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Ali Hedayati, Olivier Le Corre, Bruno Lacarrière, Jordi Llorca. Dynamic simulation of pure hydrogen production via ethanol steam reforming in a catalytic membrane reactor. *Energy*, 2016, 117, pp.316 - 324. 10.1016/j.energy.2016.06.042 . hal-01525709

HAL Id: hal-01525709

<https://hal.science/hal-01525709v1>

Submitted on 12 Sep 2023

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Dynamic Simulation of Pure Hydrogen Production via ethanol Steam Reforming in a Catalytic Membrane Reactor

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Abstract

Ethanol steam reforming (ESR) was performed over Pd-Rh/CeO₂ catalyst in a catalytic membrane reactor (CMR) as a reformer unit for production of fuel cell grade pure hydrogen. 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. A static model for the catalytic zone was derived from the Arrhenius law to calculate the total molar production rates of ESR products, i.e. CO, CO₂, CH₄, H₂, and H₂O in the catalytic zone of the CMR (coefficient of determination R² = 0.993). The pure hydrogen production rate at steady state conditions was modeled by means of a static model based on the Sieverts' law. Finally, a dynamic model was developed under ideal gas law assumptions to simulate the dynamics of pure hydrogen production rate in the case of the fuel flow rate or the operational pressure set point adjustment (transient state) at isothermal conditions. The simulation of fuel flow rate change dynamics was more essential compared to the pressure change one, as the system responds much faster to such an adjustment. The results of the dynamic simulation fitted very well to the experimental

40 values, which proved the robustness of the simulation based on the Sieverts' law. The
41 simulation presented in this work is similar to the hydrogen flow rate adjustments needed to set
42 the electrical load of a fuel cell, when fed online by the pure hydrogen generating reformer
43 studied.

44

45 **Keywords:**

46 Ethanol Steam Reforming, Pure hydrogen production, Membrane reactor, Dynamic simulation,
47 Sieverts' law

48

49 **Highlights:**

- 50 • Ethanol steam reforming (ESR) experiments were performed in a Pd-Ag membrane
51 reactor
- 52 • The model of the catalytic zone of the reactor was derived from the Arrhenius law
- 53 • The permeation zone (membrane) was modeled based on the Sieverts' law
- 54 • A dynamic model was developed under ideal gas law assumptions
- 55 • Pressure and fuel flow rate adjustments were considered for dynamic simulation

56

57 **1. Introduction**

58

59 Renewable energy resources are now considered as one of the fastest and most feasible
60 solution to achieve the targets of clean electricity production; however, some challenges such
61 as dependency on the geographical and local conditions and infrastructures, and transmission
62 of produced electricity to the end users remain among the challenges to be encountered. In this
63 regard, on-site electricity production at the place/time where needed is beneficial.

64

65 Being compatible with modern energy carriers such as hydrogen, fuel cells are considered as
66 the efficient (45-50% electrical efficiency) and environmentally friendly energy converters of the
67 future power generation systems [1–3]. Fuel cells have proved potentials in different
68 applications and can be applied in sub-MW size at any condition, independent from
69 geographical factors such as local climate conditions. Although production of hydrogen-rich
70 gases can offer flexible fuels for fuel cells [4], the pollution-free efficient performance of a fuel
71 cell is reached when pure hydrogen is used [5]. Accordingly, the main challenge remains in the
72 requirements of the special installations and infrastructures for production, distribution, and
73 delivery of hydrogen as it is needed in highly pure state [6]. Production of hydrogen – for
74 example via reforming processes – at the same place/time needed can make pure hydrogen
75 storage/transportation unnecessary [7].

76

77 The use of renewable biofuels such as bio-ethanol as a source of hydrogen is highly beneficial
78 due to the higher H/C ratio, lower toxicity, and higher safety of storage that distinguishes ethanol
79 over other substrates. Bio-ethanol is cheaply and easily obtained from biomass and organic
80 waste and can be used directly in catalytic steam reforming processes to produce hydrogen
81 since it contains large amounts of water [8]. Concerning the production of fuel cell grade
82 hydrogen, the application of catalytic membrane reactors (CMRs) is beneficial where the
83 production and separation of hydrogen from the mixture of produced gases take place in the
84 same reactor vessel simultaneously. In the case of Pd-Ag metallic membrane reactors,
85 hydrogen purity up to 99.999% is obtained, which is suitable for direct low-temperature fuel cell
86 feeding [9,10].

87

88 The application of the CMRs in pure hydrogen production (as a reformer unit) is still under
89 investigation. The effect of the co-presence of steam reforming byproducts (CO, H₂O, CO₂ and
90 CH₄) on the performance of the membrane in terms of pure hydrogen permeation rate is still a

91 challenge to be overcome. Hou et al. [11] reported that the hydrogen inhibition effect of CO,
92 CO₂, and H₂O in the case of a Pd-Ag membrane could be classified as H₂O>CO>>CO₂ in terms
93 of the competitive adsorption capability of the gases on the Pd-Ag membrane surface. In the
94 study by Unemoto et al. [12] the comparison between CO, CO₂, and H₂O showed that at T<600
95 K, CO had the strongest influence on the hydrogen permeability of the Pd membrane. They
96 suggested that at T>873 K, the effect of co-existence of other species for a membrane with a
97 thickness higher than 10 μm is negligible. On the contrary, Patrascu and Sheintuch [13]
98 concluded that the effect of very small amount of CO on hydrogen permeation inhibition could
99 be notable even in presence of H₂O. The strong effect of low concentration of CO on the
100 membrane permeation behavior at different temperatures was reported also in other studies
101 [14–18]. Catalano et al. [19] stated that CH₄ acted as inert gases in terms of hydrogen inhibition.
102 Barreiro et al. [20] showed that the hydrogen flux was reduced in presence of water at 593-723
103 K, while CO₂ had no influence on the permeation rate of hydrogen.

104
105 Overall, the literature does not provide a consistent idea on the hydrogen inhibition
106 phenomenon due to the competitive adsorption of CO and H₂O on the surface of the metallic Pd
107 membrane, the effect of reverse reactions of water gas shift (WGS) and methane steam
108 reforming (MSR), and the effect of operating at high pressure and temperature in the real
109 atmosphere of the ESR. It is not totally agreed if CO₂ and CH₄ are considered as inert gases as
110 their reactions with water via reverse WGS and MSR can lead to a more complicated situation
111 regarding the influence on the hydrogen permeation. According to the review given by Cornaglia
112 et al. [21], it can be understood that the hydrogen inhibition phenomenon caused by the ESR
113 products especially in presence of H₂O, is a very complicated issue. It is inevitable to study each
114 fuel reformer system specifically in terms of the properties of the membrane, operating
115 conditions, and the composition of the fuel fed into the reformer reactor.

116

117 If a fuel cell is fed online by pure hydrogen generating system (hereafter referred to as
118 “reformer”), the dynamics of pure hydrogen supply must be fitted to the load variations (dynamic
119 behavior) of a fuel cell. Considering the dynamic energy demand of an end user – for example a
120 building – a reformer must be able to realize and track the dynamic electrical output of the fuel
121 cell in charge of electricity supply of the end user. Adjustment of the flow rate of pure hydrogen
122 provided by a reformer is a crucial phase to respond promptly and aptly to the electrical load
123 modifications of a fuel cell, aiming to optimize the whole system (reformer + fuel cell)
124 performance. Although a few studies are reported in the literature regarding the dynamic
125 performance of the fuel cells, the works devoted to the investigations of the dynamic
126 performance of the online fuel reformers – corresponding to the load variation of the fuel cells –
127 are not sufficiently reported in the literature [22].

128

129 Garcia et al. [23] developed a dynamic model for a three module reformer made up of ethanol
130 dehydrogenation, acetaldehyde steam reforming, and water gas shift units for feeding hydrogen
131 to a fuel cell. They simulated the dynamic response of the reforming unit in terms of the
132 selectivity of the products of the ESR reaction rate to the changes in concentration of the feed
133 (ethanol + water). The same authors in another study [24] focused on the controllability and the
134 dynamics simulation of the same system as they reported in [23] by acting on the feed
135 concentration at isothermal conditions. A dynamic numerical model for the methane fuel
136 processor of a PEMFC was developed by Funke et al. [25] aiming at optimizing the reaction
137 conditions and heat integration especially during start up, shut down, and load change. The
138 effect of two constructions (the reactor and the evaporator with and without thermal coupling) on
139 the temperature profile, reaction rates, and methane conversion was investigated and it was
140 reported that hydrogen yield is higher when the reactor and the evaporator are not thermally
141 coupled. John and Schroer [26] presented a dynamic model of a methane steam reformer for a
142 residential fuel cell system. The dynamic model covered the full operating range including the

143 startup and shut down, and described the dynamics of the hydrogen yield and thermal behavior
144 of the reformer when the flow rate of water or natural gas changed. The thermal system was
145 affected by increasing the flow rate of the water. Higher hydrogen yield and lower methane
146 concentration at the outlet were reported at higher temperature, i.e. lower concentration of inlet
147 water. A dynamic model for an interconnected reformer and PEMFC stack was developed by
148 Stamps and Gatzke [27] with emphasis on the influence of various design and operating
149 parameters on system performance. It was concluded that operating at higher temperature
150 results in higher system performance.

151

152 A dynamic modeling study of a catalytic steam reformer by Kvamsdal et al. [28] showed that
153 the steam or gas (CO , CO_2 , H_2 , and CH_4) supply interruption affects the reactor wall
154 temperature, which can directly lead to material failure or coke formation. Lin et al. [29] modeled
155 the dynamics of an experimental multi stage methane reformer in charge of providing hydrogen
156 to a PEMFC to design a control system to provide the responsiveness of the fuel reformer to the
157 alterations in the hydrogen demand. The response of the fuel reformer to changes in the
158 process variables such as CH_4 feed flow rate, $\text{H}_2\text{O}/\text{CH}_4$ feed ratio, O_2/CH_4 feed ratio and the
159 reformer inlet temperature was studied. Tsourapas et al. [30] presented a dynamic model based
160 on thermodynamics and energy balance for a JP5 fuel reformer in connection with a membrane
161 separator (SEP) and a PEM fuel cell to investigate the effects of the operating set point of SEP
162 on the overall system efficiency. They concluded that the open loop response of the system is
163 shown to be satisfactory in terms of the response time and hydrogen production. It was shown
164 that there is a trade-off between the SEP efficiency and the overall efficiency of the system.

165

166 In another work by Koch et al. [10], a dynamic model of an ethanol steam reformer (as the fuel
167 reformer for pure hydrogen production to feed a PEMFC) was developed to implement an
168 adaptive and predictive control. The static behavior of the reformer system was described by

169 means of several maps developed in Matlab. Further, the dynamics of the fuel reformer in
170 connection with a PEMFC by acting upon reactor pressure and feed flow rate (ethanol + water)
171 was studied. They proposed an efficient controller that reduced the response time of the
172 reformer by a factor of 7 down to 8 s in terms of following the dynamics of a fuel cell load by
173 acting simultaneously on the fuel flow rate and pressure. However, such advanced controllers
174 require internal models and simulations for further development.

175

176 The purpose of this paper is to present a simpler approach mainly based on physical laws
177 (adapted Arrhenius model, mass balance, ideal gas law, and Sieverts' law). Such a model can
178 be applied for the development of controllers, which is out of the scope of the paper. A dynamic
179 model of a reforming system (the CMR) is given to simulate the dynamics of the pure hydrogen
180 production rate at unsteady state conditions (between two steady state points) under fuel flow
181 rate and pressure set-up steps. The model considers the kinetics of the catalytic reforming
182 reactions regarding the molar production of ESR products, especially hydrogen inside the
183 reactor at unsteady operating conditions. Moreover, the dynamic simulation is based on the real
184 dynamic experiments using a Pd-Ag membrane reactor module (where production and
185 separation of hydrogen takes place in the same reactor) for production of fuel cell grade
186 hydrogen via ethanol steam reforming. Additionally, application of the CMR makes it possible to
187 investigate the effect of the byproducts of the ESR (CO, CO₂, H₂O, and CH₄) on the
188 performance of a real case Pd-Ag membrane based on the observed reaction kinetics
189 (concentration of the ESR products). The latter is an important factor in monitoring and
190 simulation of the performance of the membrane in ESR environment so that many works have
191 been reported on the investigation of the effect of the gaseous byproducts on the permeation
192 behavior of the membranes.

193

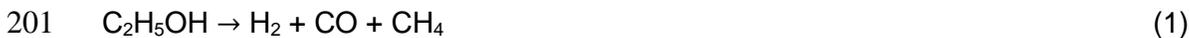
194 **2. Materials and methods**

195

196 2.1. Experimental

197

198 The Pd-Rh/CeO₂ catalyst (0.5% Pd – 0.5% Rh) was deposited over cordierite pellets of about 1
199 mm following the procedure described by López et al. [31]. When ESR is performed over Pd-
200 Rh/CeO₂ catalyst, the major reforming reactions are [32,33]:



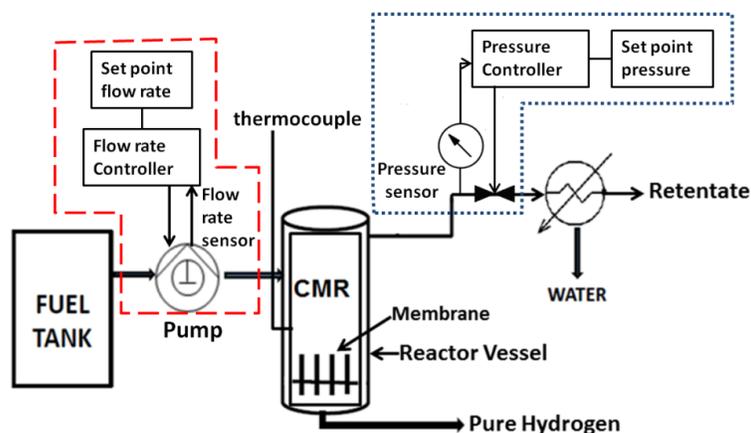
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206 Equations 1-3 represent the ethanol decomposition, water gas shift, and methane steam
207 reforming reactions, respectively. Equation 4 is the overall ESR reaction.

208

209 The laboratory setup used for the ESR experiments (fuel reformer) consisted essentially of a
210 fuel tank, a liquid pump, a CMR, a pressure transducer and a condenser. A detailed description
211 of the reformer setup can be found in [34]. A schematic plan of the fuel reformer system is
212 shown in Fig. 1.

213



214

215

Fig. 1. Scheme of the Reformer.

216 The dashed and dotted lines represent the fuel flow rate and pressure controlling systems,
 217 respectively. The CMR (provided by Reb Research and Consulting [35]) was 10 in. tall and 1 in.
 218 in diameter. There were four Pd-Ag membrane tubes selective to hydrogen inside the reactor;
 219 each one 3 in. tall and 1/8 in. diameter in order to separate hydrogen from the gases produced.
 220 To perform the experiments, the reactor was filled with the catalysts so that the metallic
 221 membranes were fully covered. The retentate pressure was adjusted by a back-pressure
 222 regulator (transducer). No pressure regulation was implemented on the permeate side and no
 223 sweep gas was used so that pure hydrogen was obtained at atmospheric pressure. The flow
 224 rate of pure hydrogen (permeate) was measured with a mass flow meter and fluctuated within
 225 ± 2 ml/min. The composition of retentate gases (waste gases) was analyzed on a dry basis using
 226 an online Gas Chromatograph ($\pm 3\%$) (Agilent 3000A MicroGC using MS 5 Å, PlotU and
 227 Stabilwax columns) every 4 minutes.

228

229 The operating conditions of the experiments under steady conditions are summarized in Table
 230 1. The experiments were performed at isothermal conditions.

231

232

Table 1. Experimental conditions

Temperature $T^{set\ point}$ (K)	923
Pressure $p^{set\ point}$ (bar)	6-10
Fuel flow rate $F_F^{set\ point}$ ($\mu\text{l}/\text{min}$)	50-200
Steam to carbon ratio SC	3

233

234 At 923 K, the ESR over the Pd-Rh/CeO₂ catalyst is optimized in terms of hydrogen selectivity,
 235 hydrogen recovery, and ethanol conversion [31,32,36,37]. At SC ratio of 3, the highest value of
 236 hydrogen recovery was obtained during the experimental work that is attributed to the

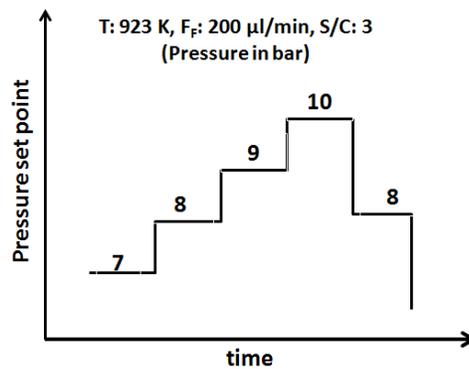
237 availability of water for the reforming reactions. On the other hand, coke formation is less prone
238 to occur at a higher SC ratio with respect to the stoichiometric value.

239

240 Two types of dynamic tests were performed in this study: pressure change and flow rate
241 change. In the case of pressure change dynamic tests, both increasing and decreasing steps
242 were considered. As presented in Fig. 2, the pressures range of 7-10 bar was selected because
243 at these pressures the efficiency of the fuel reformer is maximum [38].

244

245



246

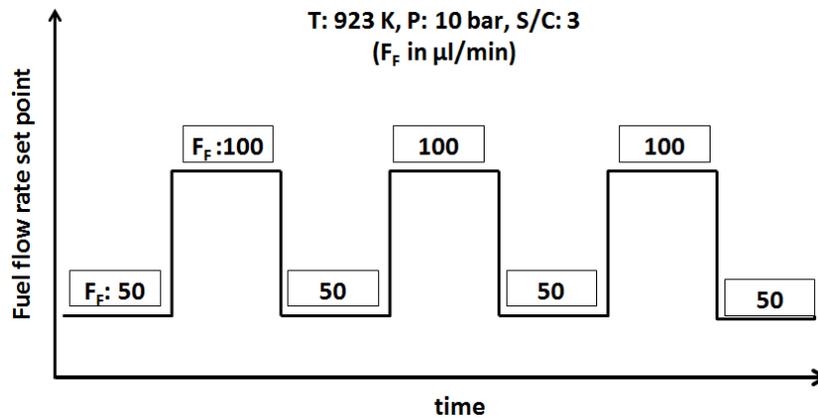
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248 Fig. 2. Scheme of the pressure change for the dynamic tests.

249 Dynamic tests regarding the response of the system to the fuel flow rate changes were
250 performed through intervals of 50 $\mu\text{l}/\text{min}$ as shown in Fig. 3.

251

252



253

254

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

255

The changing cycles were run more than one time to observe the durability of the performance

256

of the reforming system. According to the membrane limitations, higher flow rates were not

257

taken into account.

258

259

2.2. CMR isothermal model

260

261

For the modeling task, the CMR was divided into two sections, i.e. the catalytic zone, and the

262

permeation zone (the membrane) as shown in the Fig. 4. The ESR reactions were supposed to

263

occur in the catalytic zone, resulting in total production of the retentate gas plus the permeated

264

hydrogen. The permeation zone (the membrane) stands for the pure hydrogen generating step

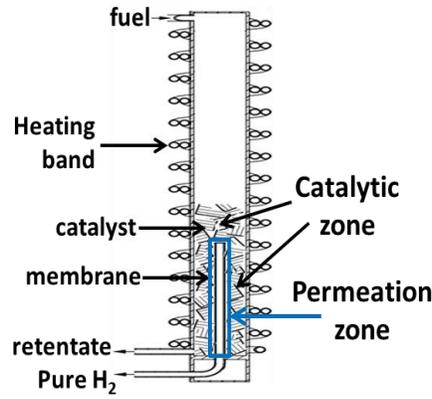
265

for which the dynamic model was developed. The outputs of the catalytic zone model were used

266

as the input of the static models of the permeation zone (i.e. the membrane).

267



268

269

Fig. 4. The catalytic zone and the permeation zone of the CMR

270

271

It is assumed that the fuel (ethanol+water) is in its gas phase at the entrance of the volume of the CMR and the ideal gas law is applied. The CMR model is splitted into a static model and a first order transfer function, i.e. ESR products are driven by the operating conditions (pressure and temperature) under steady state conditions.

275

276

2.2.1. Static model of the catalytic zone

277

278

A static model for the catalytic zone was developed to calculate the total molar production rate of species present in the catalytic zone of the CMR, i.e. CO, CO₂, CH₄, H₂, and H₂O as the products of the catalytic conversion of ethanol (around the membrane). The static model was derived following the Arrhenius law as a function of fuel flow rate and operating pressure in the form of:

283

$$\dot{n}_{specie} = f_{specie} \times \exp\left(-\frac{g_{specie}}{RT}\right) \quad (5)$$

$$f_{specie} = \alpha_{specie} \times F_F^{\beta_{specie}} \quad (6)$$

$$g_{specie} = \theta_{specie} \times P + \gamma_{specie} \quad (7)$$

287

288 \dot{n}_{specie} [mol/s] is the molar production rate of each species produced in the CMR via ESR over
 289 the catalyst (and around the membrane). F_F [m³/s] and P [Pa] represent the fuel (ethanol +
 290 water) flow rate and the reactor pressure, respectively. ' f_{specie} ' represents a function of fuel flow
 291 rate as pre-exponential factor, and ' g_{specie} ' represents the energy of activation as a function of
 292 pressure. α_{specie} , β_{specie} , θ_{specie} , and γ_{specie} are the fitting parameters of the equations. The
 293 introduced model was applied to calculate the molar production rate of the ESR products,
 294 mainly to calculate the partial pressure of hydrogen ($P_{\text{H}_2,r}$ in eq. 9) around the membrane
 295 surface (right before the permeation zone).

296

297 **2.2.2. Static models of the permeation zone**

298

299 The model of hydrogen permeation through the membrane at steady state was derived from the
 300 Sieverts' law. Hydrogen permeation phenomenon through a Pd-Ag membrane is explained by
 301 Sieverts' law based on the mass transfer and surface reactions principals [19,39]. As stated by
 302 the Sieverts' law, the hydrogen permeation rate through Pd-Ag membrane is a temperature
 303 activated phenomena driven by the difference between the partial pressure of hydrogen at two
 304 sides, i.e. the retentate side (inside the reactor, around the membrane) and the permeate side
 305 (right after the membrane) [31,33]:

306

$$307 \quad J_{\text{H}_2} = \frac{Q_0}{\delta} e^{\frac{-E_a}{RT}} (\sqrt{P_{\text{H}_2,r}} - \sqrt{P_{\text{H}_2,perm}}) \quad (8)$$

308

309 Where J_{H_2} is the pure hydrogen production rate obtained via the Sieverts' law. δ is the thickness
 310 of the membrane and Q_0 is the pre-exponential factor. E_a , R , and T are the activation energy,
 311 universal gas constant, and temperature, respectively. $P_{\text{H}_2,r}$ and $P_{\text{H}_2,perm}$ are the partial pressure
 312 of hydrogen at the retentate and permeate side, respectively.

313 The partial pressure of hydrogen inside the reactor was calculated based on the hydrogen
314 fraction in the gas phase assuming that the only present species in the catalytic bed (and
315 around the membrane) are CO, CO₂, CH₄, H₂ and H₂O. Therefore:

316

$$317 \quad P_{H_2,r} = P \times y_{H_2,r} \quad (9)$$

318

319 Where P and $y_{H_2,r}$ represent the reactor pressure and the molar fraction of hydrogen in the
320 catalyst bed, respectively. The reactor pressure simulation method is explained in section 2.2.3.
321 The activation energy (E_a) and the pre-exponential factor (Q_0) are calculated by means of
322 permeation experiments during which pure hydrogen at known temperature and pressure is
323 purged and the permeation rate of hydrogen through the membrane is measured (atmospheric
324 pressure at the permeate side) [40–45].

325

326 As discussed before, the published open literature offers no robust model/analysis on the effect
327 of different species on the performance of the membrane in the real atmosphere of methane
328 steam reforming and water gas shift reactions. It was concluded that to understand the influence
329 of co-existence of ESR products on the permeation performance of the membrane, specific
330 models must be developed regarding specific operational conditions of the ESR environment.

331

332 Accordingly, a model was developed for hydrogen permeation through the Pd-Ag membrane;
333 specifically for the ESR environment at the operating conditions presented in this work. It is
334 assumed that the concentrations of CO and H₂O affect the permeation performance of the
335 membrane differently at different operating conditions. The hidden effect of CH₄ and CO₂ are
336 taken into account considering the ESR reactions (eq. 1-3). Firstly, the model presented in the
337 section 2.2.1 (catalytic zone) was used to fit the molar flow rate of the species present in the
338 retentate gas, i.e. CO, CO₂, CH₄, H₂, and H₂O (to calculate the partial pressure of hydrogen at
339 the retentate side).

340

341 Regarding equation 9, the activation energy (E_a) was taken from the work by Papadias et al.
342 [46] as they used the same membrane module as the one used in this work, with the same
343 characteristics and synthesized by the same manufacturer (REB Research & Consulting [35]).

344 Therefore, the term $\frac{e^{-\frac{E_a}{RT}}}{\delta}$ in eq. 9 was calculated, which is equal to $54.9 \text{ [m}^{-1}\text{]}$. Then, the term ' Q_0 '
345 was obtained firstly from the experimental results (Q_0^{measure}), and then modeled (Q_0^{model}) by
346 means of a static model as a function of the reactor pressure (P) and fuel flow rate (F_F):

347

$$348 \quad Q_0^{\text{measure}} = \frac{J_{H_2} \times \delta}{e^{-\frac{E_a}{RT}} \times (\sqrt{P_{H_2,r}} - \sqrt{P_{H_2,perm}})} \quad (10)$$

349

$$350 \quad Q_0^{\text{model}} = k_1 \times F_F \times \exp(k_2 \times P) \quad (11)$$

351

352 Where ' k_i ' is the fitting parameter. $P_{H_2,r}$ in eq. 10 is obtained via eq. 9 by using the modeled
353 values of the molar production rate of ESR products (eq. 5-7) to calculate the hydrogen fraction
354 in the catalytic zone. In fact, this factor was used to fit the results of the Sieverts' law based
355 model to the experimental ones.

356

357 Accordingly, the hydrogen permeation rate at steady state conditions was modeled to be used
358 in the simulation of the dynamics of hydrogen permeation rate at transient conditions, i.e.
359 between two steady state points.

360

361 **2.2.3. Isothermal dynamic simulation of the permeation zone**

362

363 Prior to the dynamic simulation of the permeation zone, the reactor pressure was modeled in
364 the case of pressure set point adjustment during which the pressure valve of the reforming

365 systems acts on the retentate gas flow rate to adjust to a higher or lower pressure. The ideal
366 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
367 are reactor pressure, the volume of the reactor, reactor temperature, and the molar mass of the
368 fuel mixture, respectively. 'm' is the accumulated mass of the fuel added to the reactor volume.
369 It was assumed that the accumulation rate of the pumped fuel into the constant volume of the
370 reactor at constant temperature, results in pressure rise as the pressure valve acts on the outlet
371 of the system to block the retentate stream when pressure increase is required. Conversely, to
372 decrease the pressure, the pressure valve lets the retentate gas be released, so that the inlet
373 mass flow rate of the fuel gets lower than the outlet mass flow rate. Regardless of the action of
374 the pressure valve on the retentate gas stream, hydrogen constantly permeates through the
375 membrane. Therefore, the added mass to the reactor volume is the difference between the fuel
376 flow rate, and the retentate gas flow rate plus hydrogen permeation rate, so that:

377

$$378 \quad \frac{dm}{dt} = \dot{m}_{fuel} - \dot{m}_r - \dot{m}_{H_2,perm} \quad (12)$$

379

380 Where \dot{m}_{fuel} and $\dot{m}_{H_2,perm}$ represent the fuel flow rate and hydrogen permeation rate, respectively,
381 both in [kg/s]. Then, the ideal gas law is written as:

382

$$383 \quad \frac{dP}{dt} = \left(\frac{RT}{VM_w} \right) \times \frac{dm}{dt} \quad (13)$$

384

385 Where $\frac{dm}{dt}$ is the rate of the accumulation of the mass in the reactor volume. In this work, the
386 CMR is a packed bed reactor running at isothermal conditions, with negligible axial mixing. The
387 temperature and concentration difference is neglected, so that the models are considered as
388 ideal plug flow pseudo-homogenous ones [47].

389

390 The dynamic simulation was performed to predict the dynamic behavior of the pure hydrogen
391 production rate (permeate zone) in the transient periods during which the reforming system
392 alters between two steady state points, as a result of the fuel flow rate or operating pressure set
393 point adjustments. To develop the dynamic model of the permeate zone, a first order function
394 was used:

$$396 \frac{J_{H_2}^D}{F_F} = \frac{J_{H_2}}{1+\tau s} \quad (14)$$

397
398 $J_{H_2}^D$ is the pure hydrogen production rate obtained by the dynamic model. The superscript “D”
399 stands for the dynamic model. J_{H_2} represents the hydrogen permeation rate calculated via the
400 static model based on the Sieverts law, considering every single operating point as steady state.
401 The time constant is presented as τ . The measured dynamic of fuel flow rate was faster than the
402 sampling time (1 second). Therefore, the fuel flow rate is always equal to its set point value:

$$404 F_F = F_F^{set\ point} \quad (15)$$

405
406 Finally, equation 14 is written as:

$$408 \frac{J_{H_2}^D}{F_F^{set\ point}} = \frac{J_{H_2}}{1+\tau s} \quad (16)$$

409
410 Where $F_F^{set\ point}$ is the fuel flow rate set point (see Fig. 3).

411
412 The simulation was performed by means of Ordinary Differential Equation (O.D.E) solver.

413

414 **3. Results and discussion**

415

416 Least Square Method (LSM) was applied to obtain all the fitting parameters regarding the static
417 models. The time constant was estimated from a set of trials and errors.

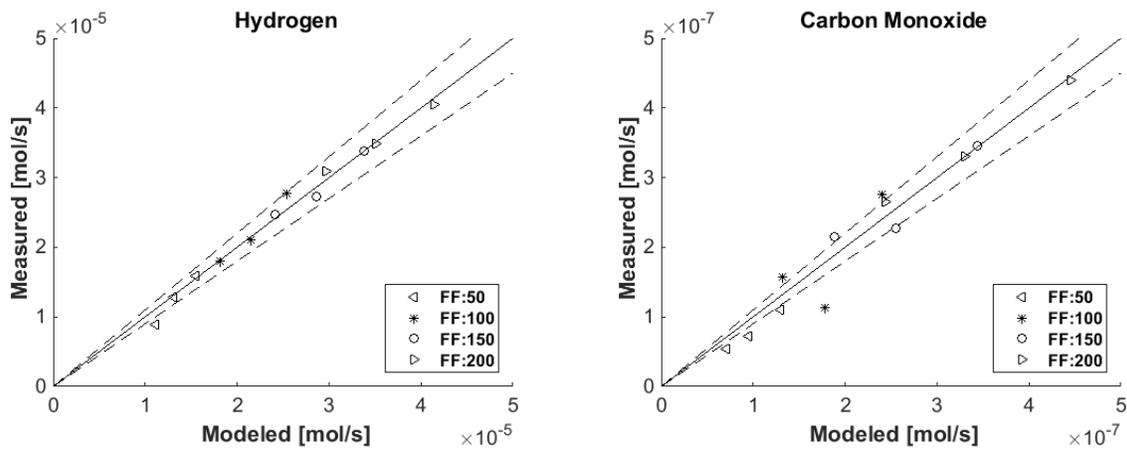
418

419 3.1. Static models of the permeation zone

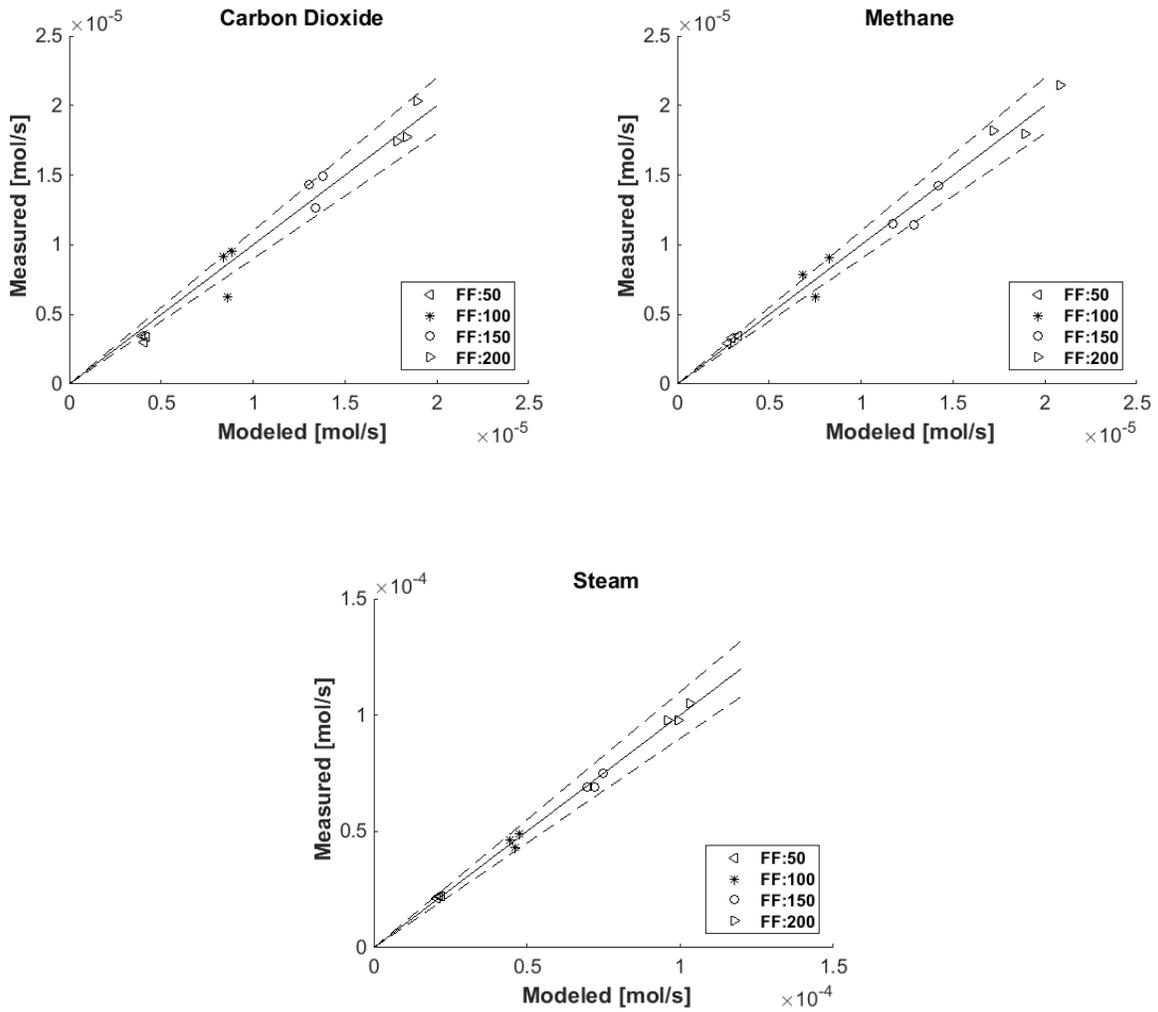
420

421 The products of ESR (H_2 , CO , CO_2 , CH_4 , and H_2O) and the pure hydrogen permeation rate was
422 modeled at four different fuel flow rates, i.e. 50, 100, 150, 200 $\mu\text{l}/\text{min}$ and three different
423 pressures (6, 8, and 10 bar). As mentioned before, the molar production rate of all the ESR
424 products was needed in order to calculate the partial pressure of hydrogen in the catalytic zone
425 (around the membrane). The calculated molar production rates of the ESR products (catalytic
426 zone) are presented in Fig. 5. The dashed lines represent the 10% error (discrepancy between
427 experiment and measurement). The x-axis (modeled) and y-axis (measured) are referred to the
428 values calculated by the static model and obtained via experiments, respectively.

429



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Fig. 5. Parity plots of the ESR products calculated by the static model (eq. 5-7).

435

The modeled values could fit the experimental results within the 10% error, especially in the

436

case of production rate of hydrogen. The values of the fitting parameters (eq. 6 and 7) for all the

437

gases are given in Table 2.

438

439

440

441

442 Table 2. Fitting parameters of the static model for the ESR products production rate model (eq.
 443 6 and 7)

specie	$\alpha_{\text{specie}} [\text{mol.m}^{-3}]$	$\beta_{\text{specie}} [-]$	$\theta_{\text{specie}} [\text{J.mol}^{-1}.\text{Pa}^{-1}]$	$\gamma_{\text{specie}} [\text{J.mol}^{-1}]$	R^2
H ₂	1.0873	0.7096	8.3800×10^{-7}	-0.0665	0.9954
CO	75.5364	0.8930	-1.5028×10^{-6}	-4.2727	0.9849
CO ₂	133.8928	1.0915	-1.4717×10^{-7}	1.1520	0.9911
CH ₄	560.2602	1.3303	-4.7941×10^{-7}	3.7000	0.9950
H ₂ O	226.0976	1.1131	-1.7989×10^{-7}	2.6771	0.9992

444

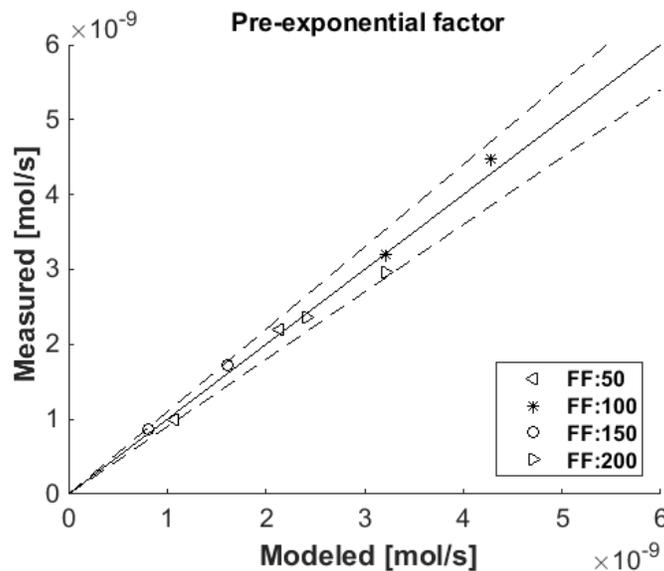
445 Keeping in mind equations 5-7, it can be seen that the values of $P \times \theta$ are very small compared
 446 to γ , except in the case of hydrogen. As mentioned before, the most effective factor on the
 447 hydrogen permeation is the partial pressure of hydrogen in the reactor; hence, the value of $P \times \theta$
 448 is higher in this case. The same explanation can be given regarding the parameter β . In the
 449 case of hydrogen, the effect of pressure in the CMR configuration is dominant in comparison
 450 with the fuel flow rate, resulting in the smallest value of β in the case of hydrogen. Conversely,
 451 the value of β in the case of CH₄ is the highest among the gases because the only source of
 452 CH₄ is the ethanol decomposition reaction (eq. 1). At complete ethanol conversion, the higher
 453 the fuel flow rate is, the higher the production rate of CH₄ is. The value of β in the case of H₂O is
 454 nearly one, which is very relevant since the ESR reaction were performed at SC=3, where there
 455 is a large amount of excess water. It can be concluded that the molar flow rate of water is
 456 proportional to the inlet molar flow rate of water in the fuel mixture (ethanol + water). At SC=3, a
 457 large portion of the inlet water (70-90%) leaves the reactor in the form of steam as unreacted
 458 water. The value of θ in the case of CO is one order of magnitude smaller than other gases,
 459 which is attributed to the very small amount of CO detected at the outlet of the reactor. The
 460 values of θ proves that at higher pressures, less byproducts (CO, CO₂, CH₄, and H₂O) and more

461 hydrogen are generated, which is totally in agreement with the experimental results and the aim
462 of application of the CMR, where ESR reactions are promoted (the shift effect).

463

464 The value of the pre-exponential factor model (eq. 11) showed a good correlation ($R^2=0.91$) with
465 the calculated values (Fig. 6) except at P=6 bar; this is interpreted to the fact that at this
466 pressure the membrane starts to be effective for hydrogen separation.

467



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470

471 Fig. 6. The result of the pre-exponential factor model (eq. 11) at P>6 bar. The dashed lines
472 show the 15% error range.

473

474 The values at P=6 bar are not presented due to membrane diffusion limitation at pressures
475 lower than 6 bar. The fitting parameters considering the static models for the permeation zone
476 (eq. 11) are given in Table 3.

477

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Table 3. Fitting parameters of the pre-exponential factor model (eq. 11)

483

Parameter	k_1	k_2	R^2
value	0.602	-3.4823×10^{-6}	0.91
Unit	$[\text{mol.m}^{-2}.\text{Pa}^{-0.5}]$	$[\text{Pa}^{-1}]$	$[-]$

484

485

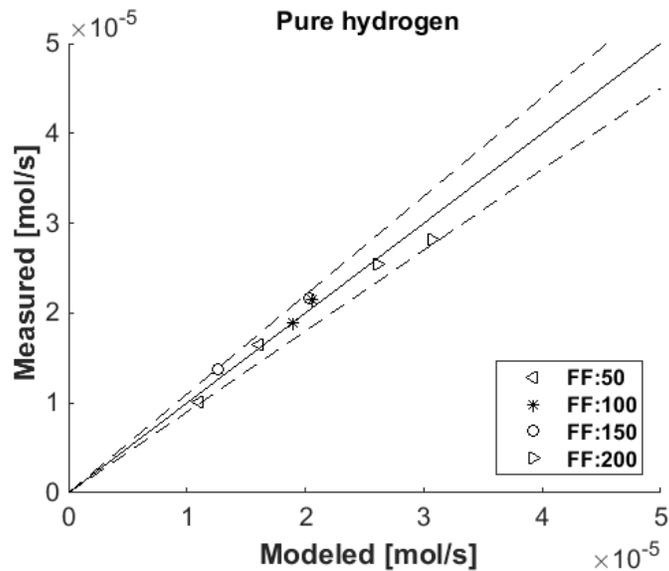
486 Regarding the value of k_2 , the diverse effect of pressure is obvious (see eq. 11). This is
487 attributed to the fact that at higher pressure, the concentration of hydrogen is higher around the
488 membrane (permeation zone) leading to the lower concentration of the other gases, which
489 directly means that the permeation performance of the membrane is less affected. This is
490 completely in agreement with the experimental results and the assumption of the negative effect
491 of the byproducts of the ESR reactions on the permeation behavior of the Pd-Ag membrane.

492

493 The result of the Sieverts' law model (permeation zone) is shown in Fig. 7 ($P > 6$ bar; $R^2 = 0.86$).

494 The partial pressure of hydrogen in the reactor (obtained based on the molar production rates of
495 the ESR products calculated by the Arrhenius based static model) was used in the Sieverts' law
496 to obtain the pure hydrogen permeation rate.

497



498
499

500 Fig. 7. Parity plots of the hydrogen permeation rate obtained by the Sieverts' law model

501

502

503

504 3.2. Isothermal Dynamic simulation

505

506 3.2.1. Pressure change simulation

507

508 To develop the dynamic model of the reforming system in the case of pressure change, firstly,

509 the reactor pressure was simulated. Keeping in mind the configuration of the CMR, when the

510 pressure of the reactor is set at a higher value, the outlet of the reactor is blocked so that the

511 inlet fuel is added to the volume of the reactor to increase the pressure gradually with time.

512 When the pressure is increased, the flow rate of the retentate gas (\dot{m}_r) is zero (see eq. 12). On

513 the contrary, when reactor pressure is set at a lower value, the pressure valve is opened so that

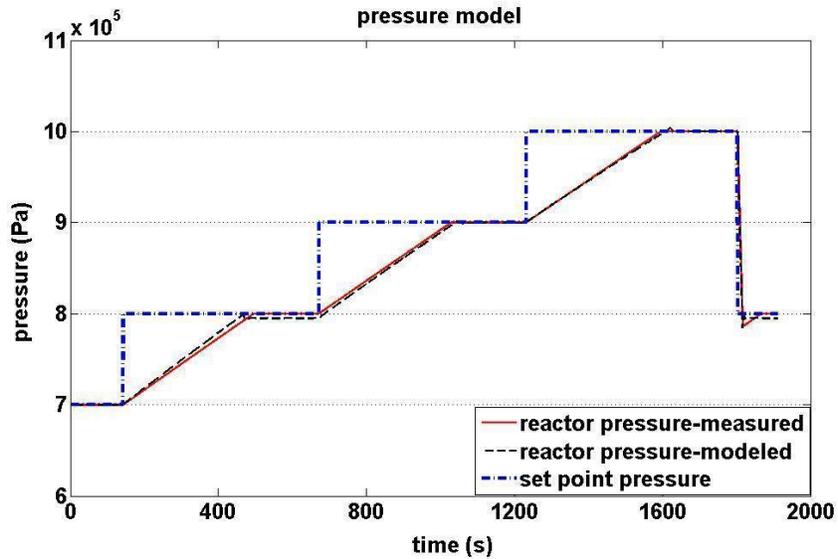
514 gas is released leading to sudden pressure drop in the reactor. The different behavior of the

515 system during pressure increasing and decreasing steps is due to the different act of the

516 pressure controlling system on the pressure valve (see Fig. 1). Therefore, the dynamics of the

517 system pressure control differ in different steps. The importance of such a performance lies in
518 the dependency of pure hydrogen permeation rate through the membrane on the partial
519 pressure of hydrogen in the reactor. The simulated pressure change behavior of the reformer
520 system is shown in Fig. 8.

521



522

523

524 Fig. 8. Measured and simulated reactor pressures in the pressure change dynamic tests. $T=923$

525

$K, F_F=200 \mu\text{l}/\text{min}.$

526 It is clear that the results of simulation of reactor pressure by means of the ideal gas law fit the
527 measurement very well.

528

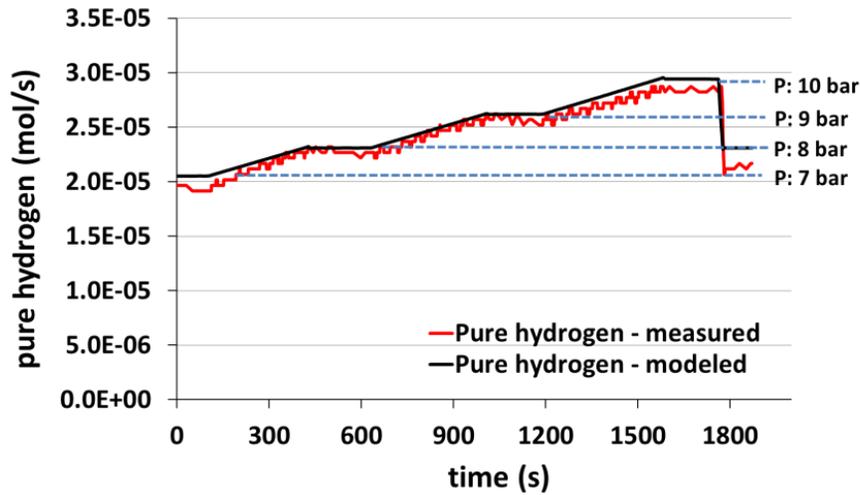
529 As mentioned before, the hydrogen partial pressure difference at the retentate and permeate
530 sides is the driving force for hydrogen permeation, which is stated by the Sieverts' law (eq. 8).

531 Therefore, consideration of the Sieverts' law as the base of simulation of hydrogen permeation

532 dynamic performance is essential. The simulated dynamic performance of the reforming system

533 in the case of pressure change dynamic tests is shown in Fig. 9.

534



535

536

537 Fig. 9. Simulation of the dynamics of the pure hydrogen production rate for pressure change

538 tests. $T=923$ K, $F_F=200$ $\mu\text{l}/\text{min}$.

539

540 The small fluctuations of the pure hydrogen measurement during the experiments are attributed
 541 to the small variations of the pressure inside the reactor, as the pressure valve acts on the outlet
 542 retentate stream. This fluctuation is ca. 10^{-6} mol/s of pure hydrogen. As expected, at constant
 543 temperature and fuel flow rate, pure hydrogen production rate follows the variation of reactor
 544 pressure by time. The CMR time constant in the case of pressure change tests was 200
 545 seconds. The simulation of the pressure change steps fitted the experimental observation very
 546 well, proving the successful modeling and application of the Sieverts' law.

547

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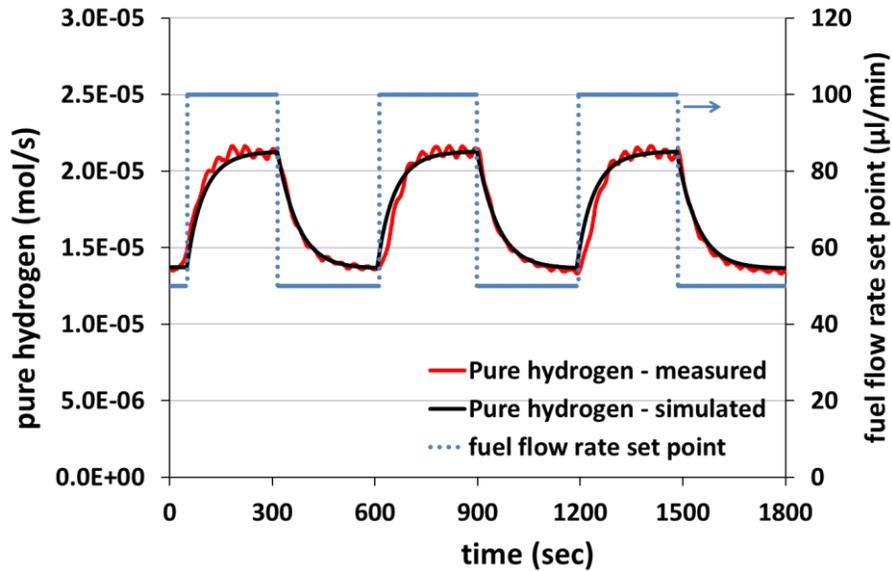
549 **3.2.2. Fuel flow rate change simulation**

550

551 In comparison with the pressure change models, it is more essential to develop a model on the
 552 fuel flow rate change. The importance of fuel flow rate change model lies in the fact that acting
 553 on fuel flow rate is much faster than the operating pressure. The CMR time constant (eq. 14) in

554 the fuel flow rate change tests was 55 seconds, which is nearly four times shorter than the
555 pressure change tests (200 seconds). The simulation result of the pure hydrogen production
556 rate for fuel flow rate change tests is presented in Fig. 10.

557



558

559

560 Fig. 10 . Simulation of the dynamics of the pure hydrogen production rate for fuel flow rate
561 change tests. T=923 K, P=10 bar.

562

563 The Sieverts' law simulation results in the case of the fuel flow rate change (Fig. 10) fitted very
564 well to the experimental observation. This is an outstanding result since the accuracy of the
565 prediction of the pure hydrogen dynamics together with fast response of the reforming system to
566 the fuel flow rate adjustments can build up a robust essential step toward further control studies.

567

568 The isothermal dynamic simulation of pure hydrogen production via ESR in the CMR
569 considering the fuel flow rate and pressure changes can play an essential role for a general
570 model of the dynamic performance of the system when connecting to a fuel cell for its online
571 feeding and control. The simulations presented in this work were able to predict the dynamics of

572 hydrogen permeation rate with high accuracy; however, the significance of the simulation based
573 on fuel flow rate modifications lies in the faster response of the reformer to reach the steady
574 state regarding the new set point.

575

576 **4. Conclusion**

577

578 Ethanol steam reforming (ESR) over Pd-Rh/CeO₂ catalyst was performed in a CMR at 923 K, 6-
579 10 bar, and fuel flow rates of 50 to 200 µl/min using a mixture of ethanol and distilled water. A
580 static model was proposed based on the Arrhenius law to calculate the molar production rate of
581 ESR products inside the reactor (catalytic zone). The pure hydrogen production rate at steady
582 state conditions was simulated by means of Sieverts' law model. Finally, the dynamics of the
583 pure hydrogen production rate (permeation zone) in the case of the operating fuel flow rate or
584 pressure set point adjustment was simulated under the ideal gas law assumptions at isothermal
585 conditions. The effective critical factors such as hydrogen partial pressure in the CMR and the
586 influence of the co-existence of the ESR products on the permeation behavior of the membrane
587 were taken into account by the Sieverts' law model. Both pressure and fuel flow rate change
588 steps simulations fitted the experimental values very well. However, the simulation of the
589 dynamics of the fuel flow rate change was more essential, as the system responds much faster
590 to such an adjustment. The future work will be devoted to the simulation of the startup and shut
591 down dynamics, the effect of the composition of the inlet fuel, and the temperature profile aiming
592 to provide a controlling system.

593

594 **Acknowledgements**

595 Funding from MINECO project ENE2015-63969-R is acknowledged. A.H. gratefully
596 acknowledges Erasmus Mundus Joint Doctoral Program SELECT+. J.L. is Serra Hünter Fellow
597 and is grateful to ICREA Academia program.

598

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