INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 40 (2015) 7559–7567

Available online at www.sciencedirect.com

ScienceDirect

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

Fixed bed membrane reactor for hydrogen production from steam methane reforming: Experimental and modeling approach

Gioele Di Marcoberardino[*], *Francesco Sosio*, *Giampaolo Manzolini*, *Stefano Campanari*

Politecnico di Milano, Dipartimento di Energia, Via Lambruschini 4, 20156 Milano, Italy

ARTICLE INFO

Article history:
Received 1 September 2014
Received in revised form
29 October 2014
Accepted 7 November 2014
Available online 3 December 2014

Keywords:
Hydrogen
Membrane reactor
Fixed bed
Palladium membrane
One-dimensional model
Steam methane reforming

ABSTRACT

This work describes the results from experimental tests on the membrane reactor in terms of hydrogen recovery factor and fuel conversion at different operating conditions. A test bench for a fixed bed membrane reactor, placed in the Laboratory of Micro-Cogeneration (LMC) of Politecnico di Milano, is designed to operate in a wide range of operating conditions: the maximum temperature and pressure are respectively 923 K and 700 kPa. An hydrogen permeability value of $5.16 \cdot 10^{-11}$ mol/(msPa$^{0.71}$) at 723 K have been determined. The best operating conditions (873 K, 500 kPa) allow to reach a methane conversion of 47.4% and an hydrogen recovery factor of 28.1%. Results are used to validate a one-dimensional finite volume model of the overall membrane reactor, solved in Matlab®.

Introduction

The current topics of energy saving and reduction of CO_2 emissions must deal with the significant energy demand in residential area. Indeed electricity and heat consumptions, in industrialized countries, are responsible for a large share of consumption of primary energy. In this context, an increasing interest has been built up on innovative solutions for small scale power generation, focusing on the field of Proton Exchange Membrane fuel cell (PEMFC) based systems, potentially characterized by high net electric efficiency and very low emissions targeting the application to distributed heat and power co-generation (CHP) in the urban areas.

Fuel cells have high electric efficiencies even at small scale together with low pollution emissions. The PEM cell type also have (i) a high power density, (ii) a fast start and (iii) low operating temperatures. All these advantages lead to say that the production of electric energy, through a fuel cell system, can allow low costs and high efficiencies even on a range of net electric power output that goes from 100 to 3000–5000 W, corresponding to the energy needs of a residential user.

The main disadvantage of the PEM cells is that they require high purity hydrogen as fuel, with CO concentration below 10 ppm (at least for the LT-PEM type). Since there isn't a hydrogen distribution network nowadays, the vast majority of PEM-based CHP systems are fed with natural gas which is widely present in major cities; moreover, the use of other fuels as bio-ethanol is of growing interest for stand-alone and off-

* *Corresponding author*. Tel.: +39 02 2399 3935.
E-mail address: gioele.dimarcoberardino@polimi.it (G. Di Marcoberardino).
http://dx.doi.org/10.1016/j.ijhydene.2014.11.045

grid locations. So these systems require a fuel processor upstream the fuel cell.

In this context, palladium alloy membranes are a promising technology for integration into a fuel processor involving pure hydrogen generation from a liquid or gas fuel. In the field of hydrogen-selective membranes, they feature high permselectivity but limited permeation flux as well as the ability to operate at high temperatures and pressures [1]. The advantages of this innovative solution are both economic (conversion and separation take place in a single reactor), and thermodynamic: the hydrogen production and separation are performed minimizing temperature swing with energy and exergetic advantages [2]. These characteristics make membranes suitable for small-scale stationary generation based on PEM fuel cell system [3–5].

This work analyzes the performances of a fixed bed membrane reactor in terms of hydrogen production rate and methane conversion at different operating conditions, which were compared with some experimental and prediction results appearing in the literature. Experimental data are used to validate a mathematical model in terms of kinetics reactions efficiency. Results were compared with some prediction results appearing in the literature.

Membrane reactor model

The flexibility of the finite volumes 1D model in Matlab® gives the opportunity to simulate a wide variety of membrane reactor configurations differing in geometry, flow patterns and reactants composition. The model considers the system at steady state conditions and the velocity profiles are in first approximation fully developed in the entry region. Therefore, the profiles of the variables are determined along the z-coordinate alone, corresponding to the length of the reactor, as shown in Fig. 1. The differential equations are traced to polynomial expressions where the unknowns are functions of the coordinate z. Starting from the input data of the system (geometric parameters, inlet stream and his composition and the reactor operating conditions), the numerical model calculates the main variables trend: the composition (or the molar flow rates of the chemical species) and the temperature of the mixtures that pass through the reactor. The process is governed by the material balance and energy balance: these have been written for both the reaction zone and the permeating zone.

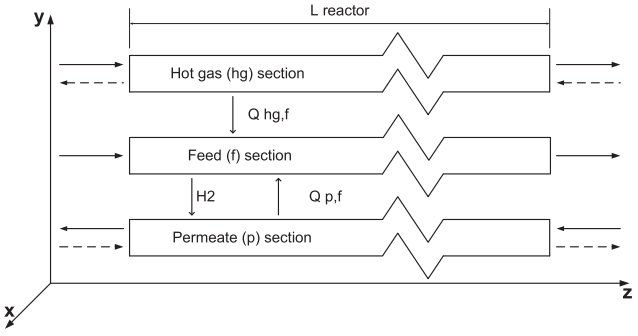

Fig. 1 – Scheme of 1D Membrane Reactor model.

Regarding the mass balance on the feed section implemented in the 1D model, the reaction equations, kinetic and adsorption parameters have been extracted from Xu & Froment [6]: all parameters are summarized in Table 1. The terms η1 and η2 are defined as the kinetic efficiency for the first two reactions: experimental results are used to validate the numerical model through the evaluation of these costants (chapter 4.3).

The expression to calculate the hydrogen permeation flux through the membrane J_{H_2} [mol/m^{2}s] is shown in Eq. (1). Hydrogen flux is a function of the hydrogen partial pressure difference between feed and permeate sides and of the reaction temperature.

$$J_{H_2} = \frac{P_0 \cdot e^{-Ea/RT}}{t} \cdot \left(p_F^n - p_P^n\right) \tag{1}$$

The term inside the bracket is the driving force [kPa^n]. Eq. (2) shows the mass balance equations in the feed section for all species (i) and reaction product/reagents (j), expressed in mol/m·s, where, the term J_i differs from zero only for the hydrogen, by using a membrane infinitely selective to hydrogen (assumed in this study).

$$\frac{dN_i}{dz} = \rho_{cat}\frac{V}{L} \cdot \sum_{j=1}^{3} \upsilon_{ij} r_j - J_i \cdot \frac{S_{mem}}{L_{mem}} \qquad \text{where} \quad i = 1, \ldots, n_{species} \tag{2}$$

As explained above, differential equations are traced to a polynomial expression along the coordinate z: Eq. (3) defines the mass balance, expressed in mol/s, where the reactor is divided in several cells with a definite volume length L_k.

$$N_{i,k}^{OUT} = N_{i,k}^{IN} + \frac{V}{L} L_k \cdot \rho_{cat} \cdot \left(\sum_{j=1}^{3} \upsilon_{ij} r_j\right)_k - J_{i,k} \cdot \pi D_{mem} \cdot L_k$$
$$\text{where} \quad k = 1, \ldots, n_{cells} \& n_{cells} = \frac{L_k}{L} \tag{3}$$

The same mass balance is also used for the permeate and hot gas sections: in the first, r_j is equal to 0 and the hydrogen permeated flux has the opposite sign, while, in the hot gas stream both reaction term and permeation term are not take into account.

For the energy balance, there is a set of equations for the three sections of the reactor: the hot gas, the feed and the permeate. The energy balance, expressed in Watt, in the feed section is presented in Eq. (4).

$$H_{out,f}\left(T_{f,k+1}\right) = H_{in,f}\left(T_{f,k}\right) + Q_{hg,f}\left(T_{hg,k}\right) + Q_{p,f}\left(T_{p,k}\right) + H_{H_2,p,k} \tag{4}$$

where the terms $Q_{hg,f}$ and $Q_{p,f}$ stand for the conductive heat transfer between the feed flow and the hot gas and the feed and permeate flows respectively; the term $H_{H_2,p}$ refers to the heat transport of the hydrogen permeate flux as shown in Eq. (5).

$$H_{H_2,p,k} = J_{H_2,k} \cdot S_{mem,k} \cdot MM_{H_2} \cdot \int_{298K}^{T_{f,k}} C_{p,H_2}(T)\,dT \tag{5}$$

Experimental setup and tests

Membrane reactor test bench

The membrane reactor test bench is shown in Fig. 2. The membrane reactors can be fed with three different gases, CH_4,