



Polymer electrolyte membrane fuel cell grade hydrogen production by methanol steam reforming: A comparative multiple reactor modeling study



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HIGHLIGHTS

- A noble process scheme to generate pure H₂ is proposed.
- High residence time enhances H₂ recovery and H₂ yield.
- Exit gas composition is reduced to permissible discharge limit.
- Produced pure H₂ can operate a 470 W PEMFC stack.

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ABSTRACT

Analysis of a fuel processor based on methanol steam reforming has been carried out to produce fuel cell grade H₂. Six reactor configurations namely FBR1 (fixed bed reactor), MR1 (H₂ selective membrane reactor with one reaction tube), MR2 (H₂ selective membrane reactor with two reaction tubes), FBR2 (FBR1 + preferential CO oxidation (PROX) reactor), MR3 (MR1 + PROX), and MR4 (MR2 + PROX) are evaluated by simulation to identify the suitable processing scheme. The yield of H₂ is significantly affected by H₂ selective membrane, residence time, temperature, and pressure conditions at complete methanol conversion. The enhancement in residence time in MR2 by using two identical reaction tubes provides H₂ yield of 2.96 with 91.25 mol% recovery at steam/methanol ratio of 1.5, pressure of 2 bar and 560 K temperature. The exit retentate gases from MR2 are further treated in PROX reactor of MR4 to reduce CO concentration to 4.1 ppm to ensure the safe discharge to the environment. The risk of carbon deposition on reforming catalyst is highly reduced in MR4, and MR4 reactor configuration generates 7.4 NL min⁻¹ of CO free H₂ from 0.12 mol min⁻¹ of methanol which can provide 470 W PEMFC feedstock requirement. Hence, process scheme in MR4 provides a compact and innovative fuel cell grade H₂ generating unit.

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1. Introduction

In last few decades, fuel cells have attracted considerable attention as leading power generating engines due to their high efficiency and low emission of pollutants. Among many types of fuel cells, polymer electrolyte membrane (PEM) fuel cell used widely in mobile and stationary applications, has received increased attention due to their attractive features such as high energy density, rapid start up and response, low operating temperatures and compactness [1]. Hydrogen is used as a fuel for PEM fuel cell. For portable fuel cells applications, a fuel processor using

high energy renewable liquid fuels to produce on board H₂ is desirable [2–4]. Methanol, a renewable liquid fuel, is recognized as a promising and potential fuel for hydrogen production. Methanol offers a number of advantages for H₂ production via catalytic reforming as it can be reformed at low temperatures (473–573 K) and provides high H/C ratio compared to other hydrocarbons [5,6]. Hydrogen is obtained from methanol using various catalytic reforming processes such as steam reforming, decomposition, oxidative steam reforming, partial oxidation and autothermal reforming. Among these processes, steam reforming is the most widely used industrial process for large scale production of hydrogen [7,8].

Methanol steam reforming is carried out over various non-noble metal (Cu, Ni) catalysts and noble metal catalysts (Pd, Pt, Rh) [9–13]. During reforming, formation of many undesired products

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reduces the quantity and quality of desired product H₂. It is well known that PEM fuel cell requires highly pure H₂ containing CO less than 10 ppm. High CO content (≥ 10 ppm) leads to detrimental effect on low temperature PEM fuel cell performance [14]. For this reason, many research works have been reported in the literature to treat reformat gas before sending to fuel cell. In these studies, the reformer has been followed by the combinations of low temperature water gas shift (WGS) reactor, high temperature WGS reactor, preferential CO oxidation (PROX) reactor, and pressure swing adsorption unit [2,15,16]. Thus, the whole fuel processing unit becomes quite difficult to carry and handle, and cannot be comfortably used in automotive fuel cell applications [17]. Additionally as a general outcome, these combinations provide low content of H₂ with large amount of CO₂ which on feeding fuel cell stack, reduces the fuel cell efficiency. Therefore, a recent research debate is emerging over fuel cell grade H₂ production in a compact device. The reformer equipped with H₂ selective membrane provides a compact device to get pure hydrogen stream from the outlet of the reformer. This H₂ stream can be directly sent to PEM fuel cell. In the literature, very few studies are reported which are concerned with the methanol reforming in the membrane reactor [18,19].

The catalytic reformer equipped with H₂ selective membrane increases the methanol conversion by shifting the equilibrium of reforming reaction toward product formation, and thus enhances the production of H₂ [20]. It is known that Pd and Pd-alloy dense membranes are highly hydrogen selective membranes and exhibit good mechanical stability. Alloying Pd with Ag membrane offers high permeation rate of H₂, good stability as well as lower material cost [21]. Removal of H₂ from the reformat gas through H₂ selective membrane increases the conversion of CO via water gas shift reaction to produce more H₂ and thereby reduces the CO concentration. The concentration of CO, however, is far away from the permissible limit. Therefore, preferential CO oxidation (PROX) reactor may be hooked up with the reformer to reduce CO.

In the present modeling work, one dimensional steady state mathematical models have been developed for fixed bed reactor and fixed bed membrane reactor. Three types of reactors namely, fixed catalytic bed reforming reactor, fixed catalytic bed H₂ selective membrane reactor for reforming, and fixed catalytic bed reactor for preferential oxidation of CO are considered. Six reactor configuration modules are selected for simulation where each reactor configuration consists of either one reactor or two reactors with identical dimensions connected in series. The simulations are carried out to

compare the performance of each reactor configuration. Two schemes are explored to identify the possibility of getting either fuel cell grade H₂ with high yield or pure H₂ with high yield in conjunction with emission of exit gases within permissible discharge limits. New corrected H₂ permeation rate through H₂ selective Pd-alloy membrane is incorporated in the model by considering all inhibiting effects of coexisting gaseous components. Additionally, the reactor configuration in which minimum carbon formation occurs on the catalyst has been identified thermodynamically.

2. Kinetic model

Various possible reaction routes have been proposed for converting methanol into hydrogen through many intermediate formation reactions. Katiyar et al. [8] carried out thermodynamic analysis on methanol steam reforming and reviewed the literature to assess the possibility of formation of various intermediates and undesired products such as CH₄, which might depend on the use of various types of catalyst. Highly undesired methanation and carbon formation reactions are found thermodynamically feasible. They identified that the Cu-based catalysts were the most efficient and suitable catalysts for the production of fuel cell grade hydrogen by methanol steam reforming. In view of these findings, most widely accepted route for hydrogen production by methanol steam reforming contains three reactions namely, steam reforming of methanol (SRM), methanol decomposition (MD), and water gas shift (WGS), represented as R₁–R₃ respectively (Table 1). Since undesired methanation reactions responsible for CH₄ production are completely kinetically suppressed on Cu-based catalyst [8], these reactions are not considered in the present study.

Although, many kinetic models for methanol steam reforming on Cu-based catalysts are available in the literature [22–28], the most reliable and widely used intrinsic kinetic model given by Peppley et al. [22] on Cu/ZnO/Al₂O₃ catalyst is considered in the present work. Peppley et al. [22] carried out steam reforming of methanol in a conventional isothermal fixed bed tubular reactor in the presence of Cu/ZnO/Al₂O₃ catalyst with composition as 40/40/20 (wt%). The reactor consisted of 0.30 m long stainless steel pipe with 0.0221 m inner diameter. In order to explain the complete range of observed product compositions in kinetic analysis, three reactions namely steam reforming of methanol, methanol decomposition and water gas shift reactions were included in the kinetic analysis. Although, the methanol decomposition was observed to

Table 1
Reactions and reaction rate expressions for reformer and PROX reactor.

Reactions	Rate expressions	Eq. no.
Reformer (Cu/ZnO/Al ₂ O ₃ Catalyst) [22]		
(R ₁) SRM CH ₃ OH + H ₂ O ↔ CO ₂ + 3H ₂ ΔH _{JT0} = +49.24	$r_1 = \frac{k_1 K_1 (p_{\text{CH}_3\text{OH}} - (p_{\text{H}_2}^3 p_{\text{CO}_2} / K_{R_1, T} p_{\text{H}_2\text{O}})) C_{S1} C_{S1a} S_g}{(p_{\text{H}_2}^{0.5} + K_1 p_{\text{CH}_3\text{OH}} + K_2 p_{\text{CO}_2} p_{\text{H}_2} + K_3 p_{\text{H}_2\text{O}})(1 + K_4^{0.5} p_{\text{H}_2}^{0.5})}$	(1)
(R ₂) MD CH ₃ OH ↔ CO + 2H ₂ ΔH _{JT0} = +90.41	$r_2 = \frac{k_2 K_5 (p_{\text{CH}_3\text{OH}} - (p_{\text{H}_2}^2 p_{\text{CO}} / K_{R_2, T})) C_{S2} C_{S2a} S_g}{(p_{\text{H}_2}^{0.5} + K_5 p_{\text{CH}_3\text{OH}} + K_6 p_{\text{H}_2\text{O}})(1 + K_7^{0.5} p_{\text{H}_2}^{0.5})}$	(2)
(R ₃) WGS CO + H ₂ O ↔ CO ₂ + H ₂ ΔH _{JT0} = -41.17	$r_3 = \frac{k_3 K_1 p_{\text{H}_2}^{0.5} (p_{\text{CO}} p_{\text{H}_2\text{O}} - (p_{\text{H}_2} p_{\text{CO}_2} / K_{R_3, T})) C_{S1}^2 S_g}{(p_{\text{H}_2}^{0.5} + K_1 p_{\text{CH}_3\text{OH}} + K_2 p_{\text{CO}_2} p_{\text{H}_2} + K_3 p_{\text{H}_2\text{O}})^2}$	(3)
PROX Reactor (Pt–Fe–Al ₂ O ₃ Catalyst) [2]		
(R ₄) CO Oxidation CO + 0.5O ₂ ↔ CO ₂ ΔH _{JT0} = -283	$r_4 = 3.528 \times 10^2 e^{(-33.092/RT)} p_{\text{CO}}^{0.5} p_{\text{CO}_2}^{-0.1}$	(4)
(R ₅) H ₂ Oxidation H ₂ + 0.5O ₂ ↔ H ₂ O ΔH _{JT0} = -241.81	$r_5 = 20.53 e^{(-18.742/RT)} p_{\text{O}_2}^{0.5}$	(5)
(R ₆) WGS CO + H ₂ O ↔ CO ₂ + H ₂ ΔH _{JT0} = -41.17	$r_6 = 4.402 \times 10^3 e^{(-34.104/RT)} \left(p_{\text{CO}} p_{\text{H}_2\text{O}} - \frac{p_{\text{CO}_2} p_{\text{H}_2}}{K_{R_3, T}} \right)$	(6)

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