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Two dimensional modeling of a membrane reactor for ATR of methane

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ABSTRACT

A theoretical study of a multitubular membrane reactor for the autothermal reforming of methane over a Ni/Al₂O₃ catalyst is presented. A 2-D model is selected to account for the strong composition and temperature gradients along the axial and radial coordinates. The effect of the degree of reduction of the Ni catalyst on the reforming reaction rates is taken into account in the model. The influence of the main operating conditions on the reactor behavior is studied. The results suggest that the membrane reactor is a promising alternative to carry out ATR of methane at milder conditions than those commonly found in a conventional reactor. The axial distribution of the O₂ fed to the reactor is a powerful tool to influence the axial temperature profiles. Nevertheless, a careful design is necessary to avoid risky conditions such as oxygen accumulation in the tubes.

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1. Introduction

Hydrogen is considered as a nonpolluting, inexhaustible, efficient, and cost-attractive future energy carrier with a fuel cell as its converter [1]. PEM fuel cells have important advantages over other types of cells, e.g., high energy density, fast time of ignition and response, low operating temperatures and compact system. These characteristics make PEMFC suitable for automotive transport [2].

The inconveniences related with the distribution and storage of H_2 due to its low volumetric energy density at constant pressure and temperature, make necessary the production of H_2 in situ from other fuels [3]. Although H_2 can be produced from a wide variety of resources using a range of different technologies, its production from fossil fuels is the most widely used in the present (near 96% of the total primary energy comes from fossil fuels [4]).

Natural gas is generally preferred and will remain the major feedstock for manufacturing of H_2 in the near future [5,6]. Steam reforming (SR) of natural gas is the most important process for the production of H_2 and has been widely investigated [5,7]. In this process, steam reacts with methane in presence of an appropriate catalyst to produce synthesis gas. Even though SR process can lead to high yields, the strong endothermicity of the reactions makes it necessary to provide a large amount of heat by fuel burning (commonly natural gas) in the furnace chamber. Because of this

demand of energy, the reformer configuration becomes very large and impractical for fuel cells in mobile appliances.

Hydrogen production using autothermal reforming (ATR) has attracted considerable attention due to its high energy efficiency with low investment cost due to its simple design [8]. In ATR the heat for the reforming reactions is supplied by internal combustion. Consequently, there is no need to supply heat from an external source. The overall chemical reactions taking place in the ATR include total oxidation (Eq. (1)), steam reforming (Eqs. (2) and (4)), and water gas shift (Eq. (3)). The energy generated from the oxidation reaction is used for SR, leading to a local decrease in temperature, which favors the equilibrium of the water gas shift reaction (WGSR).

 $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H_{r1} = -802.30 \text{ kJ/mol}$ (1)

$$CH_4 + H_20 \leftrightarrow CO + 3H_2 \quad \Delta H_{r2} = 206.10 \,\text{kJ/mol}$$
 (2)

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{r3} = -41.15 \text{ kJ/mol}$$
(3)

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad \Delta H_{r4} = 165.00 \text{ kJ/mol}$$
 (4)

The main advantages of the use of the ATR process with respect to the SR process are related to economics of scale. Besides, ATR reactor is a very compact unit considered an attractive alternative to mobile fuel cells [3].

However, a common problem in ATR reactors is the evolution of the axial temperature profiles, which can exhibit pronounced hot spots near the reactor inlet [8–10]. These high temperatures introduce considerable stress on the reactor materials and can damage the catalyst, particularly when a Ni catalyst is employed [3,11].



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f

g

i

fluid

reaction *i*

gas

Nomenclature			
A:	pre-exponential factor reaction dependant		
B_0	geometric parameter. m ²		
Ci	molar concentration of component <i>j</i> , kmol/m ³		
\dot{C}_{pj}	specific heat of component <i>j</i> , kJ/(kmol K)		
d_p	equivalent diameter of the catalyst pellet (Eq. (8)),		
	m		
d _S	shell diameter, m		
d _T	internal tube diameter, m		
$D_{j,-K}^{c}$	elective knudsen antusion coefficient of compo-		
D	nent j , m^2/s		
D _{er} f	friction factor, dimensionless		
J F.	motion factor, dimensionless molar flow of component <i>i</i> Nm ³ /h or kmol/h (Fa		
1	(10))		
Fr	reduction factor, dimensionless		
F _{S0}	feed flowrate of O ₂ (shell side), Nm ³ /h		
F_{T0}	total feed flowrate, Nm ³ /h		
G	mass flux, kg/(m ² s)		
Jj	permeation flow of component <i>j</i> , $\text{kmol}_j/(\text{s}\text{m}^2)$		
k_{1a}, k_{1b}	kinetic constants of r_1 kmol/(kg _{cat} s Pa ²)		
K_2	kinetic constants of r_2 , kinol Pd ^{oio} /(kg _{cat} S)		
k_3	kinetic constants of r_4 kmol Pa ^{0.5} /(kg _{out} s)		
K ₀	geometric parameter. m		
K _{ea.2}	equilibrium constants of r_2 , Pa ²		
$K_{eq,3}$	equilibrium constants of r_3 , dimensionless		
$K_{eq,4}$	equilibrium constants of r_4 , Pa ²		
Kj	adsorption constant for component <i>j</i> in reforming		
wΟX	and water-gas shift reactions, Pa ⁻¹		
Kin	adsorption constant for component j in combustion		
T	reaction, Pa		
L M:	molecular weight of component $i \ kg/kmol$		
n_T	number of tubes, dimensionless		
p_i	partial pressure of component <i>j</i> (tube side), Pa		
P	total pressure, Pa		
P_m	average pressure between membrane sides at each		
	axial position, Pa		
r	radial coordinate, m		
r _i R	1 $(11^{\circ} S)$ $(11^{\circ} S)$ $(11^{\circ} S)$ $(11^{\circ} S)$ $(11^{\circ} S)$		
Re	oxygen feed ratio $(F^0_{\alpha\alpha}/F^T_{\alpha\alpha})$, dimensionless		
R_T	internal tube radius, m (Fig. 1)		
T	temperature, K		
<i>u</i> _s	superficial velocity, m _f ³ /m _r ² s		
U	overall heat transfer coefficient, $W/(m^2 \circ C)$ or		
	$kJ/(h m^2 K) (Eq. (10))$		
<i>x</i> ₀₂	oxygen conversion, dimensionless		
y_j	avial coordinate m		
Z	axial cooldinate, in		
Subscrip	ts		
0	at the axial coordinate <i>z</i> = 0		
cat	catalyst		
CH ₄	methane		
C0	carbon monoxide		
CO_2	carbon dioxide		
H ₂ H ₂ O	nyurogen water		
1190	Water		

	j O ₂ r rm s	component j oxygen reactor radial mean values superficial shell side			
	S T	tube side			
	Superscr	ipts			
	0	at the axial coordinate $z=0$			
	OX	combustion reaction			
	S	shell side			
	Т	total			
	Greek Letters				
	α	heat transfer coefficient, W/(m ² °C)			
	δ	membrane thickness, m			
	ΔH_{ri}	heat of reaction <i>i</i> , kJ/kmol			
	ΔP_i partial pressure difference of component <i>j</i> between membrane sides at each axial position. Particle P				
	6.5	hed porosity dimensionless			
	c_B beta pointsity, uniteristonicess n_i effectiveness factor for reaction <i>i</i> dimensionless				
	$\lambda_{\rm or}$ radial effective conductivity $W/(m^{\circ}C)$ or $kI/(sm^{\circ}C)$				
	Ner -	(Eq.(7))			
	μ_i	viscosity of component <i>j</i> , Pa s			
	v_{ij}	<pre>stoichiometric coefficient (reaction i, component j)</pre>			
	ρ_B	bed density, kg/m ³			
	$ ho_g$	gas density, kg/m _f			
	$ ho_P$	catalyst density, kg/m ³			
	Abbrevic	itions			
	autothermal reforming				
	HGR	heat generation rate, $GJ/(m^3 h)$ (<i>HGR</i> =			
	PEMFC	$\eta_1 r_1(-\Delta H_{r_1}) + \sum_{i=2}^{*} F_r \eta_i r_i(-\Delta H_{r_i}))$ proton-exchange (or polymer electrolyte) mem-			
		brane fuel cell			
	SR	steam reforming			
	VDR	varying degree of reduction			
	WGSR	water gas shift reaction			

A possible alternative to reduce or eliminate the hot spots is the distribution of the oxygen feed along the reactor length by dividing the packed bed into stages and splitting the oxygen stream [12–14]. This controlled feed of oxygen can also be obtained by means of an inorganic membrane, aiming to operate the reactor under milder autothermal conditions and high hydrocarbon conversion.

Membrane reactors have been widely investigated as controlled reactant distributors [15,16]. Relevant studies were performed for oxidative coupling of methane [17,18] and dehydrogenation of low alkanes [19–21]. Some authors have also explored the methane oxidative reforming using membranes as oxygen distributors [6,22–26]. Most of these investigations are focus on fluidized bed membrane reactors. In spite of the multiple advantages of this configuration (mainly for its efficient heat removal), it becomes impractical for mobile appliances.

A packed bed membrane reactor is proposed in the present work to carry out the ATR of methane. An inorganic porous membrane is selected to axially distribute the required oxygen. The inert membrane tubes are assumed to be filled with catalyst particles, and oxygen is dosed from the shell side through the membrane into the tubes, as shown in Fig. 1. Although dense oxide membranes have been used for oxygen distribution in the ATR of methane showing reasonable permeation rates [27], dense membranes show limited



Fig. 1. Schematic representation of the membrane reactor for ATR of methane.

thermal and chemical stability upon aging [15,28,29]. Conversely inorganic porous membranes allow higher permeation fluxes than those of dense membranes [19,30,31] and have been extensively used in catalytic reactors showing high stability [32,33].

In this article, a theoretical study of a multitubular packed bed membrane reactor for the ATR of methane over a Ni/MgOAl₂O₃ catalyst is presented. By means of a 2D pseudohomogeneous model, the convenience of this novel design to produce hydrogen to feed a PEM fuel cell for mobile appliances is analyzed. The influence of the main operating variables on the reactor performance is also addressed.

2. Mathematical model

A two-dimensional, pseudo-homogeneous, steady-state model is proposed to represent the ATR of methane in a multitubular packed bed membrane reactor. In the present design, the inert membrane tubes are filled with catalyst particles. A stream of methane, steam and (optional) O_2 is fed by the tube side while a fraction of oxygen is distributed from the shell side through the tubular porous membrane (Fig. 1).

To simulate the ATR membrane reactor, the following hypotheses have been assumed:

- axial dispersion of mass and energy and external transport limitations are neglected because of the high total flowrates through the catalyst bed,
- internal mass transport limitations are accounted for by means of constant effectiveness factors for the four reactions under consideration [9],
- the catalyst particle is assumed to be isothermal,
- bed porosity is assumed to be radially constant [16],
- ideal gas law holds true,
- resistances to heat and mass transfer offered by gas films on both sides of the membrane wall are neglected,
- the reactor shell is assumed to be properly isolated, with negligible heat losses to the environment.
- Ergun's friction factor is employed to predict the pressure drop inside the tubes [34], while isobaric conditions are selected for the O₂ flowing on the shell side.

From these assumptions, the governing equations of the reactor are given below:

Reaction side (catalyst tubes)

Total mass balance

$$\frac{\partial(u_s\rho_g)}{\partial z} = \frac{4}{d_T} J_{O_2} M_{O_2} \tag{5}$$

Component mass balances

$$\frac{\partial(u_s c_j)}{\partial z} = D_{er} \left(\frac{\partial^2 c_j}{\partial r^2} + \frac{1}{r} \frac{\partial c_j}{\partial r} \right) + \sum_{i=1}^4 v_{ij} \eta_i r_i \tag{6}$$

Energy balance

$$\frac{\partial T}{\partial z} = \frac{1}{u_s \sum_{j=1}^6 c_j \, C p_j} \left[\sum_{i=1}^4 \eta_i r_i (-\Delta H_{ri}) + \lambda_{er} \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) \right] \quad (7)$$

 $j = O_2$, CO_2 , CH_4 , H_2O , CO, H_2 Momentum equation

$$\frac{dP}{dz} = -\frac{G}{\rho_g d_P} \left(\frac{1 - \varepsilon_B}{\varepsilon_B^3}\right) \left[\frac{150(1 - \varepsilon_B)\mu_g}{d_P} + 1.75G\right]$$
(8)

Retentate side (shell)

Mass balance

$$\frac{dF_j^S}{dz} = -J_j \pi \, d_T n_T \quad j = O_2 \tag{9}$$

Energy balance

•

$$\frac{dT_S}{dz} = \frac{U\pi \, d_T n_T (T - T_S)}{F_j C p_j} \quad j = O_2 \tag{10}$$

Boundary conditions

• At z = 0, $\forall r$ (inlet condition):

$$c_j = c_{j0}, T = T_0, P = P_0, T_S = T_{0S}, P_S = P_{0S}$$
 (11)

• At r = 0, $\forall z$ (symmetry condition):

$$\frac{\partial c_j}{\partial r} = 0 \quad \text{for } j = O_2, CO_2, CH_4, H_2O, CO, H_2$$
 (12)

$$\frac{\partial T}{\partial r} = 0 \tag{13}$$

• At $r = R_T$, $\forall z$ (tube wall condition):

$$\frac{\partial C_j}{\partial r} = 0 \quad \text{for } j = CO_2, CH_4, H_2O, CO, H_2$$
(14)

$$\frac{\partial c_j}{\partial r} = \frac{J_j}{D_{er}} \quad \text{for} \, j = \, O_2 \tag{15}$$

$$\frac{\partial T}{\partial r} = \frac{U}{\lambda_{er}}(T_S - T) \tag{16}$$

where the permeation flux is quantified by the following expression [35]:

$$J_j = \Delta P_j \left(\frac{D_{j,k}^e}{RT\delta} + \frac{B_0}{RT\delta\mu_j} P_m \right) \quad j = O_2$$
(17)

$$D_{j,k}^{e} = K_0 \sqrt{\frac{8RT}{\pi M_j}} \tag{18}$$

The overall heat transfer coefficient (*U*) is evaluated as resistances in series on the tube and shell sides. The heat transfer coefficients (α_T and α_S) are calculated from the data fitted by Yagi and Kunii [36] and the Delaware method [37], respectively.

The radial effective diffusion coefficient (D_{er}) is adopted from Froment and Bischoff [34], and the radial effective conductivity (λ_{er}) is calculated following the guidelines suggested by Zehner and Schlünder [38].

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Table 1

Geometrical and transport parameters and operating conditions of the simulated membrane reactor.

Tube length, L	1 m
Internal tube diameter, d_T	0.0156 m
Shell diameter, d _S	0.3048 m
Number of tubes, n_T	90
Feed pressure, P ₀	25 atm
Shell side pressure, P _S	25.7–26.9 atm
Inlet tube temperature, T ₀	535–650 °C
Inlet shell temperature, T _{S0}	535–650 °C
Total feed flowrate, F _{T0}	3.9407 kmol/h
Shell O ₂ flowrate, F _{S0}	3 kmol/h
F^{0}_{H20}/F^{0}_{CH4}	1.4 [10]
F^{T}_{O2}/F^{0}_{CH4}	0.598
F_{H2}^{0}/F_{CH4}^{0}	0.0003
$R_f = F_{02}^0 / F_{02}^T$	0.001
Catalyst	30% Ni/Al ₂ O ₃
Catalyst diameter, dp	0.001 m
Catalyst density, ρ_P	2355.3 kg/m ³
Bed porosity, ε_B	0.4
Membrane thickness, δ	0.00175 m
Geometrical membrane parameter, K ₀	$23.1 \times 10^{-10} \text{ m}$
Geometrical membrane parameter, B ₀	$11.5 \times 10^{-17} m^2$
Overall heat transfer coefficient, U	30.53-30.94 W/(m ² °C)
Heat transfer coefficient tube side, α_T	408.87-1635.16 W/(m ² °C)
Heat transfer coefficient shell side, α_S	33.00-31.54 W/(m ² °C)
Effective radial diffusion coefficient, Der	0.1127-0.2638 m ² /h
Radial effective conductivity, λ_{er}	0.3654-0.5260 W/(m°C)
Ergun Friction factor, f	44.25-45.58

In order to avoid the multiplicity of steady states inherent to countercurrent operation, a cocurrent flow configuration between the process gas and the coolant (O_2) streams is adopted.

The thermodynamic properties of the components are extracted from the literature [39,40]. Gas properties in the model depend on the temperature and composition of the gas mixture at each axial position.

A commercial tubular microfiltration membrane (SCT, Inocermic), modified by deposition of silica in order to attain the desired permeation characteristics [41], is selected for the simulations. The original membrane material is α -Al₂O₃. The parameters K_0 and B_0 , are obtained from Pedernera et al. [42]. The geometric parameters of the reactor, catalyst and membrane, together with the transport parameters and operating conditions used in the simulations, are given in Table 1.

The diameter and density of the catalyst particles, as well as the bed porosity are extracted from literature [43]. The length and disposition of the tubes for the proposed design are adopted from the guidelines suggested by Kern for heat exchangers [44].

Eqs. (5)–(10) are integrated by means of a Gear algorithm, after a discretization procedure along the radial coordinate has been done.

The reaction scheme considered in the present contribution includes the complete combustion of methane, the steam reforming reactions and the WGSR [9,11,12]. The kinetic expressions of

Table 2Reaction rate expressions.

$$\begin{split} r_{1} &= \frac{k_{1a}p_{CH_{4}}p_{O_{2}}}{\left(1+K_{CH_{4}}^{ON}p_{CH_{4}}+K_{O_{2}}^{ON}p_{O_{2}}\right)^{2}} + \frac{k_{1b}p_{CH_{4}}p_{O_{2}}}{\left(1+K_{CH_{4}}^{ON}p_{CH_{4}}+K_{O_{2}}^{ON}p_{O_{2}}\right)} \\ r_{2} &= \frac{k_{2}/p_{H_{2}}^{2.5}\left(p_{CH_{4}}p_{H_{2}O}-p_{H_{2}}^{3}p_{CO}/K_{eq,2}\right)}{\left(1+K_{COPCO}+K_{H_{2}}p_{H_{2}}+K_{CH_{4}}p_{CH_{4}}+K_{H_{2}O}p_{H_{2}O}/p_{H_{2}}\right)^{2}} \\ r_{3} &= \frac{k_{3}/p_{H_{2}}(p_{CO}p_{H_{2}O}-p_{H_{2}}p_{CO_{2}}/K_{eq,3})}{\left(1+K_{CO}p_{CO}+K_{H_{2}}p_{H_{2}}+K_{CH_{4}}p_{CH_{4}}+K_{H_{2}O}p_{H_{2}O}/p_{H_{2}}\right)^{2}} \\ r_{4} &= \frac{k_{4}/p_{H_{2}}^{3.5}\left(p_{CH_{4}}p_{H_{2}O}^{2}-p_{H_{2}}^{4}p_{CO_{2}}/K_{eq,4}\right)}{\left(1+K_{CO}p_{CO}+K_{H_{2}}p_{H_{2}}+K_{CH_{4}}p_{CH_{4}}+K_{H_{2}O}p_{H_{2}O}/p_{H_{2}}\right)^{2}} \end{split}$$

the system of reactions are shown in Table 2. The combustion of methane (reaction (1)) is evaluated by means of the kinetic model proposed by Trimm and Lam [45], while the steam reforming (reactions (2) and (4)) and WGS (reaction (3)) are assessed using the kinetics by Xu and Froment [46]. The kinetic constants and adsorptions parameters of the involved reactions are reported in Table 3. The adsorption constants for methane and oxygen on Ni catalyst are extracted from De Smet et al. [11]. The expressions of equilibrium constants corresponding to reactions (2)–(4) are reported in Table 4 [47].

An important problem in the modeling of the partial oxidation of methane is the degree of reduction of the Ni catalyst required for the steam reforming. According to the observations reported by Dissanayake et al. [48], the steam reforming would be consecutive to the complete combustion of CH₄. This has been accounted for in the present simulations by multiplying the rates of the steam reforming reactions and the WGS reaction by a reduction factor (*Fr*), which is a power function of the fractional oxygen conversion. This approach was called *Varying Degree of Reduction Model (VDR)* by De Groote and Froment [9].

2.1. Model validation

The adopted model is validated against industrial and modeling data available in the open literature [9]. Table 5 shows the validation results. The 1-D version of the model (Eqs. (5)–(17)) was used in the simulations. After a fitting procedure in the reduction factor (*Fr*) proposed by De Groote and Froment [9], most of the variables are reproduced satisfactorily by the present model (Table 6). However, some discrepancies are observed in the value of the hot-spot (T_{max}) and its axial position $L(T_{max})$. These differences can be attributed to the space time (bed density) adopted in this work, probably different from that used by De Groote and Froment [9] (data not reported by the authors). The simulated outlet temperature (T_{out}) is higher than that of the industrial reactor (heat losses have been neglected): accordingly, the methane slip is slightly underestimated.

Table 3

Kinetic and adsorption parameters values for combustion, reforming, and water-gas shift reactions [45,46].

Kinetic parameters of reaction (r_i)			Adsorption parameters of component j		
$k_i = A_i \exp\left(\frac{-E_{a,i}}{RT}\right)$			$K_j = A(K_j) \exp\left(rac{-\Delta H_j^0}{RT} ight)$		
k _i	A_i^a	$E_{a,i}$ (kJ/mol)	K_j	$A(K_j)^{\mathrm{b}}$	ΔH_j^0 (kJ/mol)
k _{1a}	8.11×10^{-2}	86.0	K _{CH}	1.26×10^{-6}	-27.3
k_{1b}	$6.82 imes 10^{-2}$	86.0	$K_{02}^{0X^4}$	$\textbf{7.87}\times 10^{-12}$	-92.8
<i>k</i> ₂	3.66×10^{14}	240.1	K _{CH4}	$6.65 imes10^{-9}$	-38.3
k3	$5.41 imes 10^{-3}$	67.1	K _{CO}	8.23×10^{-10}	-70.7
k_4	8.83×10^{13}	243.9	K_{H_2}	$6.12 imes10^{-14}$	-82.9
			K_{H_2O}	$1.77 imes 10^5$	+88.7

^a Units: $(A_{1a}), (A_{1b})$: kmol Pa⁻² kg_{cat}⁻¹ s⁻¹; (A_2) : kmol Pa^{0.5} kg_{cat}⁻¹ s⁻¹; (A_3) : kmol Pa⁻¹ kg_{cat}⁻¹ s⁻¹; (A_4) : kmol Pa^{0.5} kg_{cat}⁻¹ s⁻¹.

^b Units: $A(K_{CH_4}^{OX})$, $A(K_{O_2}^{OX})$, $A(K_{CH_4})$, $A(K_{CO})$, $A(K_{H_2})$: Pa⁻¹; $A(K_{H_2O})$: dimensionless.

Table 4 Equilibrium constants [47].

Reaction	Units	Expressions
<i>r</i> ₂	Pa ²	$K_{eq,2} = 1.026676 \times 10^{10} \exp\left(-\frac{26830.0}{T} + 30.11\right)$
<i>r</i> ₃	-	$K_{eq,3} = \exp\left(\frac{4400.0}{T} - 4.063\right)$
r_4	Pa ²	$K_{eq,4} = K_2 K_3$

Table 5

Reactor dimension and operating conditions of a conventional ATR reactor.

	Industrial reactor [9]	De Groote and Froment simulations (VDR Model) [9]	This work
F ⁰ CH ₄ (Nm ³ /h)	3483	3483	3483
P_0 (atm)	25	25	25
<i>T</i> ₀ (°C)		535	535
$F^{T}_{02}/F^{0}CH_{4}$	0.598	0.598	0.598
$F^{T}_{H20}/F^{0}CH_{4}$	1.4	1.4	1.4
$F^{T}_{H2}/F^{0}CH_{4}$		0.0003	0.0003
y ⁰ 02		0.19945	0.19945
у ⁰ сн4		0.33352	0.33352
у ⁰ н2		0.0001	0.0001
y^{0}_{CO2}		0	0
у⁰ н20		0.46693	0.46693
$d_T(\mathbf{m})$		1.2	1.2
<i>L</i> (m)		3	3
$d_p(\mathbf{m})$		0.005	0.005
$\rho_B (kg_{cat}/m^3R)$		-	1413.18

Table 6

Validation results.

Parameter	Industrial ATR reactor [9]	De Groote and Froment simulations (VDR Model) [9]	This work
T _{max} (°C)	-	1167	1177
$L(T_{max})(\mathbf{m})$	-	1.37	0.3986
<i>y</i> ₀₂	0	0.00026	~ 0
Усн4	0.008	0.0055	0.00351
Ун2	0.456	0.458	0.46272
усо	0.160	0.156	0.16499
<i>y</i> _{C02}	0.07	0.06	0.06035
<i>у</i> _{H20}	0.306	0.318	0.30842
T_{out} (°C)	950	974	1007
F_{H2} (Nm ³ /h)	6976	6925	7043
F_{CO} (Nm ³ /h)	2444	2355	2511

shows the reactor dimension and operating conditions of the conventional ATR reactor considered for comparison purposes. Table 6

3. Results and discussion

3.1. Comparison between 2D and 1D models

Fig. 2 shows the radial mean temperature calculated from the 2D model for the reference condition of the membrane reactor, as well as the temperature evolution corresponding to an equivalent 1D model [49]. Both models predict a strong hot spot in the middle of the reactor, followed by a tube section where a continuous increase of temperature is observed. Although the 1D model tracks satisfactorily the radial mean temperature, it predicts a hot-spot value 24 °C lower than that of the 2D model, and the location of this local maximum slightly shifted to the entrance (see detail in the figure). Since the gas flowing through the shell side is acting as a cooling medium, its temperature (T_S) increases monotonically along the axial position. Near the hot spot location, the temperature rise in T_S is particularly significant, because of the high heat-transfer rate towards the shell side. As shown in Fig. 3, oxygen is



Fig. 2. Axial temperature profiles for the reference condition. Results from the 2D (radial mean values) and 1D models. $T_0 = 535 \degree \text{C}$, $F_{02}^{-T}/F^0_{CH4} = 0.598$.

accumulated in the first half of the membrane tubes (reaction side), because the consumption rate by combustion (reaction (1)) is lower than the permeation rate through the membrane. Once the reaction temperature reaches high enough values, a sudden oxygen consumption occurs, which is associated to a fast heat release by reaction (1) causing the significant hot spot in Fig. 2. Ahead of the hot spot, a fast temperature decrease is observed, which is related to the overcoming evolution of the reforming reactions (2)–(4). In fact, the hydrogen production begins at this axial coordinate, i.e., $z \sim 0.45$ m (Fig. 3, left ordinate), beyond the position where the Ni catalyst reaches the appropriate degree of reduction to be active for steam reforming.

Near the hot spot location, strong temperature and composition gradients in the radial direction appear. This can be seen in Figs. 4 and 5, respectively, for two axial positions close to the temperature peak shown in Fig. 2. In spite of the small diameter of the membrane tubes (d_T = 15.6 mm), temperature differences up to 80 °C are predicted between the tube center and the membrane wall, and the maximum temperature (at r = 0) can exceed the radial mean temperature in more than 40 °C (Fig. 4). On the other hand, the 1D model can underestimate the radial mean temperature significantly (e.g., for z = 0.567 m), which is clearly non conservative. The profiles of oxygen molar fraction also show important gradients in the radial direction (Fig. 5). Due to the permeation fluxes through



Fig. 3. Axial profiles of H_2 production (left ordinate axis) and O_2 molar fraction (right ordinate axis), for the conditions of Fig. 2. Results from the 2D (radial mean values) and 1D models.



Fig. 4. Radial temperature profiles at axial positions close to the hot spot. Operating conditions of Fig. 2.



Fig. 5. Radial profiles of oxygen molar fraction at axial positions close to the hot spot. Operating conditions of Fig. 2.

the membrane pores, more oxygen is available for the combustion reaction near $r = R_T$; conversely, at radial positions close to the tube center the O₂ has been partly consumed, the atmosphere is less oxidative and a higher degree of reduction of the catalyst is reached. Under these conditions, the hydrogen production is favored in the central region of the tube. For other axial positions close to the reactor outlet, the oxygen becomes completely depleted in the tube center, and the radial temperature profiles are much flatter, showing slight minima at r = 0 (results not shown). Fig. 5 also points out that the predictions of the 1D model can differ significantly from the radial mean values, particularly at axial positions where high reaction rates take place.

These results confirm that a two dimensional model is necessary to accurately predict the strong composition and temperature gradients occurring in the membrane tubes, and to account for the influence of the selected tube diameter on these radial variations. Clearly, small diameters would be necessary not only to provide high membrane areas for oxygen permeation, but also to avoid excessive temperatures that could damage the catalyst.



Fig. 6. Axial profiles (radial mean values) in the MR for three different feed temperatures, T_0 = 535, 600 and 650 °C. (a) Temperatures on reaction and shell sides; (b) H₂ production (left ordinate axis) and molar fraction of oxygen (right ordinate axis).

3.2. Influence of the feed temperature in the membrane reactor for ATR of methane

Fig. 6a shows the temperature variation inside the membrane reactor for three different feed temperatures. The flowrate and composition of the feed stream, as well as the total amount of permeated oxygen, were kept constant at their reference values (Table 1). The curve for $T_0 = 535 \,^{\circ}\text{C}$ corresponds to that of the 2D model in Fig. 2. Under these conditions the membrane reactor presents a hot spot of around 941 °C, whereas the outlet temperature of the process gas is around 875 °C. When the feed temperature is increased (e.g., $T_0 = 600 \,^{\circ}$ C), the outlet temperature follows the same trend, due to the higher enthalpies of the process gas and oxygen streams at z=0. However, a significant reduction in the value of the hot spot is predicted. This phenomenon is confirmed for the curve corresponding to 650 °C, which shows the lowest hot spot (around 774°C) and the highest outlet temperature. Besides, the location of the hot spot shifts to the reactor inlet as T_0 is increased. This type of "inverse response" of the hot spot value with respect to the feed temperature is an interesting phenomenon that was found for other operating conditions in the membrane reactor and does not appear for the conventional fixed bed reactor [49]. The results can be explained by inspection of Fig. 6b, where the H₂ flowrate and O₂ molar fraction inside the membrane tube are presented for the same conditions of Fig. 6a. As shown, the higher T_0 , the lower the oxygen accumulation phenomenon, because the rate of reaction (1)(combustion of methane) increases considerably in the first section of the tube. This attenuates the heat generation rate at the position where the maximum in the oxygen profile appears. As it was described in Fig. 2, the fast oxygen consumption at $z \sim 0.55$ m is the cause of the strong hot spot established for $T_0 = 535 \,^{\circ}$ C. Increasing T_0 also leads to improving the H₂ production at the reactor outlet (Fig. 6b). This is consistent with the higher temperatures observed in Fig. 6a at z = 1 m. For higher feed temperatures, the model also predicts that the H₂ production starts closer to the entrance, where the catalyst would reach the necessary degree of reduction to carry out the endothermic reforming reactions.

The results shown in Fig. 6 are consistent with the overall heat balance in the membrane reactor. Since the same amount of O_2 is being converted for the three analyzed temperatures (same total O_2 is fed, same residual O_2 at the outlet), the total heat generation by



Fig. 7. Axial profiles at different radial positions (r=0, $r=R_T/2$, $r=R_T$ and radial mean value: rm), for one of the operating conditions of Fig. 6: $T_0 = 650 \degree C$. (a) O_2 molar fraction. (b) Heat generation rate.

combustion is approximately constant. The total heat consumption resulting from the reforming reactions is slightly higher when T_0 is augmented (H₂ production improves). Thus, the increase in the outlet temperatures predicted by the model is mainly explained by the higher inlet temperatures of both the process gas and shell side streams.

In order to analyze the strong heat effects along the axial position in the membrane reactor for ATR, Fig. 7 shows the O₂ molar fraction and the heat generation rate $(HGR = \eta_1 r_1(-\Delta H_{r_1}) +$ $\sum_{i=2}^{4} F_r \eta_i r_i (-\Delta H_{ri})$ along the tube length, for different radial coordinates and a feed temperature of 650°C. Up to the position z = 0.12 m, only the combustion reaction takes place (see the null H₂ evolution in Fig. 6b); therefore, the HGR is positive at all the radial coordinates, which means that heat is being released by chemical reaction. The value of the HGR rises together with the molar fraction of O_2 , up to an axial position where the permeation flux is balanced by the combustion rate. Beyond this maximum in the oxygen content, the lower O₂ concentrations lead to a higher degree of reduction of the catalyst. Then, the endothermic reactions (2) and (4) start and the HGR goes down and becomes negative. This reactor zone shows the temperature decrease observed in Fig. 6a after the hot spot. From this point onward, (z > 0.45 m), the heat released by combustion prevails over the heat consumption associated to the reforming reactions, and a mild temperature increase is observed.

It is important to note in Fig. 6 that significant amounts of non converted oxygen appear at z = 1 m for the three feed temperatures analyzed ($\sim 2\%$ of O₂ in the reformed gas). These O₂ slips are clearly undesirable and should be avoided for safety reasons.

Different strategies have been proposed to overcome this problem [3,17,29,30,49]. A possible alternative could be increasing the membrane area. Fig. 8 shows the axial profiles corresponding to the same operating conditions of Fig. 6, but the reactor length is now 1.8 m. The general trends of Fig. 6 are also found in Fig. 8, i.e., lower hot spots, higher H_2 productions and higher outlet temperatures take place as the feed temperature increases. However, the hot spots are significantly lower than those of Fig. 6. In all the cases analyzed, the maximum reactor temperature is not located at an intermediate axial position but at the reactor outlet. This behavior of the membrane reactor could be advantageous from an operative standpoint, and does not appear in a conventional process



Fig. 8. Axial profiles (radial mean values) in the MR, for three different T_0 values. (a) Temperatures on reaction and shell sides; (b) H₂ production (left ordinate axis) and molar fraction of oxygen (right ordinate axis). Reactor length: L= 1.8 m.

for which all the O_2 is fed at the reactor mouth. As the membrane area is 80% higher than that in Fig. 6 and the total amount of oxygen being permeated is the same, the local O_2 fluxes through the membrane are lower and consequently the phenomenon of O_2 accumulation inside the tubes is considerably attenuated (compare Figs. 6b and 8b). Even though the amount of catalyst in the second case (Fig. 8) is 80% higher than that in the first (Fig. 6), the outlet H₂ productions do not increase significantly. This result suggests that, for these conditions, the H₂ production in the membrane reactor is not controlled by the space time. Nevertheless, the use of longer membrane tubes results in milder operating conditions, and the O_2 slips are minimized: the reformed gas now contains only 1.27% of O_2 (Fig. 8b).

Another way of increasing the total conversion of the permeated oxygen is by dividing the membrane tube into two sections: a porous first segment, followed by a non porous one. Fig. 9 shows the



Fig. 9. Axial profiles (radial mean values) in the MR, for $T_0 = 650$ °C and two different lengths of the non-porous section of the membrane. (a) Temperatures on reaction and shell sides; (b) H₂ production (left ordinate axis) and molar fraction of oxygen (right ordinate axis). *L* = 1 m. Total feed of O₂ kept constant.

axial profiles corresponding to two different membrane designs: 20% and 0% of non-porous tubes. To compare the results, the total feed of O_2 (F_{O2}^T) is the same for both cases, which is achieved by adjusting the pressure in the shell side. As a consequence of the null permeation in the final non porous section, the total conversion of O_2 increases (see the O_2 slips in Fig. 9b), i.e., the total amount of heat released by combustion is higher. This is accompanied by a higher outlet temperature and also a higher production of H₂. However, as less membrane area is available, the local O_2 fluxes through the membrane have to be increased to permeate the same total amount of O_2 . Therefore, more O_2 is accumulated in the tubes (Fig. 9b) and more pronounced hot spots are observed (Fig. 9a).

4. Conclusions

A simulation study of a membrane reactor for ATR of methane has been carried out. The main results suggest the following conclusions:

- For the conditions studied, a 1D model underestimates the radial mean temperature at axial positions close to the hot spot and is clearly non conservative. Even for membrane tubes of small diameters, significant radial gradients of temperature and composition can occur.
- The balance between the local permeation fluxes and the oxygen consumption rate by chemical reaction is a key factor, because it affects the degree of reduction of the Ni catalyst at each axial location and therefore the evolution of the reforming reactions.
- The membrane reactor for ATR can exhibit an inverse response with respect to the feed temperature. Due to the lateral feed of oxygen, an increase in the feed temperature of the process gas can minimize the accumulation of oxygen in the catalyst bed, leading to lower hot spots located nearer the reactor inlet. This behavior is not found in conventional fixed-bed reactors.
- For a fixed total amount of O₂ to be fed to the ATR reactor, an increase in the permeation area can reduce considerably the hot spots. This improvement results from lower local fluxes through the membrane, i.e., from a more efficient axial distribution of one of the reactants.
- The oxygen slips constitute an important safety problem that can be minimized by means of a final section of non porous membrane, a decreasing porosity profile or higher membrane areas.

Finally, it is important to note that an important challenge still holds, concerning the mechanical stability of the membranes subjected to high temperatures and strong thermal gradients. Too severe operating conditions may result in membrane failures, which in turn may lead to reactor runaway or the formation of explosive mixtures.

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