DEVELOPMENT OF A HYDROGEN MEMBRANE REFORMER BASED CO_2 EMISSION FREE GAS FIRED POWER PLANT

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ABSTRACT

The aim of this CO_2 Capture Project (CCP) funded work has been to develop novel dense hydrogen mixed conducting ceramic membranes (HMCM) with sufficient H_2 transport rates and stability under normal steam reforming conditions, and further develop a techno-economically viable Pre-Combustion De-Carbonisation (PCDC) process applying said materials. A large number of candidate membrane materials have been synthesized and characterized followed by hydrogen permeability measurements in atmospheric laboratory tests at both the University of Oslo (UiO) and SINTEF. Based on the measurements and theoretical evaluations, a main candidate materials system, was selected. Supported membrane tubes have been fabricated and one tube was tested in a pressurized hydrogen flux test rig under relevant process conditions (20 bar and 1000 °C). The measured hydrogen flux compared favorably with model predictions based on the atmospheric laboratory tests. However, the tested membrane tube was not gas impervious and improved membranes tubes need to be fabricated and tested to verify the project results.

The novel HMCM based concept allows close to 100% CO_2 capture and the loss in efficiency is estimated to be only 5%-points compared with a conventional combined cycle power plant without CO_2 capture. This includes compression of purified CO_2 to 150 bar. The novel hydrogen process will generate a diluted hydrogen fuel containing about 40% H_2, 40% N_2 and 20% H_2O. The low hydrogen concentration in the fuel is a major advantage since this will depress formation of nitric oxides in the combustion chamber. A reactor model has been developed and temperature profiles, concentration profiles, hydrogen flux and required membrane area for the different membrane reactor steps at real process conditions are presented.

INTRODUCTION

The CO_2 Capture Project (CCP) is an international effort by eight leading energy companies to develop new technology to capture and store CO_2 currently emitted by fixed sources such as turbines, heaters and boilers. Both post combustion, pre-combustion and "oxy-fuel" approaches have been studied. In the pre-combustion approach fossil fuel is converted to hydrogen fuel and CO_2 is recovered for storage. Methane Steam Reforming (MSR) and water CO shift reactions are commonly used in hydrogen production from natural gas followed by separation of CO_2 by means of e.g. amine scrubbing. This technique gives high CO_2 purity, but is quite energy intensive.

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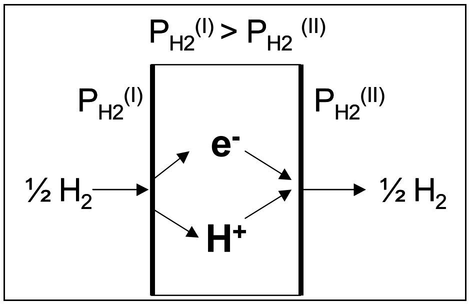

Figure 1: Schematic drawing of the HMCM transport process

An alternative method is to separate hydrogen from the synthesis gas using hydrogen selective membranes (Figure 1). Since MSR is favoured by high temperature it is advantageous to develop membranes that can operate at high temperatures (> 700 °C). Several oxides possessing the perovskite structure are known to be protonic conductors [1-2]. The challenge in the present work, however, has been to develop a material with both high electronic and protonic conductivity [3]. Since this transport process is based on ion diffusion the selectivity of the membrane is infinite as long as the membrane is gas impervious. This work has been based on Hydro IPR covering Ceramic Conducting Materials, Reactor Design and Process Design, [4-6].

THE HYDROGEN MEMBRANE REFORMER SYSTEM

A novel hydrogen membrane reformer concept has been developed. It combines Steam Methane Reforming and HMCM, Figure 2. Desulphurized natural gas fuel at 30 bar, mixed with steam and preheated to 700°C, is fed to the retentate side of the membrane section, and undergoes endothermic steam reforming, producing a hydrogen rich syngas at about 950 °C. The retentate side surface can either be coated with an appropriate methane steam reformer catalyst or designed with interstage adiabatic catalyst beds. Hydrogen is transported through the membrane and is in step 1 reacted with air extracted from the gas turbine compressor (about 9%, 17 bar) to generate a nitrogen and steam containing sweep gas. This sweep gas is used to recover most of the hydrogen in a step 2 generating a high pressure hydrogen fuel containing about 40% H_2, 40% N_2 and 20% H_2O. This fuel is cooled and recompressed to 18 bar. The hydrogen fuel mixture is then combusted with air in the gas turbine. The low hydrogen concentration in the fuel is a major advantage since this will depress formation of nitric oxides in the combustion chamber to 15 ppmv or below [7]. The amount of sweep gas generated in step 1 is determined by the heat demand on the reformer side, but the sweep gas amount can be increased by using oxygen depleted air from the residual syngas oxidation unit. Unconverted CO in the residual synthesis gas is shifted with water to CO_2 and H_2. Similar to step 1 air is used to oxidize permeated hydrogen thus driving the CO shift reaction to completion. CO_2 can then be captured at about 25 bar simply by condensation of the water vapour. CO_2 is further dried, compressed and liquefied and pumped to actual injection pressure. A relatively large portion of the gas turbine compressed air (about 50-60%) is preheated in this section.

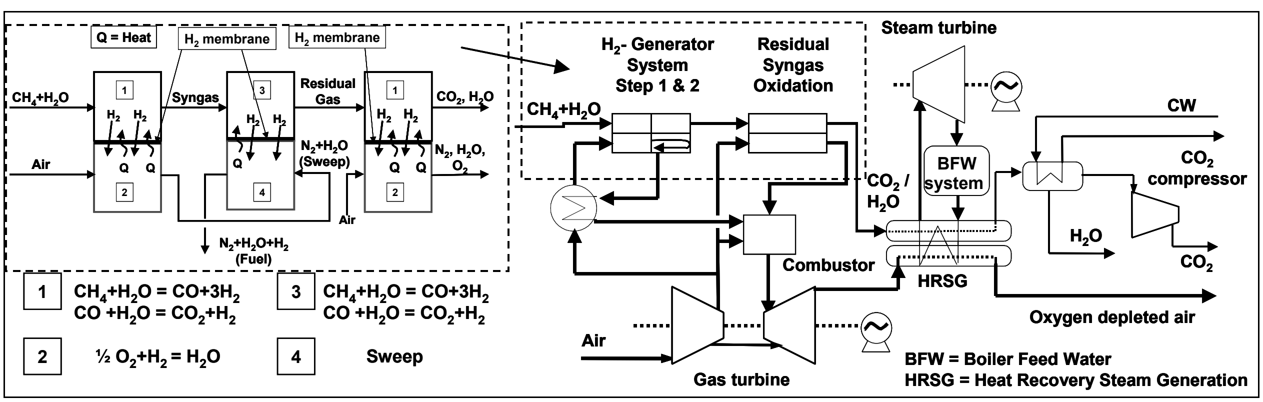

Figure 2: The Hydrogen Membrane Reformer system (left) and the integrated power plant (right)

The loss in efficiency is estimated to be only 5%-points compared with a conventional combined cycle power plant. This includes compression of purified CO_2 to 150 bar. A comparison with a 395 MW_{LHV} conventional combined cycle power plant is shown in Table 1.

TABLE 1: POWER PLANT PERFORMANCE SUMMARY

	HMCM Power Cycle	Conventional Power Cycle
Total Fuel Consumption, MW_{LHV}	681.0	681.0
Net power output, MW_{LHV}	361.9	395.0
Thermal efficiency inclusive CO_2 compression, %	53.1	58.0
CO_2 emission, metric tons/h	Close to zero	144.1

MEMBRANE PRODUCTION AND MEASUREMENTS

Small membrane disks were produced and characterized by Hydro and further tested at the University of Oslo (UiO) and SINTEF. The two locations have essentially identical experimental set-ups, i.e. a measurement cell with two chambers separated by the membrane disk placed on a support tube. Powders for the preparation of membranes were produced either by combustion spray pyrolysis, wet complexing routes (e.g. citric acid) or by conventional solid state reaction using oxides and carbonates. After calcination the powders were milled and uniaxially pressed to disks and in some cases also by cold isostatic pressing. These disks were finally sintered to approximate diameters of either 10 or 20 mm and about 1.5 mm thickness. A mixture of hydrogen, nitrogen and helium with hydrogen contents of 10%, 20%, 50% or pure H_2 humidified to 0.022 atm was used as feed gas. On the secondary side, argon was used as sweep gas, either dry or humidified to 0.022 atm. The sweep gas exiting the cell was analysed by a gas chromatograph (GC).

Tubular porous thick-walled (1-2 mm) support tubes were fabricated by Hydro. The powder was produced by a wet complexing route, mixed with cornstarch, and cold isostatically pressed to 10-15 cm long tubes. These tubes were coated with a thin (50 μm) dense membrane layer and tested at relevant process conditions in a pressurised hydrogen flux measurement test rig. Figure 3 shows a picture of the membrane tube which was mounted inside a zirconia tube. The zirconia tube acts as a mechanical support and it was installed in a high pressure test reactor tube.

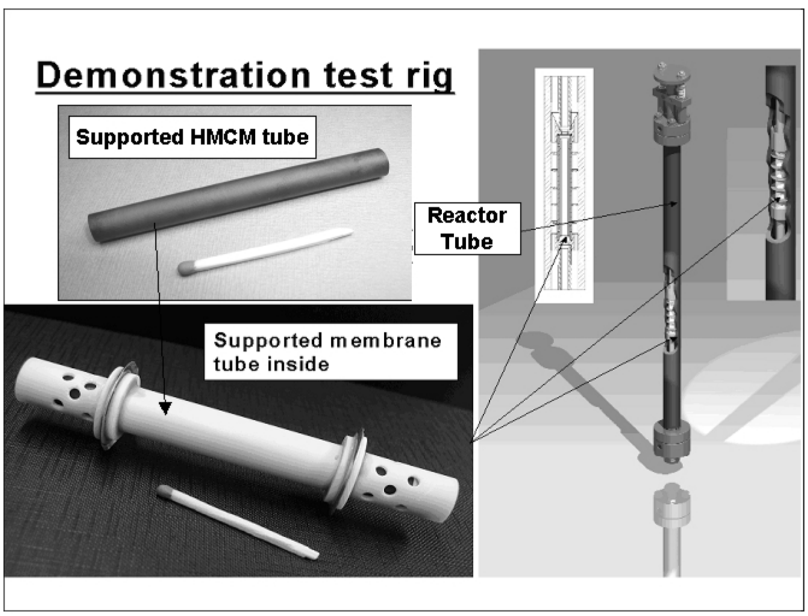

Figure 3: Test reactor with supported membrane tube

REACTOR MODEL

A model of the hydrogen membrane reactor system has been developed, and implemented in Matlab by SINTEF. A kinetic model for methane steam reforming from the literature [8] and a membrane flux equation developed by Hydro has been included (eq.1). J_{mj} is radial flux (kmol/m^2/s) of hydrogen (component j) in membrane (m) P_{rj} and

P_{sj} are the partial pressures (in bar) of component j at the reaction layer side (r) and the support (s) side, respectively.

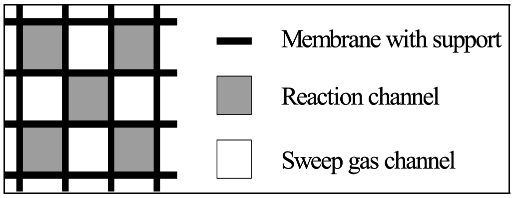

Figure 4: The membrane reactor channels perpendicular to the flow direction

$$J_{mj} = \frac{Q_j}{\delta x_m}\left[\frac{1}{k_1\sqrt{P_{sj}}+1} - \frac{1}{k_1\sqrt{P_{rj}}+1}\right] \qquad (1)$$

Q_j is the permeability and δx_m is the membrane thickness. It is assumed that the membrane has 100% selectivity for hydrogen. Both the permeability Q_j and the constant k_1 depend on the temperature by an Arrhenius type of expression. The modelled reactors consist of small squared channels of reactor and sweep gas compartments with the membrane in between, see Figure 4. The reforming reactions on the methane/steam side generate hydrogen, which passes through the membrane and reacts with oxygen on the air side. The membrane reactor model may be used in both co-current and counter current mode, and the program combines these to modes into a system of two membrane reactors in series, see Figure 2.

As an example Figure 5 depicts the membrane with support for the first membrane reactor, i.e. Methane Steam Reforming (MSR) with air oxidation. On the MSR side, methane and water diffuse into a thin reaction layer where the conversion to H_2, CO and CO_2 takes place. Part of the hydrogen flows through the membrane, and in the support at the other side of the membrane it reacts with oxygen diffusing from the sweep gas. Supposing that the reaction rate between hydrogen and oxygen is almost instantaneous, the reaction will take place in a very small region, just where the oxygen and hydrogen meet each other. This "reaction front" is calculated by the model and will typically start at the membrane surface at the reactor inlet, and then move towards the support surface as the oxygen is being consumed (see Figure 5).

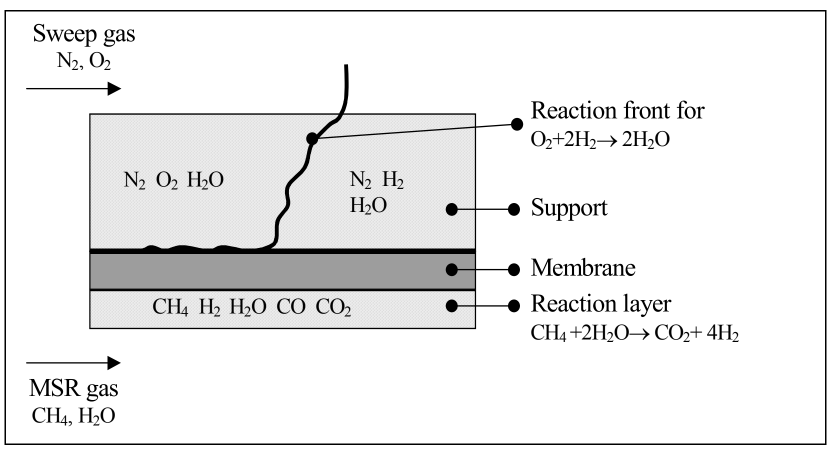

Figure 5: The membrane with support and reaction layer along the flow direction (step 1)

The following main assumptions are made:

- The MSR reactions are assumed to take place in the thin porous layer close to the membrane. This layer is assumed to be catalytic active and potential reactions in the gas phase is disregarded.
- The reaction kinetics of Xu [8] for a Ni/MgAl2O4 catalyst is assumed to be an adequate description of the MSR reactions in the layer. It is only necessary to include an effectiveness factor to cope with the differences in activity.

- Radial concentration or temperature gradients in the thin reaction layer (50 μm) are disregarded in the reaction kinetics calculations. This assumption was supported by estimates showing that radial temperature gradients in membrane and support (approx. 1 mm) will be maximum 1 °C.
- The reaction rate for the oxidation of hydrogen is assumed to be infinite. Consequently, all the hydrogen that permeates through the membrane will react with the oxygen, and as long as the oxygen is not consumed completely, the reaction rate of hydrogen will be equal to the permeation rate. Another consequence is that the reaction will occur in a small reaction front in the support, or in the gas film outside the support.
- Any thermal radiation is neglected in the energy balance. Radiation from one wall to another is disregarded because the temperature at the membrane wall is assumed to be constant at any axial position. The radiation between the membrane and the gas phase is also disregarded.

For most of the thermodynamic calculations the source is the book of Reid et al [9]. Thermodynamic properties for each of the component are collected from the end of this book. The model assumes that the compressibility factor is constant in the reactor

RESULTS FROM THE MATERIALS WORK

A total number of 40 candidate membrane materials were synthesized and characterized and more than 35 hydrogen permeability measurements were performed. Based on the measurements and theoretical evaluations, a main candidate materials system was selected. Measured hydrogen flux data of the selected candidate material are shown in Figure 6. A hydrogen flux model (based on the Wagner equation and solution thermodynamics, see eq. 1) was developed to explore the permeation rates one may expect in actual processes using the selected materials. The model was fitted to the measured flux data of the selected membrane material as shown in Figure 6.

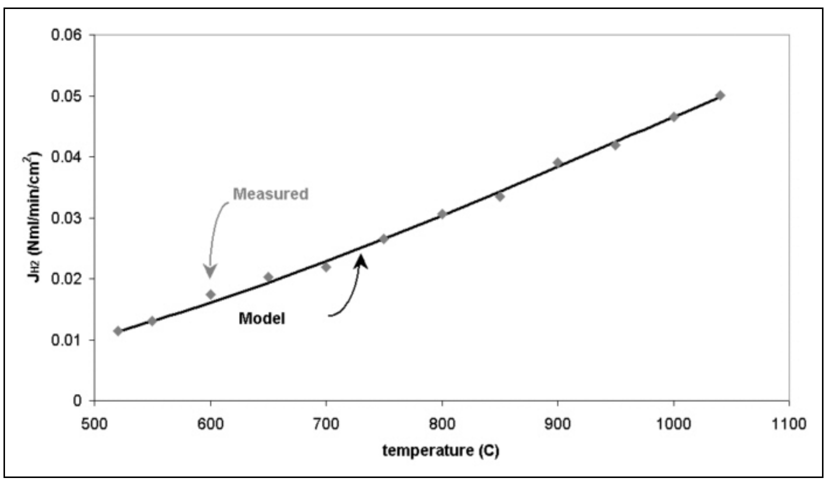

Figure 6: Measured hydrogen flux data of selected candidate material

Disks pressed from very fine powders (0.1-0.2 μm) sintered to gas impervious specimens at 1715°C under thoroughly controlled atmosphere. However, despite using the same powders and sintering conditions, the membrane coatings of the supported tubes did not fully densify to form gas impervious layers. To obtain fully sintered gas impervious coatings, an increase in the sintering temperature without sacrificing atmosphere control is required. Unfortunately we did not have access to suitable high temperature equipment when the tubes were made. Two membrane tubes with approximately 50 μm thick crack free coatings were made. One was tested. The tubes had final dimensions represented by a length of 10 cm, an outer diameter of 8 mm, and a wall thickness of 2 mm (Figure 3).

The test was performed at a temperature of 1000 °C and a pressure of 20 bar. Humidified hydrogen was used at the reactor side (inside of tube) and humidified nitrogen at the sweep side (outside of tube). Since the membrane tube coating was not 100% gas impervious, an overpressure of approximately 50 mbar at the nitrogen side was applied to minimize leakage of hydrogen into the sweep stream. The volume flow data under these conditions calculated from gas chromatography (GC) data as well as total flow measurements are given in the first part of Table 2. To quantify the contribution of hydrogen flux to the total transport, the degree of interdiffusion was checked.

TABLE 2: VOLUME FLOW DATA (Nml/min) FROM FLUX MEASUREMENTS

Type of measurement	Gas specie	Reactor side		Sweep side	
		Inlet	Outlet	Inlet	Outlet
Flux measurement with hydrogen. GC analyses of both gas streams.	H_2	2400	1700-1800	0	600-700
	N_2	0	600-700	3000	2300-2400
	H_2O	600	Not analyzed	600-800	Not analyzed
Leakage correction measurement. GC analyses of sweep side stream.	N_2	1988	2456*	1896	1428
	CO_2	337	326*	0	11
	O_2	0	131*	504	373
Leakage correction measurement. GC analyses of reactor side stream.	N_2	1988	2542	1896	1342*
	CO_2	337	348	0	-11*
	O_2	0	143	504	361*

*Calculated from GC analyses of opposite gas stream.

The quantification of interdiffusion was carried out by flowing a gas mixture of 14.5 vol% CO_2 in N_2 at the reactor side and air at the sweep side under otherwise similar conditions to the measurements with hydrogen. Volume flow data are given in the second and third parts of Table 2. The total transport (leakage) of sweep gas to the reactor side is similar to the run with hydrogen, which is expected when the pressure difference between sweep and reactor side is the same. Also expected is the lower transport of reactor side gas to the sweep gas since there is no flux and since CO_2 and N_2 may diffuse slower than H_2. This difference in transport across the membrane is manifested by a significant increase in total reactor side gas flow and consequently reduction in sweep gas flow. For the quantification of hydrogen diffusion the transport of CO_2 to the sweep side of 11 Nml/min was used as a basis (N=Normal conditions: 22.4 m^3/kmol). This number which is regarded accurate within 30%, is determined from the direct measurement of the CO_2 concentration in the sweep exit gas and the total volume flow of sweep exit gas. The translation of this number to hydrogen diffusion is carried out by the most conservative measure by assuming Knudsen diffusion. In Knudsen diffusion mode the diffusivity of gas molecules are inversely proportional to the square root of their masses. Hence, H_2 is expected to diffuse $\sqrt{(44/2)}$ = 4.7 times faster than CO_2. The transport through diffusion is proportional to the difference in partial pressure of the diffusing specie. In the case of hydrogen the average difference is approximately 0.6 bar, while the difference for CO_2 is 0.14 bar. The expected transport of hydrogen through diffusion is therefore 4.7*(0.6bar/0.14bar)*11Nml/min = 220 Nml/min.

The average value of total hydrogen transport from reactor side to sweep side in the flux measurements is 660 Nml/min. Correcting for the gas diffusion contribution of 220 Nml/min given above, it appears that 440 Nml/min of hydrogen was transported through the membrane by hydrogen flux. By taking account of the membrane area of 25 cm^2, the measured hydrogen flux was 18 Nml/min/cm^2. The measured hydrogen flux then compares favorably with model predictions, yielding 10-15 Nml/min/cm^2 at test conditions.

HYDROGEN MEMBRANE REACTOR MODELLING RESULTS

The reactor model has been used to estimate temperature profiles, concentration profiles, hydrogen flux and required membrane area for the different membrane steps at real membrane reformer process conditions (see Table 3). Hydrogen flux model predictions is based on the atmospheric laboratory tests as described above. Reactor design is based on monolith structures with small channels (see Figure 3) and an area to volume ratio of approximately 700 m^2/m^3. The reactor design is similar to what has been proposed for the AZEP (Advanced Zero Emission Power plant) technology [10]. Target average hydrogen flux was initially set to 5 Nml/min/cm^2 based on an initial in-house economic assessment. Table 3 shows the estimated membrane volume for a 362 MW_{LHV} combined cycle power plant for different membrane thickness and for target H_2 flux inclusive H_2 transport rates (step 1 and 2).

TABLE 3: ESTIMATED MEMBRANE VOLUME FOR A 362 MW_{LHV} POWER PLANT FOR DIFFERENT MEMBRANE THICKNES AND FOR TARGET H_2 FLUX AND INCLUSIVE H_2 TRANSPORT RATES (STEP 1 AND 2)

Membrane thickness (*Target flux and H_2 transferred*)	Membrane Reactor Volume (Step 1)	Membrane Reactor Volume (Step 2)
25 μm	18 m^3	91 m^3
30 μm	20 m^3	102 m^3
50 μm	27 m^3	148 m^3
Target H_2 flux(5 $Nml/cm^2/min$)	35 m^3	82 m^3
Hydrogen transferred (kmol/h)	*3300*	*7700*

This shows that the target hydrogen flux according to the model can be easily achieved in step 1. A membrane thickness close to 20 μm is needed in step 2, which is in the lower range of what can be practically and reliably manufactured. Although the hydrogen flux in step 2 can be increased somewhat by increasing the membrane reactor temperature, the modelling shows that a thin membrane layer will be essential in this step. A membrane thickness of 50 μm on step 1 and 25 μm on step 2 will give a hydrogen flux close to target.

In the modelling it was assumed that the membrane surface is coated with a 50 μm thick porous Steam Methane Reformer catalyst layer. The catalyst activity was varied between 10 and 100% relative to the rate constants given in [5], but this had only minor impact on the required reactor volume.

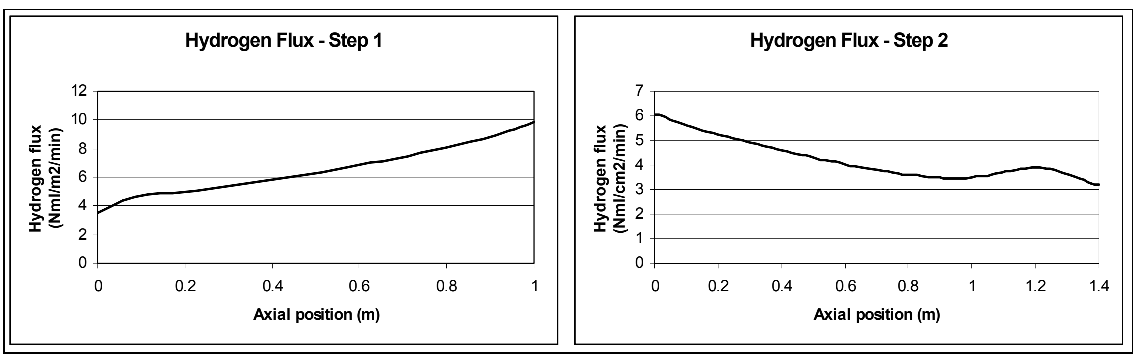

Figure 7: Hydrogen flux Hydrogen Membrane Reformer step 1 and 2

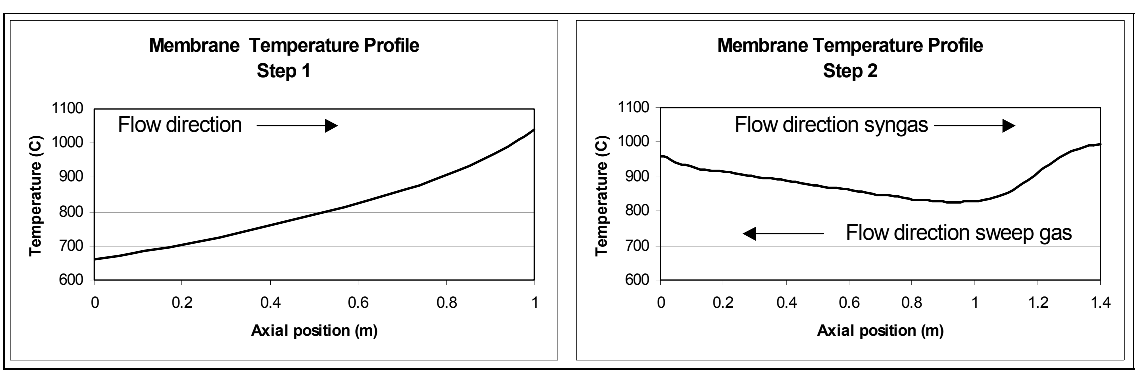

Figure 8: Membrane temperature profiles for step 1 and 2

The modelled flux versus axial position for step 1 and 2 is shown in Figure 7. The relative reformer catalyst activity was set to 50% and the membrane thickness to 50 μm in step 1 and 25 μm in step 2. Corresponding modelled temperature profiles are shown in Figure 8. The heat consuming reforming of methane causes the drop in temperature in the step 2 reactor. In order to avoid substantial temperature drop on step 2 the methane slip from step 1 must be controlled. If the reformed gas from step 1 is far from equilibrium it can be fed to an adiabatic steam reformer (similar to the catalyst bed in an Auto Thermal Reformer – ATR, that is used in conventional ammonia plants). This will prevent the undesirable temperature drop on stage 2.

Figure 9 showing concentration profiles along the axial position at step 2 indicates that most of the methane is converted after 1.2 m. On the sweep gas side the estimates show that a hydrogen concentration exceeding 40% can be achieved which is a perfect gas turbine fuel.

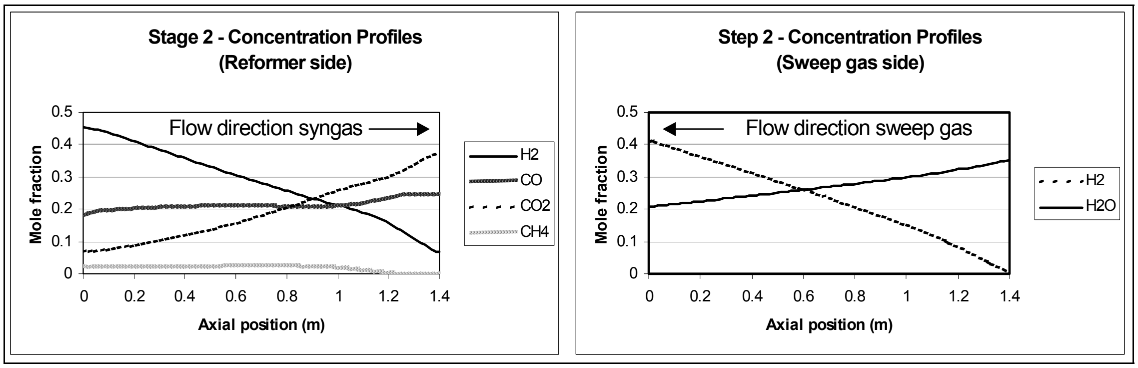

Figure 9: Concentration profiles step 2

The residual syngas oxidation section was simulated using the same geometry as in step 1 and 2. The modelled hydrogen flux is shown in Figure 10 (left side). The concentration profiles (Figure 10 right side) show that most of the CO are converted to CO_2, but there is still about 2% CO left in the residual gas while about 0.5% is an acceptable level.

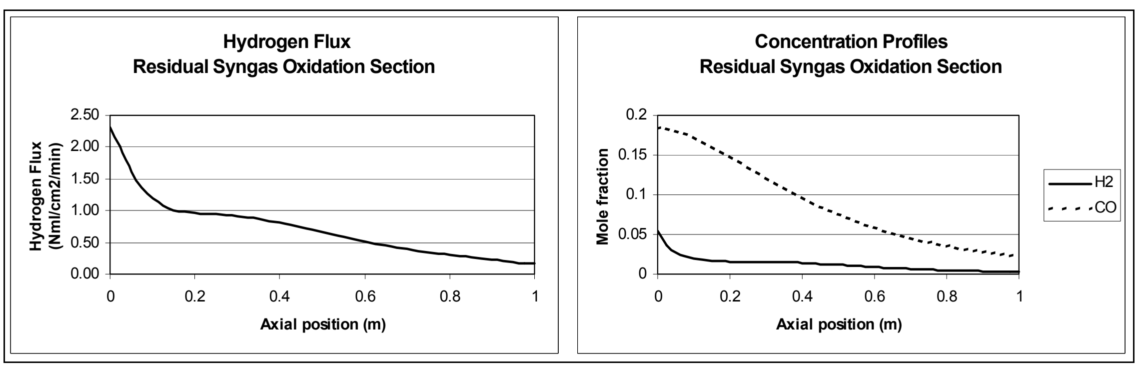

Figure 10: Residual syngas oxidation section. Hydrogen flux and concentration profiles.

DISCUSSION

The high pressure test combined with the laboratory atmospheric tests have shown that the selected HMCM material has the potential for a high hydrogen flux. However, since the tested membrane tube was not gas impervious, improved membranes tubes need to be fabricated and tested to verify the project results. To obtain fully sintered gas impervious coatings, an increase in the sintering temperature without sacrificing atmosphere control is required. A suitable high temperature kiln is purchased and improved tubes will be fabricated in a 6 month CCP extension project started June this year. New high pressure tests will hopefully be performed within the end of 2004.

The reactor modelling has shown that a quite high CO slippage is likely in the HMCM based residual syngas oxidation section for a reasonable reactor size due to low average H_2 flux. In order to improve the driving force for ion transport oxygen transport membranes should be evaluated as an alternative in the next phase of this project

The 50-60% extraction of combustion air from the compressor section of the gas turbine is outside vendor's experience. A next phase of the project should evaluate alternatives that can reduce the amount of extracted air.

CONCLUSIONS

There is significant technical challenge in the membrane development and its integration into a PCDC process, but promising results have been obtained. A ceramic hydrogen mixed conducting membrane (HMCM) for use at high temperatures (700-1100°C) has been developed. Supported membrane tubes have been fabricated and one tube was tested in a pressurized hydrogen flux test rig under relevant process conditions. The measured hydrogen flux compared favorably with model predictions based on the atmospheric laboratory tests. The tested membrane tube, however, was not gas impervious and improved membranes tubes need to be fabricated and tested to verify the project results.

The novel PCDC concept allows close to 100% CO_2 capture and the loss in efficiency is estimated to be only 5%-points compared with a conventional combined cycle power plant without CO_2 capture. The novel hydrogen process will generate a diluted hydrogen fuel containing about 40% H_2, 40% N_2 and 20% H_2O. The low hydrogen concentration in the fuel is a major advantage since this will depress formation of nitric oxides in the combustion chamber.

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