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Development of membrane reactor technology for power production with pre-combustion CO₂ capture

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Abstract

Hydrogen membrane reactors are an advanced technology for pre-combustion CO₂ capture at gas fired power stations. Developments in the field of membrane manufacturing, bench scale testing, module modeling and techno-economic evaluations are discussed. Semi-commercial modules with membranes up to 50 cm length are currently available. A bench scale multi-tube membrane reactor with a capacity up to 8 parallel tubes has been successfully operated for separation, membrane water-gas shift and membrane reforming experiments. A membrane module model has been developed that is a key element in the scale-up of membrane reactors. Techno-economic evaluation of membrane reactors indicates that for CO₂ capture at gas fired power plants membrane water-gas shift has a better potential than membrane reforming and than conventional pre-combustion CO₂ capturing using Selexol.

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1. Introduction

One possible route for pre-combustion CO₂ capture in gas fired power plants involves the conversion of natural gas into syngas, a mixture with carbon monoxide (CO) and hydrogen (H₂), through reforming with subsequent conversion of CO into CO₂ through the water-gas shift (WGS) reaction and capture of CO₂. The H₂ and CO₂ are separated; H₂ is used for power production and CO₂ is available for underground storage. An advanced technology with the potential of efficiency and cost improvements is the use of hydrogen selective membranes. These Pd-alloy membranes are able to separate H₂ from syngas at elevated temperature (250-600°C). It is also possible to combine the separation with reaction which gives additional opportunities for efficiency and cost efficiency improvements. This paper gives an overview of recent achievements in the development of membrane reactor technology, which have been achieved at ECN and in cooperation with project partners. Here reactor/module design, bench scale testing, modeling and techno-economic analysis are used in a combined approach.

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The working principle of membrane reactors is depicted in Figure 1. Two main types of hydrogen membrane reactors can be distinguished: membrane reformers (M-REF) and membrane water-gas shift reactors (M-WGS). In the M-REF (left) a mixture with natural gas and steam (coming from an upstream pre-reformer) is fed to the feed side chamber of the membrane reformer. Here the steam methane reforming (SMR) reaction is taking place parallel with selective removal of H_2 through the membrane. The selective removal of the product H_2 pulls the reaction to high conversions. The feed side product is a retentate mixture with a high concentration of CO_2 that (after clean-up and compression) is available for underground storage. The product H_2 is removed through the lower pressure permeate side of the membrane reformer. It is used in the gas turbine of the combined cycle in which the membrane reactor is integrated. A sweep gas is used to increase the driving force for permeation. The heat of reaction for the endothermic reforming reaction is supplied by heat from a separate combustion section. In M-WGS the natural gas feed has been converted first by means of reforming (e.g. autothermal reforming ATR and a pre-shift reactor). The feed side reaction is the water-gas shift (WGS) reaction, also with parallel removal of H_2 and the feed product being a CO_2 rich stream. The WGS reaction is slightly exothermic so a combustion section is not required.

In the case of a M-WGS reactor an alternative configuration is to move the catalyst from the feed side of the reactor to a separate upstream packed bed WGS reactor (hence changing the membrane *reactor* into a membrane *separator*) and use multiple stages of WGS reactors and separators in series instead.

Membrane reactor technology at ECN is primarily developed for CO_2 capture technology at natural gas fired power plants and industrial hydrogen production e.g. for ammonia manufacturing. Other potential applications are the use in IGCC, small scale reformers and hydrogen recovery in industry (with or without the combination with CO_2 capture and storage). This paper is restricted to the results relevant for natural fired power plants only.

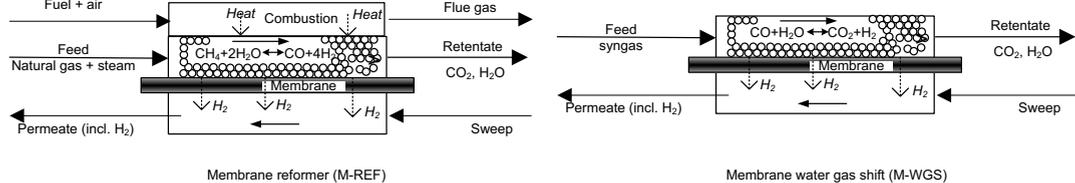


Figure 1: Working principle of hydrogen membrane reactors for CO_2 capture.

In the past years significant progress has been made on the development of hydrogen selective membranes. ECN has developed ceramic supported Pd membranes that are available with a length of 50 cm (standard) up to 90 cm. Membrane supports are manufactured from commercial alumina tubes by adding two additional alumina layers for improved surface smoothness. The Pd (alloy) membrane separation layer with a layer thickness of around $3 \mu m$ is then applied by electroless plating. ECN has available a patented sealing technology to form a gastight connection between the ceramic/metallic membrane tubes to the steel membrane reactor/modules. Commercialization has recently progressed by offering complete single tube or multitube membrane separator modules on a semi-commercial basis [1]. Similar 50 cm thin layer membranes are being developed by partner institutes [2, 3]. The Dalian Institute of Chemical Physics (DICP) from China manufactures Pd alloy membranes by electroless plating employing a proprietary method for support modification [4], which has been applied to ECN supports within the CACHET project. SINTEF from Norway manufactures PdAg foils by magnetron sputtering that are then transferred to a porous steel membrane support.

Special demands are made on catalysts in membrane reactors with respect to activity, stability and cost. Therefore commercial and in-house developed catalysts are being tested at membrane reactor and simulated membrane reactor conditions. During reforming the H_2 withdrawal makes that low H/C ratio are encountered. This, in combination with the relatively low temperature compared to conventional reforming could induce catalyst deactivation due to carbon formation. It has been shown that both Ni-based catalyst as well as precious metal catalyst are subject to deactivation under simulated membrane reformer conditions at $600^\circ C$. However, experiments showed that Ni based catalyst, preferred because of their low costs, are outperforming precious metal based catalyst and can effectively be improved by doping with additives to prevent carbon formation [5]. For M-WGS reactions

the activities are aimed at investigating activity of commercial high temperature shift Fe-Cr and novel base metal catalysts. A highly active catalyst will allow for low amount of catalyst per unit of membrane surface area which reduced the path length of the transport of H_2 to the membrane surface area and thus lowers the mass transfer resistance in the catalyst bed [6].

2. Reactor/module concept development and bench scale testing

In previous work [7], a systematic synthesis and selection of reactor concepts for a full scale power plant application has been performed. From this the preferred concept for reforming that was selected was the ‘box concept’ which is derived from an industrial tubular steam reformer where the reformer furnace contains a large number of reactor tubes, each with a membrane tube inside. Manifolding is done using headers with flanges. Heat is supplied from a furnace (‘box’) surrounding the membrane tubes. For M-WGS a similar concept could be used (omitting the heating since WGS is exothermic), but alternatives shell-and-tube concepts are under consideration.

This concept was translated into the design of a bench scale multitube process development unit (PDU) which can accommodate up to 8 membranes (Figure 2). Manifolding is done as with the anticipated full scale concept. The heat supply is not done by gas burners but is, for practical reasons, by an electrical furnace surrounding the tubes.

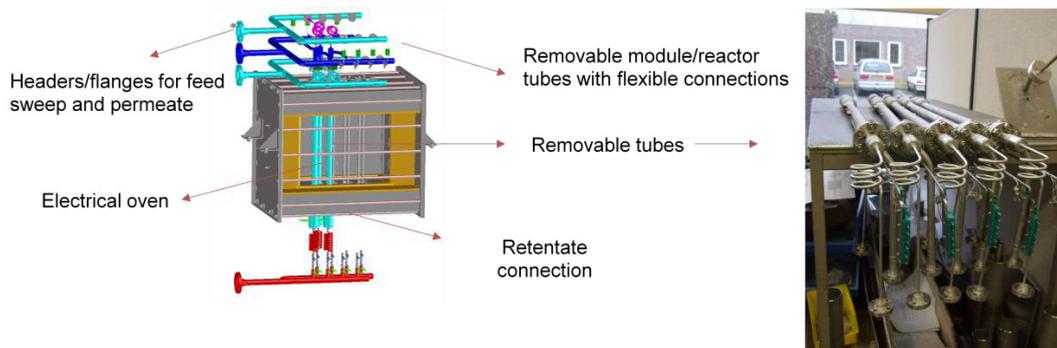


Figure 2: Process development Unit (PDU) multi-tube module/reactor

Membranes are fixed in the module by means of an extension tube with a fixing disk that is clamped in the top, see Figure 3. Mounting the membranes in the tube proved not to be problematic for the membranes up to 50 cm, but likely for membrane with significantly higher lengths (larger than 1 meter), special measures must be taken to achieve proper alignment of membranes in the tube. For both WGS and reforming (pre-)commercial shift of reforming catalyst was successfully placed into the annulus between the membrane reactor wall. To limit the mass transfer resistance the thickness of the annulus has been chosen to be only 6.4 mm which means that catalyst is required with a small particle size: <1 mm average.

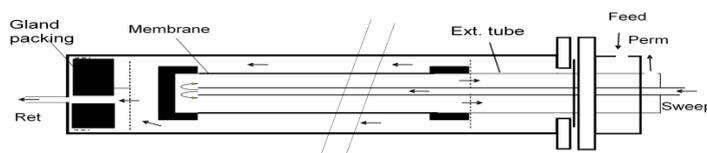


Figure 3: Membrane reactor/module tube configuration.

A gland packing was used at the bottom of the reactor tubes to allow for easy exchange of membrane tubes. The design chosen gives a membrane reactor that in operation fulfills all the necessary demands. During operation it was shown that a good flow distribution was achieved between the individual reactor/module tubes. The difference in gas composition of the main components (H_2 , CO_2 , CH_4) was less than 8% relative between the parallel tubes. This

was also the case in the experiments with catalyst. This was achieved by placing an orifice in a flange in each of the feed and sweep headers. The temperature profile was identical between all parallel tubes, a maximum top-to-middle difference of 15°C in reactor tube skin temperature was found during experiments at 550 °C.

With the PDU multiple experiments have been conducted that demonstrate the concept of membrane reactors on a multi-tube scale, and that provide data for reactor and process development. The membranes used in all tests were pure Pd membranes prepared by DICP according to their proprietary method [4] on ceramic supports made by ECN. These experiments include ([8, 9]):

- Pure hydrogen and pure nitrogen permeation experiments, dual gas (H₂/N₂ mixture) experiments at 400/550°C
- Synthesis gas mixtures separation experiments at 400 °C
- Integrated water-gas shift reaction experiments at 400 °C
- Membrane reformer experiments at 550 °C.

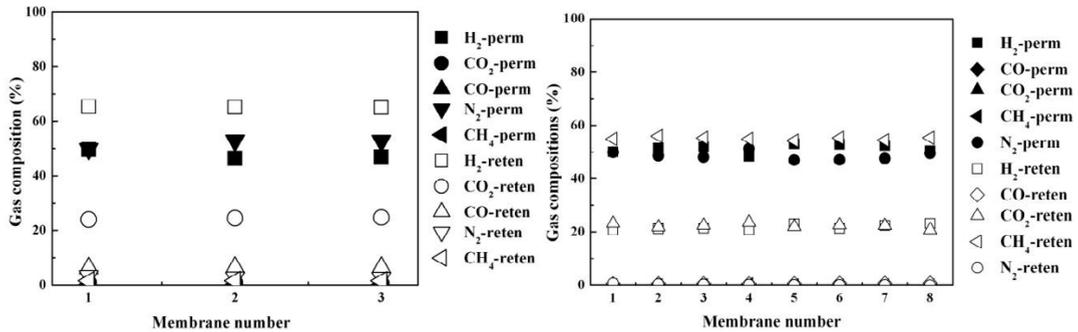


Figure 4: Comparison of individual gas product compositions of parallel membrane tubes for a separation test at 400 °C and a membrane reforming test at 550 °C. Sweep gas N₂ used in both tests

A good gas distribution between the parallel tubes in the setup is essential for obtaining an even performance. Figure 4 shows the gas distribution between the individual reactor/module tubes during a separation test using a syngas feed and a M-REF test (while using catalyst). The product composition of the retentate and permeate are very much alike between the tubes indicating an even flow distribution and very similar performance of the membrane tubes in both tests. The temperature distribution was similar among the tubes within a difference of 3 °C.

The left hand part of Figure 5 gives the impact of feed pressure during M-WGS feeding a synthesis gas mixture. It can be seen that hydrogen recovery increases significantly with feed pressure due to the increased partial pressure difference between feed and permeate. In conventional shift reactors the CO conversion is not affected by the pressure. In M-WGS however, the increasing H₂ withdrawal with increasing feed pressure increases CO conversion.

The right hand side of figure 5 gives the feed pressure effect in a M-REF test. The feed is a synthetic gas mixture with the composition of a natural gas/steam mixture after passing through a pre-reformer (equilibrium composition at 550°C). The equilibrium of the SMR reaction ($\text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow 4\text{H}_2 + \text{CO}_2$) dictates reduced conversions with increasing pressures. However, it is observed that increasing feed pressure the conversion is increased, which is a direct result of the increase of hydrogen recovery with pressure, shifting the reaction to higher conversion. The maximum CH₄ conversion and H₂ recovery was achieved as 73% and 92% at a feed/permeate pressure of 35/5 bara. For application in an NGCC, however, the hydrogen fuel should be available at a pressure of approx. 22-25 bar for entry into the combustion chamber of the gas turbine. When increasing the permeate pressure from 5 bara to 25 bara, the CH₄ conversion decreased to 8.6%. Therefore these high pressures cannot be used in power plant applications which makes that lower pressures in combination with compression to the desired gas turbine inlet pressure of 22 bar or higher is required, which causes a significant energy penalty. Even then, the low driving force makes that high membrane surface areas are required as is later shown in the economic evaluation. The apparent permeance found during these experiments was typically $4.9 \cdot 10^{-7} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$ for the M-WGS case at a feed/permeate pressure of 35/15 bar and for the M-REF experiments using thicker membranes it was typically $3.7 \cdot 10^{-7} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$ at a 35/5 bara for the M-REF experiments.

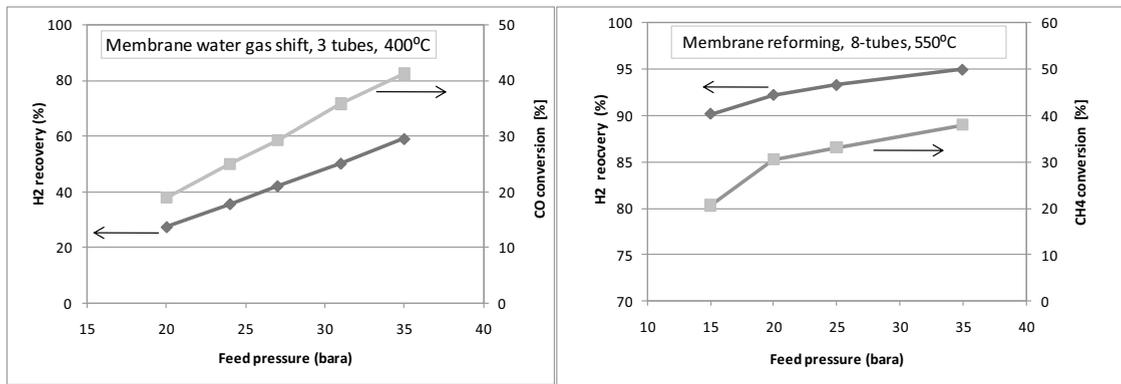


Figure 5: Results of a M experiment, feeding a syngas mixture at WGS conditions (left) and of a integrated M-REF test (right). Multiple parallel membrane tubes of 44 cm effective length, 1.4 cm OD, permeate at 15 bar for M-WGS, 5 bar for M-REF.

3. Reactor/module modeling and scale-up

For development of membrane reactor technology it is crucial to integrate the various disciplines in order to make the right choices in membrane, reactor/module and process development. A special role here is for the modeling of membrane reactors and separator modules. Modeling forms the key in understanding the phenomena that are important in membrane reactor/module technology and the translation thereof into full scale application for CO₂ capture. Figure 6 illustrates the central position of membrane reactor/separator modeling. On one hand it serves as a tool to translate experiments into the characterization of membranes, while on the other hand it is a tool to translate membrane and experimental results into a full scale design. To obtain the inherent properties of hydrogen selective membranes it is necessary to translate the ‘apparent overall’ permeance for effects of depletion of hydrogen at the feed side and enrichment of hydrogen at the permeate side, and to account for effects of mass transfer. This will give the permeance of hydrogen as it is in a mixture relevant for the application. The modeling can also be used for evaluation of module/reactor design on mass transfer, and will allow for reliable scale up based on measured membrane performance and obtaining the required full scale membrane surface area.

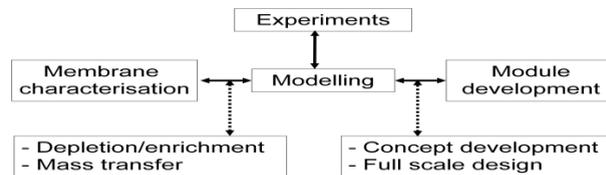


Figure 6 : Interrelation between experimental, modelling and design activities

An important underlying issue in the development and design of membrane reactors is that the hydrodynamic conditions change with scale-up. At bench scale conditions short membrane tubes are used (up to 0.5 m) given that currently membrane manufacturing technology is limited to these values. To obtain the most accurate measurement hydrogen recoveries and conversions of around 50% should be used - although rarely acknowledged in literature. The scale up of membrane reactors towards the application in full size gas fired power plants will imply both increasing the number of parallel tubes as well as increasing the length of the membranes. This makes that gas flow are much higher. This will have an impact on the mass transfer, but possibly also on the flow regime, the reactor sizing and design, and perhaps even the preferred reactor concept.

To assess the impact of this change in feed flow and other operating conditions a 2-dimensional (2-D) axisymmetric membrane separator model has been developed [10]. The model is based on solving the incompressible

Navier Stokes equations and accounts for mass transport by convection and Fickian diffusion on both the feed and sweep side as well for selective permeance of H₂ through the membrane. An important feature is that it accounts for the distortion of the flow pattern by the radial transport of hydrogen towards the membrane. In Figure 7 this approach is illustrated for a simulation of a typical counter-current hydrogen separation experiment in the PDU. In the middle of the grid (r=7) the membrane is situated. Clearly in the left hand figure the enrichment of at the sweep side and the depletion on H₂ at the permeate side can be observed. Also it can be seen that the axial concentration of H₂ is not evenly distributed so a mass transfer resistance is present. The velocity profile on the right hand side is disturbed significantly by the transport of H₂ through the membrane.

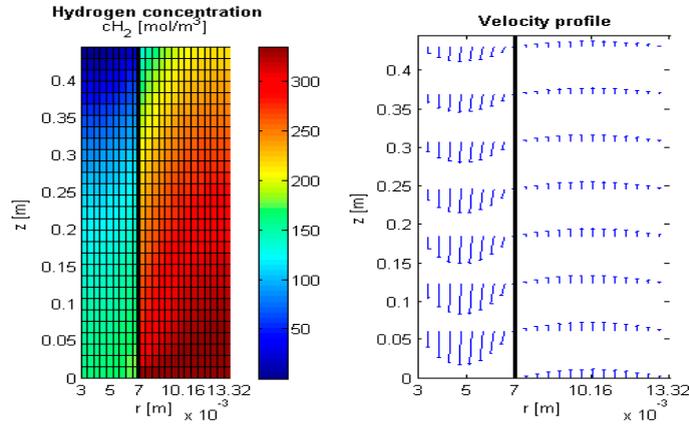


Figure 7: Typical result of 2-D separator modelling. Hydrogen concentration (left) and velocity profile (right) in axi-symmetrical representation of the PDU module. Sweep channel (r=3-7 mm), membrane support 3-5 mm, membrane separation layer (r=7 mm), feed side channel (r=7-13 mm).

The 2-D model can be used to separate the effect of mass transfer from the H₂ permeance and use it for prediction studies. Figure 8 shows the results of a H₂/N₂ separation experiment using 3 membrane tubes at 400 °C. Using the results of a pressure variation experiment, in the 2-D model the permeance has been used for fitting of the membrane permeance. The n-value (power in pressure dependency in the permeance equation) had been previously obtained from a pure H₂ experiment (not shown). Fixing this value for the permeance the model has been run to predict the effect of feed flow on H₂ recovery, including the effect of decreased mass transfer resistance with increasing feed flow rate. A good match between model prediction and the experimental data is obtained. In a similar fashion, in future work this approach can be used for prediction of the performance of large scale applications from bench scale experiments.

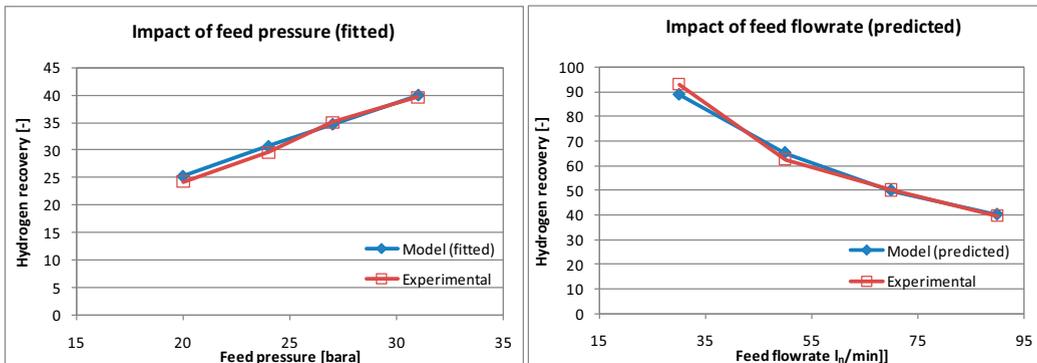


Figure 8: Approach for use of the model illustrated with experimental and modelling results. Left: permeance is fitted to experimental. Right: the fitted permeance is used for successful prediction of the effect of feed flow rate.

4. Techno-economic assessment studies

System assessment studies serve two main goals. Firstly they are used for developing process scheme in which CO₂ capture technologies are integrated. This provides the working conditions and the performance targets for the CO₂ capture technologies which serve as input for the experimental programs. Secondly they provide the thermodynamic and economic performance of the CO₂ capture technologies when integrated in a power plant. This information is used in evaluation of the potential of the various capture technologies and is used for setting priorities in the CO₂ capture program. For this a full power plant model in Aspen Plus as well as an economic evaluation has been performed [11]. The method and starting points applied are tailored for easy comparison of a variety of technologies which make that values obtained differ slightly from those obtained by partners in [3], end-conclusions however do not differ. The main results are illustrated in Figure 9.

One of the main issues has been the comparative assessment of membrane reforming (M-REF) with membrane water-gas shift (M-WGS). For the latter, two different upstream natural gas conversion technologies have been assessed: autothermal reforming (ATR) and gas heated reforming (GHR). Steam methane reforming (SMR) had been considered in the past but has been discarded on the basis of too low CH₄ conversions under required conditions for CO₂ capture. For reference a base case natural gas combined cycle (NGCC) and a pre-combustion scheme with ATR and a Selexol CO₂ capture unit have been included. An economic analysis of the ‘box’ concept suggested that a more compact design would be preferred for economic reasons; therefore the membrane reactor costs have been assessed based on shell and tube arrangements. Both membrane reactor technologies outperform the pre-combustion Selexol case in terms of specific CO₂ avoidance costs, but require a higher specific investment. For M-WGS, of the different upstream reforming options the gas heated reforming option performs best both in thermodynamic as in economic terms.

Comparing M-WGS to M-REF, it is seen that the increased complexity of the M-REF option is not reflected in a significant higher efficiency and that the costs per ton of CO₂ avoided as calculated are even worse for the M-REF case. It is concluded that the complexity and uncertainty encountered in M-WGS reactors are much lower, and the efficiency is not much different from that of M-REF reactors and considerably less membrane surface area is required. Therefore, for power production with CO₂ capture the preferred concept is that of M-WGS reactors. One of the main reasons is the combination of a demand for high conversion combined with a H₂ being needed at high pressure in the gas turbine of the power plant. For other applications (industrial capture or industrial H₂ production) or when using high alloys allowing operation at higher temperatures, M-REF still is an option to be considered.

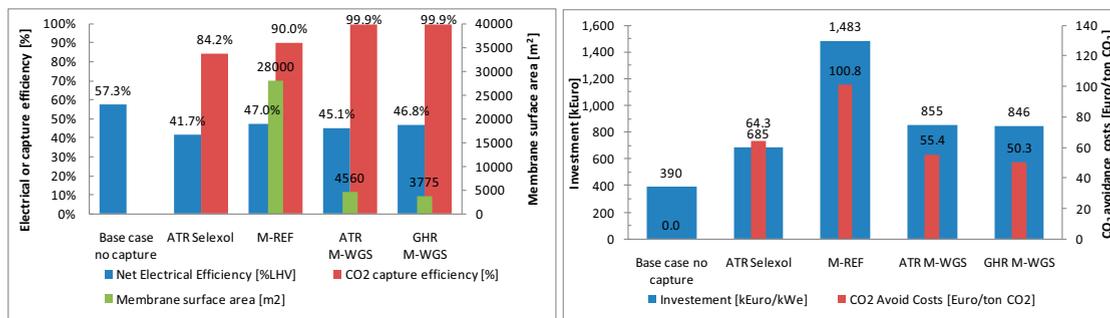


Figure 9: Summary of results of system assessment studies thermodynamic and economic performance for several M-WGS concepts compared to M-REF integrated in a gas fired power plants with CO₂ capture.

5. Conclusions

An overview of results in various activities in the development of membrane reactor technology for pre-combustion CO₂ capture is provided. A multi-tube bench scale reactor has been successfully operated for tests of membrane water-gas shift and membrane reforming. The design fulfilled its demands but future generations should focus on a more compact design. For interpretation of the experiments a 2-dimensional module model has been developed which is used for translating bench scale data to full scale conditions. The results of techno-economic

analysis indicate that membrane water gas shift has better prospects for CO₂ capture than membrane reforming. The most promising is the combination of MWGS with Gas heated Reforming (GHR) and efficiencies are higher and CO₂ avoidance costs are lower than conventional pre-combustion CO₂ capture using Selexol.

6. Acknowledgements

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7. References

- [1] ECN. Hydrogen separator modules, www.hysep.com. 2009.
- [2] Eide LI. Carbon dioxide capture for storage in deep geological formations - Results from the CO₂ capture project. Volume 3: Advances in CO₂ capture and storage technology results (2004-2009). CPL Press; 2009.
- [3] Beavis R. The FP6 CACHET Project - Final Results. 10th International Conference on Greenhouse Gas Control Technologies, GHGT10; 19-23 Sept 2010.
- [4] Hou S, Jiang K, Li W, Xu H, Yuan L. A metal palladium composite or alloy palladium composite membrane and their preparation methods. WO2005/065806 A1.
- [5] Pieterse JAZ, Boon J, Delft YCv, Dijkstra JW, Brink RWvd. On the potential of nickel catalysts for steam reforming in membrane reactors. Accepted for publication in *Catalysis Today* 2010.
- [6] Bi Y, Xu H, Li W, Goldbach A. Water-gas shift reaction in a Pd membrane reactor over Pt/Ce_{0.6}Zr_{0.4}O₂ catalyst. *International Journal of Hydrogen Energy* 2009 Apr; 34 (7):2965-71.
- [7] Jansen D, Dijkstra JW, van den Brink RW, Peters TA, Stange M, Bredesen R, et al. Hydrogen membrane reactors for CO₂ capture. *Energy Procedia* 2009 Feb;1(1):253-60.
- [8] Li H, Dijkstra JW, Pieterse JAZ, Boon J, Brink RWvd, Jansen D. Towards full-scale demonstration of hydrogen-selective membranes for CO₂ capture: Inhibition effect of WGS-components on the H₂ permeation through three Pd membranes of 44 cm long. *J Membr Sci* 2010; In Press.
- [9] Li H, Pieterse JAZ, Dijkstra JW, Munck Sd. Testing membrane reactors at scale: Separation of WGS-mixtures and WGS-experiments with three Pd membrane tubes of 50 cm long. 10th International Conference on Greenhouse Gas Control Technologies, GHGT10; 19-23 Sept 2010.
- [10] Boon J, Li H, Dijkstra JW, Pieterse JAZ. -Dimensional Membrane Separator Modelling: Mass Transfer by Convection and Diffusion. 10th International Conference on Greenhouse Gas Control Technologies, GHGT10; 19-23 Sept 2010.
- [11] Dijkstra JW, Raju G, Peppink G, Jansen D. Techno-economic evaluation of membrane technology for pre-combustion decarbonisation: water-gas shift versus reforming. 10th International Conference on Greenhouse Gas Control Technologies, GHGT10; 19-23 Sept 2010.