outlet CO_2 concentration on the gas side over time.
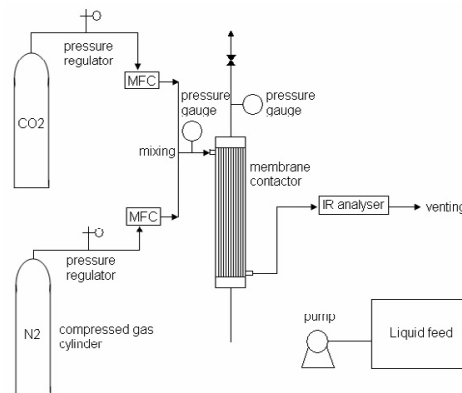

Figure 3 Absorption experiments on hollow fibers membrane contactors set-up.

3. Results

3.1. Flat sheet membrane screening

We now detail the different results obtained throughout this work, on native and aged membranes. We first report the average of contact angles obtained on both sides of native and aged flat sheet membranes (Table 2).

Table 2 Native and aged membranes contact angles averaged over the different material samples.

Material	Native	Aging		
		A	B	C
PTFE	120	120	112	112
PVDF	105	105	91	0
PP	123	121	111	111
Nylon	128	0	0	0

The different native materials display contact angles between 100° and 140°; all the membranes are therefore hydrophobic. For the same kind of material we observe small variations of the contact angle from one provider to another. After aging protocol A, all materials but Nylon display roughly the same contact angle as the native membranes. When a water droplet is put down on top of the

Nylon sample; the material is immediately impregnated with water, i.e. the polymer is now hydrophilic. When membranes samples are dipped into MEA for 1 week at T=40°C (aging protocol B), we clearly observe a general decrease of the contact angle as values are now between 90°C and 110°. PTFE and PP membranes are still hydrophobic (θ>90°) but some of the PVDF membranes have a contact angle θ<90°C and are therefore considered as hydrophilic as an increase of the contact temperature seems to enhance the aging of PVDF membranes by the MEA solution. Finally, the trend observed at T=40°C is confirmed when the membranes are aged with the MEA solution at T=80 °C (aging protocol C). Clearly, PTFE membranes are the most resistant whereas PVDF membranes are now completely hydrophilic. We also observe a stability of the contact angle for the PP membrane which seems to indicate that either the membrane is resistant or the aging is reversible.

Gas permeability measurements are performed on the series of native and aged (protocol A) membrane samples. Figure 4 shows examples of results for each type of polymer (samples from the same polymer behave in the same way).
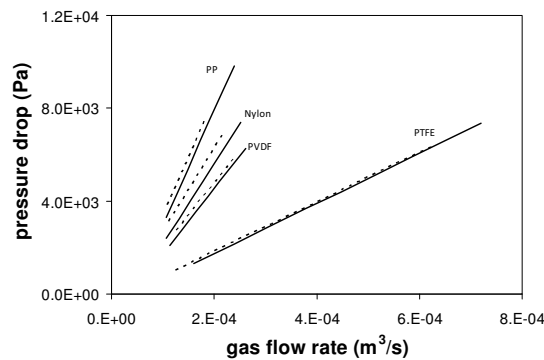

Figure 4 Gas permeability of native (solid line) and aged (protocol A, dashed lines) membranes.

PTFE native membranes show a larger gas permeability than other membrane probably due to their open structure inherited from their preparation technique based on a stretching operation. Conversely, the PP native membrane, shows the smallest effective permeability likely resulting from the small material porosity. From Figure 4, we can notice that PTFE shows a remarkable stability in contact with MEA, even after two months. A significant evolution of the PP membrane is observed after two months of contact with the solvent. This is in agreement with the observations reported in the literature on the evolution of PP membranes when exposed with MEA[5]. PVDF shows a behavior close to PP. Based on the literature review, this last result seems new since, to our knowledge, no clear observation on the degradation of PVDF by aqueous MEA solutions has been reported up to now. Nylon shows a strong degradation in contact with MEA.

Finally, the analytical methods described previously are operated on membranes following aging protocols B and D, and results are compared with those of native membranes. Both PVDF and Nylon membranes do not shown real modification after applying aging protocol B, but are no longer self-supported after two months operated under protocol D conditions at T=80°C (see figure 5). PP and PTFE membranes do not show any sign of degradation as the TGA and TMA curves as well as IR spectra of aged samples are similar to those of native samples. Aging tests on PP and PTFE membranes are still in progress to evaluate their stability on a longer period of time.

In conclusion, a systematic material screening based on different experimental characterization gives consistent results between the evolution of the contact angle, the changes in the membrane gas

permeability and the structure evolution of the 4 different polymers. In view of these results, we can conclude that PTFE is the most efficient material screened in this work and will be used as a material for hollow-fiber geometry tests.

Figure 5 Pictures of PVDF (left) and Nylon (right) membranes after 2 months operated under protocol D conditions.

3.2. Mass transfer measurements

Following the lab-scale screening tests, a series of CO_2 absorption experiments are performed on the lab-scale set-up with a PTFE module containing about 130 fibers. No liquid breakthrough over time is observed with 1 bar cross-membrane pressure and the gas absorption performance remains stable with time. Results of CO_2 absorption for two different gas velocities are shown in Table 3.

Table 3 Results of absorption experiments for PTFE module, 15% wt. CO2, 30% vol. MEA, liquid velocity $2.7*10^{-3}$ m.s^{-1}.

Gas velocity (m/s)	CO_2 capture ratio (%)
$1.31\ 10^{-2}$	99.7
$5.82\ 10^{-2}$	81.3

The CO_2 capture ratio (R) is calculated through:

$$R = \frac{Q_{in}(\%CO_2)_{in} - Q_{out}(\%CO_2)_{out}}{Q_{in}(\%CO_2)_{in}} \tag{1}$$

with Q_{in} and Q_{out}, the inlet and outlet gas flowrate and $(\%CO_2)_{in}$ and $(\%CO_2)_{out}$, the volume fraction of CO_2 at the gas inlet and at the gas outlet. A decrease of capture ratio with increasing gas velocity is logically observed, due to a smaller gas-liquid contact time. Based on the results, it is possible to determine a global rate constant K.a, which incorporates the overall mass transfer coefficient K and the gas-liquid specific interfacial area a. This lumped parameter is very convenient in order to evaluate the global absorption capacity of a given process, but its application demands several hypotheses to hold:

- the reaction is assumed to be pseudo-first order (this implies a large excess of MEA)
- K is constant
- plug-flow conditions are supposed in the gas phase (no dispersion)
- gas velocity is constant (CO_2 absorption does not significantly modify u_G)

The rate constant can be obtained through:

$$\kappa = -\frac{u_G}{L}\ln(1-\eta) \tag{2}$$

with u_G the gas velocity, L the length of the fibers and η the capture ratio. A value of $\kappa=0.52$ s^{-1} is obtained, in accordance with literature data ($\kappa=0.43$ s^{-1}[6] and $\kappa=0.40$ s^{-1}[7] for PTFE and absorption of CO_2 in MEA (5M)). Moreover, knowing the interfacial area (a=2067 m^{-1}), an overall mass transfer coefficient of $2.52*10^{-4}$ m.s^{-1} can be determined. It can be concluded from the mini-module experiments that a good stability of performances over time is achievable for PTFE membrane, with no liquid breakthrough and high efficiency.

4. Conclusions

We present a complete development of hollow-fiber membrane contactor module from flat sheet membrane screening to lab-scale mass transfer measurements. First, a series of 10 different commercially available flat sheet membrane materials, based on 4 different polymer types (PP, PVDF, PTFE and Nylon) are selected. Experimental screening tests are then performed on native and aged membranes leading to a ranking of polymers in term of material stability and resistance to contact with MEA solution. PTFE is selected for the conception of a lab-scale module. The stability of non wetting conditions and the overall absorption performances under steady state operation are determined in this module and mass transfer measurements are under way. These results have been used to design a 10m^2 pilot plant module currently operating at IFP New Energy (see figure 6). Results on this pilot module will be used to build a rigorous modeling of the process and to obtain an technico-economical estimation of hollow fiber membrane contactor efficiency for CO_2 capture.

Figure 6 Picture of the 10m^2 pilot plant module.

5. References

[1] de Coninck H. Advocacy for carbon capture and storage could arouse distrust. Nature 2010; 463, 293.
[2] Rao AB, Rubin ES. A Technical, Economic, and Environmental Assessment of Amine-Based CO_2 Capture Technology for Power Plant Greenhouse Gas Control. Environ. Sci. Technol. 2002; 36, 4467-4475.
[3] Rochelle GT. Amine Scrubbing for CO_2 capture. Science 2009; 325, 1652-1654.
[4] Mansourizadeh A, Ismail AF. Hollow fiber gas-liquid membrane contactors for acid gas capture: A review. J. Hazard. Mater. 2009; 171, 38-53.
[5] Wang R. Influence of the membrane wetting on CO_2 capture in microporous hollow fiber membrane contactors. Separation and Purification Technology 2005; 46, 33-40.
[6] Nishikawa N, Ishibashi M, Ohta H, Akutsu N, Matsumoto H, Kamata T, Kitamura H. CO_2 removal by hollow-fiber gas-liquid contactor. Energy Conversion and Mgnt 1995; 36, 415-418.
[7] Yeon SH, Sea B, Park YI, Lee KH. Determination of mass transfer rates in PVDF and PTFE hollow fiber membranes for CO_2 absorption. Separation Sci. and Technol. 2003; 38, 271-293.

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