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Modeling and 3D-simulation of hydrogen production via methanol steam reforming in copper-coated channels of a mini reformer

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HIGHLIGHTS

- Maxwell-Stefan model is more close to experimental data than mixture-averaged one.
- Here is an optimum value for the steam to carbon ratio that maximizes H_2 flow rate.
- Using the narrow channels increases the H_2 production rate as well as the CO content.
- Cylindrical microchannels show better performance compared to rectangular ones.

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ABSTRACT

Modeling and CFD simulation of a three-dimensional microreactor includes thirteen structured parallel channels is performed to study the hydrogen production via methanol steam reforming reaction over a $Cu/ZnO/Al_2O_3$ catalyst. The well-known Langmuir-Hinshelwood macro kinetic rate expressions reported by Peppley and coworkers [49] are considered to model the methanol steam reforming reactions. The effects of inlet steam to methanol ratio, pre-heat temperature, channels geometry and size, and the level of external heat flux on the hydrogen quality and quantity (i.e., hydrogen flow rate and CO concentration) are investigated. Moreover, the possibility of reducing the CO concentration by passing the reactor effluent through a water gas shift channel placed in series with the methanol reformer is studied. Afterwards, the simulation results are compared with the experimental data reported in the literature considering two different approaches of mixture-averaged and Maxwell-Stefan formulations to evaluate the diffusive flux of mass. The results indicate that the predictions of the Maxwell-Stefan model is in better agreement with experimental data than mixture-averaged one, especially at the lower feed flow rates.

1. Introduction

Minimization, miniaturization or micro process engineering is a technology which reduces the equipment size and weight while increases the performance of the heat and mass transport phenomena due to a reduction of the characteristic length [1,2]. This ability has led to extensive feasibility studies for industrial production of high added value chemicals using microreactors [3–11]. This idea goes back to 1970, in which some institutions and universities such as MIT and Newcastle Universities, and Battelle Pacific and Northwest National Laboratory Research institutions studied some features of the microreactors for production of diverse chemicals. Since, the construction of the microreactors is considerably expensive, simulation studies can promote our knowledge of the behavior of the reacting flows in micro structured reactors, which in turn improves the reactor design and reduces the construction cost and operation.

Hydrogen, a clean fuel with high energy density, is the most common fuel used to supply the fuel cells as an on-board power source in the vehicles with electric motors including automobiles, buses, airplanes and etc. To this end, onboard production of hydrogen via onboard storage of methanol and subsequent catalytic reforming into hydrogen has been suggested. Microreactors, due to their small size and high heat and mass transport efficiencies, are highly effective for the implementation of this idea. In this regard, based on the available hydrocarbon feed stocks, there are many catalytic processes for hydrogen production using microreactors.

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Some of them are based on the traditional endothermic routes such as steam and carbon dioxide reforming and others have been established based on the new oxidation ones such as catalytic partial oxidation and auto-thermal reforming reactions. In all the aforementioned processes, due to stringent considerations about the catalyst deactivation, only using feedstocks that are free of sulfur, nitrogen and organometallic compounds are allowed. In order to fulfill this matter, natural gas, due to its abundance and ease of refinement, has been taken into consideration.

Methanol is a clean liquid fuel (i.e., is free of sulfur, nitrogen and organometallic compounds), which is produced industrially from natural gas through syngas precursor, and can be converted to hydrogen in the presence of copper-based catalysts [12–20]. Moreover, such as gasoline and gas oil, methanol can be safely charged and used in the vehicle's fuel tank. In addition to what was mentioned, methanol (as an oxygenated hydrocarbon) steam reforming reaction is performed at lower operating temperatures compared to methane (as a saturated hydrocarbon) steam reforming reaction to produce hydrogen [21].

Hence, in the recent years, many theoretical and experimental investigations have been performed to study the diverse features of hydrogen production via methanol using microreactors [22–36]. Among these, Pattekar and Kothare [22] investigated the behavior of a microreactor experimentally and theoretically for in-situ production of hydrogen from methanol. They simulated a microreactor in 2D with channels of 230 μm × 1000 μm. Surface reactions were performed on a thin layer of copper catalyst with thickness of 33 μm and gas phase reactions were completely ignored. A binary mixture of water and methanol was used to calculate the physical properties. They studied the effects of operating pressure and temperature on methanol conversion, and also determined the minimum thermal energy required for continuous operation. A simulation study was carried out by Choi and Stenger [23] to investigate the effect of the number of inlet and outlet flows of a copper-coated microreactor on methanol conversion. The 1D-plug flow approximation was used to model the reactor behavior. Terazaki et al. [24] experimentally examined the catalytic conversion of methanol by steam reforming reaction. They theoretically evaluated the minimum temperature required for reaction initiation and compared it with the experimental values. A one-dimensional model including spiral flow and axial heat diffusion was applied by Kawamura et al. [25] to find the optimum number of inlet and outlet flows in microreactors used to produce hydrogen by methanol steam reforming. Kim and Kwon [26] investigated the behavior of a microreactor including six parallel rectangular channels. In this study, all microchannels were insulated in all dimensions except one was exposed to heat flux. Moreover, it is assumed that the reaction mixture behaves like an ideal gas. Yakoob et al. [27] experimentally studied the methanol steam reforming and compared the ability of some catalysts to reduce the production rate of carbon dioxide. Furthermore, Suh et al. [28] used a 1D model to examine the effect of several heating methods on the production rate of carbon dioxide. Fazeli and Behnam [29] investigated different geometries to minimize the energy consumption by methanol steam reforming reaction using a 2D model. They assumed steady state conditions and ignored the gas phase reactions. In one of the latest CFD studies on methanol steam reforming, a theoretical comparison was carried out between the performance of fractal-design and parallel-channel microreactors by Haung et al. [36]. They found that the fractal design relative to the parallel channel pattern not only increased the methanol conversion but also decreased the carbon monoxide concentration.

In the present work, a three-dimensional model was established by a CFD approach to study the effect of some parameters and features affecting the performance of methanol steam reforming performed in straight channels of a microreactor. The effects of channel dimensions and operating conditions on the performance of the methanol steam reforming process (i.e., methanol conversion and hydrogen purity) were investigated based on two different viewpoints of a constant inlet mass flow and a constant inlet velocity. Moreover, the ability of both multicomponent and mixture-averaged formulations to model the mass transport phenomenon and predict the experimental results was examined.

2. Model development and description

A three-dimensional CFD model was developed to investigate the thermal and kinetics behavior of the methanol steam reforming process using a rectangular parallel channel microreactor. The pattern of rectangular channels is considered according to what was proposed by Kim and Kown [26]. In this pattern, the microreactor includes thirteen parallel channels with dimensions of 1 mm × 0.5 mm × 20 mm in which all surfaces are insulated except the bottom subjected to a constant heat flux. As regards the reactants are uniformly distributed between the channels of the microreactor and that the heat fluxes are identical, it can be expected that the behavior of the reaction mixture in a single channel represents the performance of the whole mini reformer. Accordingly, only one of the microchannels is selected as the simulation domain.

2.1. Governing equations

In narrow channels of a microreactor, the formulation of the fluid mechanics depends on the ratio of molecules mean free path (λ) to channel characteristic length (L_c); this ratio is defined as Knudsen number ($K_n = \lambda/L_c$) [37]. According to the value of this ratio, there are two different formulations of statistical and continuum mechanics. At low Knudsen numbers (less than 10^{-3}), the continuum approach is proper for modeling the microchannels [37]. In this paper, regarding to the channel dimensions, the minimum characteristic length is 0.5 mm. The mean free path can be evaluated for all molecules of the reaction mixture (i.e., CH_3OH, H_2O, CO, CO_2, H_2) using the following equation developed by gas kinetics theory [37]:

$$\lambda = \frac{K_B T}{\sqrt{2}\pi\sigma^2 P}, \quad (1)$$

where K_B and σ denote the Boltzmann constant and molecular diameter and T and p are the operating temperature and pressure, respectively. At a pressure of 1 atm and maximum operating temperature of 250 °C, which are correspond to the worst case in this study, the Knudsen number for methanol, steam, carbon dioxide, carbon monoxide and hydrogen is 1.65×10^{-4}, 0.31×10^{-3}, 0.4×10^{-3}, 0.4×10^{-3} and 0.54×10^{-3}, respectively, that all of them are less than 10^{-3}. Accordingly, the continuum mechanics can well describe the mechanical behavior of the fluid flows through the microchannels. To this end, and as regards the flow through the narrow channels is laminar, the three-dimensional Navier-Stokes equations were applied to accurately model the heat and mass transport phenomena in the micro reformer. As regards the methanol steam reforming reactions are carried out at a nearly atmospheric pressure, the density of the reaction mixture can be evaluated using the ideal gas law. In addition to the above, the channels of microreformer subject to the following assumptions:

- At the reactor inlet, the feed completely evaporates due to high temperature. So, all components are considered in the gas phase.