Computational fluid dynamics study of hydrogen generation by low temperature methane reforming in a membrane reactor

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ABSTRACT

Concentrated solar energy can be used to drive highly endothermic reactions, such as methane reforming. An attractive route is the parabolic trough technology, which is mature and relatively inexpensive but limited to temperatures below 600 °C, when methane conversions are low. However, high conversions are achievable if hydrogen is continuously removed from the reactive stream by a membrane selective to hydrogen. In this study, low temperature methane reforming in a membrane reactor is analyzed numerically by computational fluid dynamics over a wide range of operating parameters. Effects of temperature, steam-to-carbon ratio and space velocity on conversion, hydrogen recovery and carbon monoxide selectivity are specifically investigated. Our results show that concentration polarization can be significant. Below 500 °C the reactor performance is kinetically limited by the reforming reaction, while above this temperature hydrogen separation is a limiting factor. High hydrogen recovery is achievable even at high, industrially relevant space velocities. Importantly, hydrogen separation enhances water gas shift, reducing the concentration of carbon monoxide, the main source of coke formation at low temperatures.

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Introduction

Most of the energy used worldwide is derived from fossil fuels by direct combustion, leading to excessive emission of carbon dioxide (CO_2) that contributes to global warming [1]. An alternative fuel is hydrogen (H_2) that have several advantages over fossil fuels, such as clean and more efficient combustion, and can be used for highly efficient and environmentally friendly electricity generation using fuel cells [2]. Hydrogen is also an important chemical feedstock with applications ranging from desulfurization, hydro treating, petroleum refining and production of chemicals [3]. Hydrogen is typically produced from hydrocarbons (mostly natural gas) by partial oxidation, autothermal reforming, dry reforming or steam reforming. Electrolysis can be used to generate H_2, but currently is too expensive to be deployed at large scale [4]. Among all methods mentioned above, steam methane (CH_4) reforming (SMR) is the cheapest and the most widely used method to produce H_2 on a commercial scale [5]. The use of steam as an oxidant is advantageous and relatively high H_2-to-carbon monoxide (CO) ratios obtainable by SMR are favorable for H_2 production [6].

The process of CH_4 reforming by steam can be described by the following reactions:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H^{\circ}_{298} = 206 \text{ kJ/mol} \qquad (1)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H^{\circ}_{298} = -41 \text{ kJ/mol} \qquad (2)$$

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \qquad \Delta H^{\circ}_{298} = 165 \text{ kJ/mol} \qquad (3)$$
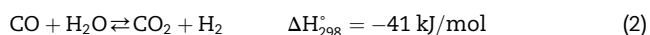
Reaction (1) is SMR, reaction (2) is the water gas shift (WGS), and reaction (3) is the overall process, which is reversible (H_2 generation is favored at low pressures) and highly endothermic, requiring large heat inputs. In commercial installations, reformer tubes containing a Ni-based catalyst are heated by burning a fraction of natural gas (ca. 30%) and the CO produced is reacted with steam at lower temperatures in downstream WGS reactors catalyzed by Fe and Cu catalysts to produce more H_2. To prevent coking, high steam-to-carbon ratios are required for SMR (ca. 2–4), since running the process with stoichiometric feed composition leads to severe coking deactivation of Ni-based catalysts [7]. Nonetheless, Ni is inexpensive and features reasonably high catalytic activity. Platinum group metals have been also identified as excellent reforming catalysts but their implementation is hindered by the exceedingly high cost associated with current catalyst formulations that feature prohibitively high metal loadings (typically ranging from 1 to 5 wt%). Progress toward the use of platinum group metals for low temperature SMR was outlined in a recent review [8].

An attractive route to produce H_2, reduce CO_2 emissions, and save the otherwise combusted fraction of CH_4, is to use concentrated solar energy to provide the heat required for SMR [9–12]. This way, solar energy is used to upgrade the energy content of the hydrocarbon feedstock (e.g. natural gas) by converting it to a "solar" fuel consisting of a mixture of H_2 and CO (syngas) or H_2 (if additional steps of WGS and/or purification are implemented). The resulting "solar" H_2 can be used as a fuel for electricity generation in gas turbines or as a

chemical feedstock. The high temperatures required for SMR historically limited the choice of a solar concentrator to solar dishes and central receivers [9–12] that have limited economic viability due to high capital costs. An alternative route is to use the mature and relatively inexpensive parabolic trough technology that can provide temperatures of ca. 400–600 °C when molten salts are used as heat carriers. In addition to high operational temperature, molten salts have other important advantages over conventional heat carriers such as steam and mineral oils, including low operational pressure, high heat capacity and density, high heat transfer coefficient and non-flammability. The solar heat is applied to the reformer indirectly, through the molten salt heat transfer fluid [13–16]. However, these temperatures are well below the operating temperature of conventional SMR reformers (850–950 °C). Therefore, to apply parabolic trough technology to SMR, it is critical to design an appropriate reforming system that can operate effectively at temperatures below 600 °C.

To overcome the thermodynamic limitations on CH_4 conversion imposed by low operating temperatures, membrane reformers can be implemented to continuously remove H_2 from the reactive stream and to shift the equilibrium towards the formation of products according to Le Chatelier's principle [17–21]. In a membrane reformer, complete CH_4 conversions are achievable well below 600 °C [22], thereby enabling the use of parabolic troughs for solar thermal SMR. The selective removal of H_2 can be effectively done by means of palladium (Pd)-based membranes, which are permeable exclusively to H_2 [23,24]. Though the cost of Pd is a prohibitive factor, recent developments provide a potential for mass production of Pd-based membranes at economically feasible costs [20]. Importantly, there is no additional energy investment for creating a pressure drop required to effectively separate H_2 by a Pd membrane (ca. 10 bar), since natural gas is already at pressures that exceed by far this requirement. In a recent experimental work reported by Patrascu and Sheintuch, SMR in a Pd membrane reformer designed specifically for solar thermal applications using molten salts as heat carriers was studied [25]. The reformer was packed with the Pt–Ni/CeO_2 catalyst supported on the SSiC ceramic foam (to improve heat transfer) and the membrane area was 175 cm^2. As a first step, the reformer was heated by an electrical furnace. Over 90% CH_4 conversion and over 80% H_2 recovery were achieved at 525 °C.

The separation characteristics of Pd-based membranes and their implementation in membrane reactors have been thoroughly investigated [20–24,26–30]. Goto et al. [28] studied H_2 permeation rate through a composite membrane with a Pd film coated on a porous ceramic tube and defined a numerical model based on the combined resistances of the Pd film and the composite support. Coroneo et al. [26,27] investigated mass transfer characteristics of Pd–Ag membrane H_2 separation modules experimentally and numerically using Computational Fluid Dynamics (CFD). Though porous ceramic membranes provide higher permeabilities, dense Pd membranes perform much better in SMR due to their exceptional selectivity. Uemiya et al. [17] compared the SMR performance of a supported Pd membrane and a porous Vycor glass membrane in a membrane reactor in a temperature range of 623–773 K. While the Pd membrane efficiently exceeded the equilibrium conversion, only a small change in equilibrium