

AUTOTHERMAL PACKED-BED MEMBRANE REFORMER FOR HYDROGEN GENERATION BY METHANE STEAM REFORMING

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Summary

An autothermal membrane reformer composed of three separated compartments, methane oxidation catalytic bed, methane steam reforming catalytic bed and hydrogen separation membranes, is optimized for hydrogen production by steam reforming of methane in order to power polymer electrolyte membrane fuel cells. Capitalizing on a recent experimental demonstration of hydrogen production in such a reactor we develop here an appropriate model, validate it with experimental data and then employ it for the hydrogen generation optimization in terms of the reformer efficiency and power output. The optimized reformer, with more separation area, reduced heat loss and recycling of SR compartment effluents to the oxidation feed, is suitable for fueling kW-range PEM fuel cell stacks, providing efficiency of up to 0.8, which is expected to provide an overall efficiency of a combined reformer-fuel cell unit of ~0.48.

Keywords

hydrogen production

Introduction

Hydrogen is a very promising environmentally friendly fuel; however, unless produced on-site, hydrogen has to be compressed or liquefied, stored, transported and distributed to the end user. This, as well as the complexity and high energy demands of the conventional hydrogen generation processes, reduces significantly the overall efficiency of the hydrogen-based energy pathway and makes the price of hydrogen uneconomical. On-board high-purity hydrogen generation by methane steam reforming (MSR) using autothermal portable membrane reformers is a very promising approach that can save costs of hydrogen storage and distribution. This process combines two reactors, heat exchange between them and hydrogen separation into one compact and thermally independent unit, while the conventional steam reforming is a multistage process that includes several reaction steps followed by hydrogen separation. For the autothermal packed bed membrane reformer (ATPBMR) to be economical and practical its energetic efficiency should be better than the ratio of combustion engine (<30%) to fuel-cell efficiency (~60%), and its power density (power to volume ratio) should be similar to that of FC, ~1 kW/L.

While many numerical¹⁻³ and experimental⁴⁻⁷ investigation of hydrogen generation by MSR using membrane reformers has been reported, none demonstrated complete autothermal behavior in a packed bed. The authors have recently demonstrated that hydrogen production can be achieved using ATPBMR composed of three separated and concentric compartments: methane oxidation catalytic bed, methane steam reforming catalytic bed and hydrogen separation membran⁶. Yet, Hydrogen Recovery (HR) in that unit, defined as ratio of hydrogen effluent to methane feed flow (Eq. 1) was too small to be economical (Fig. 1, HR~0.6 compared with 3.3 the thermodynamic adiabatic limit).

$$HR = F_{H_2}^M / (F_{mf}^{SR} + F_{mf}^{Ox}) \quad [1]$$

The objective of this study is to develop a thorough experimentally-validated model and to extend it with the aim of the hydrogen generation optimization. It is shown

that energy efficient and power-dense ATPBMR can be achieved.

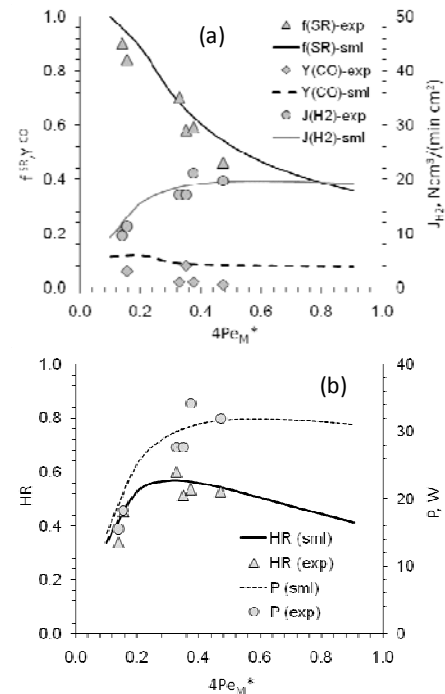


Figure 1: Simulations vs. experiments: $y_{mf}^{Ox/SR}=0.075/0.3$, $SV^{Ox}=1000 h^{-1}$, $SV^{SR}=160-560 h^{-1}$. (a) SR conversion (f^{SR}), CO selectivity (Y_{CO}), and hydrogen flux ($J_{H_2}^M$) and (b) hydrogen recovery (HR) and power output (P) vs. $4Pe_M^*$

Model Definition and Validation

The previously reported *adiabatic* model² was extended to account for heat losses and was found to predict well the experimental data, as it is shown in Fig. 1, where SR conversion, CO yield, HR and expected power output are plotted vs. $4Pe_M$, the ratio of methane feed to hydrogen transport capacity (evaluated at 650 °C).

$$Pe_M = F_{mf}^{SR} / F_{H_2}^M = F_{mf}^{SR} / S^M A_{H_2} \sqrt{P_1^{SR} \exp[-E_a / (R_g T)]} \quad [2]$$

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The model kinetic and thermodynamic parameters were based on literature data, while the heat transfer parameters were determined by adjusting to experimental data.

Optimization

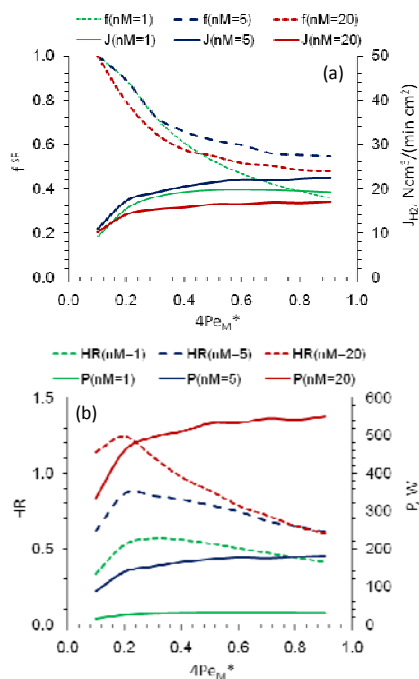


Figure 2: (a) SR conversion (f^{SR}) and J_{H_2} (hydrogen outlet flux) and (b) hydrogen recovery (HR) and power output (P) vs. $4Pe_M^*$ for increasing separation area: $a_v^M=11.5, 57.6, 230.5\ m^{-1}$, $nM=1, 5, 20$ and $SV^{Ox}=1000, 5000, 10000\ h^{-1}$, respectively; $y_{mf}^{SR}=0.33$.

The operation was further optimized by applying several steps: (i) Increasing membrane area, that allows in turn to increase SR throughput (with some adjustment of Ox flow) and diminish the effect of heat loss; (ii) Recycling the SR compartment effluent, which includes unreacted methane and some hydrogen, to the oxide feed will improve efficiency (this was verified by the authors experimentally⁷); (iii) Reducing the heat loss, as will be expected in larger units and/or by better thermal insulation.

Figure 2 shows that $\sim 500\ W$ of power is expected from same unit just by increasing the separation area (nM – number of membranes), also increasing significantly hydrogen recovery to ~ 1.2 (compare with an adiabatic thermodynamic limit of ~ 3.3 with complete heat recuperation and ~ 2.7 in a normal co-current operation mode). The effect of reduced heat loss coefficient in simulations performed with 20 membranes is presented in Fig. 3, in terms of the process efficiency ($\eta=HR/3.32$) and power output (P) as a function of methane utilization (MU) defined as

$$MU = F_{mf}^{Ox} / F_{mf}^{SR} \quad [3]$$

Note that there is an optimal η as MU is increased, and it is shifted to lower MU values, as the heat losses are reduced. An efficiency of ~ 0.7 and the power output of $600\ W$ are obtainable for the reformer, when the separation area is increased, the heat losses are reduced and the

methane utilization is optimized. This is very close to the *adiabatic* efficiency limit for co-current operation (~ 0.8). The volumetric power density of the simulated reformer, corresponded to $600\ W$, is $0.96\ kW/L$.

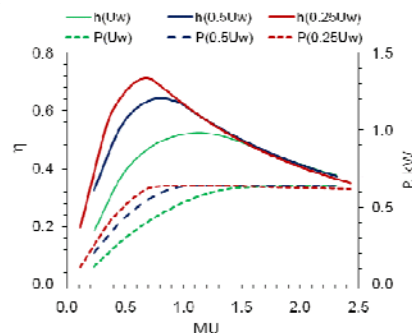


Figure 3: efficiency (η) and power output (P) vs. methane utilization (MU) for decreasing heat loss coefficient: $U_w, 0.5U_w, 0.25U_w$; $y_{mf}^{Ox/SR}=0.07/0.33$, $a_v^M=230.5\ m^{-1}$, $SV^{SR}=4000\ h^{-1}$

Concluding Remarks

A comprehensive model with no adjustable kinetic or thermodynamic parameters has been developed, verified versus experimental data and further extended for the ATPBMR design optimization. The model describes the results satisfactorily. The optimized reformer, with more separation area, reduced heat loss and recycling of SR effluents to Ox feed, it suitable for fueling kW-range PEM fuel cell stacks, providing efficiency up to 0.8, which is expected to give the overall efficiency of a combined ATPBMR+PEMFC unit of ~ 0.48 (0.8×0.6).

Notation: y – mole fraction, SV – space velocity, α_s – membrane surface to volume ratio, A_{H_2} – membrane permeability; *superscripts:* SR – of steam reforming, Ox – of oxidation, M – of membrane; *subscripts:* mf – of methane feed

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