



Design concepts of a scaled-down autothermal membrane reformer for on board hydrogen production

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HIGHLIGHTS

- An autothermal membrane reactor for H₂ production by MSR is rigorously analyzed.
- MSR effluent is recycled to an oxidation reactor to supply the heat for reforming.
- Temperature increases with feed flow rate when operating with full recycle.
- Axially distributing the oxidation reactor feed improves temperature uniformity.
- Efficiency and permeate flow improves with temperature; hence with feed flow rate.

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ABSTRACT

The design of an on-board autothermal membrane reactor producing pure hydrogen at atmospheric pressure, while recuperating heat, is analyzed mathematically. The suggested design incorporates two reactors exchanging heat; an endothermic methane steam-reforming (MSR) reactor embedding Pd membranes to separate pure H₂, and an exothermic methane oxidation (MOx) reactor fed by the MSR effluent. The analysis is conducted at three levels of details: (i) Thermodynamics reveals that the minimum operating temperature for high thermal efficiency under adiabatic conditions with full recycle of MSR effluents is 550 °C. Feeding the oxidation reactor with added fuel does not improve efficiency. (ii) A kinetic model that accounts for the permeance of the Pd membranes suggests even higher temperatures should be considered when operating with limited membrane area. The effect of catalytic kinetics is small. (iii) A transient detailed one-dimensional model considering heat exchange between the reactors, heat losses to surroundings and axial distribution of the MOx feed is used to study the performance of a 1.3 L system in terms of thermal efficiency and permeate flow rate. Efficiency and H₂ output are favored by higher flow rates, which result in higher temperatures. Combustion of recycled effluent produces hot spots, but distributing the feed axially mitigates the non-uniformity, and improves efficiency and permeate flow rate. Some distinct dynamical aspects are presented.

We conclude that such a nonadiabatic autothermal system can operate at efficiencies of ~66% and expected power density of 0.5 kW/L at maximum MSR temperature of 700 °C, when feeding the MSR reactor with liquid H₂O instead of pre-vaporizing it. This represents significant improvement over previous designs, and is currently tested experimentally.

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1. Introduction

The interest in hydrogen production, to be used in the environmentally friendly proton exchange membrane fuel cells (PEMFC) as energy carrier, is increasing. Hydrogen is almost exclusively produced from methane by reaction set (1). These reactions are conducted commercially in packed beds tubes filled with Ni based

catalyst which are placed in a furnace supplying the heat of reaction through the burning of fuel. Typical operation conditions are pressure of ~25 bar and temperatures as high as 1000 °C for full conversion of methane steam reforming (MSR) to syngas (mixture of CO and H₂). This step is followed by high temperature water gas shift (WGS) (on robust Fe–Cu–Cr catalyst) and low temperature WGS (on Cu based catalyst) to produce as much H₂ as possible. The Cu based catalysts are not used at the high temperature stage due to sintering. These steps are followed by pressure swing adsorption (PSA) for CO₂ removal and methanation (reverse steam

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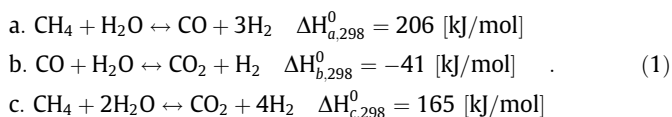
Nomenclature

A_m	pre-exponential factor of membrane permeance [mol/m ² s√bar]	U	overall heat transfer coefficient [kW/m ² K]
A^{Ox}	pre-exponential factor of CH ₄ oxidation reaction [m ³ /kg ^{cat} s]	V	reaction zone volume [m ³]
C_p	specific heat [kJ/mol K] for gas, or [kJ/kg K] for solid	x	conversion
d^i	outer diameter of compartment $i = Ox, SR, SS, m$ [m]	X_j	fraction of MOx flow to j th feed port
D_e	effective axial diffusion coefficient [m ² /s]	y_i	molar fraction of component 'i'
E^m	activation energy for hydrogen transmembrane flux [kJ/mol]	z	axial coordinate [m]
E^{Ox}	activation energy for CH ₄ oxidation reaction [kJ/mol]	<i>Greek letters</i>	
F	molar flow [mol/s]	α_{ij}	stoichiometric coefficient of component 'i' in reaction 'j'
k_e	effective conductivity [kW/mK]	χ	fraction of MSR effluent being recycled to MOx reactor
k_l	Arrhenius expression for reaction l in MSR [mol√bar/kg ^{cat} s] for $l = a, c$, [mol/kg ^{cat} s bar] for $l = b$	ε	porosity of bed
K_l^{eq}	equilibrium constant of reaction l , [bar ²] for $l = a, c$, unitless for $l = b$	η	thermal efficiency
L	total reactor length [m]	κ_i	selectivity factor (1 for H ₂ , 0 for all other components)
L_{II}	length of zone II; the heat recuperation zone [m]	θ	dimensionless temperature
L_m	membranes length, also equals length of zone I [m]	ρ	density [kg/m ³] for solid, or [mol/m ³] for gas
N_m	number of membrane tubes	ζ	dimensionless axial coordinate
P_i	pressure [bar]	<i>Subscripts</i>	
P_i	partial pressure of component i [bar]	g	gas phase
P_{FC}	power of a FC working at 60% efficiency fed by H ₂ produced by the reactor [kW]	i	component i
Q	volumetric flow [m ³ /s]	max	axially maximal
R_l	rate of reaction l in MSR reactor, $l = a, b, c$ [mol/kg ^{cat} s]	s	solid phase
R_g	gas constants, 8.31447×10^{-3} [kJ/mol K]	0	feed
R^{Ox}	rate of methane oxidation reaction [mol/kg ^{cat} s]	<i>Superscripts</i>	
S	reaction zone cross section [m ²]	m	related to the membrane interior, i.e. the permeate
t	time [s]	Ox	related to the methane oxidation reactor
T	temperature [K]	SR	related to the methane steam reforming reactor
		SS	related to the stainless steel exterior

reforming) for clearing any residual CO [1]. Clearly this production scheme, which is adopted in large scale production ($\sim 10^5$ Nm³/h) and in an efficient way, is too complicated for a scale down process aimed at producing small on demand amounts of H₂ (0.1–10 Nm³/h).

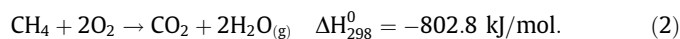
The use of highly selective Pd based membranes for pure H₂-production in integrated membrane reactors has been investigated in the last two decades; see recent reviews by Shigarov et al. [2] and Gallucci et al. [3]. Recent advances in Pd membranes production techniques have led to higher H₂ fluxes, and along with the increasing demand for clean H₂ production, either on board or in decentralized fueling stations, serve as the main incentive for optimizing process design of these complex systems. Process design and catalyst selection for these scaled-down units require conditions different than those of the commercial process (low H₂ partial pressure, low temperatures etc.). These conditions may also accelerate deactivation.

The current research is aimed at developing new scaled down membrane reformers configurations for efficient production of pure H₂ by methane steam reforming (MSR): the process comprises the MSR reaction (Eq. (1)a), followed by WGS (Eq. (1)b), and the combined reaction (Eq. (1)c). Thermodynamic analysis of (1)(a) or (c) shows that, without product separation, hydrogen conversion is favored by high steam-to-carbon ratio (S/C), high exit temperature and low pressure.



With hydrogen separation methane conversion is favored by high pressure (as well as by hydrogen transport which also increases the CO conversion), and the system can operate therefore at lower temperatures, and consequently lower S/C can be used for deactivation prevention purposes.

Most work on membrane reactors for H₂ production has focused on electrically heated systems [4–10]. This configuration holds meaningful drawbacks: First, the system has to be connected to the electric grid, and thus unable to support portable or isolated remote applications (transportation, offshore drilling rigs, cellular antennas etc.). Secondly, a loss of thermal efficiency is related with the unconverted methane at the effluent, as full MSR conversion is impractical. A scaled down autothermal unit for the production of H₂ from methane should couple the endothermic MSR with a heat source and increase thermal efficiencies which, in turn, implies increased conversion beyond closed-system equilibrium; this can be achieved in membrane reactors. Initial process designs combined methane oxidation (MOx) (2) with MSR.



The issue of coupling exothermic and endothermic reactions is an active field of research [11] and its implications for a membrane reactor raises new issues:

- (i) *Direct or indirect contact:* The reactions can be conducted within the same vessel (direct heat coupling) or in different reactors (indirect coupling). The former approach will dilute the hydrogen and diminish its membrane transport and we choose the latter one (see Section 2 for further discussion).

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