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# Techno-economic evaluation of membrane technology for pre-combustion decarbonisation: water-gas shift versus reforming

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## Abstract

A techno-economic evaluation of the application of membrane reactors in natural gas combined cycles with CO<sub>2</sub> capture is presented. The electrical efficiency, capture efficiency, required membrane surface area and cost of CO<sub>2</sub> avoided are presented for power plants integrated with membrane reformers as well as membrane water gas shift reactors. For applications in CO<sub>2</sub> capture, membrane water-gas-shift is more suited than membrane reforming. The lower hydrogen partial pressure in a membrane reformer compared to membrane WGS causes high investment costs, because the membrane area is high and compression of the hydrogen fuel before entering the gas turbine is necessary. A significant increase in operating temperature, possibly combined with a higher feed pressure could improve the performance of membrane reformers. For the various options of upstream reforming in membrane water-gas shift, gas heated reforming is the preferred option with autothermal reforming as second best.

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## 1. Introduction

In pre-combustion CO<sub>2</sub> capture at natural gas fired power plants, the energy content of the fuel is transferred to H<sub>2</sub> while a separate stream of CO<sub>2</sub> is made available for underground storage. For this, the fuel is first converted in a reforming step, giving a synthesis gas mixture (a mixture of H<sub>2</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>O). The CO then reacts with steam via the water-gas shift reaction to form CO<sub>2</sub> and additional H<sub>2</sub>. CO<sub>2</sub> and H<sub>2</sub> are then separated. For natural gas as a feed various methods of reforming can be used (steam reforming, autothermal reforming, gas heated reforming etc), as well as several methods for H<sub>2</sub>/CO<sub>2</sub> separation. Conventional methods for H<sub>2</sub>/CO<sub>2</sub> separation make use of liquid phase solvents for which both physical solvents (e.g. Selexol) and chemical solvents (e.g. amines) can be used, depending on the CO<sub>2</sub> concentration. A more advanced method makes use of high temperature hydrogen selective membranes. The membranes anticipated in this study are thin palladium (alloy) membranes supported by a porous ceramic or metallic support having a high flux and very high selectivity towards hydrogen permeation [1, 2]. Hydrogen selectively permeates through the tubular shaped membrane as a result the difference in partial pressure of

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hydrogen between both sides of the membrane. These allow for separation of hydrogen at elevated temperature, which provides a potential for better efficiency and costs by limiting the need for cooling and heating in the cycle. Furthermore the  $\text{CO}_2$  is made available at high pressure.

If the membrane separation step is combined with the water-gas shift or reforming step thus creating *membrane reactors*, additional benefits can be expected. These include less process steps and therefore potentially lower investments, more favorable process conditions, and an even higher efficiency. An important choice is whether to combine the hydrogen separation step with only the water-gas shift reaction, or to also combine it with the steam methane reforming reaction. The attractive point of combination with reforming is that an integrated one-step process at high temperature from fuel to  $\text{H}_2$  and  $\text{CO}_2$  is obtained. This with a low number of unit operations and high temperatures that might allow for good heat integration. On the other hand high temperatures put higher demands on membrane stability. Combination with only the water-gas shift reaction requires that an upstream separate reforming type step is required; the advantage is however a milder temperature and a higher hydrogen content of the streams. To evaluate the potential of hydrogen membrane reactors and to make a comparative assessment between the two options a techno-economic evaluation has been conducted in which both options are compared.

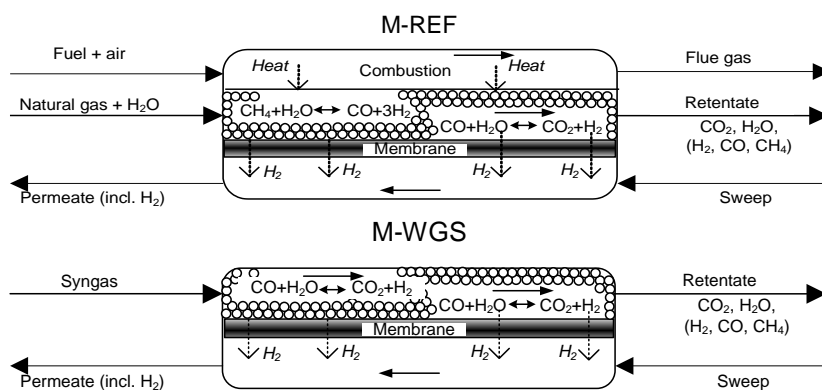


Figure 1 Membrane reformer (M-REF) and membrane water gas shift (M-WGS) working principles

The working principle of hydrogen membrane reactors is depicted in Figure 1. A membrane reformer (M-REF) is fed with a mixture of natural gas and steam. The reforming reaction and water-gas shift reaction are carried out at the feed side with the aid of a catalyst. Parallel to the reaction, hydrogen is removed through a hydrogen selective membrane. The selective removal of the product hydrogen shifts the equilibrium of both reactions to the right, which allows for a high conversion at a relatively low temperature (500 – 600 °C) compared to conventional steam methane reforming without a membrane. Since the overall reaction is highly endothermic, natural gas or  $\text{H}_2$  is combusted with air in a third zone to provide heat. A water-gas shift membrane reactor (M-WGS) is fed with a synthesis gas (syngas) mixture from an upstream reformer. The selective removal of the  $\text{H}_2$  product shifts the equilibrium to the right. The reactor is operated adiabatically at around 350-400°C.

The integration of both the membrane reactors in natural gas fired power plants is schematically illustrated in Figure 2. For M-REF case natural gas is mixed with steam and fed to a pre-reformer to convert higher hydrocarbons and increase the  $\text{H}_2$  content of the feed gas. It is then fed to the membrane reactor M-REF. The resulting  $\text{CO}_2$  rich retentate is sent to the  $\text{CO}_2$  clean-up and compression. The heat for the reaction is supplied by combusting natural gas (or hydrogen, not depicted) in the combustion zone. The off gas is mixed with steam and used as a sweep gas. Hydrogen produced by the steam reforming reaction permeates through the membrane. The permeation is enhanced by using a sweep gas. Following cooling and water removal, the  $\text{H}_2$  is compressed and used for power generation in the gas turbine and steam cycle.

For the M-WGS case natural gas is mixed with steam and oxygen from an air separation unit (ASU). This is fed to a reformer for which several options exist (SMR/ATR/GHR/HIR, see below). The resulting syngas is fed to the membrane water-gas shift reactor (M-WGS). The sweep gas consists of compressed nitrogen from the ASU and

steam. Retentate handling is identical to the M-REF system, permeate is sent to the gas turbine combined cycle. Now however without the need for extensive cooling water knock-out and recompression (see also below).

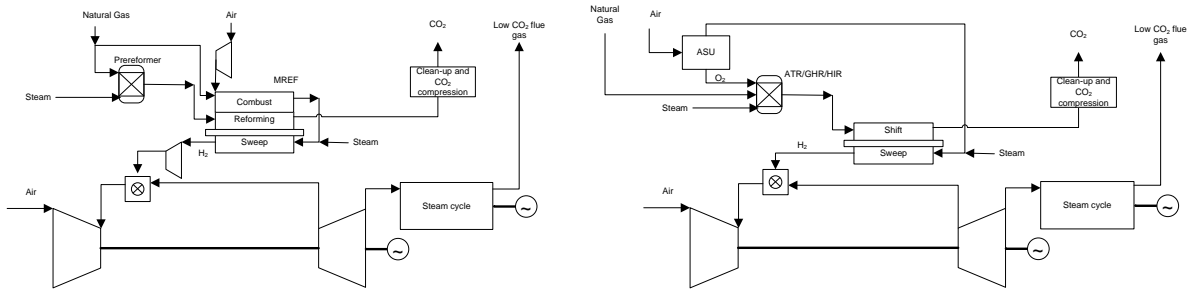


Figure 2 Simplified system schematic of natural gas fired power plants with M-REF (left) and M-WGS (right) for CO<sub>2</sub> capture.

For the upstream reforming step in M-WGS several options exist. These options are (see Figure 3.) Steam Methane Reforming (SMR), Autothermal Reforming (ATR), Gas Heated Reforming (GHR) or Heat Integrated Reforming (HIR). The SMR system features the endothermic steam methane reforming reaction ( $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ ) which requires external heat supply. For ATR in the same reactor the exothermic partial oxidation of natural gas ( $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$ ) is carried out additionally, which supplies heat to the SMR reaction. In the case of gas heated reforming the ATR and SMR are carried out in series where the hot off-gasses of the ATR are used for heat supply to the SMR reaction. In the case of the novel Heat Integrated Reformer (HIR) [3] with is an integrated reactor in which the two steps are carried out in a parallel scheme with heat exchange between the two steps, the outlet streams are then mixed before being sent to the M-WGS reactor.

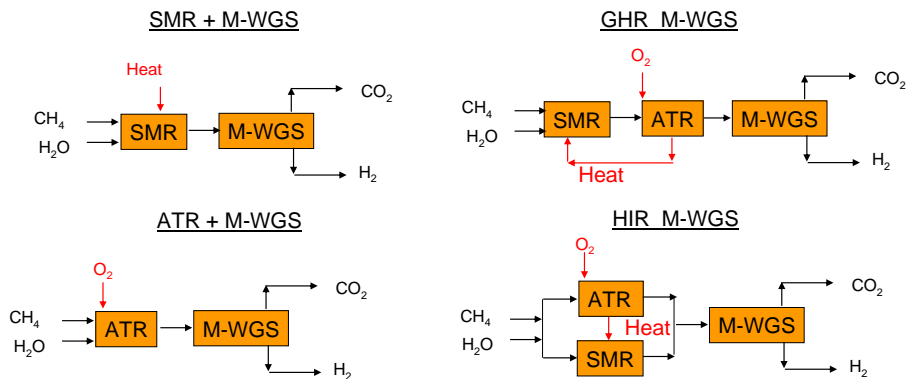


Figure 3 Schematic of different options for M-WGS systems.

## 2. Methodology

A techno-economic assessment has been performed for conventional and advanced pre-combustion membrane technologies. For comparison an ATR Selexol case has been included: oxygen fed autothermal reforming of natural gas, conventional water-gas shift followed by cooling down and H<sub>2</sub>/CO<sub>2</sub> separation using conventional Selexol absorption. Also a no-capture reference case, a natural gas combined cycle (NGCC), is included in the study. The system simulations have been performed using flow sheeting in Aspen Plus. Economic evaluation was done using an in-house developed modular costing tool. For the system design a simplified approach for the detailing of the plant heat integration has been used that allows for a fast comparison evaluation of a various system options. The methodology simplifies the steam cycle of the combined cycle to a single pressure cycle and by making use of multi-stream heat exchanger blocks in which the heat integration is performed on a pinch-technology approach basis without fully specifying the exact matches between all the streams. The main starting points for the system design are listed in Table 1. The permeance includes mass transfer effects. The M-WGS permeance depicted is averaged

over the inlet/outlet and is higher for than for M-REF because lower temperature allows for thinner membranes. The starting points for the gas turbine and the steam cycle have been tuned to match that of industrial performance data for the NGCC considered [4]. It is assumed that these starting points are not affected by integration of membrane reactors in the system. The gas turbine fuel must be at least 22 bar, allowing for 5 bar of control margin for the gas turbine fuel valve. No limitations have been accounted for on the gas turbine fuel composition.

Table 1: Main starting points of the study

Component	Specification	Component	Specifications
Natural gas	46.899 MJ/kg, 40 bar [5]	M-WGS	Adiabatic, 400°C inlet
Ambient conditions	1 atm, 15°C	Feed/permeate press.	40/22 bar
Gas turbine	Siemens V94.3A, PR=16.9, TIT=v=1238.5 °C	Membrane permeance	$1 \cdot 10^{-6}$ mol/m <sup>2</sup> .s.Pa
ATR	Tout=989°C, S/C=1.4	Hydrogen recovery	98%
GHR	Tmax=998°C, Tout=650°C, S/C=1.4	M-REF	Isothermal, 600°C
HIR	Tout=500°C, S/C=1.72	Feed/permeate press.	40/10 bar
Compressors	85% isentropic efficiency	Membrane permeance	$8 \cdot 10^{-7}$ mol/m <sup>2</sup> .s.Pa
		Hydrogen recovery	90.5%
		Membrane selectivity	100%
		ASU	O <sub>2</sub> purity 95%, 250 kWh <sub>el</sub> /ton O <sub>2</sub>

The membrane reactor model used is an in-house 1-dimensional model [6] describing the reaction kinetics, permeation as function of the local hydrogen partial pressure at both sides of the membrane and heat effects. The model calculates the profiles of concentrations along the membrane reactor length accounting for effects of feed side hydrogen depletion and permeate side hydrogen enrichment and their effects on permeation and reaction kinetics. The model is implemented as a user sub-routine in Aspen Plus and allows for assessment of trade-off between system efficiency and membrane reactor size. The Selexol CO<sub>2</sub> absorption unit was modelled as a black box separator using separation factors from literature.

The plant investments are calculated based on sizing of equipment, based on the result of flow sheeting calculations and selection of the construction materials. The total capital costs are then calculated using surplus charges (for piping, instrumentation etc. etc.) [7]. An exception to this approach is ‘all inclusive equipment’ as e.g. the ASU and the combined cycle for which literature has been used. The other exception are ‘special materials’ as membranes and catalysts which are accounted for in the investment and operating costs but for which surcharges are not applied. For the M-WGS reactor the costing has been done based on the costs of shell-and-tube heat exchangers having the same surface area as the membrane surface area of the membrane reactor, applying a surcharge for extra manifolding. The M-REF membrane reactor costs have been estimated accounting for the separate contributions of shell, tubing manifolding etc.. The starting points for the economic model have been taken from IEA GHG [5]. Here a net present value approach is used which accounts for the benefits and costs over the construction period and operating life of the power plant.

### 3. Results

The system design was developed for all the cases discussed above and presented in Figure 4 for the M-REF case and in Figure 5 for the ATR M-WGS case. The SMR M-WGS case proved to suffer from a low methane conversion in the SMR step so this option was abandoned in an early stage and the results will not be presented. For the other M-WGS cases the lay-out is quite similar to the latter, with small differences in heat integration. The black, blue and red streams indicate the main flow path, water/steam cycle and power production/demand respectively.

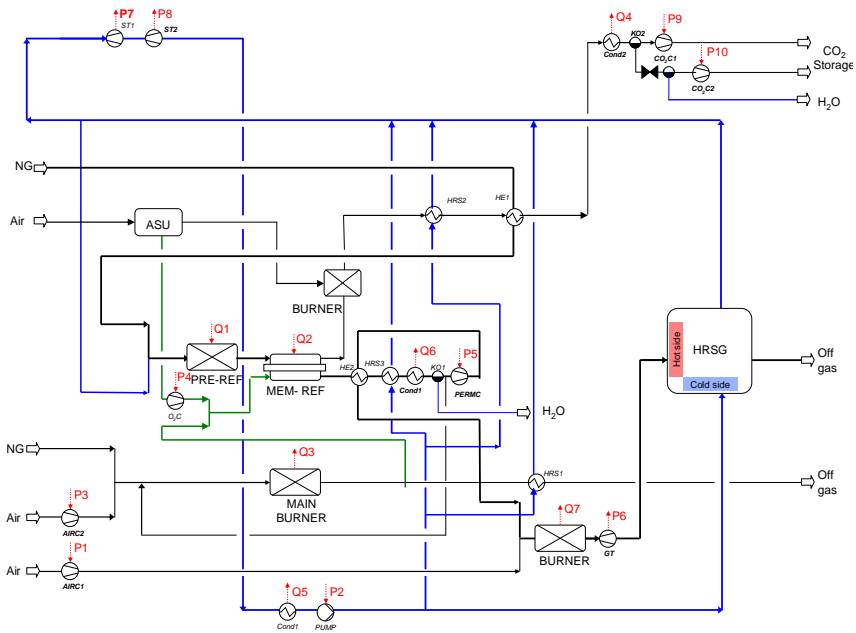


Figure 4 M-REF system design

The M-REF system in Figure 4 gives the detailed lay-out of the scheme presented in Figure 2(left). The membrane reformer burner ('main burner') is integrated in the membrane reformer but is simulated as a separate step in the flow sheeting model. The unconverted  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{H}_2$  in the retentate are catalytically combusted using oxygen from a small air separation unit ('ASU'). The resulting  $\text{CO}_2/\text{H}_2\text{O}$  stream is then sent to water removal and  $\text{CO}_2$  compression. The sweep is a low pressure bleed steam from the steam cycle. The resulting permeate  $\text{H}_2/\text{H}_2\text{O}$  is cooled down, water is knocked out, and  $\text{H}_2$  is compressed to the required gas turbine fuel pressure. After combustion the exhaust stream is expanded in the gas turbine and used for steam generation in the heat recovery steam generator HRSG.

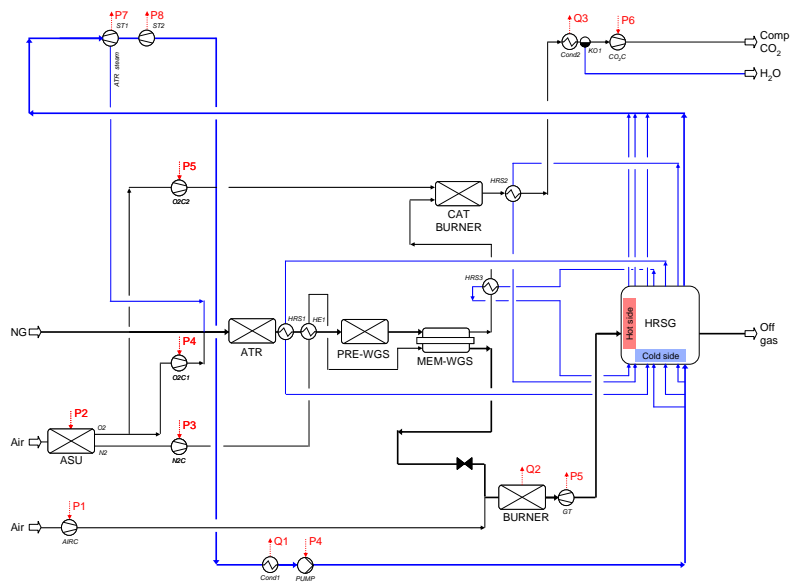


Figure 5 M-WGS system design

The M-REF system in Figure 5 gives the detailed lay-out of the left-hand scheme presented in Figure 2. It features feed mixing, an ATR and then the M-WGS reactor. The retentate goes again to a catalytic burner to convert remains of CO and H<sub>2</sub> after which it enters compression and drying. The sweep gas is a mixture of N<sub>2</sub> from the ASU and steam. The permeate stream leaves the M-WGS reactor at 22 bar, so can be directly fed to the gas turbine without the necessity of a compression step. The ATR exhaust stream is used for making saturated steam only; superheating steam is not considered because of the risk of metal dusting.

The results of system modelling are presented in Figure 6. The capture efficiency of the M-REF was chosen at 90% by tuning the ratio between H<sub>2</sub> and NG fuel to the M-REF burner. A higher capture efficiency could be achieved by burning more H<sub>2</sub>, at the cost of a lower electrical efficiency. The capture efficiency of the ATR Selexol option is slightly lower than that of M-REF. The capture efficiencies of the M-WGS systems are all close to 100% given that the membrane is assumed 100% selective and retentate CO, H<sub>2</sub> etc. are captured by catalytic oxyfuel combustion in the catalytic burner. The LHV efficiency of the membrane cases is significantly higher than that of the reference ATR Selexol system. The M-REF system has an electrical efficiency that is only slightly higher than that of the M-WGS cases. Making a comparison between the three M-WGS cases it is shown that the GHR M-WGS case is the most efficient followed by ATR-WGS and HIR M-WGS. The membrane surface area of the M-REF options is drastically larger than that of the different M-WGS options. This will be discussed in more detail later. The GHR M-WGS system has the lowest membrane surface area compared to ATR M-WGS and HIR M-WGS. Although the GHR itself is more expensive than an ATR, the total investments are lower, because the higher efficiency and better heat integration pays off in lower investments for the ASU, and the steam system. This makes that the overall CO<sub>2</sub> avoidance costs are highest for the M-REF case as a result of the high investment costs combined with only a minor efficiency benefit. The M-WGS systems, ATR M-WGS and especially GHR M-WGS, have the best economic prospects in terms of investments as well as CO<sub>2</sub> avoidance costs. The HIR also has no economic advantage so it is concluded that is not very suitable for CCS applications but more in chemical synthesis in which it features good possibilities for product gas flexibility.

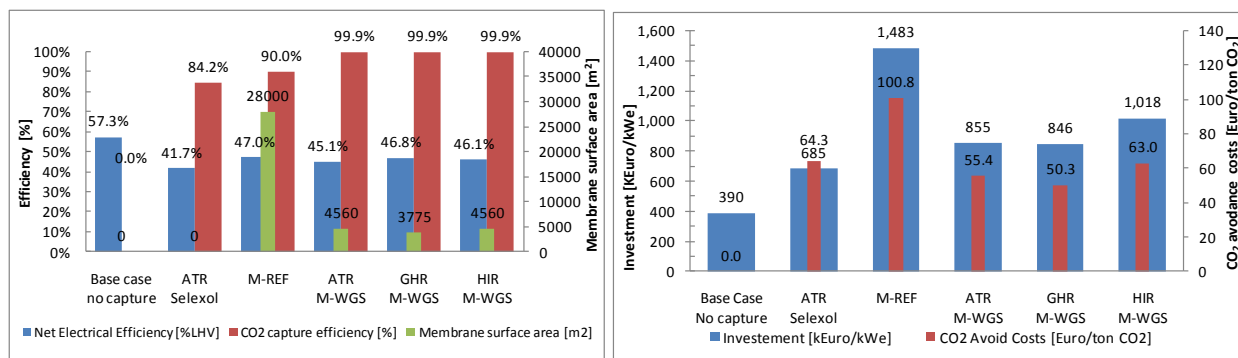


Figure 6 Summary of results of system assessment studies thermodynamic and economic performance for several M-WGS concepts compared to M-REF integrated in a gas fired power plants with CO<sub>2</sub> capture.

#### 4. Analysis

Analysing the reasons for the drastically higher membrane surface area required for M-REF compared to M-WGS the partial pressures in the system were analyzed. Figure 7 schematically presents the partial pressure profiles along the main flow path of the system. It can be seen that feed side H<sub>2</sub> profiles for a system with pre-reforming followed by subsequent M-REF show lower overall H<sub>2</sub> partial pressures than the flow path consisting of ATR followed by pre-shift and M-WGS, or SMR followed by pre-shift and M-WGS. This is because when reaching the membrane separation step in the process, the overall reaction from CH<sub>4</sub> into H<sub>2</sub> and CO<sub>2</sub> has proceeded much further towards full conversion in the M-WGS cases. Given that the total feed pressures are virtually equal for both cases, thus the partial pressure of hydrogen is much lower resulting in a lower driving force for permeation.

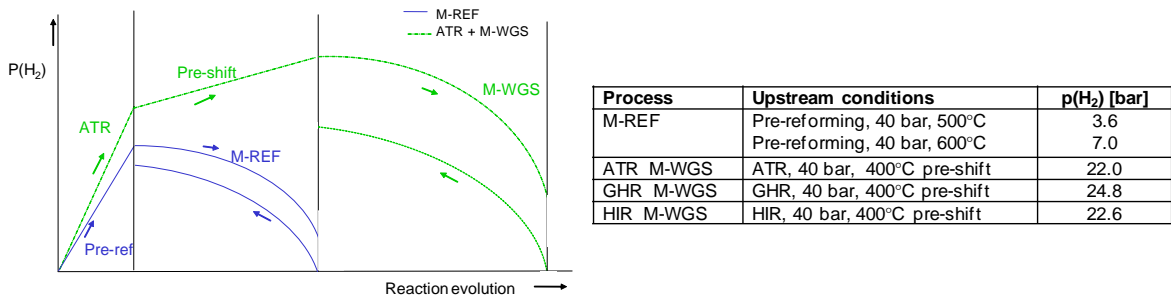


Figure 7 Schematic representation of  $\text{H}_2$  partial pressure  $P(\text{H}_2)$ . In blue solid lines from left to right for M-REF: pre-reforming of NG feed and membrane reforming. In green dashed lines from left to right for M-WGS: ATR of NG feed, pre-shift and membrane WGS. Sweep/permeate streams counter-current from right to left. The Table shows the partial pressure of hydrogen at the membrane reactor feed side inlet.

The limiting conditions for the membrane reactor are found at the feed side inlet/sweep outlet. It is seen in Figure 8 that in the case of M-WGS for each of the upstream reforming technologies (ATR, GHR, HIR) the hydrogen partial pressure is significantly higher than that in the case of M-REF. While for all M-WGS cases the sweep gas pressure can be chosen equal to that of the gas turbine, M-REF is hindered by low hydrogen partial pressures which makes that a low permeate pressure is required. Figure 8 (right) shows that at 22 bar sweep pressure, the hydrogen recovery (HR, ratio between hydrogen in the permeate and maximum amount of hydrogen that can be produced in the case of full conversion and permeation of all hydrogen) remains below 50%. To reach the required 95-98% recovery, a sweep pressure of 10 bar is necessary. This implies that retentate cooling, water-knock out and compression to 22 bar is required, which reduces efficiency and increases investment costs. For the M-REF to be cost competitive with M-WGS the membrane surface area needs to be significantly reduced. Furthermore, investments and electrical efficiency need to be improved by increasing the permeate pressure to 22 bar to be able to feed the hydrogen permeate to the gas turbine without the need for recompression. Figure 8 (left) shows that significant increase in the temperature could significantly reduce the required membrane surface area for M-REF, but temperatures will exceed the current upper limit of Pd-alloy membranes that is around 600°C.

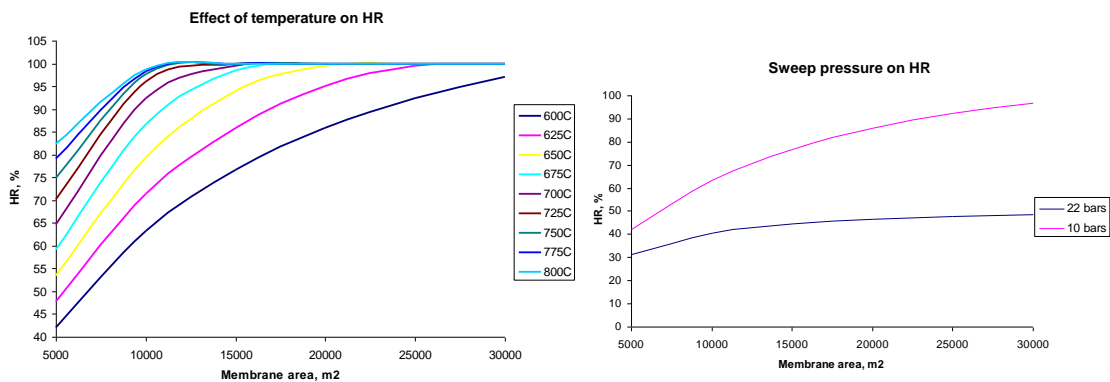


Figure 8 Effect of temperature and feed pressure on the hydrogen recovery (HR) for M-REF. (600°C, 40 bar feed, 22 bar permeate pressure)

Figure 9 shows the result of further investigations on the possibility of operating at 22 bar permeate pressure. It can be seen that only at 800°C the required hydrogen recovery of around 95-98% achieved. Increasing the feed pressure is less effective in increasing recovery, but could help in combination with increased temperatures.

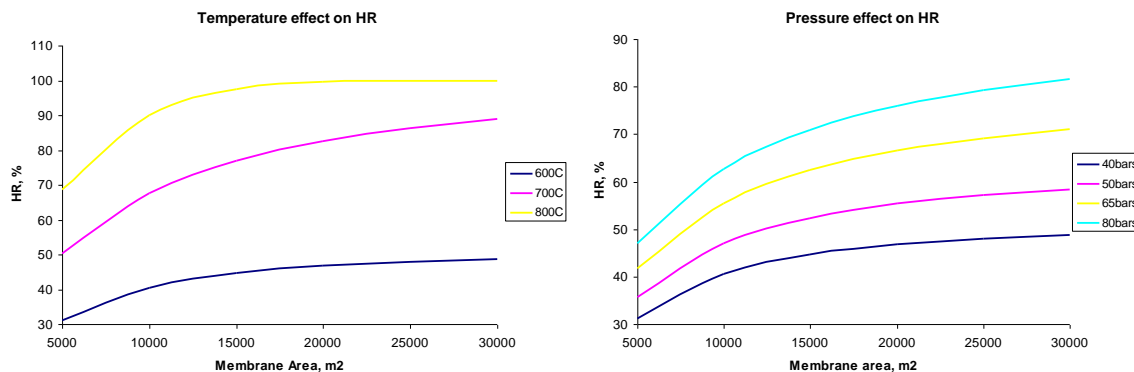


Figure 9 Hydrogen recovery (HR) at 22 bar permeate pressure for increased temperature (at 40 bar feed) and feed pressure (at 600°C).

## 5. Conclusions

A techno-economic evaluation indicates that hydrogen membrane reactors can be used for more cost and energy efficient capture of CO<sub>2</sub> at natural gas fired power plants. Compared to membrane reformers, membrane water gas show a slightly lower efficiency penalty, but show much higher membrane surface area and CO<sub>2</sub> capture costs. It has been shown that this is inherently due to the low hydrogen partial pressure in membrane reformers, and that only a significant increase in operating temperature, or a combination thereof with a higher operating pressure could overcome this. Therefore, for applications of CO<sub>2</sub> capture in natural gas fired power plants, membrane water-gas shift is preferred over membrane reforming. For other applications with a low pressure H<sub>2</sub> this could however be different. For the various options of upstream reforming in membrane water-gas shift, gas heated reforming is the preferred option being followed by autothermal reforming.

## 6. Acknowledgement

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