Dynamic Modeling of Pure Hydrogen Production via Bio-ethanol Steam Reforming in a Catalytic Membrane Reactor

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Abstract
Ethanol steam reforming was performed in a catalytic membrane reactor (CMR) containing Pd-Ag membrane tubes selective to hydrogen and Pd-Rh/CeO_2 catalyst. Experiments were performed at 923 K, 6-10 bar, and fuel flow rates of 50 to 200 µl/min using a mixture of ethanol and distilled water with steam to carbon ratio of 3. Moreover, dynamic experiments were carried out to observe the behavior of the CMR and obtain the time constant in case of desired pressure or fuel flow rate adjustment. A static model for the catalytic zone based on the experimental results was derived from the Arrhenius law as a function of fuel flow rate and operating pressure to simulate the production of H_2 in the CMR. Based on the static model, pure hydrogen production rate was also simulated and a dynamic zonal model was proposed under ideal gas law assumptions to simulate the behavior of the CMR system regarding the production of pure hydrogen in isothermal conditions. This model resembled hydrogen flow rate adjustments needed to set the electric load of a fuel cell fed by the studied CMR system.

Keywords:
Hydrogen, Membrane reactor, Modeling, Dynamic behavior

1. Introduction

The conventional fossil fuel-based engines are no longer considered as the only power generating option for portable purposes such as automotive industry due to low efficiency, emission of harmful gases, and dependency on oil. Electric vehicles have been in the center of attention as a movement toward zero-emission technology. The electric engine of a vehicle can run on battery cells. However, some challenges such as charging requirement, heaviness, and costly production of such batteries have hindered the technology to grow as a certain option for the future of new generation electric engines. Besides, batteries need a huge space, especially for long tracking purposes.

Hydrogen combustion engines deliver high amount of energy while giving water vapor off as the exhaust. Still, conversion to electricity and heat by means of fuel cells is known as the highest efficient energy producing process [1]. High efficiency of the fuel cells (normally 45-60%) - comparable to the complicated conventional energy production cycles - is attributed to the single-step energy conversion pathway. In a fuel cell, chemical energy is converted to electrical energy resulting in prevention of thermodynamic losses to a large extent [2]. Fuel cell technology has shown proven potentials for different tasks and can be applied at any condition independent from local factors such as weather, geographical factors, etc. Pure hydrogen is used as the main fuel for fuel cells to produce electrical power particularly in low temperature fuel cells such as Proton Exchange Membrane Fuel Cells (PEMFCs), which dominate the market of portable applications. The main challenge nowadays remains in the requirements of special installations and infrastructures for production and distribution of fuel

cell grade pure hydrogen as it is needed in highly pure state [3]. Production of hydrogen at the refilling stations or right in the vehicle itself could make pure hydrogen storage/transportation unnecessary. For this purpose, reforming processes for hydrogen production are beneficial [4].

Hydrogen is directly produced by fuel reforming via three main catalytic conversion routes i.e. steam reforming (SR), partial oxidation (POX), and autothermal reforming (ATR). The main products of a reforming process are hydrogen and carbon dioxide; however, other light side products such as CO, CH_4, and C_2H_6 are also present. Concerning the production of fuel cell grade hydrogen, the application of catalytic membrane reactors (CMRs) is beneficial since the production and separation of hydrogen from the mixture of produced gases take place in the same reactor vessel simultaneously. In Pd-based metallic membranes hydrogen purity up to 99.999% is obtained, which is suitable for direct fuel cells feeding [1-5].

Ethanol is a hydrogen rich fuel with hydrogen to carbon ratio of 3. This product is not considered as a toxic liquid and its special molecular structure makes it easier for C-C breakage in reforming processes [6]. Bio-ethanol as a renewable fuel is produced via conversion of biomass (fermentation or enzymatic catalysis) [6]. The mixture of water and ethanol in the form of bio-ethanol can be used directly as a feedstock for reforming processes leading to significant reduction in global energy consumption by omitting the costs of the distillation process and the additional alcohol purification unit operations [7]. Regarding the catalytic conversion, it is proven that noble metals not only are able to convert ethanol efficiently due to their significant reactivity, but also hinder carbon deposition on the active sites [8-9]. This distinctive property together with robust behavior and formation of only CH_4 and CO as byproducts has attracted the attention of a lot of research groups toward noble metals for ethanol reforming application [6]. In this work, ethanol steam reforming (ESR) reactions over Pd-Rh/CeO_2 catalyst have been performed in a CMR using a mixture of water and ethanol as fuel. The highest amount of hydrogen is obtained by steam reforming of ethanol (6 moles of hydrogen is formed theoretically per one mole of ethanol in the feed). If ESR is performed over Pd-Rh/CeO_2 catalyst, the major reforming reactions are [9-10]:

$$C_2H_5OH \rightarrow H_2 + CO + CH_4 \quad (1)$$
$$CO + H_2O \leftrightarrows H_2 + CO_2 \quad (2)$$
$$CH_4 + 2H_2O \leftrightarrows 4H_2 + CO_2 \quad (3)$$
$$C_2H_5OH + 3H_2O \leftrightarrow 2CO_2 + 6H_2 \quad (4)$$

Equation 4 is the overall ESR reaction.

A large piece of work on ESR in the CMRs using different catalysts and reactor configurations can be found in the literature. A comprehensive literature survey is given in [11]. Concerning modelling studies, theoretical models have been reported in the literature under steady state conditions for ESR simulation in CMRs for hydrogen production. Generally, ESR in membrane reactors have been simulated based on experimental results, aiming at mathematical modeling, activation energy calculation, and pre-exponential factors estimation. Kinetic studies derived from conventional power-law based have been performed using experimental data at different operating conditions (temperature, pressure, and S/C ratio) mainly to model the reaction rates, ethanol conversion, and the selectivity of reforming products [12-18]. In another work by Koch et al. [1], a model was developed by performing ESR in a staged membrane reactor to implement an adaptive and predictive control. This

model was used to study the dynamics of the fuel reformer in connection with a PEMFC by acting upon reactor pressure and feed flow rate (ethanol + water).
In this work, a static model was developed to calculate the rate of hydrogen production via ESR in a CMR as a result of the catalytic conversion of ethanol based on experimental results. A general static model for the catalytic zone based on the experimental results was developed and reported in [21]. The model was derived from the Arrhenius law as a function of the operating conditions with a general form of:

$$\dot{n}_{H2} = f \times e^{\frac{-g}{RT}} \quad (5)$$

$$f = a \times F_F^b \times (S/C)^c \quad (6)$$

$$g = d \times P + e \quad (7)$$

$\dot{n}_{H2}$ [mol/s], F_F [m^3/s], P [Pa], S/C, and T [K] represent the molar production rate of hydrogen, the fuel flow rate, pressure, steam to carbon ratio, and temperature, respectively. R is the universal gas constant. 'f' represents a function of fuel flow rate and steam to carbon ratio as pre-exponential factor, and 'g' represents the energy of activation as a function of pressure. 'a', 'b', 'c', and 'd', and 'e' are the fitting parameters of the equations. In this study, a more specific model was used as the dynamic tests were performed at constant temperature and S/C ratio.

Pure hydrogen production (permeation through Pd-Ag membranes) was measured via dynamic experiments. Then a model was developed based on the experimental results to simulate the pure hydrogen production rate during fuel flow rate and pressure change cycles. The application of the model is in the design and control of a hydrogen producing system capable of online feeding a fuel cell with the possibility of instant adjustments of pure hydrogen stream following changes on the fuel cell electric load.

2. Materials and methods

2.1. Experimental

The Pd-Rh/CeO_2 catalyst (0.5% Pd – 0.5% Rh) was deposited over cordierite pellets of about 1 mm following the procedure described by López et al. [19]. The laboratory setup used for the ESR experiments (fuel reformer) consisted essentially of a fuel tank, a liquid pump, a CMR, a pressure transducer and a condenser. A detailed description of the reformer setup can be found in [20]. A schematic plan of the fuel reformer system is shown in Fig. 1.

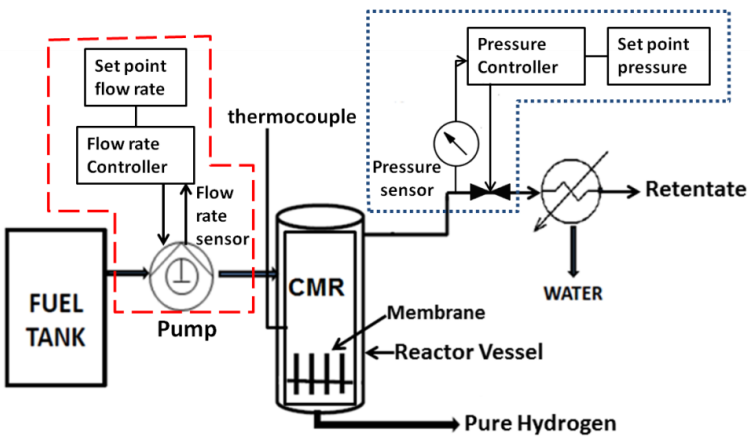

Fig. 1. Scheme of the Reformer.

The dashed and dotted lines represent the fuel flow rate and pressure controlling systems, respectively. The CMR was 10 in. tall and 1 in. in diameter. There were four Pd-Ag membrane tubes selective to hydrogen inside the reactor; each one 3 in. tall and 1/8 in. diameter in order to separate hydrogen from the gases produced (provided by Reb Research). To perform the experiments, the reactor was filled with the catalysts so that the metallic membranes were covered. The retentate pressure was adjusted by a back-pressure regulator (transducer). No pressure regulation was implemented on the permeate side (pure hydrogen outlet). So the permeate side pressure is kept automatically at ambient pressure and besides no sweep gas was used so pure hydrogen was obtained at atmospheric pressure to directly feed a fuel cell. The flow rate of pure hydrogen (permeate) was measured with a mass flow meter and fluctuated within ±2 ml/min. The composition of retentate gases (waste gases from the upper part, the retentate) was analyzed on a dry basis using an online Gas Chromatograph (±3%) (Agilent 3000A MicroGC using MS 5 Å, PlotU and Stabilwax columns) every 4 minutes. The operating conditions of the experiments are summarized in Table 1.

Table 1. Experimental conditions

Temperature (K)	923
Pressure (bar)	6-10
Fuel flow rate (μl/min)	50-200
S/C	3

Methane steam reforming (see (3)) is favored at higher temperatures because of the endothermic nature of the reaction. As a result, hydrogen production reached the highest value at 923 K. Temperatures higher than 923 K were not considered due to the limitations of the experimental setup. At S/C ratio=3, the highest value of hydrogen recovery was obtained during the experimental work that is attributed to the availability of water for the reforming reactions. On the other hand, coke formation is less prone to occur at higher S/C ratio. Accordingly, the dynamic experiments were carried out at 923 K and S/C ratio of 3.

In order to monitor pure hydrogen flow rate variations in the case of fuel flow rate or pressure set point adjustments, the dynamic performance of the reforming system was studied. A controlling computer program was used to apply the set pressure or fuel flow rate changes to the system. The reforming system was given time to reach the steady state conditions in terms of pure hydrogen flow rate as the new fuel flow rate or pressure was set.

Two types of dynamic tests were performed in this study. In the case of pressure change dynamic tests, both pressure increasing and decreasing steps were considered. As presented in Fig. 2, the pressures range of 7-10 bar was selected because at these pressures the efficiency of the fuel reformer is maximum [15].

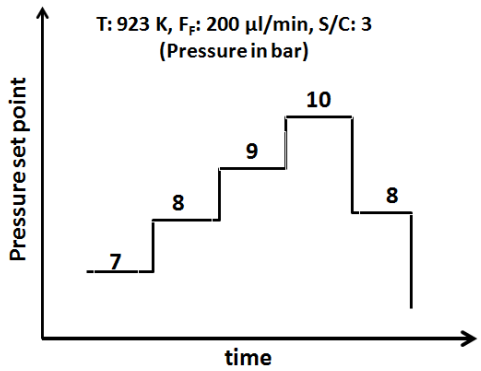

Fig. 2. Plan of the pressure change for dynamic tests.

The ideal gas law in the form of $PV = \frac{mRT}{M_W}$ was used to model the pressure of the reactor. P, V, T, and M_W are reactor pressure, volume of the reactor, temperature, and the molar mass of the fuel mixture, respectively. m is the amount of mass added to the reactor volume. It was assumed that the accumulation rate of the pumped fuel into the reactor at constant temperature and volume leads to pressure increase as the pressure valve acts on the outlet of the system to block the retentate stream when pressure increase is required. Then:

$$\frac{dP}{dt} = \left(\frac{RT}{VM_W}\right) \times \frac{dm}{dt} \tag{8}$$

Where $\frac{dm}{dt}$ is the rate of the mass added to the reactor volume. Since hydrogen is permeating at the same time as fuel is being added to the reactor volume, the added mass is the difference between the fuel flow rate and hydrogen permeation rate, so that:

$$\frac{dm}{dt} = \dot{m}_{fuel} - \dot{m}_{retentate\ gas} - \dot{m}_{pure\ hydrogen} \tag{9}$$

Where $\dot{m}_{fuel}$ and $\dot{m}_{pure\ hydrogen}$ represent fuel flow rate and hydrogen permeation rate, respectively, both in [kg/s]. Conversely, the pressure valve is opened, letting a lot of gas to release instantly when pressure is set at a lower point.

Dynamic tests regarding the response of the system to the fuel flow rate changes were performed by means of variations equal to 50 µl/min, as shown in Fig. 3.

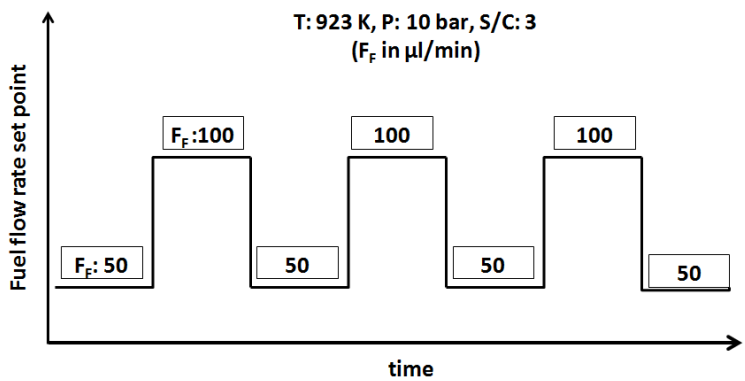

Fig. 3. Plan of the fuel flow rate change for dynamic tests.

The changing cycle of 50-100-50 µl/min was run several times to observe the durability of the performance of the reforming system. Lower fuel flow rates were not considered due to low

hydrogen production rate. According to the membrane limitations, higher flow rates also were not taken into account. The simulation was performed by means of Ordinary Differential Equation (O.D.E) solver.

2.2. CMR model

For the modeling task, the CMR was divided into two sections i.e. the catalytic zone, and permeation zone (the membrane). The model of the catalytic zone (static model) was developed in Matlab and was used as one of the inputs of the model of the permeation zone (the membrane). Dynamic model of the reforming system was developed by means of Simulink using the permeation zone model as a sub-model in charge of prediction of the pure hydrogen flow rate.

2.2.1. Static model

A static model was proposed to analyze the performance of the ESR in terms of the molar production rate of H_2 inside the reactor (around the membrane):

$$\dot{n}_{H2}^{s} = f_1 \times e^{-g_1} \quad (10)$$

$$f_1 = \alpha \times F_F^{\beta} \quad (11)$$

$$g_1 = \theta \times P + \gamma \quad (12)$$

$\dot{n}_{H2}^{s}$ is the molar production rate of hydrogen in the CMR via ESR calculated by the static model. α, β, θ, and γ are fitting parameters. This model was derived at 923 K and S/C of 3, as a function of fuel flow rate in the pre-exponential factor and reactor pressure in the activation energy term.

2.2.2. Membrane model for dynamic modeling

Hydrogen permeation through the membrane (pure hydrogen production) as the product of CMR system was modeled to simulate a pure hydrogen producing unit that can directly feed a fuel cell system. A model was developed as a function of the reactor pressure and the molar production rate of hydrogen obtained by the static model ($\dot{n}_{H2}$):

$$J_{H2}^{s} = A \times \dot{n}_{H2}^{s}{}^{B} \times P^{C} + D \quad (13)$$

J_{H2}^{s} is the pure hydrogen production rate calculated by the static model. A, B, C, and D are the fitting parameters. Another model as a function of only molar production rate of hydrogen (B=1 and C=0) was also proposed to understand if pure hydrogen production rate can be modeled independent from the reactor pressure. Partial pressure of hydrogen inside the reactor is known as the driving force of hydrogen permeation through a membrane and has been a purpose of modeling [16-18].

To develop the dynamic model of hydrogen production via ESR as a result of catalytic activity, a first order function was used:

$$\frac{J_{H2}^{D}}{F_F} = \frac{J_{H2}^{s}}{1+\tau s} \quad (14)$$

τ is the time constant. The measured dynamic of fuel flow rate was faster than the sampling time (1 second). Thefore:

$$F_F = F_F^{set\ point} \tag{15}$$

Accordingly, (14) is written as:

$$\frac{J_{H2}^{D}}{F_F^{set\ point}} = \frac{J_{H2}^{S}}{1+\tau s} \tag{16}$$

Where $F_F^{set\ point}$ is the fuel flow rate set point (see Fig. 3). The time constant was obtained by means of Least Square Method (LSM) applying on the experimental measurements.

3. Results

3.1. Hydrogen production in the reactor-static model

The hydrogen production rate in the reactor via ESR was modeled at four different fuel flow rates, i.e. 50, 100, 150, 200 µl/min and three different pressures. As shown in Fig. 4, the values obtained via modeling placed in the range of 5% error compared to the experimental results. A Least Square Method (LSM) was applied to fit the static measurement of the hydrogen production rate in the reactor (CMR).

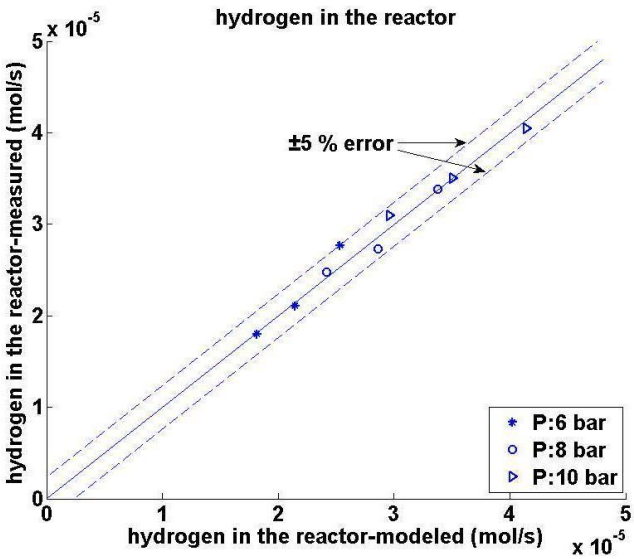

Fig. 4. Parity plot of the modeled and measured hydrogen production rate in the reactor.

α, β, θ, and γ are equal to 1.0873 [mol.m^{-3}], 0.7096 [-], 8.3×10^{-7} [J.Kg^{-1}.K^{-1}.Pa^{-1}], and -0.0665 [J.Kg^{-1}], respectively.

3.2. Pressure change-dynamic model

To create the dynamic model of the reforming system in case of pressure change, firstly, reactor pressure was simulated. Keeping in the mind the configuration of the system and ideal gas law, when pressure of the reactor is set at a higher value, the outlet of the reactor is blocked so that the inlet fuel is added to the volume of the reactor to increase the pressure

gradually with time. On the contrary, when reactor pressure is set at a lower value, the pressure valve is opened so that huge amount of gas is released leading to sudden pressure drop in the reactor. The different behavior of the system during pressure increasing and decreasing steps is due to the different act of the pressure controlling system on the pressure valve (see Fig. 1). Therefore, the dynamic of the system pressure control varies in different steps. The importance of such a performance lies in dependency of pure hydrogen permeation rate through the membrane on the partial pressure of hydrogen in the reactor. The simulated pressure change behavior of the reformer system is shown in Fig. 5.

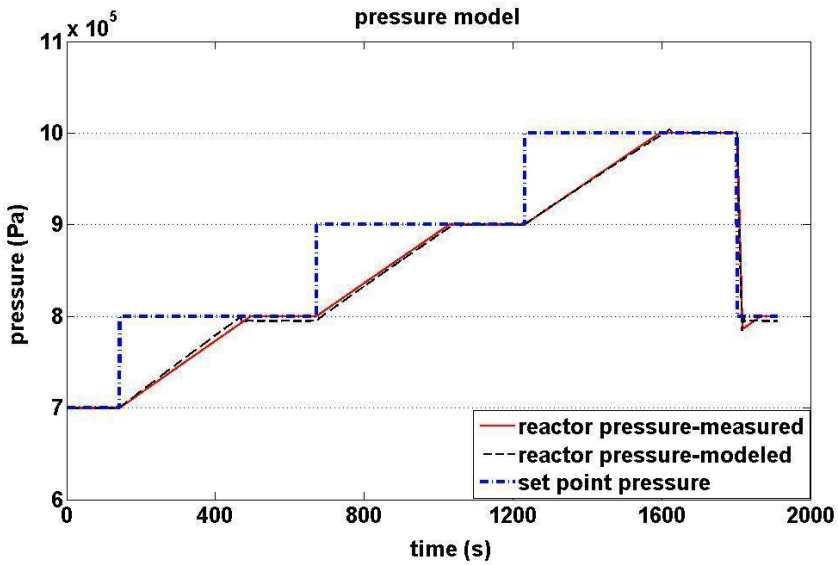

Fig. 5. Simulation of reactor pressure in pressure change dynamic tests.

It is clear that the results of simulation of reactor pressure by means of the ideal gas law fit the measurement very well. The pure hydrogen flow rate was simulated as a function of hydrogen production rate inside the reactor and the reactor pressure (see (13)). As expected, at constant temperature and fuel flow rate, pure hydrogen production rate follows the variation of reactor pressure by time.

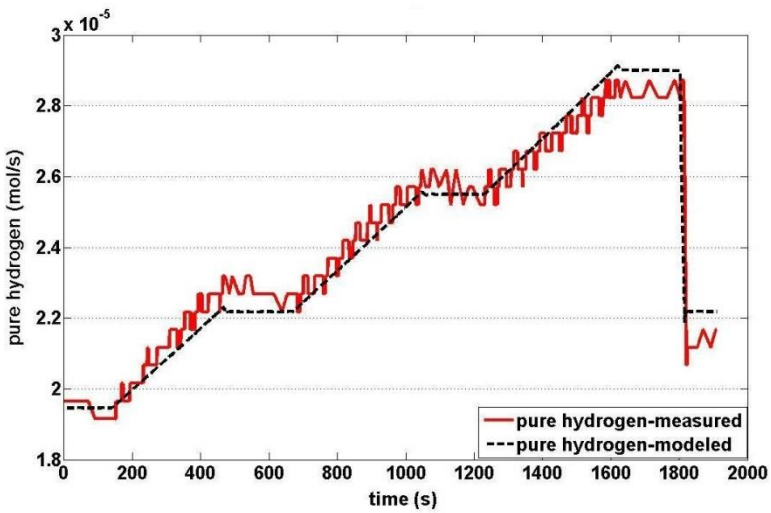

Fig. 6. Pure hydrogen model as a function of hydrogen production rate inside the reactor and the reactor pressure for pressure change dynamic tests

The small fluctuations of pure hydrogen measurement during the experiments are attributed to the small variations of the pressure inside the reactor, as the pressure valve acts on the outlet retentate stream. This fluctuation is equal to ca. 0.11×10^{-5} mol/s of pure hydrogen. Considering (13), the values of A, B, C, and D are 3.78×10^{-8} [Pa^{-1}], 0.716 [-], 0.987 [-], and 5.88×10-6 [$mol.s^{-1}$], respectively. As mentioned before, the dependency of pure hydrogen production (hydrogen permeation rate) on operating pressure is expected. Bearing this fact in mind, another model was proposed as a function of hydrogen production flow rate in the reactor ($\dot{n}_{H2}$). In this case, the constant values of (13) are A=0.965 [-], B=1 [-], C=0, and D=1.1×10^{-5} [$mol.s^{-1}$]. The result of this model is presented in Fig. 7.

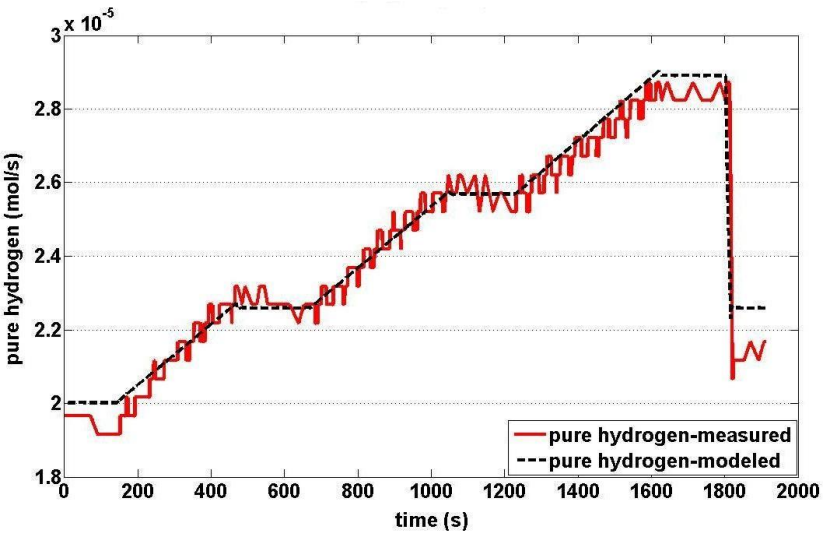

Fig. 7. Pure hydrogen model as a function of hydrogen production rate inside the reactor for pressure change dynamic tests

The similarity of the two models proves that the pure hydrogen production rate can be simulated independent from the operating pressure. This is an interesting result since the driving force of hydrogen permeation through the membrane is known to be the partial pressure of hydrogen around the membrane.

3.3. Fuel flow rate change-dynamic model

Intervals of 50 µl/min were considered to model the dynamic behavior of the reformer system. The results of the model are illustrated in Fig. 8. Measured values were obtained via dynamic experiments at constant pressure.

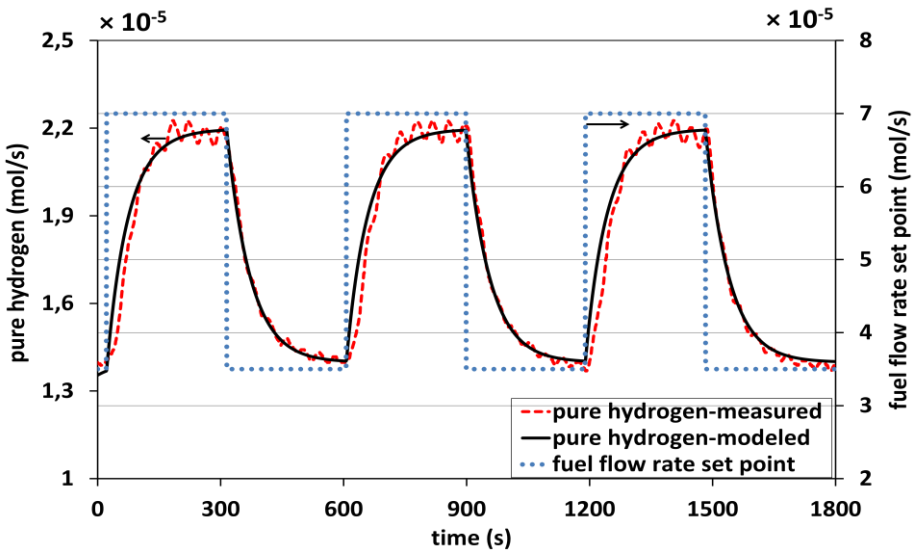

Fig. 8 .Experimental and simulation results of pure hydrogen production for fuel flow rate change dynamic tests

The time constant value is 55 seconds. At constant pressure, only hydrogen production rate inside the reactor was considered as the variable of the model. The model fits the experimental results very well, capable of prediction of the pure hydrogen flow rate variation with high accuracy. In comparison with pressure change model, it is more essential to develop a model on fuel flow rate change. The importance of fuel flow rate change model lies in the fact that acting on fuel flow rate is much faster than acting on system pressure. The time constant in fuel flow rate change tests (55 seconds) is nearly 45 times shorter than pressure change tests (200 seconds).

Dynamic model of the reforming system fits the experimental results very well, being able to predict variations of pure hydrogen production rate when reactor pressure is changed according to the set point value adjustments.

The static model of hydrogen production via ESR, together with both fuel flow rate and pressure change simulated behaviors can play an essential role for a general model of the dynamic performance of the system when connecting to a fuel cell for its online feeding and control. The model offered in this work is able to predict pure hydrogen alterations as a function of fuel flow rate and reactor pressure variations with high accuracy.

4. Conclusion

Ethanol steam reforming (ESR) over Pd-Rh/CeO_2 catalyst was performed in a CMR unit at 923 K, 6-10 bar, and fuel flow rates of 50 to 200 µl/min using a mixture of ethanol and distilled water with steam to carbon ratio of 3. A static model was proposed from the Arrhenius law as a function of fuel flow rate, pressure, steam to carbon ratio, and temperature for the catalytic zone. The model was based on experimental results and predicted correctly the performance of the ESR in terms of the molar production rate of H_2 inside the reactor (catalytic zone). Based on the static model, pure hydrogen production rate (permeation zone) was also simulated by means of two different models as functions of the production rate of H_2 and reactor pressure. Besides, dynamic performance of the system in case of the fuel flow rate or pressure change was studied experimentally and a a dynamic model was constructed under ideal gas law assumptions to simulate the behavior of the CMR system regarding the

production of pure hydrogen under isothermal conditions. The model was able to predict pure hydrogen production rate as a function of fuel flow rate and reactor pressure with high accuracy. This dynamic model resembled hydrogen flow rate adjustments needed to follow changes in the electric load of a fuel cell.

Acknowledgements

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