

GHGT-11

"Application of hydrogen selective membranes to IGCC"

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Abstract

This study considers the integration of Pd-based H₂-selective membranes in integrated gasifier combined cycles (IGCC) from both technical and economical point of view. The selected gasification system is based on Shell technology. Two different dry feeding systems are investigated: the first is a state-of-the-art nitrogen-based lock hopper charger while the second uses CO₂ as pressurization gas. The net electric efficiency of the two plants is evaluated as a function of the hydrogen recovery factor (HRF) and the membrane feed pressure in order to minimize the membrane surface area. 90% HRF and 54 bar feed pressure are the best operating parameters which correspond to a net electric efficiency of 39% both for N₂ and CO₂ feeding system. The cost of CO₂ avoided is calculated as a function of a parameter named MI which represents the membrane development in terms of performances and costs. Results show that an improvement of membrane technology is necessary to match the state-of-the-art CO₂ capture plant, even though membranes show good potentiality for cost abatement.

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1. Introduction

This paper discusses the application of Hydrogen selective membranes to Integrated Gasification Combined Cycles for capturing the CO₂. The selected gasifier is based on Shell dry feed technology as also selected within European Benchmark Task Force (EBTF) [1]. Two different membrane types are going to be investigated both developed in the CACHET 2 project.

The first is a pure Pd membrane showing a high H₂ permeance, but no tolerance towards sulphur [2], and the second is a Pd-alloy based membrane which has a reduced permeance but can support sulphur content up to 1-2 ppm without reducing the flux to a large extent [3]. Considering the different behavior

towards sulphur of the membranes, a different acid gas removal process up-stream has been included: Rectisol for pure Pd membrane and Selexol for the Pd-alloy based membranes.

The adoption of a dry feed gasifier with high carbon conversion (>99%) leads to higher gasifier efficiency (measured in terms of cold gas efficiency) and higher plant efficiency, when compared to slurry fed gasifiers. The main drawback of this technology when applied to a membrane-integrated process is the significant inert concentration in the syngas, mostly nitrogen used as fuel carrier. This leads to: i) lower H_2 partial pressure in the membrane feed and consequently lower H_2 fluxes through the membrane, and ii) lower CO_2 purity after the hydrogen separation which may not meet the product specification for geological storage or enhanced oil recovery (EOR). For this reason, advanced feeding technologies or advanced CO_2 purification processes should be investigated to overcome this issue. Two investigated options are summarized in Figure 1.

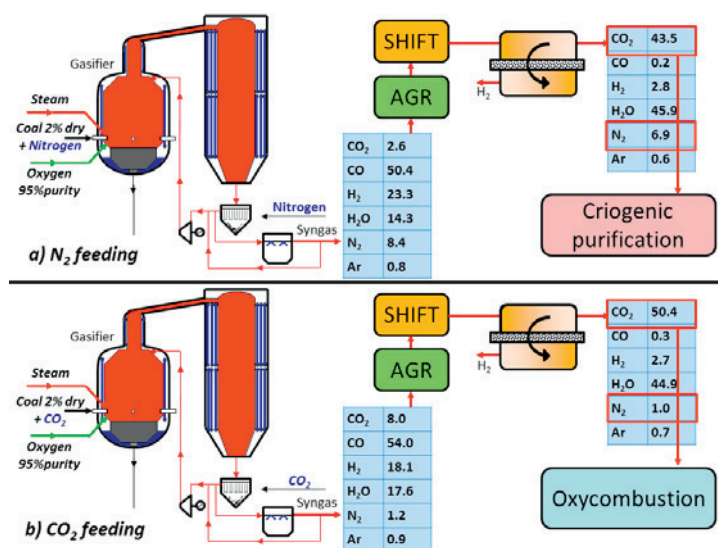


Fig. 1. Schematic of two lay-outs investigated and corresponding syngas compositions: a) N_2 feeding system and b) CO_2 feeding system

Based upon assessments of technoeconomics and operationability, the CACHET 2 project decided to develop membrane separator modules instead of membrane reactors (no WGS reaction is performed together with hydrogen separation) [4] [5]. For this reason, the non-integrated reaction and separation section configuration is based on several membrane modules in series (number range between two and three) with adiabatic high temperature shift (HTS) reactor in between to increase the CO conversion. The number of HTS depends on the target HRF: very high HRF requires additional HTS in order to convert as much CO as possible. Moreover, the adoption of membrane modules instead of membrane reactors reduces temperature variation inside the reactor and along the membranes; significant temperature gradients (>50-100°C) inside the reactor can be detrimental for the membrane as consequence of the differential thermal expansion between the membrane layer and the porous support.

2. Investigated cases

The first lay-out presented is based on conventional IGCC feeding and, consequently, cryogenic CO_2 purification [6] (N_2 feeding). Membrane modules are applied to IGCC adopting all conventional

components in the rest of the plant. In particular, two different acid gas removal (AGR) sections are going to be considered depending on the membrane tolerance towards sulphur. Lay-out of investigated cases shown in Figure 2 is equal to the reference case without capture until the AGR; this allows the obtained results to be consistent with the reference cases [7],[8]. CO shift conversion is carried out after the sulphur removal section reducing CO₂ venting in AGR and steam condensation exergy losses. The gasification pressure is set at 44 bar, as indicated by Shell, this is a trade-off between efficiency, which take advantage of lower pressures, and gasifier size [9].

The power plant size is based upon one gasification train generating syngas for one gas turbine combined cycle. Oxygen is produced in an ASU partially integrated to the gas turbine compressor: 50% of the air at the ASU distillation column comes from the GT compressor. An expander between the gas turbine compressor and the ASU is adopted to decouple the pressures and recover part of the compression work. This configuration was proposed as reference from the EBTF. N₂ produced in the ASU is compressed and partly used in lock hoppers for coal feeding, and partly sent to the membrane modules as sweep gas reducing the hydrogen partial pressure leading to a decrease in membrane surface area required. Moreover, nitrogen reduces the stoichiometric flame temperature limiting NO_x formation. Syngas exits the scrubber at about 170°C and then is sent to a catalytic bed for COS hydrolysis. Low temperature heat is recovered producing hot water for the saturator. Syngas is then further cooled with water and sent to acid gas removal (AGR) unit after condensate separation.

H₂S is removed in the Acid Gas Removal (AGR) section by means of a Selexol process resulting in a cleaned syngas sulphur content between 10 to 20 ppm, or a Rectisol process resulting in a H₂S syngas content lower than 1ppm. After the AGR unit, syngas is saturated and additional steam is added in order to achieve 2.0 S/CO ratio at WGS. Saturator allows increasing water content in the syngas, which is generated by recovering low-temperature heat and reducing the amount of steam to add. This steam comes from the IP steam generated in the gasification island and, if necessary, bled from the steam turbine at high pressure section outlet (usually named cold RH).

Both in Pd case and in Pd-alloy membrane cases, the maximum membrane temperature is set at 400°C. Since there is no reaction occurring in the module, the maximum temperature coincides with the feed inlet temperature, while at the outlet, the temperature is slightly lower because of the cooling effect of the sweep gas. This assumption affects mainly the membrane surface area rather than system efficiency since the fuel temperature at combustor inlet is set at 350°C.

Three different hydrogen recovery factor (HRF) are assumed in order to outline its influence over electric efficiency and CO₂ capture ratio. The feed pressure was varied from 35 bar to 54 bar: higher total pressure increases H₂ permeation driving force reducing the membrane surface area. As sweep gas, it is used nitrogen from ASU compressed to 25 bar with an intercooled compressor. The amount of sweep gas as reference case is set in order to have a H₂ concentration of 40% at reactor outlet, to reduce the membrane surface area required. The retentate stream, which mainly consists of CO₂, H₂O and unconverted H₂ and CO, is cooled down to ambient temperature producing high pressure steam for the HRSG and IP water economization. Because of the high steam content and pressure, a part of condensation heat can be recovered for water economization (dew point is at about 200°C). At 35°C, CO₂ molar concentration, volume dry, is 76% and 82% at 90% and 98% of HRF respectively. In order to achieve a CO₂ purity above 96% and recover most of hydrogen and carbon monoxide, a cryogenic separation process has been adopted. The cryogenic process has a CO₂ capture ratio ranging from 91 to 95%: this depends on the CO₂ purity at the inlet of the process, which is function of HRF.

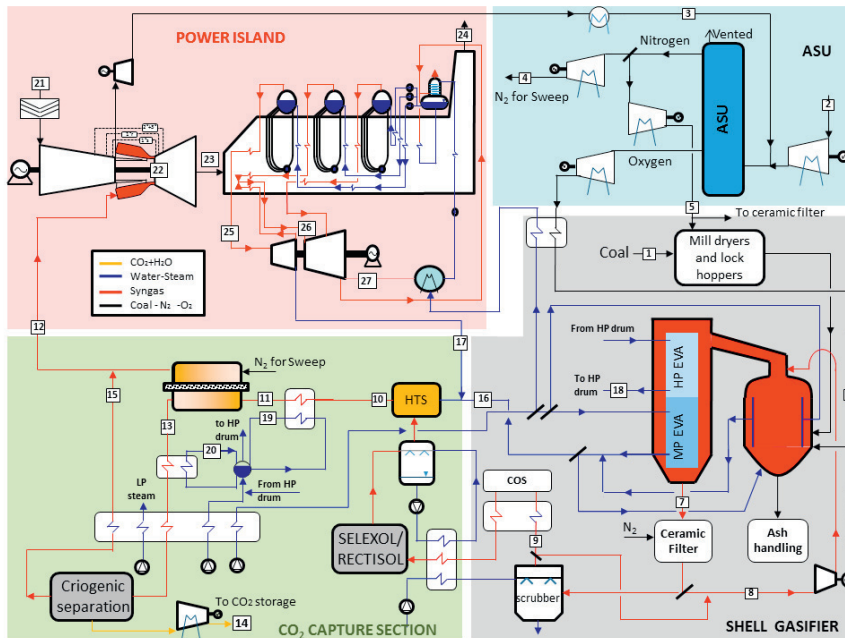


Fig. 2. Layout for the IGCC with membrane and low temperature AGR; CO₂ purification via cryogenic process.

The adoption of CO₂ as fuel carrier (CO₂ feeding) reduces the inert concentration in the produced syngas allowing a more conventional purification process as oxy-combustion. Moreover, equipment can be the same as for the previous case. The amount of CO₂ considered for coal feeding is determined keeping the same volumetric flow as in the nitrogen case, hence doubling the mass flowrate [1]. With the current feeding technology, about 50% of the fuel carrier is vented in atmosphere during the charging process. This is because nitrogen venting has neither economic nor environmental drawbacks, while it is the easiest option. If the fuel carrier adopted is the CO₂, venting even a single molecule of CO₂ reduces the CO₂ capture ratio with significant thermodynamic and economic penalties. It is expected that the feeding technology can be improved reducing venting, if necessary, although not all the CO₂ could be recovered. The calculated syngas composition was determined with a reduced order modelling keeping the same geometry of the gasifier and coal and oxygen flowrates of the N₂ case [7]. The temperature and compositions at the gasifier outlet have been determined accordingly. A description of the plant lay-out is shown in Figure 3.1. As for the previous cases, the lay-out coincides with the reference case until the AGR section. The CO₂ for fuel feeding is compressed together with the CO₂ captured. CO shift conversion is carried out after the sulphur removal section reducing CO₂ venting in AGR and steam condensation exergy losses.

After the AGR, the syngas is saturated using hot water, which is heated by recovering low-temperature heat. The additional steam in order to achieve the required S/C ratio at WGS inlet originates from the IP steam generated in the gasification island and, if necessary, bled from the steam turbine at high pressure section outlet (usually named cold RH).

Three different hydrogen recovery factors (HRF) are investigated in order to outline its influence over the electric efficiency and CO₂ capture ratio. The feed pressure was varied from 35 bar to 54 bar: higher total pressure increases H₂ permeation driving force reducing the membrane surface area. As sweep gas, nitrogen from the ASU is used, and compressed to 25 bar with an intercooled compressor. The amount of sweep gas as reference case is set in order to have 40% H₂ concentration at reactor outlet, to minimize the membrane surface area. The retentate stream, which mainly consists of CO₂, H₂O and unconverted H₂ and

CO, is burned with oxygen in order to exploit the remaining heat value of the retentate while keeping a high CO₂ purity. The oxygen is taken from the ASU after the pump. Cases with membrane feed pressure above gasification conditions require an additional pump (which can be either in series or in parallel) in order to achieve the desired pressure. After combustion, the retentate is cooled down to ambient temperature producing high pressure steam for the HRSG, pre-heating feed water for HRSG and the water for the saturator. Water pre-heating is fundamental because of the high steam content in the stream: dew point occurs at about 200°C. At 35°C, CO₂ molar concentration volume dry is 96.1% and 96.4% at 90% and 98% of HRF respectively.

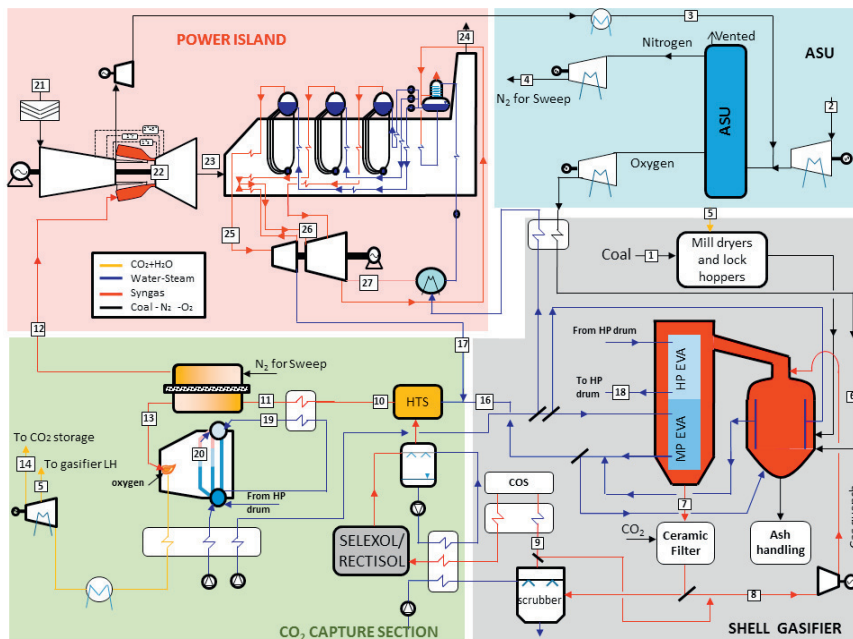


Fig. 3. Layout for the IGCC with membrane and low temperature AGR; retentate oxycombustion

3. Methodology

Heat and material balances have been estimated by a proprietary computer code developed to assess the performances of advanced power plants [10]. The Rectisol, Selexol and CO₂ compression systems are simulated with Aspen Plus™. Calculation methodology and assumptions are the same used and approved in EBTF [1]. Main simulation assumptions are summarized in Table 1. The hydrogen pressure at combustor inlet (23.5 bar) is set in order to have an overpressure of 5 bar with respect to the air).

Template of the economic assessment methodology is the EBTF work which deals with the reference cases with and without carbon capture [1]. A summary of the most important equipment and consumables are summarized in table 2. The coal cost is assumed equal to 3 €/GJ_{LHV}. The reference CO₂ capture plant has a cost of CO₂ avoided equal to 36 €/t_{CO2} as in EBTF.

The membrane surface area was determined with a two-dimensional model developed by SINTEF within the CACHET 2 project. The simulation tool accounts for bulk-phase feed side mass transfer characteristics, permeability and mass transfer resistance associated with the membrane deposition layer, mass transfer characteristics through the ceramic support tubing and at the bulk-phase permeate side of

the membrane. The input parameters of the model for the pure Pd membrane are: thickness equal to 7.266×10^{-6} m, permeability at reference conditions ($T=400$ °C) equal to 9.592×10^{-13} kmol m^2 s Paⁿ, activation Energy of 12.8 kJ/kmol and n equal to 0.676 [4] and [5]. When a sulphur tolerant membrane is considered, the permeability is assumed reduced by 60% [3]

Table 1 - Main assumptions adopted for plant simulations.

<i>Douglas Premium coal characteristics</i> [2]	
Coal LHV	25.17 MJ/kg
CO ₂ specific emission	349.0 [g/kWh _{LHV}]
<i>Gas turbine</i>	
Pressure ratio	18.3
Gas mass flow rate at the turbine inlet	650 kg/s
TIT	1360 °C
Pressure loss at inlet	1 kPa
<i>Steam cycle</i>	
Pressure levels, bar	144, 54, 4
Maximum temperature SH e RH	565 °C
<i>Gasifier</i>	
Gasifier outlet pressure	44 bar
Gasifier outlet temperature	1550 °C
<i>Acid Gas Removal</i>	
Electrical energy consumption	5.66 kWh/kg _{H₂S} (Rectisol), 0.54 kWh/kg _{H₂S} (Selexol)
Thermal energy consumption	15 kWh/kg _{H₂S} (Rectisol), 5.8 kWh/kg _{H₂S} (Selexol)

Table 2 - Main assumptions for investment cost assessment. [1][7]

Component	Scaling parameter	Reference Cost (M€)	Reference Size	Scale factor
Gasifier,	Thermal input [MW]	90.0	828.0	0.67
Gas turbine package,	GT _{Net Power} [MW]	49.4	272.12	0.3
HRSG, ducting and stack,	U*S [MW/K]	32.6	12.9	0.67
Steam turbine package,	ST _{Gross Power} [MW]	33.7	200.0	0.67
Low temperature heat recovery	Thermal input [MW]	6.1	828.0	0.67
Air separation Unit (ASU)	O ₂ produced [kg/s]	26.6	28.9	0.7
Selexol CO ₂ separation system	CO ₂ captured [kg/s]	28.1	69.4	0.8
CO ₂ compressor and condenser,	Compr. Pow. [MW]	9.9	13.0	0.67

Since the Pd-alloy membrane technology is still under development, it will not be provided a lumped figure for the cost of CO₂ avoided, but it will be determined as a function of the membrane performances and membrane module costs. In particular, a coefficient MI representing the membrane technologies improvement is introduced and it is defined as follows:

$$MI = \frac{\text{Membrane module costs}}{\text{Membrane performances}}$$

MI equal to 1 represents current status of membrane development assuming the abovementioned performances and a specific cost equal to 5000 €/m². Then, values of MI equal to 0.6 and 0.4 are considered representing an improvement of only performances, only costs or both. For example, a MI coefficient equal to 0.6 can either represent (i) a 40% costs reduction with no performances improvement (ii) either improved performances by 66% with no cost variation or (iii) the combination of the two as cost reduction to 80% and performances improvements of 33%.

4. Results

Overall energy balances for the two membrane cases combined with the reference cases are shown in Tab.3.

Table 3 - Main assumptions for investment cost assessment

		IGCC Reference	IGCC Selexol Cap	Membrane- N₂ feeding	Membrane- CO₂ feeding
HRF		--	--	90	90
Membrane inlet pressure		--	--	54	54
<i>Power production</i>					
Gas Turbine	[MW] _{el}	290.2	305.0	323.1	308.5
Steam Cycle gross	[MW] _{el}	197.7	179.2	175.0	235.1
Expander ASU	[MW] _{el}	8.5	10.2	9.8	12.3
<i>Auxiliaries Consumptions</i>					
Coal handling	[MW] _{el}	1.7	1.9	1.9	2.1
Ash handling	[MW] _{el}	0.5	0.6	0.6	0.6
Sulphur adsorption	[MW] _{el}	0.4	19.3	4.5	6.5
N ₂ LH compressor	[MW] _{el}	9.2	11.1	12.0	-
N ₂ dilution compressor	[MW] _{el}	32.1	24.0	38.9	60.0
ASU compressors	[MW] _{el}	22.7	26.6	26.0	32.7
Syngas quench blower	[MW] _{el}	1.1	1.3	1.2	1.1
Membrane feed compressor	[MW] _{el}	--	--	5.0	5.6
CO ₂ compressor	[MW] _{el}	--	22.9	9.6	4.0
HRSG pumps	[MW] _{el}	3.1	3.2	3.1	2.0
Heat rejection	[MW] _{el}	2.48	2.5	2.4	3.7
BOP	[MW] _{el}	0.7	1.3	1.2	2.9
<i>Overall Balances</i>					
Net power output	[MW] _{el}	422.4	379.6	401.4	434.8
Thermal Input	[MW] _{th}	888.8	1044.4	1020.0	1101.7
Auxiliary drying fuel	[MW] _{th}	7.8	9.1	8.9	9.5
Overall Efficiency	[%]	47.1	36.0	39.0	39.1
Specific Emission	[g/kWh]	732.1	98.5	105.3	20.6
SPECCA	[MJ/kgCO ₂]	--	3.7	2.5	2.2

The membrane feed pressure and the hydrogen recovery factor are set at 54 bar and 90% respectively; these are the operating conditions which guarantees the lowest cost of CO₂ avoided. Applying the CO₂ capture, the power output penalty is lower than the corresponding efficiency penalty, due to the higher fuel input. In the CO₂ feeding case, the net power output is even higher than the reference IGCC without capture. Gas turbine net power is higher for carbon capture cases because of the lower heating value of the syngas. Comparing N₂ and CO₂ cases, it can be noted that the first has a higher GT power output and a lower steam turbine power output.

This is a consequence of the purification process and the resultant use of the hydrogen in the retentate: in the N₂ case, the cryogenic separation makes it available for the GT combustor, while in the CO₂ case it is burned with pure oxygen, increasing the thermal input to the HRSG. The ASU compressor work is higher for the CO₂ case as a consequence of the retentate oxycombustion. On the other hand, the CO₂ compression work decreases: as a matter of fact, the cryogenic separation requires an inner expansion of the purified stream in order to supply the cooling effect while this is not required in the oxycombustion. As overall efficiency, both membrane cases show a 39.0% value, which is 3% point higher than the reference case; considering that the CO₂ specific emissions are similar between the N₂ and the Selexol case the resulting SPECCA lowers to 2.5 MJ/kg_{CO2}. This is stressed in the CO₂ case where the oxycombustion significantly decreases the emissions and consequently the SPECCA (2.2 MJ/kg_{CO2}); however this value is calculated assuming that all the CO₂ used as fuel carrier is recovered (in the actual technology all the coal carrier but the last lock hopper vessel is vented; an improve in the lock hopper vessel system could recover almost all the vented gas).

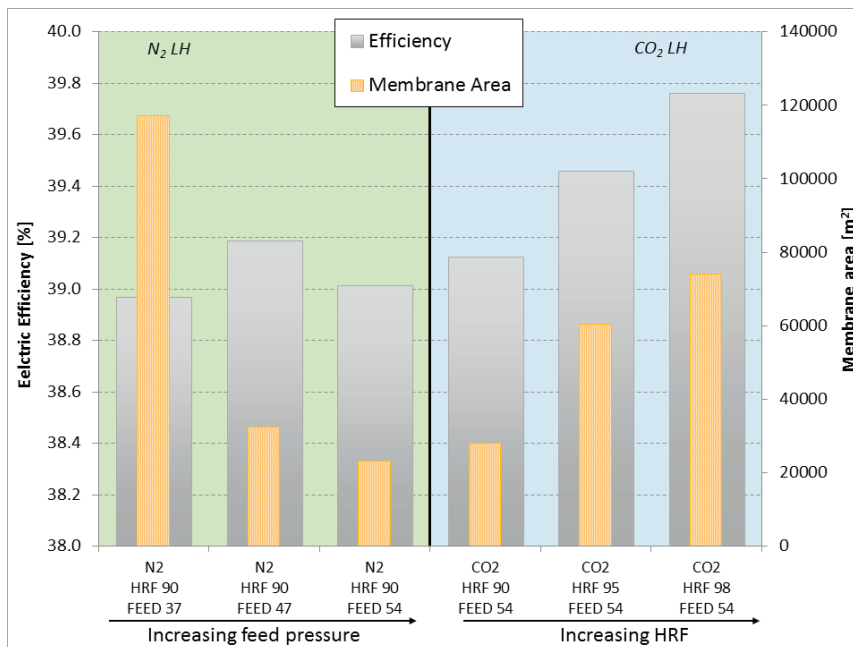


Fig. 4. Efficiency and membrane surface for the two investigated configurations as a function of feed pressure (left side) and HRF (right side)

Focusing on the membrane operating conditions in the N_2 feeding case, the feed pressure and the HRF do not affect the net electric efficiency whilst strongly change the membrane surface area. For example, an increase in the feed pressure from 37 to 54 bar reduces the membrane surface area of 80%. Concerning the CO_2 feeding case, both the membrane area and the plant efficiency are affected by the membrane operating conditions; this is explained by the low efficiency of the oxy-combustion compared to the cryogenic separation which enhances the case with HRF as high as possible.

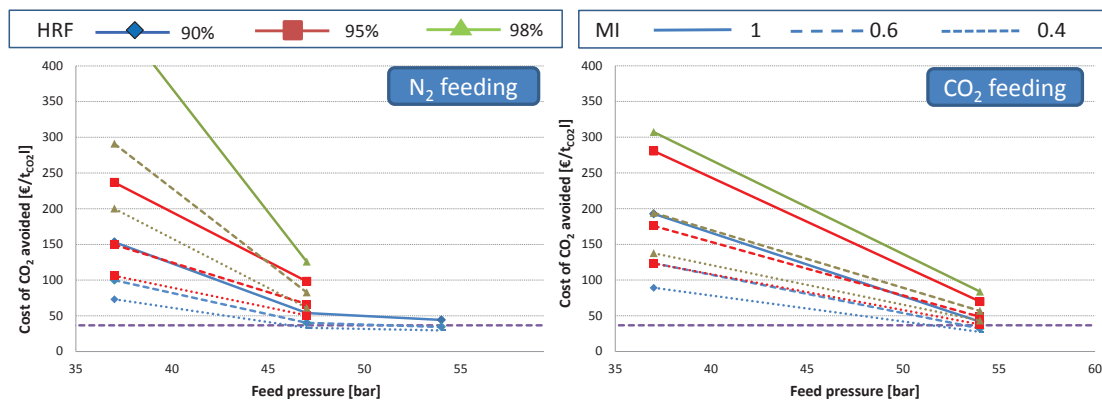


Fig. 5. Cost of the CO_2 avoided for the N_2 LH (left side) and CO_2 LH (right side) as a function of the feed pressure, HRF and MI.

If sulphur tolerant membranes are assumed, hence with Selexol as AGR instead of Rectisol, the efficiency and CO_2 avoided improves, but the membrane surface area doubles as a consequence of the assumed lower permeance of this type of membrane. The cost of CO_2 avoided as a function of the MI coefficient for the pure Pd membranes is shown in Figure 5 for both N_2 feeding and CO_2 feeding.

From the figure it can be noted that: i) feed pressure reduces the membrane surface area with significant economic benefits and, ii) the adoption of high HRF is not justified from economic point of view. Hence, the membrane operating conditions are the governing parameter for the investigated cases. Between the two different configurations investigated, no significant differences can be outlined, but CO_2 feeding has the highest potentiality when CO_2 vented during coal charging is reduced compared to actual performances. Finally, actual membrane performances (represented by MI equal to 1) have a cost of CO_2 avoided higher than the reference case (about 20%). However, with a reduction of MI of 0.4, the resulting cost of CO_2 avoided matches the reference case. Considering the expected cost of membrane modules for large scale application (in the range of 2000 €/m²) [11], it can be noted that the membrane potentialities to reduce the cost of CO_2 avoided are significant.

5. Conclusions

This work discussed the application of hydrogen selective membranes to Integrated Gasification combined Cycle for CO_2 capture. Two different CO_2 purification processes were investigated in combination to different gas as coal carrier (N_2 and CO_2). From economic point of view, actual costs are higher than reference technologies; however it can be expected a potential decrease thanks to the estimated cost reduction and performances improvement. Moreover, membrane advantages over

competitive technologies can be even more significant when a warm gas clean-up is applied: within CACHET 2, a sorbent with good perspectives for H₂S at high temperature has been developed .

Acknowledgements

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