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***Energy recovery system on a gas turbine cycle
combining CO₂ capture by membranes: Overall
efficiency improvements***

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Abstract

Post combustion Carbon Capture and Storage (CCS) is currently intensively investigated as a key issue for the mitigation of greenhouse gases emissions. A very large number of studies is dedicated to coal power plants. In this paper, the possibility to achieve carbon capture on a gas turbine, based on a combination of flue gas recycle and membrane separation is reported. Membrane processes are effectively known to offer attractive performances in terms of energy efficiency, as soon as concentrated and/or pressure mixtures have to be treated. Two different flow schemes have been simulated and compared: flue gas recycle with air combustion and flue gas recycle with an oxygen enriched feed mixture. The energy requirement of the different processes, expressed in GJ (thermal basis) per ton of recovered CO₂, and the size of the membrane capture process (expressed in m² of membrane area) have been systematically estimated for different membrane separation performances. It is shown that an overall energy requirement down to 2.6 GJ per ton can possibly be achieved when optimal operating conditions, based on oxygen enriched air combustion together with a highly selective membrane (CO₂/N₂ selectivity of 200) are combined. Additional possibilities in order to minimize the energy penalty of the process are discussed.

1. Introduction

Carbon Capture and Storage offers tremendous scientific and technological challenges as a key issue for greenhouse gases emissions mitigation [1]. More specifically, numerous studies address the design challenge of the CO₂ capture step, which represents the largest contribution in the overall CCS cost [2]. In terms of CO₂ sources, studies generally focus on coal power plants, which represent the major part of world CO₂ emissions from the power sector. Different strategies such as oxycombustion, precombustion and postcombustion and different capture processes (absorption, adsorption, cryogeny, membranes) have been proposed. Surprisingly, few studies have however addressed the problem of post-combustion CO₂ capture on gas turbines [3-6], even though this technology represents a significant and increasing part of power plants throughout the world. Gas turbines show indeed attractive performances in terms of energy efficiency and ease of use; one of their major drawback is however to produce diluted CO₂ in the flue gas (typically 4%, while coal combustion processes generate 14% CO₂ in flue gas). This specificity complicates the capture and concentration step compared to other flue gases, a more diluted flue gas logically translating into a larger energy requirement for the capture step [7]. Consequently, the development of a carbon capture process on a gas turbine is extremely challenging. This situation is investigated in purpose in this study.

Different strategies have been explored for the specific case of a gas turbine, in order to achieve carbon capture: absorption, oxycombustion, water cycle, Graz cycle, Hazep concept... [3-6, 8-9]. Surprisingly, the analysis of a post-combustion CO₂ capture strategy based on a membrane separation process combined to a gas turbine remains however essentially unexplored. Some papers were recently published on membrane processes for post-combustion capture, but they were exclusively dedicated to coal power plants [10-17]. For instance, Kotowicz et al. recently analyzed the influence of a membrane CO₂ separation

on the energy efficiency; the energy penalty of the capture process was very high compared to other capture processes (around 15 percentage points)[12]. Based on this conclusion, it could be anticipated that the use of membrane processes together with a gas turbine shows no interest, membranes being known to lead to very large energy requirements for diluted CO₂ mixtures [18-19]. Nevertheless, membrane processes also show a very high parametric sensitivity in terms of energy efficiency when different CO₂ contents have to be treated [18]. In fact, very low energy requirements can be achieved, as soon as a CO₂ mole fraction of 0.3 or more is attained in the feed mixture. This observation logically suggests to explore the potential interest of a carbon capture strategy based on a flue gas recycling loop together with a membrane CO₂ capture process, in order to generate a higher CO₂ mole fraction in the flue gas. The interplay of the membrane unit feed pressure and the flue gas recycling ratio, will obviously be a key issue if a minimal energy penalty is aimed. This study intends to analyze, through simulations, a carbon capture process based on this concept: the performances of a hybrid gas turbine / membrane separation process, including a recirculation loop, have been investigated in order to identify the possibilities and limitations of the approach. The overall energy requirement of the CO₂ capture, typically expressed in GJ (thermal basis) per ton of CO₂ recovered, will be taken as a major target variable and compared to the reference case, namely absorption in MEA, which typically requires 3.5 GJ per ton of CO₂ [19-23]. A reference gas turbine of 250 MW has been taken as a base case, and different flow schemes and flue gases recirculation conditions have been tested, based on a series of four different set of data for the membrane separation performances.

In a first step, the modelling and simulation framework will be described (gas turbine with partial flue gas recycling, membrane process) and the key performance parameters will be detailed. The results of the simulation and the optimal operating conditions will be discussed in the second part.

2. Modelling and simulation framework

2.a General framework

A general flow sheet of the process which is investigated in this paper is shown on Figure 1. Natural gas, assumed to be pure methane, is burnt in a turbine either with air or Oxygen Enriched Air (noted OEA). The characteristics of the gas turbine cycle which have been used for the simulations are closed to the 250 MW gas turbine (GE MS9001FA) and are summarized in Table 1. The main specifications of the CO₂ capture unit (based on a gas permeation membrane module) are also shown.

Gas turbine	Methane mass flow	1 kmol.s ⁻¹
	Pressure ratio	17 :1
	Turbine Inlet Temperature	1200 °C
	Pressure drop	5%
	Isentropic efficiency (compressors and turbine)	0.9
CO ₂ capture unit (membrane module)	CO ₂ purity on the permeate side (y)	0.9
	CO ₂ capture ratio (R)	0.9
	Permeate pressure	1 bar

Table 1: Characteristics of the gas turbine cycle and capture unit specifications used for simulations in this study

The principle of the process is shown on Figure 1. The fuel (gas) flow rate is fixed at 1 kmol.s⁻¹. The oxidant compressor C_{ox} is fed by air or OEA and an excess of “air” (*e*) is needed in order to ensure complete combustion conditions. The OEA quality is defined by the mole fraction of O₂ (*X*_{O₂}). The Turbine Inlet Temperature (TIT) [24] is controlled by

dilution at the exit of combustion chamber with flue gas recirculation and also with air excess. In this study, TIT is maintained constant at 1200°C , corresponding to a conventional gas turbine [25]. At the turbine exit, the flue gases are cooled down to 25°C and supposed to be dried. Thanks to the compressor C_{FGR} , a fraction Z of the flue gases, called Flue Gas Recirculation Ratio (FGR), is recycled to the combustion chamber in order to enhance the CO_2 mole fraction (X_{IN}) in the membrane module.

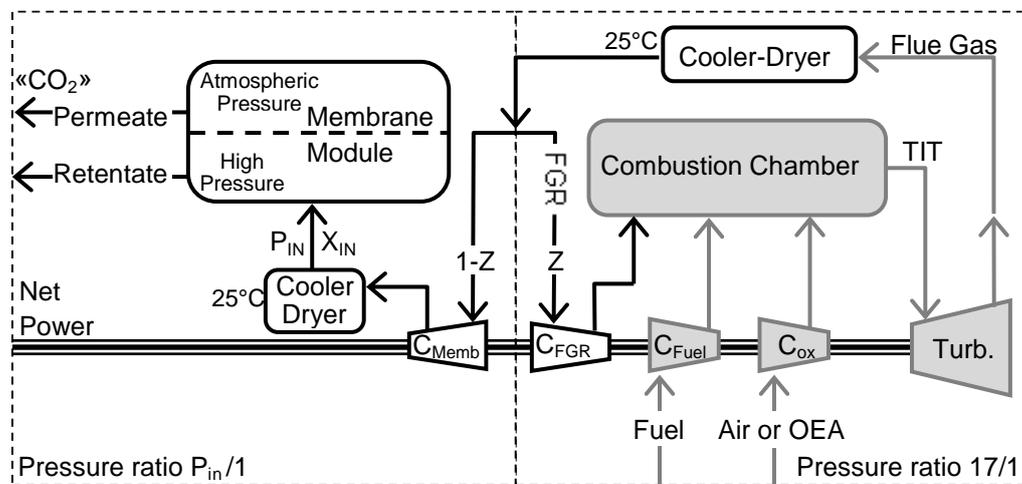


Figure 1: Diagram of the process investigated in this study. Grey blocks: reference gas turbine cycle. White blocks: additional equipment required for flue gas treatment and CO_2 capture. Z corresponds to the flue gas recycle ratio, P_{IN} to the inlet membrane module pressure. Concentrated CO_2 is recovered on the permeate side of the membrane module under atmospheric pressure conditions, before being compressed, transported and stored. CO_2 purity is fixed at 90% volume fraction.

The remaining part ($1-Z$) is sent to the membrane capture unit through the second compressor C_{Memb} under a pressure P_{IN} . In order to minimize compression and transportation cost, two typical targets are often taken as a design constraint for CCS studies [1, 2, and 21]: a CO_2 purity (y) of 0.9 (volume basis), together with a CO_2 capture ratio (R) of 0.9. The CO_2 capture ratio being defined as the percentage of CO_2 which is effectively recovered by the capture unit.

It has to be noted that the CO₂ rich mixture is generated on the low pressure (permeate) side, no membrane material being able to permeate N₂ faster than CO₂ under steady state conditions [26]. Moreover, the permeate pressure of the membrane module is maintained at atmospheric pressure. This enables a direct comparison with other capture technologies such as absorption in chemical solvents, which usually deliver the concentrated CO₂ at 1 Bar before compression, transport and storage [20-21].

The simulation of this new thermal cycle is performed thanks to EES code [27] assuming an isentropic efficiency of 0.9 for each compressor and turbine and a combustion chamber pressure drop of 5% [28-29]. The thermal properties of gases (O₂, N₂, CO₂, H₂O and CH₄) are extracted from the EES library for real gases [27]. The combustion temperature is calculated assuming a complete and adiabatic combustion. Thermal dissociation is neglected because the temperature at the exit of the combustion chamber is lower than 1400°C [30].

2.b Membrane module performances

Apart from the turbine characteristics discussed above, the separation performances of the membrane separation unit shown on Figure 1 have to be predicted depending on the set of operating conditions. The modelling framework of a single stage membrane module working under steady state conditions has been already detailed in several studies and it will be only briefly described hereafter. Basically, the CO₂ purity y , the CO₂ inlet content X_{IN} and the capture ratio R being fixed, the membrane separation performances can be computed based on two main variables:

- The membrane selectivity α , a characteristic which depends on material structure and properties, and corresponds to the ratio of the permeabilities of CO₂ over N₂

$$\alpha = \frac{P_{CO_2}}{P_{N_2}} \quad (1)$$

This expression 1 assumes the two gases to permeate independently in the material (no flux coupling) and is used in numerous publications dedicated to CO₂/N₂ separation by polymeric membranes. In fact, this assumption has been shown to hold for gas permeation processes in polymers, especially for rubbery materials [31-33].

- The pressure ratio, which corresponds to the inlet pressure P_{IN} divided by the permeate pressure (P_{OUT} , with P_{OUT} fixed at 1 Bar in this study, as mentioned before).

Assuming the so-called cross-plug flow conditions, the separation performances can be computed through numerical resolution of the characteristic mass balance equations. This design methodology has been tested in a great number of cases and it is considered to offer realistic predictions of the performances of a membrane gas separation module [34-35]. Details of the system of equations and resolution method (based, for instance, on DASSL software [36]), can be found elsewhere [12, 15, 18]. An example of simulation results of membrane module performances is shown on Figure 2. The interplay between the inlet pressure P_{IN} , the inlet CO₂ content in the feed mixture X_{IN} and the capture ratio R is represented for a membrane selectivity of 100 and a target CO₂ purity (y) of 0.9. It can be shown that an increase of the CO₂ content in the feed mixture enables the target capture ratio $R = 0.9$ to be attained, together with a decreasing inlet pressure P_{IN} . For a membrane selectivity of 100, the flue gas should contain 30% or more of CO₂ (obtained thanks to the flue gas recirculation and/or to OEA combustion) in order to achieve the target capture ratio $R=0.9$.

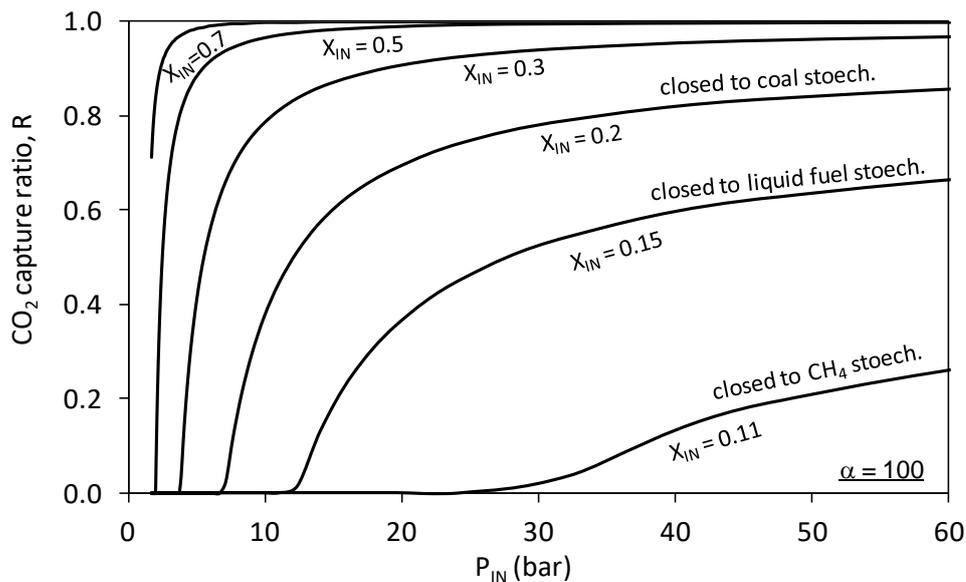


Figure 2: An example of simulation results for a single stage membrane module. Influence of CO₂ inlet fraction and inlet pressure on the CO₂ capture ratio (R). A membrane selectivity α of 100 and a CO₂ purity on the permeate side (y) of 0.9 have been imposed for the calculations.

Membrane selectivity obviously plays a key role in the attainment of the CO₂ capture specifications. Numerous studies have been reported on possible membrane materials for CO₂ capture such as polymeric membranes [37], ceramic [38], zeolite [39] or liquid membranes [40]. Different polymeric membranes, based on a physical separation process (so called solution-diffusion mechanism), have been reported with selectivities in the range of 50 [41] to 75 [42]. A selectivity – permeability trade-off is known to occur in this case and the combination of a moderate selectivity (typically around 50) combined to a very high permeability has been reported to be more appropriate from a technico-economical point of view.

Nevertheless, the selectivity-permeability trade-off can be circumvented, for membrane materials which do not imply a solution-diffusion mechanism. Improved selectivity and/or permeability compared to the trade-off limit have been indeed reported for membrane materials such as mixed matrix membranes, nanoparticle filled polymers, zeolite membranes

or liquid membranes). For the CO₂/N₂ gas pair, high selectivity data have been reported for membrane based on a chemical separation mechanism (such as Fixed Site Carrier Membranes) or zeolite materials [43-45]. In order to evaluate the role of membrane selectivity and permeability on the overall process performances, four set of membrane performance data have been selected in this study for simulation purposes. More specifically, increasing selectivity data (α), namely 50, 75, 100 and 200, associated to increasing CO₂ permeances have been tested. These four different cases, detailed in Table 2 and shown on a trade-off graph Figure 3, are expected to cover the different current or hypothetical future possibilities of membrane materials for post-combustion CO₂ capture.

Membrane reference	CO ₂ /N ₂ selectivity (α)	Membrane CO ₂ permeance (GPU)	Comments
1	50	500	Performances corresponding to currently commercially available polymeric membranes and modules [17] <i>Material type : MTR Polaris membrane.</i>
2	75	1000	Likely upper limit performances for improved polymeric membranes based on a physical separation mechanism [42] <i>Material type : poly(ethylene oxide) poly(butylenes terephthalate) block copolymers.</i>
3	100	2000	Level of selectivity already reported on lab scale materials based on a chemical reactivity [38,43], associated to a high, unreported permeance level <i>Material type : polyvinyl amine (PVAm) and polyvinyl alcohol (PVA) blend membrane.</i>
4	200	200 000	Upper theoretical limit of (currently unavailable) zeolite membranes [39] <i>Material type : metal-organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs)</i>

Table 2: Summary of the four different set of data tested for membrane performances in this study, together with the corresponding current or future situation.

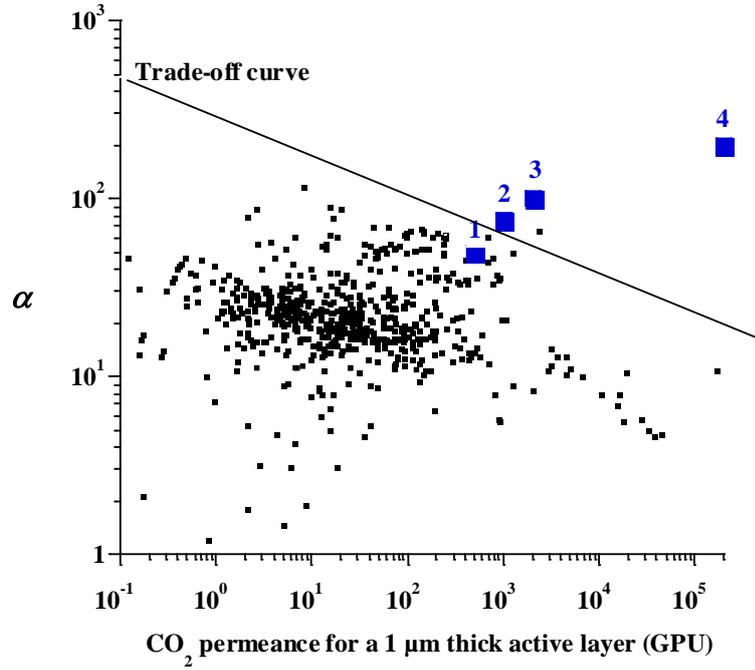


Figure 3: Trade-off curve showing the CO₂/N₂ selectivity (α) data of different membrane materials (dots) versus CO₂ permeance for a 1 μm thick membrane. The theoretical trade-off limit, calculated according to a model proposed by Freeman [46] for a strict physical separation mechanism to take place (i.e. solution-diffusion) is also shown. The characteristics of the four different membranes tested in this study and detailed in Table 2 are represented by the filled squares.

It should be stressed that materials 3 and 4 are by no means currently commercially available and can be considered as highly prospective. The main objective of our study is however to evaluate their potential interest in a carbon capture context. From a material science point of view, it is essential to evaluate whether more selective membrane materials show any interest for carbon capture.

Apart from the process separation performances, the dimensionless membrane surface area St has been simultaneously computed. The corresponding real membrane surface area (expressed in m^2) can be determined from the dimensionless membrane surface area St through:

$$S = \frac{\delta}{\phi_{CO_2}} Q_{V,in} \frac{St}{P_{IN}}$$

(2)

Where δ is the membrane thickness, ρ_{CO_2} is the permeability of pure CO₂ in the considered membrane, P_{IN} the inlet pressure in the membrane module and $Q_{v,in}$ the volume flowrate of the feed mixture.

2.c Thermal efficiency and overall energy requirement for CO₂ capture

The ultimate objective of this study is to evaluate, similarly to any study on CO₂ capture, the overall energy requirement per unit mass of recovered CO₂ (typically expressed in GJ per metric ton of CO₂, on a thermal basis). This key data, noted C_{CO_2} has been calculated as follows for the hybrid process described on Figure 1:

$$C_{CO_2} = \frac{P_{capture} + P_{O_2}}{\dot{m}_{CO_2 captured}} \quad (3)$$

$P_{capture}$ and P_{O_2} are respectively the energy requirement corresponding to the capture process (membrane unit) and to the air separation unit (i.e when OEA is used). $P_{capture}$ can be directly deduced from the difference between the net mechanical power of the reference cycle without CO₂ capture and the cycle with CO₂ capture both defined by their thermal efficiencies respectively η_{ref} (here 0.385) and η_{therm} and by the Low Heating Value of the fuel ($LHV_{CH_4} = 50 \text{ MJ/kg}_{CH_4}$). P_{O_2} is a function of O₂ mass flow rate $((1+e) \dot{O}_2^0)$ and of OEA unit production cost (C_{unit-O_2}), which depends on oxygen purity. e is the excess of oxygen and \dot{O}_2^0 is the mass of O₂ necessary to burn 1kg of fuel ($\dot{O}_2^0 = 4 \text{ kg}_{O_2}/\text{kg}_{CH_4}$). The mass flow rate of CO₂ captured ($\dot{m}_{CO_2 captured}$) depends on the total CO₂ mass-flow rate $[(CO)_2^0]$ and on the capture rate (R) of the membrane which is a function of P_{IN} , X_{IN} and α . $(CO)_2^0$ is the mass of CO₂ produced by the combustion of 1 kg of fuel ($(CO)_2^0 = 3.67 \text{ kg}_{CO_2}/\text{kg}_{CH_4}$)

After simplification, the CO₂ capture cost, which will be discussed in the next paragraphs, can be expressed as:

$$C_{CO_2} = \frac{LHV \times (\eta_{ref} - \eta_{therm}) + (1+e) \times O_2^0 \times C_{unit_{O_2}}}{CO_2^0 \times R} \quad (4)$$

In summary, for the different simulations which will be described afterwards, the key outputs data will be the overall CO₂ energy requirement (C_{CO_2}) expressed in GJ for the capture of one ton of CO₂ and the corresponding membrane surface area (in m²), which will play a key role in the capital cost of the capture process.

In a first step, the energy penalty induced by a given flue gas recirculation ratio and inlet membrane module pressure will be studied. Next, the simulation results of the air feeding process will be described and discussed. Finally, the results of the OEA feeding process, which require the oxygen production (P_{O_2}) cost to be taken into account together with the capture costs, will be detailed.

3. Results & discussion

3.a Influence of recirculation ratio and inlet membrane module pressure on the overall gas turbine efficiency

Before investigating the hybrid process (turbine + membrane unit), it is of interest to explore the influence of the two key boundary parameters of the membrane unit, imposed by the gas turbine operating conditions. In fact, it is important to notice that, for the process described in Figure 1, the membrane module can be fed by a gas mixture which will show a variable CO₂ content (X_{IN}) (which depends on the set of operating conditions, namely Z) and a variable inlet pressure P_{IN} . These degrees of freedom logically address the question of the influence on the energy penalty. A dedicated parametric study has been undertaken for that

purpose. Figure 4 shows the results of thermal efficiency η_{therm} and CO_2 concentration X_{IN} as a function of the recirculation rate (Z) and membrane inlet pressure (P_{IN}). The figure is separated in two parts. The first part, from $Z = 0$ to 0.669 corresponds to the cycle fed with air; for a Z value exceeding 0.669, combustion becomes rich and then incomplete. These conditions correspond to the upper CO_2 concentration (namely $X_{IN} = 11.7\%$) in the flue gases which can be obtained when air combustion is applied. OEA combustion is needed if a Z value larger than 0.669 is wanted. Thus, the second part of Figure 4, from $Z = 0.669$ to 0.95, corresponds to the cycle fed with OEA.

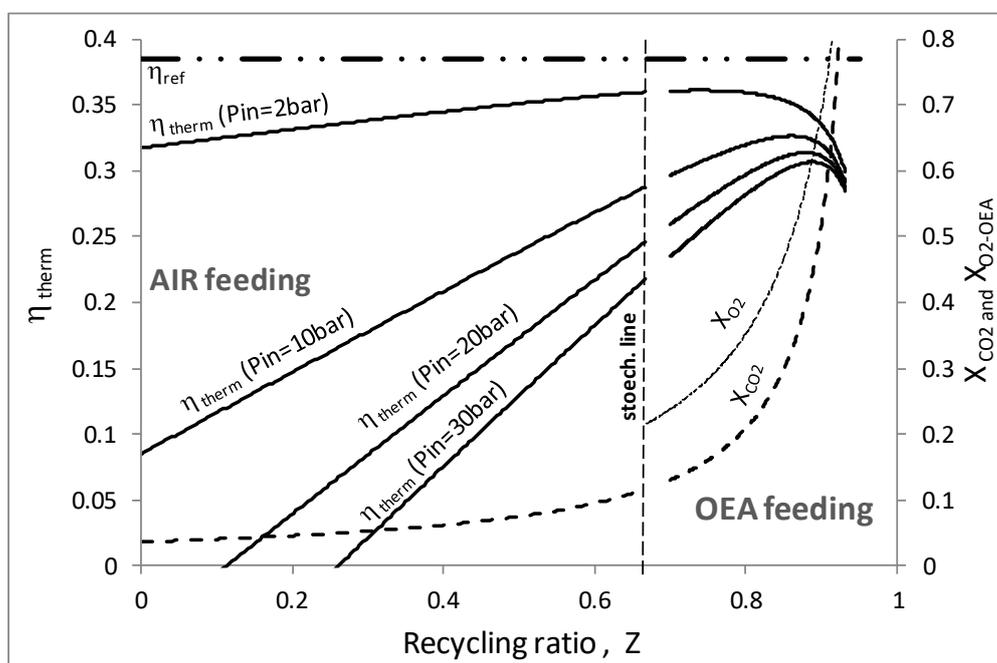


Figure 4: Evolution of the thermal efficiency of a gas turbine as a function of recirculation ratio Z and capture process inlet membrane pressure (indicated on each curve). The corresponding O_2 inlet and CO_2 turbine outlet mole fraction are indicated (dotted lines). Left side: air feeding, right side : OEA feeding.

Due to the CO_2 concentration effect of the flue gases recirculation, we can notice that the CO_2 mole fraction (X_{IN}) increases, as expected, with recirculation rate (Z). Due to the additional compression work of the membrane compressor, the thermal efficiency logically decreases as membrane inlet pressure (P_{IN}) increases. Moreover, in the OEA feeding part

and for a constant membrane pressure (P_{IN}), the thermal efficiency interestingly passes through a maximum value as the recirculation rate increases.

In the next paragraph, the interplay between the recirculation ratio (Z), the inlet pressure (P_{IN}) and the possibilities and limitations of the capture process, expressed through the maximal capture ratio R and the associated overall CO₂ capture energy requirement (C_{CO_2}) are more specifically examined.

3.b Hybrid process: Performances for air feeding conditions

For air feeding conditions, the cost of oxygen production is obviously null. The capture cost (eq. 4) depends only on $\Delta\eta$, the thermal efficiency difference and on the capture ratio R . As described before (Figures 2 and 4), these two variables strongly depend on P_{IN} , X_{IN} and Z . In order to simultaneously achieve a minimal energy requirement and complete combustion conditions, simulations have been performed closed to the stoichiometric point, but with a small air excess. A value of $e = 0.1$ has been selected, leading to $Z = 0.657$ and $X_{IN} = 11.3\%$.

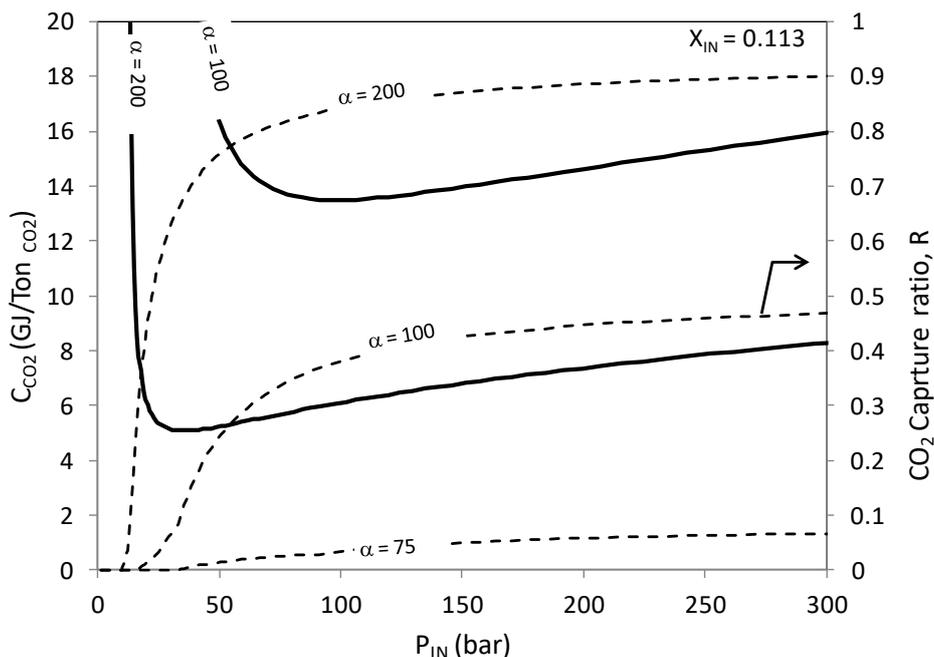


Figure 5: Evolution of the CO₂ capture cost (full line) and capture rate (dashed line) as function of membrane pressure for different membrane selectivities α . For the simulations shown on this graph, the recirculation ratio has been set to $Z=0.657$, corresponding to a CO₂ volume fraction in flue gases of $X_{IN}=0.113$.

The results of capture energy requirement (C_{CO_2}) and capture ratio (R) are plotted in Figure 5 for constant $X_{IN}=11.3\%$, as a function of P_{IN} and for different membrane selectivity data (75,100 and 200). The fourth case, namely a selectivity of 50, leading to a very high energy requirement and a very low capture ratio, is not shown. As expected, the capture ratio R increases as membrane selectivity increases. For the study domain ($P_{IN} = 2$ Bar to 100 Bar), a selectivity of 200 (α) is the only condition which enable a capture ratio of 90% to be attained. The two other membrane selectivity performances show lower, possibly non-acceptable, capture ratios.

As the inlet pressure increases, the capture cost first decreases drastically, but reaches later a minimum value and finally slowly increases. For $\alpha = 75$ (not shown) and for $\alpha = 100$, the minimum cost is respectively 110 and 13.5 GJ/Ton_{CO₂}. These data largely overwhelm the MEA performances (3.5GJ/ton_{CO₂}) and suggest that CO₂ membrane capture is not appropriate. For $\alpha = 200$, the minimum capture cost which is reached (at 35 bar) is equal to 5GJ/ton with a corresponding capture ratio of 70% only. To obtain a capture rate of 90%,

the capture cost increases until 8GJ/ton and the membrane pressure which is required becomes too high (290 Bar).

Although clearly not competitive with the process of MEA absorption, these results show however that the CO₂ enhancement by FGR allow to significantly decrease the CO₂ capture energy requirement, at the condition that a highly selective membrane is available ($\alpha=200$). To enhance the efficiency of the membrane separation unit, it is necessary to significantly increase the inlet CO₂ concentration. This observation is in agreement with other parametric studies on membrane processes for CO₂ capture [17,18]. In the following part, the combination of OEA feeding and Flue Gases Recirculation, which enables a much higher inlet CO₂ concentration to be attained, is studied.

3.c Hybrid process: Performances for oxygen enriched air (OEA) feeding conditions

In case of OEA feeding, we again impose 10% of oxygen excess, in order to always lead to a complete combustion and minimize the OEA production cost. As shown in equation 3, the capture cost is now calculated from $\Delta\eta$ (Fig.3), R (Fig.2), and OEA energy requirement. The latter is shown on Figure 6, which represents the energy requirement of cryogenic OEA as function of oxygen purity (X_{O_2}) [47].

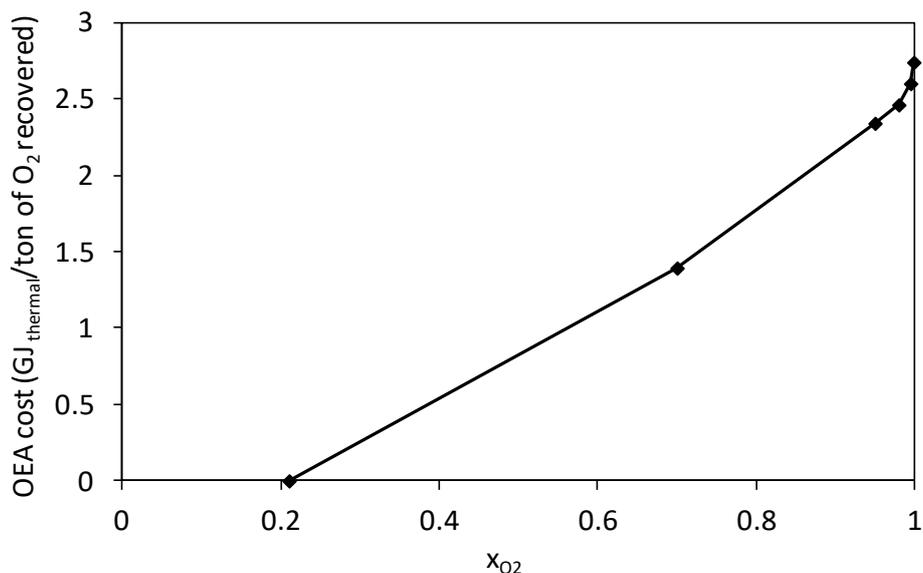


Figure 6: Evolution of the energy requirement for cryogenic production ($\text{kWh}_{\text{elec}}/\text{kg}_{\text{EPO}}$) of oxygen as function of oxygen mole fraction [47].

The energy requirement is expressed in $\text{kWh}_{\text{elec}}/\text{kg}_{\text{EPO}}$ and must be multiplied by 2.58 to take into account the production and transport of electricity [48]. As expected, OEA production energy is maximum for high oxygen purity ($X_{O_2} > 0.95$). Values up to 1 kWh electric per kg of equivalent pure oxygen (EPO) can be obtained, which non-linearly decrease down to zero for a composition corresponding to air ($X_{O_2} = 0.209$).

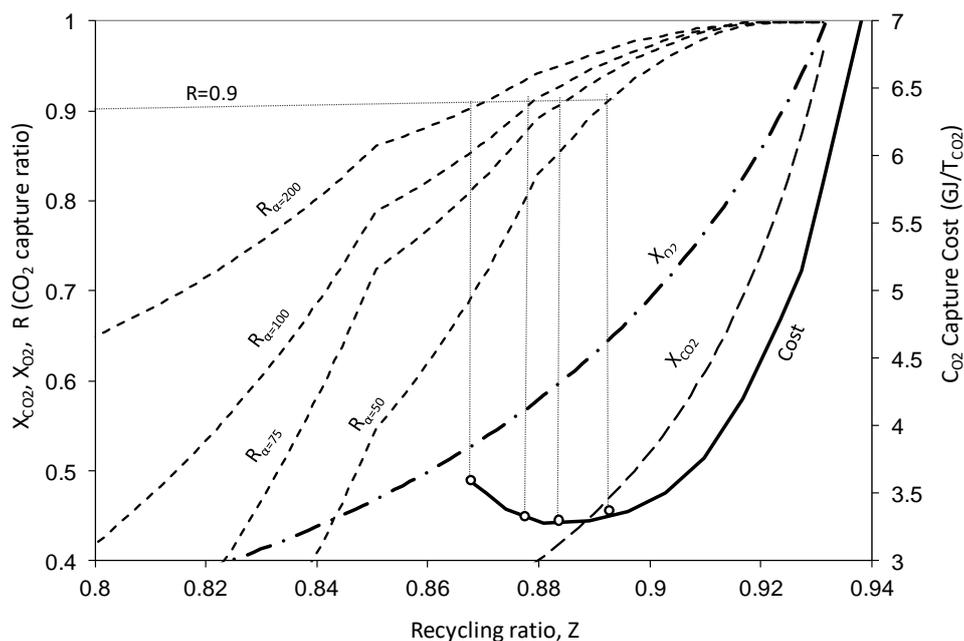


Figure 7: Energy requirement for CO₂ capture (line “cost”) and CO₂ capture ratio (R, dotted lines) as a function of the recirculation rate (Z) for different oxygen contents in OEA. The numbers on the dotted lines correspond to the different membrane selectivity performances ($\alpha = 50, 75, 100$ and 200). For each R curve, the recirculation rate corresponding to the minimal energy requirement at 90% CO₂ recovery ($R = 0.9$) have been identified (circles). A membrane inlet pressure of 10 Bar ($P_{in}=10\text{bar}$) has been imposed for this illustrative chart.

For each set of inlet pressure data (such as for $P_{in} = 10$ Bar in Figure 7), CO₂ capture energy requirement can be calculated as function of recirculation rate, for different oxygen volume fractions in OEA. The data which enable the target CO₂ purity (y) to be attained together with a capture ratio (R) of 90% have been collected for the different membrane selectivity data. The corresponding energy requirement, membrane surface, oxygen content in OEA and CO₂ content in flue gases are shown in Figures 8 and 9.

Figure 8 shows that for the less selective membrane ($\alpha = 50$) the minimal energy requirement of capture (3.2 GJ/ton CO₂) is close to the reference MEA absorption process (3.5 GJ/ton). As membrane selectivity increases, the CO₂ capture energy requirement decreases. The minimal energy requirement is 3.2, 2.95, 2.8 and 2.62 GJ/ton for $\alpha = 50, 75, 100$ and 200

respectively. Moreover, the corresponding inlet membrane pressure (18, 22, 18 and 12 Bar) seems to be realistic for classical industrial compressors [29].

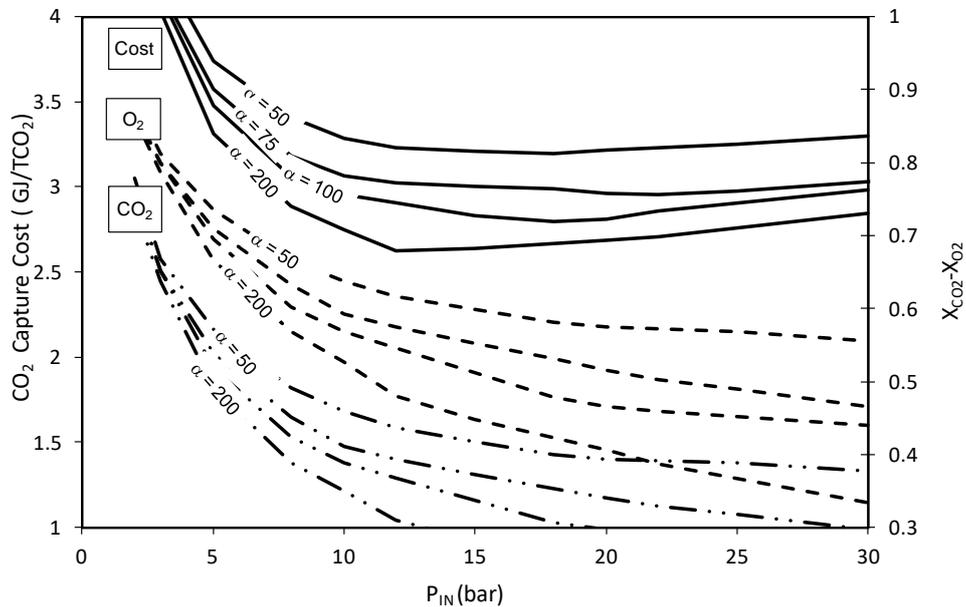


Figure 8: Evolution of CO_2 capture energy requirement, $X_{CO_2 IN}$ and X_{O_2} as function of inlet membrane pressure for different membrane selectivities. (CO_2 purity y and capture ratio R are fixed at 0.9).

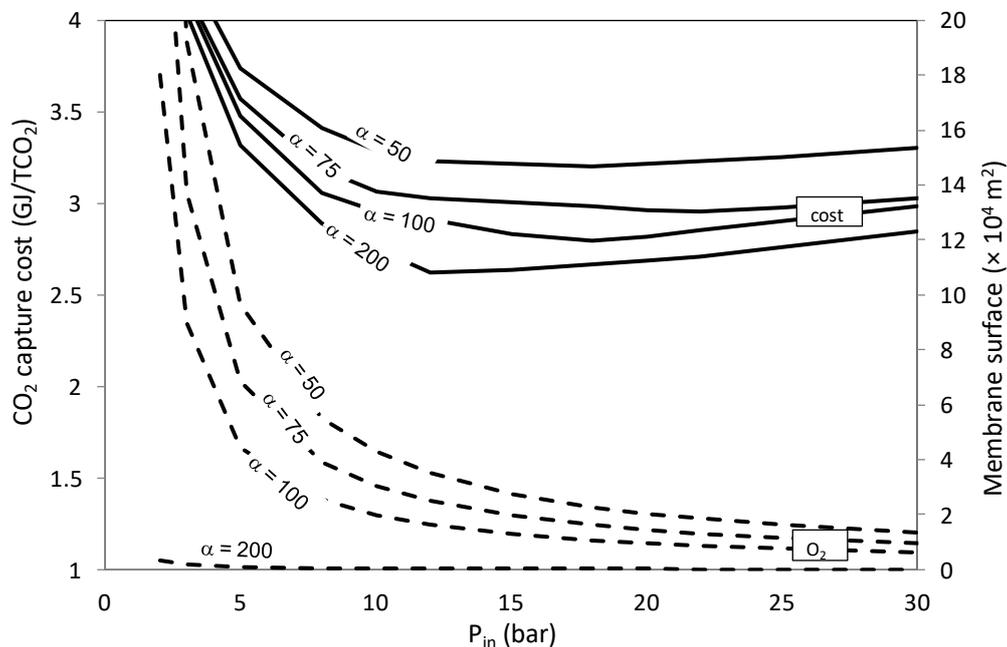


Figure 9: Evolution of CO_2 capture energy requirement and membrane surface as function of inlet membrane pressure for different membrane selectivities (CO_2 purity y and capture ratio R are fixed at 0.9).

Interestingly, the corresponding oxygen volume fraction in OEA X_{O_2} (Fig.8) is close to 50% (respectively 53, 46, 45 and 48%). Thus, the OEA production process must be designed to produce a medium oxygen purity. Alternative technologies to cryogenic production (such as PSA or membrane air separations) could possibly be investigated in this range of oxygen purity [49-50]. Finally, the capital expenses (CAPEX) will depend, among others, on the membrane surface. For the four cases which have been investigated, 22700, 13100, 10500 and 310m² are required, respectively, for the 250 MW gas turbine. Taking into account the fact that a specific surface area of several thousands of square meters per m³ can be achieved with membrane gas separation modules [34,35], these data again appear to be industrially feasible and acceptable in terms of footprint.

The different set of data which correspond to the gas turbine base case, and to the optimal membrane CO₂ capture conditions (i.e. minimal energy requirement conditions) with air or OEA feeding, are summarized in Table 3.

Finally, it should be noted that, based on the turbine / membrane unit strategy, several process modifications could be explored in order to further minimize the energy requirement for CO₂ capture:

- i) An Energy Recovery System (ERS) such as a turbine could be installed on the retentate (high pressure) exit of the membrane unit. This option is often proposed for gas separation units in order to improve the energy efficiency of the separation process [34]. For CO₂ capture, the ratio of the feed flowrate which effectively permeates through the membrane (namely the stage-cut) is most often quite low [17,18]. Consequently, a large proportion of the compressed stream (up to 70% in some cases) is released on the high pressure side. Where favourable nearby geological circumstances should fortuitously

permit, this high pressure stream can be used for the enhanced recovery of hydrocarbons, thereby dramatically reducing the energy cost of CO₂ capture. Historical such examples include the use of such gases (with 15% CO₂ content) by Exxon to enhance oil production, and the injection by Amoco of nitrogen into deep coal seams to produce the natural gas contained therein. Wherever possible, these especially attractive geological opportunities should therefore be investigated. More commonly, a turboexpander may be used to recover a portion (up to 24% in some cases [17]) of the otherwise wasted energy. A potential additional advantage could be also obtained by an expander based on Joule-Thompson cooling effect (retentate decompression). This could be used for cooling the inlet air of the gas turbine in order to increase the power output [51]. Another option consists to cool the flue gases prior to the membrane (e.g. down to 5 C), in order to reduce the volume of the flue gases and increase membrane selectivity [52]. In addition, there may be opportunities to use a cooling-induced temperature difference as a supplementary driving force across the membrane, especially where a cross-flow or counter-flow configuration is adopted [17], including for the permeate vacuum case outlined immediately below.

ii) A different driving force operation could also be explored for the membrane unit, based on a vacuum operation on the downstream side, in place of the sole feed compression strategy explored in this study. A moderate permeate vacuum (e.g. 0.1 Bar), together with a slight feed compression (2 Bar) is effectively known to be more energy efficient for post-combustion CO₂ capture by membrane processes [17,18]. For the different OEA combustion case studies shown in Table 3, the optimal pressure ratios range between 12:1 and 22:1. These moderate values are likely to be compatible with a slight vacuum/compression combination. However, it is important to notice that a very much larger membrane area will be required in this case, compared to the feed

compression option. The physical footprint for the membrane facility would however likely still remain a small fraction of that required for the more widely-considered amine plant CO₂ capture approach. Consequently, an exhaustive technico-economical analysis, tackling the trade-off issues of a minimal energy requirement (in favour of vacuum) and a minimal membrane area (in favour of feed compression) would be necessary in order to evaluate the potential interest of such a modification.

iii) The optimal operating conditions which are reported in Table 3 are based on cryogenic process, the reference oxygen production technology. These set of data are valid only for the oxygen production performances shown on Figure 6, which have been used for the evaluation of the P_{O_2} term in equation 3. Given the moderate oxygen purities which are obtained in Table 3, it might be that alternative oxygen production technologies could decrease the overall energy requirement. PSA (Pressure Swing Adsorption) or membrane separations (based on dense polymers) show indeed a lower energy requirement compared to cryogenic processes if a moderate oxygen purity (typically 0.3 to 0.5) is needed [53]. This observation suggests to re-examine the hybrid process proposed in this study (gas turbine / membrane capture unit) through different OEA production technologies in order to possibly find a lower overall energy requirement. This may especially be the case if steam derived from the turbine exhaust gases is used as a motive force to run the compressors, as has been done in the past with large LNG Trains.

iv) Finally, the wasted heat in the chamber exhaust gases can also be used in order to produce steam and additional mechanical work. This strategy which corresponds to a combined cycle (NGCC turbine) could be proposed in order to improve the overall efficiency of the turbine + carbon capture process.

4. Conclusion

The objective of this study was to evaluate the possibilities and limitations of a hybrid process based on a gas turbine and a membrane carbon capture unit, with a special emphasis on the overall energy requirement for carbon dioxide capture (expressed in GJ/ton of CO₂). Four different membrane characteristics, covering a broad range of currently commercially available and hypothetical materials have been investigated, with 0.9 CO₂ purity and 0.9 CO₂ capture ratio specifications. Based on a feed compression strategy for the inlet membrane module, with purified CO₂ recovery under atmospheric conditions, the following conclusions can be drawn:

- For combustion in air, even with a flue gas recirculation strategy (in order to increase the CO₂ concentration the flue gases), unacceptable energy requirement levels are obtained. The best performances, logically obtained with the most selective membrane ($\alpha = 200$), induce indeed an energy requirement of more than 8 GJ/ton. This value is much larger than the 3.5 GJ/ton needed for the reference post-combustion capture process (absorption in MEA).
- A completely different picture is obtained if an Oxygen Enriched Air (OEA) strategy is applied. In that case, energy requirements down to 2.6 GJ/ton can be attained. Interestingly, the membrane selectivity performances (tested between $\alpha = 50$ and $\alpha = 200$ here) play a key role on the overall energy requirement. This situation differs from the direct “end of pipe” post-combustion carbon capture, where no significant improvement on the energy requirement is observed as soon as the membrane selectivity reaches a value of $\alpha = 50$ [17,18]. Thus, the search for highly selective membranes, far above the performances of the actual membrane materials, is of major interest for the gas turbine /

membrane capture process investigated in this study. Additionally, moderate inlet pressure values (12-22 Bar), together with moderate oxygen purities (45-53 %) are needed for optimal OEA conditions.

The promising results reported for the OEA combustion strategy call for a more in depth analysis of this hybrid process. It can be noted first that the concept can hardly be extended on a straightforward way to a coal power plant. The coal power plant framework is indeed very different from gas turbines: CO₂ is more concentrated, which is beneficial for membrane separations, but simultaneously, flue gas conditions (composition, pressure) are very different and the combustion constraints have to be completely reconsidered compared to a gas turbine. The conclusions driven from simulations are thus specific to gas turbines.

Several unexplored issues could be investigated in future works. The possibility to further decrease the energy requirement, discussed in the previous section is clearly of major interest. Apart from CO₂ and N₂, the fate of minor flue gas compounds, such as H₂O, NO_x, O₂... could be also investigated through simulations performed for multicomponent mixtures, both in the combustion chamber and membrane permeation unit. Finally, an experimental validation of the concept, as well as a technico-economical analysis of the hybrid process (including operating costs but also capital costs such as membrane modules) are urgently needed in order to better evaluate the potential of the concept proposed in this paper.

Case study	Membrane CO ₂ capture unit							OEA		Gas Turbine Cycle					
	α	δ	ρ_{CO_2} (Barrer)	X_{IN-CO_2}	Pin (bar)	S (m ²)	C** (GJ/ton)	X_{O_2-OEA}	OEA %***	Z	$\Delta\eta$ (%pt)	C_{OEA} (kg/s)	C_{FGR} (kg/s)	C_{memb} (kg/s)	Turbine (kg/s)
Reference*	-	-	-	0.036	-	-	-	0.21	-	-	$\eta_{Ref} = 38.9\%$	819	-	-	836
Air / FGR	200	1 μ m	200k	0.113	295	17	8.20	0.21	-	0.66	-39	285	509	265	810
OEA/FGR	50	1 μ m	0.5k	0.40	18	22700	3.20	0.58	53%	0.88	-7.4	105	630	86	752
OEA/FGR	75	1 μ m	1k	0.33	22	13100	2.95	0.50	46%	0.86	-7.9	121	626	101	764
OEA/FGR	100	1 μ m	2k	0.33	18	10500	2.80	0.48	45%	0.85	-7.6	126	624	107	768
OEA/FGR	200	1 μ m	200k	0.31	12	310	2.62	0.48	48%	0.85	-6.7	126	625	106	767

Table 3: Optimal configuration for air or OEA combustion, with 90% CO₂ purity and a 90% CO₂ capture ratio specifications. The natural gas (methane) mass flow rate is set at $Q_{CH_4} = 16 \text{ kg}\cdot\text{s}^{-1}$.

*: Air combustion, no CO₂ capture

** : Overall energy requirement for CO₂ capture

***: Percentage of the overall energy requirement corresponding to OEA production

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Notation

C_{CO_2}	Overall carbon capture energy requirement (GJ/ton CO ₂ recovered)
LHV	Low Heating Value (J.kg ⁻¹)
m	Recovered CO ₂ mass flow rate (kg.s ⁻¹)
P_{IN}	Membrane module inlet pressure (bar)
P_{OUT}	Membrane module permeate pressure (bar)
ρ	Membrane permeability coefficient (mol.m ⁻¹ .s ⁻¹ .Pa ⁻¹)
Q	Volume flow rate (m ³ /s)
R	Carbon dioxide recovery/capture ratio [-]
S	Membrane surface area (m ²)
St	Total non-dimensional membrane surface area (-)
T	Temperature (K)
X	Mole fraction (-)
y	CO ₂ mole fraction on membrane permeate side (-)
e	Excess of oxygen (-)
Z	Flue Gases Recirculation Rate (-)

Greek letters

α	Membrane selectivity [-]
δ	Membrane thickness [m]
η	Thermal efficiency [-]
γ	Adiabatic gas expansion coefficient [-]

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