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MEMBRANE REACTORS: KEY TECHNOLOGY FOR PRODUCTION OF DE-CARBONISED ENERGY CARRIERS

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Abstract

Pre-Combustion De-Carbonisation (PCDC) has been identified as promising concept to capture CO₂ in power generation systems. Membrane reactors are expected to play a key role in the development in novel PCDC schemes, next to gas turbines and fuel cells. This paper focuses on the application of membrane reactors with hydrogen separating membranes. A generalized layout of systems for power production with H₂ membranes is discussed. An analysis revealed that the systems all exhibited certain key elements, with several options to fulfil the function in that element.

The combination of a shift membrane burner (SMB) and an SOFC offer the possibility for high-efficiency power generation with CO₂ capture. The impact of the fuel efficiency on the system efficiency and key system parameters is discussed. Optimum efficiency was found at a fuel utilisation of 75.5%.

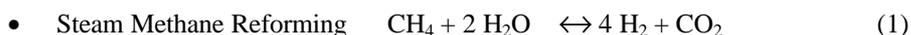
The integration of a membrane reformer (MREF) in a gas turbine cycle offers the possibility for power production with a low carbon capture penalty. The results of an economic analysis are provided, which give targets for membrane development. The membrane flux target is 50-100 kW/m² at corresponding membrane costs of 700-1400 €/m².

Introduction

A sustainable use of fossil fuels in the future will undoubtedly be based on concepts where the energy content of the fossil fuel is first transferred to hydrogen. The driving force for these concepts is that in this way the CO₂ can be captured elegantly. However the major drawback of this de-carbonisation approach is currently the associated efficiency penalty leading to cost for avoided CO₂ of over 50 €/tonne. This will make the economic feasibility of such an approach very questionable and in order to get a broad public acceptance for these concepts it is inevitable to reduce this associated efficiency penalty and costs. Looking carefully into the efficiency drop clearly reveals that the CO₂ concentration step is the major cause of this efficiency penalty.

Extensive assessment studies, evaluating more integrated approaches of the conversion technologies i.e. electricity or hydrogen production with the CO₂ capture, showed that additional primary energy use can be reduced. Membranes give great opportunities for the earlier mentioned new integrated approach. This paper discusses in detail schemes for CO₂-free electricity production in cycles where hydrogen is playing a major role as an energy carrier. In these cycles, a membrane reformer or water gas shift membrane reactor is the enabling technology for more efficient and “lower” cost CO₂ capture. The objectives for membrane based (after)burners in both gas turbine and SOFC systems are reduction of the energy efficiency penalty with 50% compared to conventional amine scrubbing.

ECN identified Pre-Combustion De-Carbonisation (PCDC) as a viable concept (in technical and economic respect) to capture CO₂ in power generation systems. In PCDC concepts the carbon containing fuel (coal, natural gas or biomass) is first reacted with oxygen and/or steam to produce a mixture of carbon monoxide, carbon dioxide and hydrogen (see equation 1). Subsequently in a second step (see equation 2) the carbon monoxide is reacted with steam to produce additional hydrogen and CO₂. Finally, the hydrogen and CO₂ are separated, either by removing the CO₂ from the mixture or by removing hydrogen from the mixture (step3).



All three steps are well known technologies (processes) that are currently used for the generation of high purity hydrogen for chemical and refining use. Today there are, however, no good prospects for application of these processes in power generation systems. This is because of the

associated costs and efficiency penalty. More advanced schemes are required for this, which incorporate novel technologies and integration of process steps. Integration of process steps may lead to lower investments, but also to more favourable process conditions and higher efficiencies. Membrane reactors are expected to play a key role in the development of novel PCDC schemes, next to gas turbines and fuel cells. This paper focuses on the application of membrane reactors with hydrogen separating membranes.

Overview of systems for pre-combustion decarbonisation with membrane reactors

A literature study has been performed into systems proposed in literature for climate neutral electricity production using hydrogen permeating membrane reactors. To give a more complete overview of possible systems, also systems proposed for climate neutral hydrogen production (again only those systems employing hydrogen permeating membrane reactors) were studied, since these systems can usually be easily adapted to generation of electricity. In total, some 15-20 relevant systems were found. An analysis of the systems revealed that the systems all exhibited certain key elements, which are shown in Figure 1. These elements are direct consequences of the membrane reactor's properties. Per key element several options for fulfillment of the function in that element exist.

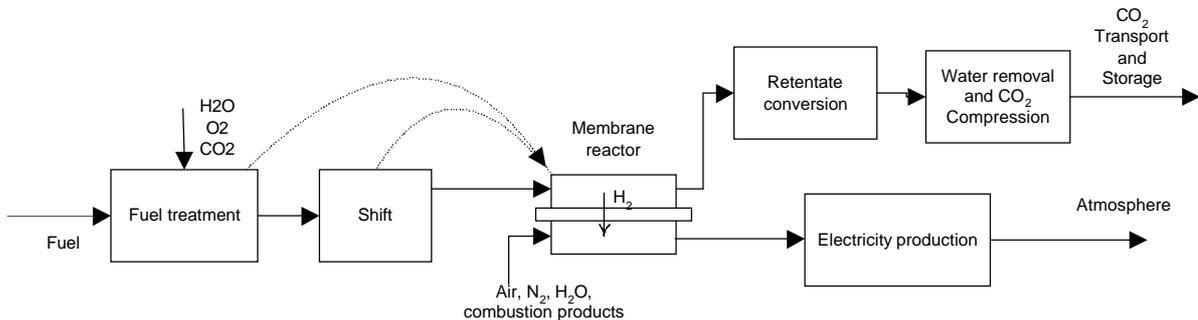


Figure 1: General building blocks discerned in systems found for climate neutral electricity production

The first step is fuel treatment. Fuel treatment is done using steam and/or (relatively) pure oxygen with possibly carbon dioxide. Depending on the fuel the reactions present are gasification, reforming and/or partial oxidation. Dilution of this stream with nitrogen should be avoided. Air is not acceptable as a fuel treatment agent: it has to be separated first to produce oxygen. The fuel pretreatment step is then followed by the water gas shift reaction.

Next, the hydrogen is separated from the stream originating from the fuel treatment process. The shift reaction and (part of) the fuel treatment process are integrated into the membrane reactor. For solid and liquid fuels, the fuel treatment will most likely take place outside the membrane reactor. An important advantage of removing the hydrogen in the membrane reactor is that it shifts the equilibrium to the product side. This leads to increased H_2 production, at more favorable conditions. To enhance hydrogen permeation rates, it is favorable to reduce the hydrogen partial pressure at the permeate side. This can be done by changing (absolute) operating pressures, but also by using an inert sweep gas (such as steam, nitrogen or combustion products) or by oxidation (combustion) of the hydrogen on the permeate side using oxygen.

Depending on the specifications for CO_2 for sequestration, it might be required to include a retentate conversion step in which unconverted fuel and combustion intermediates (CO and H_2) are converted to CO_2 and H_2O . Retentate conversion with oxygen, air or the use of a second membrane reactor based on oxygen conducting membranes are possible. Finally, after water removal, the CO_2 is compressed to the conditions for transport and storage. The electricity production step can be done with a variety of conventional and advanced technologies of which gas turbines (GTs) and fuel cells (SOFC) are expected to play a key role.

ECN develops thin layer palladium alloy membrane technology for PCDC concepts because this technology is expected to reduce the cost of CO_2 avoided to a level < 25 €/ton. This paper will now focus further on two options: a shift membrane burner/SOFC combination and a membrane reformer system.

Development of a shift membrane burner (SMB)

The shift membrane burner (SMB)/SOFC combination has been proposed and discussed in [1], [2]. A simplified system is depicted in Figure 2. Fuel is fed to the anode side of an SOFC (that produces electricity). The anode outlet stream consists of CO_2 and H_2O , with CO and H_2 as a result of the SOFC having a maximum fuel utilisation of 85%. The anode outlet stream is fed to the feed side of a shift membrane burner (SMB). Here the CO is converted with the shift reaction (2), while hydrogen permeates through a hydrogen separating membrane. At the permeate side the hydrogen is burned with air. Though Figure 2 suggests otherwise, the SMB streams inside the SMB flow in a co-current arrangement. The SOFC with SMB is placed inside a gas turbine cycle (producing additional electricity), with a heat exchanger to obtain the required membrane reactor inlet temperature and a combustion chamber that is used raise the turbine inlet temperature.

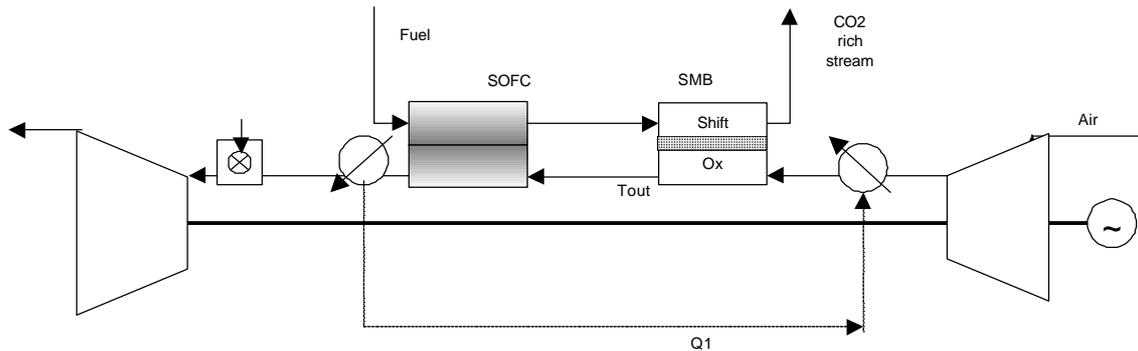


Figure 2: Simplified system structure, with important heat exchange steps.

A system model has been prepared to assess the system efficiency and to determine the impact of important design parameters. One important design parameter, which had not yet been explored before is the SOFC fuel utilisation. A higher fuel utilisation gives a higher SOFC electricity production but a higher required SOFC area. The SMB has to convert less CO and H_2 , leading to a lower membrane surface area, inlet/outlet temperature difference for the membrane reactor, and also to a higher heat exchanger duty Q_1 . Since the temperature difference of the combustion chamber is limited by a carbon capture percentage constraint, the turbine inlet temperature is lower and the gas turbine power production less. As a result, the system efficiency, turbine inlet temperature and gas turbine mole flow are influenced. The SMB (retentate and permeate) outlet temperature has been fixed at the SOFC inlet temperature.

Table 1: Impact of fuel utilisation on the membrane reactor

Fuel utilisation	SMB temperature difference	Total system efficiency	Turbine inlet temperature	GT compressor mole flow [kmol/hr]
0.85	111° C	60.17%	536° C	2624
0.80	170° C	61.03%	667° C	2233
0.755*	242° C	62.11%	841° C	1882
0.75	250° C	61.82%	849° C	1847
0.70	364° C	56.68%	873° C	1466

* = Optimum in total electrical efficiency

In table 1 the impact of the fuel utilisation is depicted. Figure 3 gives a graphic representation of the results. It can be seen that the system efficiency has an optimum at a fuel utilisation of 75.5%. The optimum is a result of the opposing effects of a higher power production in the SOFC and a higher GT power production with increasing fuel utilisation. The inlet/outlet temperature difference of the SMB is 242° C. This is expected to be too high for a single membrane reactor, so networking of several membrane reactors to obtain a higher effective inlet outlet temperature difference is required. A lower fuel utilisation leads to a lower SOFC cooling demand, thus to a lower GT compressor mass flow. The turbine inlet temperature is considerably lower than that of conventional gas turbines. Raising the turbine inlet temperature is not possible because more additional firing with natural gas or an anode off-gas bleed, will result in a carbon capture rate below the target value of 80%.

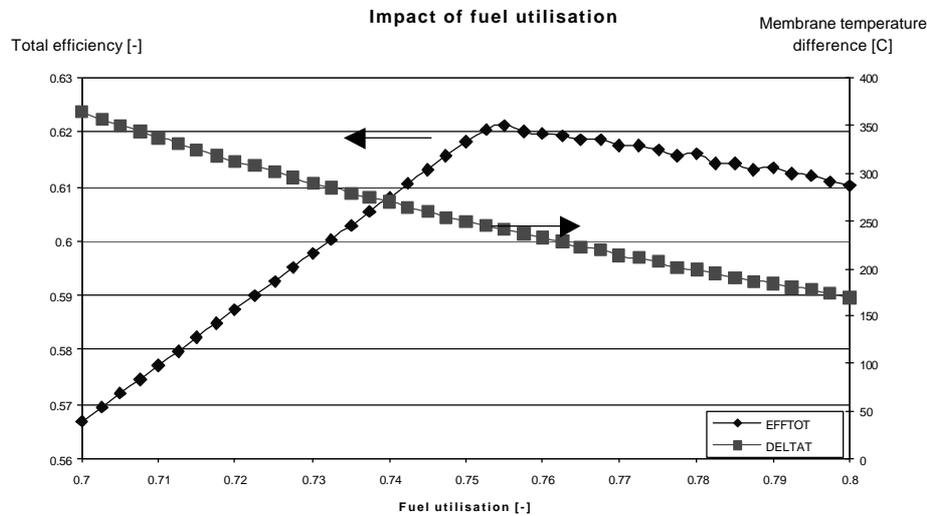


Figure 3: Impact of fuel utilisation on efficiency and membrane reactor temperature difference

Development of a membrane reformer (MREF)

The second system discussed is that of a membrane reformer (MEMREF) placed in a GT cycle. The combination of separation and reaction, as foreseen in membrane steam reforming, offers higher conversion of the reforming reactions at lower temperatures due to the removal of hydrogen from these equilibrium reactions as shown in equations (1) and (2) respectively. Thus a membrane reactor allows one-step reforming with WGS reaction and parallel hydrogen separation. The retentate gas consists of predominantly CO₂, a small fraction of non-recovered hydrogen, and some CO and CH₄ and excess steam. Unlike conventional reforming or WGS, membrane reforming/WGS benefits from high pressure of operation due to the increased H₂ partial pressure differential across the membrane which acts as the driving force for hydrogen permeation

The system proposed consists of a membrane reactor with a permeate side steam sweep, placed in a gas turbine cycle. In the membrane reactor both steam reforming and the water gas shift reaction take place on the feed side. The hydrogen permeate stream is led to the gas turbine combustor. The heat Q of the steam reforming reaction is provided by external combustion of e.g. natural gas.

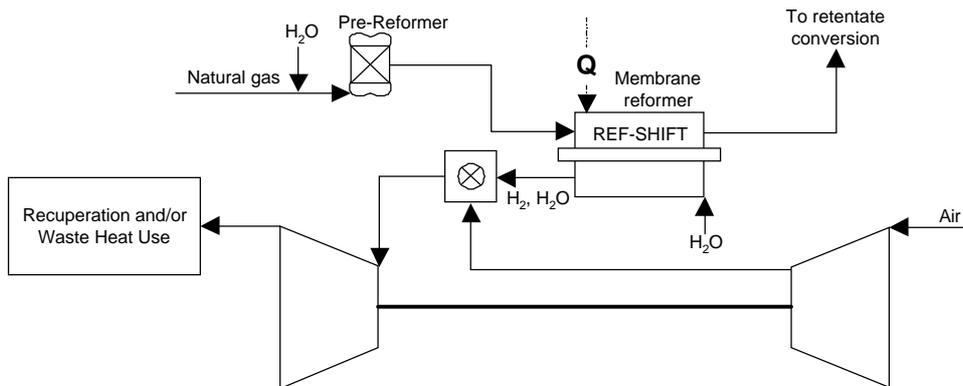


Figure 4: System lay-out of a gas turbine with a membrane reformer for power production with CO₂ capture.

An economic analysis has been performed to determine the technology development targets. Starting points were a CO₂ capture energy reduction target of 50% compared to conventional amine absorption technology (resulting in an efficiency penalty target of 4-5 %-points LHV) and a reduction of CO₂ avoided costs <25 €/ton. A membrane lifetime target >2 years has been set, which is in the same order as the lifetime of noble metal based catalysts in the chemical industry. The result of the economic analysis is a combined cost and performance target. Assuming that the membranes amount to 70% of the incremental capture investments (excluding CO₂ compression), a combined investment and membrane flux target can be calculated. The permeation rate target is expressed as the Lower Heating Value (LHV) flux of hydrogen permeating through the membrane (the product of molar flux and molar LHV of hydrogen). For a flux target of 50-100 kW/m² the corresponding membrane cost target is 700-1400 €/m² membrane. So at a flux of 100 kW/m² the membrane cost target is 1400 €/m².

Experimental results show that the membrane performance is feasible with ECN in-house manufactured membranes. Figure 5 gives the results of permeation experiments with a Pd/Ag membrane on an alumina support at simulated reforming conditions. [3] The flux is in accordance with the 50-100 kW/m² target. Furthermore stable operation for 3 months and a H₂/CO₂ selectivity of around 4000 has been proven. Thermal cycling in N₂ had no negative impact on the membrane performance.

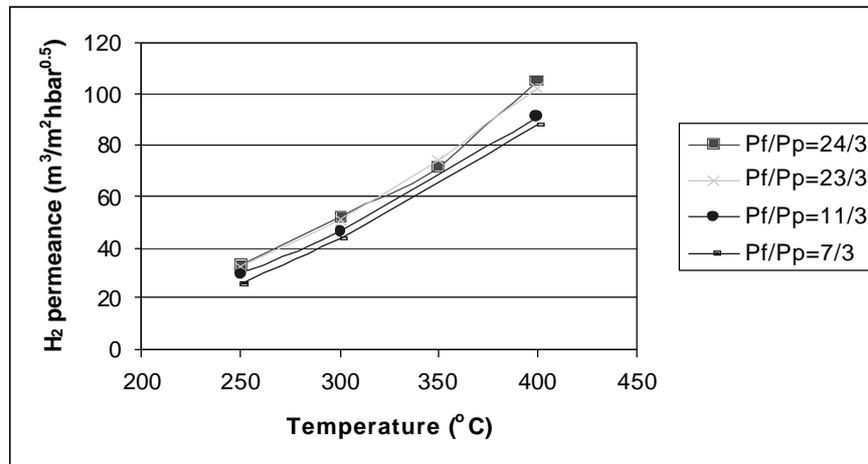


Figure 5: Permeance of a Pd/Ag membrane as a function of temperature and feed/permeate pressure (barg).

Conclusions

Membrane reactors have been identified as a promising option for power production with capture of CO₂. An analysis of systems found in literature revealed that these systems all exhibited certain key elements. Per key element several options for fulfillment of the function in that element exist. An analysis of the impact of the fuel utilisation in SOFC/SMB system revealed that system efficiency has an optimum at a fuel utilisation of 75.5%, resulting in an SMB temperature difference of 242° C. The optimum is a result of the opposing effects of a higher power production of the SOFC and a power production in the gas turbine at increasing fuel utilisation. Networking of several membrane reactors to obtain a higher effective inlet outlet temperature difference is expected to be required.

An economic analysis has been performed to determine the development targets for a membrane reformer for implementation in a gas turbine cycle. Starting with an efficiency penalty of 4-5% points (50% of conventional capture methods) and CO₂ avoided cost <25 €/ton the targets have been set at a membrane price of 1400 €/m² and a membrane flux of 50-100 kW/m² (LHV). Experimental results indicate that the membrane flux is feasible with current in-house membranes.

Acknowledgements

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