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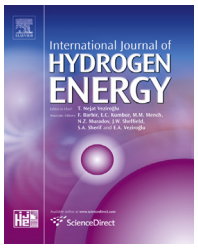

A numerical study of the effectiveness factors of nickel catalyst pellets used in steam methane reforming for residential fuel cell applications

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ABSTRACT

A numerical study is performed to evaluate the effectiveness factors of commercial nickel catalyst pellets commonly used in small-scale steam methane reformers for residential fuel cell applications. Based on the intrinsic reaction kinetics of the steam reforming process, the standard composition of the partially reformed gas mixture is determined as a function of the methane conversion. The heterogeneous reforming reactions inside the spherical catalyst pellets are then modeled by considering the distributed reaction, multi-component diffusion and permeation, and conductive and convective heat transfer in the porous media. Various operating conditions, including the reforming temperature, steam-to-carbon (S/C) ratio, operating pressure, and geometrical parameters, such as the pellet diameter and mean pore size, are simulated. The effectiveness factors calculated for each condition are presented as a function of the methane conversion. Finally, simple correlations for the effectiveness factors are presented, and their accuracies are assessed.

Introduction

The steam reforming of hydrocarbons is currently a primary source of hydrogen for industrial applications. Hydrogen can be produced by large-scale tubular reactors filled with nickel (Ni) catalyst pellets, operating at temperatures between 500 °C and 800 °C and pressures between 20 and 40 bar [1–3]. However, advancements in fuel cell technologies have led to a steady increase in the need for small-scale, distributed hydrogen production by reforming hydrocarbon fuels. For example, residential fuel cells require on-site hydrogen production by reforming natural gas or methane.

A residential fuel cell is a miniature version of combined heat and power (CHP) systems that typically generate approximately 1–3 kW of electricity and a similar amount of heat for household purposes [4–6]. Of the many fuel cell types, polymer electrolyte membrane fuel cells (PEMFCs) are mainly employed in residential fuel cell applications due to their good properties for short-term, repeated operations. In general,

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residential fuel cells are designed to operate with city gas supplied via well-developed pipeline infrastructures. Thus, residential PEMFCs are equipped with fuel processing units to convert methane into hydrogen before the fuel gas enters the fuel cell stack.

The fuel processor for residential PEMFCs is typically composed of four catalytic reactors: the desulfurizer, steam reformer, shift converter, and carbon monoxide (CO) remover [4]. In the desulfurizer, sulfur compounds additives, which are used as odorants, are removed from the city gas to prevent poisoning of the reforming catalyst. Subsequently, methane is converted into hydrogen in the steam reformer via reforming reactions. At this stage, the reformed gas contains approximately 10% CO, and the CO concentration is reduced to 0.5–1.0% in the shift converter through the water–gas shift reaction. The CO concentration should be further reduced to less than 10 ppm to prevent poisoning of the electrochemical catalyst in PEMFCs. This process is performed in the CO remover, which preferentially oxidizes CO into CO_2 with a small amount of oxygen (selective oxidation).

The catalyst pellets used for steam methane reforming are made of nano-sized Ni particles dispersed on porous alumina (Al_2O_3) or spinel ($MgAl_2O_4$) support. The Ni content is typically 7–15% [1–3]. In general, the steam methane reforming is modeled by three global reaction steps: (I) the methane reforming reaction, (II) the water–gas shift reaction, and (III) the reverse methanation reaction. The reforming process is endothermic, indicating that thermal energy is required to convert methane into hydrogen. The intrinsic kinetics determined by Xu and Froment [7] have been widely used to predict the operation of catalytic reformers in fuel cell applications. This kinetic model was also used to determine the effectiveness factors of commercial Ni–$MgAl_2O_4$ pellets under the operating conditions of large-scale industrial hydrogen production [8,9].

The catalyst surface in porous pellets cannot be fully utilized during heterogeneous reactions because the pore structure in the pellets hinders the mass transport. Specifically, heterogeneous reactions at the catalyst surface are retarded because the reactant concentration decreases while the product concentration increases in the interior of the porous pellets. In addition, the temperature inside the pellet also decreases as thermal energy is consumed by the endothermic reaction, further reducing the reaction rate. The effectiveness factor is a dimensionless parameter defined as the ratio of the apparent reaction rate in the pellets to the intrinsic reaction rate [10,11] and thus measures how effectively the catalyst is utilized. The effectiveness factor is generally governed by the relative magnitudes of the reaction and diffusion rates in the catalyst pellets. The effectiveness factor approaches unity for the ideal situation with a high diffusion rate and negligible concentration gradient, indicating full utilization of the catalyst.

For the successful operation of residential PEMFCs, it is important to properly design the reformers for hydrogen production. Numerical and computational fluid dynamics (CFD) simulations have been performed to predict the reformer operation and optimize the reactor design [12–14]. In these studies [12–14], a constant catalyst effectiveness factor between 0.03 and 0.07 is generally assumed for each reforming reaction step because it is impractical, though not impossible, to consider the detailed reaction and diffusion inside the catalyst pellets in the computation. To accurately simulate the steam reforming process in the reformers, the effectiveness factor should be determined accurately as a function of the reforming temperature, pressure, and gas composition. Several studies [8,9,15,16] have investigated the effectiveness factors of commercial Ni catalyst pellets in steam reforming reactions. However, the reforming conditions considered in those studies [8,9,15,16] are significantly different from those employed in reformers installed in residential PEMFCs.

Therefore, this study aims to investigate the effectiveness factors of commercial Ni catalyst pellets under the steam reforming conditions relevant to small-scale hydrogen production for the residential fuel cell applications. The reaction kinetics proposed by Xu and Froment [7] are employed to determine the intrinsic reaction rate on the Ni catalyst surface. The dusty-gas model is employed to calculate the multicomponent diffusion, Knudsen diffusion, and viscous flow inside the spherical, porous catalyst pellets. The conductive and convective heat transfer in the pellets is also considered to account for the endothermic nature of the steam reforming process. The effectiveness factors are obtained as a function of the methane conversion for various operating conditions and geometrical parameters. In particular, the reforming temperature, steam-to-carbon (S/C) ratio, operating pressure, pellet diameter, and mean pore size are varied. In addition, simple correlations are proposed to estimate the effectiveness factors with reasonable accuracy, which can be used in numerical simulations to design and optimize compact reformers for residential fuel cell applications.

Theory and calculation

Physical model

Fig. 1(a) presents a typical compact reformer for steam methane reforming, which consists of spherical catalyst pellets packed in a cylindrical container. Randomly packed, equal-sized spherical particles have a bulk porosity of around 0.4 [17]. A preheated mixture of methane and water vapor (steam) with a specified S/C ratio flows through the packed bed reactor. Due to the highly endothermic nature of the

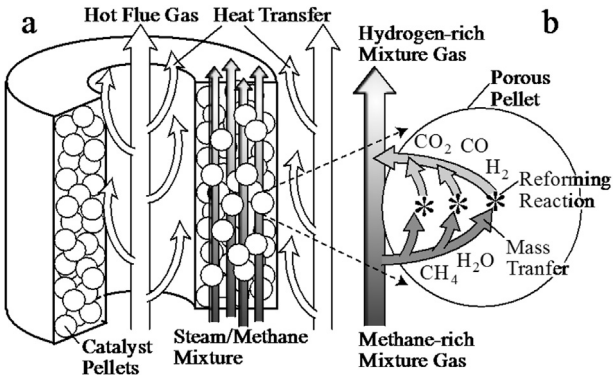

Fig. 1 – Schematic of the (a) overall operation of and (b) pellet processes in a compact steam methane reformer.