

The best hydrogen membranes deserve the best reactors

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The recent availability of ultra thin, highly permeable and highly selective H₂ membranes has led to the development of novel membrane reactor concepts for the production of ultra-pure hydrogen. Integrating these membranes in a reactor can result in a large degree of process integration and intensification. Our research has focused on novel reactor configurations which decrease the amount of membrane area required for a target hydrogen production, minimize heat and mass transfer limitations and, when possible, also attain an integrated CO₂ capture.

Production of ultra-pure hydrogen by reforming of methane has been evaluated in both fluidized bed (FBMR) and packed bed membrane reactors (PBMR). The results show that the PBMR requires significantly more (in some conditions twice) the membrane area compared to FBMR thanks to the excellent bed-to-membrane mass transfer in fluidized beds. High performance membranes should therefore be integrated into fluidized bed membrane reactors.

Introduction

Most of the hydrogen today is produced by steam reforming of methane. This process consists of feed gas preheating and pre-treatment, primary and secondary reforming, high and low temperature shift conversion, CO₂ removal and methanation. Often Pressure Swing Absorption is used to achieve the desired hydrogen purity. Steam reforming is highly endothermic, therefore, and in view of thermodynamic limitations, heat transfer must take place at high temperatures (850-950°C). An excess of steam is used to avoid carbon deposits (typical feed H₂O/CH₄ molar ratios of 2 to 5).

A high degree of process integration and process intensification can be obtained by integrating hydrogen

perm-selective membranes in the steam reformer. The number of process units can be sharply decreased and the total required reactor volume can be much reduced, while higher methane conversions and hydrogen yields beyond thermodynamic equilibrium limitations can be achieved, at lower temperatures and with higher overall energy efficiencies. Both packed bed membrane reactors and fluidized bed membrane reactors for the reforming of methane (see Fig.1) have already been described qualitatively in the literature and pros and cons of both concepts have been discussed. In this paper a direct quantitative comparison between the two concepts has been made using detailed theoretical models for ultra-pure hydrogen production via methane reforming.

Reactor configurations

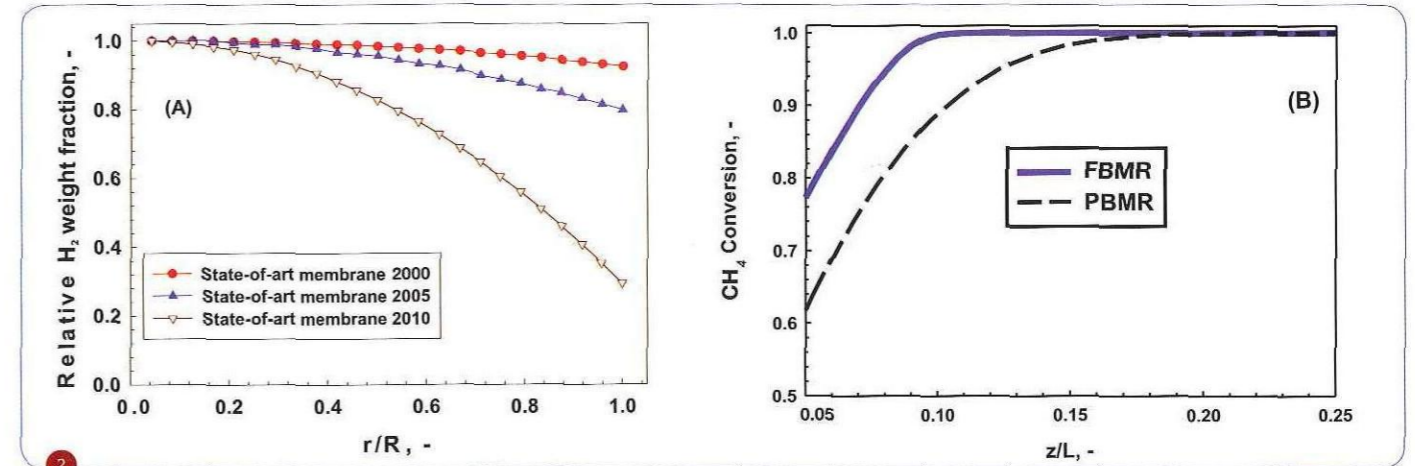
Packed bed membrane reactor

In this work the typical tube-in-tube packed bed membrane reactor configuration (Fig 1 A) was considered. A detailed 2D model was used in order to identify the extent of bed-to-membrane mass transfer limitations (also known as concentration polarization) and their effect on the reactor performance. Membrane research has produced thinner membranes with higher hydrogen permeability which will result (Fig. 2A) in higher mass transfer limitations in packed bed membrane reactors (even with small reactor diameters) and consequently in larger membrane area required for the same hydrogen separation. Moreover, packed bed reactors are always non-isothermal, where the first part of the reactor has a lower temperature, resulting in lower reaction rates and lower permeation rates through the membrane.

Fluidized bed membrane reactor

In a typical fluidized bed membrane reactor (Fig 1B), pure hydrogen is recovered by Pd-based membranes inserted into the fluidized catalyst bed. A virtually isothermal condition can be achieved and bed-to-

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Relative H₂ weight fraction for the isothermal packed bed for different membranes (A) and comparison between conversion in a staged fluidized bed and a packed bed equipped with the same membrane area (B)

membrane mass transfer limitations are largely avoided due to the strong catalyst circulation inside the reactor. In addition, bubble-to-emulsion phase mass transfer limitations and the extent of gas back-mixing can be much decreased by compartmentalizing of the fluidized bed with the insertion of the membranes inside the bed and the extraction of gas through the membranes. The effect of bubble-to-emulsion phase mass transfer limitations and gas back-mixing have been quantified with the help of a two-phase reactor model. The bubble-to-emulsion phase mass transfer limitation increases with increasing bubble diameter, which itself increases by increasing the reactor length. The membrane area that is needed increases by up to 2.4 times compared to the case without limitations. The bubble diameter (and thus the mass transfer limitations) can however be reduced by inserting, for instance, wire mesh (which cuts the bubbles) at different reactor heights (i.e. staging the fluidised bed reactor). Simulations show that the required conversion can already be achieved with the original membrane area at 3-4 stages.

Direct comparison between FBMR and PBMR

Fig. 2B shows a comparison in terms of methane conversion between the staged fluidized bed membrane reactor and the packed bed membrane reactor. The effect of bed-to-wall mass transfer limitations in the packed bed reactor results in a lower methane conver-

sion as compared with the fluidized bed membrane reactor. Simulations show that in the worst case the packed bed membrane reactor requires almost double the membrane area compared to the fluidized bed membrane reactor.

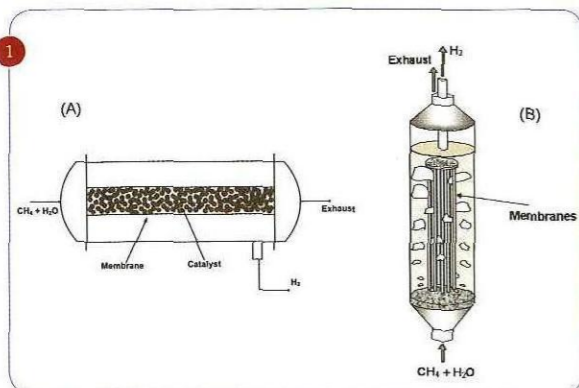
Conclusions

In this work, two different membrane reactor concepts have been quantitatively compared using detailed models. It has been pointed out that both concepts suffer from mass transfer limitations. For the FBMR the problem can be easily solved by staging the fluidized bed with consequent break-up of bubbles and decrease of mass transfer limitations. For the packed bed membrane reactor, the mass transfer limitations occur between the catalytic bed and the membrane surface and cannot be avoided, while these limitations increase by using better performing membranes. Moreover, in packed bed reactors axial temperature profiles are always present (causing deterioration of the permeation flux), while in fluidized bed an isothermal condition can be attained.

In conclusion, it has been shown that a better membrane deserves a better reactor concept. ●

Acknowledgment

The authors are grateful to the Dutch Ministry of Economic affairs for financial support of this work in the EOS program (Project EOSLT05010 carried out at University of Twente) and the partners in the project: ECN, HyGear bv and Continental Engineers bv.



Packed bed membrane reactor configuration (A) and fluidized bed membrane reactor configuration (B) for methane reforming