

# Experimental demonstration of the reverse flow catalytic membrane reactor concept for energy efficient syngas production. Part 1: Influence of operating conditions

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## Abstract

In this contribution the technical feasibility of the reverse flow catalytic membrane reactor (RFCMR) concept with porous membranes for energy efficient syngas production is investigated. In earlier work an experimental proof of principle was already provided [Smit, J., Bekink, G.J., van Sint Annaland, M., Kuipers, J.A.M., 2005a. A reverse flow catalytic membrane reactor for the production of syngas: an experimental study. *International Journal of Chemical Reactor Engineering* 3 (A12)], but compensatory heating was required and problems related to the mechanical strength of the powder-based YsZ catalyst and the steel filter were reported. Therefore, in Part 1 the performance of a Rh–Pt/Al<sub>2</sub>O<sub>3</sub> catalyst with improved mechanical strength and porous Al<sub>2</sub>O<sub>3</sub> membranes with excellent temperature resistance was tested in an isothermal membrane reactor. For this purpose a novel sealing technique was developed that could withstand sufficiently high pressure differences and temperatures. Very high syngas selectivities close to the thermodynamic equilibrium could be achieved for a considerable period of time without any increase in pressure drop and without any decrease in syngas selectivity. Using the Rh–Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, several experiments were performed in a RFCMR demonstration unit and the influence of different operating conditions and design parameters on the reactor behaviour was investigated. It is shown that very high syngas selectivities (up to 95%) can be achieved with a maximal on-stream time of 12 h, without using any compensatory heating and despite inevitable radial heat losses. In Part 2 a reactor model is discussed that can well describe the experimental results presented in this part.

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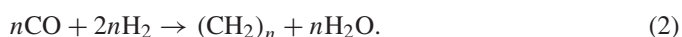
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## 1. Introduction

In the next decades natural gas will become a more and more important energy source in view of the decreasing oil reserves and the rising oil prices. Natural gas is predominantly available at remote locations and therefore it is preferably converted to liquid fuels for use in the transport sector via the so-called gas-to-liquid (GTL) process.

In the GTL process firstly syngas is produced via the partial oxidation of CH<sub>4</sub> with pure O<sub>2</sub> (obtained by cryogenic air

separation), which is subsequently converted to higher hydrocarbons via the Fischer–Tropsch reaction:



GTL processes are currently being commercialised by SasolChevron, Shell and other companies, with which enormous investment costs (about 25,000 US\$/daily barrel) are associated. An important part of both the investment ( $\pm 50\%$ ) and operating costs (i.e., CH<sub>4</sub> losses) of these first generation GTL plants is related to the cryogenic air separation and syngas production units. An alternative air separation and/or heat integration in the syngas unit could substantially reduce these costs for next generation GTL plants.

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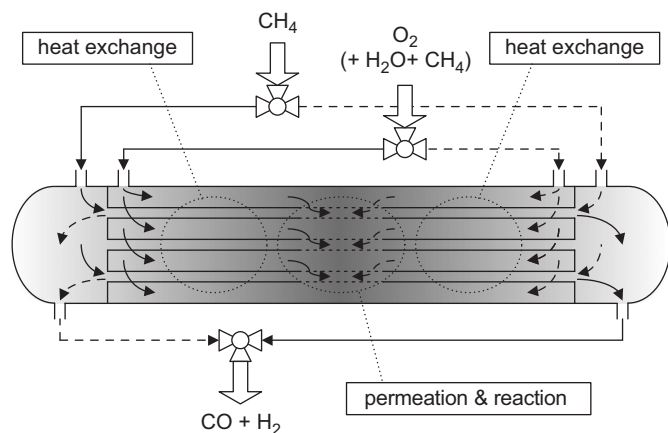


Fig. 1. Schematic overview of the RFCMR concept with porous membranes in a shell-and-tube configuration. The colour gradient represents the axial temperature profile, a darker colour indicates a higher temperature.

In previous contributions we have developed two novel reactor concepts for syngas production via catalytic partial oxidation (CPO) of  $\text{CH}_4$  with improved efficiency. In the first concept, a reverse flow catalytic membrane reactor (RFCMR) with porous membranes, recuperative heat exchange is integrated inside the partial oxidation reactor via the reverse flow concept, resulting in reduced pure  $\text{O}_2$  consumption and higher syngas selectivities (Smit et al., 2005b). Another key feature of this concept is the distributive feeding of  $\text{O}_2$  to  $\text{CH}_4$ , which circumvents problems such as possible formation of hot spots and explosive mixtures that arise when a reverse flow reactor with a premixed feed of  $\text{CH}_4$  and  $\text{O}_2$  would be used for syngas production (Blanks et al., 1990; De Groote and Froment, 1996; Gosiewski et al., 1999; Gosiewski, 2000, 2001). A porous membrane reactor with distributive feeding of  $\text{O}_2$  was proposed and studied experimentally by Alibrando et al. (1997), but for limited temperatures and accordingly also limited syngas selectivities were obtained.

In the second RFCMR concept, also air separation is integrated using  $\text{O}_2$  perm-selective perovskite membranes rather than porous membranes (Smit et al., 2003), which avoids the need of a very expensive air separation unit. Although this concept has a higher cost saving potential, there are still important issues that need to be resolved with respect to temperature control (Zhang et al., 2007; Smit et al., 2007), and the chemical and mechanical stability of the perovskite membranes.

In Fig. 1, a schematic overview of the RFCMR concept with porous membranes is presented, in which the  $\text{O}_2$  and syngas compartments are arranged in a shell-and-tube configuration. Obviously, also other configurations could be considered provided that a good heat transfer between the compartments can be achieved. The  $\text{O}_2$  and syngas compartments are separated by a porous membrane in the centre of the reactor and impermeable walls at the in- and outlets. The gas streams are fed co-currently to the compartments and the flow directions are periodically alternated to create the reverse flow behaviour. At the centre, the syngas compartment is filled with catalyst for the partial oxidation reaction, while at the in- and outlet of this

compartment inert material is positioned for additional heat capacity and to prevent back-reactions.

To control the temperature in the centre of the RFCMR, some steam is co-fed with the  $\text{O}_2$ , which is used for endothermic steam reforming in order to counterbalance the reaction heat of exothermic partial oxidation reactions and increase the syngas yield. Furthermore, to establish the plateau temperature outside the membrane section, also a small amount of  $\text{CH}_4$  is added to the  $\text{O}_2$  feed, which is combusted just before the membrane section over a combustion catalyst. Via modelling (Smit et al., 2005b) and experimental (Smit et al., 2005a) studies the conceptual and technical feasibility of this RFCMR concept was already demonstrated.

In this contribution the technical feasibility of the RFCMR concept with porous membranes/filters is further investigated. In earlier work an experimental proof of principle has been given (Smit et al., 2005a), but compensatory heating was required and problems related to the mechanical strength of the powder-based Rh/YsZ (Ytria stabilised Zirconia) catalyst as well as to the steel filter were reported. Therefore, in Part 1 firstly the performance of a Rh-Pt/ $\text{Al}_2\text{O}_3$  catalyst with improved mechanical strength will be tested in an isothermal membrane reactor. Furthermore, in this set-up  $\text{Al}_2\text{O}_3$  membranes will be tested, which have an excellent temperature resistance. A novel sealing procedure to connect the membrane to the support tubes will be discussed, which can withstand high temperatures and reasonable pressure differences.

Subsequently, new experimental results of the RFCMR demonstration unit will be presented to investigate the influence of different operating conditions on the reactor performance. For these experiments, an IR/TCD analyser has been used that allowed for on-line measuring of the syngas composition due to its short analysis time, which was not possible with the Micro-GC used in the previous study (Smit et al., 2005a). Furthermore, in the present study no compensatory heating was required due to increased flow rates and improved catalyst performance compared to the previous study.

In Part 2 of this contribution, a reactor model will be developed that can describe the experimental results presented in this first part.

## 2. Experimental set-up and procedures: isothermal membrane reactor

A shell-and-tube membrane reactor was constructed, consisting of an  $\text{Al}_2\text{O}_3$  shell ( $\text{OD} \times \text{ID} \times L = 26 \times 18 \times 500$  mm) and a ceramic porous membrane, which was filled with a CPO catalyst and connected to two  $\text{Al}_2\text{O}_3$  support tubes ( $\text{OD} \times \text{ID} \times L = 12 \times 9 \times 400$  mm) that were filled with dense  $\text{Al}_2\text{O}_3$  particles (3 mm spheres). A detailed flow-sheet of the experimental set-up is given in Fig. 2. The shell was placed in a special 3-zone oven (Elicra, 2 kW) with a very flat temperature profile in the central zone.  $\text{CH}_4$  was fed to the tube and air to the shell compartment. Air was used instead of pure  $\text{O}_2$  for safety reasons, but the dilution by inert  $\text{N}_2$  does not affect the conclusions drawn from the experimental results in a qualitative

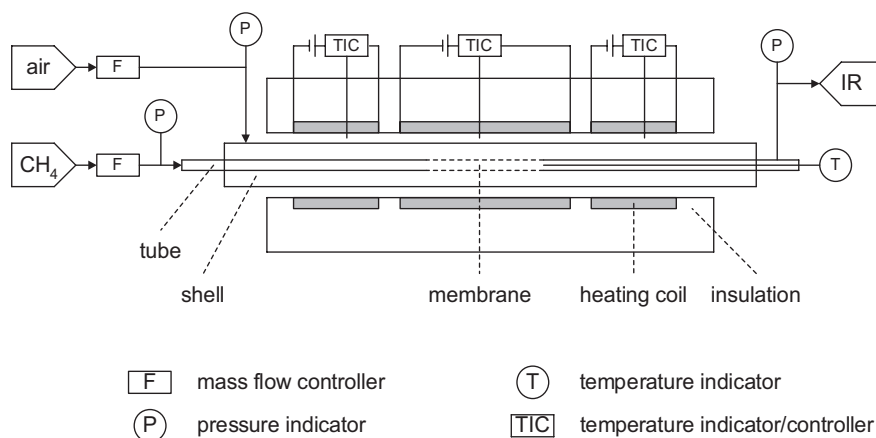


Fig. 2. Flow-sheet of the isothermal membrane reactor experimental set-up.

sense. The gas feed flow rates were controlled with mass flow controllers (Brooks Instruments, 5850s; Bronkhorst, F201).

To measure the temperature at the end of the catalyst bed, a thermocouple (Rössel, k-type, OD  $\times$  L = 1.6  $\times$  500 mm) was placed inside the tube. Pressures were measured with analog transmitters (Econosto) and the pressure at the tube outlet was regulated at about 1.3 bar in order to provide for a sufficiently large flow rate to the gas analysis equipment. The gas composition was analysed with an IR/TCD-analyser (Sick-Maihak, s710) equipped with two modules. The first module was a Multor (IR), which measures the CH<sub>4</sub> (0–5%), CO (0–20%) and CO<sub>2</sub> (0–5%) mole fractions. The analysis time of this module was about 24 s (non-synchronous). The second module was a Thermor (TCD), which enabled the measurement of the H<sub>2</sub> mole fraction with very high temporal resolution. Before feeding the tube outlet stream to the IR/TCD analyser, the syngas was passed through an ice-cooled condenser to prevent water condensation in the IR/TCD analyser.

To distributively feed the air to the CH<sub>4</sub>, a porous Al<sub>2</sub>O<sub>3</sub> membrane provided by Membraflow was used, consisting of a macro-porous support (OD  $\times$  ID  $\times$  L = 11  $\times$  6.5  $\times$  120 mm) coated with a micro-porous layer (thickness of 23  $\mu$ m, average pore size of 150 nm) on the inside. This membrane was selected due to its excellent resistance to high temperatures. The micro-porous layer provided for a reasonable but not too large pressure difference over the membrane (relative to the axial pressure drop inside the membrane), so that the air could indeed be fed distributively to the CH<sub>4</sub>. The permeability as specified by Membraflow is 300 000 l/h/bar/m<sup>2</sup> (STP), which was confirmed with separate permeability experiments.

To establish a gas-tight connection between the support tube and the membrane a special sealing technique was developed. The ends of the support tube and membrane were conically polished and in the spare space between the membrane and the support tube a special glass sealing with a high melting temperature (Schott, 8252) was applied (see Fig. 3). The principle of the sealing technique is that when an over-pressure is applied in the shell compartment, the viscous glass will be pushed into the very small space between the membrane and the support tube.

Because this space is very small and due to the conically polished ends, no glass can slip through, thereby effectively preventing gas leakage. In the sealing procedure, firstly the glass was crushed and milled to a powder with an average particle size of 64  $\mu$ m, which was suspended in alcohol. The suspension was then applied into the spare space between the membrane and the support tube. The membrane and support tube were placed in an oven, which was heated up slowly (5  $^{\circ}$ C/min) to 1100  $^{\circ}$ C. After sealing for 1 h the oven was cooled down again. The sealing was found to be gas tight for temperatures up to 1000  $^{\circ}$ C and a pressure difference of 1.5 bar for several hours (longer periods of time were not investigated).

CPO catalysts have been extensively researched in the last decades (e.g. York et al., 2003), but not many CPO catalysts in the form of spherical particles (or pellets) are offered commercially. At the scale at which CPO is carried out in this study (undiluted feeds, high flow rates), it is essential that, besides a high activity and high selectivities towards CO and H<sub>2</sub>, the CPO catalyst also has a sufficient mechanical strength and high-temperature resistance to prevent fracture of the particles. Furthermore, coke formation on the catalyst should be very limited to avoid blocking of the reactor.

In previous work (Smit et al., 2005a) a powder-based Rh/YSZ catalyst was used, which gave high CO and H<sub>2</sub> selectivities as well as minimal coke formation, but the mechanical strength of this catalyst was poor leading to particle break-up and a continuously increasing pressure drop during the experiments. To circumvent these problems, also a commercial Pt/Al<sub>2</sub>O<sub>3</sub> combustion catalyst (3 mm spheres) from Engelhard (Escat 26) was tested. According to the specifications, the Pt loading is 0.5 wt% and the specific surface area 80 m<sup>2</sup>/g. This catalyst was found to have a good mechanical strength, high-temperature resistance and minimal coke formation, but the CO and H<sub>2</sub> selectivities were unacceptably low. Therefore, the Pt/Al<sub>2</sub>O<sub>3</sub> particles were crushed and sieved to obtain particles of 1.4–2 mm, which were then impregnated with an aqueous RhCl<sub>3</sub> solution to obtain a Rh loading of 1 wt%. This catalyst gave very satisfactory results, as will be discussed in the next section.

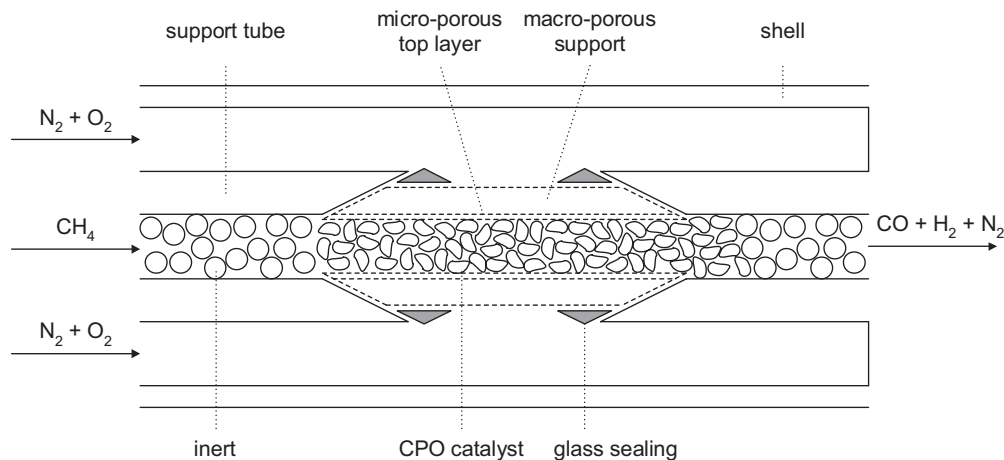


Fig. 3. Detailed drawing of the isothermal membrane reactor.

It might be argued that by impregnation of the particles the Rh might not be as well distributed inside the particles as in the powder-based particles of the Rh/YsZ catalyst and that the Rh is mainly located on the particle surface. However, this is not necessarily a disadvantage, but rather an advantage, because of the generally very low particle effectiveness factors of CPO catalysts due to intra-particle diffusion limitations (e.g. Smit et al., 2005b), so that only the active sites close the catalyst outer surface can be effectively used.

### 3. Experimental results: isothermal membrane reactor

With the isothermal membrane reactor, experiments were carried out to study the performance of the Rh/Al<sub>2</sub>O<sub>3</sub> catalyst at different feed flow rates of air and CH<sub>4</sub> (maintaining stoichiometric feeds) and different temperatures.

#### 3.1. Syngas composition

In Fig. 4 the dry syngas composition normalised to the CH<sub>4</sub>, CO, CO<sub>2</sub> and H<sub>2</sub> mole fractions (thus excluding N<sub>2</sub>) is given as a function of the measured temperature at the end of the catalyst bed for CH<sub>4</sub> feed flow rates of 0.5 and 1 l/min (STP). Also included in this figure are the equilibrium compositions calculated with a Gibb's free energy minimisation method discussed elsewhere (Smit et al., 2004). Because air was used instead of pure O<sub>2</sub>, also N<sub>2</sub> was taken into account in these calculations. However, solid carbon was not taken into account, because hardly any coke formation was observed during the experiments as will be discussed in more detail later.

The CO and H<sub>2</sub> mole fractions in Fig. 4 are very close to the equilibrium values for both flow rates and the CO<sub>2</sub> mole fractions are slightly below the equilibrium values. This is also reflected in the CO selectivity, defined as

$$S_{\text{CO}} = \frac{x_{\text{CO}}}{x_{\text{CO}} + x_{\text{CO}_2}}, \quad (3)$$

which is given in Fig. 5 as a function of the temperature measured at the end of the catalyst bed. The CO selectivity is above

the equilibrium value for all temperatures and exceeds 95% already at 1000 K. The H<sub>2</sub>/CO ratio is slightly above 2 and very close to the equilibrium value (Fig. 5), indicating that also the H<sub>2</sub> selectivity, defined as

$$S_{\text{H}_2} = \frac{x_{\text{H}_2}}{x_{\text{H}_2} + x_{\text{H}_2\text{O}}}, \quad (4)$$

is at least as high as the CO selectivity.

The measured CH<sub>4</sub> mole fractions given in Fig. 4 are above the equilibrium value and accordingly the CH<sub>4</sub> conversions, defined as

$$\zeta_{\text{CH}_4} = \frac{x_{\text{CO}} + x_{\text{CO}_2}}{x_{\text{CH}_4} + x_{\text{CO}} + x_{\text{CO}_2}}, \quad (5)$$

are lower than the equilibrium conversions (Fig. 5), but this is attributed mainly to a small mismatch in the CH<sub>4</sub> and air feed flow rates, since the differences between the measured and equilibrium values are almost constant and independent of temperature.

The mismatch in the CH<sub>4</sub> and air feed flow rates was confirmed by calculating the O<sub>2</sub>/CH<sub>4</sub> ratio from the overall C, H and O mass balances at the tube outlet. In these calculations it was assumed that all CH<sub>4</sub> consumed was converted to CO and CO<sub>2</sub> and furthermore that all O<sub>2</sub> was converted. These assumptions were verified by analysis with a Micro-GC. For a CH<sub>4</sub> feed flow rate of 0.5 l/min (STP), the calculated O<sub>2</sub>/CH<sub>4</sub> ratio was about 0.46–0.47 and for 1 l/min (STP) the calculated O<sub>2</sub>/CH<sub>4</sub> ratio was typically 0.47–0.48, which explains why the CH<sub>4</sub> conversions are somewhat higher for a flow rate of 1 l/min (STP) than for 0.5 l/min (STP). Concluding, the reactor effluent was very close to its thermodynamic equilibrium.

#### 3.2. Discussion

In the experiments a maximal CH<sub>4</sub> feed flow rate of 1 l/min (STP) was used, whereas the catalyst mass was 3.86 g. This corresponds to a gas hourly space velocity (GHSV), defined as the volumetric flow rate of reactants divided by the catalyst volume, of  $1.5 \times 10^4 \text{ h}^{-1}$ . Hohn and Schmidt (2001) obtained

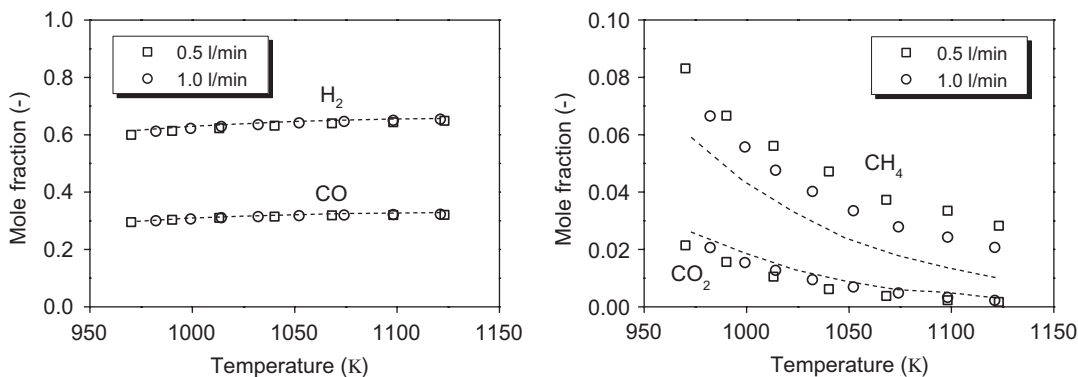


Fig. 4. Measured (markers) and equilibrium (dashed line) dry outlet mole fractions of CO, H<sub>2</sub> (left) and CH<sub>4</sub>, CO<sub>2</sub> (right) as a function of the temperature in the isothermal membrane reactor for different CH<sub>4</sub> flow rates.

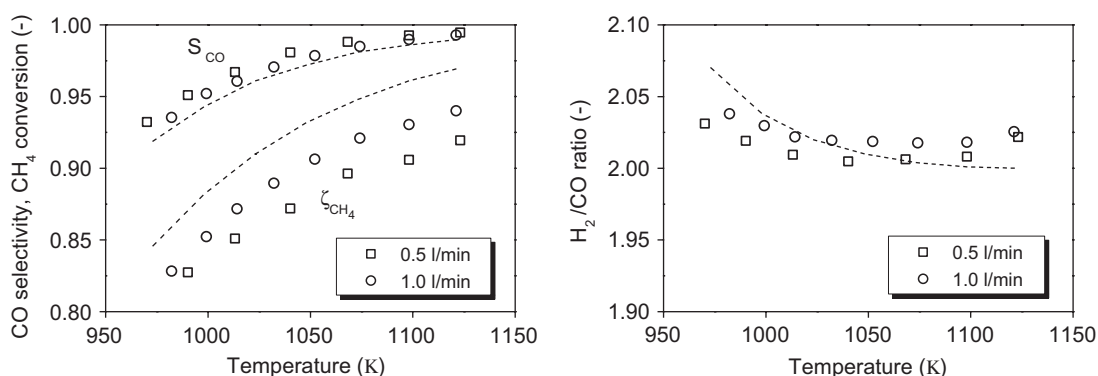


Fig. 5. Measured (markers) and equilibrium (dashed line) CO selectivity, CH<sub>4</sub> conversion (left) and H<sub>2</sub>/CO ratio (right) as a function of the temperature in the isothermal membrane reactor for different CH<sub>4</sub> flow rates.

reasonably high H<sub>2</sub> and CO selectivities using Rh impregnated Al<sub>2</sub>O<sub>3</sub> spheres as catalyst for GHSVs as high as  $1 \times 10^6 \text{ h}^{-1}$ , but their Rh loading was more than a factor of 10 higher and moreover in their experiments equilibrium compositions were not yet reached. Since the syngas compositions obtained in this study are virtually at equilibrium, probably even higher flow rates and GHSVs could have been used while retaining the high CO and H<sub>2</sub> selectivities, but this was not possible due to the pressure limitations of the experimental set-up. To increase the GHSV without increasing the axial pressure drop inside the membrane and the pressure difference over the membrane, larger particles and membranes with higher permeabilities should be used. Obviously the optimal Rh loading, catalyst geometry and membrane permeability have to be optimised for industrial applications.

The experimental set-up was operated continuously for over 7 h with negligible increases in the pressure difference over the membrane and the axial pressure drop over the catalyst bed during the experiments, demonstrating the high-temperature resistance and mechanical strength of the Rh–Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, the porous Al<sub>2</sub>O<sub>3</sub> membrane and the glass sealing. Also the obtained syngas compositions were very reproducible. Obviously, longer on-stream times are required to fully assess the technical feasibility. Some minor coke formation was observed

on the Rh–Pt/Al<sub>2</sub>O<sub>3</sub> catalyst at the beginning of the catalyst bed, probably due to CH<sub>4</sub> cracking:



Also on the “inert” Al<sub>2</sub>O<sub>3</sub> particles some coke formation was observed just after the end of the catalyst bed, which is probably due to the Boudouard reaction:



To prevent coke formation, the inert Al<sub>2</sub>O<sub>3</sub> could be replaced by SiC particles, whereas YsZ might be used as support for the CPO catalyst. Alternatively, the coke could be burned off periodically.

#### 4. Experimental set-up and procedures: RFCMR demonstration unit

The demonstration unit that was used to study the technical feasibility of the RFCMR concept with porous membranes/filters previously, was also used for the present study. It consists of single shell-and-tube configuration and a flow-sheet is provided in Fig. 6. A detailed description can be found in Smit et al. (2005a).



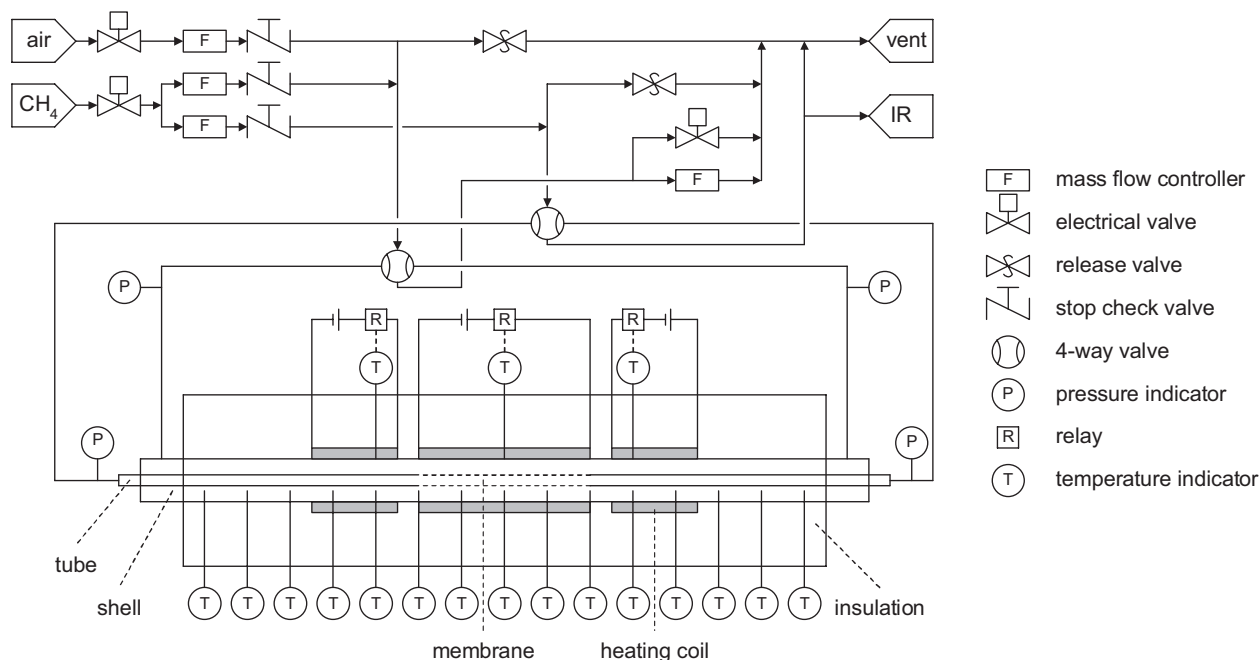


Fig. 6. Flow-sheet of the RFCMR demonstration unit.

Although porous Al<sub>2</sub>O<sub>3</sub> membranes were successfully applied in the isothermal membrane reactor, it proved to be very difficult to implement these membranes and the Al<sub>2</sub>O<sub>3</sub> support tubes in the RFCMR demonstration unit. The difficulty is mainly related to the differences in mechanical properties between Al<sub>2</sub>O<sub>3</sub> and stainless steel. Al<sub>2</sub>O<sub>3</sub> is very rigid and also quite fragile, so that the tube has to be placed very precisely into the shell to avoid any stresses. Furthermore, the presence of particles (inert particles and combustion catalyst particles) in the shell compartment leads to additional radial stresses.

To circumvent the mechanical problems of ceramic tubes, steel filters were used as an alternative because of their superior mechanical strength and flexibility. Furthermore, they do not require a high-temperature sealing but can simply be welded to stainless steel (AISI 316) support tubes, which greatly simplifies the assembly. Firstly, sintered metal filters made from high-temperature resistant steel (Inconel 600, Hastelloy X; purchased from GKN-filters) were tested. However, these filters sintered over time, resulting in a continuously increasing pressure difference over the filter. As a result the on-stream time was limited to only a few hours before the maximal allowed pressure in the shell compartment was reached.

As an alternative to the sintered metal filters, a filter was developed consisting of a high-temperature resistant steel tube (Inconel 600, OD × ID × L = 10 × 8 × 200 mm) in which a number (96) of tiny holes (diameter of 0.2 mm) were made with a laser. The filter was filled with the Rh/Al<sub>2</sub>O<sub>3</sub> catalyst particles described in Section 2 and the steel support tubes were filled with inert particles (3 mm Al<sub>2</sub>O<sub>3</sub> spheres). The shell compartment was filled with inert parti-

cles (3 mm Al<sub>2</sub>O<sub>3</sub> spheres) at the in- and outlet and 0.5 wt% Pt/Al<sub>2</sub>O<sub>3</sub> combustion catalyst particles (3 mm spheres) in the centre.

In this study the syngas composition was analysed with an IR/TCD-analyser (as described in Section 2), with which the H<sub>2</sub> mole fraction could thus be followed with high temporal resolution during a cycle. In previous work (Smit et al., 2005a) a Micro-GC was used, with which only one sample could be analysed during a cycle, because of the much longer analysis time of the Micro-GC compared to that of the IR/TCD-analyser.

A disadvantage of using an IR/TCD-analyser is that the mole fractions of CH<sub>4</sub>, CO and CO<sub>2</sub> can only be measured with intervals of 24 s (non-synchronous). As a result, dips and peaks in these mole fractions due to switching losses (caused by combustion of part of the produced syngas at the moment of switching of the flow direction and also by unconverted CH<sub>4</sub>) might or might not be present around the moment of switching of the flow direction. To avoid misinterpretation, the measured values for CH<sub>4</sub>, CO and CO<sub>2</sub> during the first 40 s of the semi-cycle have been omitted from the figures presented in the next section.

Because of the large radial heat losses of the small-scale demonstration unit, much larger air feed flow rates are required to create the desired trapezoidal temperature profile than would be required for an industrial scale reactor (Smit et al., 2005a). Due to pressure drop limitations in the tube compartment, it was not possible to increase the CH<sub>4</sub> feed flow rate to the tube compartment accordingly and therefore it was necessary to use a by-pass flow at the shell outlet, which was controlled by a separate mass flow controller. Since air is used instead of pure O<sub>2</sub> for safety reasons, the mismatch in flow rates to the

shell and the tube is even larger, because the steepness of the temperature fronts and the height of the plateau temperature in the reverse flow section of the reactor are dependent on the total flow rate in the shell. At industrial scale dead-end permeation can be used, as was demonstrated by Smit et al. (2005b).

Although in principle the CPO reaction is slightly exothermic, the released reaction heat is small compared to the radial heat losses. Furthermore, since a relatively large amount of CH<sub>4</sub> is combusted in the shell compartment to compensate the radial heat losses, considerable amounts of CO<sub>2</sub> and H<sub>2</sub>O flow through the filter to the tube compartment, so that the heat produced by the partial oxidation is counterbalanced by the endothermic CO<sub>2</sub> and H<sub>2</sub>O reforming of CH<sub>4</sub> and additional syngas is produced:



For isothermal operation at industrial scale, a molar H<sub>2</sub>O/O<sub>2</sub> ratio of about 0.25 is required in the shell feed (see Smit et al., 2005b). Because of the increased CH<sub>4</sub> mole fraction in the air feed due to the radial heat losses, the molar (CO<sub>2</sub> + H<sub>2</sub>O)/O<sub>2</sub> ratio in the shell compartment just after the combustion section is also about 0.25. Therefore, it was not necessary to add any additional H<sub>2</sub>O to the air feed to avoid runaways.

Regarding the self-sustainability of the RFCMR demonstration unit, it was found that for a sufficiently large permeation rate through the filter of 10 l/min (STP) and an accompanying CH<sub>4</sub> feed flow rate to the tube of about 4 l/min (STP), no compensatory heating was required to maintain stable reactor operation and to achieve high syngas selectivities. In the previous study (Smit et al., 2005a), compensatory heating was required due to the lower flow rates.

## 5. Experimental results: RFCMR demonstration unit

With the RFCMR demonstration unit numerous experiments were carried out at different operating conditions, where the switching time, the length of the combustion catalyst section, the CH<sub>4</sub> fraction in the air feed and the total air feed flow rate were varied. Furthermore, the influence of compensatory heating was investigated.

### 5.1. Operating conditions and time-averaged results

The operating conditions of the cases studied are listed in Table 1. The different cases have been labelled starting from F to distinguish them from the experimental results that were obtained by operating the demonstration unit as a conventional reverse flow reactor (Smit et al., 2005a), which will also be used to validate the reactor model in Part 2.

The dry syngas compositions that were measured at the tube outlet of the demonstration unit in the cyclic steady-state (after at least 7200 s) for cases F–K are given as a function of time during several semi-cycles in Fig. 7. In Fig. 8 the accompanying axial temperature profiles that were measured in the

Table 1  
Operating conditions used in the RFCMR demonstration unit for cases F–K

Case	F	G	H	I	J	K
$L_{\text{Pt}/\text{Al}_2\text{O}_3}$ (m)	0.42	0.42	0.42	0.42	0.30	0.30
$t_{\text{switch}}$	240	120	240	240	120	240
$T_{\text{feed}}$ (K)	298	298	298	298	298	298
$T_{\text{heating}}$ (K)	off	off	off	1023	off	off
$x_{\text{CH}_4, \text{in}}^{\text{S}}$	0.01	0.01	0.02	0.01	0.01	0
$\phi_{\text{v, by-pass}}^{\text{S}}$ (l/min, STP)	15	15	15	15	15	0
$\phi_{\text{v, CH}_4, \text{in}}^{\text{I}}$ (l/min, STP)	4.0	4.0	3.8	4.0	4.0	4.2
$\phi_{\text{v, total, in}}^{\text{S}}$ (l/min, STP)	25	25	25	25	25	10

demonstration unit are presented at the end of a forward and backward semi-cycle. The CH<sub>4</sub>, CO, CO<sub>2</sub> and H<sub>2</sub> mole fractions were again normalised by excluding N<sub>2</sub>.

In Table 2 the time-averaged CH<sub>4</sub>, CO, CO<sub>2</sub> and H<sub>2</sub> mole fractions are given for each case. The mole fractions were time-averaged over multiple semi-cycles, but the first 40 s of every semi-cycle were not included, thus excluding switching losses. Furthermore, also the CO and H<sub>2</sub> selectivities, the overall O<sub>2</sub>/CH<sub>4</sub> ratios in the feeds, the H<sub>2</sub>/CO ratios, the CH<sub>4</sub> conversions and the switching losses have been included in Table 2. The CO selectivities, H<sub>2</sub>/CO ratios and CH<sub>4</sub> conversions were directly calculated from the measured tube outlet compositions, whereas the H<sub>2</sub> selectivities and O<sub>2</sub>/CH<sub>4</sub> ratios in the feeds were calculated from the element mass balances at the tube outlet (see Section 2). The switching losses were calculated by comparing the time-averaged H<sub>2</sub> mole fraction of the entire semi-cycle and the time-averaged H<sub>2</sub> mole fraction of the entire semi-cycle minus the first 40 s.

From Table 2 and Fig. 7 and 8 it can be concluded that for almost every case very high syngas selectivities, high CH<sub>4</sub> conversions and ideal H<sub>2</sub>/CO ratios can be achieved even with plateau temperatures as low as 1000 K. Furthermore, no hot spots were observed in the filter section, while steep temperature gradients are located outside the filter section, resulting in low temperatures at the in- and outlet. The influence of the different operating conditions on the obtained results will now be discussed in more detail below.

### 5.2. Effect of switching time

Comparing cases F and G, it is observed that a shorter switching time gives somewhat higher CO and H<sub>2</sub> selectivities and a higher CH<sub>4</sub> conversion because of the somewhat higher plateau temperature, but the differences are small. More importantly, shorter switching times give higher switching losses. For a switching time of 120 s (case G) the switching losses are 2.27%, but for a switching time of 240 s (case F), the switching losses reduce to 1.26%. Since the movement of the temperature profile is relatively small, even longer switching times could be used with even lower switching losses. Furthermore, two 3-way valves could be used instead of one 4-way valve to switch the flow direction in the tube compartment, so that the dead volumes between the tube in- and outlet and the 4-way valve are eliminated.

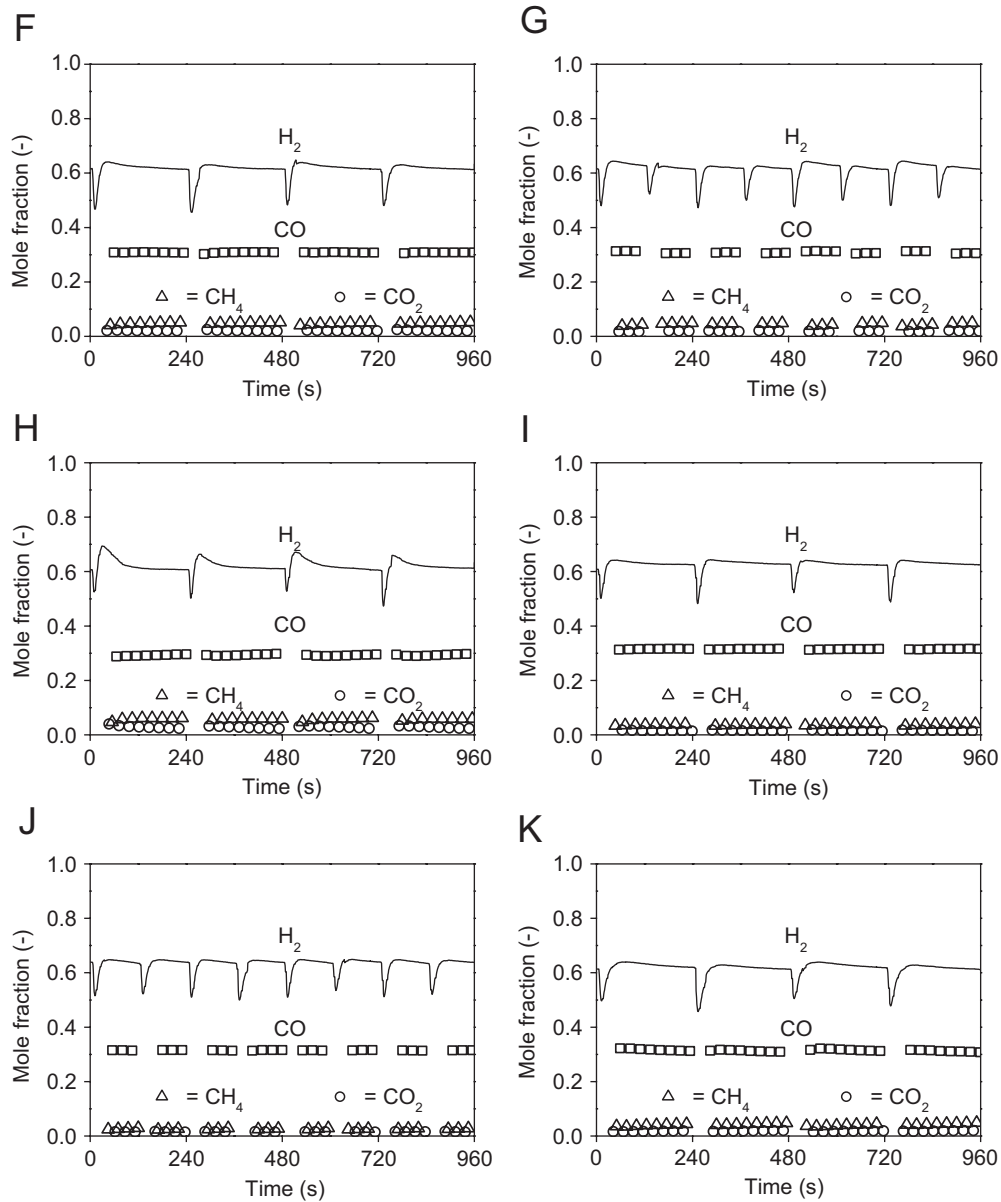


Fig. 7. Measured (dry), normalised mole fractions at the tube outlet of the RFCMR demonstration unit as a function of the time for cases F–K. See Table 1 for the operating conditions.

### 5.3. Effect of amount of $\text{CH}_4$ added to the air feed

With respect to the influence of the  $\text{CH}_4$  fraction in the air feed, it is observed that a higher  $\text{CH}_4$  fraction (case H) gives much higher temperature peaks just before the beginning of the filter, leading to significantly higher  $\text{H}_2$  fractions at the beginning of a semi-cycle compared to the remainder of the semi-cycle, which explains the very low switching losses that were calculated. Surprisingly, the CO selectivity and  $\text{CH}_4$  conversion measured for case H are the lowest of all cases studied, whereas the  $\text{H}_2/\text{CO}$  ratio is the highest and also the  $\text{H}_2$  selectivity is very high. The most likely explanation for these observations is that inside the filter,  $\text{CH}_4$  and  $\text{O}_2$  are primarily converted via the very fast CPO reaction (Eq. (1)), whereas the  $\text{CO}_2$  and  $\text{H}_2\text{O}$

produced during the  $\text{CH}_4$  combustion in the air compartment are converted via  $\text{CO}_2$  (Eq. (8)) and  $\text{H}_2\text{O}$  (Eq. (9)) reforming of  $\text{CH}_4$ , respectively.  $\text{CO}_2$  reforming is much slower than the CPO and  $\text{H}_2\text{O}$  reforming reactions and apparently the residence time in the filter was too short to convert all  $\text{CO}_2$ .

### 5.4. Effect of compensatory heating

As discussed earlier, the radial heat losses in the demonstration unit severely affect the reverse flow behaviour of the reactor. However, in previous work (Smit et al., 2005b) it was found that the temperature profiles in the reverse flow section and the membrane section are established relatively independently. To assess the importance of the radial heat losses in



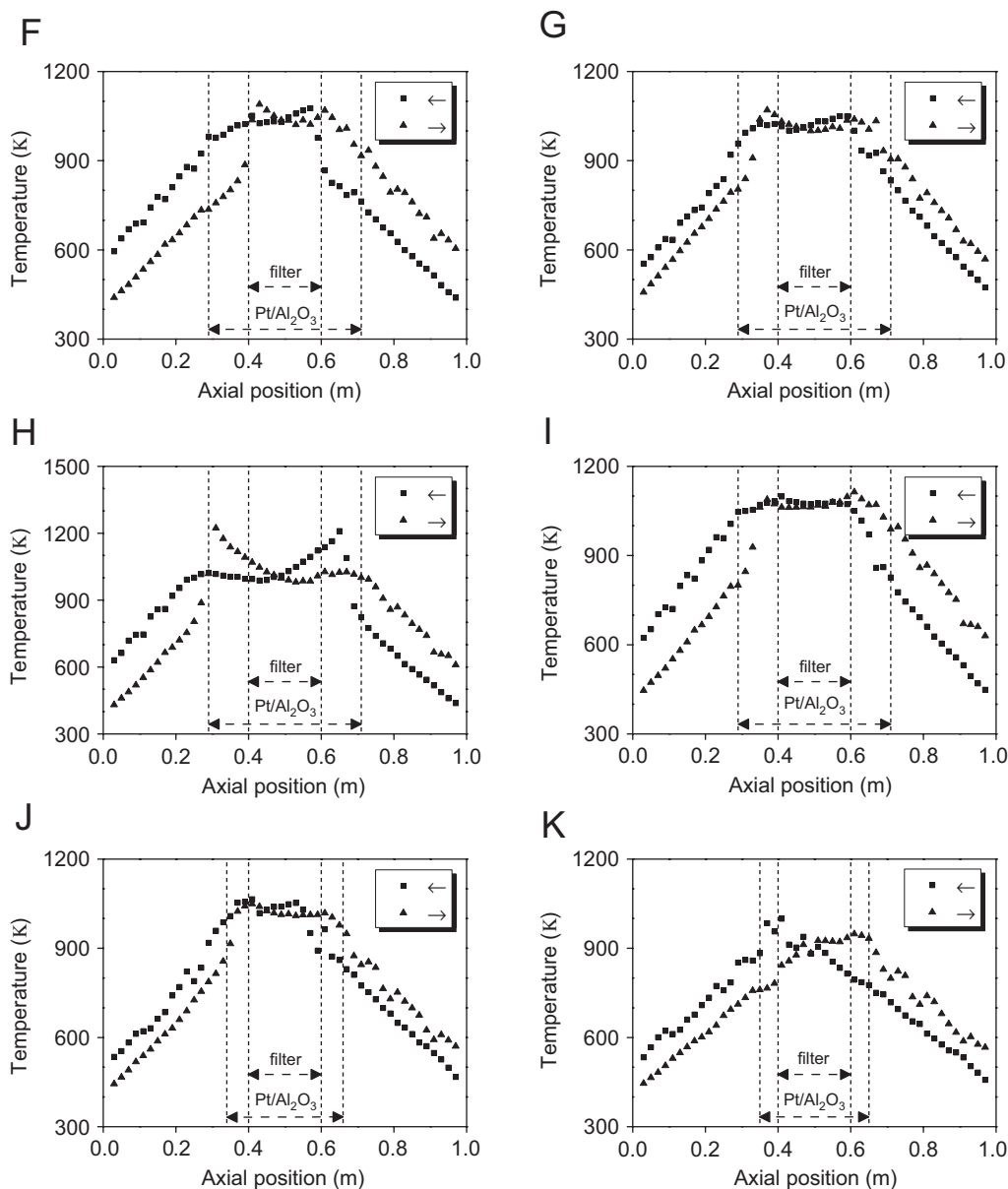


Fig. 8. Measured axial temperature profiles in the RFCMR demonstration unit at the end of forward ( $\rightarrow$ ) and backward ( $\leftarrow$ ) semi-cycle for cases F–K. “Pt/Al<sub>2</sub>O<sub>3</sub>” indicates the location of the combustion catalyst and “filter” the location of the metal filter with the Rh–Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. See Table 1 for the operating conditions.

the filter section, also an experiment was carried out in which compensatory heating along the filter was used.

For case F the temperature measured just outside the shell wall in the (axial) centre of the reactor was typically about 925 K, which is considerably lower than the plateau temperature at the tube wall (about 1050 K), indicating quite steep radial temperature gradients. In case I identical operating conditions to those in case F were used, but the central heating coil was controlled in such a way that a temperature of 1025 K was established just outside the shell wall in the (axial) centre of the reactor. The resulting temperature plateau observed for case I is about 100 K higher than for case F and accordingly also the CO and H<sub>2</sub> selectivities and CH<sub>4</sub> conversion are higher. Obviously,

additional compensatory heating or absence of radial heat losses in the case of an industrial scale reactor would lead to even higher plateau temperatures and thus higher selectivities and conversions, but then H<sub>2</sub>O should be added to the air feed to prevent runaways.

##### 5.5. Effect of combustion catalyst section length

To study the effect of the length of the combustion catalyst section, an experiment was performed with a somewhat shorter length (case J). Comparing the axial temperature profiles for cases G and J, the length of the temperature plateau is shorter for case J and the temperature peaks due to the CH<sub>4</sub>

combustion are located inside the filter section resulting in higher temperatures in this section because the radial heat losses are counterbalanced by the combustion reactions. As a result also the syngas selectivities and CH<sub>4</sub> conversion are significantly higher for case J. The switching time that was used for case J is relatively short (120 s) and accordingly the switching losses are relatively high (2.19%). Longer switching times might lead to lower switching losses for case J, but the overall syngas yield does not necessarily increase. For longer switching times the combustion of CH<sub>4</sub> in the shell compartment occurs well within the filter section at the end of the semi-cycle, leading to significantly lower temperatures at the beginning of the filter section, so that at the beginning of the next semi-cycle the temperatures at that location will still be relatively low and accordingly also the syngas selectivities and CH<sub>4</sub> conversions will be significantly lower.

### 5.6. Need of CH<sub>4</sub> combustion in the air compartment

In previous work (Smit et al., 2005b) it was found that it is desirable for the RFCMR concept to add a small amount of CH<sub>4</sub> to the air feed to create the trapezoidal temperature profile and allow to control the temperatures in the heat exchange and membrane sections separately, but also that this is not strictly essential to achieve high syngas selectivities. To confirm these findings, also an experiment (case K) was carried out in which dead-end permeation (thus no by-pass at the outlet of the shell compartment) was used and furthermore no CH<sub>4</sub> was added to the shell feed. Indeed, still very high CO and H<sub>2</sub> selectivities and CH<sub>4</sub> conversions can be achieved despite very low temperatures at the beginning of the filter section, because for this case the maximum temperature was established at the end of the filter section.

The high selectivities and conversions also result from the fact that no CO<sub>2</sub> has to be converted by the relatively slow CO<sub>2</sub> reforming reaction, since no CH<sub>4</sub> is combusted in the shell compartment. This is reflected by the relatively low H<sub>2</sub>/CO ratio measured for case K. The switching losses are somewhat higher compared to other cases with a switching time of 240 s, because of the low temperatures at the end of the filter at the beginning of the semi-cycle and as a result the H<sub>2</sub> mole fraction reaches its semi-stationary value relatively slowly. Longer switching times are probably not possible for this case though, because then a blow-out could occur.

### 5.7. Discussion

The results presented in Table 2 and Figs. 7 and 8 have shown that with the RFCMR demonstration unit very high syngas selectivities and CH<sub>4</sub> conversions can be achieved, higher than typical values encountered in industrial practice (Brejč and Supp, 1989; Aasberg-Petersen et al., 2001), without using any heating and despite the radial heat losses. This clearly demonstrates the technical feasibility and potential of the RFCMR concept for energy efficient syngas production. However, the

Table 2

Dry, normalised syngas compositions and related quantities measured in the RFCMR demonstration unit for cases F–K

Case	F	G	H	I	J	K
$x_{\text{CH}_4, \text{out}}^t$	0.049	0.045	0.058	0.038	0.027	0.042
$x_{\text{CO}, \text{out}}^t$	0.308	0.309	0.293	0.315	0.315	0.315
$x_{\text{CO}_2, \text{out}}^t$	0.021	0.019	0.029	0.015	0.016	0.018
$x_{\text{H}_2, \text{out}}^t$	0.614	0.612	0.619	0.625	0.643	0.625
$S_{\text{CO}, \text{out}}^t$ (%)	93.6	94.2	91.1	95.3	95.3	94.6
$S_{\text{H}_2, \text{out}}^t$ (%) <sup>a</sup>	94.3	95.5	96.4	95.5	96.8	93.7
$R_{\text{O}_2/\text{CH}_4}^t$ <sup>a</sup>	0.513	0.504	0.492	0.510	0.508	0.524
$R_{\text{H}_2/\text{CO}, \text{out}}^t$	2.02	2.03	2.12	2.00	2.04	1.98
$\zeta_{\text{CH}_4, \text{out}}^t$ (%)	87.1	87.9	84.6	89.8	92.6	88.7
H <sub>2</sub> loss (%)	1.26	2.27	0.08	1.04	2.19	1.65

<sup>a</sup>Calculated from the element mass balances at the tube outlet.

maximal on-stream time of the RFCMR demonstration unit was limited to about 12 h for two reasons.

One limiting factor was coke formation in the support tubes, resulting in a slowly increasing axial pressure drop over time. The coke could be (partially) burned off by temporarily shutting off the CH<sub>4</sub> feed to the tube compartment, so that the tube compartment was flushed with air. This resulted in significant temperature peaks at the in- and outlet of the reactor. Similar to the isothermal membrane reactor, the coke formation is probably caused by the Boudouard reaction occurring on the Al<sub>2</sub>O<sub>3</sub> particles. Therefore, particles made of a different material such as SiC are to be preferred, which makes operation with longer on-stream times possible. Alternatively the coke has to be burned off periodically.

The second reason for the limited on-stream time was a decrease in the permeation rate through the filter over time. Previously this was attributed to sintering (Smit et al., 2005a), but inspection with a microscope revealed that apparently very small pieces of the combustion catalyst accumulated inside the tiny holes of the filter, which resulted in a gradually increasing pressure difference over the filter. To circumvent this problem, a glass wool blanket was wound around the filter. This effectively prevented the fouling by small pieces of combustion catalyst, but instead fouling by small threads of glass wool was observed, so that the maximal on-stream time was increased but still limited. Clearly, fouling of the filter is a serious problem that has to be solved. Possible solutions could be periodic back-flushing to clean the holes or using another combustion catalyst which is less prone to break-up. Alternatively, filters have to be used with much smaller pore sizes (i.e., porous membranes).

## 6. Conclusions

In the first part of this contribution, the technical feasibility of the RFCMR concept with porous membranes/filters was further investigated experimentally. Firstly, a Rh–Pt/Al<sub>2</sub>O<sub>3</sub> catalyst and porous Al<sub>2</sub>O<sub>3</sub> membranes were tested in an isothermal membrane reactor. A novel sealing technique was presented, which enabled a gas-tight connection between the membrane and support tubes at very high temperatures and reasonable pressure differences.

With the isothermal membrane reactor it was shown that very high syngas selectivities close to the thermodynamic equilibrium could be achieved for a considerable period of time without any increase in pressure drop and without any decrease in syngas selectivities, demonstrating the good mechanical strength and temperature resistance of the catalyst, the porous  $\text{Al}_2\text{O}_3$  membrane and the glass sealing.

Although the porous  $\text{Al}_2\text{O}_3$  membranes were successfully applied in the isothermal membrane reactor, it proved to be very difficult to implement them in the RFCMR demonstration unit due to their rigidity and fragility. Therefore, steel filters were used instead, which showed a superior mechanical strength.

With the RFCMR demonstration unit the influence of different operating conditions and design parameters on the reactor behaviour were investigated. The syngas composition was measured on-line and it was found that for almost all cases studied syngas with very high CO and  $\text{H}_2$  selectivities (up to 95%) could be produced from undiluted  $\text{CH}_4$  feeds, without using any compensatory heating and despite the inevitable radial heat losses of the small-scale demonstration unit.

As expected, shorter switching times result in higher switching losses, but also in higher syngas selectivities. Increasing the  $\text{CH}_4$  weight fraction in the air feed leads to higher temperatures outside the filter section, but remarkably to a lower CO selectivity and a lower  $\text{CH}_4$  conversion. This is attributed to the fact that  $\text{CO}_2$ , which is generated during the combustion in the shell compartment, is converted very slowly to syngas in the tube compartment. This problem can be overcome by locating also some catalyst just outside the filter section. With respect to the length of the combustion section it was observed that it should not be too long and not too short to prevent low temperatures at the end of the filter section just after switching the flow directions. Obviously these operating conditions and design parameters have to be further optimised. In principle, it is not necessary to add any  $\text{CH}_4$  to the air feed to obtain reasonably high syngas selectivities, but only if the switching time is relatively short. As an alternative to adding some  $\text{CH}_4$  to the air, some air could be added to the main  $\text{CH}_4$  feed instead to obtain a trapezoidal axial temperature profile, but this was not investigated in the present study.

The maximal on-stream time of the RFCMR demonstration unit was about 12 h and was limited by coke formation in the support tubes and by fouling of the filter. Another type of inert particles in the support tubes and further optimisation of the filter design or the use of porous alumina membranes, which were successfully tested in the isothermal membrane reactor, may solve these problems.

## Notation

ID	inner diameter, m
$L$	length, m
$L_{P_T/\text{Al}_2\text{O}_3}$	length combustion catalyst section, m
OD	outer diameter m

$R$	molar ratio
$S$	selectivity
$t_{\text{switch}}$	switching time, s
$T_{\text{feed}}$	feed temperature, K
$T_{\text{heating}}$	temperature at shell wall controlled with the heating coil, K
$x$	mole fraction

## Greek letters

$\zeta$	conversion
$\phi_v$	flow rate, l/min (STP)

## Subscripts

by-pass	by-pass
in	at the inlet
out	at the outlet
total	total flow

## Superscripts

$s$	shell
$t$	tube

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