



Design and operation of a compact microchannel 5 kW_{el,net} methanol steam reformer with novel Pt/In₂O₃ catalyst for fuel cell applications

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ABSTRACT

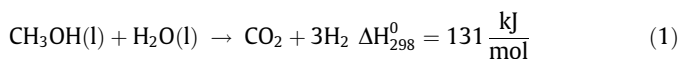
A methanol reformer was designed, built and tested, which allows hydrogen production for high temperature PEM fuel cells for mobile applications applying micro-structured plate heat-exchanger technology and a novel, highly active catalyst formulation for oxidative steam reforming of methanol at temperatures exceeding 300 °C. It is one of the first micro-structured methanol reformers with integrated anode off-gas combustion, which works in the kW scale. The reformer was operated under conditions of start-up, steady state and under dynamic conditions, in connection with a 1 kW high temperature PEM fuel cell and finally integrated into a fuel processor, which contained an external evaporator and a heat-exchanger for super-heating the reformer feed. The thermal power of the hydrogen produced by the reformer amounted to 20 kW_{thermal}, which corresponds to 6.5 kW_{el} of a fuel cell at 40% efficiency and 80% hydrogen utilization.

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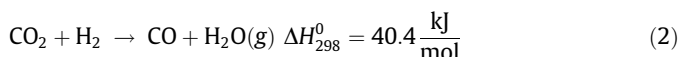
1. Introduction

Methanol has received increasing attention as an attractive energy carrier for future distributed and mobile power generation owing to the viability of sustainable production routes, its high storage stability and energy density compared to liquefied or compressed hydrogen. By application of reforming technology, it may serve as a hydrogen source for fuel cell applications [1], which is the subject of the current development work.

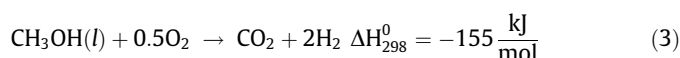
Methanol is converted to hydrogen containing reformat by endothermic steam reforming [1] as shown in the following equation:



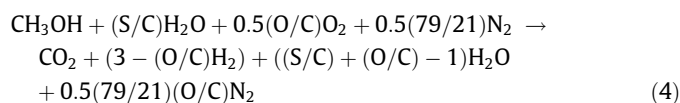
Besides hydrogen and carbon dioxide usually the reformat of methanol steam reforming contains significant amounts of unconverted steam. To a lower extent some unconverted fuel and carbon monoxide are present, the latter being formed by the reverse reaction of water–gas shift according to the following equation:



Partial oxidation of methanol is exothermic as indicated by the following equation:



Oxidative steam reforming uses air and steam as reformer feed:



S/C is the molar steam to carbon (here methanol) ratio, O/C is the ratio of atomic oxygen in the oxidant to carbon in the fuel. The hydrogen content in the reformat follows from:

$$x(\text{H}_2) = (3 - (\text{O}/\text{C})) / (3 + (\text{S}/\text{C}) + 0.5(79/21)(\text{O}/\text{C})) \quad (5)$$

The enthalpy of the reaction at a given temperature *T* is:

$$\Delta H_{298}^0 = (1 - (\text{O}/\text{C}))\Delta H_{\text{R}}^T(\text{STR}) + (\text{O}/\text{C})\Delta H_{\text{R}}^T(\text{PO}_x) \quad (6)$$

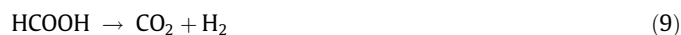
For S/C = 1.5 and O/C = 0.2 at 350 °C reaction temperature, the feed composition results in a hydrogen content of 57.4 vol.% in the wet reformat and the enthalpy of reaction amounts to 15 kJ/mol, i.e. the reaction is still endothermic. It should be noted, that heat losses are not included into the calculations, which require additional energy. This energy could be delivered by further increasing the oxygen content in the feed or by integrated anode off-gas combustion, as was performed in the system described below.

The maximum hydrogen concentration in the reformat is gained at S/C 1. However, to minimize the carbon monoxide concentration in a practical system and to avoid coke formation, a surplus of steam is required. Therefore practical systems operate at

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S/C ratios between 1.3 and 2.0. By-products of methanol steam reforming are formic acid and methyl formate (HCOOCH_3), which are both harmful at least for low temperature PEM fuel cells. These by-products are formed because both species are intermediate products of methanol steam reforming as proposed by Takahashi et al. [2]:



The decomposition of formic acid is a fast reaction [3]. Another by-product of methanol steam reforming is dimethyl ether, formed by methanol dehydration:



Dimethyl ether formation is favored by decreasing reaction temperature [4].

Catalyst development in the field of methanol steam reforming for de-centralized applications had been focused on ZnO-based catalysts such as Cu/ZnO and Pd/ZnO which exhibit high activity and low selectivity towards carbon monoxide. However, both catalyst formulations have significant disadvantages. Once Cu/ZnO catalysts are activated by reduction, they exhibit pyrophoric nature upon exposure to an oxidizing environment. At reaction temperatures exceeding 300 °C, the catalysts suffer from copper sintering and consequently deactivation takes place. Finally, Cu/ZnO catalysts are good catalysts for water–gas shift and carbon monoxide is formed by reverse water–gas shift under conditions of partial load of a methanol reformer when operated with this catalyst type, as soon as the methanol present in the feed is consumed. This makes them little suited for small and de-centralized applications. Pd/ZnO-based catalysts show higher activity because they can be operated at higher temperature, while the selectivity towards carbon monoxide remains low [5,6]. However, extensive catalyst development work performed by the group of the authors of the current paper revealed, that Pd/ZnO-catalysts are extremely sensitive to the preparation procedure bearing always the danger of formation of metallic palladium, which then leads to the formation of large quantities of carbon monoxide. Pd/In₂O₃/Al₂O₃ catalysts were identified as viable alternatives [7,8]. Pt/In₂O₃/Al₂O₃ catalysts proved to be even more active, especially under conditions of oxidative steam reforming. They show an activity of an order of magnitude higher compared to Cu-based systems when operated at reaction temperatures exceeding 325 °C [9]. The catalyst initially shows (when exposed for the first time to methanol and steam) some methane formation [9]. The higher activity is crucial when catalytic wall reactors are applied, because the catalyst mass which can be deposited onto the channel walls is limited while catalyst cost is less of an issue in such reactors owing to the considerably improved catalyst utilization compared to fixed beds. The catalyst formulation has proven 2000 h long term stability and low selectivity towards carbon monoxide during start/stop cycles and when operated at partial load [10].

Apart from microreactors developed for methanol steam reforming, which were designed as testing devices for catalyst development [11–15], many micro-methanol reformers and complete methanol fuel processors were developed for small scale applications in the power range of a few Watts and less as power supply of electronic devices such as mobile phones [16–34].

Methanol reformers and complete fuel processors in the power range of a few hundred Watts have been reported, which were based upon microstructured plate heat-exchanger technology. Creemers et al. [35] developed a micro-fixed bed reactor with integrated heat exchange. The reactor had 60 micro-fixed bed

passages and 62 heating passages and was designed to produce hydrogen for a fuel cell with 500 W power output. Heating oil, which was heated by an external burner served as the heat source for the reformer. The methanol conversion exceeded 90% at 250 °C reaction temperature. Pan and Wang developed a reformer integrated with a catalytic burner for methanol steam reforming [36], which was designed as a cross-flow heat-exchanger. It contained an integrated evaporator for methanol. Owing to the low activity of the Cu/ZnO catalyst applied, small fixed beds were used for steam reforming, but surprisingly also for catalytic combustion. To avoid hot spot formation, perforated fins were introduced into the afterburner fixed beds to distribute the added hydrogen over the length of the catalyst bed but despite this a temperature difference of almost 50 K was observed over the reactor length axis [36]. This deteriorated the performance of the reformer. The poor heat transfer between the fixed catalyst beds led to a temperature difference between the combustion bed and the steam reforming bed in the range of 40 K. Full methanol conversion was achieved at a low S/C ratio of 1.2 and reaction temperatures of less than 250 °C, while the low carbon monoxide concentration never exceeded 1 vol.%, because reverse water–gas shift occurred only to a minor extent at the low reaction temperature. Later, Pan and Wang built a reactor which was 14 times larger [37] and operated it for 1000 h. The methanol conversion decreased from 100% to about 93% in this period while the carbon monoxide concentration in the reformat could be maintained below 2 vol.%. Recently Pan et al. developed a methanol fuel processor, which contained an integrated methanol reformer/ catalytic burner and a water–gas shift reactor in a concentric design [38]. The device had 74 mm diameter and 100 mm height, while the hydrogen produced had a thermal energy of 160 W. The fuel processor was operated for 1600 h and showed good stability. Park et al. [39] described the development of a microstructured methanol steam reformer with an electric power equivalent of 28 W, which combined steam reforming with catalytic combustion. The reactor was sealed by brazing. While the steam reforming catalyst was wash-coated onto the channels, the catalytic burner contained a small fixed bed [39]. Kolb et al. reported of the development of an integrated microstructured fuel processor with a electrical net power output of 100 W [40]. The fuel processor worked very stably both under full and partial load. A very narrow temperature profile of only 3 K was achieved in the reformer, which was crucial for the Pd/ZnO catalyst technology applied. The fuel processor was coupled to a high temperature fuel cell, which generated an electrical power output of 103 W.

Numerous methanol fuel processors of the kW scale, which were based upon ‘conventional’ technology such as fixed beds, ceramic or metallic monoliths and integrated membrane separation have been developed. The famous HotSpot fuel processor developed by Johnson Matthey was actually a fixed bed reactor [41,42]. By initial methanol combustion the reactor was pre-heated and then able to produce hydrogen containing reformat under autothermal conditions. The power density of the HotSpot reactors was 3 kW/L. Owing to the high reaction temperature, the carbon monoxide content of the reformat supplied by the reformer was ranging between 2 vol.% and 3 vol.%. Very prominent fuel processor systems had been developed for automotive applications, which were implemented into the NECAR 3 and NECAR 5 by Daimler-Benz [43–45]. Schuessler et al. [46] from XCells respectively Ballard presented an integrated methanol fuel processor system based upon autothermal reforming with 0.5 L volume and 1.8 kg weight at 1.2 m³/h hydrogen output [46]. The reactor was built from copper powder by a sintering technique performed at temperatures between 500 °C and 700 °C, which were low enough to avoid damage of the catalyst. Toyota developed a methanol-fuelled fuel cell vehicle, which had a range of 500 km and a maximum power of

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