

# Post-combustion CO<sub>2</sub> capture from natural gas combined cycles by solvent supported membranes

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## Nomenclature

DES	Deep eutectic solvents
E	Specific CO <sub>2</sub> emissions [kg/MWh]
e.m.	electric motor
GT	Gas turbine
HRSG	Heat recovery steam generator
J	Flux through membrane [mol/s/m <sup>2</sup> ]
k	Permeance [gpu] or [mol/s/m <sup>2</sup> /Pa]
NGCC	Natural gas combined cycle
ref	Reference power plant without CO <sub>2</sub> capture
SILM	Supported ionic liquid membranes
SPECCA	Specific primary energy consumption for CO <sub>2</sub> avoided [MJ <sub>LHV</sub> /kg <sub>CO2</sub> ]
TIT	Turbine inlet temperature (total temperature at 1 <sup>st</sup> rotor inlet)

## Greek

$\eta_{pol}$	Polytropic efficiency
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## 1. Introduction

Membranes for CO<sub>2</sub> separation are receiving growing attention for application in the field of CCS. They allow CO<sub>2</sub> separation by means of a continuous process, they do not lead additional water consumption and they do not need steam for regeneration, thus not affecting steam turbine operations in power plants. In addition, being CO<sub>2</sub> separators with no need of thermal duty, CO<sub>2</sub> membranes can be applied in energy intensive industries both as post-combustion and pre-combustion separators.

Technical challenges in the development of CO<sub>2</sub> membranes are related to the improvement of their permeability and selectivity, in order to limit the area required for a given separation efficiency and obtain a high purity of the CO<sub>2</sub> separated. It is well known that performance of polymeric membranes, the most investigated CO<sub>2</sub> membrane technology, are characterized by an 'upper bound' that correlates the maximum permeability and selectivity [1]. In other words, polymeric membranes with high permeability usually have low selectivity and vice-versa.

More recently, a new class of membranes has been receiving attention, namely solvent supported membranes. In these devices, a solvent with a negligible volatility which provides the necessary selectivity is incorporated in a porous membrane. Ionic liquids represent good candidates to be used in such membranes and superior performance of supported ionic liquid membranes (SILMs) over polymeric membranes has been obtained [2]. Other promising solvents for such application are deep eutectic solvents (DES), which is a class of solvents which can be obtained from precursors that are solids at ambient temperature. [3]. DES can be prepared readily from renewable, non-toxic naturally occurring chemicals, are relatively inexpensive and can be tailored to specific uses by a wide variety of formulations [4]. The use of ionic liquids and DES in membrane separators also represents an alternative maybe more suitable application for these solvents with respect to conventional absorption systems based on absorption and desorption columns. As a matter of fact, the extremely high viscosity of these solvents makes their circulation in a column based absorption system extremely difficult and requires high energy consumption.

In addition to membrane materials, research has been conducted on CO<sub>2</sub> membranes focused on their integration in power plants. The application as post-combustion capture systems in coal fired power plants has received the largest attention from researchers [5-9]. Different configurations with two or more membrane modules in series or parallel to achieve high CO<sub>2</sub> capture rate and high purity with the lowest cost have been examined. Integration of CO<sub>2</sub> membranes in natural gas combined cycles (NGCCs) is more challenging, due to the much lower CO<sub>2</sub> content in the flue gases with respect to coal plants. In order to increase the CO<sub>2</sub> concentration in the membrane feed, Merkel et al. [10] proposed a novel configuration with two membranes in series, where the second membrane allows for a selective CO<sub>2</sub> recycle to the gas turbine (GT) compressor inlet, significantly increasing the CO<sub>2</sub> partial pressure in the flue gas.

The aim of this paper is to assess the thermodynamic performance and economics of the integration of solvent supported CO<sub>2</sub> membranes in NGCCs according to the process configuration proposed by Merkel et al. [10]. Reference is made to solvent supported membranes due to the novelty of such technology and the expected wide variability in their performance and cost, but the same considerations made throughout the paper are also valid for polymeric membrane.

## 2. Methodology

### 2.1. Plant description

The NGCC power plant integrated with CO<sub>2</sub> separation membranes is shown in Fig. 1. The system is based on two membranes operating in series on the cooled flue gas from the heat recovery steam generator (HRSG). The first one is a 3-port membrane (i.e. with no sweep gas inlet on the permeate side), using a vacuum pump to keep a sub-atmospheric pressure of 0.2 bar in the permeate stream. CO<sub>2</sub> separated by this membrane is sent to storage after intercooled compression up to 150 bar. The second membrane is a 4-port membrane (i.e. with a sweep gas inlet stream, flowing counter-currently), where fresh air for the GT is used as sweep gas on the permeate side. Thus, this second membrane allows a selective CO<sub>2</sub> recycle, by producing a CO<sub>2</sub> enriched gas as working fluid in the GT. In the first membrane, separation of 90% of the CO<sub>2</sub> generated by NG combustion is set. In the second membrane, the flow rate of CO<sub>2</sub> separated is determined to obtain the target GT turbine inlet temperature (TIT), while the air flow is such that an O<sub>2</sub> concentration of 2.5%vol. at the combustor outlet is obtained.

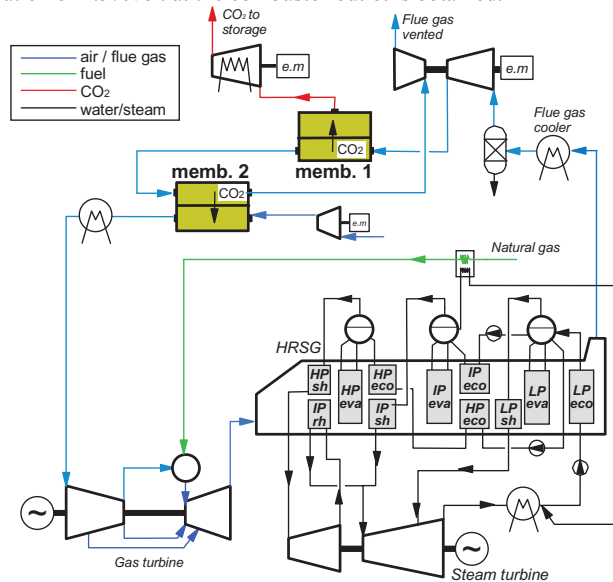


Fig. 1 Process configuration of the NGCC power plant with CO<sub>2</sub> membranes assessed in this work.

A flue gas compressor ( $\eta_{\text{pol}}=85\%$ ) is used to increase the feed pressure of both membranes and reduce the membrane area. An expander ( $\eta_{\text{pol}}=90\%$ ) is then used at the retentate outlet of the second membrane to recover the pressure energy from the exhaust gas. Feed and vacuum pressures of the first membrane are varied in this work in the sensitivity analysis, while a pressure drop on the feed side of both membranes of 6% in total is assumed. Nearly atmospheric pressure is always kept on the permeate side of the second membrane and an air fan is simply used on the fresh air to balance the pressure drop in the membrane and in the downstream gas cooler (total pressure drop of 5% is assumed) and obtain a 1 atm pressure at the GT compressor inlet. A gas cooler is used to cool the permeate

gas from the membrane to the GT compressor inlet temperature of 30°C. Such cooling is needed due to the relatively high temperature of the gas permeating through the second membrane, due to a temperature increase resulting from the flue gas compression.

The gas turbine flow conditions are calculated considering a pressure ratio of 18.1 and a TIT of 1360°C, in line with large scale state of the art heavy duty GTs. It must be said that commercial GTs could probably not be adapted for operating under the conditions imposed on this plant. The increase of CO<sub>2</sub> content in the GT working fluid (25-30% vol. at the compressor inlet) leads to modified properties of the working fluid and requires a redesign of the machines and the combustor. In this work, the gas turbine flows are calculated with the model presented in [11], by assuming a dedicated machine design, but considering the current technological level, i.e. keeping the maximum blade temperature unchanged with respect to the benchmark GT cycle with no gas recycle.

The heat recovery steam cycle is based on a 3 pressure level with reheat HRSG (130/28/4 bar, 565/565/300°C) with pinch point ΔTs of 10°C. Steam is expanded in a steam turbine with HP/IP/LP section isentropic efficiency of 94/92/88% and condensed at 0.048 bar by cooling water from a cooling tower. All the main assumptions for the power cycle are based on [12]. A constant fuel input of 711 MW<sub>LHV</sub> is assumed in all the cases, as estimated for the benchmark NGCC without capture.

Mass and energy balances are solved with the in-house code GS, developed at the Department of Energy of Politecnico di Milano [13], except CO<sub>2</sub> compression, for which Aspen Plus V8.2 with the Peng Robinson equation of state and default binary interaction parameters has been used.

## 2.2. Membrane model

Permeation through the membrane is calculated through eq.(1). The flux  $J$  (flow per unit of time per unit of membrane area) of each gas species  $i$  is proportional to the difference in partial pressures  $p \cdot x$  on the two sides of the membrane, with a proportionality related to the membrane permeance  $k_i$ .

$$J_i = k_i \cdot (p_{feed} \cdot x_{i,feed} - p_{perm} \cdot x_{i,perm}) \quad (1)$$

Calculation of the membrane performance is achieved by dividing the membrane area in 20 steps of equal surface, where the equation above is applied. The stream on the permeate side is considered to flow perfectly counter-current with respect to the feed stream. The membrane has been modelled with a Matlab code, which adjusts the membrane surface area to achieve the target CO<sub>2</sub> separation efficiency. A selectivity of CO<sub>2</sub> with respect to all the other species (N<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, Ar) of 70 is assumed.

## 2.3. Economic analysis

The economic analysis has been performed by using the CO2CRC method [6]. The main assumptions for the economic analysis and the methodology for the calculation of the capital cost are shown in Table 1 and Table 2.

The total capital costs are calculated as shown in Table 2. For the membrane, a specific cost has been used and defined as the cost per square meter divided by the permeability ( $US\$ \cdot Pa / (mol/s)$ ). A baseline membrane cost of 0.025 US\$/m<sup>2</sup>/gpu has been assumed, corresponding for example to a membrane with a permeability of 2000 gpu<sup>1</sup> and a specific cost of 50 US\$/m<sup>2</sup>, similar to the polymeric membrane used in [10].

For the gas turbine, HRSG and steam cycle, the EBTF cost functions from [12] have been used, corrected to US\$2012 using the CEPCI index and currency conversion for €/€ based on 2012 values. For the GT, a 20% additional cost has been assumed for the plants with selective flue gas recycle to take into account the costs for the development for the machines operating with CO<sub>2</sub>-enriched gas.

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<sup>1</sup> 1 gpu is equal to 10<sup>-6</sup> (Ncm<sup>3</sup>/s)/(cm<sup>2</sup>\*cmHg) and hence corresponds to 2.7\*10<sup>-3</sup> (Nm<sup>3</sup>/h)/(m<sup>2</sup>\*bar)

Table 1 Main assumptions for the economic analysis

Currency	US\$2012
Discount rate	7 % pa (real)
Project life	25 years
Construction period	2 years
Plant load factor	90%
Price of natural gas	4 \$/GJ LHV
Price of electricity	43 \$/MWh
General and maintenance cost	6% Capex
Cooling water cost	0.025 \$/m <sup>3</sup>
Expected membrane life	3 years

Table 2 Capex calculation methodology

Parameter	Value
A Process equipment cost (PEC)	Sum of all equipment cost
B General cost	30% PEC
C Total equipment cost (TEC)	A + B
D Instrumentation	15% TEC
E Electrical	7% TEC
F Piping	20% TEC
G Total installed cost (TIC)	A+B+D+E+F
H Set-up cost	8% TIC
I Engineering	5% TIC
L Owners cost	7% (G+H+I)
M Engineering, procurement, construction and owner's cost (EPCO)	G+H+I+L
N Contingency	10% EPCO
O Total capital cost (CAPEX)	M+N

### 3. Results

#### 3.1. Mass and energy balance

In Figure 2, the effect of membrane feed pressure on the net plant efficiency and on the total specific membrane area (i.e. the sum of both membrane areas) is shown. The specific membrane area shown is defined to be independent of the membrane and corresponds to an inverted permeation driving force (i.e. units equivalent to [(mol/s)/Pa]<sup>-1</sup>). Units usual to membrane technology are used and this specific membrane area is calculated as the membrane area (in million of square meters) multiplied by the membrane permeability (in gpu). For example, for the case with 2 bar membrane feed pressure, a specific area of about 1500\*10<sup>6</sup> m<sup>2</sup>\*gpu is required. This means that if a membrane with a permeability of 1000 gpu is used, a total membrane area of 1.5\*10<sup>6</sup> m<sup>2</sup> is needed.

The energy balance of the plants is reported in Table 3, together with data for the benchmark NGCC without capture. Compared to alternative technologies, competitive efficiencies are obtained for moderate flue gas pressurization, with net efficiencies over 50% for pressurization lower than 2.5 bar and up to 53% for a membrane feed pressure of 1.5 bar. The efficiency reduces as the membrane feed pressure increases due to the need for flue gas pressurization before entering the membrane system. Flue gas compression is responsible for an efficiency reduction of about 2% points for a 1.5 bar feed pressure (while accounting for pressure energy recovery on expansion), 3.4% points for a 2 bar feed pressure and up to 7.4% points for a 4 bar of feed pressure.

The specific primary energy consumption for CO<sub>2</sub> avoided (SPECCA), defined in eq.(2), can be used to evaluate with a single index the energy and environmental performance of plants with CO<sub>2</sub> capture. The values of 2-2.6 MJ<sub>LHV</sub>/kg<sub>CO2</sub> obtained for the cases with moderate membrane feed pressurization are highly competitive with alternative technologies based on MEA absorption that have a SPECCA of the order of 3 MJ/kg [12].

$$SPECCA = \frac{3600 \cdot (1/\eta - 1/\eta_{ref})}{E_{ref} - E} \quad (2)$$

It is also important to note that the high CO<sub>2</sub> concentration at the inlet to the first membrane (>30% vol.) achieves CO<sub>2</sub> purities of 95% or more (and up to 96.7% for a 4 bar feed pressure), which may be sufficient for storage sites (e.g. aquifers) where extremely high purities (>99%) are not required.

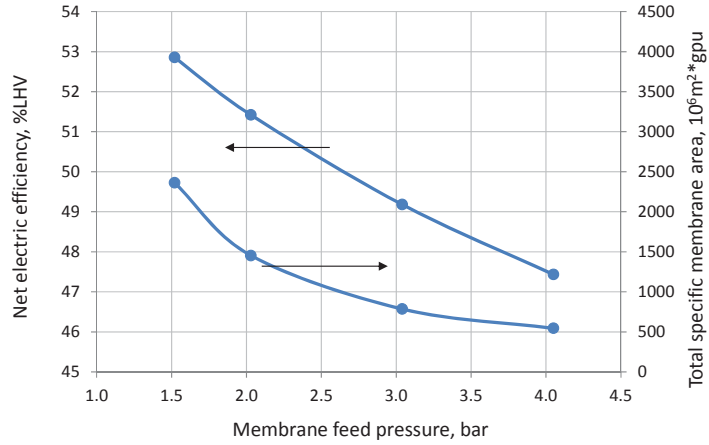


Fig. 2 Effect of membrane feed pressure on efficiency and total membrane surface area.

Table 3 Power balance of the investigated membrane cases

	Ref. NGCC	Membrane cases			
First membrane feed pressure, bar		1.52	2.03	3.04	4.05
Power balance, MW:					
Gas turbine net power	272.1	249.8	249.4	249.2	249.0
Steam turbine gross power	147.1	167.3	167.6	167.7	168.0
Steam cycle pumps	-1.79	-2.13	-2.14	-2.14	-2.15
Aux. for cond. heat rejection	-1.86	-2.05	-2.05	-2.05	-2.05
Aux. for heat reject. other than cond.		-0.77	-0.82	-0.90	-0.98
Fresh air fan		-2.08	-2.05	-2.03	-2.01
Flue gas compressor		-25.55	-45.44	-76.60	-100.8
Flue gas expander		11.65	21.25	36.46	48.03
CO <sub>2</sub> compression		-19.20	-19.02	-18.89	-18.59
Gross Power, MW	419.2	417.1	417.0	417.0	416.9
Net Power, MW	415.6	376.9	366.7	350.8	338.4
Heat input, MW, LHV	711.3	711.3	711.3	711.3	711.3
Net efficiency, %LHV	58.4	53.0	51.6	49.3	47.6
CO <sub>2</sub> capture efficiency, %		90.0	90.0	90.0	90.0
Specific emission, kg/MWh	353.7	40.3	41.5	43.3	44.9
CO <sub>2</sub> avoided, %		88.6	88.3	87.8	87.3
SPECCA, MJ/kg		2.01	2.63	3.66	4.55
CO <sub>2</sub> purity, %mol dry		95.2	96.0	96.5	96.7

### 3.2. Economic analysis

The breakdown of the cost of electricity for the different case studies is shown in Fig. 3. The COE calculated for the reference NGCC is lower than reported by NETL [14] (41.0 \$/MWh vs. 59.6 \$/MWh). The difference in cost is

due to the different fuel costs assumed (4 US\$/GJ in our case vs. 6.1 \$/GJ in [14]) and the electrical efficiency of the plant (58.4% vs. 55.7%LHV).

For the plants with CO<sub>2</sub> capture, the COE increases by about 22 \$/MWh to 40 \$/MWh compared to the reference plant. Fig. 3 shows that as the feed pressure increases, so does the COE. This is because as the feed pressure increases, larger compressors and expanders are needed, although a smaller membrane is required. This is also clear from Fig. 4, where the equipment cost breakdown and the effect of the membrane feed pressure on membrane and flue gas compressor/expander cost is shown. As a consequence, the increase in capital cost due to the flue gas compressor and expander and the increase in the fuel cost on the COE offset any capital cost reduction from the smaller membrane. The membrane case with the lowest cost of electricity is at 1.5 bar feed pressure. In this case, the COE is 63.8 \$/MWh

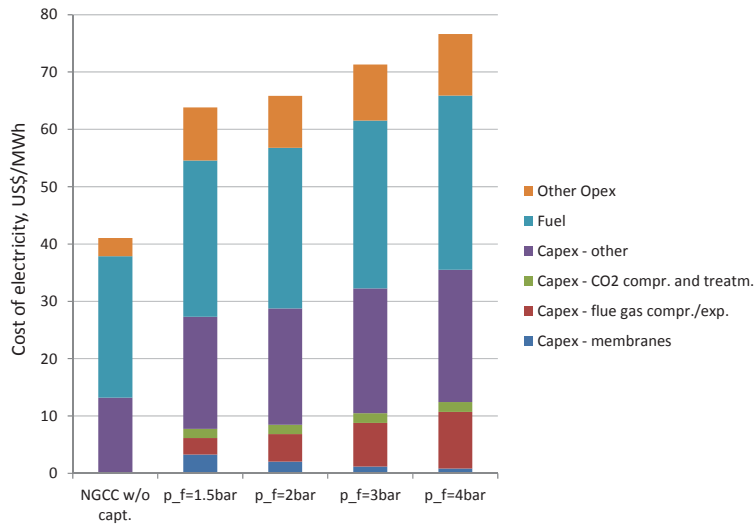


Fig. 3 Effect of membrane feed pressure on efficiency and total membrane surface area.

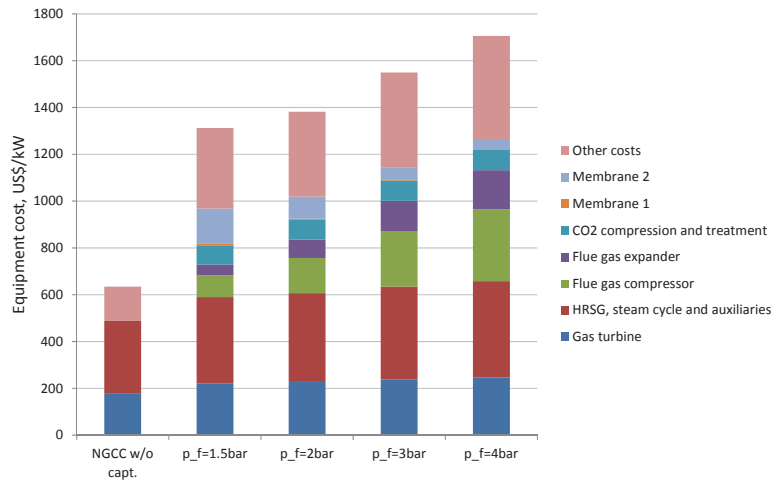


Fig. 4 Breakdown of the specific equipment cost.

The cost of the CO<sub>2</sub> avoided and its breakdown is shown in Fig. 5. The overall trend reflects the one for COE; with the lowest capture cost for the case with 1.5 bar for the membrane feed pressure at a cost of 73.5 \$/t CO<sub>2</sub> avoided. The capture cost for this case is mainly driven by the capital cost of the compressor and membrane system that account for over 50% of the cost. The energy operating cost, which takes into account the lost revenue due to the lower power output of the plants with CO<sub>2</sub> capture, is relatively low (accounting for about 20% of the capture cost) due to the moderate energy penalty of this case (9%). The costs estimated here are lower than those reported for the NETL NGCC baseline case with CO<sub>2</sub> capture by MEA, where a cost of 96 \$/t CO<sub>2</sub> avoided is reported. This suggests that the membrane properties selected here may be competitive for NGCC capture compared to traditional solvent systems.

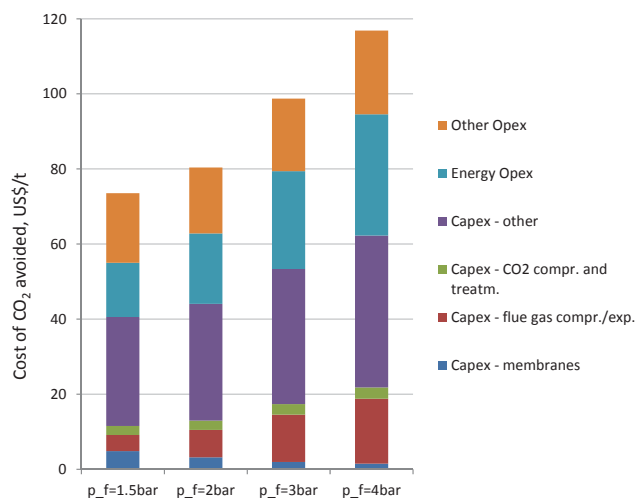


Fig. 5 Effect of membrane feed pressure on efficiency and total membrane surface area.

#### 4. Conclusions

This study has presented a techno-economic analysis of NGCC plants integrating a two-CO<sub>2</sub> membrane system for CO<sub>2</sub> capture and a selective flue gas recycle. The results show that when a moderate pressurization of the feed gas to the membrane system is utilized, a high net efficiency (53.0%) and a moderate cost of 73.5 \$/t CO<sub>2</sub> avoided is achieved, which is highly competitive with benchmark MEA-based CO<sub>2</sub> absorption. Also CO<sub>2</sub> purities of higher than 95% are achieved, which may be sufficient for most storage applications, thus reducing the need for downstream purification. These results of course depend on the assumed membrane performance and cost, which could be considered as a target by the developers in the new and promising field of solvent supported membranes.

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