

CO₂ Separation by Membrane Technologies: Applications and Potentialities

Giuseppe Barbieri^{1*}, Adele Brunetti¹, Francesco Scura¹, Enrico Drioli^{1,2}

¹National Research Council - Institute for Membrane Technology (ITM-CNR),
Via Pietro BUCCI, c/o The University of Calabria, cubo 17C, 87030 Rende CS, Italy

²The University of Calabria - Department of Chemical Engineering and Materials

1. Introduction

Flue gas from power plants is actually the major source for generation of carbon dioxide in the atmosphere. Since CO₂ can act as a trap for UV rays, the reduction of CO₂ emissions is an important area of research. The regulation of the carbon dioxide emissions implies the development of efficient CO₂ capture technologies that can be retrofitted to existing power plants as well designed into new plants with the goal to achieve 90% of CO₂ capture limiting the increase in cost of electricity to no more than 35% (Ciferno et al., 2009). In particular, the identification of a capture process which would fit the needs of target separation performances, together with a minimal energy penalty, is a key issue. Currently, the main strategies for the carbon dioxide capture in a fossil fuel combustion process are (Davdison and Metx, 2005):

- Oxy-fuel combustion: This option consists in performing the oxygen/nitrogen separation on the oxidant stream, so that a CO₂/H₂O mixture is produced through the combustion process. The advantage of feeding an oxygen-enriched gas mixture (95% oxygen) instead of air, is the achievement of a purge stream rich in CO₂ and water with very low N₂ content, therefore the CO₂ can be easily recovered after the condensation of the water vapour.
- Pre-combustion capture: This solution is developed in two phases: i) the conversion of the fuel in a mixture of H₂ and CO (syngas mixture) through, e.g., partial oxidation, steam reforming or auto-thermal reforming of hydrocarbons, followed by water-gas shift; ii) the separation of CO₂ (at 30-35%) from the H₂ that is then fed as clean fuel to turbines. In these cases, the CO₂ separation could happen at very high pressures (up to 80 bar of pressure difference) and high temperatures (300–700 °C).
- Post-combustion capture: In this case, the CO₂ is separated from the flue gas emitted after the combustion of fossil fuels and the separation is realized at relatively low temperature, from a gaseous stream at atmospheric pressure and with low CO₂ concentration (ca. 5–25% if air is used during combustion). SO₂, NO₂ and O₂ may also be present in small amounts. This possibility is by far the most challenging since a diluted, low pressure, hot and wet CO₂/N₂ mixture has to be treated. Nevertheless, it also corresponds to the most widely applicable option in terms of industrial sectors (power, kiln and steel production for instance). Moreover, it shows the essential advantage of being compatible to a retrofit strategy (i.e. an already existing installation can be, in principle, subject to this type of adaptation) (Favre, 2007). This is the main reason why in this paper we will focus on the post combustion capture.

The conventional separation processes suitable to be used also in post-combustion are: absorption (with amines), adsorption (with porous solids with high adsorbing properties such as zeolite or active carbon) and cryogenic separation (Drioli and Romano, 2001, Simmonds et al., 2003). Amine-based absorption with an aqueous monoethanolamine (MEA) solution is the most common technology since it allows to achieve high level of CO₂ capture (90% or more) from flue gas due to fast kinetics and strong chemical reaction (Favre, 2007). However, the corrosivity of the amines, their easy degradation by trace flue gas constituents (particularly sulphur oxides) and the significant amount of energy (in the range 4–6 MJ/kgCO₂ recovered) required in the regeneration step make their use by far to be the best available technology. In fact, DOE/NETL (Department of Energy – National Energy Technology Laboratory) has estimated that MEA-based process for CO₂ capture will increase the cost of the electricity for a new power plant by about 80-85%, also reducing the plant efficiency of about 30%. A relatively novel CO₂ capture technology is based on cryogenic removal of CO₂ (Eide et al., 2005). This technology relies on the assumption that all components of the flue gas are removed except for the N₂ and CO₂ prior to cooling. After this removal, the remaining gas is sent into a cryogenic chamber where the temperature and pressure are manipulated to cause the CO₂ to liquefy. Under the right conditions CO₂ will condense whereas N₂ remains as a gas. This distillation allows N₂ to escape through an outlet at the top of the chamber and the highly concentrated liquid CO₂ can be collected at the bottom of the chamber. Great advantages of cryogenic CO₂ capture with respect to absorption are that no chemical absorbents are required and that the process can be operated at atmospheric pressures. The main disadvantages of this system are the several costly steps required for removing the water content from the feed stream before cooling units as well as the drops in process efficiency due to the progressive formation of an increasing layer of solid CO₂ onto heat exchanger surfaces during the capture cycle. The use of this technology for CO₂ capture from flue gas is, thus, far from the application that can be justified only for the treatment of large streams. Membrane operations are now being explored, particularly because of their fundamental engineering and economic advantages over competing separation technologies in other gas separation sectors. Membranes are a low cost mean of separating gases, when high purity gas streams are not vital and many literature studies propose the use of membranes for CO₂ separation. However, there are a number of issues associated with the capture of carbon dioxide from flue gases which limit the use of membranes. The concentration of CO₂ in flue gases is low, which means that large quantities of gases will need to be processed. Additionally, creating a pressure difference through the membrane will require significant amounts of power, which will in turn lower the thermal efficiency of the power plant. Each of the three separation technologies is based on different separation principles and, thus, the project characteristics differ significantly. The choice of the technology suitable for the specific separation is, thus, related on different parameters like economics, stream conditions, product target and, also, on design considerations (Brunetti et al. 2010).

In this work we will analyse the potentialities and the applications of gas separation (GS) in the post combustion capture giving general guidelines on some design parameters to take into account in the choice of a technology suitable for the CO₂ separation. In addition, the attention was focused on some general maps as useful tool for the evaluation of the right direction of work also in dependence of specific considerations, strictly related to the output to be obtained.

2. Engineering Considerations for CO₂ post Combustion Capture

The main advantages and drawbacks of the described technologies in CO₂ separation are indicated in Table 1. The selection of the separation process may be driven by specific considerations, strictly related to the output to be obtained. The feed composition (CO₂%), the feed conditions (pressure and temperature), the product purity and the final destination of the product strongly affect the choice (Table 2).

Table 1 - Advantages and drawbacks of the technologies for CO₂ separation

| ABSORPTION | | ADSORPTION | | CRYOGENIC | | MEMBRANE SYSTEMS | |
|-----------------------------------|---|----------------------------|--|---------------------------------------|--|--------------------------------------|--|
| <i>Advantages</i> | <i>Drawbacks</i> | <i>Advantages</i> | <i>Drawbacks</i> | <i>Advantages</i> | <i>Drawbacks</i> | <i>Advantages</i> | <i>Drawbacks</i> |
| Recycling of the sorbent | Corrosion of carbon steel facilities due to oxygen | Recycling of the sorbent | Not able to handle large concentrations of CO ₂ | No requirement of chemical absorbents | Several costly steps required to remove all water traces | No moving parts and modularity | Current low selectivity of membrane material |
| Non-dependence on human operators | Degradation of the solvent due to SO _x and NO _x | High operating flexibility | Adsorption also of gases smaller than CO ₂ | Atmospheric pressures | Increasing layer of solid CO ₂ onto heat exchanger surfaces | Instantaneous response to variations | Limitation on the suitable operating temperature |

Table 2 – Comparison among the three units as function of feed and product conditions

| | <i>Absorption</i> | <i>Adsorption</i> | <i>Cryogenic</i> | <i>Membrane System</i> |
|--|-------------------|-----------------------------|--------------------------|-------------------------------|
| CO ₂ in the feed, (% molar) | >5 | >10 | >5 | >15 |
| CO ₂ purity, % | >95 | 75-90 | 99.99 | 80-95 ^(*) |
| CO ₂ recovery, % | 80-95 | 80-95 | 99.99 | 60- 80 ^(*) |
| Energy requirement, MJ/kgCO ₂ | 4-6 (Favre 2007) | 5-8 (Brunetti et al., 2010) | 6-10 (Eide et al., 2005) | 0.5-6 (Bounaceur et al. 2006) |

*Considering a CO₂/N₂ selectivity of 50 in one stage process

The composition of the feed and the product target are best considered together when selecting a CO₂ separation process because the four processes have drastically different economies of scale and these parameters strictly influence the performance, reliability and pre-treatment required by the three upgrading processes. It must be considered that, even the recovery and purity achievable with the cryogenic separation are significantly higher than that of the other technologies, however, this technology is suitable for the

treatment of large stream volume ($> 50000 \text{ m}^3 \text{ (STP) h}^{-1}$), owing to the high costs related to energy requirements. The direct competitor of membrane systems is, thus, the ammine absorption. Considering a typical membrane system (CO_2/N_2 selectivity= 50), the membranes can compete with the absorption only for CO_2 concentration in the feed stream higher than ca. 15%. This is a crucial consideration in the membrane design because the flue gas stream arrives to the capture system with an inlet pressure slightly higher than one bar and the net pressure difference through the membrane provides the driving force for the separation. Concerning the CO_2 recovery and purity they are strictly related to the membrane properties (selectivity and permeance). With the membranes currently available on the market, the absorption show better performances with respect to membrane technology, when a single stage process is considered. The current membrane systems, in fact, cannot offer, in the mean time, high recovery and high purity, therefore, the improvement of the membrane properties and, in particular, the increase in the selectivity is the bigger challenge for making one stage membrane process competitive with absorption. However, the use of multistage systems allows, already now, higher recovery and purity to be obtained (Baker et al. 2008).

3. Membrane System Performance

From the above considerations, it appears clear that the membrane operations can represent a suitable alternative to the traditional separation processes for CO_2 capture, particularly for the treatment of streams containing more than 15% of CO_2 , like that coming out from steel production plants. However, moving in the perspective of having available on the market improved materials, at the moment only present at lab scale, exhibiting higher selectivities, it is very interesting to analyse the possible application of membrane GS in the treatment of the flue gas coming out from a power plant. Hence, the potentialities of the membrane GS for the separation of a stream containing 10-15% of CO_2 (typical flue gas coming from power plant) has been proposed, focusing the attention on the application of one stage membrane system. In particular, a simple tool taking into account the influence of the most important parameters affecting the membrane system performance has been introduced in terms of general maps of CO_2 purity versus CO_2 recovery (Error. Il segnalibro non è definito. Brunetti et al. 2010). A dimensionless 1D mathematical model for the multi-species steady-state permeation in no sweep mode and co-current configuration (Brunetti et al. 2010) has been used for the calculations. In the equations, Θ_i and ϕ are the parameters affecting the performance of a one stage membrane system, the permeation number and the feed to permeate pressures ratio, respectively.

$$\Theta_{\text{CO}_2} = \frac{\text{Permeance}_{\text{CO}_2} A^{\text{Membrane}} p^{\text{Feed}}}{x_{\text{CO}_2}^{\text{Feed}} Q^{\text{Feed}} \phi} \quad (1)$$

$$\phi = \frac{P^{\text{Feed}}}{P^{\text{Permeate}}} \quad (2)$$

The permeation number expresses a comparison between the two main transport mechanisms involved. A high permeation number corresponds to a high residence time for the stream and, then, to a high permeation through the membrane with respect to the total flux along the module.

For given feed composition, membrane properties (species permeance and selectivity), module geometry (total installed membrane area and module length) and fixed

operating conditions (feed flow rate and pressures) the solution of equations system provides the species dimensionless flow rate profiles and composition along the module length for both the membrane sides.

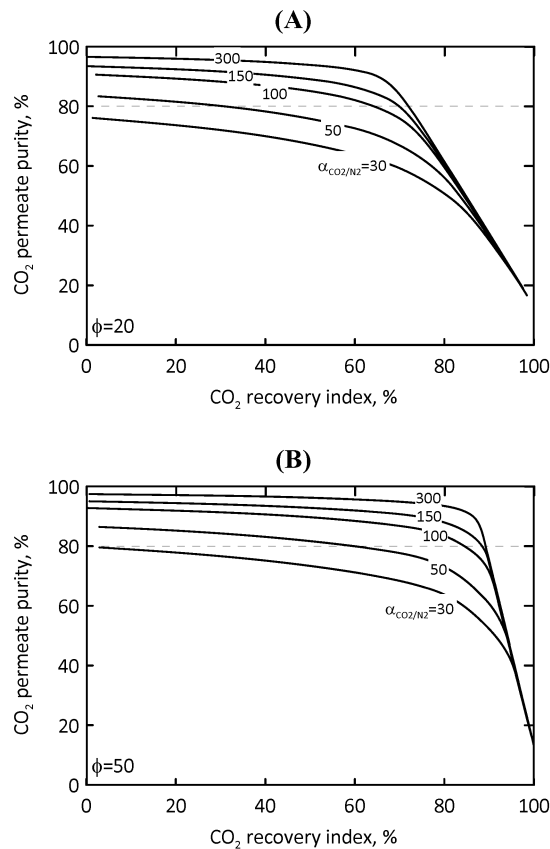


Figure 1 - CO_2 permeate purity versus recovery index for pressure ratio of 20 (A) and 50 (B), at different CO_2/N_2 ideal selectivity from 30 to 300. CO_2 feed concentration=13%. $\Theta_{\text{CO}_2}=20$. “Reprinted from *Journal of Membrane Science*, 359, Brunetti A., Scura F., Barbieri G., Drioli E., *Membrane technologies for CO_2 separation*, 115–125, Copyright (2009), with permission from Elsevier”

Different membrane selectivities ranging from 30/50 (commercial membranes) up to 150 and 300 (of most promising membranes) and different feed pressure ratios were considered. The results showed that, with currently available membranes (selectivity up to 50), it is not possible to get, simultaneously, high CO_2 recovery and purity (80% CO_2 in permeate stream). In order to fit this target, the mathematical simulations showed the fundamental role played by the operating pressure ratio more than selectivity. In fact, with a selectivity of 100 (value already reached in the lab by some membrane materials), shifting the pressure ratio from 10 to 20 or 50, the CO_2 recovery passes from 22% to more than 60% or 80%, respectively. A high pressure ratio is necessary also when high selective (100-150) membranes are operated (Figure 1).

4. Conclusions

The comparison between membrane process and traditional technologies for CO₂ separation indicated that the membrane systems offer relevant gains in terms of flexibility, reliability, modularity and that they require energy intensity generally lower, or, at least, comparable with that of the absorption. Significant efforts are still required in order to improve the membrane transport properties so that obtaining, in one stage, purities and recoveries comparable to that of traditional operations. However, by means of a simple tool, taking into account the influence of the most important parameters affecting the membrane system performance, it has been demonstrated that with the membranes already available on the market it is possible to achieve, in one stage, high recovery and purity only when a high pressure ratio is imposed.

5. References

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