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Hydrogen membrane reactors for CO_2 capture

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Abstract

In the European FP6 research project CACHET palladium-based hydrogen membrane reactors for pre-combustion CO_2 capture from natural gas combined cycles are being developed. In the project both the electroless plating method used by DICP and the SINTEF two-stage membrane preparation method based on magnetron sputtering have been successfully up-scaled to produce membranes with a length of 50 cm. The membranes have been tested extensively with hydrogen/nitrogen gas mixtures and with simulated feed gas for reforming and water gas shift conditions. The membrane performances in terms of flux, stability and separation efficiency were sufficient to start at ECN the design and the construction of a membrane reactor test facility, the Process Development Unit (PDU), in which membrane reactor tests under relevant process conditions will be performed. The process synthesis and techno-economic analysis indicate overall efficiencies between 46.7 and 47.4 % LHV for natural gas combined cycle power plant with hydrogen membrane reactors for CO_2 capture. The cost of electricity is estimated to be 73 and 92 €/MWh. These figures are based on 2008 cost data and the membrane performance after two years of development.
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Keywords: Membrane reactors, CO₂ Capture, Natural gas combine cycle, Costs

1. Introduction

In the European FP6 research project CACHET [1] (Carbon Dioxide Capture and Hydrogen Production from Gaseous Fuels), hydrogen membrane reactors for pre-combustion CO_2 capture are collaboratively being developed by the Dalian Institute of Chemical Physics (DICP) from China, SINTEF from Norway, National Technical University of Athens (Greece), Process Design Center (PDC) from Germany and the Energy research Centre of the Netherlands (ECN).

Hydrogen membrane rectors are seen as an attractive technology for pre-combustion CO_2 capture in gas fired power stations because they combine [2], all in one reactor, the efficient conversion of natural gas into H_2 for power production with capture of the remaining CO_2 (see Fig. 1). The membrane reactor is integrated in a conventional power cycle, where the hydrogen is used for power generation, while the remaining gas stream contains mainly CO_2 and some non-recovered hydrogen and steam at relatively high pressure. Subsequent condensation of the steam leaves concentrated CO_2 at high pressure, reducing the compression energy for transport and storage.

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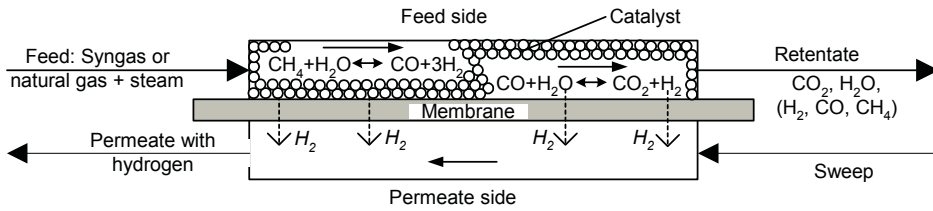*E-mail address*:jansen@ecn.nl.

Figure 1: Operating principle of a membrane reactor

The overall goal of the three year CACHET project is to develop innovative technologies, which will substantially reduce CO_2 capture cost in power generation from fossil fuels. CACHET targets a reduction to 20 to 30 €/tCO_2 with 90% capture rate (reference year 2005) and CO_2 delivered at pipeline pressure for storage. A summary of the status after the 2nd project years has been presented recently [3].The more specific objective of the membrane work package in CACHET is to develop and evaluate the potential of H_2 membrane reactors using Pd or Pd/Ag membrane reactor technology for the pre-combustion capture of CO_2. With regard to the development of hydrogen membrane reactors, the article gives an overview of the results obtained during the first two years of the CACHET project.

2. Process synthesis and techno –economic analysis

The membrane- and membrane reactor developments have been guided and supported by process synthesis and techno-economic analysis. Two process schemes for H_2 membrane reactor integrated in natural gas combined cycles have been evaluated: (a) an Integrated membrane Water Gas Shift Combined Cycle (ImWGSCC) and (b) an integrated membrane Reformer Combined Cycle (ImRCC). The basic block schemes of these two concepts are given in Fig. 2.

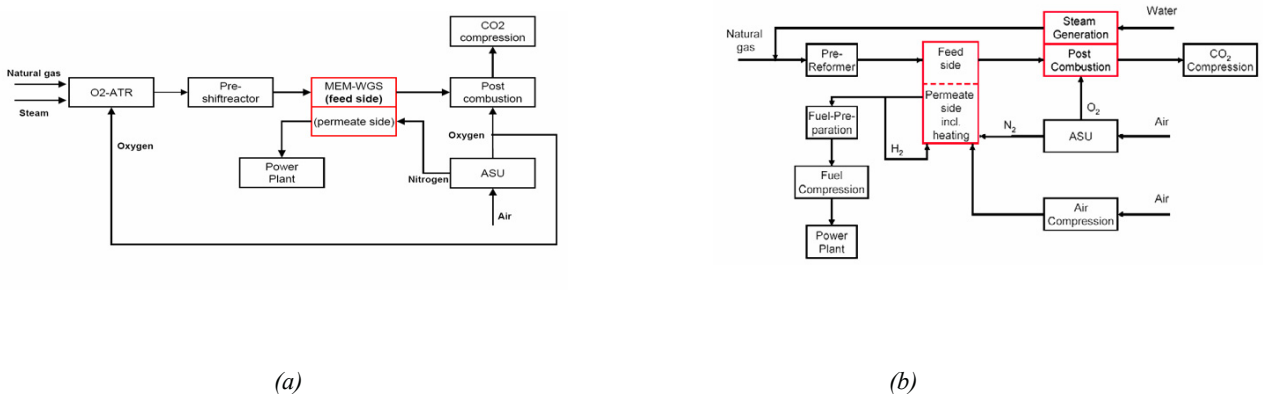*(a)*   *(b)*

Figure 2   Process block schemes for (a) an Integrated membrane Water Gas Shift Combined Cycle (ImWGSCC) and for (b) an Integrated membrane Reformer Combined Cycle (ImRCC)

The ImWGSCC converts the natural gas in the presence of "pure" oxygen in the partial oxidation/combustion reaction (reforming reaction: oxygen-blown Auto thermal Reforming (O2-ATR)). The oxygen is produced by an air separation unit (ASU). A major fraction of the off-gas removed from the ATR consists of carbon monoxide. To completely convert the CO into carbon dioxide the membrane supported water gas shift reactor (MWGS) is applied and is operating at 400 °C and 4.4 MPa. The nitrogen from the ASU is used as sweep gas ensuring a permeate side pressure of 2.5 MPa.

In the ImRCC case, the membrane reactor is operating at 550 to 600 °C and 4.7 MPa. The steam reforming and water gas shift reaction are carried in one reactor. The permeate side pressure is selected to be 1.0 MPa maximizing the driving force for the hydrogen separation and thus reducing the membrane area.

At the start of the project, Preliminary Performance Criteria (PPC's) for both the membrane reactors and membrane tubes have been established. These PPC's were derived from capture cost studies performed by the IEA-GHG programme for natural gas-fuelled combined cycles, and from assessment studies on integrated membrane reactor power generation concepts available in the open literature [4]. The standardized IEA "cash flow procedure" to assess and compare different CO_2 capture technologies (pre- and post-combustion) in power plants has been adopted to derive the PPC's. For this the IEA-procedure is applied

backwards, which resulted in the PPC's shown in Table 1. The values served as early targets for technology development within the project.

Tabel 1   PPC's for H_2 membrane tubes to reach 25 € per ton of CO_2 avoided at a fuel price of 5€/GJand power plant efficiency with CO_2 capture of 50% LHV.

	ImWGSCC	ImRCC
Operating temperature (^{o}C)	400	600
Average hydrogen flux (kW/m^2)	150	100
Allowable membrane cost (€/m^2)	1100 -1500	1040 – 1500
Target permeance (mol·m^{-2}·s^{-1}·Pa^{-1})	$1.3 – 1.6*10^{-6}$	$3.0 – 4.6*10^{-6}$
Lifetime membranes and catalyst (year)	2 to 3	2 to 3

Based on the extensive membrane reactor modelling work and techno-economic analysis both options have been evaluated with respect to the electricity production cost and cost of CO_2 avoided. A summary of the techno-economic analysis (based on membrane performance data after two years of membrane development) is shown in Table 2. While the membranes developed at SINTEF and DICP meet those performance targets for ImWGSCC and ImRCC, if pure H_2 is fed, the effective H_2 permeances are considerably lower, if WGS or steam reforming mixtures are fed. For the calculation of the membrane area an "apparent" permeance of $8.0*10^{-7}$ mol·m^{-2}·s^{-1}·Pa^{-1} was used in the ImWGSCC case. In the ImRCC case, the membrane area is calculated on basis of the target permeance given in table 1 and a correction for the reduction of the flux for feeding a steam reforming mixture. This is done since no representative value was available yet for the "apparent" permeance. For the investment cost estimation membrane cost of 1500 €/m^2 were used. The cost of produced power includes both the operating cost and capital cost (reference year 2008) depreciation over 25 years and the fuel prices was set at 5€/GJ.

Tabel 2   Economic comparison of the two membrane cases

	ImWGSCC	ImRCC
Fixed capital (million €)	437	566
Efficiency (%)	47.4	46.7
Membrane area (m^2)	6000	10500
Cost of power (€/MWh)	73	92
Cost of CO_2 capture (€/ton CO_2)	58	101
Cost of CO_2 avoidance (€/ton CO_2)	70	124

For the ImWGSCC case the overall LHV efficiency is 47.4% whereas for the ImRCC case the overall LHV efficiency is 46.7%. The higher cost and the lower efficiency of the ImRCC are caused by the combination of the moderate operating temperature, 550 - 600 ^{o}C, and the elevated operating pressure, 4.7 MPa, of the membrane reformer. As a result, the equilibrium composition of the syngas mixture at the inlet of the membrane reformer reactor is low in hydrogen. Therefore, the driving force for separation, given by the difference of the partial pressure of hydrogen on the feed and permeate side of the membrane, is also low. This obviously leads to a very large membrane area and thus, very high capital costs. In an attempt to reduce the membrane area, and thus the cost of CO_2 capture, the overall pressure at the permeate side has been lowered to 1.0 MPa. This lower cost of capture is unfortunately at the expense of a lower overall efficiency as additional compression of the fuel gas i.e. hydrogen is needed. For the ImWGSCC case, the driving force for hydrogen separation is higher. Therefore, the total membrane area required is lower; moreover the permeate side can be operated on the gas turbine pressure level. Consequently no fuel gas compression is needed. Meanwhile, more membrane performance data under relevant reforming conditions have been obtained indicating that the "apparent' permeance for the ImRCC case could be higher as assumed. This higher permeance will have positive effects on the economics of the ImRCC case. Besides, several additional options for improvement of the ImRCC case have been identified and these will be assessed in the last year of CACHET.

3. Membrane development and fabrication

In the first two years of CACHET, both SINTEF and DICP have successfully scaled-up their membrane preparation methods. SINTEF produces 50 cm Pd-23w%Ag membranes prepared by a two-step method in which first a thin defect-free Pd-alloy film is prepared by sputtering deposition onto a 'perfect surface' of a silicon wafer. In a second step the membrane is removed from the wafer and transferred to a porous stainless steel support, see Fig. 3). This allows the preparation of very thin (approximately 2 μm) defect free high-flux membranes supported on macro-porous substrates, which can be operated at elevated pressures and temperatures up to 400 ^{o}C [5,8]. SINTEF focuses on application of their membranes in the water gas shift membrane reactor.
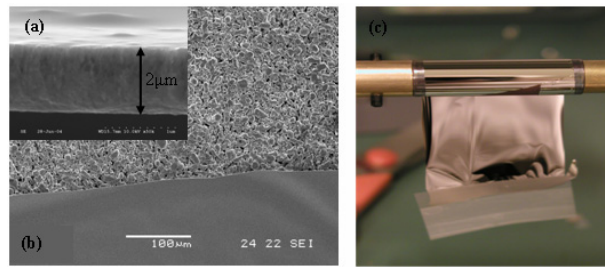
Figure 3   (a) Cross-section of the unsupported Pd-23w%Ag film; (b) Top-view of the stainless steel support showing the interface with the Pd-23w%Ag film; (c) Tubular supported membrane.
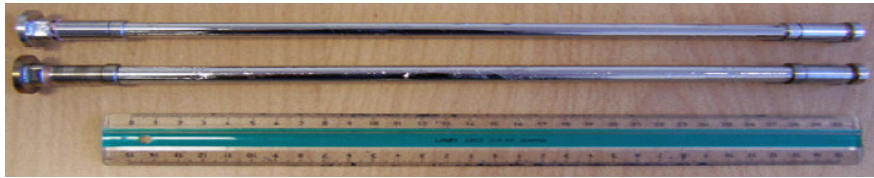

Figure 4   2 µm thick Pd-23w%Ag membranes on porous stainless steel support produced by SINTEF

DICP produces 50 cm long pure Pd membranes (Fig. 5) on a ceramic support made by ECN and capped with new high temperature/high pressure sealing (designed for 700 °C and 3.9 PMa), also provided by ECN. Prior to deposition of the Pd layer (2-3 µm) by electroless plating, the pores of the support tubes were pre-filled with an inorganic gel to obtain a smooth surface and prevent Pd from entering into the pore structures [6]. These were re-opened after completion of the Pd deposition by decomposing the gel at 500 °C in H_2, leaving a micro-porous ceramic residue. The DICP membranes can be applied in both water gas shift and steam reforming membrane reactors.
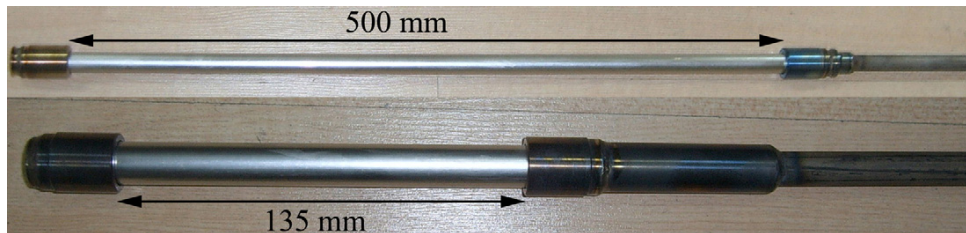

Figure 5   Pd membranes from DICP with ECN's high pressure, high temperature sealings

4. Membrane testing

Permeance

Both types of membranes have been tested extensively with hydrogen/nitrogen gas mixtures and with simulated feed gases for water gas shift and reforming [6]. Pure H_2 permeance of DICP membranes at 500 °C is in the range of $7.2*10^{-6}$ to $9.7*10^{-6}$ mol·m^{-2}·s^{-1}·Pa^{-1} at 100 kPa pressure difference. The pressure dependence of the single gas H_2 fluxes deviates from Sieverts' law with typical pressure exponents n around 0.64 [7]. Pure H_2 permeance of SINTEF membranes up to $1.4*10^{-5}$ mol·m^{-2}·s^{-1}·Pa^{-1} at 400 °C have been obtained. Permeances in gas mixtures representative for the CACHET application are lower than those in pure H_2 due to the presence of mass transfer and surface effects on the hydrogen flux while measuring in gas mixtures [8]. Measurements by SINTEF in a typical water gas shift gas mixture showed H_2 permeances up to $8*10^{-7}$ mol·m^{-2}·s^{-1}·Pa^{-1} at 15% H_2 recovery. DICP measurements under reforming conditions at 600 °C showed permeances of $1.4*10^{-6}$ mol·m^{-2}·s^{-1}·Pa^{-1} with 16% H_2 being recovered on the permeate side. To conclude, the permeance of the membranes produced by DICP and SINTEF are within the range required.

Membrane selectivity

There is no absolute selectivity target for the membranes set within CACHET. However, to satisfy the target of capturing 90% of the CO_2, an (H_2/N_2) permselectivity in the order of 400 is needed [9]. Long-term stability testing at a feed pressure of 10 bars of the SINTEF membranes showed after 250 days process time H_2/N_2 selectivities of approximately 1000. In separation experiments at temperature up to 500 °C DICP membrane tubes with ECN sealings showed H_2/N_2 selectivities of approximately 2500. To conclude, both types of membranes have sufficient selectivity for capturing 90% of the CO_2.

Membrane stability

The long-term stability of the SINTEF Pd-23%Ag/stainless steel composite membranes has been examined in H_2/N_2 mixtures as a function of both temperature and feed pressure. During continuous operation, the membrane shows a good stability at 400°C while the N_2 leakage increases very slowly at a temperature of 450°C (P_{feed} = 1.0 Mpa) [9]. After 100 days of operation (P_{feed} = 5-20 bars, T = 350-450°C), the N_2 permeance equals $7.0 \cdot 10^{-9}$ mol·m^{-2}·s^{-1}·Pa^{-1}, which indicates that the H_2/N_2 permselectivity still lies around 500, based on a H_2 permeance equal to $3.0 \cdot 10^{-6}$ mol·m^{-2}·s^{-1}·Pa^{-1}. Despite the generation of small pinholes, a membrane life-time of several (2-3) years (T ≤ 425°C) is estimated for the experimental conditions employed based on long-term stability tests over 100 days. To investigate the membrane stability in WGS conditions, the behaviour over a period of 500 hours operation was followed (Fig. 6). An initial fairly constant hydrogen permeance of $1.3 * 10^{-6}$ mol·m^{-2}·s^{-1}·Pa^{-1} in equimolar feed of H_2 and N_2, was reduced to $8.1 * 10^{-7}$ mol·m^{-2}·s^{-1}·Pa^{-1} on changing the feed to WGS conditions: 57.5% H_2, 18.7% CO_2, 3.8% CO, 1.2% CH_4 and 18.7% steam [8].
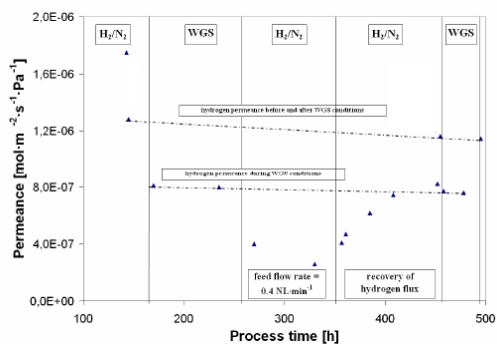

Figure 6 Long-term stability of a SINTEF membrane
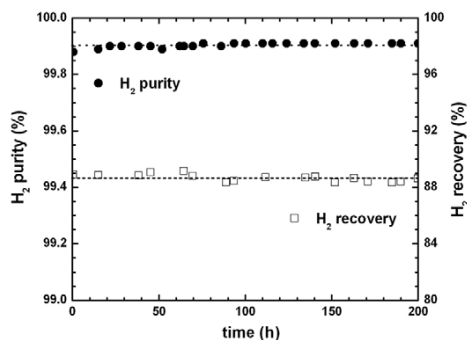T=400°C, P = 2.6 MPa [8].

Figure 7 H_2 recovery and purity during 200 hour reformate separation experiment with a DICP membrane [7].

The stability of the DICP membranes during separation of various reformate mixtures was studied using short membranes [6]. Figure 7 shows the performance of an 8 cm long Pd membrane during a 200 h test at 400 °C and 1.1 MPa feed pressure in an un-shifted reformate (ca. 58.9% H_2, 22.6% H_2O, 5.9% CO_2, 11.6% CO, balance: N_2, CH_4). H_2 recovery and purity remained practically constant at 88.7% and 99.9%, respectively, throughout the test. Stable H_2 recovery (90%) and H_2 purity (99.95%) were also observed during a 500 h separation test under similar conditions with a 10 cm long Pd membrane using a dry WGS-shifted reformate. At ECN Pd membranes from DICP have successfully undergone continuous operation at 450 °C during 14 days, temperature cycles in N_2 atmosphere and temperature cycles in H_2 atmosphere (to 150 °C with a ramp rate of 1 °C/min). To enhance the long-term stability of the DICP membrane at operation temperatures of 600 °C thicker membranes are probably needed because the degradation could go faster at this temperature in the reformate mixtures. Therefore DICP now develops and tests thicker Pd membranes. Based on the stability tests performed so far it is concluded that membranes, sufficiently stable to be used for tests in a bench scale reactor, can be fabricated by SINTEF and DICP. However, membrane stability is an issue that needs to be explored further as data on the long-term stability of the membranes under realistic conditions is still limited.

5. Design of the bench scale membrane reactors

The design of the bench scale membrane reactor is based on a full-scale membrane reactor. Both applications correspond with several thousands of square meters of membrane surface area, which implies that multiple reactors must be used. The most important concepts found in literature for membrane reformers are plate type membrane reactors from Tokyo Gas/MHI [10] and a fixed bed concept with membrane and heating tubes from Shell [11]. For membrane water gas shift reactors the most important concepts are both shell-and-tube based concepts published by ECN [12] and BP [13]. On basis this concept inventory and an initial concept definition, a long list of design concepts has been made using a systematic design methodology. Three promising concepts for the reformer reactor have been selected for a final assessment.

These concepts are:
- Catalyst in shell concept   Shell and tube based concept with catalyst in the shell (Fig. 8a)
- Catalyst in annulus concept   Shell and tube based concept with catalyst in an annular space around the membrane (Fig. 8b)
- Box concept   Conventional steam methane reformer based concept with membrane in reformer tubes, and manifolding with headers and pigtails (Fig. 9).

For evaluation of these three concepts, a multi-criteria scoring method has been used, in which scoring was done by a multi disciplinary panel. The box concept was the best scoring concept in the analysis. This concept is derived from the design of a conventional steam reformer adapted for addition of membranes in the reformer tubes. In this membrane reactor concept a rectangular shaped atmospheric box is used. The catalyst is placed in an annular space around the membrane tubes. Conventional burners are placed in the box. Sweep gas is introduced through an insert tube. Feed is introduced at the top of the reactor, while retentate is removed at the bottom of the reactor.

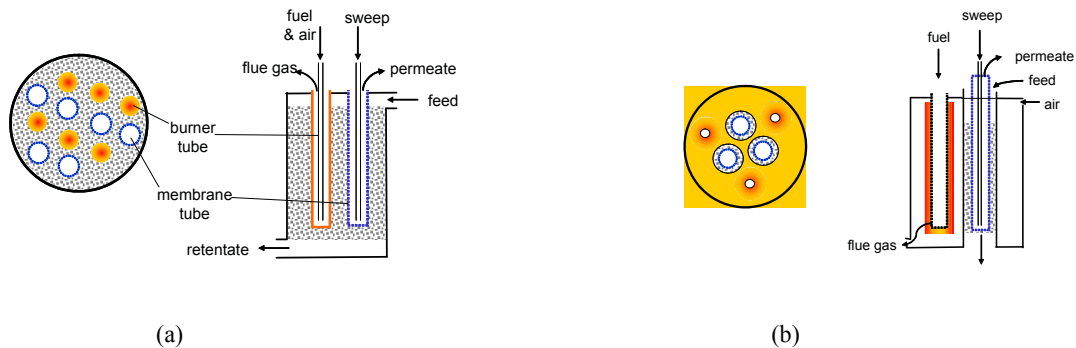(a)   (b)

Figure 8   Catalyst in shell' design (a) and Catalyst in annulus' design for reforming (b).

For the water gas shift membrane reactor also three concepts were selected, all analogies to the reformer concepts. The water gas shift reactor is however fundamentally different from the reformer since heating is not required for shift applications, thus burners can be omitted. The three concepts scored comparable, so more detailed information is required for a final selection. For ImWGSCC, a sequential membrane and water-gas-shift catalyst set-up has the advantage of a lower reactor complexity. This set-up has consecutive conventional shift reactors and membrane permeators. Calculations indicated that for membrane water gas shift reactors 4 stages will give a sufficiently high CO conversion. For a sequential membrane steam reformer, however, up to 30 stages still gave insufficient methane conversion.
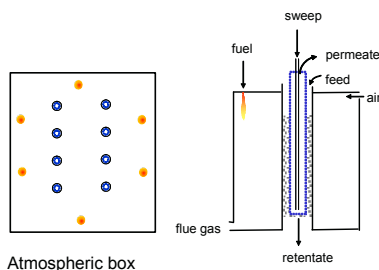

Figure 9   'Box' concept for reforming

6. Process development unit

The developed membranes will be tested under relevant process conditions in a Process Development Unit (PDU) for membrane reactor testing for both steam reforming and water-gas-shift (sequential and integrated). The PDU is commissioned at the end of October 2008 and first experiments are foreseen in December 2008. The PDU setup will consist of two main sections (figure 10):
- The test rig. This will provide gasses with the required composition, flow, and process conditions, will safely discard the used gasses and will perform all necessary gas analyses.

- The membrane reactor. Different reactor concepts can be tested in the PDU. The current membrane test reactor is a downscaled version of the full-scale membrane reactor (box design). It will however also provide information on the design of other concepts. It features the membrane reactor configuration as in the full scale application including manifolding of multiple membranes. The reactor consists of maximum 8 tubes, placed in two rows, heated by radiant electric heating elements placed in the walls. Each reactor tube can accommodate catalyst and membranes up to 50 cm length. The reactor will be tested at a scale of 3 tubes for shift to 8-tubes for reforming.
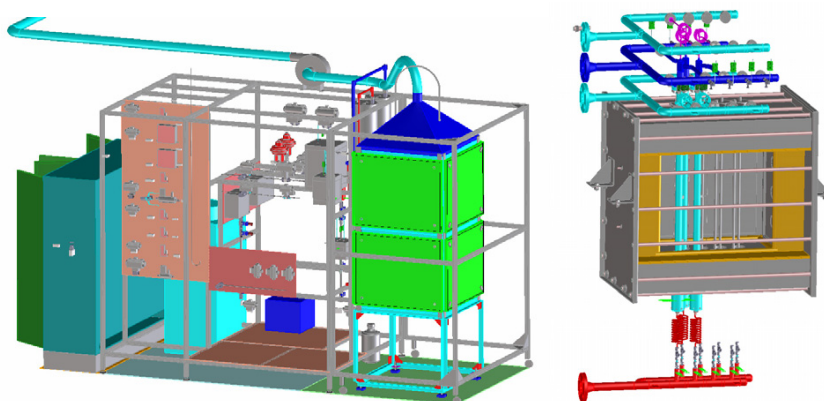

Figure 10 Design of the process development unit (left) and the membrane test reactor (right).

7. Conclusions

The first two years of CACHET have shown important progress in the development of Pd-based membrane reactors for pre-combustion CO_2 capture for natural gas combined cycles. Thin Pd-Ag membranes (2 µm thickness) on 50 cm long macroporous (2 µm pore size) tubular stainless steel supports have been prepared by the SINTEF two-stage method. The performance of these Pd-alloy membranes are within the range of the required performance criteria derived for the integrated membrane Water Gas Shift Combined Cycle (ImWGSCC) option. DICP produces 50 cm long pure Pd on low cost ceramic supports capped with new high temperature/high pressure sealing. The performance of these Pd /ceramic membranes in reforming conditions is within the performance range needed for the Integrated membrane Reformer Combined Cycles (ImRCC) option.

Both SINTEF and DICP membrane tubes show sufficient selectivities to satisfy the CACHET target of capturing 90% of the CO_2 in a natural gas combined cycle power plant. Besides, based on long-term stability tests it is concluded that stability of the membranes so far is sufficient for the membrane reactor test in the bench scale process development unit.

Cost estimates for electricity production for NGCC cycles with pre-combustion CO_2 capture show that integration of the WGS-membrane reactor gives lower cost compared to the membrane reformer case. Still, the cost is relatively high mainly due to the currently high natural gas price and the rather low efficiencies calculated. However, improvements are foreseen as performances of the membranes is still enhancing.

For the ImRCC, the preferred reactor concept is the so-called box concept, derived from a conventional steam reformer. For the ImWGSCC several feasible options were identified. A preference however exists for the sequential sub-type of the concepts that separates the reaction and separation steps.

A Process Development Unit has been constructed which features a scaled down version of the reactor concepts for integrated membrane steam reformer and integrated/sequential water gas shift. The reactor will be tested at a scale of 3 to 8-tubes of 50 cm length. These tests will produce input data for the efficiency and capture cost calculations and provide input for further technology development.

8. Acknowledgement

9. References

1.http://www.cachetco2.eu

2. D. Jansen; P. P.A.C. Pex, J.W. Dijkstra, and S.C.A. Kluiters, Membrane reactors: key technology for production of de-carbonised energy carriers, The Seventh International Conference on Greenhouse Gas Control Technologies (GHGT-7), Vancouver, Canada 5th -9th September, 2004.

3. A. Gottschalk, Pre-Combustion CO2 Capture Technologies Treating Gaseous Fuels - EU-FP6-Project CACHET,
15th International Conference on the Properties of Water and Steam 2008 (15th ICPWS), Berlin, Germany, 7-11 September 2008, ISBN 978-3-931384-64-7.

4. G. Manzolini, E. Macchi, J. W. Dijkstra, D. Jansen, Technical Economic Evaluation of a System for Electricity Production With CO_2 Capture Using a Membrane Reformer With Permeate Side Combustion, ASME paper GT2006-90353, ASME Turbo Expo 2006, Barcelona, Spain, 8-11 May 2006.

5. R. Bredesen, H. Klette, US Patent 6.086.729, 2000.

6. S. F. Hou, K. Jiang, W. Z. Li, H.Y. Xu, L. X. Yuan, "A metal palladium composite membrane or alloy palladium composite membrane and their preparation methods," WO patent 2005/065806.

7. K. Jiang, A. Goldbach, C. Bao, C. Y. Yu and H. Y. Xu, Proceedings of the 10th International Conference on Inorganic Membranes ICIM 10, Tokyo, 2008, paper 1a07.

8. T.A.Peters, M.Stange, H.Klette, R.Bredesen, Journal of Membrane Science 316 (2008) 119.

9. T.A.Peters, W.Mekonnen, A.Ramachandran, M.Stange, J.C.Walmsley, R.Holmestad, A.Borg, R.Bredesen, 2008.

10. Yasuda, I; Shirasaki, Y; Tsuneki, T.; Asakura, T.; Kataoka, A.; Shinkai, H. & Yamaguch, T (2004) Development of Membrane Reformer for HydrogenProduction from Natural Gas, ICCMR-6, July 1906-30 September 2004.

11. Shell Oil Company; Miglin, M. T.; Matzakos, A. N.; Wellington, S. L.; Clomburg, L. A.; Veenstra, P.; Munshi, A. W.; Jean, R.; Elliot, G. W. & Groeneveld, M. J. (2004c) Apparatus and process for production of high purity hydrogen, Anon., patent number WO2004/022480,

12. P.T. Alderliesten; M.Bracht, An attractive option for CO_2 control in IGCC systems: water gas shift with integrated H_2/CO_2 separation (WIHYS) process; Phase 1: Proof of Principle; Final report CEC Project JOU2-CT92-0158, ECN Energy research Centre of the Netherlands, ECN-C--97-097.

13. P. Middleton, P. Hurst and G. Walker, (2005) Chapter 27, Grace: pre-combustion de-carbonisation hydrogen membrane study, In Carbon Dioxide Capture for Storage in Deep Geologic Formations, Volume 1, eds. D. C. Thomas, S. M. Benson, Anon., Elsevier.