Pure hydrogen production in a membrane reformer: Demonstration, macro-scale and atomic scale modeling

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HIGHLIGHTS

- Hydrogen membrane reformers experiments are analyzed and simulated.
- Comparison shows permeance inhibition due to polarization or to competitive adsorption.
- Criterion for detection of mass-transfer effects and approximate corrections are suggested.
- Inhibition due to adsorption is assessed using DFT to calculate coefficients.
- Inhibition due to Pd-surface reaction is suggested.

ARTICLE INFO

ABSTRACT

We discuss various designs for scaled down membrane steam reformer for generating pure hydrogen onboard or in a hydrogen fuel station, motivated by the expectation of using hydrogen as an energy carrier, mainly to power the energy efficient and environmentally friendly Proton Exchange Membrane Fuel Cells (PEMFC). Pure H_2 separation is achieved by Pd or Pd/Ag membranes.

A novel concept for hydrogen generation by auto-thermal methane steam reforming (MSR) was experimentally demonstrated by our group. The reactor, built from three concentric compartments, indirectly couples the endothermic methane steam reforming (catalyzed by Ni/Al_2O_3) with the exothermic methane oxidation, while hydrogen is separated by a permselective Pd/Ag membrane. The MSR conversion is mainly determined by the membrane hydrogen flux. The system is optimized using an appropriate model, validated with experimental data using parameters from literature. The optimized reformer, is predicted to achieve a methane-to-hydrogen conversion efficiency of up to 0.8.

In a second concept, solar energy circulated by means of molten salts is used to heat the membrane reformer in a hydrogen fuel station. Laboratory scaled membrane reformer, packed with a foam wash-coated with Ni–Pt catalyst and heated externally, demonstrated the concept feasibility. Modeling this reactor suggests about 80% reduction in permeance, compared to a value measured in pure hydrogen.

We describe 1-D mathematical model that were successfully used to predict the experimental results and ask whether 2-D models are necessary. By deriving an appropriate criteria we show that concentration polarization cannot account for the large observed permeance inhibition. To understand this phenomenon we resort to DFT-calculated adsorption energies to estimate the inhibition due to surface adsorption of possible co-adsorbates like methane, CO and water. While CO adsorption is strong, CO concentration is small, and this effect is too small to account for observations, suggesting that surface reaction on the Pd membrane should be considered to estimate coverages by C, O and other intermediates.

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1. Introduction

Hydrogen is a very promising environmentally friendly fuel: its oxidation in fuel cells directly produces electricity in a pollution-free way with efficiency (claimed to be 60% for PEM fuel cells) that is much higher than that of heat engines (30% and

lower). The high energy transformation efficiency of fuel cells may decrease significantly carbon dioxide emission, even when fossil fuels are still used as a source of hydrogen. This is the motivation behind the search for new small scale efficient processes for hydrogen production that will be used either in fueling stations or on board adjacent to the FC [1–3]. The European road

Notation

A_{H_2}	permeance pre-exponent (mol/(m^2 s bar$^{0.5}$))
c_i	concentration of component i
C_p	molar heat capacity (kJ/(mol K))
D, D_{er}	diffusivity (radial dispersivity)
E_a	activation energy (kJ/mol)
f	conversion
F	molar flow rate (mol/s)
ΔG	Gibbs free energy (kJ/mol)
HR	hydrogen recovery based on total methane
HR^{SR}	hydrogen recovery based on steam reforming
ΔH	heat of reaction (kJ/mol)
J_{H_2}	hydrogen flux (N cm^3/(cm^2 min))
k_j	rate constant of reaction j
k_{ax}	axial conductivity
$K_{eq,j}$	overall equ. coefficient of reaction j
K_i	adsorption coefficient
L	reactor length (m)
P_i	partial pressure of component i (bar)
P, P_t	total pressure (bar)
P^*, P^M	pressure at permeate side
Q	volumetric flow rate (cm^3/min)
Q_H	pre-exponent of permeance
R_g	gas constant
S^{ox}, S^{sr}	cross section area
S^M	membrane area (m^2)
SV	space velocity (h^{-1})
t	time (h)
T	temperature (°C)
u, v	axial and radial velocities
V	reactor volume (m^3)
y	molar fraction
z	axial reactor coordinate (m)

Greek symbols

α_{ij}	stoichiometric coefficient
Θ	permeance correction for inhibition
ε	catalytic bed porosity
η	effectiveness factor of permeance
ρ, ρ_s	fluid and solid densities
v_m	permeance expressed as velocity

Subscripts

eff	effluent
f	feed
g	gas
H	hydrogen
m	methane
t	total
ref	at ref pressure (1 bar)

Superscripts

M	membrane compartment
Ox	oxidation compartment
SR	steam reforming compartment

Abbreviations

FBMR	fluidized bed membrane reactor
MOx	methane oxidation
MSR	methane steam reforming
PBMR	packed bed membrane reactor
Ox	oxidation
SR	steam reforming

map calls for the establishment of thousand hydrogen fueling stations by 2020.

Traditionally hydrogen is produced by steam reforming of methane (MSR) (or of natural gas) followed by high- and low-temperature water gas shift (WGS) reactions, Eq. (1), followed by separation procedures (e.g. pressure swing adsorption and selective oxidation). This implies three catalytic beds and two separation steps. Moreover, this process requires extensive heat input for the highly endothermic reaction, and high temperatures (>950 °C) due to equilibrium limitations, thus it is carried in large furnaces:

$$
\begin{aligned}
\text{MSR:} \quad & CH_4 + H_2O \rightleftarrows CO + 3H_2 & \Delta H_{298K} = 206 \ [\text{kJ/mol}] \\
\text{WGS:} \quad & CO + H_2O \rightleftarrows CO_2 + H_2 & \Delta H_{298K} = -41 \ [\text{kJ/mol}] \\
\text{overall} \quad & CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2 & \Delta H_{298K} = 165 \ [\text{kJ/mol}]
\end{aligned}
\tag{1}
$$
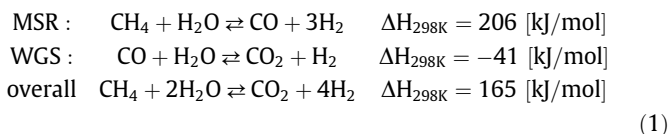
Membrane reactors (MR), comprising Pd or PdAg thin membranes to separate the hydrogen from the reacting mixture are a promising way to enable the small scale, local production of H$_2$. These membranes are known to hold essentially infinite selectivity for hydrogen (selectivities were reported to be >10^3 [11,31]). The separation of H$_2$ shifts the reaction towards the products and allows to reduce the operating temperature required for high conversions, to high (or even low) 400's°C while supplying pure hydrogen in one step. It also shifts the equilibrium to CO$_2$ rather than CO. This will have advantageous effect on separation and on preventing coking as we discuss below.

The purpose of this article is to review demonstration and modeling of membrane reactors of steam reforming of potential fuels like methane (i.e. natural gas), ethanol (renewable) or methanol to produce hydrogen, and to identify the steps that limit the system throughput: kinetics, hydrogen transport through the membrane (i.e., permeance) or heat transfer. Also, we review the model elements to inquire whether 1-D models are sufficient to accurately describe the system and whether 2-D or 3-D models should be incorporated.

Two heating approaches are envisioned for this endothermic reaction:

(i) *Wall-heated reactors:* An environmentally friendly route of supplying the required heat is the application of solar-thermal power, using molten salts. This will decrease the carbon footprint of the product; however this will require operating temperatures limited to ~530 °C. The process scheme is described below (Fig. 1a, membrane not shown). The laboratory reactor scheme using external heating is presented in Section 2 following [5]. This work is part of an effort to build a membrane methane reformer that is heated by solar energy through molten salt [6].

(ii) *Autothermal reactors:* In recent publications [1,2] we have demonstrated the feasibility of hydrogen generation in a completely autothermal packed bed membrane methane steam reformer. The reformer (Fig. 1 c) was composed of three separated compartments: a methane oxidation (MOx) catalytic bed, a MSR catalytic bed and a hydrogen separation membrane. A detailed parametric study was performed [1] and the hydrogen generation optimization was experimentally demonstrated [2]. Yet, the reactor efficiencies (defined below) were lower than 20%.