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Experimental evaluation on the CO₂ separation process supported by polymeric membranes

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Abstract

Planar polymeric membranes with hydrophilic, hydrophobic and composite (coupled or thermowelded) structures have been prepared and tested in an experimental lab-scale plant by using different liquid absorbents (amines, carbonate, H_2O) as "carrier" with the aim to optimize the process of CO_2 separation from other gas. The effect of nature of the membranes, differential pressure between gas/liquid phases and type and concentration of the absorbent were investigated as well as the carrier transport mechanism. The best performances (in terms of CO_2 permeability) have been determined for coupled membranes. Moreover, the experimental results have shown that, between the studied carriers, the 2-etanolamine is the type of adsorbent with the greater affinity toward the CO_2 .

Keywords: CO2 separation; Facilitated transport; Polymeric membranes

1. Introduction

Carbon dioxide (CO_2) is one of the gases mostly responsible of the greenhouse effect [1]. The concentration of CO_2 in the atmosphere is, for instance, in constant increasing according to the ANPA data. In the last decade, the Italy greenhouse gases emitted in atmosphere have changed from 498 to 525 million tons with an increase of +5.2% in contrast with the reduction of the European level equal to 3.5% due, above all, to the decreasing of the emissions in Germany and England. This value is insufficient to respect the commitments foreseen by the Kyoto Protocol that had predicted for the European continent, a general reduction equal to 5.2%, within 2012 [2]. The energy production for transport, electricity and heat is essentially connected today to the combustion of different fossil fuels as coke, natural gases and derived oil products that release also CO₂ to the atmosphere. The introduction of hydrogen as a new and clean energetic vector will be, nevertheless, in the near and middle term, dependent by the development of a centralized production that will always use traditional fossil combustibles, and therefore does not resolve the problem of CO₂

production [3]. Actually, the energetically more efficient process for hydrogen production (86%) is the steam reforming of the natural gas characterized by a CO_2 emission of 70g/MJ [4]. Therefore, a future vision that hypothesizes the establishment of a hydrogen economy will be based on technological solutions that would be able to limit or eliminate the issues of CO_2 associated to the process of energy production. In this aim, a strategic role will be played by the development of highly efficient, suitable and cheap CO_2 separation processes.

The main CO_2 separation technologies from exhausted gas carbon are currently: adsorption [5,6], absorption [7,8], cryogenic method [9,10] and separation with membranes [11,12].

The first three methods are more traditional and present, above all, some limitations connected to the elevated energy consumption, elevated volumes and high costs [13]. The reasons that therefore press the research toward the membrane systems have to be sought in the technical–economic advantages that they offer [14]. Some authors [15] have found the new membrane technology systems economically more advantageous than traditional plants with management costs of \$460,000 against \$340,000. As clearly showed from literature, the polymeric membranes [supported liquid membranes (SLM)] seem to be very efficient and particu-

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larly those in polyethylene fluoride (PTFE) or polyvinylidene fluoride (PVDF) [16]. Nevertheless, literature studies have emerged that a "hybrid" system (membrane absorption) offers as advantage a consistent reduction in volume due to the lack of absorbent dragging typical for the traditional columns of absorbiment, especially when working with elevated volumes and short-contact times [17]. From those considerations, we finalized our study on the development of hybrid system, in which the membrane doesn't have the assignment to separate the CO_2 but to increase the contact surface between gas and liquid, while the CO_2 separation will be connected to the absorbent performance. In the specific case of the CO₂ separation from the combusted gases [17,18], some authors have used as carrier amine solutions, getting a good degree of separation and high selectivity values [19]. In this study, with the purpose to optimize the process of CO_2 separation, we have tested different absorbents (amines, carbonate, H₂O) by using planar membranes [20] with hydrophilic (as received by suppliers) or hydrophobic or composite structures (after specific treatments).

2. Experimental

2.1. Membrane preparation

Since earlier experiments, it has been observed that the separation process proceeded in a different rate if performed on hydrophilic membranes or on hydrophobic ones. A deeper analysis of this mechanism has evidenced that, on the samples with high hydrophilic property, the absorbent liquid floods almost the totality of the membrane pores preventing the diffusion of gas phase. Furthermore, membranes with high hydrophobic characteristics show a low degree of wet ability towards the absorbent solution even if they get the pore volume available for gas diffusion. Thus, the experimental evidences lead us to design a membrane structure based on two layers with different characteristics: hydrophobic on the side contacting with gas phase and hydrophilic in that where liquid phase has to wet.

The preparation, characterization and testing of the different typologies of membranes are described in the following.

2.1.1. Hydrophobic membrane

Hydrophobic membranes (T-PVDF) were prepared by impregnation with a PTFE solution. The impregnation procedure consists to wet the membrane just from one side, with a PTFE aqueous solution (55%), to obtain a thin layer with hydrophobic properties. The PTFE solution, after stirring, has been payed in a glass container, with a diameter of approximately 10 cm, to form a uniform layer on the bottom of the container. The hydrophilic fresh membrane was leaned against Teflon layer and was carefully stirred on it in order to obtain a uniform distribution of hydrophobic agent on one surface of the membrane, avoiding a complete immersion of it in the solution. In the next step, the impregnated membranes were dried for 1 h at T=70 °C.

2.1.2. Composite membranes

In order to have a membrane with hydrophilic surface in contact with the liquid phase and hydrophobic surface in contact with the gas phase, we prepared composite structures formed by coupling two membranes, one hydrophilic and the other one hydrophobic. These membranes have been prepared by two different techniques. An earlier group of samples (S-PVDF) have been prepared by a simple mechanical coupling of two single membranes. The second group of samples (C-PVDF) have been prepared by welding two single membranes by using a laboratory hot-press with constant pressure of 2 MPa and varying the temperature and the time of press. In particular, three different operative temperatures (80, 100 and 120 °C) have been used, while the press time was varied from 15 min to 4 h.

2.2. Characterization techniques

2.2.1. Bubble pressure

The maximum radius of prepared membranes has been determined by the Bubble Pressure method, measuring the necessary pressure that allows a gas flow (e.g., N_2) to pass in the liquid phase of the membrane.

2.2.2. Scanning electron microscopy (SEM)

The morphologic and micro structural analyses of membranes have been made with a scanning electronic microscope (SEM; Philips XI-20) using an acceleration voltage equal to 10 kV. The samples have been, before, immersed in liquid N_2 in order to facilitate the breaking and was subsequently fixed to a support and covered with a gold layer in order to reduce the accumulation of charges on the surface.

All the data that relates to the characterizations are reported in Tables 1 and 2.

2.3. Experimental facilities

In order to evaluate the performance of prepared membranes, it has been designed and realized in a lab-scale

Table 1

List of the different typologies of tested membranes with measured bubble pressure and pore radius

Sample	Treatment	Bubble pressure (bar)	Pore radius (µm)
PVDF	As received	0.200	7.09
T-PVDF	PTFE deposition	0.270	5.25
C-PVDF-1	30 min press at 80 °C	0.195	7.27
C-PVDF-2	30 min press at 100 °C	0.240	5.91
C-PVDF-3	30 min press at 120 °C	0.402	3.53
C-PVDF-4	240 min press at 100 $^{\circ}\mathrm{C}$	0.287	4.94

apparatus appropriate to carry out separation tests of CO₂ from gas mixtures. The P and I of the process are shown in Fig. 1. As it is possible to notice, such system substantially is divided in two submodules, one for the liquid phase and the other one for the gas phase. The heart of the system is the reactor, where the membrane is positioned and the two phases (gas and liquid) come in contact. The hydrophobicity of membrane allows the liquid to easily penetrate in the pores and, subsequently, to come in contact with the gas that diffuse into the largest pores of the structure. The reactor is placed inside an electrical oven (Memmert) that maintains the system under isothermal conditions. The online analytical equipment of the plant concerns in a gas chromatograph (GC 6000 Carlo Erba Instruments). A pump for HPLC (mod. HP 1100), a vacuum pump to clean the gas lines faster and a membrane back-pressure regulator to maintain the pressure of the gas phase constant complete the system.

2.4. Operative conditions and results expression

The tests have been carried out in isothermal conditions $(T=28 \ ^{\circ}C)$ by using as carrier: pure H₂O, aqueous solution of 2-ethanolamine, aqueous solution of K₂CO₃. The tests have been carried out with pure gases (N₂, CO₂, CH₄, H₂) and gas mixtures that have been, alternatively, loaded into the system, at a pressure of 15,000 Pa. The operative variables investigated in our study were the nature of membranes, type of absorbent, absorbent concentration and pressure of the gas phase.

The parameters selected to characterize the prepared membranes were permeability and the maximum radius of the pores. The permeability, indicated with R, represents the volume of the gaseous species to be separated that permeate

through the membrane, in the unit of time, with respect to a specific value of partial pressure refereed to the surface and to the thickness of the membrane. The permeability is expressed in cm³ (STP) × cm/cm³ × s × cmHg (STP: standard pressure temperatures). In our experiments, *R* has been measured both for one component flow gas and multicomponent gas mixtures.

Furthermore, the differential pressure on the membrane is correlated to the radius of the pore (r_p) by the following:

$$r_{\rm P} = \frac{2\gamma}{\Delta P} \times \cos\vartheta$$

where $r_{\rm p}$ represents the pore radius; $\gamma (72,3 \times 10^{-3} \text{ N/m for H}_2\text{O})$ is the liquid superficial tension; ϑ represents the contact angle (in this case, $\vartheta \rightarrow 0^{\circ}$ and $\cos \vartheta = 1$); $\Delta P (P_{\rm gas} - P_{\rm liquid})$ is the differential pressure.

The results obtained in our tests and expressed as the largest pore radius and permeability have been reported in Tables 1 and 2, respectively.

3. Results and discussions

3.1. Experimental characterization

3.1.1. SEM

3.1.1.1. Comparison between commercial and PTFEdeposited membranes. Fig. 2 shows the SEM micrograph of the cross-section of teflonated membrane (T-PVDF). The right side of the section corresponds to the treated area and is characterized by a zone of good homogeneity due to the thickening produced by PTFE deposition. This means that



Fig. 1. Flow sheet of the experimental apparatus.

Table 2 List of tested membranes with gas composition and kind of absorbent used for the experiments as well as measured differential pressure variations and R

Membrane	Gas	Absorbent	$\Delta P/\Delta t$ (bar min ⁻¹)	$\frac{R (cm^{3}/s)}{(cm^{2} cmHg)}$
S-PVDF	N ₂	MEA 1 M	0,00E+00	0,00E+00
S-PVDF	CH_4	MEA 1 M	0,00E + 00	0,00E + 00
S-PVDF	H_2	MEA 1 M	0,00E + 00	0,00E + 00
S-PVDF	CO_2	MEA 0.01 M	3,13E - 03	5,92E - 05
S-PVDF	CO_2	MEA 0.1 M	3,01E - 03	5,69E - 05
S-PVDF	CO_2	MEA 1 M	6,21E - 03	1,17E - 04
S-PVDF	CO_2	MEA 3 M	1,67E - 02	3,16E - 04
S-PVDF	CO_2	H_2O	5,38E - 04	1,02E - 05
S-PVDF	CO_2	K ₂ CO ₃ 0.1 M	1,48E - 03	2,80E - 05
T-PVDF	CO_2	MEA 1 M	1,45E - 03	2,74E - 05
C-PVDF-1	CO_2	MEA 1 M	4,20E - 03	7,94E - 05
C-PVDF-3	CO_2	MEA 1 M	3,66E - 03	6,92E - 05
C-PVDF-4	CO_2	MEA 1 M	2,78E - 03	5,26E - 05

the hydrophobic process produces a reduction in the membrane surface porosity with a consequent loss of surface area. As consequence of this phenomenon, we detected also a lowering of the permeation rate and therefore a decrease of permeability coefficient (R) in agreement with the data shown in Table 2.

3.1.1.2. Comparison between PTFE deposited and thermowelded membranes. The micrograph in Fig. 3 shows the cross-section of one composite structure produced in the earlier experiments (C-PDVF). The different porosity of the two faces is clearly pointed out; the hydrophilic side (to the left) shows a more porous structure with respect to the hydrophobic one (to the right). Nevertheless, the morphology relative to the surface of the membrane faces doesn't show any evident alteration; this means that the preparation process doesn't damage the surface, allowing to retain the initial porosity. The micrograph shows also that the membranes are not completely joined, as highlighted from the separation area between the two faces. This defect in



Fig. 2. SEM micrograph of the PTFE-treated membrane (S-PVDF).



Fig. 3. SEM micrograph of the composite membrane (C-PVDF).

workmanship has been avoided by adjusting the temperature and time of pressing.

3.1.2. Bubble pressure measurements

The measure of the required pressure that allows the gas flow, also called bubble pressure, in the liquid phase can supply an experimental information on the porous superficial network of composite membrane after their preparation process (thermowelding or hydrophobization). Table 1 clearly shows that higher pressures characterized small-pore radius membranes. The bubble pressure value relative to the membrane (C-PDVF 1) thermowelded at 80 °C for 30 min is lower than that relative to fresh membrane (PVDF). Even if this composite membrane showed the best result of permeability, the bubble pressure characterization did not give any appreciable values because of a poor joining that caused a swelling in the central area during such a measurement test. Instead, for the rest of other membranes, we determined a very clear correlation between the bubble pressure and $r_{\rm p}$. Particularly, the results have shown that, in the preparation of composite membrane by thermowelding, the effect of temperature and time of pressing was determinant in the resulting $r_{\rm p}$; in fact, we found that $r_{\rm p}$ decreases by increasing these two parameters as shown in Table 1.

3.2. Results of tests

The "*Facilitated Transport*" is the mechanism that allows for membranes, and particularly, supported liquid membranes (SLM), the separation of a phase, CO_2 in our specific case, from gas mixtures.

The base of such mechanism is to impregnate the membrane structure with a compound, namely, carrier, that has a strong chemical affinity with the substance which must be separated. The carrier, through its ability, will react chemically with the permeate and will generate a preferential transport of the substance across the membrane. The flow sheet of the process is represented in Fig. 4. The amount of CO_2 which can be separated as a function of some parameters, like composition of the inlet gas, permeability and selectivity of the gas in the membrane, temperature, composition of the flow of gas, permeated through the membrane, pressure and temperature.

The optimization of these parameters will lead to the improvement of the overall process.

As for the tested absorbents (amine, carbonates and H_2O), the equilibrium which exists between them and CO_2 is determined by the following reactions [21]:

$$2RNH_2 + CO_2 = RNHCOONH_3R$$
(1)

$$K_2CO_3 + CO_2 + H_2O = 2 \text{ KHCO}_3$$
 (2)

$$CO_2 + H_2O = H_2CO_3 \tag{3}$$

One objective of the tests is to establish by means of the permeability measurements, which is between these carriers, the most suitable for carbon dioxide separation process when supported by our composite membranes. However, the other operating variables which interested our study were nature of the membranes, concentration of the absorbent and pressure of the gas phase.

The results concerning the performances of the absorbents supported by a polyvinylidene fluoride membrane (PVDF) are shown in Fig. 5 (bubble pressure: 0,21 bar; pore size: 5 μ m). A 2-ethanolamine solution (1 M concentration) was used as absorbent. The process gases have been, alternately, loaded in the plant at a pressure of 15,000 Pa.

As it is shown by the graphic, the pressure of gas phase remains constant when gas will be H_2 , N_2 or CH_4 . Instead, when loading the plant with CO_2 , a constant decrease of the gas pressure was detected indicating the passage of CO_2 from gaseous phase to the liquid one. These results highlight the high selectivity of this system (membrane-absorbent) that in about 25 min was able to absorb the 93.3% of CO_2 content, while the other gases didn't show any pressure fall in time. However, as expected for this type of absorbent



Fig. 4. Flow sheet of the CO_2 separation process based on absorbent/ membranes system.



Fig. 5. Variation of differential pressure of CO₂, N₂, H₂, CH₄ for a hydrophilic membrane at T=28 °C, absorbent=MEA 1 M.

membrane, the tests have also evidenced the presence of a slight crossover of water vapors on the gas phase.

With the aim to better understanding which was the driving force that produces water crossover, a set of tests were performed by using hydrophobic polymeric membranes. The results showed that the membranes hydrophobicity hindered to the absorbent to fill pores by maintaining the liquid only on the surface of the membrane. This produces a drastic reduction of exchange area between the gas and liquid phase, making it impossible to obtain an appreciable gas separation. As consequence of those results, the choice of a membrane, which was hydrophilic on one side and hydrophobic on another one, appears to be fundamental to improve the performance of the CO₂ separation process. Such a membrane would increase the superficial area available for the contact between gas and liquid, allowing a better separation of the two phases. Fig. 6 shows the trend of the gas-phase pressure as a function of the time on stream. These tests have been performed on teflonated membrane (T-PVDF) by using as adsorbent a 2-ethanolamine solution in concentration 1 M. The test with pure nitrogen showed a constant pressure of the gas phase, while this parameter decreased by loading the system with CO₂.



Fig. 6. Variation of differential pressure of CO₂, N₂ as a function of the time on stream for T-PVDF membrane at T=28 °C, absorbent=MEA 1 M.

These results can be compared with the ones obtained for the received absorbent membrane; only a decrease of the permeation rate is highlighted. This trend also resulted in agreement with the data reported in Table 1, where it is clearly showed that the treatment produces a decrease of the pore radius of the membrane (from 7.09 μ m for the received sample to 5.10 μ m for the treated sample). Thus, the lowering of the permeation rate can be probably correlated to the decrease of the pore size of the membrane as consequence of the impregnation with a solution to 55 wt.% of PTFE. This consideration is further supported by SEM micrograph of Fig. 2 that shows the hydrophobic zone of the membrane is characterized by a homogeneity not detectable on the other side that presents a superficial porous network.

The preparation method described above didn't seem suitable for the studied process due to the strong lowering of membrane porosity that affects gas permeability and the difficulty to have a good reproducibility. The need to avoid these problems leads us to investigate a different preparation procedure based on the welding of two membranes, one hydrophilic and the other hydrophobic. The composite membranes have been realized both by simple coupling or by thermowelding under pressure.

The samples, prepared by these methods, have been tested, always, in the same conditions as used for the earlier experiments (2-ethanolammine solution as absorbent in concentration of 1 M). The obtained results are shown in Fig. 7 and Table 2. As it is evident, the coupled membranes (S-PVDF) have shown a higher permeability with respect to the thermowelded ones. Furthermore, among the several samples prepared by the second procedure, we detected a clear correlation between the pressing temperature on the permeation rate that decreases with the increasing of this parameter, as evident from Tables 1 and 2 where the maximum pore radius and the measured permeability are shown. On the contrary, the time of pressing doesn't



Fig. 7. Variation of CO₂ differential pressure for different membranes (S-PVDF-1, C-PVDF-1, C-PVDF-3, C-PVDF-4) as a function of the time on stream at T=28 °C, absorbent=MEA 1 M.



Fig. 8. Variation of CO₂ differential pressure as a function of the time on stream for different absorbents on an S-PVDF membrane at T=28 °C.

strongly influence the value of permeability, while it produces a good enhancement of the welding quality. As it has been evidenced by the measurements, the variation of welding temperature from 80 °C (C-PVDF-1) to 120 °C (C-PVDF-4) has produced a lowering of *R* from 7.49 to 5.26 with a correlated variation of 42.4%. From the experiments, we detected that this variation of *R* produced an effect on the permeation rate whose index is the drop of differential pressure. From the diagram of Fig. 7, the time recorded to have a 50% of reduction in the differential pressure corresponds to 19 min for C-PVDF-1 sample while it becomes 28 min for C-PVDF-4 one, with an increase of 47.4%, that means a quite linear relationship between variations of welding temperature, increase of *R* and increase of permeation time.

The influence of the nature of absorbent on the CO_2 membranes permeability have been also investigated. Therefore, the absorbents, which industrially are used in the traditional plants, like water, K_2CO_3 solution in concentration 0,1 M and 2-ethanolamine at the same concentration, have been tested. The experiments have been made on two coupled membranes (S-PVDF), and the results are showed in Fig. 8. The best result was obtained with the amine



Fig. 9. Effect of MEA concentration on variation of CO₂ differential pressure at T=28 °C on S-PVDF membrane.



Fig. 10. Effect of pressure on variation of CO_2 differential pressure at T=28 °C on hydrophilic membrane.

solution that, at operating conditions, showed the greatest affinity with CO_2 . In fact, we have determined that, after 30 min of time on stream, the drop of differential pressure was of 11.7 % for water absorbent, 29.9% for K₂CO₃ solution absorbent and 61% for the amine solution.

To measure the influence of the concentration of the amine solution on the permeability of the CO_2 through the coupled membranes (hydrophilic and hydrophobic), three 2-ethanolamine solutions with different concentration, 0.1, 1.0 and 3.0 M, have been prepared and tested. The results of these experiments are visible in Fig. 9 from where it is clearly deducible that the CO_2 permeability greatly increases by increasing the concentration of the absorbent.

The last set of tests concern the investigation on the behavior of the membrane if operating under stressing operative conditions. Thus, we planned to perform different tests by using some membrane at an operative pressure very close to the bubble pressure of the sample. For these experiments, we selected some hydrophilic membrane (VPDF) characterized by a value of bubble pressure of 21,000 Pa. Four samples of this membrane have been tested at two different operative pressure (15,000 and 19,000 Pascal) with two different gas phase compositions (pure nitrogen and pure carbon dioxide) and by using, as absorbent, 2-ethanolamine solution with 1 M concentration. As showed in Fig. 10, the most important evidence concerns that, working at a pressure of 15,000 Pascal, the absorption of CO₂ has been detected, while no transfer of nitrogen has been found. By approaching to the bubble point pressure (tests at 19,000 Pa), we have seen that the permeability of the CO₂ remained almost unchanged; however, a significant passage of nitrogen through the membrane has been discovered. These results give us the indication that operative pressure very close to the bubble pressure produces a stress on the membranes selectivity that has losses of efficiency. The limit pressure changes with the characteristics of the membrane structure, and it can be nearly indicated as equal to 90% of the sample bubble pressure.

4. Conclusions

In this study, the use of a combined polymeric membrane (hydrophilic–hydrophobic, SLM type) has been proposed as effective support for CO_2 absorbent solutions. The hybrid process (membrane-absorbent) based on this typology of material has been studied and performed on an experimental lab-scale plant which was able to use different chemical solvents as "carrier" in order to promote a preferential transport of the CO_2 through the membrane.

The operative variables which interested this study were nature of the membranes, differential pressure between gas/ liquid phases and type and concentration of the absorbent.

The experimental results pointed out that the performances (in terms of CO_2 permeability) of the coupled membranes (S-type) are higher than that of the polymeric hydrophilic and hydrophobic membranes thermowelded or prepared by PTFE deposition.

The experimental data have also confirmed that 2-etanolamine is the type of adsorbent, between those studied, with the greater affinity with the CO_2 .

In conclusion, the feasibility of a CO_2 separation process based on a combined membrane (hydrophilic + hydrophobic) coupled with a hybrid process "membrane-absorbent" has been demonstrated.

From the obtained experimental data, the value of the CO₂ permeability, *R*, has been determined for all sample, both as received and treated by us. Values of *R* ($1.17E^{-04}$ cm³/s/cm² × PcmHg), which are perfectly comparable with the literature data, have been measured for combined membrane with amine solution.

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