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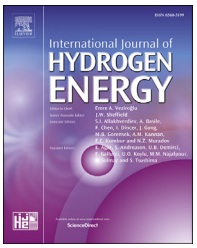

Modeling and simulation of water-gas shift in a heat exchange integrated microchannel converter

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ABSTRACT

The aim of this study is to analyze the operation of a heat exchange integrated, Pt-CeO_2/Al_2O_3 washcoated microchannel water-gas shift (WGS) reactor under fuel processing conditions by mathematical modeling techniques. In this context, operation of a single microchannel is modeled, whose outcomes are compared with experimental data obtained from the literature. Simulations show good agreement with the experimental data, with an error below 4%. Upon its validation, single channel model is used to simulate a heat exchange integrated microchannel reactor, which involves periodically located groups of reaction and air-fed cooling channels. The integrated reactor is modeled by 2D Navier-Stokes equations together with reactive transport of heat and mass. Incorporation of heat exchange function minimizes the impact of thermodynamic limitations on WGS by precise regulation of reaction temperature and gives 77.6% CO conversion, which is 67.4% in the absence of cooling. Improvement in conversion from 69.2% to 77.6% is observed upon increasing feed temperature of the reaction stream from 565 to 595 K, above which the reaction is controlled by equilibrium. Coolant feed temperature, however, changes conversion only by <1%. Isothermal conditions are obtained upon feeding reaction and coolant channels at 595 K and 587 K, respectively. Changes in the thickness and material of the wall between the channels give limited deviations in conversion. An integrated reactor with 2.37 L volume is sufficient for supplying H_2 necessary to drive a 1 kW PEMFC unit.

Introduction

Water-gas shift (WGS) is a process that is used to increase the hydrogen (H_2) contents of the effluents of catalytic steam reforming or partial oxidation. The process involves catalytic conversion of carbon monoxide (CO) with steam through the following reaction:

$$CO + H_2O = CO_2 + H_2 \quad \Delta H^\circ = -41 \text{ kJ mol}^{-1} \qquad (1)$$

WGS is widely used in industrial applications, with the most well-known one being the steam reforming of natural gas to produce hydrogen for running the hydro-processing steps involved in petroleum refining operations [1]. The reaction is also important for tuning the product distribution in gasification of renewable resources [2,3]. In industrial practice, WGS is traditionally carried out in two successive, adiabatically operating packed-bed reactors, high temperature (573–723 K) and low temperature (473–573 K) converters, which involve the use of Fe–Cr oxide type and Cu–ZnO/Al_2O_3

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catalysts, respectively [4]. The necessity of using a low-temperature unit comes from the fact that WGS is thermodynamically limited at high temperatures [5]:

$$K_{eq} = \exp\left(\frac{4577.8}{T} - 4.33\right) \quad (2)$$

Apart from its use in large scale manufacturing of H_2, WGS is an integral part of the so-called fuel processors that involve catalytic reforming of hydrocarbons into pure H_2 for powering proton exchange membrane fuel cells (PEMFCs) used to generate electricity for mobile and stationary applications up to ~2–3 kW scale [6,7]. In addition to H_2, catalytic conversion of hydrocarbons also produces CO, which is a poison for the anode of the PEMFC, and must therefore be removed from the reformate stream. For this purpose, WGS is used just after the reforming step together with a separate catalytic unit for further CO clean-up [6–8].

In contrast with the refining operations, WGS unit in the fuel processors is subject to contact with oxygen (O_2) which reduces the activity of industrial WGS catalysts due to sudden increase of temperature and subsequent sintering. In other words, their pyrophoric nature rules out the use of Cu and Fe–Cr based catalysts in the WGS units of fuel processors [4,6,8]. In this respect, catalysts need to be non-pyrophoric. Moreover, they are expected to exhibit adequate activity within the opposing constraints of thermodynamic and kinetic limitations and have high thermal stability. Compared to conventional ones involving copper and iron, catalysts with precious metals can drive WGS at higher rates, do not require activation prior to use and do not degrade upon their exposure to air [9]. Among various precious metals, Pt and Au are investigated in detail for their use in WGS run under fuel processing conditions [4].

WGS unit is expected to be compact and lightweight, as these are critical design features of fuel processors. Due to the thermodynamic limitation, WGS is hindered at high temperatures. This constraint causes WGS to be carried out at lower temperatures where the kinetic phenomena dictate the response, and higher CO conversions becomes possible only with larger reactors. Even though catalysts such as Pt-CeO_2/Al_2O_3 are active at low temperatures (473–573 K), WGS converters, which are mostly of packed-bed type, remains bulkier than those of reforming and CO purification units [6,10]. A promising strategy for decreasing WGS converter size without compromising from CO conversion is based on reducing thermodynamic constraints by fast removal of the exothermic heat from the catalyst bed. However, due to their inherently weak heat transfer properties, packed bed units suffer from low heat transfer rates [11]. An attractive alternative is to use microchannel reactors, the units composed of parallel, identical channels, each of which has a hydraulic diameter between 10^{-6} and 10^{-3} m. Small channel sizes offer enhanced volumetric intensification of the reactor surface area up to ~5×10^4 m^2 m^{-3}, which remains only ~1×10^3 m^2 m^{-3} in the packed bed units [11–15]. In contrast with the traditional particulate form, catalyst is in the form of a thin (<~1×10^{-4} m thickness) layer coated onto the inner walls of the channels. Considering the fact that the channels are machined onto thermally conductive metal plates that are bonded together to end up with the core of the multichannel reactor [12,16], exothermic heat generated on the catalyst layers can be removed with rates much higher than those involved in packed beds [17]. The reactor architecture also enables functional intensification allowing the unit to operate like a heat-exchanger which removes the heat released by WGS and, in turn, offers higher CO conversions.

Potential benefits of the microchannel units have led several groups to study its use in WGS. Majority of those studies are focused on the development of efficient catalysts suitable for microstructured devices. Kolb et al. [18] compared Pt/CeO_2, Pt-Pd/CeO_2, Pt-Rh/CeO_2 and Pt-Ru catalysts, all supported on Al_2O_3 and washcoated onto microchannels machined on stainless steel plates, on the basis of their activity and selectivity. They reported that Rh and Ru led to methanation ($CO + 3H_2 = CH_4 + H_2O$), which is found to be less in other catalysts. The authors also found that Pt/CeO_2/Al_2O_3 was the best catalyst in terms of activity and minimal methanation [18]. The effect of reactor material was reported in the study of Goerke et al. [19], in which the use of FeCrAlY instead of stainless steel increased WGS activity of Ru/ZrO_2 compared to Au/CeO_2. Wheeler et al. [20] compared the activities of alumina supported Ni, Pd, Pt, Rh, and Ru. They reported that Pt/Al_2O_3 was the most promising candidate, whose activity was improved and methane selectivity was reduced upon addition of ceria. Positive contribution of ceria, which was linked to its high oxygen storage capacity, was reported also by other groups [21–24].

Importance of simultaneous heat removal from WGS for the regulation of reaction temperature is reported in the literature. In their modeling-based study, TeGrotenhuis et al. [25] found that decreasing the temperature of the reactant stream along the reactor increased CO conversion. A similar outcome was reported by Severin et al. [26] who obtained higher CO conversion by introducing cooling function to the WGS converter of a gasoline fuel processor. Dubrovskiy et al. [27] studied a heat exchange integrated micro-structured reactor for WGS applications. The authors found that temperature of Mo-based catalyst can be changed along the reactor to obtain an optimal profile that yields in elevated CO conversions. Kim et al. [28] investigated the effect of design and operating parameters of a heat-exchange integrated, Cu-based catalyst driven WGS converter on CO conversion via mathematical models. The authors suggested that enabling cooling function in the reactor can decrease the necessary catalyst amount by half when compared to the adiabatic operation. In another study, Baier and Kolb [29] showed that the conventional two step WGS operation can be carried out in a single reactor by maximizing CO conversion through the regulation of reaction temperature by means of integrated cooling. The use of microchannel type WGS reactors in the context of fuel processing was also investigated in other studies [30].

This study involves parametric investigation of a heat exchange integrated microchannel WGS converter via computational fluid dynamics (CFD) based techniques, and aims understanding the effects of operational and structural parameters on temperature distribution and CO conversion with an approach that is not available in the literature. Development of the single channel and heat exchange integrated reactor models along with the details of numerical solution

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