



An equilibrium theory for catalytic steam reforming in membrane reactors



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ABSTRACT

The study of integrated membrane reactors for the production of pure hydrogen is attracting increasing interest. In this work, we show how these systems may be described through pure transport models, accounting for the competition between different transport mechanisms, in the limit for either infinitely fast or infinitely slow reaction. The actual performance of a reactor will lie between these two limiting-case conditions. The results of this work highlight that the behavior of these systems may be described as a continuous sequence of equilibrium states. The main novelty of the study is in the introduction of a simple model that allows to evaluate integral quantities, such as hydrogen permeate flow rate and yield, on the basis of physical parameters and not through fitting of transport coefficients. Methane steam reforming has been chosen as a case study, but the conclusions reached may be extended to other integrated reactors for which the permeation law of the product across the membrane is non-linear.

1. Introduction

Methane steam reforming is currently the most widely adopted method for hydrogen production. Its main limitations are the considerable amount of natural gas necessary, both as feed and as fuel, the need to separate hydrogen from carbon dioxide and other by-products, and that the reaction is equilibrium-limited. To overcome these drawbacks, the use of integrated membrane reactors (MRs), in which hydrogen is removed as it is being produced, is currently receiving much attention (Said et al., 2016; Patrascu and Sheintuch, 2015; Dittmar et al., 2013; Kyriakides et al., 2013; Chen et al., 2008; Lin et al., 2003; Gallucci et al., 2013). MRs take advantage of the shift in equilibrium which follows hydrogen removal, thus allowing high methane conversions at temperatures lower than those adopted in conventional steam reformers. Such reactors are also considered for methanol (Sá et al., 2011; Israni and Harold, 2011, 2010) and ethanol (Domínguez et al., 2012; Tosti et al., 2008a,b) steam reforming, water gas shift (Augustine et al., 2011; Mendes et al., 2011; Abdollahi et al., 2010; Piemonte et al., 2010; Barbieri et al., 2008), and ammonia decomposition (Itoh et al., 2014; Rizzuto et al., 2014; Li et al., 2013).

The development of efficient catalysts has made reaction kinetics very fast, and the rate of reaction rarely limits the performance of these systems. On the other hand, the behavior of membrane reactors is heavily affected by the efficiency with which hydrogen is transported towards the membrane and then permeates. As membranes with increasingly high permeability are being developed, mass transport resistances within the packed bed may become the limiting factor in the

performance of these devices (Mengers et al., 2014; Chen et al., 2008; Mori et al., 2007; Piemonte et al., 2010; Hara et al., 1999). From the above considerations, it is possible to conclude that the behavior of a MR may be described as equilibrium-limited, where the equilibrium conditions vary along the reactor as a consequence of the balance between product permeation and reaction advancement.

If the reactor is fed with an equilibrium mixture – e.g. if a pre-reforming unit is present, its performance is determined by its ability of moving away from the initial equilibrium condition, as hydrogen permeates across the membrane, and towards a new equilibrium condition, as methane reacts to form more hydrogen. In other terms, the behavior of the reactor may be seen as a continuous sequence of different equilibrium conditions. The phenomena which contribute to the performance of a membrane reactor are hydrogen permeation across the membrane and transport of hydrogen from the bulk of the packed bed to the membrane surface. Different limiting-case scenarios have been considered in this work to gain more insight on the behavior of these systems. The first case considered is one in which the reaction is infinitely slow compared to hydrogen transport and the reactor behaves as a separator. The second case is one where the reaction is infinitely fast: hydrogen is produced by SR as soon as it is removed by effect of permeation and the system is everywhere at equilibrium, even though the equilibrium conditions change from one point to another in the reactor, along both the radial and axial coordinates. In both cases, the amount of hydrogen permeating may be limited by either transport across the membrane or transport within the packed bed. In these limiting-case conditions the behavior of the system may be described

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Nomenclature*List of symbols*

a_z	geometric ratio L/R_1
d	characteristic dimension of packed bed particles (m)
\mathcal{D}_{rr}	radial dispersion coefficient (m^2/s)
\mathcal{D}_{zz}	axial dispersion coefficient (m^2/s)
\mathcal{D}	diffusion coefficient (m^2/s)
\mathbf{D}	effective dispersion tensor (m^2/s)
f	average molar weight (kg/mol)
J_h	hydrogen mass flux through the membrane [$\text{kg}_{\text{H}_2}/(\text{m}^2 \text{s})$]
k	rate constant of the methane reforming reaction [$\text{mol}/(\text{m}^3 \text{s Pa})$]
K_{eq}	equilibrium constant of the methane reforming reaction (Pa^2)
L	reactor length (m)
\mathbf{n}	unit vector normal to the membrane surface (–)
P	pressure (Pa)
P_i	partial pressure of the i -th component [Pa]
P_L	outlet pressure (Pa)
P_U	reference pressure ($\mu UR_1/\kappa$) (Pa)
\mathbb{P}_m	membrane permeability [$\text{kg}_{\text{H}_2}/(\text{m}^2 \text{s Pa}^{0.5})$]
r	radial coordinate (m)
r_i	volume-specific mass rate of production of the i -th component [$\text{kg}/(\text{m}^3 \text{s Pa})$]
\mathcal{R}	gas constant [$\text{J}/(\text{mol K})$]
R_1	inner reactor radius (m)
R_2	outer reactor radius (m)
R_m	volume-specific molar rate of methane consumption [$\text{mol}/(\text{m}^3 \text{s Pa})$]
T	temperature (K)
U	inlet gas velocity (m/s)
\mathbf{v}	mass average velocity [m/s]
W_i	molar weight of the i -th component (kg/mol)
z	axial coordinate (m)

Greek symbols

β	ratio between characteristic and inlet velocities
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$(\kappa P_{atm}/(\mu R_1 U))$ (–)	
δ	membrane thickness (m)
η	proximity to reaction equilibrium (–)
κ	packed bed permeability (m^2)
μ	gas viscosity (Pa s)
ρ	gas density (kg/m^3)
ρ_i	density of the i -th component (kg/m^3)
σ	geometric ratio, R_2/R_1
τ	packed bed tortuosity factor (–)
ν_i	stoichiometric coefficient of the i -th component (–)
Φ	intrinsic membrane permeability
ω_i	mass fraction of the i -th component (–)
Ω	linear combination of hydrogen and methane densities ($-\nu_m \rho_h + \nu_m \rho_m$) (–)
Ψ, Ψ_s	hydrogen yield (–)

Dimensionless parameters

Da	Damkholer number ($RTkR_1/U$)
Da^*	modified Damkholer number (Da/Γ)
\mathcal{D}_{rr}	dimensionless radial dispersion ($\mathcal{D}_{rr}/\mathcal{D}$)
$\bar{\mathbf{D}}$	dimensionless dispersion (\mathbf{D}/\mathcal{D})
l_p	characteristic length of permeation $2\sqrt{\rho_h^0}/\Gamma$
Pe	Peclet number (UR_1/\mathcal{D})
Pe_m	molecular Peclet number (Ud/D)
Pe_r^{eff}	effective radial Peclet number (Ud/\mathcal{D}_{rr})
Pe_z^{eff}	effective axial Peclet number (Ud/\mathcal{D}_{zz})
α	dimensionless outlet pressure (P_L/P_U)
γ	dimensionless permeability parameter ($\mathbb{P}_m RTP_{atm}^{-1/2}/W_h U$)
Γ	$2\gamma/(a_r^2 - 1)$

Subscripts

c	carbon dioxide
h	hydrogen
m	methane
w	water

through a pure transport model. The actual behavior of a reactor should fall somewhere between the conditions of $Da \rightarrow 0$ and $Da \rightarrow \infty$, representing the case of infinitely slow and infinitely fast reaction, respectively, where the Damkholer number (Da) provides a measure of the ratio between characteristic times of the reaction and of convective transport; given the recent development of catalysts for the steam reforming reaction it is reasonable to argue that in many cases the performance of the system will, in fact, be completely limited by transport, either in the packed bed or across the membrane, rather than reaction rate.

The article begins with a concise description of a complete transport-permeation-reaction model, accounting for variable density of the mixture and embedding the coupling between momentum and mass transport (Section 2). This complete model, which has been thoroughly investigated elsewhere and validated against experimental data (Murmura et al., 2016a), is here used as a benchmark to develop a simplified predictive model for the overall hydrogen permeating flux and yield. Particular emphasis has been placed on understanding the influence of pressure on the behavior of the system (Section 3). The development of the predictive pure transport model is introduced in Section 4, with a focus on the interplay between reaction and permeation in correspondence of the membrane in the limit of fast reaction kinetics. In Section 5 the model developed for the condition in

which the reaction rate has a negligible effect is introduced and is a follow-up of studies previously carried out by the authors (Murmura et al., 2016b). Section 6 introduces the pure-transport model describing the system when the reaction may be considered to be infinitely fast. The problem is here formulated in terms of an auxiliary variable, representing the linear combination between hydrogen and methane concentrations. In Section 7 the results of the model have been validated against the more complete numerical model as well as experimental data available in literature.

In most studies on membrane reactors, the procedure adopted is different from the one followed in the present work. The development of the model and the experimental campaign are usually carried out

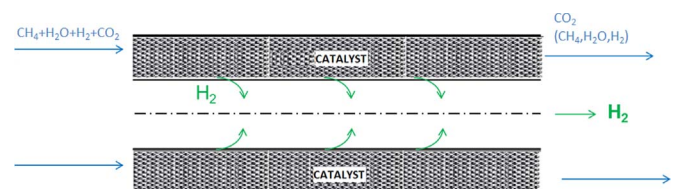


Fig. 1. Schematic representation of the problem. The reacting mixture is fed to the annular volume and hydrogen permeates across the infinitely selective membrane placed on the outer wall of the innermost tube.

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