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H_2 production with low carbon content via MSR in packed bed membrane reactors for high-temperature polymeric electrolyte membrane fuel cell

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HIGHLIGHTS

- H_2 removal diminishes the backward reaction and increases the residence time.
- Selective CO_2 removal has low effect on the CH_3OH conversion compared to H_2 removal.
- IL membranes for MSR intents require minimum permeance of $\geqslant 1 \times 10^{-6}$ mol s^{-1} m^{-2} Pa^{-1}.
- IL-based PBMRs are easier to operate and have low energy consumption.

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ABSTRACT

This work compares the hydrogen purity and recovery produced by a methanol steam reforming (MSR) packed bed membrane reactor (PBMR) equipped with a membrane selective to hydrogen (Pd-Ag) and with a membrane selective to carbon dioxide (porous membrane filled with ionic liquids-ILs). A 3-dimensional non-isothermal PBMR model was developed in Fluent (Ansys™) for simulating a PBMR equipped with these two types of membranes and simulating a conventional packed bed reactor (PBR). For the development PBMR models a MSR mechanistic kinetic model was fitted to experimental reaction rates of a commercial catalyst (BASF RP60). The results indicated that selective hydrogen removal from the reaction medium originates a significant increase in the methanol conversion, while the carbon dioxide removal has a smaller effect. CO_2-PBMR showed to be more efficient in terms of energy consumption than H_2-PMBR. The simulation results showed also that ILs membranes must have a minimum permeance of $\geqslant 1 \times 10^{-6}$ mol s^{-1} m^{-2} Pa^{-1} and CO_2/H_2 selectivity of $\geqslant$200 at 473 K to be attractive for this type of applications. The advantages and limitations of each reactor configuration are discussed based on experimental and simulated data.

1. Introduction

Hydrogen is an important energy carrier. However, it has a very low volume energy density and shows limitations regarding storage and transportation. As an alternative, internal reforming or hydrogen production *in-situ* from fuels such methane, methanol or ethanol are being considered [1–3]. High temperature polymer electrolyte membrane fuel cells (HT-PEMFC) based on PBI membranes, can be directly fed with methanol steam reforming (MSR) reformate, since this device can tolerate CO concentrations up to 0.3% [4]. The integration of hydrogen production *in-situ* by methanol steam reforming (MSR) with HT-PEMFC is already used in power supplies manufactured by few companies such as Ultracell [5], and Serenergy [6]. However, the presence of contaminants in the reformate stream (CO_2, H_2O, CH_3OH and CO) can affect the performance of the HT-PEMFC specially at high current densities, while feeding a HT-PEMFC with a purified hydrogen stream allows higher performance and lower hydrogen stoichiometry [7,8].

Membrane reactors have been successfully applied for hydrogen production and purification to few reactions: WGS reactions and hydrocarbon steam reforming [9–13]. Membranes for hydrogen production via steam reforming are typically based on palladium or palladium alloys due to their high selectivity to hydrogen and very high permeability [9,14–16]. One of the most remarkable procedures to produce Pd-alloy membrane was developed by SINTEF using a two-steps sputtering technique, enabling the production of a defect–free Pd-alloy film with a

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nominal thicknesses ranging from 2.2 to 10.0 μm [17,18]. These defect–free Pd-alloy membranes can deliverer ≈100% pure hydrogen at the permeate side with very high permeability (10^{-8} mol m m^{-2} s^{-1} $Pa^{0.5}$ at 573 K) and applied to reactors with a configuration suitable for a specified reaction where mass transfer limitations (polarization of the concentration) in the gas phase can also be reduced [18–20]. Performing the reaction of methanol steam reforming using Pd-alloy membranes in packed bed membrane reactors (PBMR) besides the hydrogen purification, benefits the selective removal of hydrogen from the retentate side (reaction bulk), which increases the methanol conversion by hindering the backward reaction [16,21]. The methanol steam reforming reaction using $Cu/ZnO/Al_2O_3$ catalysts, however, is typically performed at temperatures between 473 K and 533 K [22], lower than the optimum temperature for PgAg membranes to operate (573–673 K). Low temperatures lead to lower membrane permeability and the presence of CO in the reformate steam can adsorb on the membrane surface decreasing the hydrogen permeation flux [23].

The hydrogen purification for HTPEMFC applications can also be achieved by removing the CO_2 and condensable components from the reformate stream. Katiyar et al. [24] performed a thermodynamic analysis of the MSR reaction with and without fractional removal of hydrogen and carbon dioxide using an adsorptive reactor, a membrane reactor or an adsorptive-membrane reactor. These authors concluded that carbon dioxide removal has positive effect on the performance of the reformer and is more suitable for fuel cell applications. However, adsorbents such as zeolites or activated carbons adsorb also MSR reactants; *e.g.* zeolites are quite selective to the methanol adsorption. On the other hand, ILs membranes are very promising for producing HT-PEMFC grade hydrogen exhibiting high selectivity and permeability to carbon dioxide [25–27]. ILs membranes have been proposed as an effective process for the selective separation of different chemical species in dilute streams. Ionic liquids present very low vapour pressure, high stability at temperatures up to 573 K [28] and their solubility in the adjacent phases can be minimizing by selecting the adequate cation and anion [25]. CO_2/CH_4 and CO_2/N_2 separations have been performed successfully using ILs membranes; e.g. ionic liquids [emim+][BF_4] and [emim+][Tf_2N−] showed selectivities to carbon dioxide, 27 and 21.2 respectively [28]. On the other hand, Kasahara et al. [29] obtained one of the highest permeabilities to carbon dioxide, 14,000 Barrer, and a very high CO_2/N_2 selectivity, 100, using a membrane of tetrabutylphosphonium proline-based. Also, many ILs show higher permeabilities to carbon dioxide than to hydrogen namely [bmim+][BF_4−] that has a selectivity of $CO_2/H_2 = 11$ [30]. Other results show that permeability increases with the temperature and decreases with the increase in transmembrane pressure; furthermore, ILs membranes exhibit relatively long-term permeation stability [28].

IL membranes have not yet been considered for hydrogen production via LT-MSR in a PBMR. However, using these membranes may allow producing high-grade hydrogen via low temperature methanol steam reforming (LT-MSR) compared to traditional PBR and Pd-based PBMR [21,24]. In the present study, a CFD analysis of methanol steam reforming with hydrogen or carbon dioxide selective removal, using membrane reactors, is presented and compared with a conventional packed bed reactor (PBR). A methanol steam reforming mechanistic kinetic model was fitted to experimental reaction rates obtained using a commercial CuO/ZnO/Al2O3 catalyst operating at low temperatures (453–513 K). For the first time, IL membranes have been considered for hydrogen purification in PBMR performing the methanol steam reforming. IL membranes were found to be potentially able of selectively remove the carbon dioxide from the reaction bulk producing a HT-PEMFC grade H_2 with minimal carbon content. The required specifications of the IL membranes for hydrogen purification in a PBMR were obtained, based on a three-dimensional non-isothermal PBMR model developed on Fluent. The temperature, pressure, flow rate of reactants and sweep gas role on the performance of the PBMR has been investigated.

2. CFD model

A PBMR 3-dimensional model (Fig. 1) was developed and implemented in commercial software Fluent, Ansys™. The model describes a tubular shell with 50 mm of length and 20 mm of outer diameter, housing a tubular selective membrane with 50 mm of length and 10 mm of inner diameter, as shown in Fig. 1. The membrane was assumed impermeable for simulating the PBR, permeable to hydrogen for the H_2-PBMR, and permeable to carbon dioxide and to hydrogen, with different selectivities, for the CO_2-PBMR. The model was validated with data collected from the literature.

2.1. Membrane

At constant temperature the permeation flux can be expressed as:

$$J_i = \frac{P_e}{\delta}\left(p_{i,ret}^{1/n} - p_{i,perm}^{1/n}\right) \tag{1}$$

where J_i is the molar flux of species *i*, P_e is the membrane permeability, δ is the membrane thickness and $p_{\mathrm{i,ret}}$ and $p_{\mathrm{i,perm}}$ are the partial pressure in the retentate and permeate sides, respectively.

For Pd-Ag membranes *n* was assumed to be equal to 2, since hydrogen has a dissociative sorption on the palladium surface; with *n* equal to 2, Eq. (1) renders the Fick-Sieverts equation. For ILs membranes *n* is equal to 1. P_e follows the Arrhenius equation behaviour (Eq. (2))

$$P_e = P_{e_o} e^{-\frac{E_a}{RT}} \tag{2}$$

where P_{e0} is the pre-exponential factor, E_a is the activation energy, *R* is the ideal gas constant and *T* is the temperature.

The Pd-Ag membrane was considered only permeable to hydrogen and the permeation parameters were obtained from Ghasemzade et al. [14]. The membrane tested by Ghasemzade et al. [14] is thicker than the ones reported by SINTEF [18,19], although it shows one of the highest permeabilities to hydrogen reported in the literature [16]. The permeation parameters of the IL membrane were obtained from Shimoyama et al. [31], which considered a membrane impregnated with [bmim][Tf2N] contacting a humidified carbon dioxide stream. Table 1 shows the permeation values used for modelling the methanol steam reforming reactors.

2.2. Kinetic model

The kinetic model suggested by Peppley et al. [32] based on a steady-state analysis of the surface reaction mechanisms was used in this work for describing the MSR reaction. The kinetic parameters obtained by Peppley for catalyst BASF K3-110, did not provide a good agreement with experimental results for BASF RP60 catalyst, especially for low temperatures; BASF RP60 catalyst was considered in the present study and show to be more active than BASF K3-110. Despite the higher catalytic activity of the BASF RP60, the MSR reaction should follow the same mechanism as the presented by Peppley et al. [32] for the BASF K3-110. The new kinetic parameters were estimated based on the experimental results obtained with a tubular packed bed reactor (Table 2). The reaction was considered rate limited, since catalyst powders with particle size between 100 and 250 μm were used to minimize the mass transfer of reactants between the bulk fluid and catalytic surface. The