



**HAL**  
open science

## Hybrid membrane cryogenic process for post-combustion CO<sub>2</sub> capture

Bouchra Belaïssaoui, Yann Le Moullec, David Wilson, Eric Favre

► **To cite this version:**

Bouchra Belaïssaoui, Yann Le Moullec, David Wilson, Eric Favre. Hybrid membrane cryogenic process for post-combustion CO<sub>2</sub> capture. *Journal of Membrane Science*, 2012, 415, pp.424-434. 10.1016/j.memsci.2012.05.029 . hal-00776395

**HAL Id: hal-00776395**

**<https://hal.science/hal-00776395>**

Submitted on 28 Apr 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

***Hybrid Membrane Cryogenic Process for  
Post-Combustion CO<sub>2</sub> Capture***

Bouchra Belaissaoui<sup>1</sup>

Yann Le Moullec<sup>2</sup>

David Willson<sup>3</sup>

Eric Favre<sup>1\*</sup>

1 : LRGP-CNRS Nancy Université  
1, rue Grandville  
54001 Nancy  
FRANCE

2: EDF R&D  
Département Mécanique des Fluides, Energies et Environnement  
6 quai Watier- BP 49  
78401 Chatou  
FRANCE

3: Stanbridge Capital  
37 East 18th Street  
New York , NY 10003  
USA

\* : Corresponding author :  
tel. +33 383 17 53 90  
e-mail: Eric.Favre@ensic.inpl-nancy.fr

***Manuscript submitted to the Journal of Membrane Science (January 2012)***

## Abstract

Reducing the energy requirement for the capture step is a major challenge in Carbon Capture and Storage (CCS) technology. Different capture processes have been investigated in the literature, such as absorption, adsorption, chemical looping and membrane separation. In this paper, the potential for a hybrid process combining membrane and cryogenic separation to achieve efficient post-combustion carbon capture has been investigated through a simulation study. The hybrid process combines a first step CO<sub>2</sub> pre-concentration with a membrane unit and a second step CO<sub>2</sub> cryogenic condensation. The influence of three CO<sub>2</sub> feed contents (5, 15 and 30%), 3 different compression strategies and two membrane selectivities ( $\alpha_{CO_2/N_2}=50$  and 100) on the separation performances have been investigated for a required CO<sub>2</sub> purity of 0.9 and a capture ratio larger than 85%. It is shown that the use of feed compression with Energy Recovery System (ERS) membrane module offers the best performances when energy requirement and membrane surface area taken into account. More specifically for a CO<sub>2</sub> feed concentration ranging between 15 and 30%, the hybrid process shows a reduced energy requirement compared to the reference technology (chemical absorption in MEA).

## 1. Introduction

The reduction of greenhouse gases emissions (CO<sub>2</sub>, CH<sub>4</sub>, NO<sub>x</sub>...) from industrial processes and power plants is a major technological challenge. For CO<sub>2</sub> emissions, different Carbon Capture and Storage (CCS) options are currently intensively investigated. Generally speaking, there are three principal pathways to capture CO<sub>2</sub> from large emission sources, namely, oxyfuel combustion, pre-combustion capture and post-combustion capture. Oxyfuel combustion option involves burning the fuel (methane, coal, oil, biomass...) in a pure oxygen stream produced by an air separation technology such as cryogeny. A CO<sub>2</sub> / H<sub>2</sub>O mixture is thereby generated and a high purity CO<sub>2</sub> stream can be obtained after drying. In terms of separation process, O<sub>2</sub>/N<sub>2</sub> is clearly the key mixture to be treated in this case. Pre-combustion processes, through gasification, remove pollutants and CO<sub>2</sub> from fossil fuels before their conversion into electric power. A CO<sub>2</sub>/H<sub>2</sub> mixture under high temperature and pressure has to be treated. Under these conditions, inorganic membranes could be a promising separation process.

Unlike the two above options, post-combustion processes, as considered in this paper, treat flue gas streams which have a low pressure and a low CO<sub>2</sub> content, diluted in nitrogen (N<sub>2</sub>). A major advantage of the post-combustion option is that it can be in principle applied to any emission source (power plant, cement and steel factories, petrochemical plants...), including retrofit possibilities. However, the major difficulty of the post-combustion strategy comes from the low pressure and diluted CO<sub>2</sub> conditions, which correspond to a low driving force

for CO<sub>2</sub> capture and concentration. Gas-liquid absorption is currently considered as the most adequate technology for post-combustion applications.

For the three carbon capture strategies listed above, the cost of the capture-transport-sequestration chain is dominated by the capture step which represents 60-80% of the total cost. Furthermore, in order to minimize compression and transportation costs, two main constraints have to be satisfied [1]: CO<sub>2</sub> capture ratio (R) and CO<sub>2</sub> purity should be both high enough. A 90% capture ratio and 90% CO<sub>2</sub> purity are often considered as appropriate targets. Consequently, several processes for CO<sub>2</sub> post-combustion capture have been investigated and their ultimate success hinges on further refining and optimisation of the existing ones or on developing innovating processes than could lower the cost of CO<sub>2</sub> capture. These processes include absorption in liquid solvents such as MEA, adsorption on materials such as activated carbon or zeolites, membrane separation based on selective dense membrane and on a pressure gradient throughout the membrane, and chemical looping combustion based on oxygen carriers. In terms of process selection, the reduction of the energy required for the capture step, usually expressed in GJ (thermal basis) per metric ton of recovered CO<sub>2</sub>, is a key issue. A target of 2 GJ<sub>th</sub>/ton, including both the capture and compression steps is often mentioned and corresponds to the European Union recommendations [2]. Today, absorption in a chemical solvent (such as monoethanolamine, MEA) is considered as the best currently available technology for post combustion capture. However, a big issue that remains is to halve the energy consumption of the solvent regeneration step which currently requires approximately 3.5 GJ<sub>th</sub>/ton of recovered CO<sub>2</sub> without the compression requirement [4-6].

Among the different carbon capture processes, membrane separation generates growing interest. However, based on the existing materials performances, the target purity and capture ratio cannot be attained by a single stage unit, unless for a concentrated feed CO<sub>2</sub> content (typically 30%) [3,4]. For a 15% CO<sub>2</sub> content, which is typical of a coal power plant, multistage membrane units are needed and several studies recently addressed this complex design problem [5-8].

Generally speaking, cryogenic separation based on multi-compression stages with intercoolers has been widely investigated, especially for air separation, but studies devoted to the application of this technology in post-combustion capture are scarce. Cryogenic processes are indeed often presented as inherently too energy intensive for this application [9]. Consequently, research reports on cryogenic CO<sub>2</sub> capture remain limited to specific situations: high pressure feed streams such as natural gas treatment [10], CO<sub>2</sub>/O<sub>2</sub> combustion cycle [11] or concentrated CO<sub>2</sub> mixtures [12,13].

It is important to note that, for both membrane and cryogenic processes, the energy required will vary in a large part depending on the CO<sub>2</sub> composition in the flue gas to be treated. The required energy in cryogenic separation is low and very competitive when concentrated CO<sub>2</sub> flue gases are treated (approximately > 40%). On the other hand, membrane separation can offer attractive performance when a moderate purity in the permeate is the aim [3]. This suggests that a synergy between the two separations processes is possible and their combination could lead to a possible optimum with a minimal overall requirement. Interestingly, this strategy has been already investigated for argon production [14], hydrogen purification [15] and air separation [16] but, to our knowledge, no research addressed the post-combustion carbon capture framework.

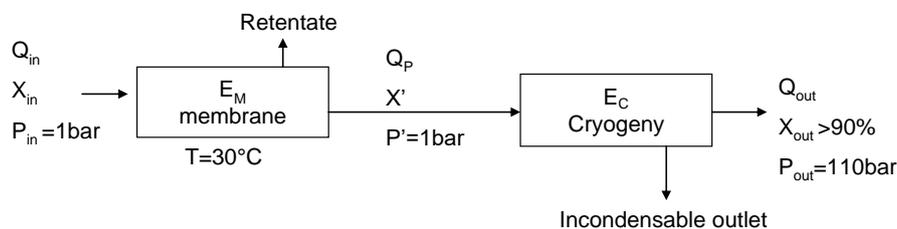
This study evaluates the value of this strategy for post-combustion carbon capture. A hybrid process combining membrane and cryogenic separation is investigated through a simulation study. It combines a first step CO<sub>2</sub> pre-concentration with a membrane process and a second step of CO<sub>2</sub> concentration and compression with a cryogenic process. Liquid CO<sub>2</sub> at high purity and under high pressure being thereby obtained, the hybrid process provides a ready to pipe transportation solution. Thus, it could possibly compete to the CO<sub>2</sub> absorption and compression steps in a classical post-combustion capture approach [17]. Given the large range of CO<sub>2</sub> concentrations which can be found in post-combustion capture, the incidence of CO<sub>2</sub> feed content will be more specifically analysed. Three different CO<sub>2</sub> concentrations will be compared: 5% (typical of a natural gas turbine exhaust), 15% (coal power plant flue gas) and 30% (steel plant or oxygen enriched air combustion). The influence of membrane selectivity and process design will be also reported, with a special emphasis on energy and membrane surface area requirement.

In a first step, the modelling and simulation framework will be described (membrane and cryogenic process). The key performances parameters (energy requirement and membrane area) will be exposed. The results of the simulation and the optimal operating conditions of the hybrid process will be discussed in the second part.

## 2. Modelling and simulation framework

### 2.1. General framework

A general diagram of the hybrid process investigated in this paper is shown on Figure 1. In this process, the inlet feed gas stream, assumed to be a dry binary mixture CO<sub>2</sub>/N<sub>2</sub> at temperature of 30°C and under atmospheric pressure, is first separated by a membrane unit to produce a more concentrated CO<sub>2</sub> purity gas stream on the permeate side. Three different composition of CO<sub>2</sub> in the inlet feed stream, noted  $x_{in}$  on Figure 1, are used to model and evaluate the performances of the process ( $x_{in} = 0.05, 0.15, 0.30$ ). The energy required for the membrane separation is noted  $E_M$ . Second, the concentrated CO<sub>2</sub> gas stream is sent to a cryogenic separation unit in order to achieve a CO<sub>2</sub> concentration to a purity of 90% or more. The energy requirement of the cryogenic unit is noted  $E_C$ . The intermediate CO<sub>2</sub> mole fraction, noted  $x'$ , is obviously a key variable to optimise in order to minimise the overall energy requirement of the hybrid process. The intermediate pressure (inlet pressure of the cryogenic unit), noted  $P'$  is fixed to 1bar.



**Figure 1:** General flow sheet of the investigated process.

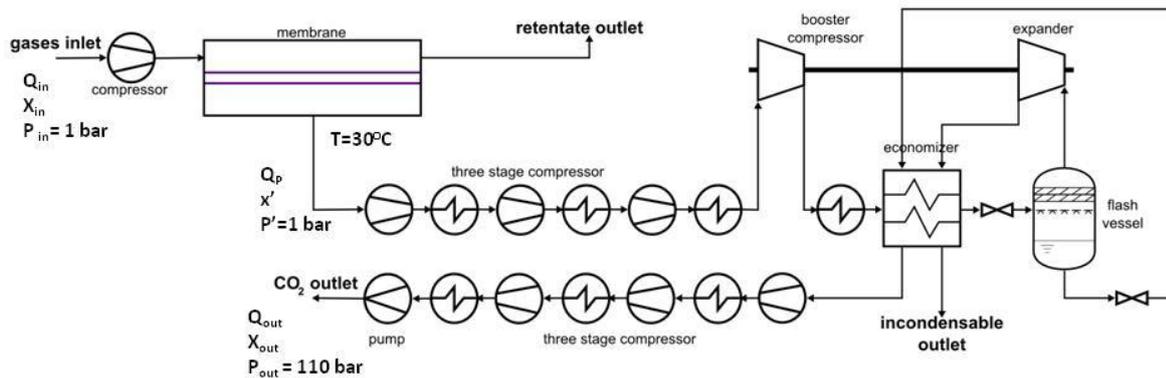
Figure 2 provides a detailed flow sheet of the process. The pre-concentration step is performed in a one stage membrane module. The CO<sub>2</sub> rich mixture is generated on the low pressure (permeate) side. No membrane material is indeed able to permeate N<sub>2</sub> faster than CO<sub>2</sub> under steady state conditions [18]. A CO<sub>2</sub> capture ratio (R<sub>1</sub>) of 0.9 is imposed for the simulations. In the case of using a feed compression strategy (case illustrated in Figure 2), the feed stream is compressed and the permeate pressure is maintained at atmospheric pressure.

As mentioned above, three different CO<sub>2</sub> gas inlet concentrations ( $x_{in} = 0.05, 0.15$  and  $0.3$ ) and two different CO<sub>2</sub>/N<sub>2</sub> membrane selectivity values ( $\alpha = 50$  and  $100$ ) were used to evaluate the interest of the process. A selectivity of 50 and a membrane permeance of 1000 Gas Permeation Unit (GPU) are typical of the best membrane materials which have been obtained to date for CO<sub>2</sub> capture thanks to dense, non reactive polymeric membranes [5]. A selectivity of 100 has been also evaluated in order to better estimate the interest of improved selectivity materials, even though this value is clearly above the performances which can be presently achieved by classical non reactive polymeric membranes.

For process design purposes, three different compression strategies, feed compression, vacuum pumping and feed compression with an Energy Recovery System (ERS), detailed in Figure 3, were studied in order to evaluate their impact on the overall process performances.

The permeate stream is sent to a cryogenic unit. Because high gas temperature is intrinsically accompanied by the gas compression and due to limiting material safety considerations, multi-stage compression with intercoolers is needed to achieve optimal separation pressures. The targets imposed in the cryogenic unit are a CO<sub>2</sub> purity ( $x_{out}$ ) higher than 94% and a CO<sub>2</sub> recovery ratio (R<sub>2</sub>) above 90%.

Table 1 summarises the hybrid process specifications used for the simulation study.



**Figure 2:** A detailed diagram of the investigated hybrid process.

**Table 1:** Key performances data of the hybrid process used for simulations in this study

<b>Feed conditions</b>	Binary mixture CO <sub>2</sub> /N <sub>2</sub>	$x_{in,CO_2} = 0.05-0.15-0.3$
	Feed pressure	1 Bar
	Gas Inlet Temperature	30°C
<b>Membrane module</b>	Compression strategies	Feed compression Vacuum pumping Feed compression-ERS
	Membrane CO <sub>2</sub> /N <sub>2</sub> selectivity ( $\alpha$ )	50-100
	Membrane permeance (GPU)	1000
	CO <sub>2</sub> capture ratio (R1)	0.9
	Compressor isentropic efficiency ( $\eta_c$ )	0.9
	Expander efficiency ( $\eta_E$ )	0.9
	Vacuum pump efficiency ( $\eta_v$ )	$\eta_v = f(\psi)$ [24] $\psi$ : membrane pressure ratio
	Thermodynamic model	Ideal gas
<b>Cryogenic separation unit</b>	CO <sub>2</sub> capture ratio (R2)	>0.94
	CO <sub>2</sub> purity ( $x_{out}$ )	>0.9
	Gas inlet temperature	30°C
	CO <sub>2</sub> delivery pressure	110 bar
	Pump Isentropic efficiency	0.8
	Compressor isentropic efficiency ( $\eta_c$ )	0.85
	Thermodynamic model	Peng-Robinson

## 2.2. Membrane module performances

The modelling of a single stage membrane module under steady state conditions is usually based on the cross-plug flow conditions. The separation performances can be computed through numerical resolution of the characteristic mass balance equations. The model used in this study has been already detailed in several studies and it will be briefly described in the following. Details of the system of equations and resolution method (based on DASSL solver in our case), can be found elsewhere [3,19,20]. This design methodology has showed to offer realistic predictions of the performances of a membrane gas separation module [21,22]. A binary dry CO<sub>2</sub>/N<sub>2</sub> mixture and isothermal separation conditions are assumed.

The inlet parameters being fixed (temperature and CO<sub>2</sub> inlet content  $x_{in}$ ), three major variables play a role on the membrane separation performances:

- i) The stage cut,  $\theta = Q_p/Q_{in}$ , is the ratio of permeate flowrate to feed flowrate. For post-combustion capture processes, it is more significant to use the carbon dioxide capture ratio discussed above,  $R = \theta \cdot x' / x_{in}$  which corresponds to the fraction of CO<sub>2</sub> in the feed which is effectively captured on the permeate stream.
- i) The membrane selectivity  $\alpha$  ( $\alpha \equiv P_{CO_2} / P_{N_2}$ ) is a key membrane material property and it corresponds to the ratio of the permeabilities of CO<sub>2</sub> over N<sub>2</sub>.

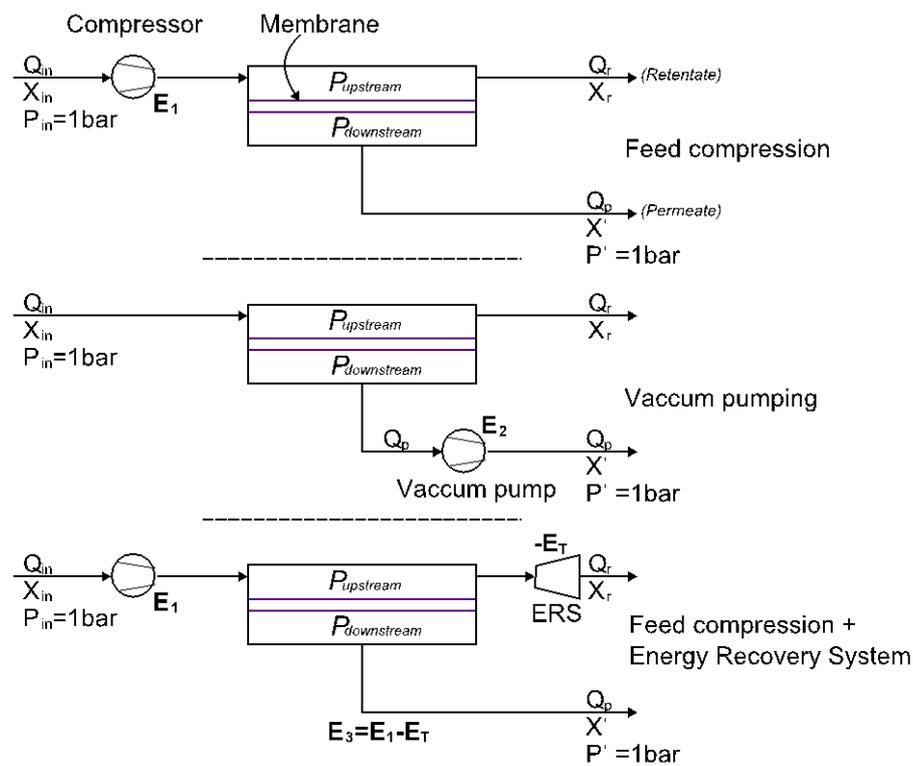
- ii) The pressure ratio ( $\psi = P_{downstream}/P_{upstream}$ ) between the upstream and downstream compartments is a key operating parameter which affects both separation performance and energy requirement.

For membrane module simulations, the feed composition ( $x_{in}$ ), membrane selectivity ( $\alpha$ ), permeate purity ( $x'$ ) and capture ratio (R) are imposed. The corresponding set of stage cut ( $\theta$ ) and pressure ratio ( $\psi$ ) are determined by numerical resolution and the energy requirement and membrane area can finally be calculated as detailed hereafter.

### 2.2.1. Membrane unit energy requirement

Simulations of the membrane unit are performed for three different compression strategies: (a) feed compression (b) vacuum pumping (c) feed compression with ERS. These strategies are illustrated on Figure 3.

The expressions used to estimate the specific energy requirement  $E_M$  of the process for each strategy are detailed in Table 2.



**Figure 3:** Schematic representation of the 3 different compression strategies of the membrane unit.

**Table 2:** Calculation of the specific energy requirement for the three different membrane compression strategies shown on Figure 3.

Compression strategy	Expression of the specific energy in GJ/ton of recovered CO <sub>2</sub> (thermal basis)
Feed compression	$E_1 = 2.7 \cdot 10^{-3} \cdot \frac{1}{\eta_c} \cdot \frac{1}{x' \cdot M(CO_2)} \cdot \frac{\gamma R T}{\gamma - 1} \left[ \left( \frac{1}{\Psi} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (1)$ <p><math>\eta_c</math> : compressor efficiency =0.90</p>
Vacuum pumping	$E_2 = 2.7 \cdot 10^{-3} \cdot \frac{1}{\eta_v(\psi)} \cdot \frac{1}{x' \cdot M(CO_2)} \cdot \frac{\gamma R T}{\gamma - 1} \left[ \left( \frac{1}{\Psi} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (2)$ <p><math>\eta_v</math> : Vacuum pump efficiency [24]: <math>\eta_v(\psi) = 0.1058 \times \ln(\psi) + 0.8746</math></p>
Feed compression with energy recovery in the retentate	$E_3 = E_1 - \eta_E * 2.7 * 10^{-3} \times \left( \frac{1}{\theta} - 1 \right) \times \frac{1}{x' \cdot M(CO_2)} \cdot \frac{\gamma R T}{\gamma - 1} \left[ \left( \frac{1}{\Psi} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (3)$ <p><math>\eta_E</math> : Expander efficiency =0.90</p>

In Table 2 expressions, the 2.7 factor corresponds to the conversion of the electrical energy which is obtained by the compression equation to a thermal energy basis, taken as reference in energy requirement for CO<sub>2</sub> capture studies [23].  $T$  is the inlet temperature (in K) and  $R$  is the ideal gas constant ( $R= 8.314$  J/(mol.K)).  $\gamma$  is the adiabatic expansion factor of the gas mixture ( $\gamma=1.4$  for nitrogen and 1.31 for carbon dioxide) defined as the ratio of the heat capacity at constant pressure  $C_p$  to heat capacity at constant volume  $C_v$ ,  $x_i$  is the molar fraction of constituent  $i$  in the mixture:

$$\gamma = \frac{\sum_{i=1}^n C_{p_i} \cdot x_i}{\sum_{i=1}^n C_{v_i} \cdot x_i} \quad (4)$$

Generally speaking, a vacuum pump shows a lower efficiency and a strong variation on pressure ratio compared to a compressor. Consequently, an expression of vacuum pump efficiency already proposed for energy estimation [24] has been used in order to take into account these specificities.

### 2.2.2. Membrane area

The dimensionless membrane surface area  $St$  has been simultaneously computed for the different simulation sets. From this variable, the real membrane surface area (expressed in m<sup>2</sup>) can be determined for a given membrane permeance. Table 3 details the expressions for different compression configurations.  $V_M$  is the molar volume of the gas ( $V_M= 22.4e^{-3}$  m<sup>3</sup>/mol),  $M(CO_2)$  is the molecular weight of CO<sub>2</sub> ( $M(CO_2) = 44$  g/mol). The permeance of the membrane is defined as a ratio between the permeability (expressed in Barrer, 1 Barrer =

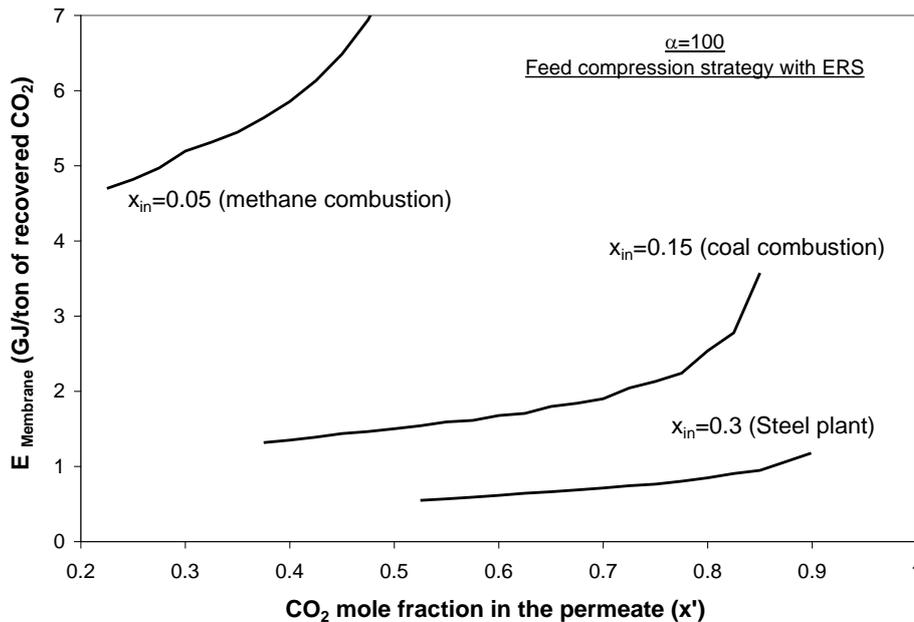
$7.6e^{-18} \text{ m}^2 \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ ) and the membrane thickness. Permeance was fixed to a value of 1000 GPU for all simulations ( $1 \text{ GPU} = 7.6e^{-12} \text{ m} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ ).

**Table 3:** Detailed expressions for the determination of the membrane surface area

Compression strategy	Expression of surface membrane area in $\text{m}^2 / (\text{Kg of recovered CO}_2 \cdot \text{s}^{-1})$
Feed compression with or without ERS	$S_1 = S_3 = \frac{1}{x' \cdot M(\text{CO}_2) \cdot 10^{-3}} V_M \frac{1}{\text{permeance}} \frac{1}{P_{\text{upstream}}} \frac{St}{\theta} \quad (5)$ $P_{\text{upstream}} = P_{\text{downstream}} / \psi, P_{\text{downstream}} = 1 \text{ bar}$
Vacuum pumping	$S_2 = \frac{1}{x' \cdot M(\text{CO}_2) \cdot 10^{-3}} V_M \frac{1}{\text{permeance}} \frac{1}{P_{\text{upstream}}} \frac{St}{\theta} \quad (6)$ $P_{\text{upstream}} = 1 \text{ bar}$

### 2.2.3. Example of simulation results

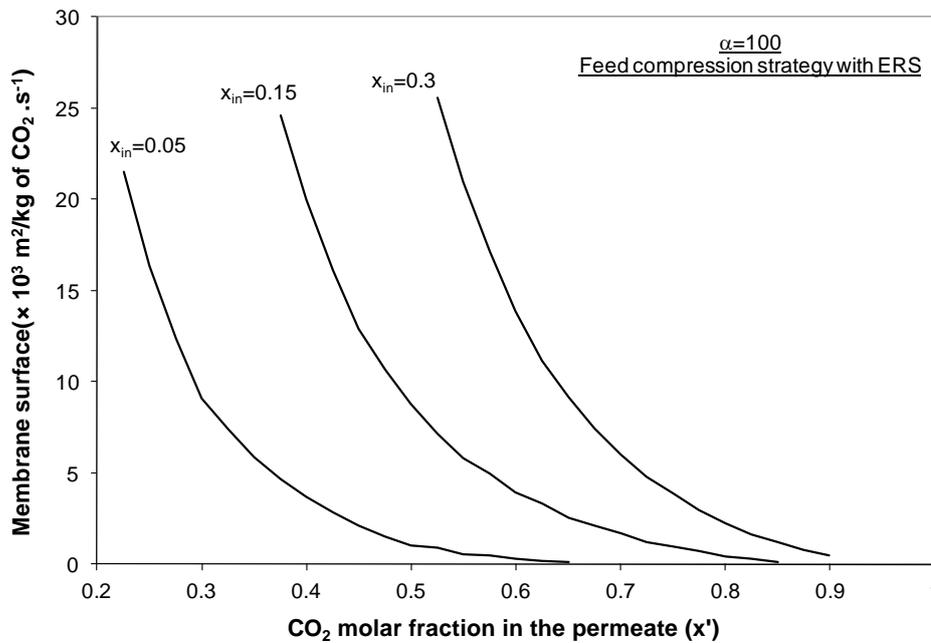
An example of simulation results of the performances of a membrane module is shown in Figures 4 and 5. A membrane selectivity  $\alpha$  of 100 and a  $\text{CO}_2$  recovery ratio of 0.9 have been imposed for the calculations. The results have been obtained for a capture step only, using feed compression with ERS strategy, but without taking into account the permeate recompression step for  $\text{CO}_2$  transport. Figure 4 shows the influence of the  $\text{CO}_2$  purity on the permeate side ( $x'$ ), on the energy requirement ( $E_M$ ) of the unit for the three characteristic inlet  $\text{CO}_2$  compositions in the flue gas.



**Figure 4:** Influence of CO<sub>2</sub> purity in the permeate ( $x'$ ) on the energy requirement of the unit for different inlet CO<sub>2</sub> content.

Figure 4 shows the very high sensitivity toward CO<sub>2</sub> content in the feed gas and that the energy decreases when a high CO<sub>2</sub> mole ratio has to be treated. Also, the plots show that the energy requirement increased with the increase of the CO<sub>2</sub> purity target in the permeate. A target of 90% CO<sub>2</sub> purity could be attainable only with a CO<sub>2</sub> inlet mole fraction  $x_{in} > 0.15$ . As shown in Figure 5, contrary to energy requirement, the membrane surface area decreases with increasing the CO<sub>2</sub> mole fraction in the permeate. Also, with the increase of CO<sub>2</sub> inlet content in the feed, more surface membrane area is needed to attain the same CO<sub>2</sub> purity.

The opposing tendencies of the membrane surface area and the energy requirement with respect to CO<sub>2</sub> purity, implies the existence of an optimum of CO<sub>2</sub> purity ( $x'_{opt}$ ) corresponding to a minimum cost of the membrane unit. In summary, for the different simulations which will be described afterwards, the key outputs data will be the energy requirement expressed in  $GJ_{th}$  for the capture of one ton of CO<sub>2</sub> and the corresponding membrane surface area in ( $m^2/kg CO_2 \cdot s^{-1}$ ).



**Figure 5:** Surface membrane area as a function of the CO<sub>2</sub> purity in the permeate ( $x'$ ) for different inlet CO<sub>2</sub> content in the feed.

### 2.3. Cryogenic separation performance

The process diagram of the chosen cryogenic separation process is shown on the right side of Figure 2. The inlet gas is compressed in three intercooled stages to an intermediate pressure and then a booster compressor raises the pressure. Afterwards, the gas is cooled down by water and cooled down further by the outlet flash vessel streams. The gas goes through a valve in order to reach the minimal necessary liquefaction pressure. The liquid CO<sub>2</sub> stream pressure is set to 6 Bar.

The incondensable gas stream pressure is reduced to 1 atm through a turbine (the turbine is coupled with the booster compressor). After being heated in the economizer, the CO<sub>2</sub> is compressed further to 90 Bar in another three intercooled stage and then pumped to the delivery pressure: 110 Bar. For the lower CO<sub>2</sub> inlet fraction, part of the CO<sub>2</sub> is still liquid after the economizer, the stream is then flashed and the liquid is directly pumped to the delivery pressure.

The inlet pressure flash is set in order to have a CO<sub>2</sub> partial pressure of 5.4 Bar ensuring a proper liquefaction of CO<sub>2</sub> and non frosting conditions (de-sublimation). The set of fixed parameters is reported on Table 1. Similarly to the membrane capture unit simulations, the inlet stream is assumed to be dry and all diluting gases are assimilated to N<sub>2</sub>.

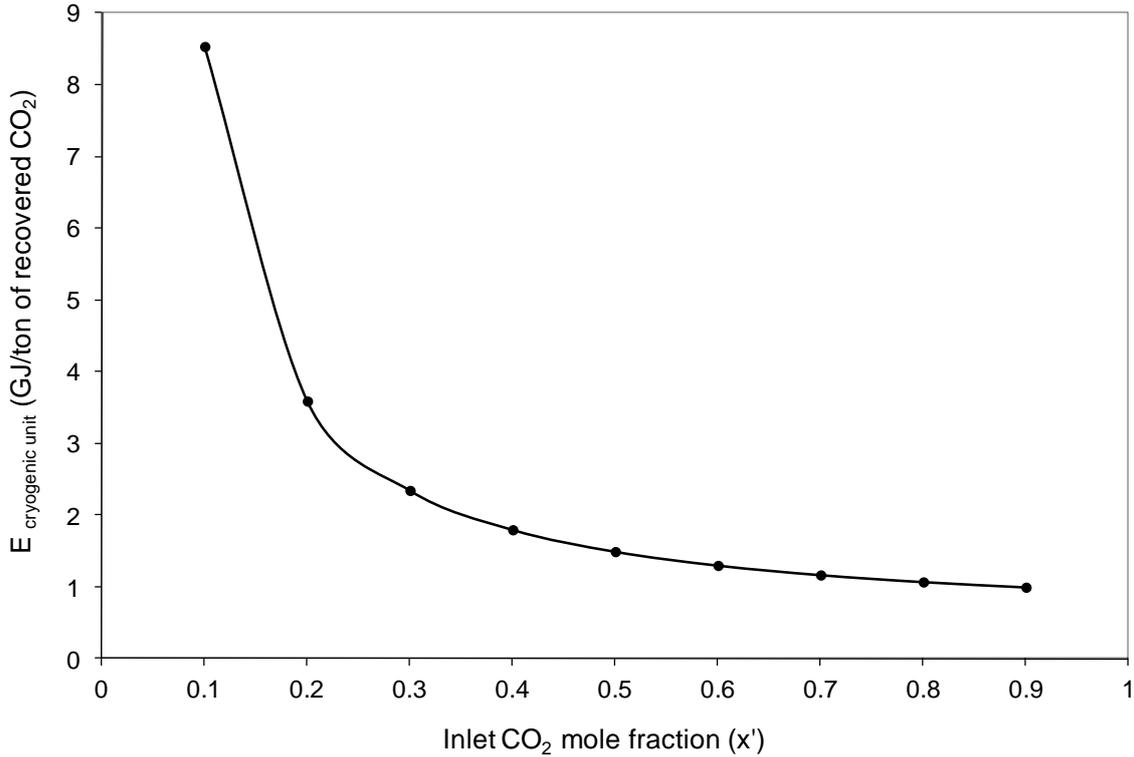
Simulation results of the cryogenic step are summarized on Table 4 and the energy requirement of the cryogenic unit is plotted as a function of inlet CO<sub>2</sub> mole fraction on Figure 6. The energy requirement obtained through simulations, based on an electricity basis (kWh/ton), has been converted to a thermal basis (GJ<sub>th</sub>/ton) thanks to the 2.7 factor mentioned in the introductory part. The cryogenic energy requirement reported on Figure 6 can be fitted by the following expression:

$$E_2[\text{GJ/ton of recovered CO}_2] = 2.7 * \left( \frac{3.718}{x'^2} + \frac{45.937}{x'} + 46.74 \right) * 3.6e^{-3} \quad (7)$$

It can be seen that the energy requirement increases very significantly with decreasing the CO<sub>2</sub> inlet mole fraction (especially for  $x' < 0.2$ ). Taking 4 GJ<sub>th</sub>/ton as the overall energy requirement of the carbon capture plus compression step for the MEA absorption unit [17], an all cryogenic process is clearly non competitive with a gas absorption unit when the feed CO<sub>2</sub> content is lower than 20%. Moreover, a standalone cryogenic process cannot reach the 2 GJ<sub>th</sub>/ton target for a feed CO<sub>2</sub> content lower than 40%. This parametric sensitivity analysis confirms the conclusion of previous carbon capture studies: cryogenic capture is too energy intensive for diluted CO<sub>2</sub> mixtures [9], but it may offer interesting energy efficiency performances when concentrated CO<sub>2</sub> streams have to be treated [12].

**Table 4:** Simulation results of the cryogenic step

Inlet CO <sub>2</sub> %	Outlet booster pressure (Bar)	Inlet flash pressure (Bar)	Outlet economizer temperature °C	CO <sub>2</sub> product purity (%)	CO <sub>2</sub> recovery (%)	Energy requirement (GJ <sub>th</sub> /ton of CO <sub>2</sub> )
10	63.0	54.0	-125	92	94	8.53
20	34.0	27.0	-108	96	95	3.55
30	24.0	18.0	-103	97	95	2.41
40	19.0	13.5	-100	98	95	1.80
50	16.0	10.8	-97	98	95	1.47
60	14.5	9.0	-93	99	95	1.28
70	13.0	7.7	-89	99	95	1.16
80	11.5	6.8	-82	99	95	1.07
90	11.0	6.0	-73	99	95	1.01



**Figure 6:** CO<sub>2</sub> recovery specific energy requirement expressed in GJ per ton as a function of inlet CO<sub>2</sub> mole fraction

As seen in the previous sections, and according to Figures 4 and 6, the energy for membrane unit increases as a function of  $x'$  (the intermediate CO<sub>2</sub> mole fraction) while the energy for cryogenic unit decreases. This suggests that the overall energy requirement of the hybrid process, defined as the sum of the energy membrane unit ( $E_M$ ) and cryogenic unit ( $E_C$ ), shows a minimum towards  $x'$ . Based on this, it is interesting to explore the possibility of an energy requirement of the hybrid process lower than that the energy required for full-cryogenic process.

In the following, the results of the hybrid process simulation are presented and discussed.

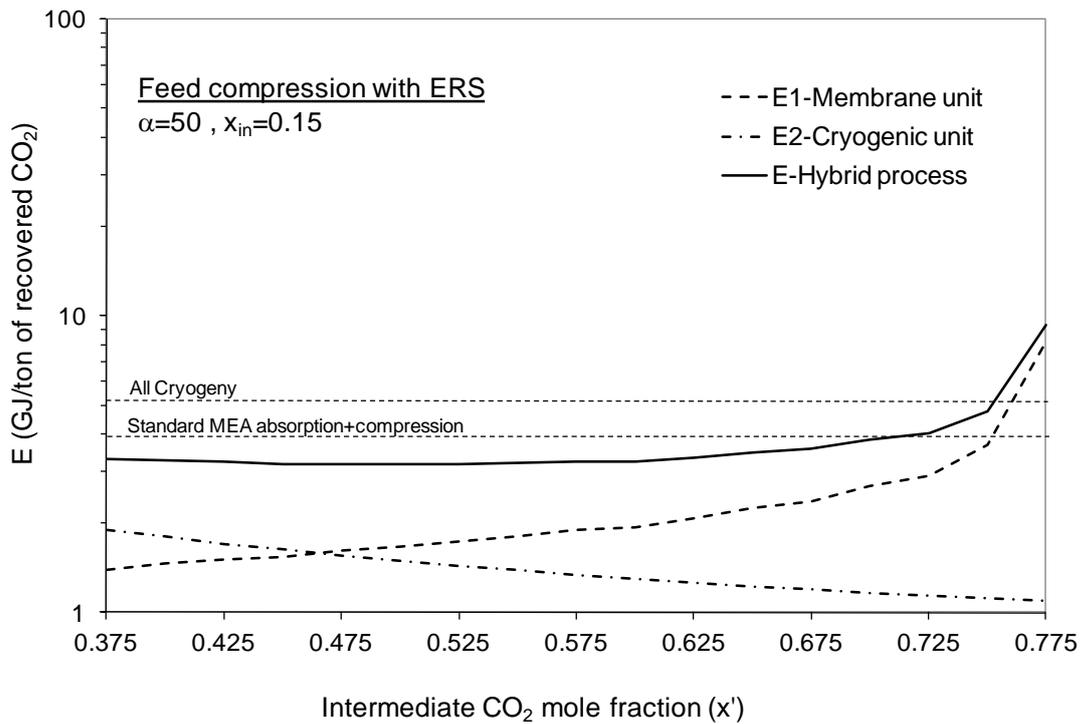
### 3. Results & discussion

First, the energy requirement of the hybrid process is computed as a function of the intermediate CO<sub>2</sub> mole fraction  $x'$  for three different compression strategies in the membrane unit. Second, the overall minimum energy  $E_{min}$  is determined for each set of operating conditions, the optimal conditions specified and the interest of the hybrid process comparing to other classical processes will be highlighted. Finally, the membrane surface area is computed for different compression strategies.

#### 3.1 Hybrid process performance: overview

In a first step, the occurrence of a minimum energy requirement has been explored for a proof of concept purpose. An illustrative example is shown on Figure 7. A power plant flue gas ( $x_{in} = 0.15$ )

is simulated with a membrane unit working with compression and an Energy Recovery System (ERS). It can be seen that the hybrid process significantly decreases the energy requirement compared to the standalone cryogeny option (upper dotted line). Moreover, under optimal conditions (i.e. for  $x'$  approximately ranging between 0.5 and 0.6), the energy requirement is competitive with the reference technology, namely the absorption + compression strategy. Thus, the hybrid strategy proposed in this study seems to offer improved performances compared to a single membrane (Figure 4) or a full cryogenic unit (Figure 7). This particularly applies for a CO<sub>2</sub> content of 15%, which is the main target of carbon capture studies.

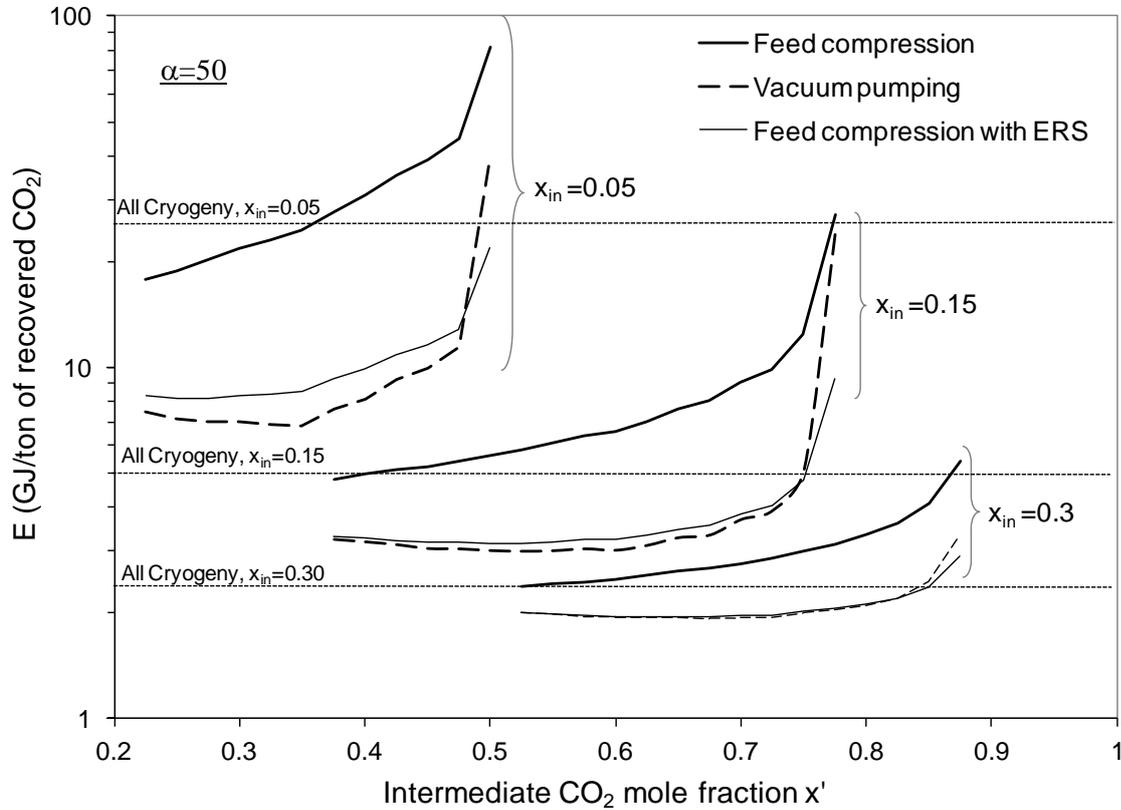


**Figure 7:** Example of a set of simulation data for the hybrid process. A 15% CO<sub>2</sub> flue gas is treated by a membrane unit working with the compression + ERS and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 50. The CO<sub>2</sub> specific energy requirement is plotted as a function of intermediate CO<sub>2</sub> mole fraction  $x'$  (permeate composition).

In a second step, the three membrane configurations and three feed compositions have been simulated for a membrane showing a selectivity of 50. The results are shown on Figure 8. The very high parametric sensitivity of the specific energy requirement vs the CO<sub>2</sub> content in the feed mixture is noticeable. This behavior reflects the peculiarities of both the membrane and cryogenic units.

It can be seen that the differences between the compression strategies is more significant with the decrease of  $x_{in}$ . Besides, as expected, the feed compression with ERS and vacuum pumping strategies allow better performances far from feed compression without ERS. Moreover, the feed compression with turbo expander and permeate vacuum strategies have generally similar values, with the permeate vacuum energy being slightly lower. Thus, the compression option without ERS, which logically corresponds to the higher energy requirement, does not appear to be a relevant strategy and will not be further considered in the following sections.

For  $x_{in}=0.05$ , the energy requirement always exceeds 6 GJ/ton. Thus, the hybrid process can by no means compete with the MEA absorption + compression option in that case, which corresponds to natural gas turbine flue gases. Nevertheless, the energy requirement drastically decreases for higher CO<sub>2</sub> contents and a more detailed analysis of the pros and cons of the hybrid process will be presented hereafter.

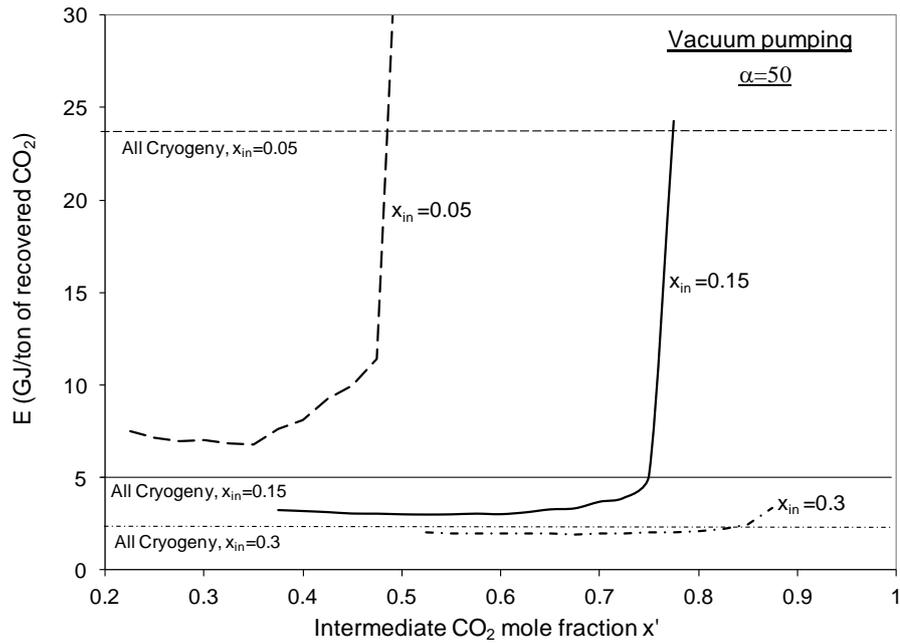


**Figure 8:** Simulation results of the hybrid process for 3 different flue gases composition and 3 membrane configurations for a membrane CO<sub>2</sub>/N<sub>2</sub> selectivity of 50. The CO<sub>2</sub> specific energy requirement of the hybrid process is plotted as a function of intermediate CO<sub>2</sub> mole fraction  $x'$  (permeate composition). The energy requirement of the all-cryogenic process is also reported for each  $x_{in}$  value (horizontal lines) for sake of illustration.

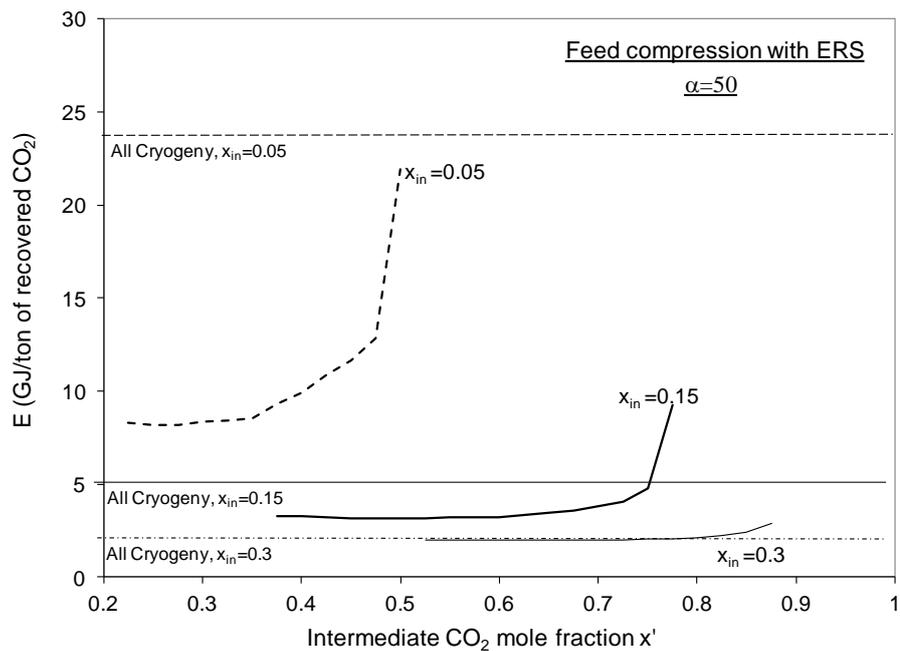
### 3.2 Energy requirement of the hybrid process

Figure 9 shows, for two different compression strategies, a detailed evolution of the energy required for the hybrid process as a function of  $x'$ . The curves are plotted for a membrane selectivity of 50 and for different inlet CO<sub>2</sub> mole fractions  $x_{in}$  (0.05-0.15-0.3). For  $x_{in}=0.05$  a minimum energy of 6.79 GJ/ton with  $x'_{opt}$  of 0.355 could be obtained. When  $x'$  exceeds 0.5, the hybrid process requires more energy than full cryogenic process. With increasing  $x_{in}$ , the energy gained comparing to full-cryogenic process decreases. For  $x_{in}=0.3$ , a minimum Energy of 1.93 GJ/ton with  $x'_{opt}$  of 0.675 could be obtained.

Consequently, the hybrid process appears to be particularly interesting for intermediate CO<sub>2</sub> contents (i.e. around 15%): for diluted flue gases (5% and below), the energy penalty is too high compared to MEA absorption, while for more concentrated streams (30% and above), the economy is almost negligible compared to a full cryogenic process.



(a)



(b)

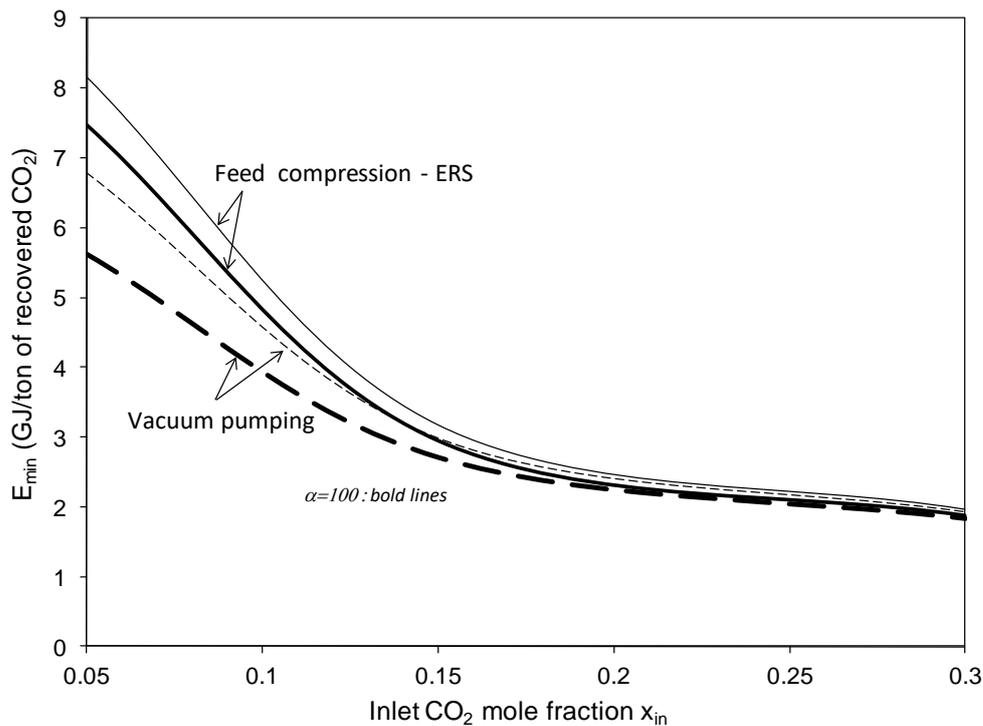
**Figure 9:** Evolution of the overall energy as a function of  $\text{CO}_2$  mole fraction  $x'$  for three different flue gas compositions:  $x_{in}=0.05$   $x_{in}=0.15$   $x_{in}=0.3$ . Membrane selectivity ( $\alpha$ ) is set at 50. The energy requirement of the all-cryogenic process is also reported for each  $x_{in}$  value (horizontal lines) for sake of illustration.

a) Vacuum pumping strategy

b) Feed compression strategy with ERS

### 3.3 Minimum energy requirement, influence of membrane selectivity

It is interesting to explore at this stage the potential interest of improved membrane materials on the energy requirement of the hybrid process. A hypothetical membrane showing a CO<sub>2</sub>/N<sub>2</sub> selectivity of 100 in place of 50 has been simulated for this purpose. Figure 10 shows a comparison of the minimum energy  $E_{\min}$  as a function of  $x_{\text{in}}$  for the two selected membrane selectivities ( $\alpha=50$  and 100) as a function of the feed mixture CO<sub>2</sub> content. Generally speaking, the minimum energy consumption of the hybrid process is very slightly influenced by membrane selectivity (50 or 100). This effect is more important for low mole fraction in the feed, typically 0.05. For  $x_{\text{in}}=0.3$ , a minimum energy of 1.88 GJ/ton is attained using a membrane selectivity of  $\alpha=100$ . Using membrane unit to achieve CO<sub>2</sub> capture on gas stream concentration of  $x_{\text{in}}=0.3$  and with the same membrane required only 1.18 GJ/ton. The energy requirement of the permeate compression step from 1 bar to 110 bar, has to be added to this value. Nevertheless, the total energy cost of the membrane + compression strategy is still slightly below the hybrid process. That suggests that for high CO<sub>2</sub> feed content (>30%), membrane process permits better performance than hybrid process. When  $x_{\text{in}}=0.05$ , a minimum energy of 5.5 GJ/ton is obtained but still very high. With low inlet CO<sub>2</sub> mole fraction, the amine absorption process clearly seems to be more appropriate.



**Figure 10:** Evolution of  $E_{\min}$  as a function of CO<sub>2</sub> mole fraction in the feed, different compression strategy and membrane selectivity ( $\alpha=50$  and 100).  **$\alpha=100$ : bold lines**

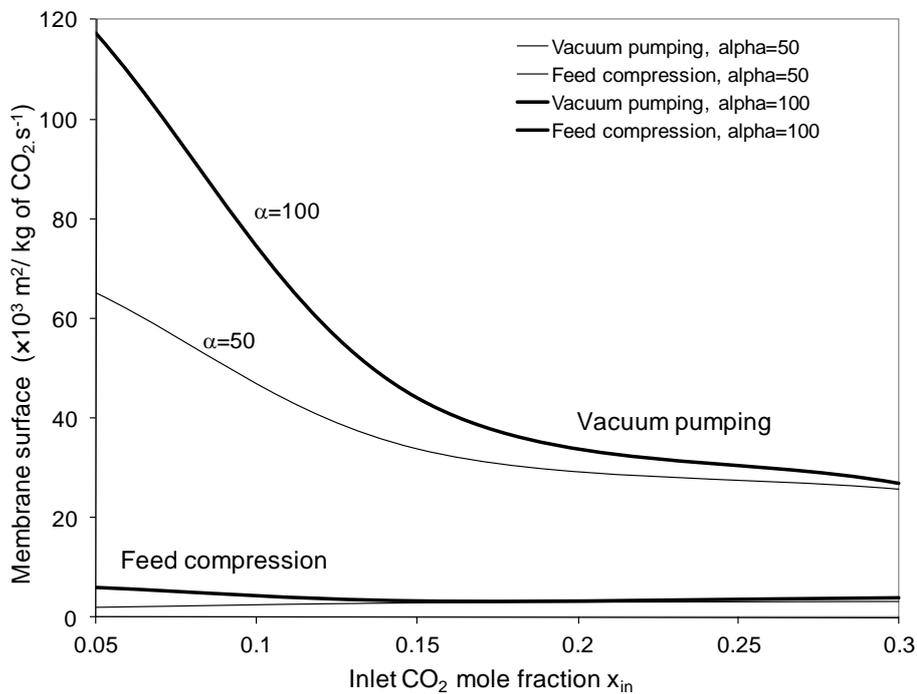
The minimal energy requirement of the hybrid process for the different situations tested and the optimal permeate concentration  $x'_{\text{opt}}$  determined for each set of operating conditions are summarized on Table 5. For sake of simplification, only results corresponding to feed compression with ERS and vacuum pumping are reported.

Table 5: **Minimum energy requirement – Summary of results**

			Vacuum pumping strategy			Feed compression with ERS		
Inlet mole fraction $x_{in}$	Membrane selectivity ( $\alpha$ )	$E_{all-cryogeny}$ (GJth/ton)	$x'_{opt}$	$P_{permeate}$ (bar)	$E_{min}$ (GJ <sub>th</sub> /ton)	$x'_{opt}$	$P_{retentate}$ (bar)	$E_{min}$ (GJ <sub>th</sub> /ton)
0.05	50	23.84	0.35	0.0031	6.79	0.25	16.4	8.16
	100		0.4	0.0035	5.62	0.35	22.22	7.47
0.15	50	5.04	0.525	0.0086	2.99	0.45	8.26	3.17
	100		0.575	0.009	2.70	0.575	11.11	2.95
0.3	50	2.34	0.675	0.16	1.93	0.625	5.13	1.96
	100		0.75	0.145	1.83	0.70	5.88	1.88

### 3.4 Membrane surface area requirement

Figure 11 presents the calculated membrane surface area corresponding to the minimum energy of the hybrid process, as a function of inlet CO<sub>2</sub> mole fraction  $x_{in}$ . The results are summarised on Table 6. One can observe that logically the required membrane surface is very high for vacuum pumping strategy compared to feed compression strategy, a factor of 20 is attained.



**Figure 11:** Evolution of membrane surface area as a function of CO<sub>2</sub> mole fraction in the feed. Two compression strategies in the membrane unit,  $\alpha=100$  (bold line).

Also, it can be seen that when vacuum pumping strategy is used, the membrane surface area is significantly increased by the selectivity of the membrane. This behavior has been already

reported in previous studies [5]. It clearly limits the interest of improved selectivity materials, which have been shown above to offer a limited impact on the energy requirement (Figure 10). Interestingly, the required membrane area of the hybrid process decreases with increasing CO<sub>2</sub> molar feed fraction. In the case of feed compression strategy, the membrane surface area is only very slightly influenced by inlet CO<sub>2</sub> mole fraction and membrane selectivity.

According to Figure 11, the feed compression strategy with ERS is clearly found to be more interesting configuration from both points of view: energy consumption and membrane surface area. An economic cost study based on these data would obviously be of great interest in order to evaluate the economic interest of the hybrid process compared to the reference MEA absorption technology.

**Table 6:** Membrane Surface Area – Summary of results

		Membrane Surface Area ( $\times 10^3 \text{m}^2 / \text{kg of recovered CO}_2 \cdot \text{s}^{-1}$ )	
Molar feed fraction $x_{in}$	Membrane Selectivity ( $\alpha$ )	Vacuum pumping strategy	Feed compression strategy
0.05	50	65.10	2.02
	100	117.23	5.89
0.15	50	33.88	2.91
	100	44.11	3.31
0.3	50	25.80	3.19
	100	26.94	3.91

## 4. Conclusion

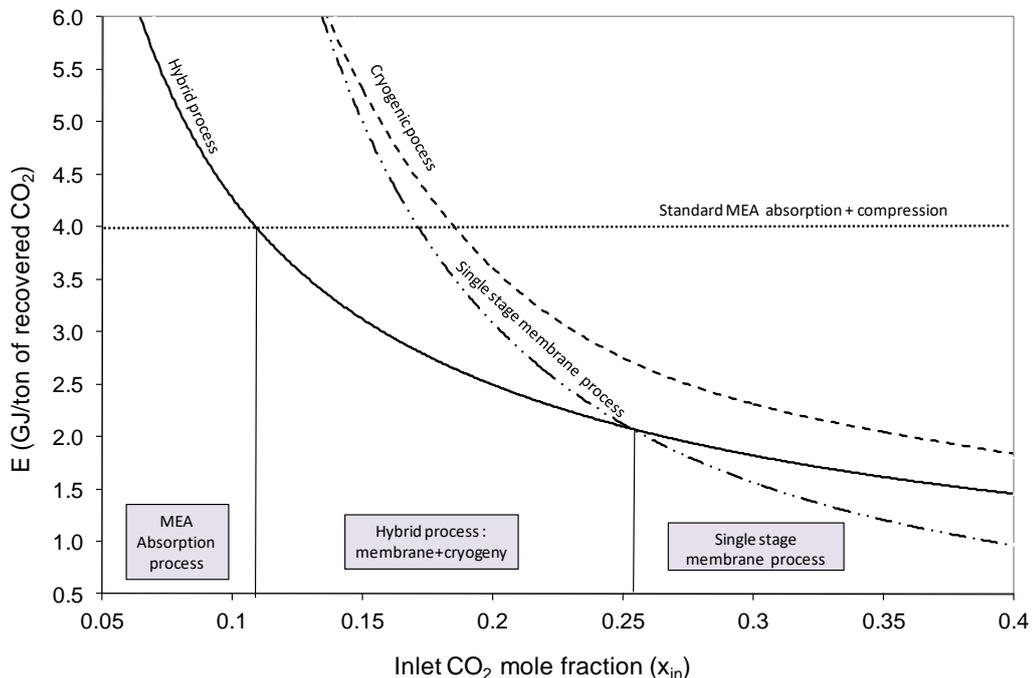
A novel post-combustion CO<sub>2</sub> capture strategy, based on a hybrid membrane/cryogenic process, has been investigated in this study. The major conclusions can be summarized as follows:

- The hybrid process effectively improves the energy efficiency compared to a standalone cryogenic approach when diluted (i.e. < 30%) CO<sub>2</sub> inlet concentrations have to be treated. The percentage energy decrease significantly increases for lower inlet CO<sub>2</sub> mole fractions.
- Compared to the reference post-combustion carbon capture technology, namely MEA absorption, the hybrid process offers improved energy performances in the 12%-25% range. This corresponds to a large proportion of emission sources, such as coal power plant flue gases (for the lower range) and oxygen enriched air combustion (for the upper range). The hybrid process is however too energy intensive for a CO<sub>2</sub> content lower than 12%, such as natural gas turbine exhaust gases.
- In terms of membrane compression strategies, the compression + Energy Recovery Systems clearly shows the best performances: the energy requirement of this option

is very close to vacuum pumping, while the membrane surface area is greatly decreased.

- From the membrane performances point of view, an improved selectivity (such as 100 in place of 50) does not offer a substantial benefit: the energy requirement is almost the same and the membrane area increases. The membrane base case (selectivity 50, permeance 1000 GPU) therefore seems to be appropriate. It is important to note that this level of performances corresponds to already available membrane modules [5].
- One major advantage of the hybrid process is that it offers a high degree of flexibility, with respect to the capture ratio and/or final CO<sub>2</sub> purity. For instance, taking 15% inlet CO<sub>2</sub> content and 98% purity, the energy requirement could be significantly reduced down to 2 GJ/ton providing that lower recovery ratio is applied.
- Finally, the hybrid process is based on two physical separation steps which make use of electricity but not steam. Because the system does not require the use of chemicals, it can be expected that no losses or secondary emissions of chemical compounds will occur. Additionally, a capture process based on electricity only may be simpler to adapt, since no modifications of the steam piping system is needed.

From a more general point of view, it is interesting to visualize the different processes and simulations reported in this study in an approximate process selection map. Similar graphs have been already reported for major separation applications such as air separation or seawater desalination. An illustrative example is shown as Figure 12.



**Figure 12:** A schematic process selection map for post-combustion CO<sub>2</sub> capture as a function of the flue gas composition (inlet CO<sub>2</sub> mole fraction)- Membrane selectivity =100 - CO<sub>2</sub> purity =90% and total recovery ratio >=85%. Framed processes correspond to the more energy efficient process for different  $x_{in}$  ranges.

Finally, this study offers several perspectives which will be addressed in future work:

- Process improvements, especially for the cryogenic step, could be investigated. For instance, with modifications such as double flash separation, two expansion turbine... an energy consumption gain of 10 % could realistically be achieved [25]. For comparison, a six stage intercooled (to 30 °C) compressor completed by a supercritical fluid pump consumes 86 kWh/t<sub>CO<sub>2</sub></sub> (0.84 GJ/ton of recovered CO<sub>2</sub>) for a compression from 1 atm to 110 Bar.
- The simulations reported in this study, similarly to most studies performed on CO<sub>2</sub> capture, have been based on a dry CO<sub>2</sub>/N<sub>2</sub> mixture. The influence of humidity, oxygen and other trace compounds of flue gases should be investigated.
- The strong parametric sensitivity of the hybrid process should be more systematically investigated. More specifically, a slight decrease of the target capture ratio (such as 85% in place of 90%) can have a very strong impact on the membrane step energy requirement. This suggests that the overall energy requirement of the hybrid process could possibly be significantly decreased if a less stringent capture ratio constraint is taken.
- One conclusion of the study is that in order to reduce the membrane area it is appropriate to seek to first increase the input CO<sub>2</sub> concentration to 15-30%. This can readily be accomplished by a mixture of flue gas recirculation, supplementary firing, and combustion with oxygen enriched air. More detailed process and simulations analyses of the possibilities of associations of these advanced fossil fuel combustion processes with the hybrid approach should be undertaken.
- An economic analysis of the hybrid membrane/cryogeny process should be undertaken. Key cost functions for the membrane, compressors, turbine, heat exchangers and pumps are obviously needed in order to achieve that purpose. This objective is beyond the scope of this paper. Nevertheless, it is hoped that the key data reported in this study will give to experts the possibility to undertake technical-economical analysis.

## Nomenclature

$E$	Overall energy requirement (GJ <sub>th</sub> /ton CO <sub>2</sub> recovered)
$E_M$	Energy required for the membrane separation (GJ <sub>th</sub> /ton CO <sub>2</sub> recovered)
$E_C$	Energy required for the cryogenic unit (GJ <sub>th</sub> /ton CO <sub>2</sub> recovered)
$P_{\text{upstream}}$	Membrane module upstream side pressure (Bar)
$P_{\text{downstream}}$	Membrane module downstream side pressure (Bar)
$P_{\text{in}}$	Feed mixture pressure of the hybrid process, fixed to 1 bar.
$P_{\text{out}}$	Outlet pressure in the hybrid process, fixed to 110 bar.
$P'$	Intermediate pressure (inlet pressure of the cryogenic unit), fixed to 1bar.
$\rho$	Membrane permeability coefficient (mol.m <sup>-1</sup> .s <sup>-1</sup> .Pa <sup>-1</sup> )
$Q_{\text{in}}$	Inlet total flow rate (mol/s)
$Q_P$	Permeate flow rate (mol/s)
$Q_R$	Retentate flow rate (mol/s)
$R$	Carbon dioxide capture ratio [-]
$R$	Ideal gas constant (8.314 J. mol <sup>-1</sup> .K <sup>-1</sup> )

St	Total non-dimensional membrane surface area (-)
T	Temperature (K)
$x_{in}$	CO <sub>2</sub> mole fraction in the feed mixture (-)
$x'$	CO <sub>2</sub> mole fraction in permeate (-)
$x'_{opt}$	Optimal intermediate CO <sub>2</sub> mole fraction (-)

#### *Greek letters*

$\alpha$	Membrane selectivity [-]
$\gamma$	Adiabatic gas expansion coefficient [-]
$\psi$	Membrane module pressure ratio [-]
$\theta$	Stage cut [-]
$\eta_C$	compressor isentropic efficiency (-)
$\eta_V$	Vacuum pump efficiency (-)
$\eta_E$	Expander efficiency (-)

#### **References**

- [1] O. Davidson, B. Metz, Special Report on Carbon Dioxide Capture and Storage, International Panel on climate Change, Geneva, Switzerland (2005) <http://www.ipcc.ch>.
- [2] P. Descchamps, P.A. Pilavachi, Research and development actions to reduce CO<sub>2</sub> emissions within the European Union. *Oil Gas Sci Technol* 59(3) (2004) 323-30.
- [3] R. Bounaceur, N. Lape, D. Roizard, C. Vallières, E. Favre, Membrane processes for post-combustion carbon dioxide capture: a parametric study. *Energy*, 31(2006) 2556-2570.
- [4] E. Favre, Carbon dioxide recovery from post combustion processes: Can gas permeation membranes compete with absorption ? *Journal of Membrane Science* 294 (2007) 50-59.
- [5] T. Merkel, H. Lin, X. Wei, R. Baker, Power plant post-combustion carbon dioxide capture: An opportunity for membranes, *Journal of Membrane Science*, 359, Issues 1–2 (2010) 126-139.
- [6] H. Herzog, What future for carbon capture and sequestration? *Environ. Sci. Technol.*, 35,7 (2001) 148–153.
- [7] J.P. Van der Sluis, C.A. Hendriks, K. Blok, Feasibility of polymer membranes for carbon dioxide recovery from flue gases, *Energy Conversion & Management*, 33, 5-8 (1992) 429.
- [8] L. Zhao, E. Riensche, L. Blum, D. Stolten, Multi-stage gas separation membrane processes used in post-combustion capture: Energetic and economic analyses, *Journal of Membrane Science*, 359, Issues 1–2 (2010) 160-172.
- [9] A. Meisen, X. Shuai, Research and development issues in CO<sub>2</sub> capture, *Energy Conversion and Management*, 38 (1997) S37-S42A.
- [10] A.Hart, N. Gnanendran, Cryogenic CO<sub>2</sub> capture in natural gas, *Energy Procedia*, 1-Issue 1 (2009) 697-706.
- [11] Z. Meratla, Combining cryogenic flue gas emission remediation with a CO<sub>2</sub>/O<sub>2</sub> combustion cycle, *Energy Conversion and Management*, 38 (1997) S147-S152
- [12] K. E. Zanganeh, A. Shafeen, C. Salvador, CO<sub>2</sub> Capture and Development of an Advanced Pilot-Scale Cryogenic Separation and Compression Unit , *Energy Procedia*, 1(2009) 247-252.

- [13] M.O Schach, B. Oyarzun, H. Schramm, R. Schneider, J.U. Repke, Feasibility study of CO<sub>2</sub> capture by anti-sublimation, *Energy Procedia*, 4 (2011) 1403-1410.
- [14] R. Agrawal, S.R. Auvil, J.S. Choe, D.W. Woodward, Membrane/cryogenic hybrid scheme for argon production from air, *Gas Separation & Purification*, 4, 2 (1990) 75-80.
- [15] R. Agrawal, S.R. Auvil, S.P. DiMartino, J.S. Choe, J.A. Hopkins Membrane/cryogenic hybrid processes for hydrogen purification, *Gas Separation & Purification*, 2 (1988) 9-15.
- [16] T. Burdyny, H. Struchtrup, Hybrid membrane/cryogenic separation of oxygen from air for use in the oxy-fuel process, *Energy*, 35, 5 (2010) 1884-1897.
- [17] R. Steeneveldt, B. Berger, T.A. Torp, CO<sub>2</sub> capture and storage: closing the knowing doing gap. *Chem. Eng. Res. & Des.*, 84-A9 (2006)739-763.
- [18] E. Favre, D. Roizard, W.J. Koros, (2009) Reverse selective N<sub>2</sub> /CO<sub>2</sub> membranes for carbon capture. *Ind. Eng. Chem. Res.*, 48 (2009) 7, 3700-3701.
- [19] J. Kotowicz, T. Chmielniak, K Janusz-Szymanska, The influence of membrane CO<sub>2</sub> separation on the efficiency of a coal-fired power plant, *Energy* 35 (2010) 841–850.
- [20] L. Zhao, E. Riensche, R. Menzer, L. Blum D. Stolten,. A parametric study of CO<sub>2</sub>/N<sub>2</sub> gas separation membrane processes for post-combustion capture. *J. Memb. Sci.* 325(2008), 284–294.
- [21] R. Zolandz, G.K. Fleming, Gas permeation applications, in *Membrane Handbook*, W.S. Ho and K.K. Sirkar Eds, Van Nostrand Reinhold, New York, (1995).
- [22] R.W. Baker, *Membrane Technology and Applications*, 2nd Ed. John Wiley & Sons, Chichester, England (2004).
- [23] L. D. Harvey, *Energy and the new reality : Energy efficiency and the demand for energy services*, Earthscan Publications Ltd, (2010) | ISBN: 1844079120.
- [24] N. Matsumiya, M. Teramoto, S. Kitada, H.Matsuyama Evaluation of energy consumption for separation of CO<sub>2</sub> in flue gas by hollow fiber facilitated transport membrane module with permeation of amine solution, *Separation and Purification Technology*, 46 (2005) 26-32.
- [25] M. Pottmann, G. Engl, B. Stahl, R. Ritter, Dynamic simulation of Oxyfuel CO<sub>2</sub> processing plants. *Energy Procedia*, 4 (2011) 951-957.