

Development of a hydrogen membrane reactor for power production with pre-combustion decarbonisation

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Abstract

At the Energy research Centre of the Netherlands (ECN) an integrated project on hydrogen membrane reactors for implementation in schemes for power production with pre-combustion decarbonisation is being carried out. Membrane development focuses on industrial applicable manufacturing methods for alumina supported PdAg membranes. Successful membrane test and membrane reactor tests have been performed. Membrane reactor design focuses on the choice of a reactor concept based on input from various tasks in the programme and on modelling results. The role of catalyst development and system development is discussed.

Keywords: Membrane reactor, palladium alloy membranes, pre-combustion decarbonisation, experimental.

Introduction

Pre-combustion decarbonisation is one of the three main routes for electricity production with low CO₂ emission. In pre-combustion decarbonisation, the fuel is converted into H₂ and CO₂, which are separated from each other. The hydrogen is used for power production in a combined cycle. The residual stream exiting has a high concentration of carbon dioxide and is available for transport and storage.

A very important step in pre-combustion decarbonisation is the H₂/CO₂ separation step. It is advantageous from both efficiency as well as a cost perspective to integrate this step with the fuel conversion step. This can be done by means of a membrane reactor. At the feed side of the membrane reactor steam reforming of natural gas is carried out, and parallel to the reaction the reaction product hydrogen is removed through a membrane. Applying this technology in a combined cycle for power production with CO₂ capture is a promising option for a low carbon capture penalty and low investment.

At the Energy research Centre of the Netherlands an integrated project on the development of a membrane reactor for implementation in pre-combustion decarbonisation schemes is being carried out. In the programme the following tasks have been defined:

- Conceptual process design
- Catalyst development
- Membrane development and testing
- Membrane reactor development
- Membrane reactor experiments

The objective is to construct a process development unit with approximately 12 kW H₂ production in 2007. For each of the tasks the key targets, approach and achievements will be presented.

Conceptual process design

Conceptual process design focuses on the development of schemes for implementation of membrane reactors in power production processes. Important subjects are development of integration schemes and the optimal choice of operational and design parameters. Other subjects are the evaluation of water gas

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shift membrane reactors vs. membrane reformers, evaluation of retentate clean-up options and exploring various system configurations. Economic evaluations are performed in which input from the reactor development is used. Results show that membrane reactors are competitive with conventional options for CO₂ capture and that using a membrane reformer in a power plant is the most competitive option compared to a system comprising of a steam reformer with a downstream water gas shift membrane reactor. In collaboration with the Politecnico di Milano a separate paper on conceptual process design is submitted to this conference [1].

Catalyst development

Catalyst development focuses on the selection and development of a reforming catalyst that is active and stable under membrane reactor conditions. Specific conditions are the combination of a low reactor temperature and the withdrawal of hydrogen, which both increase the risk of catalyst deactivation through carbon deposition. Achievements in catalyst development are:

- A pre-commercial reforming catalyst has been selected. The pre-commercial catalyst shows good activity and sufficient stability under simulated membrane reactor conditions.
- An in-house ceria–zirconia promoted Rh catalysts has been developed for use next to the pre-commercial catalyst. The catalyst shows comparable activity and stability under simulated reforming conditions to the pre-commercial catalyst.

A separate paper submitted to this conference will discuss catalyst development in more detail [2].

Membrane development and testing

The membrane is the key element in the membrane reactor. ECN has chosen for the supported thin layer Pd alloy membranes based on the ECN fabrication technology. The metal alloy is applied on a tubular porous support by electroless plating, followed by alloying. This procedure showed to be the technique offering the lowest costs and good possibilities to be scaled up for large production volumes. The manufacturing process of ECN PdAg membranes contains the following steps:

- Fabrication of porous support tube with an appropriate porous structure. The porous support is based on a commercial porous alumina tube on which typically two intermediate layers are applied. Development focuses on the controlling the pore size and defect population.
- Application of Pd seeds on the support, activation of the support. A recent achievement has been the development of an industrial applicable method of seeding, as opposed to a manually method. The new method has cost benefits and has improved reproducibility.
- Sequential electroless plating of a Pd and an Ag layer with an appropriate thickness to reach a Pd/Ag ratio of 70/30 w/o. For the plating a continuous plating bath has been developed which can hold up to 7 tubes at once. As opposed to the stationary plating bath used before, the continuous bath offers better control of the alloying process.
- Heat treatment for alloying PdAg. Here the laboratory vacuum oven procedure has been replaced with a new procedure using an industrial type atmospheric oven. The alloying procedure proved to be very important for membrane quality.

Membranes with a thickness of 3-5 μm of PdAg are obtained with lengths up to 80 cm .

Membranes are tested by permeation and separation experiments. Figure 1 gives the results of a separation experiment under simulated membrane reactor conditions. After initial activation high hydrogen permeances of 50-100 m³/m²hbar^{0.5} can be obtained with high permselectivities. The selectivity (for the 500° C experiment) is rather low for palladium alloy membranes, but this is due to leakage through the sealing at high pressures.

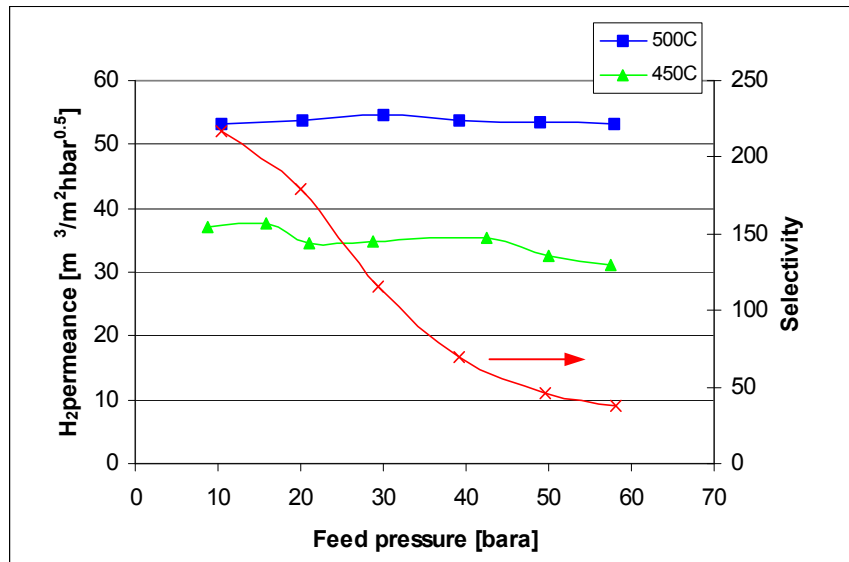


Figure 1: Results of gas separation experiments under simulated membrane reactor conditions.

Membrane reactor design

Membrane reactor design focuses on the selection of a full-scale reactor concept and design of a process development unit of approx. 12 kW H₂ production. Since various reactor concepts are still being evaluated, the methodology will be the main issue of discussion here. The role of the various modelling and inventory activities in this task is illustrated in Figure 2.

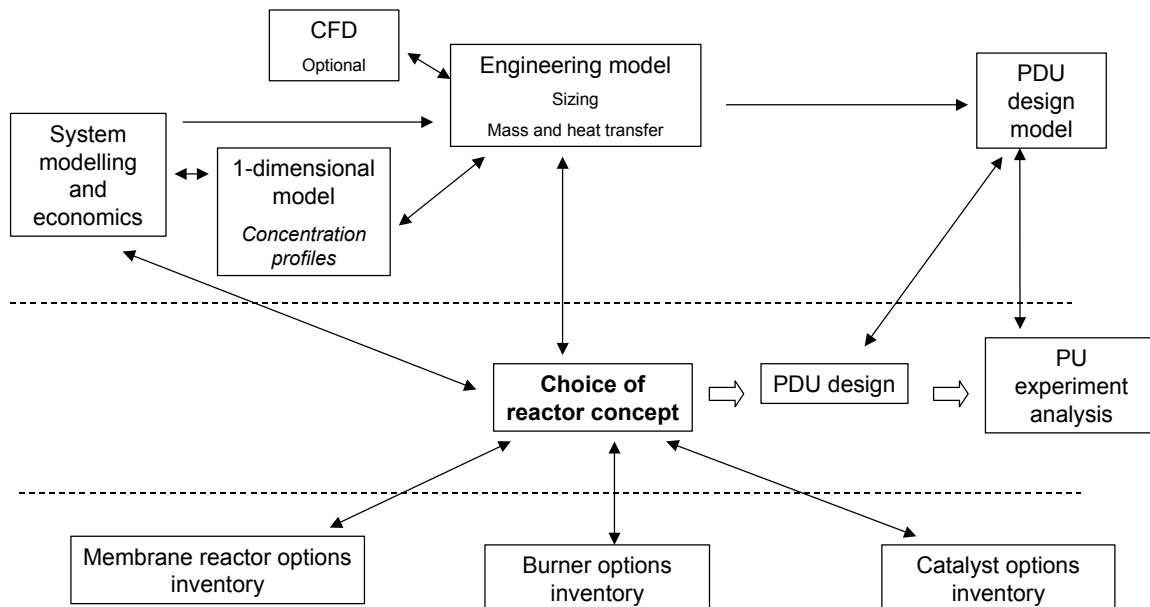


Figure 2: Role of modeling and inventory activities in reactor design.

The first activity for selection of a reactor concept has been an inventory of membrane reactor designs published in literature. A separate inventory has been made of the options for the type of burners to use in the membrane reactor. The results from this are used in the TRIZ method for systematic design [3]. In this methodology first the functions present in the membrane reactor are identified. These include membrane shape, catalyst placement, heat supply etc. for each of the functions all possible solutions are listed (e.g. catalyst placement outside membrane tubes, catalyst placement inside membrane tubes). Different combinations of solutions are combined into several alternatives for reactor concepts.

The different alternatives are scored against each other in ranking sessions. The criteria used in the ranking session proved to be of crucial importance. Quantified criteria are required, for which the scoring is obtained from results from system design, process economics, reactor design, reactor modelling and experimental work. Using only a qualitative approach, as is often used in this method, proved not give sufficient detail and confidence for a definitive choice for a reactor concept.

Various models are made which serve different objectives. An interesting example of reactor modelling is presented in Figure 3. The model is a one-dimensional type model for a membrane reactor describing the partial pressure profiles along the membrane length coordinate. The model combines mass and energy balances for each component on both sides of the membrane with expressions for reaction and permeation. The feed is a pre-reformed $\text{CH}_4/\text{H}_2\text{O}$ (3/1) mixture entering at 40 bara and the sweep is steam entering at 5 bara. The reactor is operated at 600° and in countercurrent mode. Feed is flowing from left to right, sweep in the opposite direction. Figure 3 shows the partial pressure profile of H_2 at both sides of the membrane. It can be seen that the steepest H_2 profiles are present at low length coordinates at the feed side and at the high length coordinates at both sides of the membrane. For the largest part of the reactor the profiles of sweep and permeate are quite parallel indicating that the membrane flux is there evenly distributed over the length coordinate. The model is used for estimating the required membrane surface area, which is input for system design, reactor design and process economics. Other models are used to address issues of e.g. mass and heat transfer, which are not accounted for in this model.

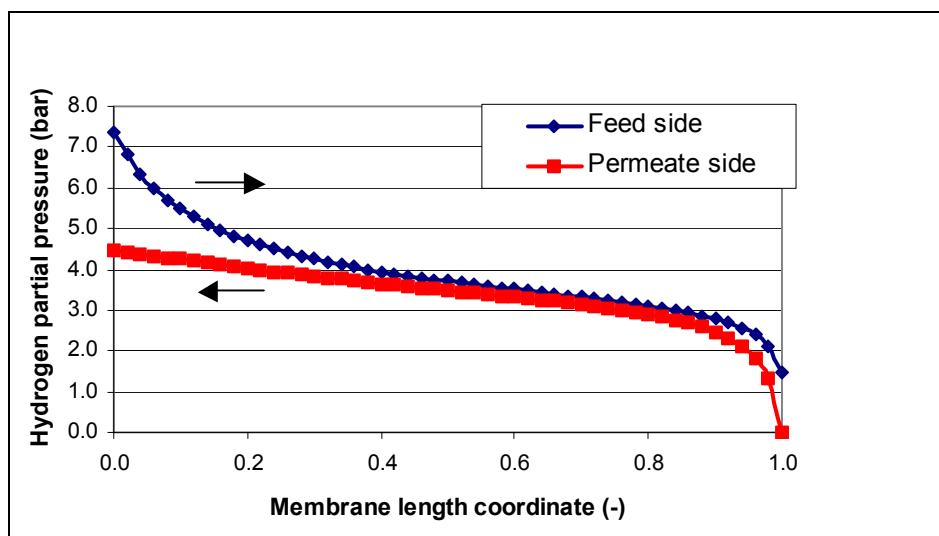


Figure 3: Hydrogen partial pressure profiles in a membrane reformer, countercurrent operation

Membrane reactor experiments

Membrane reactor experiments are performed in a single tube membrane reactor with a 17.4 cm long Pd/Ag on alumina membrane with a diameter of 1.4 cm that was placed in a bed of low temperature reforming catalyst particles. The reactor is placed in an electrically heated oven.

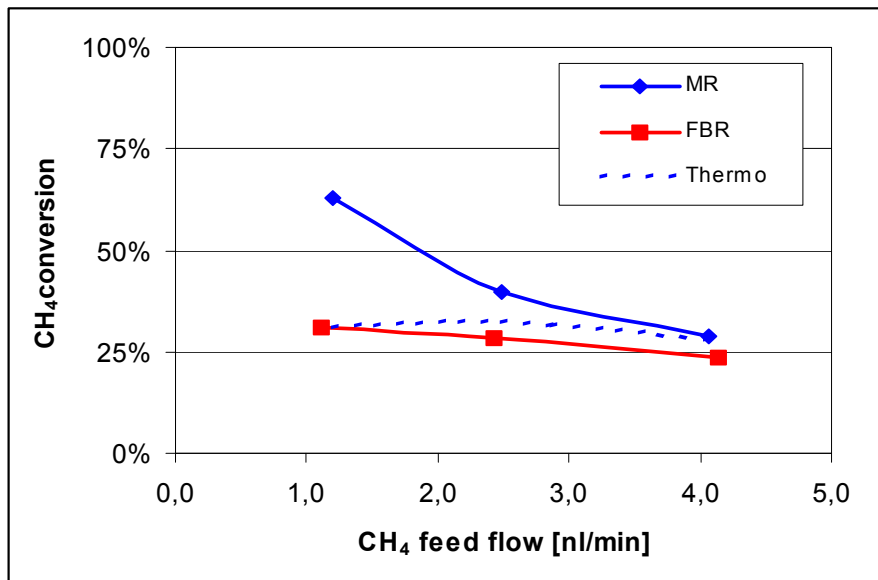


Figure 4. Membrane reactor experimental results $T=650^{\circ}\text{C}$; $P_{\text{feed}}=11$ bara. Feed composition $\text{CH}_4/\text{H}_2\text{O}=1/3$. Sweep flow 0.5 nl/min. Sweep pressure 1 bara.

Figure 4 present the results of one-tube membrane reactor reforming experimental 650°C in which the feed flow has been varied. A preheated feed stream consisting of a $\text{CH}_4/\text{H}_2\text{O}$ mixture is supplied to feed side of the membrane reactor. A nitrogen sweep stream is introduced in co-current mode to prevent back-permeation of hydrogen. The "FBR" line in Figure 4 corresponds with fixed bed operation in which no permeation through the membrane takes place. The "MR" line corresponds with membrane reactor operation, including permeation of hydrogen through the membrane. The dotted "Thermo" line corresponds with the equilibrium conversion calculated from the feed composition and catalyst bed temperature measured. It can be seen that, especially at low feed flow rates, permeation shifts the equilibrium to considerably higher conversions, and beyond the chemical equilibrium.

For practical application of membrane reactors higher conversions are required than those obtained in the experiments presented here. Membrane modeling shows that this is due to the low membrane surface area/feed flow ratio used, so for higher conversions longer membranes or lower feed flow rates are to be used.

Figure 5 gives the results of a similar single tube membrane reforming experiment at 600°C in which the feed pressure has been varied. From this figure it can be seen that permeation of hydrogen shifts the CH_4 conversion measured significantly beyond that of chemical equilibrium (CH_4 conversion calculated for chemical equilibrium and without membrane permeation). This shift in conversion increases with increasing feed pressure.

Finally a comparison with the one-dimensional model is presented. The model assumes a uniform temperature of 600°C , infinite selectivity towards H_2 and a fixed hydrogen permeance of $2.0 \cdot 10^{-6}$ mol/m²/s/Pa. This has been estimated to be the average permeance during the experiments. The model also assumes that at the beginning of the membrane the reaction is at equilibrium and assumes excess in catalyst. The modelling results are in good agreement with the experimental results at low feed pressure. The effect of feed pressure increase is more pronounced than in the membrane reactor experiments. As in the experiments also the modelling shows that the shift in conversion increases with increasing pressure. In the experiments however the conversion is still decreasing with pressure and in the model the shift in conversion is so large that the conversion increases with pressure. A possible explanation could be that the model assumes infinite selectivity whereas this experiment showed some CH_4 leakage.

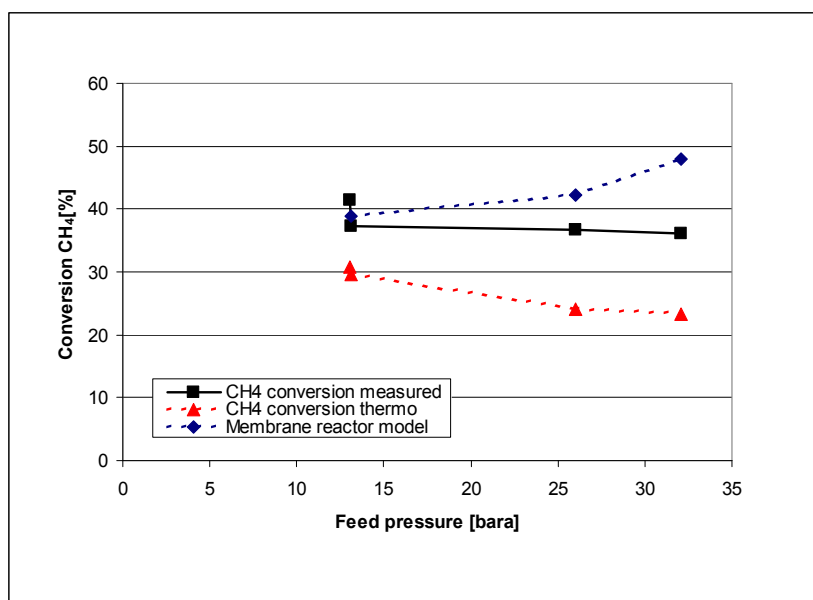


Figure 5: Membrane reforming experimental results: impact of feed pressure on CH₄ conversion. Feed composition CH₄/H₂O: 1/3. Sweep pressure 1 bar. Sweep flow 0.5 l_n/min. Feed flow 2.5 l_n/min. Comparison with thermodynamic equilibrium calculations and with results of a 1-dimensional reactor model.

Conclusions

At ECN an integrated project on hydrogen membrane reactors for implementation in schemes for power production with pre-combustion decarbonisation is being carried out. In the membrane development task it has been proven that Pd alloy membrane with a high hydrogen permeance can be manufactured. A catalyst with sufficient stability and activity under membrane reactor conditions has been developed. Application of the membrane and catalyst in membrane reactor experiments have successfully shown that it is possible to shift the methane conversion beyond chemical equilibrium by means of hydrogen withdrawal.

Acknowledgement

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