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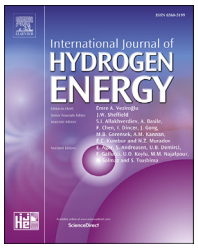

# A two-dimensional mathematical model for the catalytic steam reforming of methane in both conventional fixed-bed and fixed-bed membrane reactors for the Production of hydrogen

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ABSTRACT

A modelling and simulation study of catalytic steam reforming of methane is presented in this paper. A two-dimensional pseudo-heterogeneous model is developed to simulate a conventional fixed-bed reactor (FBR) as well as a fixed-bed membrane reactor (FBMR) with sweep gas added in both co-current modes for the two reactor configurations. The developed model is based on mass and energy balance equations for the catalyst phase and the gas phase in both FBR and FBMR reactors. Firstly, a study is done for describing that the temperature profiles of gaseous and solid phases reach to stable state as well as the component distributions in the two FBR and FBMR reactors. The model covers the aspect of the partial pressure of hydrogen in the membrane reactor with the permeation of hydrogen across a Pd-based membrane. The conversion of methane is significantly enhanced by the partial removal of hydrogen as from the shell side as a result of diffusion through the Pd-based membrane. Simulation results demonstrated that methane conversion of 97.21% can be achieved in FBR at operating temperature of 1250 K relative to methane conversion of 99.79% to 923 K in FBMR. The yield of hydrogen achieved to level from 2.154 in FBR at operating temperature of 1250 K while the yield of hydrogen reached to level from 3.731 with a thickness from 1.7 μm in FBMR reactor.



## Introduction

Steam reforming's process of light hydrocarbons has been extensively applied for industrial production of hydrogen and/or syngas. Among different hydrocarbons, methane is the most important because of plentiful resources, high energy density, ready availability and widely distributed network. Catalytic steam reforming of methane (CSRM) is nowadays considered the main process used to produce hydrogen [1–3]. Hydrogen will be the clean, efficient and pollution-free energy source in the close future. Therefore, great attention has been given to hydrogen production technology in order to obtain a stable source for hydrogen [4–6]. In conventional technology, CSRM is carried out by using multitubular fixed-bed reactors (FBRs) [7]. Due to the endothermicity of the reforming

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reactions; high temperatures favour the process [8,9]. Usually, the exit temperature from the conventional FBR is around of 850–980 °C. For this reason, the conventional reforming reactors are operated at very high temperatures imposing strong limitations for the materials employed in the reactor and using large amounts of energy for heating [10,11].

There are growing interests worldwide over climate change and greenhouse gas emissions. Environmental problems derived from different energy generation sources and the fossil fuels prices have enhanced the development of new technologies for energy production [10,12–14]. The significant diminution of carbon-dioxide ($CO_2$) emissions in energy production and fuels are requisite to ensure sustainable developments [15]. Hydrogen is also a major industrial commodity that is used as an intermediate in great number chemical processes, for example, in production of ammonia and methanol [16–20]. Most of the world's hydrogen is produced at large petroleum and chemical plants by steam reforming and/or partial oxidation of natural gas in FBRs, coupled with pressure swing adsorption (PSA) for hydrogen purification [21–25]. In steam reforming process, methane reacts with steam in the FBR and/or in the fixed-bed membrane reactor (FBMR) to produce a gas mixture of methane ($CH_4$), water ($H_2O$), hydrogen ($H_2$), carbon monoxide (CO) and dioxide carbon ($CO_2$).

Modelling is useful to investigate the effects of key operating parameters, optimization, and scale-up. The performance of the reactor systems can be explored beyond the range of parameters that can be studied experimentally due to limitations imposed by economic and safety considerations [8,9,26–30]. Physical and chemical parameters should be simultaneously of coupled way from the mathematical model (Such as fluid-solid mass transfer, fluid-solid heat transfer, adsorption and desorption, and chemical reactions). There are hydrodynamic and kinetic models describing the physical and chemical phenomena in both FBR and FBMR reactors. The hydrodynamic models should explain the physical phenomena while the kinetic model should analyze the chemical phenomena occurring in chemical reactors [31–33]. In this context, the mathematical models can be used to evaluate to high complexity in the hydrodynamic and non-ideality in chemical reactor processes.

FBMRs are largely applied for hydrogen production. Recently, numerous works have been available in the literature for describing on the advances, on catalyst, and reactor configuration [34–40]. As an intensification setup, the FBMR can be used to combine the autothermal reforming (ATR) process and water-gas shift process with a compact configuration integrating permselective membrane layer. Some concepts were experimentally studied with different operating parameters, i.e., operating temperature, operating pressure, and steam/carbon ratio [41–44]. As a typical condition, the thermodynamic equilibrium analysis (in FBMRs) provides a simple and direct basis for process practical applications. In addition, when the process achieves the thermodynamic equilibrium, the Gibbs free energy of the product gas reaches a minimum. In case of the reforming processes for hydrogen production, the insertions of permselective membranes can shift the equilibrium due to continuous removal of hydrogen [8,45–47]. For FBMRs, the permeation rate's importance on the diffusion rate needs to be included to account for radial gradients because of the effect of concentration polarization in the vicinity of the membrane.

When a gas mixture is conducted to a membrane surface by any driving force, there is an accumulation of the less permeable chemical species and a depletion of the more permeable chemical components in the boundary layer adjacent to the membrane. This phenomenon causes a concentration polarization gradient building up in the boundary layer [48–50]. From the point of theoretical view, the concentration polarization exists in all membrane separation processes due to the selective permeability of membrane [51,52]. The concentration polarization is often underestimated phenomenon affecting the membrane processes [50,53–56]. In general, the polarization effect is gradually stronger for increasing membrane selectivity and permeance. Especially in the past few years, the progress in membrane materials, membrane modifications and fabrication technology has substantially improved membrane separation properties [57–60]. The high performance membranes have great potential in various gas separation applications at industrial level and would be expected to experience the concentration polarization effect in their application [61,62]. In this context, robust mathematical models (2D-dimensional) to study the concentration polarization profiles for gas separation membrane processes have not been studied well. For this reason, a 2D approach able to systematically take into account this phenomenon is approached in this work.

The most of the researches have been experimentally and numerically investigated to produce $H_2$ at high temperature exceeding 700 °C [63–66]. The main focus of the experimental studies was to develop the robust catalysts which are resistant for carbon deposition [67,68]. On the one hand, Industrial conventional FBRs are operated between 808 and 3535 kPa and 1073–1273 K, but the equilibrium-limited process can reach a conversion of methane of about 93%. On the other hand, applications of FBMRs offer a possible form to overcome this limitation by selectively removing hydrogen from a selective membrane system resulting in higher conversions of methane at lower temperatures [69,70]. The most commonly used membranes for removing hydrogen are dense palladium membranes or silver-palladium membranes [57,71–73]. These membranes offer high selectivity over other gases because of the selective dissolution of hydrogen atoms into the metal matrix.

In this work, we present a 2D-dimensional pseudo-heterogeneous modelling to mathematically simulate the CSRM process in both FBR and FBMR reactors. Based on the energy and mass equations as well as the equations of i component balances, a mathematical model was developed for describing the governing equations of the energy and i component balances for the two FBR and FBMR reactors. Simulations performed from the governing equations provide the performance of the CSRM process in both FBR and FBMR reactors with a nickel catalyst. The performance of above reactors has been analyzed in terms of temperature profiles (at the surface of the solid phase and gas phase for two reactors), methane conversion at different temperatures, hydrogen production and the distribution of $CH_4$, $H_2O$, $H_2$, CO and $CO_2$ in the two reactors.