Chemical Engineering & Processing: Process Intensification 120 (2017) 148–160

Contents lists available at ScienceDirect

Chemical Engineering & Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

Designing the optimal geometry of a membrane reactor for hydrogen production from a pre-reformed gas mixture based on the extent of the reaction boundary layer

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ARTICLE INFO

Keywords:
Membrane reactor
Optimization
Design
Geometry
Yield

ABSTRACT

A typical hydrogen-production system consisting of a pre-reformer catalytic reactor and a membrane reactor is considered: if equilibrium conditions are achieved in the pre-reformer, the reaction in the membrane reactor can only proceed once the hydrogen partial pressure has been reduced by effect of its permeation. An accurate transport-reaction-permeation model of methane steam reforming in catalytic membrane reactors suggests that, in these conditions, only a fraction of the catalyst volume is effectively active towards the advancement of the reaction and hydrogen production is confined to a reaction boundary layer (RBL) located in the near-membrane zone, whose extent is relatively insensitive to the thickness of the catalytic bed. Based on this observation, we developed a detailed study of the structure of the RBL in a wide range of operating parameters for different reactor geometries and showed that, for an assigned value of the total mass flow rate of the process stream, the optimal reactor performance is obtained whenever the thickness of the catalyst bed is comparable to that of the RBL.

1. Introduction

Membrane reactors (MRs) are receiving significant attention for their potential application in decentralized systems for hydrogen production [1–4]. The possibility of integrating reaction and separation in a single device decreases capital costs and makes scale-down more economically sound [5]. In reference to methane reforming, a comparative study on membrane-based configurations for distributed hydrogen production has shown that steam reforming in membrane reactors can be characterized by a higher thermal efficiency compared to the conventional steam reforming process followed by pressure swing adsorption (PSA) for hydrogen recovery and also appears to be more competitive than autothermal reforming in MRs and traditional steam reforming followed by a water–gas shift MR [3]. The same work highlights the fact that an appropriate design of membrane reactors can actually reduce the capital costs compared to the traditional configuration, despite the high cost of the selective palladium membrane, because of the exclusion of the PSA unit. In point of fact, membrane reactors constitute an important example of process intensification [6,7].

The correct design of a membrane reactor must take into consideration the characteristic times of reaction, permeation, and transport through the packed bed. The degree of complexity of such a process can be appreciated by considering the number of parameters that influence the overall performance of the system, in particular: pressure, temperature, inlet flow rate and composition, catalyst activity, membrane permeability, and reactor dimensions. The traditional approach to the study of membrane reactors consists in testing them over a range of operating conditions, acting mainly on the inlet flow rate, pressure, or temperature [8–13]. Chiappetta et al. [14] have also investigated the influence of the ratios between membrane surface area and catalyst volume and between inlet flow rate of the limiting reagent and membrane surface area. However, the range of values that the operating parameters may assume is so wide that it is not possible to test all conditions of interest. In this view, the development of a model in which operating conditions are grouped in a set of dimensionless parameters is an interesting tool for the understanding of the different phenomena governing the behavior of the system.

The underlying idea of the present work has been that criteria for the design of a membrane reactor can be derived by studying the qualitative structure of the spatial profiles of intensive variables, such as component concentrations. In effect, these profiles ultimately determine the overall equipment performance. The choice of considering the presence of a pre-reforming traditional reactor (i.e. with

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http://dx.doi.org/10.1016/j.cep.2017.07.011
Received 6 April 2017; Received in revised form 12 June 2017; Accepted 11 July 2017
Available online 14 July 2017
0255-2701/

List of symbols

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$\mathscr{D}$	diffusion coefficient (m^2/s)
$\mathbb{D}$	effective dispersion tensor (m^2/s)
f	average molar weight (kg/mol)
I_h	inlet flow rate of hydrogen (kg_{H_2}/s)
J_h	hydrogen mass flux ($kg_{H_2}/(m^2\ s)$)
k	rate constant of the methane reforming reaction (mol/(m^3 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 ith component (Pa)
P_L	outlet pressure (Pa)
$\mathbb{P}_m$	membrane permeability ($kg_{H_2}/(m^2\ s\ Pa^{0.5})$)
r	radial coordinate (m)
r_i	volume-specific mass rate of production of the ith component (kg/(m^3 s Pa))
$\mathscr{R}$	gas constant (J/(mol K))
R_1	inner reactor radius (m)
R_2	outer reactor radius (m)
R_m	volume-specific molar rate of methane consumption (mol/(m^3 s Pa))
T	temperature (K)
U	inlet gas velocity (m/s)
$\mathbf{v}$	mass average velocity (m/s)
W_i	molar weight of the ith component (kg/mol)
z	axial coordinate (m)

Greek symbols

β	ratio between characteristic and inlet velocities($\kappa P_{atm}/(\mu R_1 U)$) (–)
η	proximity to reaction equilibrium (–)
κ	packed bed permeability (m^2)
μ	gas viscosity (Pa s)
Π_h	permeate flow rate (kg_{H_2}/s)
ρ	gas density (kg/m^3)
ρ_i	density of the ith component (kg/m^3)
σ	geometric ratio, R_2/R_1
ν_i	stoichiometric coefficient of the ith component (–)
ω_i	mass fraction of the ith component (–)
Ψ_s	hydrogen yield (–)

Dimensionless parameters

Da	Damkholer number ($RTkR_1/U$)
$\mathscr{D}_{rr}$	dimensionless radial dispersion ($\mathscr{D}_{rr}/\mathscr{D}$)
$\widetilde{\mathbb{D}}$	dimensionless dispersion ($\mathbb{D}/\mathscr{D}$)
Pe	Peclet number ($UR_1/\mathscr{D}$)
α	dimensionless outlet pressure (P_L/P_U)
γ	dimensionless permeability parameter ($\mathbb{P}_m RTP_{atm}^{-1/2}/W_h U$)

Subscripts

c	carbon dioxide
h	hydrogen
m	methane
w	water

impermeable walls) upstream the membrane reactor is motivated by the fact that, if the feed contained only methane and steam, the initial hydrogen concentration would be low, thus the membrane in proximity of the inlet section useless, leading to an increase in the overall cost of the reactor without any significant benefit in either methane conversion or hydrogen permeation. A similar conclusion has also been reached in other studies. For instance, Roses et al. [15] found that for a target hydrogen flux, the required membrane area of a fixed-bed MR without pre-reforming could be up to 25% larger than that of a fluidized bed MR. This difference drops to 3–10% when a pre-reformer is present. Similarly, Piemonte et al. [16] found that the presence of a membrane is useless in the first part of a water–gas shift reactor. When the transport-reaction-permeation model is applied to typical geometric configurations and operating conditions used in the experimental prototypes of membrane reactors reported in the literature, the structure of the field variables suggests that a relevant fraction of the catalyst is inactive towards the advancement of the reaction, the active region being confined to a narrow zone (henceforth referred to as reaction boundary layer, RBL) located in the vicinity of the membrane surface. Concrete examples of the structure RBL in a fixed geometric configuration are discussed in Section 3. In turn, this observation raises an obvious question as to what operating conditions and reactor geometry should be used in order to minimize the extent of the inactive catalyst volume fraction. The answer to this question clearly depends on the choice of the process variables that are kept constant when comparing the performance of different reactor geometries. Here, we choose to maintain constant the total mass flowrate entering the reactor, as this condition is expected to be the most directly relevant for providing information useful to design of the process. The implications of this choice as regards the behavior of the dimensionless parameters defining the transport-reaction-permeation model is discussed in Section 4. The comparison between the equipment performance associated with different geometries is carried out in Sections 5 and 6. The main conclusions arising from this analysis are discussed in Section 7, together with the possible directions of future work.

2. Statement of the problem

The system studied consists of an integrated membrane reactor realized with a double pipe configuration. The catalyst is placed in the annular volume between the two cylinders and a membrane, considered to have infinite selectivity with respect to hydrogen, is supported on the outer wall of the innermost tube. The methane steam reforming process was used as case study.

Since one of the advantages of using a membrane reactor is the possibility of working at low temperature, the water–gas shift reaction in the conditions of interest can be considered to be completely shifted toward the formation of hydrogen. In fact, for pressures higher than 2 bar and temperatures around 800 K, the CO molar fraction at equilibrium is always lower than 0.7%. The ability of the WGS reaction to reach completion in the temperature range of interest has been verified experimentally in previous studies [17]. For this reason, the reaction modeled is that of total steam reforming of methane

$$CH_4 + 2H_2O \rightleftharpoons 4H_2 + CO_2 \quad (1)$$

The problem has been studied under the assumption of constant and uniform temperature and zero partial pressure of hydrogen in the permeate side. The assumption of a uniform temperature is justified by the fact that, having considered the presence of a pre-reformer, the initial temperature drop that characterizes strongly endothermic reactions is confined to the pre-reformer and not experienced by the membrane reactor. Furthermore, in the range of operating