

INTERNATIONAL JOURNAL OF CHEMICAL REACTOR ENGINEERING

Volume 3

2005

Article A12

A Reverse Flow Catalytic Membrane Reactor for the Production of Syngas: An Experimental Study

J. Smit*
M. van Sint Annaland[‡]

G.J. Bekink[†]
J.A.M. Kuipers**

*University of Twente, j.smit@tnw.utwente.nl

[†]University of Twente, g.bekink@student.utwente.nl

[‡]University of Twente, m.vansintannaland@tnw.utwente.nl

**University of Twente, j.a.m.kuipers@tnw.utwente.nl

ISSN 1542-6580

Copyright ©2005 by the authors.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior written permission of the publisher, bepress, which has been given certain exclusive rights by the author.

A Reverse Flow Catalytic Membrane Reactor for the Production of Syngas: An Experimental Study

J. Smit, G.J. Bekink, M. van Sint Annaland, and J.A.M. Kuipers

Abstract

In this paper experimental results are presented for a demonstration unit of a recently proposed novel integrated reactor concept (Smit et. al., 2005) for the partial oxidation of natural gas to syngas (POM), namely a Reverse Flow Catalytic Membrane Reactor (RFCMR). Natural gas has great potential as a feedstock for the production of liquid fuels via the Gas-To-Liquid (GTL) process, but this process has not found widespread application yet, mainly due to the large costs associated with cryogenic air separation and complex heat integration. In conventional GTL processes excess O_2 (20-40 %) is used together with preheating of the feed (250-400 °C). The O_2 consumption and heat integration cost can be reduced substantially by integrating the recuperative heat exchange inside the POM reactor using the reverse flow concept. The RFCMR concept basically consists of two fixed bed compartments (e.g. in a shell-and-tube configuration) separated by a porous membrane (or filter), through which the O_2 is fed distributively to the syngas compartment, thereby avoiding possibly explosive feed mixtures and hot spots. Furthermore, the flow directions of the gas streams are periodically alternated. A small amount of CH_4 is combusted in the O_2 compartment to create the trapezoidal temperature profile. Also some steam is added to the O_2 feed to keep the center of the reactor isothermal.

To demonstrate the RFCMR concept an experimental set-up was constructed with a single shell-and-tube design, from which axial temperature profiles and the composition of the produced syngas could be measured. This set-up was first operated as a conventional reverse flow reactor and it was found that radial heat losses have a major influence on the axial temperature profiles as expected, but that suitable temperature profiles could be established. Subsequently, the demonstration unit was operated as a reverse flow catalytic membrane reactor. Syngas with high CO (93 %) and H_2 (96 %) selectivities with high CH_4 (85 %) conversions was produced from undiluted CH_4 feed. These selectivities are higher than the typically encountered values of 90 % in industrial practice, because of the lower O_2/CH_4

ratio, and could be improved even further by going to higher temperatures, but this was not possible in this study due to mechanical constraints. The temperature plateau was flat in the center of the reactor and no hot spots were observed. The experiments have clearly demonstrated the potential of the RFCMR concept for energy efficient production of syngas.

KEYWORDS: Reverse flow, partial oxidation, membrane reactor, experimental

1 INTRODUCTION

Natural gas has great potential as feedstock for liquid fuels as an alternative to conventional oil processing due to the rising oil prices. A promising process to convert natural gas to liquid fuels is the so-called Gas-To-Liquid (GTL) process, in which the partial oxidation of CH_4 (POM) is followed by the Fischer-Tropsch (FT) reaction:



GTL-processes have been subject of research for over half a century, but have not found widespread application yet due to economic reasons. Major cost drivers of a conventional GTL-plant are related to the production of pure O_2 via cryogenic air distillation and external heat exchange equipment. Therefore, an alternative air separation and/or heat integration could substantially improve the prospects of the GTL-process.

Alternative air separation has recently become possible with the development of O_2 perm-selective perovskite membranes. POM reactors with integrated air separation have already been demonstrated on lab-scale by Balachandran et al. (1995) and also on pilot plant-scale in the Air Products ITM project (Chen, 2004). If air separation is integrated inside a POM reactor, very high feed temperatures are required to achieve high syngas yields (Smit et al., 2004). Since the POM reaction is only slightly exothermic, the air and CH_4 feed streams have to be preheated. In view of the very high operating temperatures, external heat transfer is very expensive. Therefore, recuperative heat exchange is preferably carried out inside the reactor, which can be achieved with the reverse flow concept (e.g. Matros and Bunimovich, 1996). To combine the POM reaction, air separation and recuperative heat exchange into a single apparatus, a Reverse Flow Catalytic Membrane Reactor (RFCMR) with perovskite membranes was proposed by Smit et al. (2003, 2004).

Also for a conventional, pure O_2 based POM reactor, heat integration is costly. In industrial practice (Brejč and Supp, 1989; Aasberg-Petersen et al., 2001) usually O_2/CH_4 ratios of 0.6-0.7 and feed temperatures up to 400°C are used to achieve the required POM temperatures of $1100\text{-}1400^\circ\text{C}$ (see also Smit et al., 2004). The O_2 consumption and heat integration cost could be reduced by carrying out the heat integration inside the POM reactor via the reverse flow concept. A reverse flow reactor for the production of syngas was studied by Blanks et al. (1990), however, based on a premixed CH_4/O_2 feed with the accompanying disadvantages of the possible formation of explosive mixtures and low syngas selectivities. The use of a porous membrane (or another type of distributor) in a reverse flow reactor to distributively feed the O_2 may overcome these problems and therefore, a Reverse Flow Catalytic Membrane Reactor with porous membranes was proposed (Smit et al., 2005). Although air separation is not integrated, with this novel reactor concept the consumption of pure O_2 and the costs associated with heat integration can be considerably reduced in comparison with a conventional POM process, making it an interesting alternative in case a POM reactor with integrated air separation turns out to be technically and economically unfeasible to be operated on industrial scale.

The RFCMR with porous membranes basically consists of two compartments (e.g. a shell-and-tube configuration). The O_2 and syngas compartments are separated by a porous membrane in the center of the reactor and by impermeable walls at the in- and outlets, as schematically represented in Figure 1. 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 center, the syngas compartment is filled with catalyst for the POM reaction, while at the in- and outlet of this compartment inert material is positioned for additional heat capacity and to prevent back-reactions. To create the desired trapezoidal temperature profile a small amount of CH_4 is added to the O_2 feed, which is combusted at the inlet of the O_2 compartment. Furthermore, also a small amount of H_2O is added to the O_2 feed to effectively use the reaction heat released by the POM reaction to produce some additional syngas via steam reforming and to keep the center of the reactor approximately isothermal and prevent runaways.

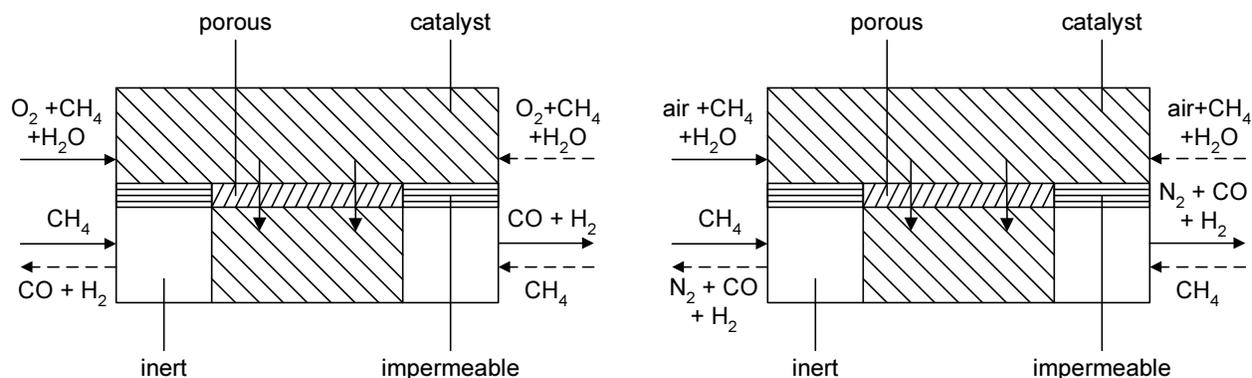


Figure 1. RFCMR concept with porous membranes with an O₂ (left) and air (right) feed.

The RFCMR concept with porous membranes and pure O₂ feed without integrated air separation is intended to produce syngas without N₂ to minimise the syngas flow rate and the size of the FT-reactor. In industrial practice usually syngas without N₂ is produced (Brejc and Supp, 1989; Aasberg-Petersen et al., 2001). However, more recently also GTL-technologies are offered (e.g. by Syntroleum), which do not use air separation and produce a syngas/N₂ mixture in a POM reactor, which is subsequently fed to the FT-reactor. Previously, it has already been demonstrated that for an air-based POM reactor the heat integration is even much more important than for a pure O₂ based POM reactor because of the N₂ dilution and that higher O₂/CH₄ ratios are required to preheat the feed (Smit et al., 2004). Therefore, the RFCMR concept with porous membranes could also be applied to an air-based process to reduce the costs of recuperative heat exchange and to minimise the air flow rate and therefore the syngas flow rate and size of the FT-reactor, which could contribute to the economical feasibility of a GTL-process without any air separation. A schematic overview of the RFCMR concept with porous membranes and an air feed is also schematically represented in Figure 1.

In this paper the feasibility of the RFCMR with porous membranes for the production of syngas is investigated by means of an experimental study. An air feed rather than an O₂ feed will be used for safety reasons, but the experimental results should support the feasibility of the RFCMR concept with porous membranes for both O₂ and air feeds. Firstly, the experimental set-up is described. Subsequently, results of experiments are discussed, where the reactor was operated as a conventional reverse flow reactor, in order to determine the operating conditions required to achieve the desired temperature profiles. Finally, the experimental results of the RFCMR are presented and the feasibility of the novel reactor concept is demonstrated.

2 EXPERIMENTAL SET-UP & PROCEDURES

A shell-and-tube reverse flow catalytic membrane reactor was constructed, consisting of a shell (OD×ID×L = 30×26×1500 mm) made from a high-temperature resistant steel (AISI 310) and a steel filter welded in between two steel support tubes (OD×ID×L = 10×8×1500 mm). CH₄ was fed to the tube and air to the shell. A schematic overview of the experimental set-up is given in Figure 2.

Although in industrial practice porous membranes or filters made from chemically inert Al₂O₃ (or another ceramic material) are probably to be preferred, steel filters with discrete holes were used in this study because of their superior mechanical strength and problems with high temperature sealings can be avoided. The size of the holes in the filter was selected in such a way that a sufficient pressure drop over the filter was established in the experiments in order to achieve a good distribution of the air feed over the filter. The disadvantage of these filters is that they can only be used for a short period of time (± 5 hours) because of the sintering of the steel, however this life time was sufficiently long for this study. In principle after some time the size of holes should no longer because of the sintering and by carefully selecting a suitable initial hole size, a steady state state should be reached. Clearly the size of the holes is a parameter that should be

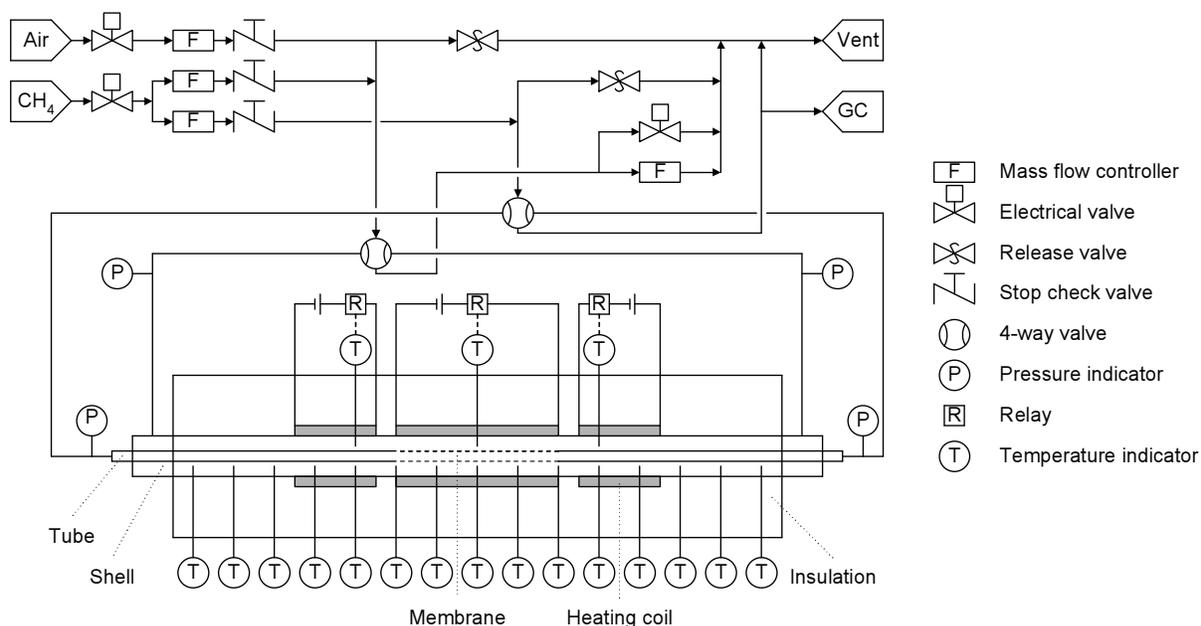


Figure 2. Flow-sheet experimental set-up.

optimized. Furthermore, the steel filter should have a sufficient chemical and mechanical life time and also the type of steel should be carefully selected. The filter (ODxIDxL = 10x8x250 mm) made from a special high temperature steel (Inconel 600), in which a number (80) of tiny holes (0.2 mm diameter) were made with a laser, was welded to the support tubes. The filter was filled with a POM catalyst, which was made from a RhCl_3 solution and a commercial Y_2O_3 stabilized ZrO_2 powder (Tosoh, TZ8Y). The Rh loading was 1 wt.% and the specific surface area was $15 \text{ m}^2/\text{g}$. The POM catalyst was first compressed to pellets and subsequently crushed and sieved to obtain particles with a diameter of 1.4-2 mm. Furthermore, the shell was filled with a commercial $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst produced by Engelhard (Escat 26) with a particle diameter of 3 mm. According to the specifications, the Pt loading is 0.5 wt.% and the specific surface area is $80 \text{ m}^2/\text{g}$. At the in- and outlet of the tube and shell inert Al_2O_3 spherical particles were used with a diameter of 3 mm.

To measure the axial temperature profile, small tubes (ODxIDxL = 4x2x25 mm) were welded to the shell, in which 48 thermocouples (Rössel, k-type, ODxL = 1.6x250 mm) were placed that were connected to a data acquisition card (Advantech PCL-818HD with PCLD-789D daughterboards). The pressure was measured with digital transmitters (Drück, PTX 1400) connected to a multi-function I/O card (National Instruments PCI-6014 with 68E wiring terminal) at the in- and outlets of the shell and tube. The gas composition was analyzed with a Micro-GC (Varian, CP-4900) with three separate columns. The first column was a Molsieve 5\AA column with He as carrier gas and was used to measure the O_2 , N_2 , CH_4 and CO concentration. The second column was also a Molsieve 5\AA column but with N_2 as carrier gas to measure the H_2 concentration. The third column was a PoraPlot Q column with He as carrier gas to measure the CO_2 and H_2O concentration. The Micro-GC was connected to a PC with data-acquisition software. The Micro-GC has a very high sensitivity (to the ppm level) and the relative error in the measured concentration was typically 1-2 %. Because the analysis time of the Micro-GC was 240 s and switching times were typically shorter, the change in gas composition during a cycle was followed indirectly by selecting a switching and analysis time in such away that a new analysis was performed 10-20 seconds further in the cycle than the previous analysis.

To minimise radial heat losses, the shell was placed in a box (HxWxL = 400x400x1000 mm) filled with an insulation material (Vermiculite). Electrical heating coils (3x600 Watt) around the shell were used to start-up the reactor and also to provide for compensatory heating. The gas feed flows were controlled with automated mass flow controllers (Brooks Instruments, 5850s/5851s). Due to the fact that the shell has

a large specific external surface area because of its small diameter, radial heat losses greatly influence the temperature profile (despite the insulation) and much larger flow rates are required to create the desired temperature profile than would be required for an industrial scale reactor with a small specific external surface area. Due to the pressure drop on the tube side, it was not possible to increase the tube side flow rate accordingly. Therefore, it was also not possible in the experimental set-up to use dead-end permeation of the air feed and consequently a by-pass flow was required. At industrial scale dead-end permeation can be used, as was demonstrated by Smit et al. (2005). To control the by-pass flow rate, a separate mass flow controller was used at the outlet of the shell.

The shell and tube inlets and outlets were connected to automated 4-way valves (Joucomatic), to achieve the periodic switching of the flow directions. Condensers were used at the outlet of the tube and shell to prevent H₂O condensation in the Micro-GC and in the mass flow controller at the shell outlet. Additionally the outlets of the tube and shell were diluted with N₂ for the same reason. To guarantee safe operation, a stand-alone hard-ware alarm system was used with temperature controllers (Eurotherm 2132), gas detectors (Dräger) and a PC-watchdog system.

3 EXPERIMENTAL RESULTS

Firstly, experimental results are discussed where the reactor was operated as a conventional reverse flow reactor without the inner tube, in order to determine the operating conditions required to achieve the desired temperature profile. Subsequently, experimental results of the RFCMR with the steel filter are presented.

3.1 Reverse Flow Reactor

As indicated in the previous section, radial heat losses will greatly influence the axial temperatures obtained in the experimental set-up, due to the relatively large specific external surface area of the shell. Therefore, the required operating conditions, such as the shell CH₄ inlet fraction, the shell inlet gas flow rate etc., to establish the desired temperature profile with respect to the reverse flow behavior, were first determined by operating the reactor as a conventional reverse flow reactor for the combustion of a small amount of CH₄ in air by removing the inner tube. Because the Pt/Al₂O₃ catalyst is already very active at low temperatures, it was found that inert sections had to be used to increase the plateau temperature (see also Nieken et al., 1994) at the membrane section of the reactor to the desired level of 900 °C, which is required to obtain high syngas yields and selectivities.

In Figure 3 typical axial temperature profiles measured in the reactor at the end of a forward and backward semi-cycle are presented for a number of cases with different lengths of the inert sections, flow rates, switching times and CH₄ inlet fractions. The operating conditions are summarized in Table 1. The axial temperature profiles were obtained for the cyclic stationary state (after at least 10 000 s) and without any heating from the heating coils. Indeed very high temperatures (1000 °C) can be obtained, which are self-sustaining, but only when employing high flow rates and high CH₄ inlet fractions (cases A and B) due to the large radial heat losses of our lab-scale reactor. For a reactor with a sufficiently large diameter the influence of radial heat losses are negligible and much lower flow rates and CH₄ inlet fractions are required to obtain the same plateau temperature. For an adiabatic reactor with inert sections, the plateau temperature

Table 1. Operating conditions RFR.

	A	B	C	D	E
L_{Pt/Al_2O_3} (m)	0.3	0.3	0.3	0.5	0.3
$t_{switching}$ (s)	120	240	120	120	120
$\phi_{v,total,in}^{shell}$ (l/min, STP)	30	30	30	30	20
$x_{CH_4,in}^{shell}$	0.018	0.018	0.014	0.018	0.018

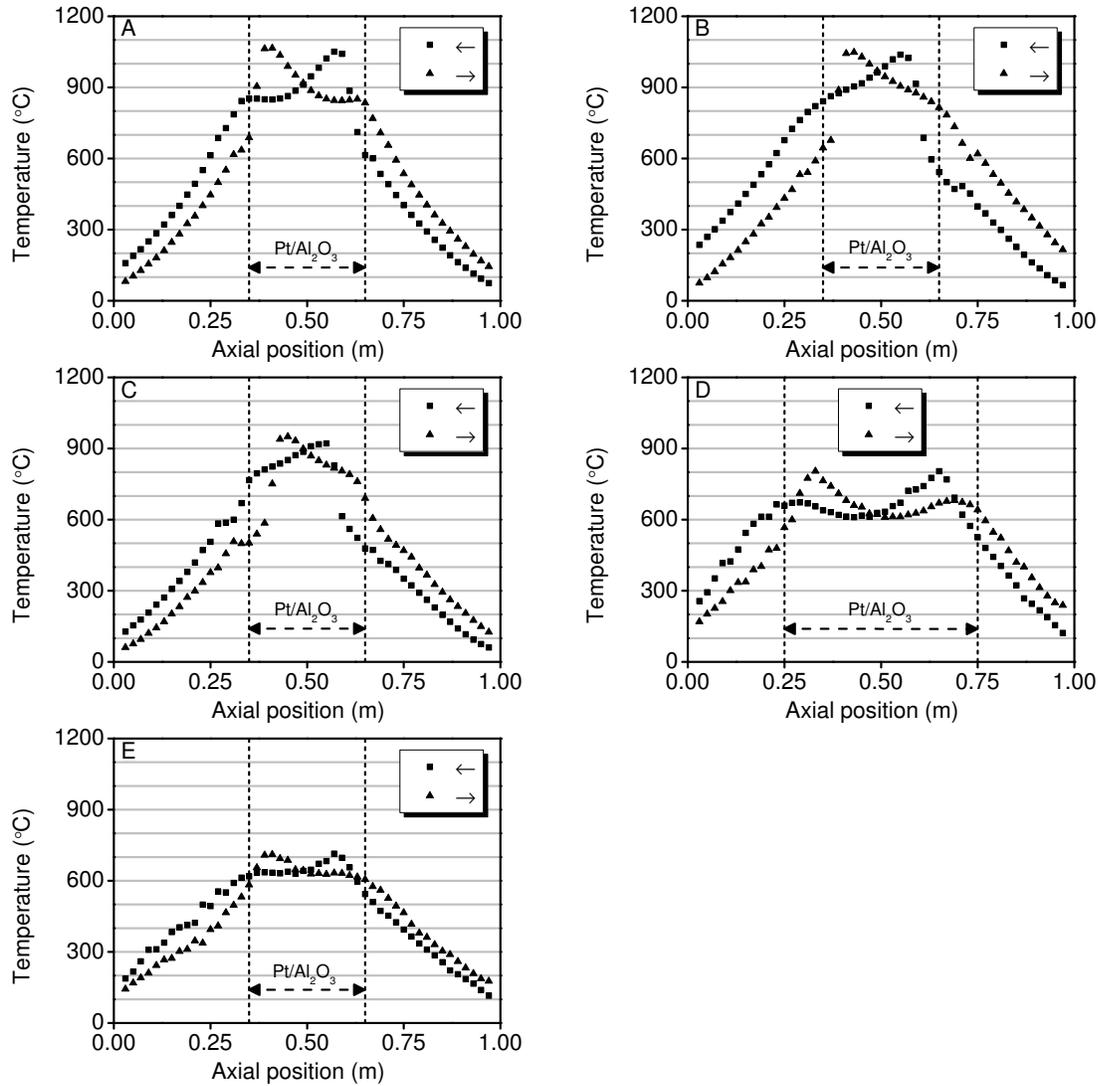


Figure 3. Axial temperature profiles in the RFR after a forward (→) and backward (←) semi-cycle for different operating conditions. See Table 1 for the operating conditions.

can be predicted with (Matros and Bunimovich, 1996):

$$T_{plateau} = T_{feed} + \Delta T_{ad} \left(1 + \frac{\rho_g v_g L_{inert}}{2\lambda_{eff}} \right) \quad (3)$$

where ΔT_{ad} is given by:

$$\Delta T_{ad} = \frac{(-\Delta H_r) w_{CH_4, in}^{shell}}{C_{p,g} M_{CH_4}} \quad (4)$$

The effective axial heat dispersion λ_{eff} can be calculated according to Gunn and Misbah (1993):

$$\lambda_{eff} = \lambda_{bed} + \frac{Re Pr \lambda_g}{Pe_{ax}} + \frac{Re^2 Pr^2 \lambda_g}{6(1 - \varepsilon_g) Nu} \quad (5)$$

with

$$Pe_{ax} = \frac{2p}{1-p} \quad (6)$$

and

$$p = 0.17 + 0.33 \exp\left(\frac{-24}{Re}\right) \quad (7)$$

and the gas-to-particle heat transfer coefficient Nu can be evaluated with (Gunn, 1978):

$$Nu = (7 - 10\varepsilon_g + 5\varepsilon_g^2) (1 + 0.7Re^{0.2}Pr^{1/3}) + (1.33 - 2.4\varepsilon_g + 1.2\varepsilon_g^2) Re^{0.7}Pr^{1/3} \quad (8)$$

The thermal conductivity of the quiescent packed can be estimated from the model of Zehner and Schlünder (1970) and physical properties from Daubert and Danner (1985) and Reid et al. (1987). According to the above equations, a plateau temperature of 900 °C could be achieved with a flow rate of and 5 l/min (STP) a CH₄ inlet fraction of 0.0018, which are at least a factor of 4 and 6 lower, respectively, than the values reported in Table 1. This clearly illustrates the large effect of radial heat losses on the temperature profiles. Nevertheless the desired trapezoidal temperature profile with a plateau temperature of 900 °C could be established.

With respect to the inert sections, it was observed that the plateau temperature was established exactly at the beginning of the combustion catalyst bed. Therefore, the combustion catalyst bed should be slightly larger (depending on the switching time) than the length of the filter in the center of the reactor.

3.2 Reverse Flow Catalytic Membrane Reactor

After the experimental set-up was successfully operated as a conventional reverse flow reactor for the combustion of CH₄ in air and the required shell side operating conditions such as the shell side flow rate, the CH₄ inlet fraction and the length of the inert sections were determined, the experimental set-up was operated as a reverse flow catalytic membrane reactor for the production of syngas. The selected operating conditions are listed in Table 2 and switching times of 115 and 230 s were used. The gas composition was analysed with the Micro-GC. Since this analysis required 240 s, only one analysis could be carried out during a semi-cycle. In order to follow the tube outlet composition as a function of time, the switching time was selected in such a way that the analysis was performed at different moments in the semi-cycle. By selecting switching times of 115 and 230 s, the analysis is performed 10 and 20 s further in the semi-cycle, respectively. Because of the high shell flow rates and CH₄ inlet fractions required to obtain a self-sustaining temperature profile, a by-pass flow at the shell outlet was required. Another implication of the radial heat losses are the temperature dips in the center of the reactor (see also Figure 3). To obtain high syngas yields and selectivities, a temperature of at least 900 °C is required in the membrane section. Although in principle the POM reaction is slightly exothermic, the reaction heat released is small compared to the radial heat losses. Furthermore, since a large amount of CH₄ is combusted in the shell compartment, a considerable amount of CO₂ and H₂O permeates to the tube compartment so that the heat produced by the partial oxidation is counterbalanced by the endothermic CO₂ and H₂O reforming of CH₄. For isothermal operation in the center of an industrial

Table 2. Operating conditions RFCMR.

$\phi_{v,CH_4,in}^{tube}$	2.1	l/min (STP)	$L_{membrane}$	0.2	m
$\phi_{v,total,in}^{shell}$	25	l/min (STP)	L_{Pt/Al_2O_3}	0.3	m
$\phi_{v,bypass,in}^{shell}$	20	l/min (STP)	T_{center}	900	°C
$x_{CH_4,in}^{shell}$	0.014	-	p^{tube}	±1.5	bar

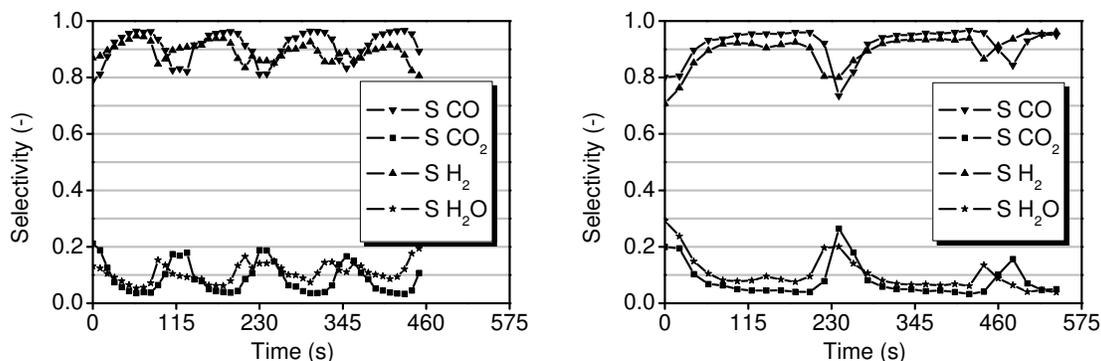


Figure 4. Syngas selectivities in the tube outlet of the RFCMR as a function of time for $t_{switch} = 115$ s (left) and $t_{switch} = 230$ s (right).

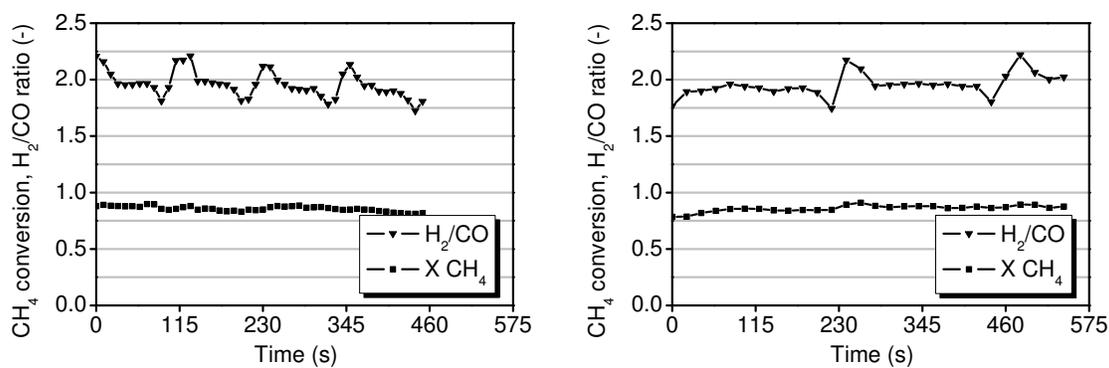


Figure 5. CH_4 conversion and H_2/CO ratio in the tube outlet of the RFCMR as a function of time for $t_{switch} = 115$ s (left) and $t_{switch} = 230$ s (right).

scale reverse flow catalytic membrane reactor, a $\text{H}_2\text{O}/\text{O}_2$ ratio of 1/4 is required (Smit et al., 2005). With the operating conditions listed in Table 2, the $(\text{CO}_2 + \text{H}_2\text{O})/\text{O}_2$ ratio is also about 1/4. Therefore, at the operating conditions used in this study, it was not required to add H_2O to the air feed. Because of the fact that no reaction heat is released in the center and because of the radial heat losses, it was thus necessary to use compensatory heating and the central heating coil at the center of the reactor was set at 900°C .

In Figure 4 the syngas selectivities (based on the converted amount of CH_4) are given as a function of time during a semi-cycle. The outlet compositions of the tube measured with the Micro-GC were corrected to account for the condensation of H_2O . Very high CO ($\pm 96\%$) and H_2 ($\pm 93\%$) selectivities were achieved during most of the semi-cycle, while the CO_2 ($\pm 4\%$) and H_2O ($\pm 7\%$) selectivities were low. This demonstrates that distributive feeding of O_2 indeed leads to high syngas selectivities and back-reactions are effectively prevented with the inert sections. The equilibrium CO and H_2 selectivities are 98% at the operating conditions used, indicating that there are some mass transfer limitations due to the particle size or that the length of the catalyst bed should be increased compared to the length of the filter. The (equilibrium) selectivities could be improved even further by going to higher temperatures, but this was not possible in this study due to mechanical constraints.

The dips in the CO and H_2 selectivities and the accompanying peaks in the CO_2 and H_2O selectivities are caused by combustion of part of the produced syngas at the moment of switching of the flow direction, referred to as switching losses. The switching losses are smeared out in time due to the dead volume between the reactor and the Micro-GC (piping, condenser). When integrating the area of the dip in the selectivity over time, taking the selectivity in the middle of the semi-cycle as a reference, it is found that the time-averaged

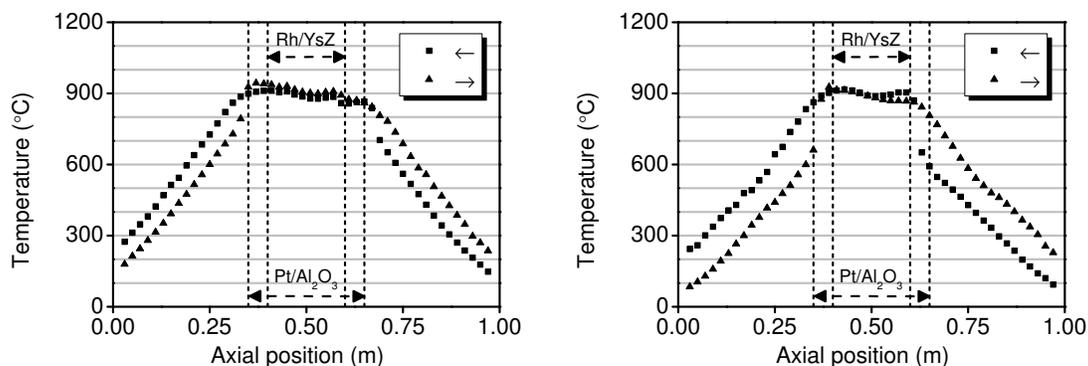


Figure 6. Axial temperature profiles in the RFCMR after a forward (\rightarrow) and backward (\leftarrow) semi-cycle for $t_{switch} = 115$ s (left) and $t_{switch} = 230$ s (right).

selectivity is decreased by about 5 % due to the switching losses. For a cycle time of 230 s the switching losses are much smaller as can be clearly observed in Figure 4 and in this case the time-averaged selectivity is decreased by only 3 % due to switching losses. Since the movement of the temperature profile for a switching time of 230 s is relatively small, even higher switching times could be used with even lower switching losses. Also two 3-way valves could be used instead of one 4-way valve to switch the flow direction of the the tube side, so that the dead volume between the tube in- and outlet and the 4-way valve is eliminated.

In Figure 5 the CH_4 conversion as well as the molar H_2/CO ratio are given as a function of time during a semi-cycle for a switching time of 115 s and 230 s. The CH_4 conversion is typically about 86 %, whereas the O_2 conversion was always 100 %. Obviously, the CH_4 conversion would be higher if all CO_2 and H_2O would be converted to syngas and the equilibrium composition would be attained. The H_2/CO ratio is typically about 1.95, which is very close to the ideal value of 2. Around the moment of switching of the flow direction, the ratio changes slightly due to the asynchronous dips in the H_2 and CO selectivities.

In Figure 6 the axial temperature profiles after a forward and backward semi-cycle are given as a function of time for a switching time of 115 s and 230 s. The temperature profiles along the membrane are very flat and no hot spots are observed, demonstrating the advantage of distributive feeding of the O_2 . At the in- and outlets steep temperature profiles are observed, demonstrating the effectiveness of the recuperative heat exchange with the reverse flow concept.

4 CONCLUSIONS

In this paper experimental results of a demonstration unit of a Reverse Flow Catalytic Membrane Reactor with steel filters for the production of syngas were presented in order to provide for an experimental proof of principle of the novel reactor concept. Firstly, the demonstration unit was operated as a conventional reverse flow reactor for the combustion of CH_4 in air in order to determine the required shell side operating conditions to establish the desired trapezoidal temperature profile. It was found that radial heat losses have a major influence on the axial temperature profiles, as expected, so that much higher flow rates and CH_4 inlet fractions were required to achieve the desired temperature plateau than would be needed for an industrial scale reactor. Nonetheless, the desired temperature profiles could be created in the lab-scale reactor. Subsequently, the demonstration unit was tested as a RFCMR with a steel filter. Syngas with high CO (96 %) and H_2 (93 %) selectivities could be produced from undiluted CH_4 feeds, which is higher than the typical values of 90 % encountered in industry (Aasberg-Petersen et al., 2001), because of the lower O_2/CH_4 ratio. These selectivities could be improved even further by going to higher temperatures, but this was not possible in this study due to mechanical constraints. Switching losses were observed, but for longer switching times they were small. Because of the large radial heat losses and the required high air flow rate and high CH_4 inlet fraction of the air feed to the shell compartment, no additional H_2O was required in the air feed. Furthermore, a flat temperature plateau without any hot spots was observed, demonstrating

the advantage of distributive feeding of O₂. The experimental results clearly demonstrate the potential of the RFCMR concept for the energy efficient production of syngas, but further optimization, scale-up and operation at industrially relevant conditions is required to determine the technical and economical feasibility.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of the Dutch Technology Foundation STW, the Energy research Center of the Netherlands ECN and the Association of Industrial Advisory Council Members of the Dutch Institute for Catalysis Research VIRAN. Furthermore, the authors thank G.J.H. Schorfhaar, B. Knaken and R.L. Brouwer for constructing the experimental set-up, J.J. Zhu for preparing the Rh/YsZ catalyst and T.H. Pünt for making the steel filters.

NOMENCLATURE

C_p	heat capacity, J/kg/K
d_p	particle diameter, m
ΔH_r	reaction heat, J/mol
$L_{membrane}$	membrane length, m
L_{Pt/Al_2O_3}	length Pt/Al ₂ O ₃ catalyst bed, m
Nu	dimensionless Nusselt number, $\alpha_{g-s}d_p/\lambda_g$
p	parameter in axial heat dispersion coefficient
p	pressure, bar
Pe_{ax}	dimensionless Péclet number for axial heat dispersion, $\rho_g v_g d_p C_{p,g}/\lambda_{ax}$
Pr	dimensionless Prandtl number, $C_{p,g}\eta_g/\lambda_g$
Re	dimensionless Reynolds number, $\rho_g v_g d_p/\eta_g$
$t_{switching}$	switching time, s
T_{center}	temperature in center of reactor, K
T_{feed}	feed temperature, K
ΔT_{ad}	adiabatic temperature rise, K
$T_{plateau}$	plateau temperature, K
v	superficial gas velocity, m/s
$x_{CH_4,in}$	mole fraction of CH ₄ in shell feed
$w_{CH_4,in}$	weight fraction of CH ₄ in shell feed

Greek symbols

α_{g-s}	gas-to-solid heat transfer coefficient, J/m ² /K/s
ϵ	porosity
η	viscosity, kg/m ² /s
λ	thermal conductivity, J/m/K/s
λ_{ax}	axial thermal conductivity, J/m/K/s
λ_{bed}	thermal conductivity of a quiescent packed bed, J/m/K/s
λ_{eff}	effective thermal conductivity, J/m/K/s
ρ	density, kg/m ³
$\phi_{v,bypass,in}$	shell by-pass flow, l/min (STP)
$\phi_{v,CH_4,in}$	tube CH ₄ feed flow, l/min (STP)
$\phi_{v,total,in}$	total shell feed flow, l/min (STP)

Subscripts

g	gas phase
-----	-----------

Superscripts

$shell$	shell side
$tube$	tube side

REFERENCES

- Aasberg-Petersen, K., Bak Hansen, J.-H., Christensen, T., Dybkjaer, I., Seier Christensen, P., Stub Nielsen, C., Winter Madsen, S., Rostrup-Nielsen, J., "Technologies for Large Scale Gas Conversion", *Appl. Catal. A-Gen.*, Vol. 4, 379–387 (2001).
- Balachandran, U., Dusek, J., Mieville, R., Poepfel, R., Kleefisch, M., Pei, S., Kobylinski, T., Udovich, C., Bose, A., "Dense Ceramic Membranes for Partial Oxidation of Methane to Syngas", *Appl. Catal. A-Gen.*, Vol. 133, No. 1, 19–29 (1995).
- Blanks, R., Wittrig, T., Peterson, D., "Bidirectional Adiabatic Synthesis Gas Generator", *Chem. Eng. Sci.*, Vol. 45, No. 8, 2407–2413 (1990).
- Brejč, M., Supp, E., "Non-Catalytic Partial Oxidation and Special Gasification Process for Higher-Boiling Hydrocarbons", in "Ullmanns Encyclopedia of Industrial Chemistry", Elvers, B., Hawkins, S., Ravenscroft, M., Rounsaville, J., Shulz, G. Eds., 5th Edition, Vol. A12, VCH Verlagsgesellschaft, Weinheim, 202 (1989).
- Chen, C. M., "Ceramic membrane reactor systems for converting natural gas to hydrogen (ITM syngas)", US Department of Energy (2004).
URL <http://www.eere.energy.gov>
- Daubert, T. E., Danner, R. P., "Data Compilation Tables of Properties of Pure Compounds", American Institute of Chemical Engineers, New York (1985).
- Gunn, D., "Transfer of Heat or Mass to Particles in Fixed and Fluidized Beds", *Int. J. Heat Mass Transf.*, 21(4), 467–476 (1978).
- Gunn, D., Misbah, M., "Bayesian Estimation of Heat Transport Parameters in Fixed Beds", *Int. J. Heat Mass Transfer*, Vol. 36, No. 8, 2209–2221 (1993).
- Matros, Y. S., Bunimovich, G. A., "Reverse-Flow Operation in Fixed Bed Catalytic Reactors", *Catal. Rev. Sci. Eng.*, Vol. 38, No. 1, 1–68 (1996).
- Nieken, U., Kolios, G., Eigenberger, G., "Fixed-Bed Reactors With Periodic Flow Reversal: Experimental Results for Catalytic Combustion", *Catal. Today*, Vol. 20, 335–350 (1994).
- Reid, R. C., Prausnitz, J. M., Poling, B. E., "The Properties of Gases and Liquids", 4th Edition, McGraw-Hill, Inc., New York (1987).
- Smit, J., Van Sint Annaland, M., Kuipers, J. A. M., "Modelling of a Reverse Flow Catalytic Membrane Reactor for the Partial Oxidation of Methane", *Int. J. Chem. React. Eng.*, Vol. 1, No. A54 (2003).
- Smit, J., van Sint Annaland, M., Kuipers, J. A. M., "Development Of Novel Reactor Concept for the Partial Oxidation of Methane to Syngas", *Chem. Eng. Res. Des.*, Vol. 82, No. A2, 245–251 (2004).
- Smit, J., van Sint Annaland, M., Kuipers, J. A. M., "Feasibility Study of a Reverse Flow Catalytic Membrane Reactor with Porous Membranes for the Production of Syngas", Accepted for publication in *Chem. Eng. Sci.* (2005).
- Zehner, P., Schlünder, E., "Wärmeleitfähigkeit von Schüttungen bei Mässigen Temperaturen", *Chem. Ing. Techn.*, 42(14), 933–941 (1970).