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# Modelling of packed bed membrane reactors for autothermal production of ultrapure hydrogen

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## Abstract

The conceptual feasibility of a packed bed membrane reactor for the autothermal reforming (ATR) of methane for the production of ultrapure hydrogen was investigated. By integrating $H_2$ permselective Pd-based membranes under autothermal conditions, a high degree of process integration and intensification can be accomplished which is particularly interesting for small scale $H_2$ production units. A two-dimensional pseudo-homogeneous packed bed membrane reactor model was developed that solves the continuity and momentum equations and the component mass and energy balances. In adiabatic operation, autothermal operation can be achieved; however, large axial temperature excursions were seen at the reactor inlet, which are disadvantageous for membrane life and catalyst performance. Different operation modes, such as cooling the reactor wall with sweep gas or distributive feeding of $O_2$ along the reactor length to moderate the temperature profile, are evaluated. The concentration polarisation because of the selective hydrogen removal along the membrane length was found to become significant with increasing membrane permeability thereby constraining the reactor design. To decrease the negative effects of mass transfer limitations to the membrane wall, a small membrane tube diameter needs to be selected. For a relatively small ratio of the membrane tube diameter to the particle diameter, the porosity profile needs to be taken into account to prevent overestimation of the $H_2$ removal rate. It is concluded that autothermal production of $H_2$ in a PBMR is feasible, provided that the membranes are positioned outside the inlet region with large temperature gradients.

*Keywords:* Modelling; Membranes; Packed bed; Chemical reactors; Hydrogen; Autothermal operation

## 1. Introduction

Production of ultra pure hydrogen for use in downstream polymer electrolyte membrane fuel cells (PEMFC) for small or medium scale applications is gaining increasing interest in recent years. On increasing scale, fuel cells are applied in the automotive industry and for distributive power generation, because of the high energy efficiency of the combination of an electromotor with hydrogen powered fuel cells (overall efficiency 38–46%) compared to the overall internal combustion engine efficiency (10–30%) (Witjens, 2004). For small scale applications (< 250 kW) in transportation or household power supply (Carrette et al., 2001) the main advantages of the PEMFC over the other types of fuel cells are its compactness, high energy density, quick start-up and response time and low operating temperature. However, ultra pure hydrogen (< 10 ppm CO) is required because of the sensitivity of the anode catalyst in the PEMFC to CO poisoning. A PEMFC can be powered directly by hydrogen or by hydrogen that is produced on site from a suitable hydrocarbon feedstock such as gasoline, natural gas and methanol (Gallucci et al., 2004; Hoang and Chan, 2004). Use of pure hydrogen as the energy carrier requires an expensive hydrogen-fuelling network leading to high costs in the fuel delivery system. Moreover, the low volumetric energy density of hydrogen at ambient conditions makes hydrogen storage uneconomical. Therefore, on site hydrogen generation from a hydrocarbon feedstock is preferred.

Hydrogen is traditionally produced via multiple reaction steps as a primary product from steam reforming of hydrocarbons such as methane, naphtha oil or methanol (Bharadwaj and

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Schmidt, 1995; Rostrup-Nielsen, 1984, 2002). On an industrial scale, most of the hydrogen is currently produced by steam reforming of natural gas. With classical steam reforming of methane (SRM) high hydrogen yields can be achieved, however, at the expense of costly high temperature heat exchange equipments and complex energy integration between a large number of process units, including reformer, high and low temperature shift reactors (HTS and LTS) and a preferential oxidation reactor (PrOX). Moreover, often a pressure swing adsorption (PSA) unit is used to achieve the desired hydrogen purity. For the production of ultra pure hydrogen for small scale applications, this route is not preferred because of the large number of process units and the associated uneconomical downscaling. A high degree of process integration and process intensification can be accomplished by integrating hydrogen permselective membranes (Adris et al., 1991; Kikuchi, 1995) in the steam reformer. Via the integration of hydrogen permselective membranes, the number of process units can be decreased and the total required reactor volume can be reduced, while higher methane conversion and hydrogen yields beyond thermodynamic equilibrium limitations can be achieved, at lower temperatures and with higher overall energy efficiencies.

Steam reforming is a highly endothermic process at elevated temperatures and requires costly external high temperature heat exchange equipment or expensive non-adiabatic reactors in order to supply the required reaction energy, which is very energy inefficient for small scale applications and adds to the complexity of the system (Hoang and Chan, 2004; Lattner and Harold, 2004). Autothermal operation with maximum hydrogen yields without external or internal heat exchange can be accomplished through a combination of steam reforming and partial oxidation. By co-feeding air or pure oxygen, part of the methane is oxidised, which generates the required reaction energy for the steam reforming in situ. This process is known as autothermal reforming (ATR). Use of air as the oxidant for the (partial) oxidation will dilute the products with nitrogen, which increases the required reactor volume and hydrogen membrane surface area. Moreover, in view of the ever-increasing environmental restrictions, the production of hydrogen from natural gas or lower hydrocarbons for use in fuel cells should ideally be realised without carbon dioxide emissions. The costly carbon dioxide sequestration due to the dilution of the products with nitrogen can be avoided by using pure oxygen instead of air as the oxidant in the oxy-steam reforming process. Depending on the type and scale of the application, pure oxygen—typically obtained via expensive cryogenic air separation—or air will be used. Although overall autothermal operation can be achieved by combining the steam reforming with the (partial) oxidation of methane, large temperature excursions close to the reactor inlet have been observed in a conventional fixed bed reactor for ATR (Ioannides and Verykios, 1998) attributed to the higher reaction rate of methane oxidation compared to the SRM. These observations have also been supported by modelling studies of partial oxidation and reforming reactions of methane (De Groote and Froment, 1996; De Smet et al., 2001). Integration of Pd based hydrogen permselective membranes in a packed bed membrane reactor for the ATR of methane should, therefore, be carried out with careful consideration of the thermal-mechanical stability of these membranes. In this study, the conceptual feasibility of packed bed membrane reactors (PBMR) for ATR of methane is investigated by means of detailed reactor simulations. To the authors' knowledge the application of PBMRs for the ATR of methane has not yet been investigated.

Many studies concerning the modelling of PBMRs have employed 1-dimensional (1D) reactor models. With these 1D models, the enhancement of the reactor performance via insertion of hydrogen permselective membranes has been demonstrated for dehydrogenation reactions, especially the dehydrogenation of ethylbenzene (Assabumrungrat et al., 2002; Basile et al., 2001; Itoh, 1987), but also for the SRM. For the SRM, Barbieri and Di Maio (1997) have demonstrated the benefits of integrating hydrogen permselective membranes with an isothermal and isobaric 1D reactor model, while Kim et al. (1999) have used a 1D non-adiabatic model, also accounting for the axial pressure drop. In these 1D models, radial gradients in the temperature and concentrations are neglected and plug flow conditions are assumed. Simulation studies of PBMRs for the dehydrogenation of ethylbenzene and cyclohexane have already shown the necessity of accounting for radial non-uniformities, especially because of the removal of hydrogen via the membranes and especially when employing membranes with a high permeability (Fukuhara and Igarashi, 2003; Itoh et al., 1994; Koukou et al., 1997; Kürten, 2003; Mondal and Ilias, 2001).

In this paper, the feasibility of integrating Pd-based membranes in an autothermal methane steam reformer for the production of ultra pure hydrogen is investigated by means of detailed reactor simulations. A two-dimensional, pseudo-homogeneous reactor model has been developed to calculate the axial and radial temperature and concentration profiles in the PBMR. The extent of temperature excursions close to the inlet of the reactor is investigated and different options to moderate these temperature peaks to prolong membrane tube life are evaluated, viz. cooling with sweep gas and staged oxygen injection. Furthermore, it is investigated whether and to what extent mass and heat transfer limitations affect the performance of the PBMR. To avoid the detrimental effects of radial mass transfer limitations in PBMRs, often a very small membrane tube diameter needs to be selected. In a PBMR with relatively large particles relative to the membrane tube diameter, a bypass flow can emerge near the membrane wall. Hydrogen is selectively withdrawn in this region of increased bed porosity and increased axial velocity reducing the contact time of the gas mixture in the catalyst bed near the membrane wall. In order to evaluate the extent of this effect, the description of the two-dimensional flow field is included in the PBMR model, following Kürten et al. (2003).

## 2. Reactor model

The packed bed membrane reactor studied, consists of a tubular, steel supported Pd-Ag membrane filled with a reforming catalyst, as schematically depicted in Fig. 1. Hydrogen is selectively withdrawn to the shell side either via a (reactive) sweep gas or by applying a vacuum. In this study the shell side was