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Water-balance Assessment in a Reformer/Fuel-cell System

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Abstract. In PEM fuel cells pure hydrogen is used as a fuel. Due to its low density, the density of its stored energy is low, too. One of the possible solutions to the problem is production of hydrogen from the energy-reach material, e.g. methanol. Conversion of methanol to hydrogen is made with reformer in a steam reforming process in which besides methanol there is also water needed. On the other hand, water is one of the products in the reaction between hydrogen and oxygen in fuel cells. The question we wanted to answer was what is the total water balance in a system consisting of a methanol reformer and a fuel-cell-based generator set and should water be supplied or removed from the system. The paper presents a model capable of assessing the water balance using some simple assumptions and commercial data from suppliers of fuel-cell systems and methanol reformers. The model shows that in normal states and by using a commercial reformer and a fuel-cell system, there is always a surplus of water present. With an example of a system consisting of the Genesis 20 LE Methanol Reformer and Nexa™ Fuel-cell Power Module it is shown how the parameters for the water-balance model can be assessed.

Keywords: Fuel cell, Fuel reformer, Methanol, Water balance

1 INTRODUCTION

PEM fuel cells use hydrogen as a fuel. Being a very light element, its energy density is small despite its high burning temperature. This means, that hydrogen storage requires a lot of space. One possible solution to the problem is a simultaneous production of hydrogen from higher-density materials, such as methanol.

Transformation from methanol to hydrogen takes place in a fuel reformer on the basis of steam reforming [1, 2]. The following reaction takes place:

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 . \tag{1}$$

The reaction inside the PEM fuel cells is as follows:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O . \tag{2}$$

We can see that inside the fuel cells water is produced, while in a fuel reformer it is used.

The aim of this work is to analyze the water balance in a reformer/fuel-cell system, or to find out if the water has to be supplied to the system or removed from it.

2 WATER BALANCE ASSESSMENT

2.1 Simple assessment

In order to obtain an insight into the topic, we can first use a simplified reformer/fuel-cell system.

As seen from the above equations, to transform one methanol molecule, we need one water molecule and the reaction yields tree hydrogen molecules. Inside the fuel cells, one water molecule is produced for each hydrogen molecule.

One can see that in this simplified model, water has to be constantly removed from the system, as more water molecules are produced in fuel cells than used in the reformer.

2.2 Detailed assessment

The actual conditions are not as simple. The CO_2 output of the reformer also contains some water and water is also present in air supplied to the fuel cells (it is not pure oxygen that is used but the air is taken from the atmosphere). Water produced in the fuel cells is partially in the form of liquid and partially in the form of steam (from which water can still be extracted). Not all of the hydrogen is used in the fuel cells; unused hydrogen is removed through the anode exhaust. In this assessment, water losses through the exhaust on the anode side of the fuel cells are neglected (some water

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may diffuse through the PEM membrane and exit the system together with unused hydrogen).

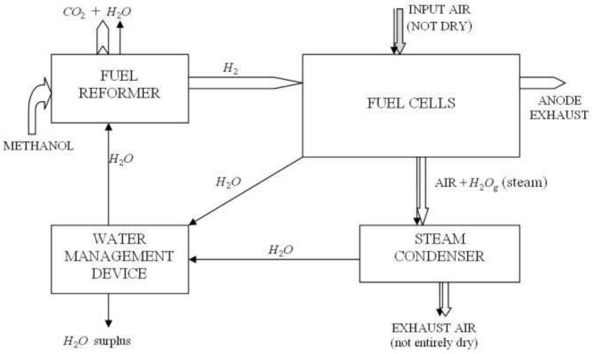

Figure 1: Schematic diagram of the system and its mass flows

For the inputs and outputs of the fuel-cell system (Fig. 1) and water flow from the fuel cells to the reformer the following equations apply:

$$\begin{aligned} n_{H_2}(used) + n_{H_2O}(air1) = n_{H_2O}(steam) + \\ + n_{H_2O}(liquid) \end{aligned}, \tag{3}$$

$$\begin{aligned} n_{H_2O}(excess) = n_{H_2O}(steam) - n_{H_2O}(exhaust) + \\ + n_{H_2O}(liquid) - n_{H_2O}(reformer) \end{aligned}, \tag{4}$$

where $n_{H_2}(used)$ is the amount of hydrogen used in reactions inside the fuel cells. According to (2), it equals the amount of H_2O in the fuel cells; $n_{H_2O}(air1)$ is the amount of H_2O in the air entering the fuel cells; $n_{H_2O}(steam)$ is the amount of H_2O in the air exiting the fuel cells; $n_{H_2O}(liquid)$ is the amount of liquid H_2O exiting the fuel cells; $n_{H_2O}(exhaust)$ is the amount of water in the exhaust (output of the dehumidifier); $n_{H_2O}(excess)$ is the amount of newly formed excess water; and $n_{H_2O}(reformer)$ is the amount of water, supplied to the reformer.

Inserting equation (3) in (4) gives:

$$\begin{aligned} n_{H_2O}(excess) = n_{H_2}(used) + n_{H_2O}(air1) - \\ - n_{H_2O}(exhaust) - n_{H_2O}(reformer) \end{aligned} \tag{5}$$

Define A as:

$$n_{H_2}(used) = A \cdot n_{H_2}(all), \tag{6}$$

where $n_{H_2}(all)$ is the amount of H_2 supplied to the fuel cells. Thus A is the ratio between H_2 used in the fuel cells and H_2 supplied to the fuel cells.

$$n_{H_2O}(air1) = \frac{m_{dryair1}}{M_{H_2O}} \cdot Rv \frac{m_{H_2O}}{m_{dryair}}(T_{environment}), \tag{7}$$

$$m_{air1} = m_{dryair1} + m_{dryair1} \cdot Rv \frac{m_{H_2O}}{m_{dryair}}(T_{environment}), \tag{8}$$

where Rv represents humidity in the environmental air (air1), $\frac{m_{H_2O}}{m_{dryair}}(T)$ describes the maximum ratio between the mass of water in air and the mass of dry air at a given temperature (i. e. when $Rv = 1$). As usually, m denotes the mass and M the molecular mass. From equations (7) and (8) it follows:

$$n_{H_2O}(air1) = \frac{m_{air1}}{M_{H_2O}} \cdot \left(1 + \left[Rv \frac{m_{H_2O}}{m_{dryair}}(T_{environment})\right]^{-1}\right)^{-1}, \tag{9}$$

and symmetrically

$$n_{H_2O}(exhaust) = \frac{m_{exhaust}}{M_{H_2O}} \cdot \left(1 + \left[Rv_{exhaust} \frac{m_{H_2O}}{m_{dryair}}(T_{exhaust})\right]^{-1}\right)^{-1} \tag{10}$$

We wish to establish the relation between $n_{H_2O}(reformer)$ and $n_{H_2}(all)$ relative to $n_{CH_3OH}(all)$ (the amount of methanol supplied to the reformer).

$$n_{H_2}(all) = 3 \cdot n_{CH_3OH}(used) \tag{11}$$

$$n_{CH_3OH}(used) = C \cdot n_{CH_3OH}(all) \tag{12}$$

$$\begin{aligned} B \cdot n_{H_2O}(reformer) = n_{H_2O}(reactionreformer) = \\ = n_{CH_3OH}(used) \end{aligned} \tag{13}$$

$$n_{H_2O}(reformer) = \frac{C}{B} n_{CH_3OH}(all) \tag{14}$$

Equations (12) and (13) define constants B and C where $n_{CH_3OH}(used)$ is the amount of methanol and $n_{H_2O}(reactionreformer)$ is the amount of water used in the reaction (1).

From the above it follows:

$$\frac{n_{H_2O}(excess)}{n_{CH_3OH}(all)} = C(3A - \frac{1}{B}) + \\ + \frac{M_{CH_3OH}}{M_{H_2O}} \frac{m_{air1}}{m_{CH_3OH}} \cdot \left(1 + \left[Rv \frac{m_{H_2O}}{m_{dryair}}(T_{environment})\right]^{-1}\right)^{-1} - \\ - \frac{M_{CH_3OH}}{M_{H_2O}} \frac{m_{exhaust}}{m_{CH_3OH}} \cdot \left(1 + \left[Rv_{exhaust} \frac{m_{H_2O}}{m_{dryair}}(T_{exhaust})\right]^{-1}\right)^{-1} \tag{15}$$

Constants A, B and C can be estimated either from the data supplied by the manufacturer [3,4], either from the measurements. The same holds true for m_{air1} and $m_{exhaust}$. The values of $\frac{m_{H_2O}}{m_{dryair}}(T\ )$ can be found in the tables, Rv is measured, $Rv_{exhaust}$ can in some cases be determined from the way dehumidification of the (cathode) exhaust is performed (e. g. if the air dehumidifier cools the air to the exhaust temperature, then $Rv_{exhaust} = 1$), otherwise it is measured.

If the ratio $\frac{n_{H_2O}(excess)}{n_{CH_3OH}(all)}$ is less than 0, water has to be supplied to the system and if the ratio is greater than 0, water has to be removed from the system.

Usually, only the data of the volumetric flows are available and not the mass flow measurements. Air can be approximated by a mixture of dry air and water steam. Therefore we can write

$$V_{air1} = V_{dryair} + V_{H_2O}, \tag{16}$$

where V_{air1} is the volume of air entering the fuel cells, V_{dryair} is the partial volume of dry air and V_{H_2O} is the partial volume of the water steam. Using the equation (16) and the below equations:

$$pV = \frac{m}{M} RT, \tag{17}$$

$$m_{H_2O} = m_{dryair} Rv \frac{m_{H_2O}}{m_{dryair}} (T_{environment}), \tag{18}$$

leads to:

$$m_{air1} = \\ = \frac{V_{air1} p M_{dryair}}{RT_{environment}} \left(\frac{1 + Rv \frac{m_{H_2O}}{m_{dryair}} (T_{environment})}{1 + \frac{M_{dryair}}{M_{H_2O}} Rv \frac{m_{H_2O}}{m_{dryair}} (T_{environment})} \right) \tag{19}$$

And similarly for the exhaust:

$$m_{exhaust} = \\ = \frac{V_{exhaust} p M_{dryair2}}{RT_{exhaust}} \left(\frac{1 + Rv_{exhaust} \frac{m_{H_2O}}{m_{dryair}} (T_{exhaust})}{1 + \frac{M_{dryair2}}{M_{H_2O}} Rv_{exhaust} \frac{m_{H_2O}}{m_{dryair}} (T_{exhaust})} \right) \tag{20}$$

For $M_{dryair2}$ the approximate value of 29 kg/kmol can be used. As the fuel cells consume oxygen, the average molecular mass of dry air changes to $M_{dryair2}$. $M_{dryair2}$ can be estimated on the basis of the known composition of dry air that is approximately 75.5 % of nitrogen (molecular mass of approximately 28 kg/kmol), 23.2 % of oxygen (32 kg/kmol) and 1.3 % of argon (40 kg/kmol). From this it follows that the molecular mass will not change significantly. Assuming that all oxygen in the fuel cells is used, the molecular mass will decrease to approximately 28 kg/kmol. To allow for a more detailed calculation, we use the following equation:

$$M_{dryair2} = \frac{\sum_i M_i n_i}{\sum_i n_i} = \frac{m_{dryair2}}{n_{dryair2}} = \\ = \frac{M_{dryair} n_{dryair} - M_{O_2} n_{O_2 used}}{n_{dryair} - n_{O_2 used}} \tag{21}$$

The following equations hold:

$$n_{dryair} = \frac{m_{air1}}{M_{dryair}} \frac{1}{1 + Rv \frac{m_{H_2O}}{m_{dryair}} (T_{environment})}, \tag{22}$$

$$n_{O_2 used} = \frac{1}{2} n_{H_2}(used) = \\ = \frac{3}{2} ACn_{CH_3OH}(all) \tag{23}$$

Now we only need to determine the volumetric flow of the exhaust:

$$V_{exhaust} = V_{dryair} - V_{O_2 used} + V_{H_2O exhaust}, \tag{24}$$

where all the volumes are measured at the same temperature (exhaust temperature).

$$V_{exhaust} = \frac{RT_{exhaust}}{p} \left(\begin{array}{l} n_{dryair} - n_{O_2 used} + \\ + \left\langle n_{dryair} \frac{M_{dryair}}{M_{H_2O}} - n_{O_2 used} \frac{M_{O_2}}{M_{H_2O}} \right\rangle . \\ .Rv_{exhaust} \frac{m_{H_2O}}{m_{dryair}} \left(T_{exhaust} \right) \end{array} \right) \quad (25)$$

Inserting equations (22) and (23) yields:

$$V_{exhaust} = \frac{RT_{exhaust}}{p} \frac{m_{air1}}{M_{dryair}} \frac{1 + \frac{M_{dryair}}{M_{H_2O}} Rv_{exhaust} \frac{m_{H_2O}}{m_{dryair}} \left(T_{exhaust} \right)}{1 + Rv \frac{m_{H_2O}}{m_{dryair}} \left(T_{environment} \right)} \quad (26)$$
$$- \frac{RT_{exhaust}}{p} \frac{3}{2} ACn_{CH_3OH} (all) \left\langle 1 + \frac{M_{O_2}}{M_{H_2O}} Rv_{exhaust} \frac{m_{H_2O}}{m_{dryair}} \left(T_{exhaust} \right) \right\rangle$$

All the above equations can be inserted into the equation (15). The result is an equation describing the number of excess water molecules (in average) produced in the system for each supplied fuel molecule.

The above equations do not take into account that when there is a lack of oxygen, chemical reactions do not run optimally. The estimated minimum air flow guaranteeing the sufficient amount of oxygen for the reaction (2) is:

$$n_{O_2} = \frac{3}{2} ACn_{CH_3OH} (all) \quad (27)$$

For oxygen in air the following applies:

$$n_{O_2} = \frac{x \cdot m_{dryair1}}{M_{O_2}} = \frac{x}{M_{O_2}} \frac{m_{air1}}{1 + Rv \frac{m_{H_2O}}{m_{dryair}} \left(T_{environment} \right)}, \quad (28)$$

where x is the relative mass of oxygen in air. From (27) and equation (28) it follows that the minimum mass flow is:

$$m_{air1} = \frac{M_{O_2}}{x} \cdot \left(1 + Rv \frac{m_{H_2O}}{m_{dryair}} \left(T_{environment} \right) \right) \cdot \frac{3}{2} ACn_{CH_3OH} \quad (29)$$

Inserting it in the below equation

$$V_{air1} = \frac{RT_{environemnt} m_{air1}}{pM_{dryair}} \left(\frac{1 + \frac{M_{dryair}}{M_{H_2O}} Rv \frac{m_{H_2O}}{m_{dryair}} \left(T_{environemnt} \right)}{1 + Rv \frac{m_{H_2O}}{m_{dryair}} \left(T_{environment} \right)} \right) \quad (30)$$

yields the minimum V_{air1} i. e. the minimum volumetric flow which (at 100 % of the oxygen consumption) still guarantees the optimal performance of the fuel cells.

3 EXAMPLE

Performance of the developed model can be examined by using a real system. Due to the lack of measured data, this example relies on the data provided by the manufacturers.

A reformer of a 75 % efficiency rate is used. It runs on a mixture of 65 % of methanol and 35 % of water [3]. On the fuel-cell side there is a Nexa Power Module plant manufactured by Ballard [4]. The exact specifications probably differ from the ones used. Also, they vary depending on the environmental conditions and load. However, the aim of this example is to demonstrate that the model parameters can easily be estimated thus enabling the water balance to be computed.

As seen from the report and papers [5,6,7], at full load, the fuel cells are supplied with 0.02771 g/s of hydrogen from which fuel cells consume 0.02651 g/s. So:

$$A = \frac{0.02651}{0.02771} = 0.96 \quad (31)$$

Assuming that the reformer has a 75 % efficiency, the ratio between the burning heat of the produced hydrogen and the burning heat of methanol is 0.75 (η). This helps us estimate parameter C. If all the methanol molecules reacted according to equation (1), there would be three times more hydrogen molecules than the number of the methanol molecules.

$$\eta \cdot n_{CH_3OH} \cdot M_{CH_3OH} \cdot HHV_{CH_3OH} = n_{H_2} \cdot M_{H_2} \cdot HHV_{H_2} \quad (32)$$

where HHV stands for specific burning heat. For hydrogen, this value is 141.9 MJ/kg and for methanol 22.7 MJ/kg.

$$\frac{n_{H_2}}{n_{CH_3OH}} = \eta \frac{HHV_{CH_3OH} \cdot M_{CH_3OH}}{HHV_{H_2} \cdot M_{H_2}} = 1{,}92 \quad (33)$$

$$C \cong \frac{1{,}92}{3} \cong 0{,}64\,. \quad (34)$$

Knowing that the reformer used a mixture of 65 % of methanol (x_1) and 35 % of water (x_2) (volumetric parts), the below parameters can be estimated:

$$n_{CH_3OH} = \frac{\rho_{CH_3OH} \cdot V \cdot x_1}{M_{CH_3OH}} \quad (35)$$

$$n_{H_2O} = \frac{\rho_{H_2O} \cdot V \cdot x_2}{M_{H_2O}} \qquad (36)$$

The water density is approximately 1000 and that of methanol is 792 kilograms per cubic meter. So:

$$\frac{n_{H_2O}}{n_{CH_3OH}} = \frac{M_{CH_3OH}\rho_{H_2O} \cdot x_2}{M_{H_2O}\rho_{CH_3OH} \cdot x_1} = 1.21 = \frac{1}{B}. \qquad (37)$$

By supplying 1.21, which would be 1 if there are no losses, we can estimate that:

$$\frac{1}{B} = 1.21 \qquad (38)$$

The mass flow of methanol was estimated on the bases of the known mass flow of hydrogen supplied to the fuel cells.

$$C \cdot n_{CH_3OH} = \frac{1}{3} n_{H_2} \qquad (39)$$

$$m_{CH_3OH} = \frac{1}{3C} \cdot \frac{M_{CH_3OH}}{M_{H_2}} m_{H_2} \cong 0.23 \text{ g/s}. \qquad (40)$$

Now we wish to know what is the ratio between the air flow and the minimum air flow. Based on equations (29) and (30), the minimum air flow was calculated to be 0.81 l/s. According to the manufacturer specifications the maximum air flow to the fuel cells is 1.5 l/s (which is approximately 1.6 l/s at 25 °C). Thus, this air flow is up to two times greater than the minimally allowed air flow at a full load that still guarantees a sufficient amount of oxygen.

Using the available data, the parameters for our system (at stationary conditions) at a full load were estimated to be:

$A \cong 0.96$,

$\frac{1}{B} = 1.21$ and

$C \cong 0.64$

with the mass flow of methanol being $m_{CH_3OH} \cong 0.23$ g/s.

Fig. 2 shows the relative amount of the excess water as a function of the relative humidity of the air entering the system. The parameter is the saturation humidity (i.e. temperature) of the input and output air (the temperature of both is assumed to be equal, which is not completely true.

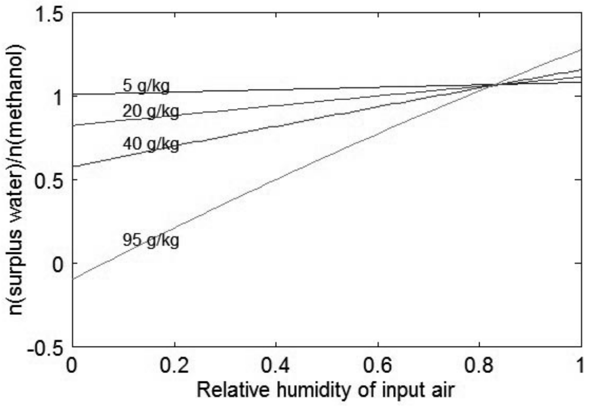

Figure 2. Excess water in the fuel cells and reformer system as a function of the relative humidity of input air

But on the other hand, it is not important weather the temperatures are the same or not and we can observe lower relative humidity which is the same as if the temperature of the input air were lower). At a temperature of 0 °C, the saturated humidity is approximately 5 g of water vapor/kg, at 25 °C approximately 20 g/kg of dry air, at 35 °C approximately 40 g/kg of dry air and at 50 °C approximately 95 g/kg of dry air. From Figure 2 we can see that the amount of produced water would be insufficient only at higher temperatures (above 50 °C) and at a simultaneous high dryness of the environmental air.

If the air pressure is 1 bar, environmental and exhaust temperature is 25 °C and air volumetric flow is 1.6 l/s, realistic conditions for operation of the fuel-cell generator Nexa are given. In such case, the water produced by the fuel cells is sufficient for preparing of a mixture of methanol and water required by the reformer.

4 CONCLUSION

The methanol reformer and the PEM fuel-cell systems are nowadays often used in practical applications as a source of electric energy. The reformer provides pure hydrogen that can be transformed into electric energy by an appropriate electrochemical reaction in the fuel cells. Byproducts of this reaction are heat and deionized water. Based on relatively little information obtained from technical documentations by the PEM fuel-cell and methanol reformer manufacturers and on some simple assumptions, this paper presents a model helping us to determine the actual water balance in the system. Based on the example of the Methanol Reformer 20LE/Nexa^{TM} Power Module system, we can draw conclusion that commercially available fuel-cell systems with realistic water production (which is a byproduct of generator operation) can be used in fuel reforming purposes in the methanol reformer. We also show that under normal operating condition and by using commercially available devices, there is always an excess of water produced by the system that can be used for various other purposes.

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