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Carbon Dioxide Absorption by Ammonia Intensified with Membrane Contactors

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Membrane gas absorption technology is a promising alternative for carbon dioxide (CO_2) removal from post combustion coal-fired flue gases. This study examines an alternative which consists in absorbing CO_2 by ammonia aqueous solution in a membrane contactor to improve the capture processes and to intensify the gas-liquid transfer. Absorption measurements through a membrane contactor have been made. The influence of the material nature constituting the membrane and operating parameters on the capture efficiency has been studied. The results have shown that it is possible to capture CO_2 from ammonia through a membrane with capture efficiency greater than 90 %. The membrane limits ammonia losses but does not eliminate it.

1. Introduction

Absorption by chemical solvents is so far the best method in CO_2 capture. This method uses mainly an aqueous solution of monoethanolamine (MEA) to absorb CO_2. This molecule has high water solubility, high absorption capacity at low CO_2 partial pressure and fast kinetics. A significant problem is degradation of amine over time and high heat requirement for its regeneration. More effective solvents for CO_2 capture are under research and development. Amman and Bouallou, (2009) have developed a new solvent, a blend amine of mehtyldiethanolamine (MDEA) activated with triethylene tetramine (TETA). Results show that the addition of small amount of TETA leads to a significant enhancement of the absorption rates compared to MDEA and increase the absorption capacity of the solvent. They conclude that this solvent is a good compromise between absorption rate and efficiency of the solvent regeneration. Another alternative is the use of ammonia solution; ammonia is more reactive than MDEA solvent (Rivera-Tinoco and Bouallou, 2010) and it has low solution enthalpy of the system NH_3-CO_2-H_2O (Toro Molina and Bouallou, 2015). The main disadvantage of using this solvent is the ammonia slip. Several authors have studied ammonia losses. They avoid ammonia slip by the use of additives with the solvent.

However, the energy cost of absorption /regeneration cycle is still very high. To improve and reduce these costs, membrane contactor, has been developed and coupled to the chemical absorption. Membrane is a physical barrier which allows a selective transfer of a component of a mixture as a result of its activity gradient. The advantages of membrane contactor are: the independence of the flow of liquid and gas, large specific interfacial area, compactness, modularity and scale-up is simple. Furthermore, problems present in conventional absorption methods, such as flooding, weeping or foaming can be avoided. Nevertheless, the use of a membrane adds a supplementary resistance to mass transfer. This resistance can be significant if the membranes are wetted by the solvent. The main problem of the membrane is pores wetting by the solvent. The used of a hydrophobic membrane, could prevents flooding problems in the membrane contactor. The most used polymers are polypropylene (PP), polyethylene (PE), polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE) membranes. However, in practice, the aqueous solutions with organic absorbents can penetrate the pores and wet the hydrophobic membrane affecting the mass transfer performances. The prevention of membrane wetting is important to maintaining high performance in CO_2 absorption. To keep the non-wetted condition a solution, a dense skin should be added in to the membrane. Composite fibres have been successfully used and tested in the prevention of membrane wetting, (Chabanon et al., 2011). The first solvent used to capture CO_2 through a membrane

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contactor was with water and then were used chemical solvents such as MEA, DEA and MDEA. The use of ammonia for capturing CO_2 through a membrane contactor has not been used so far. A good combination of solvent with the contactor can be very beneficial in the capture process. Recently, Wang et al. (2013) studied CO_2 absorption in binary amine systems in a PP hollow-fibre membrane contactor. The aqueous blends amines studied were MEA/MDEA, DEA/2-amino-2-methyl-1-propanol (AMP), and MDEA/PZ. For blended amines, solvent formulation optimization was studied intensively by theoretical analysis.
Our approach is not to explain the phenomena occurring in materials but simply to study their effectiveness for CO_2 capture.

2. Experimental

2.1 Materials

Two hollow fibres were used in this study: a house hollow fibre, membrane composite of a dense outer layer in Teflon AF® coats a support of PP and a porous membrane of Oxyphan® (PP). The hollow fibre modules have been made and supplying by LGC Toulouse. Their characteristics are summarized in Table 1. As a reference for comparison, we selected a commercial composite membrane, commercialized by membrane (Oxyplus®). Oxyplus is a dense outer layer in polymethylpentene (PMP) coats a support of polypropylene (PP).

Table 1: Characteristics on hollow fiber modules

	PP- Téflon AF®			Polypropylène (Oxyphan®)	Oxyplus®		
Number of fibers	27	54	108		27	54	210
Shell i.d. (m)	0.0124	0.0124	0.0124	0.0124	0.0124	0.0124	0.0124
Fiber o.d (µm)	383	383	383	54	380	380	380
Fiber thickness (µm)	90	90	90	2.8×10^{-4}	90	90	90
dense skin (µm)	1.6	1.6	1.6	3.8×10^{-4}	<1	<1	<1
Support thickness (µm)	~86.5	~86.5	~86.5	0.24	200	200	200
Fiber Length (m)	0.240	0.240	0.240	0.05	0.240	0.240	0.240
Interfacial area ($m^2.m^{-3}$)	245	490	980	358	243	486	1889
Packing fraction, φ	0.02	0.047	0.75		0.02	0.05	0.18

The structure of a composite fiber, the thickness of the dense skin and of the porous support is shown in Figure 1.

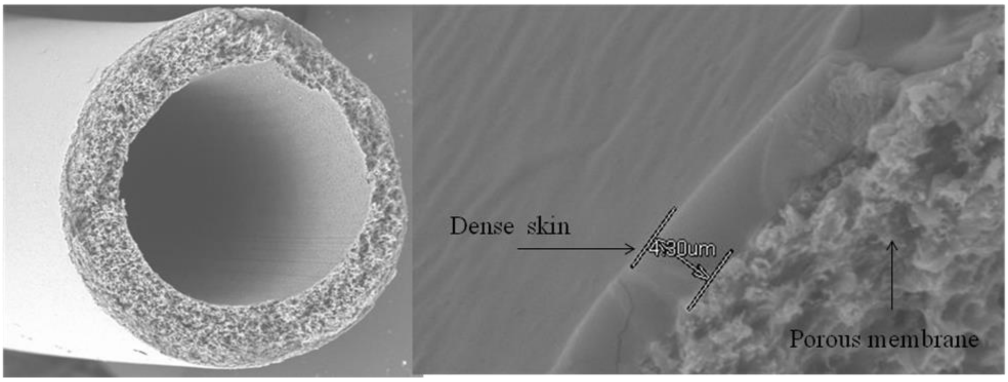


Figure 1: SEM pictures of hollow fibre membrane (LGC Toulouse)

Gas mixture: Gases were supplied by Air Liquide as pure CO_2 bottle (≥99.5 %) and pure N_2 (≥99.99 %),
Ammonia: Ammonia solution used is prepared from an ammonia solution of 3 to 20 wt%.

2.2 CO_2 absorption test

CO_2 capture efficiency (η) was experimentally determined from the inlet and outlet gas flow rate (Q) and CO_2 concentration (C_{CO2}). Steady state was achieved according to the expression given by Eq(1).

$$\eta = \frac{Q_{in}C_{CO_2 in} - Q_{out}C_{CO_2 out}}{Q_{in}C_{CO_2 in}} \times 100 \qquad (1)$$

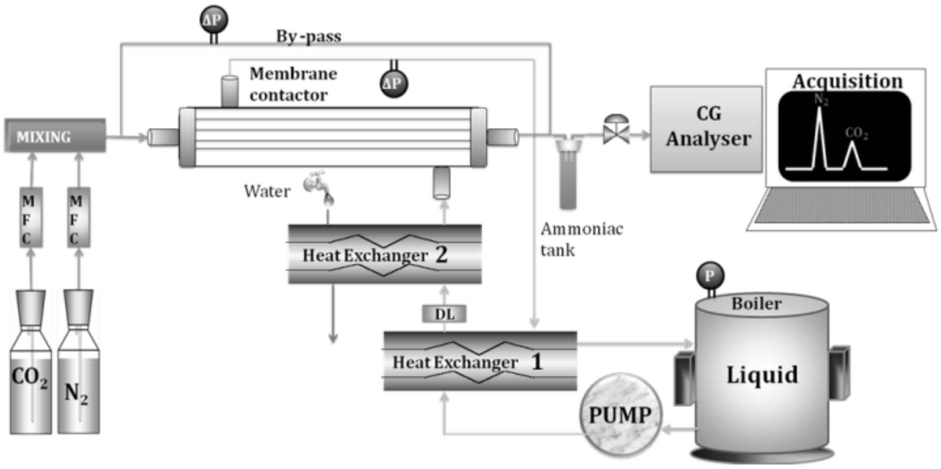


Figure 2: experimental setup used for membrane

2.3 Experimental set-up and procedures

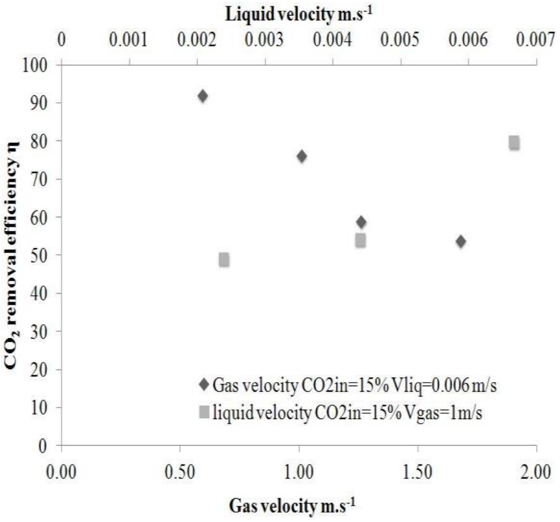
The schematic absorption–desorption system for CO_2 absorption and desorption made in our laboratory Kallas et al. (2009) and later Toro-Molina and Bouallou (2015) is shown in Figure 2. A CO_2/N_2 gas mixture (15 vol% CO_2) prepared by two mass controllers (MFC) flows on the lumen side of the membrane contactor. The composition of the gas at the absorber outlet was analysed by a gas chromatograph. The lean solution of aqueous ammonia (3 wt%), prepared by dissolution of 20 wt% NH_3 in distilled water, flowed in the module counter-currently. CO_2 transfers from CO_2/N_2 mixture through the membrane into the liquid in the shell side where it is absorbed. A tank recovers ammonia losses (ammonia passes through the membrane) during absorption process. The gas composition after absorption was analysed using the same gas chromatograph. After absorbing CO_2, the lean solution turned rich and flowed into a stripper through a first heat exchange (Heat Exchanger 1), where the lean liquid at high temperature exchanged the heat with the rich one at room temperature. In the stripper, the rich solution released CO_2 and turned lean. The lean ammonia solution was introduced into another heat exchanger (Heat Exchanger 2) until the solution was to room temperature. Ammonia solution is used for a new absorption-desorption cycle. The system was operated for 30 min to achieve a steady state condition prior to sample measurement.

3. Results and discussion

A series of experiments have been conducted to study CO_2 removal for post-combustion. A low and constant CO_2 loading is used in the experiments and is obtained through hot-regeneration. The influence of the most important parameters was investigated: gas and liquid velocities, solvent concentration, packing fraction.

3.1 Potential for the polypropylene porous hollow fiber

Figure 3 shows the effect of the velocity of the gas and liquid on the capture efficiency in a porous membrane. The increase in the velocity of gas led to a decrease of the capture efficiency up to a value of 53 % for v_{gaz} = 1.7 m/s. This decrease in efficiency is related to the decrease in the contact time between the gas and the liquid solution in the contactor. On the other hand, the increase in the liquid velocity induced an increase in the capture efficiency with a large driving force. Figure 4 shows that when the CO_2 concentration increases, capture efficiency decreases. 30 % efficiency is lost when the volume concentration of CO_2 increases from 5 % to 30 %. Figure 5 shows that the capture efficiency increases with the concentration of ammonia. However, the maximum ammonia concentration which must be used may not exceed 7 wt%. The use of ammonia concentration up to 5 wt% and temperatures below 293 K leads to the formation of a bicarbonate ammonium solid salt. This phenomenon should be avoided to providing an excellent performance of the membranes and that they are not obstructed.



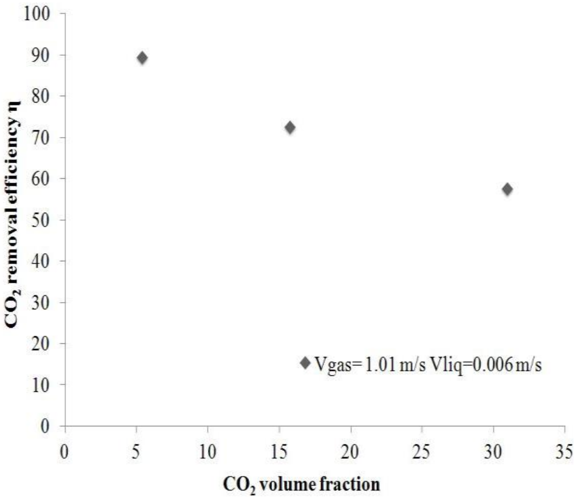
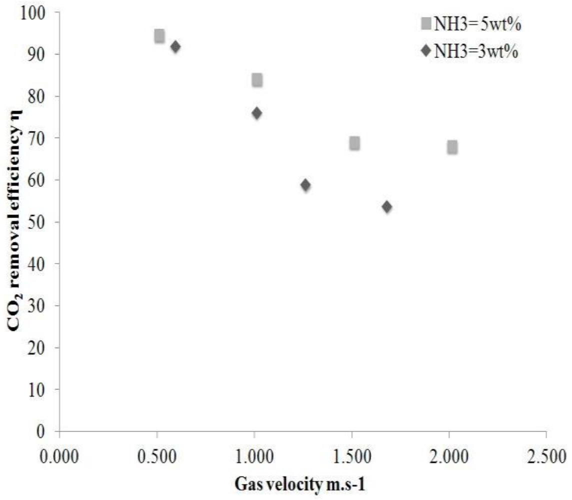


Figure 3: Effect of the velocity of the gas and liquid on capture efficiency, (NH_3 = 3 wt%, CO_2 = 15 vol%., T ≈ 294 K)

Figure 4: Effect of the volume fraction on CO_2 capture efficiency, (NH_3 = 3 wt%, v_{gaz} = 1 $m.s^{-1}$, v_{liq} = 0.006 m/s, T ≈ 294 K)



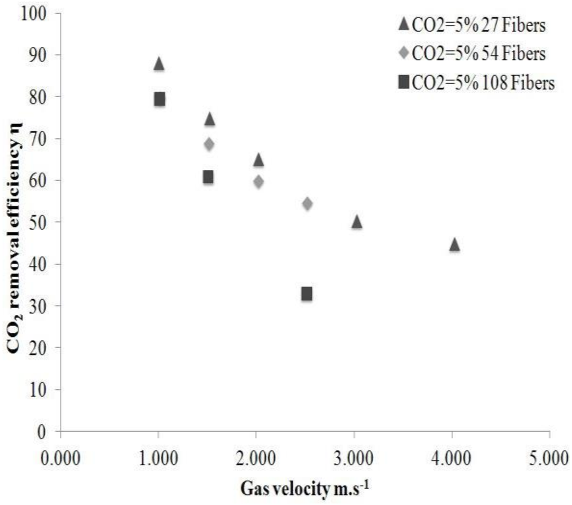


Figure 5: Effect of NH_3 concentration on capture efficiency (CO_2 = 15 %, v_{liq} = 0.006 m/s, T≈294 K)

Figure 6: Influence of packing fraction PP-Teflon AF (T ≈ 295 K, v_{liq} = 0.006 $m.s^{-1}$, NH_3 = 3 wt%)

3.2 Potential for the composite fibres PP-Teflon AF hollow fibre

Figure 6 and Figure 7 show the influence of velocity and the packing fraction on effectiveness of capture for two CO_2 concentrations: 5 % and 15 % in volume. Both concentrations are in the low and high ranges in the outlet flue gases from the thermal power plant. Three packing fractions have been assessed. A module with 27 fibres which corresponds to a packing of 0.02, a module with 54 fibres which corresponds to a packing of 0.05 and a module with 108 fibres that corresponds to a packing fraction of 0.09. For the three tested packings (0.02, 0.05 and 0.09) capture efficiency decreases with the compactness of the contactor. In addition, efficiency will decrease when the velocity of gas increases especially for a packing fraction of 0.09 and initial concentration of CO_2 by 15 %. Thus, for a velocity of 1 gas $m.s^{-1}$ with a packing fraction of 0.02, the measured capture efficiency is 80 %, while for a packing fraction of 0.09 measured efficiency is only 50 %. For three packing assessed, capture efficiency greater than 80 % was measured only when the initial CO_2 concentration was 5% and the gas velocity of 1 m/s. The reduction in the efficiency related to the compactness is probably due to heterogeneous arrangement of fibres in the liquid phase inside the contactor.

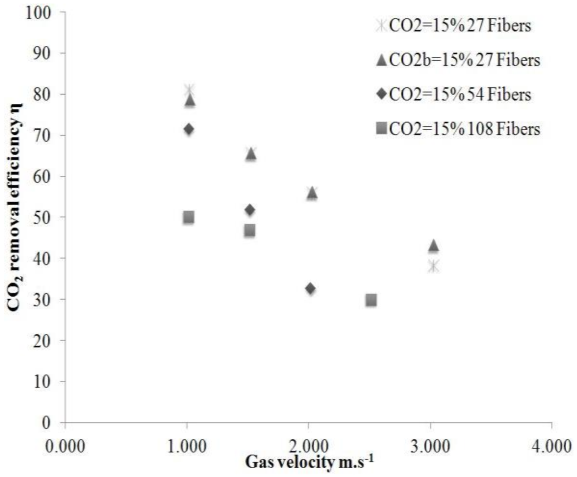


Figure 7: Influence of packing fraction PP-Teflon AF ($T \approx 295$ K, $v_{liq} = 0.006$ m/s, $NH_3 = 3$ wt%)

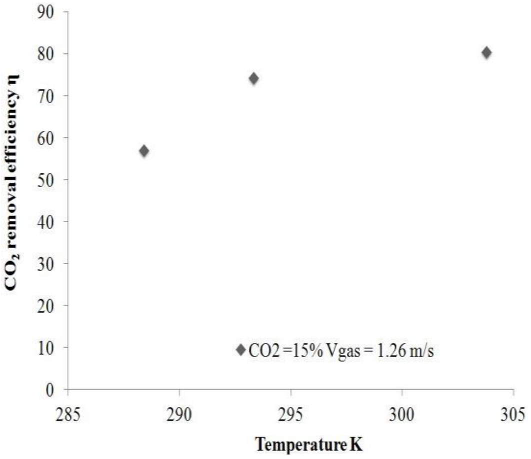


Figure 8: Influence of temperature on capture efficiency ($T \approx 295$ K, $v_{gaz} = 1.26$ m/s, $v_{liq} = 0.006$ m/s, $\varphi = 0.18$)

The Figure 8 shows that when the temperature rises, the capture efficiency increases. Thus, when the temperature changes from 288 to 293 K, capture efficiency increases by 16 %. However, when the temperature goes from 293 to 303 K, capture efficiency increases only by 6 %. This may be due to the fact that the increase in temperature increases the amount of ammonia that comes out of the side gas, gas phase and liquid phase. We recovered 10 mL of solution of ammonia for absorption test at 303 K for a time of absorption of 200 min. On the other hand, for the tests at a temperature below 293 K, the maximum of retrieved solution was 5 mL for a time of greater than 300 min capture. We conducted a trial of absorption by varying the pressure liquid side; it went from 1 to 2 bar. Capture efficiency does not vary greatly: it rose from 74 % to 76 %. Pressure liquid side has therefore no effect on capture efficiency. However, it must maintain a pressure greater than atmospheric pressure to limit losses of ammonia.

Higher capture efficiencies are observed when using membrane Oxyplus (Toro Molina and Bouallou, 2015). This may be due to the fact that dense skin of membrane Oxyplus is thinner than that of the PP-Teflon AF membrane. On the other hand, as the Oxyphan membrane is not dense skin, the difference between the values of the obtained capture efficiencies can be associated to the wetting of the membrane. The Oxyphan membrane may be wet more easily than the composite membranes; this results in a higher resistance to transfer.

3.3 Ammonia lost

The membranes used for CO_2 capture in this study are all permeable to ammonia. This permeability varies, depending on the polymer used to make fibre hollow or depending on the nature of the membrane (porous membrane or composite membrane) and leads to loss of solvent. We consider data collected from the ammonia solution retrieved (lost ammonia for absorption) in the gas outlet of the contactor in liquid or solid form. The loss of ammonia in the contactor is related to several factors: the nature of the membrane, the degree of filling of the module, the amount of NH_3 present in solution and the temperature of absorption. The amount of ammonia solution lost was greater for the Oxyphan membrane than for membrane Oxyplus, PP-Teflon AF. This confirms the hydrophobic power of dense skin. The loss of ammonia in the Oxyphan membrane is 3 mL/h during the absorption of CO_2 with a concentration of NH_3 3 wt% and 54 fibre modules. Ammonia losses are invariant regardless of the velocity of gas, that of the liquid and the CO_2 concentration. When the absorption tests carried out at a concentration of NH_3 equal to 3 wt% with the PP-Teflon AF membrane, we found droplets out of the gas of the contactor. This solution was not large enough to measure the quantity of ammonia lost during absorption. This indicates the power of the polymer Teflon AF to contain ammonia. If the ammonia concentration increases, the losses also increase. In addition, if the concentration which crosses the fibre is more important, there is a possibility to form solid ammonium carbonate salts during the reaction between CO_2 and NH_3. For trials with the Oxyplus membrane and a 3 wt% NH_3 concentration, the loss of the ammonia solution was 1.9 mL, this amount of ammonia is less than the amount lost through the Oxyphan membrane but greater than the loss of the PP-Teflon AF membrane.

4. Conclusions

In this paper, results show that composite fibres trap more ammonia then porous fibres, reducing significantly its losses. Note that, the loss of ammonia is a key parameter, because it is a very volatile chemical component. As presented in the State of the art, the ammonia solution has already been used as a solvent to absorb CO_2. However, for the ammonia the absorption of CO_2 occurs within limited operating ranges due to it is high vapour pressure (temperature absorption > 283 K or pressure absorption < 3 bar). With the use of the composite membranes, absorption pressure may be reduced without increasing losses of ammonia, which could also reduce the costs associated to the solvent compression. The influence of different parameters were evaluated. Results show that the capture efficiency is strongly dependent on the gas velocity. Capture efficiency decreases the gas velocity for all tested membrane. This is explained by the contact time reduction between the gas and liquid phase. The gas velocity must be less than 0.8 m/s to ensure a capture efficiency of 90 % with a packing fraction of 0.05. Other parameters, influencing the capture efficiency are the packing fraction switch and the volume fraction of CO_2. On the other hand, the parameters which promote absorption are: liquid velocity, ammonia concentration, intake temperature even if it increases the losses of ammonia. However, if the ammonia concentration exceeds 5 wt%, efficiency may decrease because of obstruction by the salts of ammonium in the membrane.

Acknowledgements

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