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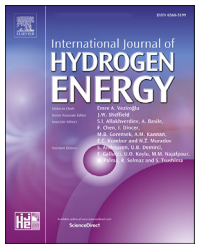

Design, modeling, and optimization of a lightweight MeOH-to-H_2 processor

Wei Wu [a,*], Shu-Bo Yang [a], Jenn-Jiang Hwang [b], Xinggui Zhou [c]

[a] Department of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan
[b] Department of Greenergy, National University of Tainan, Tainan 70005, Taiwan
[c] State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

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ABSTRACT

The conceptual design, modeling, and optimization of a MeOH-to-H_2 processor by an integration of a multi-tube annular membrane methanol reformer (MTAMMR) and the preheating system are presented. The annular membrane methanol reformer (AMMR) is a packed-bed reactor consisting of two concentric cylinders and its surface is covered with the Pd-Cu membranes. When the methanol steam reforming and the preferential oxidation reactions are carried out in the outer and the inner tubes, respectively, the countercurrent axial flow in the annular gap can ensure the thermally self-sustaining operation. Under sufficient consideration of the effect of heat integration, three plate-fin heat exchangers (PFHEs) are taken into account in the preheating system. Through a series of optimization algorithms for maximizing the H_2 permeation rate of each AMMR and minimizing the total energy demand of the preheating system, respectively, the optimal operating conditions and specifications of MeOH-to-H_2 processor are obtained. Finally, it is successfully found that the perfect weight of the optimized MeOH-to-H_2 processor is close to the H_2 tank weight for 2016 Toyota Mirai vehicle if the PFHEs use titanium material.

Introduction

Methanol is a desired liquid fuel for decentralized hydrogen production plants due to its safe, low-cost, and convenient transportability [1]. The methanol steam reforming (MSR) has some advantages including the low reforming temperature and a relatively high hydrogen-carbon ratio [2]. The MSR processes are widely applied for producing hydrogen where an integration of the methanol steam reformer, the water gas shift (WGS) reactor, and the preferential oxidation (PROX) reactor for CO-selective oxidation was a typical design of a MeOH-to-H_2 processor [3]. Moreover, the process design, modeling, and optimization of different configurations using various fuels for hydrogen production have been investigated [4–6].

In the past years, the system integration of fuel cell stacks and fuel processors has been investigated such as the PEMFC stack coupling with a MeOH-to-H_2 processor [7,8], and a 5 kW stand-alone power unit using a combination of the high-temperature PEMFC fuel cell and an autothermal ethanol reformer was addressed [9]. Notably, the process integration and the system energy integration are used to improve the power system efficiency. For fuel cell powered applications,

* Corresponding author.
E-mail address: weiwu@mail.ncku.edu.tw (W. Wu).

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the methanol reformer was more suitable for fuel cell powered submarines than the high weight of the metal hydride storage cylinders [10], and a high-efficiency, autothermal reactor using dual reforming of ethanol and methane for hydrogen production could improve driving range of fuel cell powered vehicles [11]. Recently, the novel heat exchanger MSR reactor was designed to couple with a high-temperature PEMFC utilizing its waste heat [12]. The heat integration of the assembly of internal reforming fuel cell system in a stack arrangement could be validated through experiments and computational fluid dynamics (CFD) simulation [13].

Regarding the kinetics of the miniaturized methanol reformer, Pohar et al. [14] showed that the synthesis of a novel copper–ceria catalyst promoted with gallium was successfully operated in the temperature range of 300–400 °C, Kuznetsov and Vitovsky [15] presented a kinetic model of methanol steam reforming over copper-zinc catalysts deposited on annular microchannel walls, and Wang et al. [16] presented the compact methanol reformer, which was made of aluminum alloy with multiple columns to fill up with copper/zinc oxides catalyst, can produce the syngas with an extremely low CO content (2–4 ppm). Regarding the effects of geometrical chamber and thermodynamics, Perng et al. [17] showed that a specified volume of catalyst bed can enhance the methanol conversion and hydrogen production in a cylindrical methanol reformer, and Chein et al. [18] presented different mini-scale reactors for hydrogen production coupled with liquid methanol/water vaporizer, methanol/steam reformer, and methanol/air catalytic combustor. These reactor designs are similar to tube-and-shell heat exchangers, but the issues of the reactor size and weight are not investigated yet. Regarding the mathematical modeling of mini reactor, Sari and Sabziani [19] showed the CFD simulation of a three-dimensional microreactor including thirteen structured parallel channels for the hydrogen production via methanol steam reforming reaction over a $Cu/ZnO/Al_2O_3$ catalyst, but the thermally self-sustaining operation of this microreactor was not addressed, and Fu and Wu [20] presented a double-jacketed membrane reactor to carry out the thermally self-sustaining operation, where the supported palladium (Pd) membrane can promote the endothermic reaction to higher conversion compared with a conventional reactor, but the geometric framework for studying the optimal reactor was not investigated. Recently, an experimental setup showed the direct thermal coupling of the high-temperature PEMFC stack and the low-temperature MSR. The simulations confirmed that this integrated power unit can achieve a thermally self-sustained operation [21]. However, the shape and size optimization of the integrated system was not addressed yet.

To develop the compact MSR for fuel cell applications, a microchannel methanol reformer was designed, built and tested, which allows hydrogen production for high temperature PEM fuel cells and uses the micro-structured plate-fin heat exchanger [22], and a compact methanol reformer consisting of evaporator, flow distributors, steam reformer and combustor was studied by the CFD simulations [23]. In general, the microchannel structure plays an important role in the reaction performance of MSR, where the effect of microchannel cross-section and distribution on MSR has been studied [24]. Recently, the compact design of ammonia fuel processing unit, which is a combination of a cocurrent-flow annular reactor, a membrane separator, and a preheating system configuration, was based on the theoretical modeling and simulated using gPROMS® [25].

In this article, the modeling and optimization of a compact methanol reformer are addressed by using gPROMS® and Aspen EDR software. In Section Annular membrane methanol reformer, the 3D cross-section profile is used to describe the detail configurations of AMMR. The molar, energy, and momentum balances of a packed bed reactor with kinetics in the outer and inner tubes of the AMMR are modeled in gPROMS® environment. In Section MeOH-to-H_2 processor, the detail configurations of MTAMMR and MeOH-to-H_2 processor are described. In Section Results and discussion, the sensitivity analysis and optimization of the reactor design specifications and operating conditions of the AMMR and MTAMMR are investigated.

Annular membrane methanol reformer

Configuration

An annular membrane methanol reformer (AMMR) is designed to produce the high-purity hydrogen. By Fig. 1, the 3D cross-section profile of the AMMR shows that (i) methanol and water with the prescribed operating temperature are fed into the left side of the outer tube to carry out the MSR reaction, (ii) the fresh air with the prescribed operating temperature mixed with the outlet stream of the outer tube flows into the right side of the inner tube to carry out the PROX reaction, (iii) the surface of the outer tube is covered with Pd-Cu membrane to produce the high-purity hydrogen, and (iv) four chambers with A-D are split individually by adding three inner plates where flue gas is exhausted from the A chamber, hydrogen gas is exhausted from the C chamber, the feed flow with methanol and water flows into B chamber, and the air flow flows into D chamber.

In general, the MSR reaction is composed of the following reactions,

$$CH_3OH + H_2O \xrightarrow{r_{MSR}} CO_2 + 3H_2 \quad \Delta H_{R,298} = 50\frac{kJ}{mol} \tag{1}$$

$$CO + H_2O \xleftrightarrow{r_{WGS}} CO_2 + H_2 \quad \Delta H_{R,298} = -41\frac{kJ}{mol} \tag{2}$$

$$CH_3OH \xrightarrow{r_{MD}} CO + 2H_2 \quad \Delta H_{R,298} = 91\frac{kJ}{mol} \tag{3}$$

The kinetics of the above MSR reactions over the CuO/MnO catalysts are shown in the part A in the Appendix section. Notably, the methanol conversion could be over 99%. For the endothermic MSR reactions, the more hydrogen yield is improved by increasing the operating temperature or increasing the steam to methanol (S/C) ratios [4]. The preferential oxidation (PROX) reaction is a combination of CO oxidation and H_2 oxidation reactions

$$CO + \frac{1}{2}O_2 \xrightarrow{r_{COX}} CO_2 \quad \Delta H_{R,298} = -283\frac{kJ}{mol} \tag{4}$$

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