Conceptual Design of an Integrated Thermally Self-Sustained Methanol Steam Reformer – High-Temperature PEM Fuel Cell Stack Manportable Power Generator

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Abstract

We have investigated the concept of an integrated system for small, manportable power units. The focus of this study is the direct thermal coupling of a methanol steam reformer (MSR) and a high-temperature proton exchange membrane fuel cell (HT PEMFC) stack. A recently developed low-temperature (LT) MSR catalyst (CuZnGaO_x) was synthesized and tested in a designed reforming reactor. The experimental data show that at 200 °C the complete conversion of methanol is achievable with a hydrogen yield of $45 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{CAT}}^{-1}$. An experimental setup for measuring the characteristics of the integrated system was designed and used to measure the characteristics of the two-cell HT PEMFC stack. The obtained kinetic parameters and the HT PEMFC stack characteristics were used in the modeling of the integrated system. The simulations confirmed that the integrated LT MSR/HT PEMFC stack system, which also includes a vaporizer, can achieve a thermally self-sustained working point. The base-case scenario, established on experimental data, predicts a power output of 8.5 W, a methanol conversion of 98.5%, and a gross electrical efficiency (based on the HHV) of the system equal to 21.7%. However, by implementing certain measures, the power output and the electrical efficiency can readily be raised to 11.1 W and 35.5%, respectively.

Keywords: methanol steam reformer, logistic fuel processor, PEM fuel cell, thermal system integration, modeling and optimization, computational fluid dynamics (CFD)

1 Introduction

Proton exchange membrane fuel cell (PEMFC) technology is slowly entering the market for small, manwearable and manportable power applications. This is primarily because they can attain a higher specific energy than Li-ion batteries, which results in lower weight and longer autonomy of the power unit [1]. An attractive option to further increase the energy density of PEMFC portable

applications is to use methanol instead of hydrogen as the fuel. This is not only because methanol has a higher volumetric energy density, but also because of methanol's properties with respect to storage and transportation, which are much better than those of pure hydrogen. In an earlier study [2] different fuel cell systems for small, manportable power generators were compared. It was suggested that from among all of the compared systems, only reformed methanol fuel cell (RMFC) systems meet or exceed the specific energy and energy density benchmarks of Li-ion batteries. The conclusions of a similar study [3] were that a chemical hydride fuel cell has the highest power and energy density of all the compared systems, suggesting it is best suited for manportable applications. However, it was pointed out that the use of high-temperature (HT) PEMFCs and other advances in RMFC systems might alter this situation.

Due to the highest attainable hydrogen concentration in the reformat stream, the endothermic steam reforming of hydrocarbons is more attractive than auto-thermal steam reforming (ASR) or partial oxidation [4, 5]. Since a methanol steam reformer (MSR) is a heat-consuming device it would be very convenient to form a heat-integrated system where the otherwise redundant waste heat produced by a PEMFC stack could be directly transferred to a MSR and thus effectively put to use.

Until now this was not practicable because there was a temperature gap between the operating temperatures of the PEMFC stack and the MSR. Low-temperature (LT) PEMFCs, based on perfluorosulphonic acid polymers (e.g., Nafion®), typically operate at temperatures between 60 and 80 °C [6, 7]. On the other hand, conventional HT PEMFCs based on polybenzimidazole (PBI) polymer doped with phosphoric acid (H_3PO_4) can operate within the temperature interval 100 - 200 °C [6, 7], and in some cases up to 220 °C [8]. However, most typically they operate between 140 and 180 °C, because at higher temperatures the degradation processes (e.g., losses of H_3PO_4 , Pt catalyst agglomeration, carbon support corrosion, etc.) become more rapid [6, 7]. The use of conventional methanol-reforming catalysts enables the MSR to operate between 200 and 300 °C. However, to attain close to 100% methanol conversion, normally temperatures above 250 °C are

required [9, 10]. Unfortunately, these temperatures exceed the operating temperatures of a conventional HT PEMFC.

There are two ways to bridge the aforementioned temperature gap and form a directly thermally coupled MSR/HT PEMFC system. One way is to develop novel HT PEMFCs capable of operating above 250 °C. Progress in this direction has already been made [11-13]; however, these types of novel HT PEMFCs are not yet market mature. Upon their successful commercialization, however, they can be directly thermally coupled with the MSR using conventional reforming catalysts.

The other way is to develop a MSR catalyst that is capable of operating in the temperature range of conventional HT PEMFCs. Recently, a low-temperature (LT) MSR catalyst was discovered that shows great potential for the complete conversion of methanol at temperatures below 200 °C, as well as a very low CO concentration in the reformat stream [14, 15]. This LT MSR catalyst now allows the direct thermal coupling of the HT PEMFC stack and the LT MSR into an integrated, thermally self-sustained system.

Numerical studies of RMFC systems often use Aspen Plus software for mass- and energy-balance calculations and another programmable software (e.g., Matlab, Ansys Fluent, Comsol Multiphysics, etc.) to simulate the operation of the HT PEMFC stack or the entire system [16-19]. There are studies that use Matlab/Simulink software for the creation of applicative system models that are corroborated by experimental data [20, 21]. However, in these systems the HT PEMFC stack is not directly thermally coupled to the MSR and a catalytic combustor is used as the heat source to provide heat to the endothermic MSR.

Typically, all the heat consumed in integrated MSR/HT PEMFC systems was supplied by the catalytic combustor. Examples of an all-in-one hydrogen-producing unit (HPU), intended for use with a LT PEMFC stack, comprising a MSR, a combustor, a preferential oxidation reactor and evaporator were presented in [22, 23]. A compact HPU was presented in [24], and a similar approach was adopted in [25], where in order to reduce the CO concentration, a methanator was added downstream of the

MSR. A HPU prepared for integration with the HT PEMFC stack, comprising a vaporizer, a MSR and a catalytic combustor, was presented in [26]. A similar HPU, comprising a methanol ASR, was investigated in [27]. However, 75% of the heat consumed in the ASR was still supplied by the catalytic burner using anode off-gas. In a study [28] a HPU was integrated with a LT PEMFC stack in a microelectromechanical system (MEMS) for a portable power source. At a voltage potential of 0.64 V a power density of 195 mW cm^{-2} was achieved and a specific energy of 225 Wh kg^{-1} , which surpasses the standard LI-145 military personnel battery from UltraLife (140 Wh kg^{-1} , [2]) by a factor of 1.6.

In the RMFC system the utilization of heat, produced by the HT PEMFC stack, through direct thermal contact was first shown in [29]. However, at 200°C , close to 100% methanol conversion could only be achieved at a very low hydrogen yield of around $6.7 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{CAT}}^{-1}$. A similar, but more advanced, approach was taken in [30], where a two-stage MSR was used. The first stage was in direct thermal contact with the HT PEMFC stack and the second stage was heated with the catalytic combustor using anode off-gas as the fuel. Recently, a complete numerical and experimental study [31] of an integrated system constructed from an internally RMFC stack was published, where the methanol was reformed by a catalyst incorporated into the anode compartment of the HT PEMFC. At a temperature of 210°C and a hydrogen excess ratio $\lambda_{\text{H}_2} = 1.2$, stable operation of the system was only possible up to 0.18 A cm^{-2} , due to the lower conversions of methanol at higher current densities. Most recently a study of a thermally coupled MSR and a single HT PEMFC was published [32]. The anode bipolar plate was designed in such a way that on one side a MSR catalyst was inserted into the flow-field channels, while on the other side there was a flow field for the HT PEMFC. At a temperature of 180°C the system was able to operate at current densities above 0.5 A cm^{-2} . However, the thermally self-sustained operation was not achieved; therefore, an external heating of the system was required. Also, due to the lower methanol conversions at current densities above 0.2 A cm^{-2} the reformat gas was fed to the HT PEMFC at an exact hydrogen stoichiometric ratio. Operation without excess hydrogen is possible, but presents higher risks for the degradation of the HT PEMFC due to potential local fuel starvation [6].

The first objective of this paper is to characterize the newly developed LT MSR catalyst and a two-cell stack of conventional HT PEMFCs. The experimentally obtained data is used to predict the operational characteristics of the integrated and directly thermally coupled LT MSR/HT PEMFC stack system. The second and main objective is to identify the working point where the system becomes thermally self-sustained (i.e., when all the heat produced is in balance with the heat consumed and lost to the environment). The same simulation approach (using Aspen Plus and Comsol Multiphysics interactive modeling), as explained in [17], is used to obtain the geometrical and operational characteristics of the conceived integrated system. For the proper application of the developed simulation approach it is necessary to include the experimentally obtained kinetics of the LT MSR and the characteristics of the HT PEMFC stack. Balance-of-Plant (BoP) components are not included in the calculations since the main objective is to show the concept of the integrated, thermally self-sustained system.

2 Materials and methods

In this section the materials and methods used to obtain the experimental results of the exothermic HT PEMFC stack and the endothermic LT MSR are presented. In order to predict the operational characteristics of the integrated, thermally self-sustained system, each individual fuel-processing reactor was tested separately. The obtained experimental results were later used in the modeling of the integrated system.

2.1 Fuel cell stack

The stack consists of two conventional HT PEMFCs, each with an active area of 12.9 cm^2 . The commercially available membrane electrode assembly (MEA), based on a PBI membrane doped with H_3PO_4 , was purchased from Danish Power Systems (DPS) [33]. Graphite composite bipolar plates (60 mm x 60 mm x 4 mm in width, length and thickness) were custom designed and purchased from Bac2. The flow field was made of parallel channels (0.5 mm in depth and 1 mm in width) and a land-

to-channel ratio of 1:1. A custom design was also needed for the Viton gaskets, which were developed together with the company Klander d.o.o. The stack was sandwiched between two layers of insulation (Microtherm® Board) and then compressed from both sides with aluminum alloy end plates (78 mm x 78 mm x 20 mm in width, length and thickness). The upper plate was also fitted with connectors for the inlet and outlet gases. The experimental test system and the scheme of the experimental setup are shown in Fig. 1. This experimental set-up is also prepared to conduct measurements once the LT SMR is integrated together with the HT PEMFC stack into the thermally self-sustained system.

Fig. 1 – Experimental set-up for the HT PEMFC stack (top), the HT PEMFC stack without insulation (bottom left), and the scheme of the experimental setup (bottom right).

2.1.1 Experimental setup

During the experiment hydrogen and air were used as the reactant gases and their flow rates were controlled by 5850SLA mass flow controllers (Brooks Instrument). The controllers were connected to a 0254 secondary electronic unit (Brooks Instrument), which was connected to a computer via a USB – RS232 converter and regulated by an in-house-developed Labview application.

The temperatures in the system were measured by five K-type thermocouples (TC). Low-voltage signals were collected and transformed into current signals between 4 and 20 mA by IPAQ-H transmitters (INOR). These signals were then converted back into voltage signals using standardized 150 Ω resistors that give voltage-drop signals between 0.6 and 3 V. The signals were collected via a NI-6001 data-acquisition device (National Instruments).

The stack was heated with four 15 Ω polyimide-protected heaters connected in a parallel circuit. The heaters are supplied with 12 VDC through a solid-state relay (SSR), which is controlled by a software PID controller built-in to the Labview application.

The TC probes are made from stainless sheath material and are ungrounded (not in electrical contact with the TC junction). Three of the probes were inserted into the bipolar plates of the stack, which means that they were directly exposed to their voltage potentials. Using the NI-6001 the voltage drops between the probes were measured and the voltage of each individual HT PEMFC was obtained.

The power characteristics of the stack were measured with a HP6051A electronic load (Hewlett Packard), which was connected to the computer via an USB – GPIB converter and controlled by the Labview application. The polarization curves were obtained by measuring in constant current mode, where each measurement lasted a period of 2 min (to equilibrate the conditions) before moving to the next measurement point.

2.2 Methanol steam reformer

2.2.1 Catalysts synthesis

A pH-controlled co-precipitation method was used to synthesize the highly active CuZnGaO_x catalyst with the molar ratio Cu : Zn : Ga = 5 : 3 : 2. Metal nitrate salts Cu(NO₃)₂ × 3H₂O (3.03 g), Zn(NO₃)₂ × 6H₂O (2.4 g) and Ga(NO₃)₃ × 9H₂O (2.15 g) were dissolved in 100 mL of distilled water, as well as 3.5 g of Na₂CO₃. The solutions were fed to a flask containing 300 mL of distilled water by laboratory syringe pumps. The temperature of the flask was maintained at 85 °C. A magnetic stirrer at 1200 rpm was used for mixing the solution. The nitrate solution was kept constant at 0.42 mL min⁻¹, while the carbonate solution flow rate was initially set to 0.5 mL min⁻¹, but was subsequently varied to maintain the pH at 6.5, which was monitored by a pH electrode. The procedure lasted 4 hours, during which time precipitation of the catalyst took place. Afterwards, it was aged at 85 °C for 24 h. It was then washed with distilled water for the removal of Na⁺ ions and separated from the solution by centrifugation using a laboratory centrifuge (Sigma 4–15C). The procedure was repeated 12 times. The precipitate was dried at 95 °C for 24 hours and calcined in static air from room temperature to 380 °C at 3 °C min⁻¹. Finally, the catalyst was pressed at 30 bar and grinded and sieved to the size fraction 250 - 500 μm. The bulk density of the catalyst was measured to be 1.323 g cm⁻³.

2.2.2 Reformer experimental design

A total of 6.03 g of the synthesized catalyst was inserted into the reformer. The reformer is made from three separate stainless-steel plates welded together; the design can be seen on Fig. 2. The inlet (1) and outlet (2) channels go through the upper plate. In the middle plate a reaction chamber was cut out (3), which was filled with the catalyst through the service hole (4) in the bottom plate. Two inserts with guide holes (5), for aligning the reformer to the fuel cell, were placed in the positioning holes (6) and welded onto the upper and bottom plates. A wire mesh (7) was inserted into the slots (8) at the inlet and outlet sides of the reaction chamber in order to entrap the catalyst. The planar shape of the reformer is required for the integration with the fuel cell stack.

Fig. 2 – Premanufactured LT MSR parts (top), upper side (bottom left) and bottom side (bottom right) of the constructed LT MSR.

The catalyst was activated in pure H_2 from room temperature to 300 °C at a 5 °C min⁻¹ temperature increase in a flow rate of 50 mL min⁻¹, and was kept at 300 °C for 6 hours. The reformer's operation was tested in the temperature interval between 170 and 200 °C, at liquid flow rates of 30 - 300 μ L min⁻¹, and at a steam-to-methanol ratio (SMR) of 1.3. The system was purged with N_2

prior to experimentation. A syringe pump was used for feeding the liquid methanol-water reaction mixture, which was evaporated in a coil evaporator before entering the reformer. The output gas analysis was performed with a gas chromatograph (Agilent Technologies).

2.2.3 Reformer modeling

The packed bed reactor was modeled by considering the processes of convection, axial dispersion and chemical reaction. Mass transfer to the surface of the catalyst particles was neglected due to the small size of the catalyst particles [34]. The viscosity and density of the gaseous mixture, as well as the diffusion coefficients, were calculated through appropriate equations of state [34]. The Stiel and Thodos correlation was used for the determination of the vapor viscosities of the non-polar gases [35], while the viscosities of the polar gases were calculated from the method of Chung et al. [36]. The pressure drop was calculated with the Ergun equation and the density of the gaseous mixture was calculated with the ideal-gas law. The fluid-velocity change due to the change in gas density was accounted for by the continuity equation. The axial dispersion coefficients were calculated using a correlation proposed by Delgado et al. [37]. For the determination of the diffusion coefficients, a volume-correlation method proposed by Fuller et al. [38] was used.

Purnama et al. [39] have recently shown that CO is not formed by the methanol decomposition reaction. Instead it is produced in a consecutive rWGS reaction, which is contrary to the previously accepted mechanism of methanol decomposition, followed by the water-gas shift (WGS) reaction. The chemical equilibrium constant for the WGS reaction is:

$$K_{WGS} = 10^{-1.4936e-13T^5 + 4.5026e-10T^4 - 5.6216e-7T^3 + 3.7206e-4T^2 - 1.3726e-1T + 2.4537e1} \quad (1)$$

The following power-law empirical correlation was used for a description of the reaction kinetics of the LT MSR reaction:

$$r_{MSR} = A_{MSR} e^{-\frac{E_{MSR}}{RT}} P_{MeOH}^a P_{H_2O}^b \rho_{cat} \quad (2)$$

where r_{MSR} is the rate of reaction, A_{MSR} is the pre-exponential factor, Ea_{MSR} is the activation energy, R is the ideal gas constant, T is the temperature and P_i is the partial pressure. The kinetics of the rWGS reaction was not determined, since the produced CO content was less than 1% in all the experiments performed.

The mass-balance equation for the species involved is:

$$\frac{\partial c_i}{\partial t} + \frac{\partial(v c_i)}{\partial z} - \frac{\partial}{\partial z} \left(D_{ax,i} \frac{\partial c_i}{\partial z} \right) \pm \frac{(1-\varepsilon)}{\varepsilon} v r = 0 \quad (3)$$

where c_i is the concentration, t is the time, v is the linear velocity, z is the length dimension, $D_{ax,i}$ is the axial dispersion coefficient, ε is the void fraction, and v is the stoichiometry coefficient. The Danckwerts' boundary condition was used for the inlet and outlet of the reactor:

$$v_0 c_{i,0} \Big|_{0-} = v_0 c_{i,0} \Big|_{0+} - D_{ax,i} \frac{dc_i}{dz} \Big|_{0+} \quad (4)$$

$$\frac{dc_i}{dz} \Big|_{z=L} = 0 \quad (5)$$

The steady-state solution was obtained with the finite-difference method using Matlab (MathWorks Inc.). Grid independence was assured. A regression analysis for the determination of the kinetic parameters was performed with the trust-region-reflective algorithm.

3 Simulation approach

The basic design of the prototype system (shown on Fig. 3) was developed using 3D modeling software SolidWorks. The conceptual design is based on the HT PEMFC stack shown in Fig. 1, where the LT MSR (shown in Fig. 2) and the vaporizer are added to form the integrated system. The model is used to visualize the prototype system, while it also allows detecting construction issues prior to

making changes or adaptations. Blueprints for the manufacture of individual components of the system and also geometries used in CFD modeling were generated from this model.

At first it was hypothesized that the thermally self-sustained operation of the integrated system would be possible at around 180 °C, and so the characterization of the HT PEMFC stack was carried out at temperatures to 185 °C. The experimental data of the LT MSR showed that in order to achieve sufficient methanol conversion the operating temperature of the integrated system needs to be raised to 200 °C. The corrections, for the temperature rise and the fact that pure hydrogen was used during the characterization of the HT PEMFC stack, are explained in later subsections.

Fig. 3 – Conceptual design of the integrated, thermally self-sustained system (the external insulation is transparent).

3.1 Aspen Plus modeling

Since the integrated system will operate on reformat gas instead of pure hydrogen, the experimentally obtained characteristics of the HT PEMFC stack need to be corrected. Based on the experimental results obtained in Section 4.1.2 and the modeling of the integrated system in Section 4.2.1 it was concluded that in order to achieve a sufficient conversion of methanol the operating temperature of the LT MSR needs to be 200 °C. It was shown in [40, 41] that an around 20 mV gain in voltage can be expected when the temperature is raised from 180 °C to 200 °C. As stated in the DPS instruction manual, and also shown in [42], a voltage drop of about the same order of magnitude can be expected when using reformat gas instead of pure hydrogen. Since both mentioned phenomena virtually cancel each other out, the polarization curve at 180 °C is taken as a reference in the HT PEMFC stack modeling of the integrated system where the reformat gas is used at 200 °C.

During the measurements presented in Section 4.1.1 the voltage differences between the first and the second HT PEMFC were fairly small over the whole current density range, being -7 mV at 0.1 A cm⁻² and 9 mV at 0.8 A cm⁻². That is why dividing the measured HT PEMFC stack voltages by the number of cells to get a single-cell polarization curve is a reasonable approximation. Recalculating the stack characteristics to obtain the polarization of the single HT PEMFC allows flexibility in future modeling and sensitivity analyses because the number of cells in the stack can be varied. The power-density polynomial shown in [Fig. 4](#) was used in the modeling of the integrated system.

Fig. 4 – Characteristics of the single HT PEMFC at $T = 180\text{ }^{\circ}\text{C}$, $\lambda_{H_2} = 1.5$, $\lambda_{AIR} = 2.5$ used in the modeling of the integrated system.

To properly describe the methanol conversion as a function of temperature, the methanol-water mixture flow, the catalyst loading, the reaction volume of the LT MSR, and the kinetic model proposed in Section 2.2.3 were used. The reaction equations were integrated into the RPlug model unit using the experimentally obtained kinetic parameters.

3.2 Comsol Multiphysics modeling

The heat flows calculated in Aspen Plus are presented as heat sources or heat sinks in the physical modeling of the integrated system in Comsol Multiphysics. The contact areas between the PBI membrane and the cathode gas-diffusion layer (GDL) are modeled as surface heat sources inside the HT PEMFC stack. The vaporizer, the LT MSR and the convective cooling of bipolar plates are modeled as volume heat sinks.

Also important are the material properties of the system's components (see Table 1), which significantly affect the temperature profile of the integrated system.

Table 1 – Properties of materials considered for use in the integrated systems.

Fuel processor (system component)	Material	Thickness [mm]	Heat conductivity [W m ⁻¹ K ⁻¹]	Heat transfer coefficient [W m ⁻² K ⁻¹]
End plate	Al-alloy	20	115	/
Bipolar plate	Graphite composite	4	43	/
Insulation	Microtherm® Board (internal)	5	0.07 ^a	/
		10	0.04 ^a	
		15		
	AeroZero (external)	30 (top & bottom) 20 (on the sides)	0.04 ^b	15
Vaporizer	Stainless steel	3	16.2	/
LT MSR		9		
Gasket	Viton	0.25	0.235	/
Current collector	Copper	1.5	400	/
Membrane	PBI	0.05	0.41	/
Electrode	Carbon paper	0.25	1.7 ^c (through-plane)	/
			21 ^c (in-plane)	

^a Value can be tailored by changing the density of the material (blend of filament-reinforced silica powder)

^b Value according to supplier (stock shapes still under development)

^c Value based on Toray “TGP-H” carbon paper

The vertical symmetry of the modeled system makes it possible to perform calculations on 1/2 of the system and afterwards to extrapolate the results to the whole system. A tetrahedral mesh with 1,303,981 elements was used and the steady-state solution was obtained with the finite-element method (FEM). The calculation process was stopped when the relative tolerance of successive calculated values was below 10⁻³.

4 Results and discussion

In this section the experimental results are shown first. Based on these results the modeling of the integrated system was performed. Further results of the LT MSR reactor, CFD analysis (Comsol Multiphysics) and the kinetic model in Aspen Plus, are provided in the Supplementary Material. There it is shown that the methanol conversion predicted by the Aspen Plus model agreed quite well with the experimental data, which confirmed that the model was suitable for use in simulations.

4.1 Experimental results

4.1.1 HT PEMFC stack

As advised by the attached instructions from DPS the HT PEMFC needs to be exposed for least 48 h of break-in period under constant working conditions. The stack was operated at the temperature $T = 160\text{ }^{\circ}\text{C}$, current density $j = 0.2\text{ A cm}^{-2}$, hydrogen excess ratio $\lambda_{H_2} = 1.5$ and air excess ratio $\lambda_{AIR} = 2.5$.

At a temperature of $185\text{ }^{\circ}\text{C}$ the HT PEMFC stack reached the thermally self-sustained working point, meaning that there was no heat input from the electric heaters, at a relatively high current density of 0.76 A cm^{-2} (see label HP in Fig. 5(b)). It is speculated that the main reason why the stack needed to work at such a high current density, to maintain the thermally self-sustained operation, was poor insulation of the system. The external insulation of the HT PEMFC stack was made from a soft and quite delicate polyimide foam insulation (Solimide HT-340), which has a nominal thermal conductivity $\lambda = 0.046\text{ W m}^{-1}\text{ K}^{-1}$. However, the mechanical and hence thermal properties of the insulation visibly deteriorated during the use in this and previous experiments. Gaps appeared in the joints of the material and this allowed the surrounding air to enter and cool down the stack. In future experiments, a new, mechanically more resilient, insulation based on aerogel technology (Blueshift AeroZero), which can offer thermal conductivity as low as $\lambda = 0.02\text{ W m}^{-1}\text{ K}^{-1}$, will be used to further reduce the thermal losses.

Also, the Microtherm® Board used for internal insulation layers is a compressed powder blend of filament-reinforced silica. At a nominal density of around 245 kg m^{-3} the thermal conductivity is $0.02\text{ W m}^{-1}\text{ K}^{-1}$. However, this material is extremely soft and compresses easily at pressures above 0.5 MPa . In order to prevent any creep of the material during the fastening of the bolts the material was pre-compressed. It was later discovered that the applied pressure was too high, which led to poorer insulating properties because the material was over-compressed (an increase in the density of the material also increases its thermal conductivity). This is evident by observing the temperature of

the end plates, which is around 100 °C (see labels EP1 and EP2 in Fig. 5(b)). According to the results in Section 4.1, the expected temperature should be somewhere around 75 °C.

At the highest measured current density of 0.8 A cm⁻² the temperature difference between the hottest bipolar plate in the middle BP2 and the coldest BP1 was around 2.5 °C.

Fig. 5 – Polarization curves of the two-cell HT PEMFC stack at $\lambda_{H_2} = 1.5$ and $\lambda_{AIR} = 2.5$ (a); Temperature profile of the HT PEMFC stack at 185 °C (b).

4.1.2 LT MSR reactor

The empirical kinetic parameters obtained through the regression analysis are presented in Table 1. The parameters, which accurately describe the operation of the reformer under the experimental conditions, were used for all subsequent calculations.

Table 2 – The kinetic parameters of the LT MSR reaction on the CuZnGaO_x catalyst.

A_{MSR} (mol bar ^{-(a-b)} s ⁻¹ kg _{cat} ⁻¹)	E_{aMSR} (kJ mol ⁻¹)	a	b
1.012×10^7	74	0.43	0.39

For reasons of brevity the experimental and modeling results for the methanol conversion at different liquid methanol-water flow rates and SMR = 1.3 are presented in Fig. 6(a). A 94.6% methanol conversion was achieved at 0.1 ml min⁻¹ and 180 °C, while at 200 °C and 0.2 ml min⁻¹ a 99.1% conversion was achieved. According to the thermodynamic equilibrium of the WGS reaction, the production of CO₂ is favorable at lower temperatures, while the production of CO is suppressed. A 0.3% CO content was obtained at 0.1 ml min⁻¹ and 180 °C, which is very close to the calculated thermodynamic equilibrium value of 0.55%. The product stream contained 11.6% water, 2.3% methanol, 18.7% CO₂ and 67.1% H₂. A 100% methanol conversion is readily obtainable under the appropriate conditions.

Another way of analyzing the activity of the LT MSR is to examine the methanol conversion as a function of hydrogen yield. Although the experimental data at 180 °C are slightly scattered, it can be concluded that the complete conversion of methanol is possible somewhere up to 20 cm³ min⁻¹ g_{CAT}⁻¹ of hydrogen yield. Increasing the temperature to 200 °C has a very beneficial effect on the hydrogen yield, allowing a 99.1% conversion at 62 cm³ min⁻¹ g_{CAT}⁻¹ (this corresponds to a flow rate of 0.2 ml min⁻¹). It is shown in Fig. 6(b) that the kinetic model, corroborated by experimental data, predicts that at 200 °C the complete conversion of methanol is possible at hydrogen yields of up to

45 cm³ min⁻¹ g_{CAT}⁻¹. This is a threefold increase compared to [43], where complete conversion was possible at hydrogen yields of up to 15 cm³ min⁻¹ g_{CAT}⁻¹ using one of the finest commercially available catalysts, i.e., HiFuel R120. Compared to [44], where the complete conversion of methanol was achieved at hydrogen yields of up to 9 cm³ min⁻¹ g_{CAT}⁻¹ using a CuMnAlO_x catalyst, this is a fivefold increase in the hydrogen yield. In [32], where a commercial catalyst BASF (RP-60) was used, it was shown that the full conversion of methanol was possible up to around 36 cm_N³ min⁻¹ of hydrogen volumetric production. Here, it is speculated that the index N means hydrogen under normal gas conditions (20 °C and 1.013 bar). In the study it is stated that around 18 g of catalyst was used; also taking into account the ratio of densities ≈ 1.6 (hydrogen at 20 °C and 200 °C) it is estimated that the hydrogen yield was around 3 cm³ min⁻¹ g_{CAT}⁻¹.

In addition, the results of the computational fluid dynamics (CFD) simulations (provided in Supplementary Material) show that the reformer design is appropriate, since the velocity and partial pressures are close to homogeneous for each reformer cross section (perpendicular to the flow).

Fig. 6 – Methanol conversion in the LT MSR at different temperatures and SMR = 1.3: for various methanol-water liquid flow rates (a), as a function of hydrogen yield (b).

4.2 Modeling results

4.2.1 Integrated system

The integrated system was modeled as shown in Fig. 7. Water and methanol are mixed in the MIXER unit according to the prescribed SMR. DUMMYMIX represents the methanol-water mixture, which upon mixing heats up due to the non-ideal properties of the mixture. In a real device the mixture will be premixed and pumped into the system at room temperature (about 20 °C), which is represented by stream MIX. It is assumed that the liquid mixture is preheated to 65 °C, meanwhile consuming around 0.6 W of heat, when travelling from the inlet and through the system before reaching the vaporizer. This is the average temperature of the inner insulation layer between the upper end plate and the vaporizer calculated using the Comsol Multiphysics model. The mixture consumes around 5 W of heat and exits the vaporizer slightly superheated at 90 °C, which is the average temperature of the reactor calculated in Comsol Multiphysics. The vaporized mixture travelling from the vaporizer to the LT MSR again consumes about 0.6 W of heat and is superheated to the operating temperature

before reaching the reaction chamber. Incoming air is heated up to the operating temperature on the way from the inlet to the catalytic layer on the cathode side of MEA, while consuming approximately 3.4 W of heat. The thermally self-sustained working point of the integrated system is reached at 0.8 A cm^{-2} , where the HT PEMFC stack produces 8.5 W of electricity and 17.3 W of heat.

Fig. 7 – Flowchart of the integrated system model.

In Comsol Multiphysics the calculated heat flows of the integrated system are combined with the system design (see Fig. 3), which takes into account the physical properties of the materials (see Table 1), to obtain the approximate temperature profile (see Fig. 8(a)). Also, the heat losses of the system are evaluated at around 4.8 W. At the thermally self-sustained working point, under steady-state conditions, the maximum calculated temperature inside the HT PEMFC stack is 202 °C and the average temperature of the LT MSR is around 201 °C.

To produce a sufficient amount of hydrogen, 0.2 mL min^{-1} of liquid methanol-water mixture with $\text{SMR} = 1.3$ is needed. At this volumetric flow a 98.5% conversion of methanol is achieved by the LT MSR. The incoming feed flow corresponds to 38.9 W of heat input based on the higher heating value (HHV). The anode and cathode stream exiting the integrated system still carry a substantial amount of heat, mostly because the excess hydrogen and unconverted methanol are not utilized. The model unit BURNER calculates that around 25.6 W is rejected to the surroundings when the combustible components are burned and the stream is cooled down to 25 °C. The energy flows of the integrated system are also presented in the Sankey diagram in Fig. 8(b).

It can be seen from the Sankey diagram that the presented system is relatively inefficient because a lot of heat still leaves the system without being utilized and is discarded into the surroundings. Since no BoP components are included in the simulations, only the gross electric efficiency can be given for comparison. The main operating characteristics of the presented, thermally coupled, integrated system are summarized in Table 3, labeled as Case 0 (the base case).

Fig. 8 – Temperature profile of the integrated system calculated using Comsol Multiphysics (a), Sankey diagram of the energy flows (b).

4.2.2 Sensitivity analysis

The results of the sensitivity analysis are presented in Table 3. The analysis was performed by varying the hydrogen excess ratio, the number of cells in the stack, the volume of the LT MSR reaction chamber, and in certain cases also by supplying additional heat using the anode off-gas catalytic burner. The purpose of this analysis was to predict the effects of changing the parameters on the efficiency of the system. However, this was more of a preliminary analysis using only Aspen Plus, and thus it was based on two major assumptions.

First, the heat losses of the system stay the same, even though the size of the system is slightly increased. The size of the system can be affected either by increasing the number of HT PEMFCs from 2 up to 4, this would add approximately 10 mm, or by increasing the height of the LT MSR reaction chamber from 4 mm to 6 mm (a 50% increase in volume). In some cases it is presumed that the catalytic burner is added to the system. It is estimated that this would add approximately 5 mm to the size of the system. If all the parameters are varied simultaneously, the maximum increase in the size of the system would be 17 mm.

Second, reducing λ_{H_2} from its initial value of 1.5 to 1.25 does not affect the polarization curve of the HT PEMFC. This also means that hydrogen utilization in the HT PEMFC stack would be 80%, which is a realistic objective for the RMFC.

Table 3 – Sensitivity analysis of the integrated thermally self-sustained system.

	H ₂ excess ratio /	Number of cells /	LT MSR chamber volume cm ³	Liquid feed flow ml min ⁻¹	Current density A cm ⁻²	Power output W	Methanol conversion %	Gross electric efficiency ^a %	Additional heat ^b W
Case 0	1.5	2	5.168	0.20	0.80	8.5	98.5	21.7	0
Case 1	1.5	2	5.168	0.16	0.65	7.7	100	24.7	1.7
Case 2	1.25	2	5.168	0.14	0.68	7.9	100	28.9	0
Case 3	1.5	4	5.168	0.16	0.32	9.7	100	31.0	3.6
Case 4	1.25	4	5.168	0.20	0.48	12.9	98.5	32.8	0
Case 5	1.25	4	5.168	0.16	0.39	11.1	100	35.5	1.4
Case 6	1.5	4	7.752	0.29	0.58	14.5	99.0	25.7	0
Case 7	1.5	4	7.752	0.24	0.48	13.0	100	27.6	1.5
Case 8	1.25	4	7.752	0.19	0.47	12.7	100	33.6	0

^a Based on the higher heating value

^b Value of 0 W represents the systems operating at the thermally self-sustained working point without a catalytic burner

The highest power of 14.5 W was achieved in Case 6, where the stack of four HT PEMFCs was used. The hydrogen excess ratio remained the same, but the LT MSR reaction chamber was enlarged, which allowed a methanol conversion of 99%. Although, compared to the base case, the efficiency was raised to 25.7%, this was not the most efficient system configuration. The most efficient configuration was achieved in Case 5, where a four-cell HT PEMFC stack produced 11.1 W of power, while the efficiency of the system was 35.5%. Due to the reduced λ_{H_2} the volume of the LT MSR reaction chamber was left the same as in the base case. Also, the stack was operated at such a current density that the LT MSR still achieved a 100% conversion. However, due to the more efficient operation of the stack, less heat was produced, and hence, additional heat was supplied to the system by the catalytic burner in order to achieve the thermally self-sustained operation. Another attractive option is Case 4, where the base-case system configuration was only changed by adding two additional HT PEMFCs and by reducing the λ_{H_2} . The thermally self-sustained working point was achieved without the additional catalytic burner and the volume of the LT MSR was unchanged, while still achieving a 98.5% conversion at a relatively high power of 12.9 W and an electrical efficiency of 32.8%.

4.3 Discussion

The power output of the presented base-case system $P_0 = 8.5$ W is relatively small, but it can be increased by adding more cells to the HT PEMFC stack. An even greater gain in the power output can be achieved by increasing the MEA active area of the HT PEMFC. The MEA active area $A_0 = 12.9$ cm², used in this study, is relatively small compared to $A_i = 50$ cm² reported in [31]. Assuming that the system components are proportionally increased (MEA, LT MSR, etc.), and hence, the system retains its operating characteristics of the current density and the methanol conversion, the power output of the enlarged system P_i can be estimated as:

$$P_i = P_0 \cdot \frac{A_i}{A_0} \quad (6)$$

The derived proportionality factor is 3.876, which means that the enlarged integrated system with the two-cell HT PEMFC stack would produce around 33 W. If measures based on Case 4 (see Table 3) are applied, the four-cell HT PEMFC stack would produce around 50 W of power while consuming around 0.77 ml min⁻¹ of liquid feed flow and utilizing a LT MSR reaction chamber of around 20 cm³.

According to [45] there is a negligible effect of methanol slip on the HT PEMFC if the methanol conversion in the MSR is maintained above 90%. Compared to [31, 32] the simulations imply that, due to the much higher activity of the LT MSR catalyst, high conversions of methanol (above 98.5%) are possible even at high current densities, and most importantly, during operation at the thermally self-sustained working point. High current densities allow the HT PEMFC stack to produce the same power output using fewer cells, which leads to a more compact design of the system. However, as seen from the preliminary sensitivity analysis in Section 4.2.2, there is always a tradeoff between the power output and the efficiency of the system.

There are several ways to increase the efficiency of the system, some of them were already used in the sensitivity analysis, and are discussed here. The first and the easiest measure would be to reduce the hydrogen excess ratio because no modification of the integrated system is required. Reducing

λ_{H_2} would mean that less methanol-water mixture is needed, which would also reduce the heat consumption for vaporization and LT MSR. Also, at lower feed rates the conversion inside the LT MSR would be higher and approaching 100%. However, reducing λ_{H_2} will affect the polarization curve of the HT PEMFC because the mass transport of hydrogen to the active sites of the catalyst will become hindered by other species present in the reformat gas. Accurately predicting the benefits of λ_{H_2} reduction is only possible on the basis of measurements where the reformat gas is used. Although, as shown in [31, 45], operating at $\lambda_{H_2} = 1.2$ is readily possible for the RMFC.

Recycling the anode off-gas stream inside the HT PEMFC stack is also a possibility, but it is not considered to be very practical. The streams inside the system would need to be rerouted and a miniature pump or a passive pump system (e.g., a venturi pump) for the recycled stream would be needed. In addition, a purging mechanism would need to be developed because gradually the concentration of inert components (e.g., CO_2 and excess steam) would build up and inhibit normal operation.

An attractive option is to increase the number of HT PEMFCs in the stack, which can also lead to a larger vaporizer and LT MSR, or to the addition of one or more units of the same size, depending on the number of cells added. However, enlarging the system slightly with additional components would not change its heat losses much. This means that proportionally less heat would be needed to sustain the thermally self-sustained operation and consequently the HT PEMFC stack could operate at a lower current density. This would indirectly lead to a lower methanol consumption and further to a lower heat consumption of the LT MSR and also a higher methanol conversion. Also, due to a lower operating current density the electrical efficiency of the stack and consequently of the whole integrated system would be increased. In addition, increasing the number of cells would also increase the power output of the system, as was shown in Section 4.2.2.

Another possibility is to add to the anode off-gas stream a standardized catalytic combustor. In this way part of the heat produced by the combustor could be used in a traditional way and supply extra

heat to the vaporizer and/or the LT MSR. This would add a certain complexity to the system, but on the other hand it would reduce the need for the heat produced by the HT PEMFC stack. Again, lower methanol consumption, lower heat consumption of the LT MSR and higher methanol conversion would be the result of this action. From a future perspective, the incorporated catalytic combustor could also be used for the system start-up.

Since there is still a significant proportion of heat left in the outlet streams, especially if the catalytic combustor is used, an external process or a device could be used for heat recuperation. Incorporating a thermo-electric generator (TEG), which converts heat into electric power, the heat carried by the outlet streams can also be partially utilized.

The insulating of the system is also very critical, because it can reduce the heat losses, which again indirectly reduces the fuel consumption and raises the efficiency of the system. As discussed in Section 4.1.1, the inner insulation layers need to prevent the end plates from becoming too hot because they have a relatively large surface area and can cause a substantial increase in heat losses. The outer insulation is also of vital importance. The material needs to have exceptional thermal properties and be rigid enough to support the weight of the system, while still maintaining its form and thus not allowing any gaps for the surrounding air to pass through and cool down the system.

The best option for the system's optimization is a combination of the measures listed above. From experience and our preliminary sensitivity analysis of the integrated system, it appears that the most efficient option is to reduce the λ_{H2} , increase the number of HT PEMFC in the stack, and add a catalytic combustor to produce some additional heat that can be used for vaporization or even in the LT MSR. However, a more in-depth sensitivity analysis of the integrated system is needed to identify the most relevant and practical measures for the system's optimization.

5 Conclusions

This article demonstrates the concept of a compact integrated system where the HT PEMFC stack and the LT MSR are directly thermally coupled. Issues that need to be resolved prior to the construction of the prototype system are pointed out and also certain solutions or measures for solving them are discussed.

For the purpose of this study the newly developed LT MSR catalyst (CuZnGaO_x), capable of operating at temperatures below 200°C , was successfully synthesized. The LT MSR reactor prepared for integration with the HT PEMFC stack was designed and built. The CuZnGaO_x catalyst was tested in this reactor under operating conditions that correspond to those in the proposed integrated system. The experimental data show that the complete conversion of methanol is achievable up to $45\text{ cm}^3\text{ min}^{-1}\text{ g}_{\text{CAT}}^{-1}$ of hydrogen yield. This is a threefold increase compared to a relevant study [43] where the commercially available catalysts HiFuel R120 was used. Based on these experimental data the kinetic parameters were obtained and used in the modeling of the integrated system.

An experimental setup for measuring the characteristics of the integrated system was designed. This setup was used to perform measurements on the two-cell stack of HT PEMFCs, which is prepared for the integration with the LT MSR. These experimentally obtained characteristics were also used in the modeling of the integrated system. Also, the inadequate internal insulation (an over-compressed powder blend of filament-reinforced silica) and external insulation (a delicate soft polyimide foam) caused the HT PEMFC stack to reach the thermally self-sustained working point at a high current density of 0.76 A cm^{-2} . This shows the importance of proper material selection and the design of the system's insulation in order to achieve the desired temperature profile of the system.

The simulations show that it is feasible to integrate the directly thermally coupled LT MSR/HT PEMFC stack into the thermally self-sustained system, which also includes the vaporizer for the liquid feed. For the base-case scenario, which was based on experimental data, the thermally self-sustained working point was achieved at a current density of 0.8 A cm^{-2} , a power output of 8.5 W , a methanol

conversion of 98.5%, and a gross electrical efficiency (based on the HHV) of 21.7%. These results imply that, due to the much higher activity of the LT MSR catalyst, high conversions of methanol are possible even at high current densities, and most importantly, during operation at the thermally self-sustained working point. High current densities allow the HT PEMFC stack to produce the same power output using fewer cells, which leads to a more compact design of the system.

The sensitivity analysis showed that, due to minimal modification of the system, the most attractive scenario was the one where the hydrogen excess ratio was reduced to 1.25 and two additional HT PEMFCs were added to the stack. As a result, the power output and the electrical efficiency would be raised to 12.9 W and 32.8%, respectively. By adding the catalytic combustor to the anode off-gas stream the additional heat produced could be used within the system, and consequently, the electrical efficiency could be raised to 35.5%, while achieving a power output of 11.1 W. The obtained results provide the basis for the construction of a prototype system and lay the grounds for an experimental proof-of-concept.

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