Experimental control of a methanol catalytic membrane reformer (O-13H-V)

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1. Introduction

On-site and on-demand hydrogen production from liquids has been gaining more attention in recent years. For that purpose, it is recommended to use low temperature processes and compact reformers which make methanol a good candidate because methanol does not involve the cleavage of C-C bonds and the reforming can be done at low temperature [1]. Catalytic membrane reactors are a good choice for a compact reforming unit since they have the production, separation and purification phase in the same reactor volume [2].

There are 3 main reactions in the methanol steam reforming process:

$$CH_3OH_{(g)} + H_2O_{(g)} \leftrightharpoons CO_{2(g)} + 3H_{2(g)} \quad \Delta H^{\circ}_{298} = +49.4 \text{ kJ mol}^{-1} \quad (1)$$

$$CH_3OH_{(g)} \leftrightharpoons CO_{(g)} + 2H_{2(g)} \quad \Delta H^{\circ}_{298} = +92 \text{ kJ mol}^{-1} \quad (2)$$

$$CO_{(g)} + H_2O_{(g)} \leftrightharpoons CO_{2(g)} + H_{2(g)} \quad \Delta H^{\circ}_{298} = -41.1 \text{ kJ mol}^{-1} \quad (3)$$

Eq. 1 is the direct methanol steam reforming reaction (MSR), Eq. 2 corresponds to the methanol decomposition reaction and Eq. 3 is the water–gas shift reaction (WGS).

These reforming units can be portable and produce hydrogen on-site with only a heat source and a liquid methanol reservoir. However, a control system is necessary to maintain a stable production of high purity hydrogen [3,4,5].

This work focuses on the design and implementation of a Single Input Single Output (SISO) controller that controls the production of pure hydrogen (permeate flow) from a catalytic membrane reactor (CMR) for the methanol steam reforming process. The reformer reactor of this work uses a supported catalyst based on PdZn alloy particles anchored over $ZnAl_2O_4$ spinel supported on Al_2O_3 pellets (SASOL® 2.5/210, 2.5 mm diameter), which was developed and tested in a previous work [6]. A PI controller with scheduled gain is tunned with the use of transfer functions - based model and then implemented in the experimental CMR setup. The system's PI controller actuates on the high-pressure liquid pump that injects the methanol and water into the CMR.

2. Controller design process

2.1 Experimental set-up

A $PdZn/ZnAl_2O_4/Al_2O_3$ catalyst was used for the methanol steam reforming in a pellet form. A commercial Inconel membrane reactor from REB Research & Consulting® was used as CMR. The reactor has 4 membranes of 3 in. tall, 1/8 in. diameter dead-end tubes coated with a 30 µm thick Pd–Ag active layer.

Several dynamic tests were carried out to obtain information about the behaviour of the system. The dynamic behaviour tests of the system have been carried out using the same experimental setup as in the previous work (Fig. 1) [6]. A liquid mixture of methanol and water with a steam to carbon ratio of 1 (S/C=1) was used in all the experiments. A set of experiments were performed and registered under dynamic conditions at different operating pressures (6, 8, 10 and 12 bar). These tests have been carried out applying step-type variations in the inlet liquid flow (mixture of methanol and water). Three step variations have been made at the different pressures, so that the behavior of the reactor at low, medium and high flow rates was obtained. The temperature was always kept at a constant value of 450 °C.

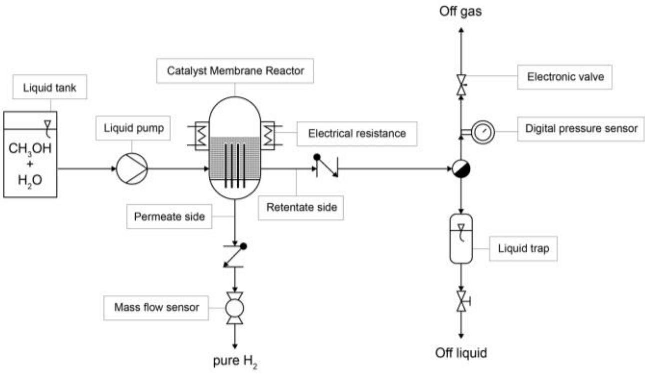

Fig. 1. Scheme of the experimental set-up.

2.2 Controller design and system indentification

The controller design strategy shown in Fig. 2 has been followed to achieve the objectives planned for this work. In which it consisted of obtaining data on the dynamic behavior of the system to then carry out an identification of the system through transfer functions. Thanks to the transfer functions, a mathematical model was made in which a PI controller was incorporated. Finally, the PI controller was tested in the experimental plant.

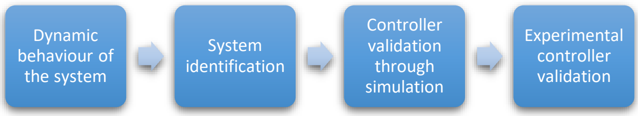

Fig. 2. Scheme of the controller design strategy.

There are three possible actuators that can modify the permeated hydrogen flux: the liquid inlet pump (which affects the inlet mass flow), the digital pressure regulator (which affects the reactor pressure) and the electrical resistance that provides heat to the reactor (which affects the reactor temperature). However, for a fast response of the catalytic membrane fuel reformer, the temperature is not a proper actuator since the changes are too slow. On the other hand, pressure changes are faster, but membrane efficiency changes with the pressure, so a high pressure is necessary to achieve a high separation efficiency of the membrane. In contrast, modifying the liquid inlet flow rate is fast, affects only the total hydrogen production and does not have a significant impact on the separation efficiency of the membrane. Consequently, we used the liquid pump as the selected actuator of the PI controller.

Catalytic membrane fuel reformers are non-linear systems since the metallic membrane of the reactor does not manage to separate more hydrogen after a certain inlet liquid flow. This occurs because mass transfer limit problems appear. This phenomenon is also called membrane saturation. To solve this non-linear system into a linear one, three different transfer functions have been obtained for three variations in the inlet flow while maintaining a fixed pressure and temperature. These three transfer functions have been divided into: low flow zone (50–65 μL_{liq}/min), medium flow zone (100–130 μL_{liq}/min) and high flow zone (150–195 μL_{liq}/min).

Once the transfer functions were obtained and verified, a mathematical model of a PI controller was developed using SIMULINK®. With the simulation model, the PI controller parameters were obtained and then, simulations were made to test the robustness of the PI controller.

Finally, experimental PI tests were carried out using LabVIEW® to control the high-pressure liquid pump. Thus, is was verified the operation of the real PI in contrast to the modeling in SIMULINK®.

3. Experimental results and discussion

3.1 Dynamic behaviour of the system

The behaviour of the system against step changes in the inlet liquid flow are shown in Fig. 3 for inlet flow step of 50-65 μL_{liq}/min at 12 bar.

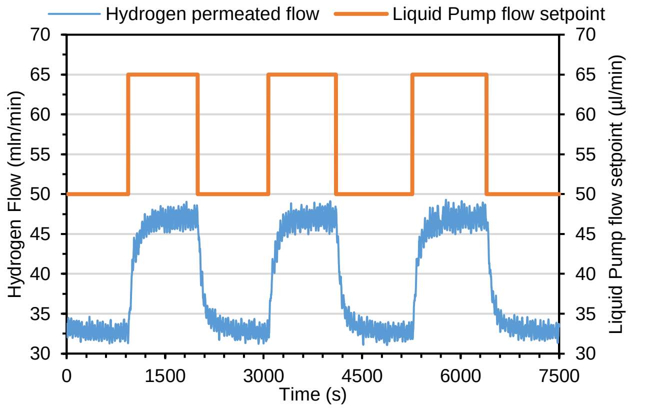

Fig. 3. Behaviour of the system against step changes in the inlet liquid flow. Inlet flow step of 50-65 μL_{liq}/min at 12 bar.

For all cases (not shown), oscillations were observed in the output of permeated hydrogen. This is due to the type of liquid pump used. It uses a piston mechanism which makes the flow rate non-uniform. As a preliminary view, a behaviour of a first-order system was observed. However, it was observed that working at higher pressures the dynamics of the system was faster.

3.2 System identification

The experimental results of dynamic behaviour of the system in the previous section were used to obtain a set of transfer functions using the commercial software MATLAB®, which were implemented to develop a computational piecewise model using the commercial software SIMULINK®. All the resulting transfer functions are first order with a time delay (Eq. 4).

$$G(s)=\frac{k_p}{\tau_p \cdot s+1} \cdot e^{-T_s \cdot s} \tag{4}$$

3.3 Mathematical model of the controlled system

Once the transfer functions were obtained and verified, a mathematical model of the controller was developed using SIMULINK®. For each calculated transfer function, a different PI controller was tuned (Eq. 5) using the Ziegle Nichols second method criteria. Then, a PI control with gain scheduled was implemented for the three operating flow ranges (low, medium and high). The derivative part of the PID was neglected due the nature of the system detected.

$$\text{PI control}=K_c\left(1+\tau_i \frac{1}{s}\right) \tag{5}$$

In Table 1 and Table 2 the optimal Kc and τi parameters for the PI modelled controller are shown for the different operation pressures and inlet flows. Due to the similarity of the results for the tested pressures, it was decided to use an average value of the K_c and τ_i parameters for all the pressure values.

Table 1. Optimal K_c values of the PI controller modelled at different pressures and inlet flows.

Pressure (bar)	K_c Low flow (50 – 60 µL$_{liq}$/min)	K_c Medium flow (100 – 130 µL-$_{liq}$/min$_l$)	K_c High flow (150 – 195 µL$_{liq}$/min)
6	3.87	3.19	2.82
8	2.54	3.96	2.64
10	3.52	3.56	2.75
12	3.73	2.17	2.76
Average values	3.42	3.22	2.74

Table 2. Optimal τ_i values of the PI controller modelled at different pressures and inlet flows.

Pressure (bar)	τ_i Low flow (50 – 60 µL$_{liq}$/min)	τ_i Medium flow (100 – 130 µL$_{liq}$/min)	τ_i High flow (150 – 195 µL$_{liq}$/min)
6	0.015	0.048	0.085
8	0.015	0.037	0.055
10	0.012	0.027	0.047
12	0.013	0.032	0.036
Average values	0.014	0.034	0.051

3.4 Experimental PI controller

The commercial software LabVIEW® was used to implement the gain scheduled PI in the real system. In the tests carried out, the K_c and τ_i parameters of the controller had to be slightly modified from the ones simulated to improve the response of the system.

In Fig. 4 is shown the test realized in the experimental system with the PI controller with gain scheduled (only is shown at 12 bar). The set-point was on the permeated hydrogen flowrate. The controller actuated on the liquid pump which modified the inlet liquid flow to ensure following the set-point.

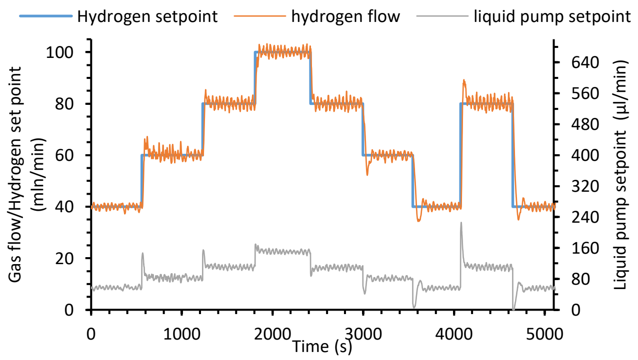

Fig. 4. Experimental results with the PI controller in the liquid pump for permeated hydrogen at 12 bar.

The controller managed to always maintain the set-point. There was a small ripple of about ±5 H_2 mL/min, but an average of the data gives the value imposed by the set-point. When changing the set-point from 40 H_2 mL/min to 80 H_2 mL/min, a small overshoot is observed, which is normal due to the large change in operation range, being quickly attenuated in the subsequent seconds.

4. Conclusions

It was possible to obtain the dynamic behaviour of the system from experimental data and identify the system from step-type changes and then modelling it through transfer functions. The model allowed the development of a PI controller with gain scheduling which was tested under real conditions with proper results. The obtained controller manages to maintain the set-point for any operating range with an acceptable response time and remarkable robustness.

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