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Experimental Evaluation of a Pt-based Heat Exchanger Methanol Reformer for a HTPEM Fuel Cell Stack

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Abstract

Fuel cell systems running on pure hydrogen can efficiently produce electricity and heat for various applications, stationary and mobile. Storage volume can be problematic for stationary fuel cell systems with high run-time demands, but it is especially a challenge when dealing with mobile and automotive applications. Using a liquid hydrocarbon as e.g. methanol as the hydrogen carrier and reforming it to a hydrogen rich gas can solve some of these storage issues. The work presented here examines the use of a heat exchanger methanol reformer for use with a HTPEM fuel cell stack. Initial experimental results and conclusions are presented for this reformer.

1 Introduction

Fuel cell systems are very efficient alternatives in power systems using electricity and heat. One of the great challenges of using the fuel cell technology in mobile applications is the storage of hydrogen for these systems. Hydrogen is the preferred fuel for fuel cells but is often inconvenient because of the very low density even at high pressures (0.014 kg/L @ 300 bar) or cryogenically (0.043 kg/L) [1]. Much higher volumetric energy densities can be achieved using liquid hydrocarbons as e.g. methanol [2]. A hydrocarbon as methanol can be derived from e.g. biomass ([3, 4, 5, 6]) and be used directly in a PEM fuel cell (DMFC), but with a poor performance and often complicated water management system. Another way of using methanol in a fuel cell is by steam reforming it over a catalyst to hydrogen.

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \qquad (49.4\frac{kJ}{mol}) \qquad (1)$$
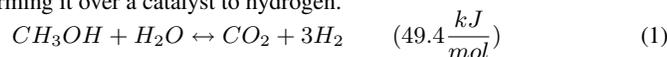
Included in this reaction is the decomposition of methanol, which produces CO:

$$CH_3OH \leftrightarrow CO + 2H_2 \qquad (90.5\frac{kJ}{mol}) \qquad (2)$$
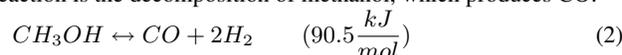
And the water-gas-shift reaction, where CO can be removed by adding extra water:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (-41.1\frac{kJ}{mol}) \qquad (3)$$
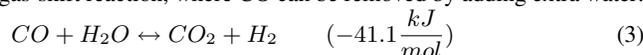
The resulting hydrogen gas from such processes, can under the right temperature and purity be used in a fuel cell, in most cases with an improved system efficiency compared to DMFC. At the same time, the volumetric challenges in storing pressurized hydrogen are avoided. Nafion based low temperature PEM fuel cells are typically intolerant to CO in the anode gas, and require very pure hydrogen with only up to 100 ppm CO or even less [7]. Another type of PEM fuel cells, the PBI based high temperature PEM (HTPEM) operates at high temperatures (160-180^oC), and has a much higher tolerance towards CO (up to 1-2%) [8].

This work examines the possibilities and initial tests when using a catalyst coated plate heat exchanger for the reforming process of methanol. Figure 1 (Right) shows a picture of the methanol reformer which has been designed to produce hydrogen for a 1 kWe HTPEM fuel cell stack.
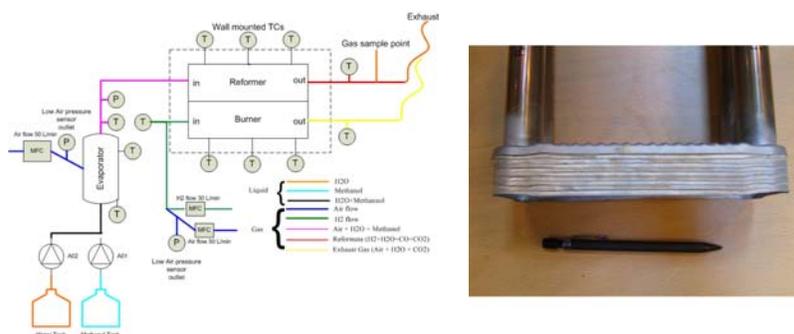
Figure 1: Left: Schematic of the reformer test system. Right: Picture showing the uninsulated catalyst coated heat exchanger.

Similar to a traditional plate heat exchanger, a heat exchanger reformer (HER), will have the advantages of, good heat transfer, compact design and low thermal mass for quick start up. Because of the endothermic nature of the steam reforming process and thus need for external heat supply, the heat exchanger is divided into a reformer side, and a burner side. The reformer consists of 10 plates and as a result, 5 burner plate volumes and 4 reactor plate volumes. The volume of the reformer is 0.4 L and the weight around 1 kg (excluding inlet and outlet pipes). The input for the reforming side is a steam based mixture of water and methanol, with the possibility of adding air for running the reformer autothermally to enable faster start-up using the heat released in the combustion reaction:

$$CH_3OH + 1.5O_2 \leftrightarrow CO_2 + 2H_2O(-675.4\frac{kJ}{mol}) \tag{4}$$
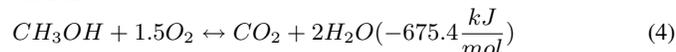
The burner side input is air, and a combustible gas which for these initial tests will be hydrogen. Figure 1 (Left) shows a schematic of the reformer test setup, with an included methanol and water evaporator, where electrical heaters supply heat for the evaporation of water and methanol. In the final system a heat exchanger will supply the heat from the burner exhaust. This setup works as a test setup to examine the usability of such a system together with a HTPEM fuel cell stack. These preliminary tests will determine the general operation of the reformer revealing the thermal dynamics, gas compositions at different temperatures and the effects of changing the steam-to-carbon ratio (SC). The reformer is expected to be able to supply a 1 kWe HTPEM fuel cell stack, and the performance is evaluated and conclusions are drawn on the suitability of using this reformer with such a stack.

To monitor the different system temperatures, thermocouples have been mounted in the in- and outlet streams of the heat exchanger and also directly on the heat exchanger to identify possible significant temperature gradients. The fuel and water pumps used are Grundfos DME 12 and the air and hydrogen supplies are controlled by Bürkert mass flow controllers. The datalogging and control of the system is carried out using a National Instruments CompactRIO 9012. To analyze the reformer outlet gas composition a Pfeiffer Omnistar mass spectrometer is used, calibrated for measuring the gas content of H_2, CO_2, CO and CH_4.

2 Chemical equilibrium

To assist in the identification of the preferred operating conditions and the effects of changing the SC and reaction temperature, a model of the chemical equilibrium can be defined by minimizing the Gibbs free energy. Using an efficient method of computing the reaction equilibrium by using Lagrange multipliers [10] a set of equations relating N species is set up. The Gibbs energy G will be minimal in equilibrium at constant pressure ($p=p^0$=1.013 bar) and temperature:

$$G = \sum_{i=1}^{N} n_i \left[G_{mi}^0(T) + RT \left(ln \left(\frac{p}{p^0} \right) + lnX_i \right) \right] \qquad (5)$$

Where i is the i'th specie. This equilibrium will be with respect to the molar balance of the A'th atom.

$$\hat{A}_j = \sum_{i=1}^{N} b_{ji} n_i - a_j = 0; j = 1...A \qquad (6)$$

The following two equations can then be solved and the solution (with correct initial guesses) can yield the molar fractions of the chemical equilibrium.

$$\frac{\partial L}{\partial n_i} = G_{mi}(T) + RT \left(ln \left(\frac{p}{p^0} \right) + lnX_i \right) + \sum_{j=1}^{A} \lambda_j b_{ji} \qquad (7)$$

$$\frac{\partial L}{\partial \lambda_j} = \hat{A}_j \qquad (8)$$

Fig. 2 shows the molar fractions as a function of temperature at two different SC ratios.
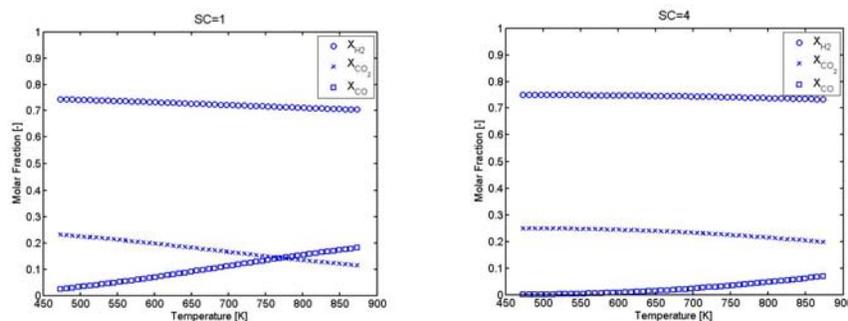
Figure 2: Left: Reformate gas composition at SC=1. Right: Reformate gas composition at SC=4.

The chemical equilibrium is used as a guideline for choosing the proper operating conditions. Furthermore the composition of the catalyst sets the range of reforming temperatures, because the PGM-catalyst for the WGS-catalyst only becomes significantly active at temperatures above 350^oC (623K). Reforming methanol can also be done at lower temperatures (around 200^oC) [9], but often involve copper-based catalysts, which are unsuitable for autothermal operation, because of the increased oxidation of copper at elevated temperatures. Using the precious metal catalyst coating from

Catator avoids these problems, at the cost of higher reforming temperatures and associated higher CO concentrations. The construction materials used limits the maximum operating temperature to 500-600 ^{o}C.

3 Experimental work

The experimental work has been divided into the following parts:

- Start-up procedure
- Operation

The following sections will present experimental data involving these two parts in the typical operation of the HER reformer.

3.1 Start-up procedure

To operate the reformer, an initial start-up of the evaporator and burner is carried out. A catalytic combustion of hydrogen is started in the burner by using 2 $\frac{L}{min}$ H_2 and 30 $\frac{L}{min}$ Air. The effect of this combustion is quickly seen on the temperature measurements on the HER as seen in figure 3 (Right).
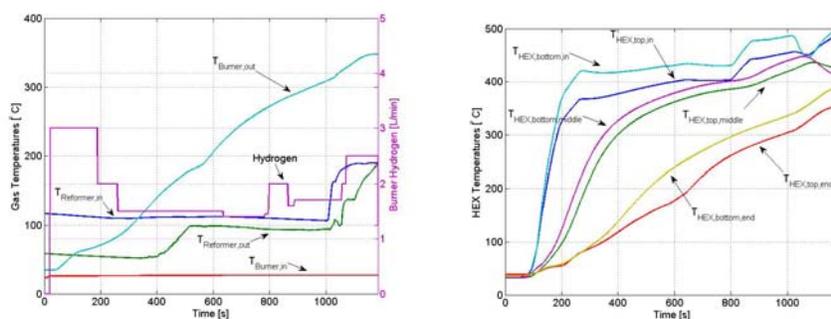
Figure 3: Left: In- and output gas temperatures during start-up. Right: Local HER temperatures.

The catalytic combustion process takes place from room temperature and the temperature gradient increases rapidly when the burner reaches 70-90 ^{o}C. The burner outlet gas temperature also experiences an increase in temperature as seen on figure 3 (Left). Because of the low mass of the reformer, the start-up time is around 1000s at the chosen hydrogen and air inlet flows. This time is expected to be reduced further by balancing the air and hydrogen flows properly, e.g. by lowering the burner stoichiometry. The average temperature of the initial steam reforming is 300-400 ^{o}C with this unit. During the HER heating, the evaporator which evaporates the water and methanol mixtures is heated electrically to around 250°C and when the reformer temperatures are at the desired values, the fuel mixture is introduced to the evaporator to avoid liquid water forming in the reformer. The steam/methanol mixture is evaporated in the bottom of the evaporator and super heated on its way through the rest of the evaporator, before it enters the reformer. Initiation of the endothermic steam reforming process reduces the temperature of the reformer if the burner power input is not increased, so the hydrogen

flow is slightly adjusted to maintain the temperature of the reformer. With a steady control of the reformer temperature and the evaporator temperature, the output reformate gas can be analyzed, which is presented later.

3.2 Operation

In the general operation of the reformer it is important to balance the heat generation and consumption, this is primarily done by changing the hydrogen/air flow into the burner. The effect on the reformer temperature, when changing the hydrogen flow into the burner was also seen, e.g. in figure 3 (Right) at around 800s, when the hydrogen flow is increased from 1.7 $\frac{L}{min}$ to 2.5 $\frac{L}{min}$ for at few seconds. The temperature rise is seen immediately and should be controlled carefully to avoid the reformer reaching critical temperatures. Figure 4 (Left) shows the somewhat constant reformer temperatures with at slight increase in temperature from 1500-4200s, it is seen that there is a significant temperature gradient through the reformer, of about 150 ^{o}C.
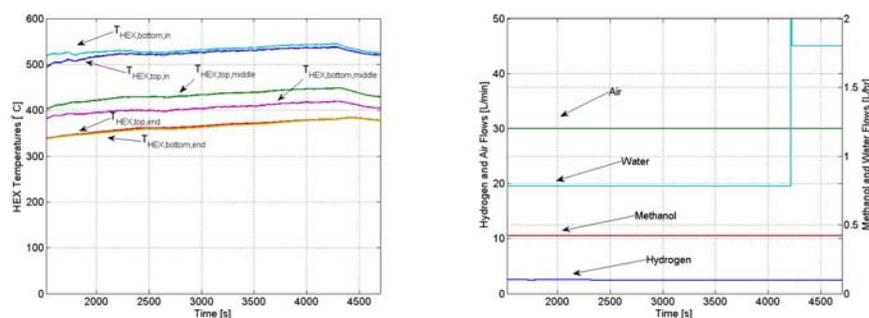
Figure 4: Left: Local reformer temperatures. Right: Methanol, water, hydrogen and air flows into the system.

The input flows in this operation example is shown in figure 4 (Right). The methanol and water flows are run constantly at 0.42 $\frac{L}{hr}$ and 0.78 $\frac{L}{hr}$ respectively. This corresponds to a SC of around 4. This is expected to yield a high CO concentration according to the chemical equilibrium. The airflow is kept constant at 30 $\frac{L}{min}$ and the hydrogen is adjusted manually to maintain a constant temperature. In the test carried out, a simple PI-controller was tested for controlling the evaporator temperature. Problems with large overshoots and oscillations are experienced, as shown in figure 5 (Left) of in- and outlet gas temperatures. From 2500-3000s the evaporator setpoint temperature is set to 300°C and changed at 3000s to 350°C. The PI-controller used showed oscillations in the controlled temperature with amplitudes of up to 20 ^{o}C. At higher amplitudes, the oscillations will also cause oscillations in the gas composition, but as seen in the reformer outlet temperature measurement, no oscillations are seen here, only a steadily increasing outlet temperature. In the last part of the measurement, the water flow is increased to a very large SC, to further check the response of the evaporator control.

The reformer will be generating a hydrogen rich gas as soon as the methanol/water mixtures is introduced to the reformer. This gas could be used directly in a fuel cell stack depending on the gas composition which is analyzed throughout the duration of this initial test. In this initial test setup the mass spectrometer for measuring the gas concentration has access to the outlet reformate gas through a large condenser to avoid introducing liquid water in the mass spectrometer. The gas analysis made during this initial testing is shown in figure 5 (Right), and is based on the dry gas composition.
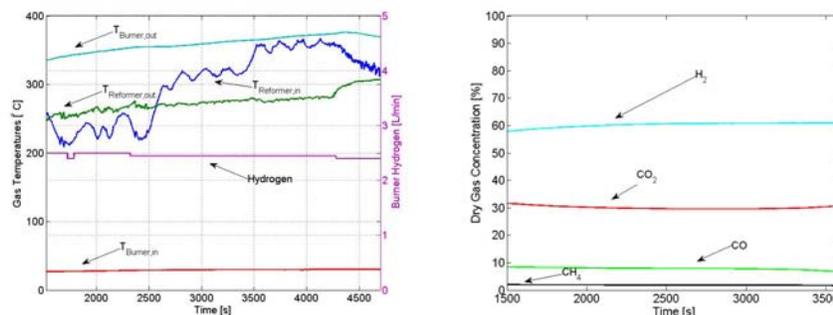
Figure 5: Left: In- and output gas temperatures during operation. Right: Graph of the species concentration out of the reformer.

The gas concentration is quite steady during the measurement but with a slightly falling CO concentration and a slightly rising CO_2 concentration, this suggests an increasing activity of the water-gas-shift reaction, which was also expected for this particular catalyst as explained earlier. The changes in the gas composition is due to the temperatures rise in the overall reformer temperature. The final measurement showed a reformate gas (dry) with 60.9% H_2, 30.6% CO_2, 6.8% CO and 1.6% CH_4. The gasses included and calibrated for in this analysis are H_2, CO_2, CO and CH_4. The presence of other gasses and vapors are considered negligible. The results of the chemical equilibrium will, under the same operating conditions as the last measurement with the average reformer temperature of 438 ^oC, show values of 74.3%H_2, 23.1%CO_2 and 2.6%CO. The measured values of the CH_4 can be considered as H_2 and CO_2 by the steam reforming reaction of CH_4, to enable a comparison of the measured results with the chemical equilibrium:

$$1.6CH_4 + 3.2H_2O \leftrightarrow 1.6CO_2 + 6.4H_2 \tag{9}$$

This explains some of the differences in the results of the measurement and the chemical equilibrium. Adding the H_2 and CO_2 generated from the reforming of methane yields values of 63.7%H_2, 29.9%CO_2 and 6.4%CO. When inputting the average reformer temperatures from the measurement into the model of the chemical equilibrium the results appearing is as shown in figure 6.
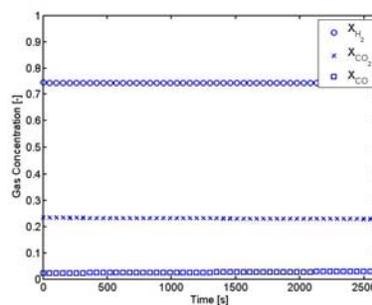
Figure 6: Species concentration of chemical equilibrium using measurements of temperature and SC as model input.

Comparing this to the results from the chemical equilibrium shows a difference which relates to the composition of the catalyst. The water gas shift reaction with this particular catalyst is very temperature dependent as explained earlier, and a more advanced model including the catalyst kinetics is needed for better results. The exact reforming temperatures inside the reformer could also be significantly different from the measurements in the simulation. The CO concentration being lower in the simulation than in the measurement is due to low activity of the catalyst. But even if completely removing the CO by a water gas shift process from the measured values, the H_2 and CO_2 concentrations should results in 75% H_2 and 25% CO which doesn't occur. This suggest some unresolved issues with respect to the measurement of the gas composition, which could be due to an extra specie in the reformate gas. Improvements could also be made by using other calibration gasses.

The formation of CH_4 and CO_2 will only act as diluents in the fuel cell. From a system perspective the methane component is not important since the anode waste gas will be used as fuel for the reformer burner side after exiting the fuel cell stack. To enable the use of the reformate gas in a high temperature PEM fuel cell, the CO concentration is to be lowered to a value around 1-2%. The reformer temperatures of this analysis are quite low, and a lower CO concentration is expected, at higher temperatures, which is also seen in the experiment, where the CO concentration is decreasing with the increasing temperatures. The CO concentration is also expected to be reduced by increasing the steam to carbon ratio, which fuels the water-gas-shift further. A few experiments where carried out with autothermal operation, but due to overlapping primary peaks in the mass spectres of N_2 in the atmospheric air and CO, these measurements did not give satisfactory results.

4 Conclusions

The results of the initial experiments with the methanol reformer yield input for the further analysis for designing and controlling a HTPEM fuel cell system running on reformed methanol. The experimental outputs of such a system setup can be used to verify developed models of the system, and assist in the overall system integration, with development of possible control strategies and the final implementation of the system with a HTPEM fuel cell stack.

Future work on the present reformer will include, fast start-up strategies using a richer hydrogen/air mixture and also increasing the reformer temperature further by adding air to the reformate side of the HER. The design of a robust closed loop control of the burner is also desired to handle sudden inlet changes to the reformer. To enable a more detailed characterization of the reformate gas, other methods of measuring the gas composition should also be examined. An implementation of a small water-gas-shift should be carried out to lower the CO content of the reformate gas for use in a fuel cell stack. More detailed modelling of the evaporator should be carried out to assist in designing a more stable controller. Finally a mobile field testable system should be constructed enabling the system to be tested under real conditions.

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