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# Study of different designs of methanol steam reformers: Experiment and modeling





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#### ABSTRACT

Three reformers with different designs (multi-channel, radial and tubular) were developed for thermal integration with a high temperature polymeric electrolyte membrane fuel cell (HT-PEMFC). They were characterized experimentally at temperatures between 443 K and 473 K, using the commercial catalyst G66 MR from Süd-Chemie (CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>). The reactors were modeled and simulated using a computational fluid dynamics (CFD) analysis. The models were validated using experimental data.

The results showed that the multi-channel design is the best solution for thermal integration with a HT-PEMFC, presenting high methanol conversion and low pressure drop. Regarding the heat transfer ability, the multi-channel showed also the best performance, presenting the lowest temperature sink among the studied reformers. The low flow velocities and the absence of metallic surfaces in the radial reformer had detrimental effect on the heat transfer. Concerning the flow distribution a coefficient of variation of 0.6% was observed in the multichannel reformer. A quasi plug flow behavior was found in the tubular and a multichannel (channels region only) reformer, while in the radial a not fully developed laminar flow was found.

At temperatures lower than 473 K was found that the reformate stream did not require further purification to be fed to a HT-PEMFC due to the low CO concentration (<1600 ppm).

The advantages and limitations of each design is discussed based on experimental data and CFD modeling.

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### Introduction

Polymer electrolyte membrane fuel cells (PEMFC) are compact electrochemical devices that convert chemical into electrical energy in an efficient way. They require high purity hydrogen as a feeding fuel, especially with very low carbon monoxide content. Hydrogen, however, has a very low volume energy density and shows limitations regarding storage and transportation. To overcome these challenges, *in-situ* hydrogen

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production from fuels such as methane, methanol or ethanol is being considered. Methanol under standard conditions has a much higher volume energy density ( $1.8 \times 10^4$  kJ dm<sup>-3</sup> [1]) than hydrogen (13 kJ dm<sup>-3</sup> [1]) and it is easier to handle, store and particularly due to absence of C–C bonds has a low reforming temperature (513 K–533 K).

The integration of *in-situ* hydrogen production by methanol steam reforming (MSR) with HT-PEMFC is already used in power supplies manufactured by few companies such as Ultracell [2], AixCellSys [3] and Serenergy [4]. In most cases, as the power supplies developed by the previous companies, the MSR reactor operates as a standalone device (external reforming) [5]. It presents the advantage of not being restricted to the fuel cell stack configuration, allowing different arrangements reformer/fuel cell and higher operation temperature. As a drawback, external reforming does not take the advantage of the heat released in the electrochemical reaction for the reforming reaction.

#### Advantages of internal reforming

Methanol steam reforming (MSR) reaction occurs simultaneously with two secondary reactions, water gas shift (WGS) and methanol decomposition (MD), as described below:

(MSR) 
$$CH_3OH + H_2O \rightleftharpoons CO_2 + 3H_2 \quad \Delta H_{298K}^{\circ} = +49.7 \text{ (kj mol}^{-1}\text{)}$$
  
(1)

$$(WGS) \quad CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H_{298K}^{\circ} = -41.2 \quad (kj \ mol^{-1})$$

$$(2)$$

(MD) 
$$CH_3OH \rightleftharpoons CO + 2H_2 \quad \Delta H_{298K}^{\circ} = +90.7 \text{ (kJ mol}^{-1}\text{)}$$
 (3)

A fuel cell is an exothermic device that wastes ca. 50% of the input chemical energy while MSR reaction is endothermic. The integration of a cellular methanol steam-reforming reactor (MSR-C) intercalated with a PEMFC in a stack arrangement, in order to take advantage of this synergetic effect, should be a very advantageous approach. However, fuel cells operate typically at around 363 K (LT-PEMFC) or 443 K (HT-PEMFC), and a MSR operates at 523 K. Due to this operating temperature mismatching, many authors have chosen to study the two systems in a separated way. But, if the operation temperature of the FC (HT-PEMFC) is increased and the operating temperature of the MSR [6,7] is decreased, internal integration would be possible. The two systems should operate at temperatures ca. 453 K, but for this arrangement a more active catalyst is required. At 453 K, the conversion of the commercial catalyst CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> for a  $m_{cat}/F_{MeOH}$  of 30 kg s mol<sup>-1</sup> is around 13% [8]. To obtain an acceptable methanol conversion (>95%) at this temperature, larger amounts of catalyst are required.

The thermal integration of MSR/HT-PEMFC was first investigated by Pan et al. [6], who studied the performance of a two-cell stack (HT-PEMFC) coupled with a reformer operating at temperatures between 453 K and 473 K. However, the heat required to carry out the MSR reaction was not coming exclusively from the electrochemical reaction, but also from electrical heaters. Avgouropoulos et al. [7,9] proposed a direct internal reforming setup, coupling the electrochemical reactions and the MSR reaction at the FC anode chamber. The reaction was carried out between 473 K and 483 K using a PEM from ADVENT TPS, and a CuMnO<sub>x</sub> reforming catalyst. This application allowed a continuous electrochemical hydrogen removal from the reforming reaction, enhancing the methanol conversion. However, the membranes showed to be intolerant to the high methanol concentrations, resulting in low power output [9].

The thermal integration of a MSR-C with a FC in a stack arrangement relies on the catalyst activity at low temperatures; nevertheless a new generation of catalysts for low temperature methanol steam reforming (LT-MSR) is expected to overcome this issue [10].

#### Design of the reformers

To achieve an efficient integration of MSR/HT-PEMFC, the reformer must be optimized to maximize the heat transfer with a uniform flow distribution and low pressure drop. Typically the MSR reaction is carried out in a tubular packed bed reactor, due to its simplicity and low cost. However, well-structured flat micro or mini reactors are more suitable and present advantages, such as higher surface-to-volume ratio, better heat and mass transfer properties and flow patterns that fit with the reaction needs [11].

Most studies describing well-structured flat reactors for MSR reaction have flow fields based on single channel design or based on a series of parallel channels, as discussed below.

#### Single channel reformers

Different reformer designs, such as coil-shaped or serpentineshaped, can be obtained from a single channel design. The performance of single channel reactors lays between plug flow and laminar reactors [12]. This type of design improves significantly the mixing, reaction and heat-transfer rates [13–15].

Compared to other designs, single channel designs show even flow distributions and higher flow velocities, which reduces the stagnant film adjacent to the channel walls and improves the heat-transfer rates [13–16]. High reaction rates are also observed in this designs which lead higher conversions. Despite the advantages, single channel designs impose a significant pressure drop penalty that may be a limitation for compact applications [14].

#### Multi-channels reformer

Reformers with parallel channels have been intensively reported in literature [17–19]. Based on parallel channels, several other designs can be obtained, such as wavy, pinhole and oblique-fin [14]. They are relatively easy to manufacture, show high conversions and low-pressure drop. However, parallel channels designs are more prone to uneven flow distributions. By adjusting the channels width [18] or by imposing a considerable pressure drop at the entrance of the channels, the flow distribution can be optimized. In fixed bed reactors, depending on the specific design of the reactor, the

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