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Comparison of packed bed and fluidized bed membrane reactors for methane reforming

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Abstract In this work the performance of different membrane reactor concepts, both fluidized bed and packed bed membrane reactors, have been compared for the reforming of methane for the production of ultra-pure hydrogen. Using detailed theoretical models, the required membrane area to reach a given conversion and the prevailing temperature profiles have been compared. The extent of mass and heat transfer limitations in the different reactors have been evaluated, and strategies to decrease (or avoid) these limitations have been proposed.

Keywords: Hydrogen production, Membrane reactors, fluidized bed, Heat and Mass Transfer limitations

1. Introduction
On an industrial scale, most of the hydrogen is currently produced via steam reforming of methane (SRM). The traditional SRM process consists of different process steps such as feed gas preheating and pre-treatment (such as hydrodesulphurisation), primary and secondary reformers (often multi-tubular fixed-bed reactors) and high and low temperature shift converters, CO₂ removal and methanation units. Often a PSA (Pressure Swing Adsorption) unit is used to achieve the desired hydrogen purity. In view of thermodynamic limitations and the high endothermicity of steam reforming, heat transfer at high temperatures (850-950 °C) is required, where excess of steam is used to avoid carbon deposition (typical feed H₂O/CH₄ molar ratios 2-5). For the production of ultra-pure hydrogen for small scale application, this route is not preferred because of the large number of process units with complex heat integration and the associated uneconomical downscaling. A high degree of process integration and process intensification can be accomplished by integrating hydrogen perm-selective membranes in the steam reformer. Via the integration of hydrogen perm-selective membranes, the number of process units can be strongly decreased and the total required reactor volume can be largely reduced, while higher methane conversions and hydrogen yields beyond thermodynamic equilibrium limitations can be achieved, at lower temperatures and with higher overall energy efficiencies (Gallucci 2004, Patil 2007).

The use of both packed bed membrane reactors (see e.g. Tiemersma 2006) and fluidized bed membrane reactors (Gallucci 2008a,b) has already been presented in literature for the reforming of methane and pros and cons of both concepts have already been discussed. In this paper a direct comparison between the two concepts has been performed for ultra-pure hydrogen production via methane reforming using detailed theoretical models. The extent of mass and heat transfer limitations in the different reactors have been evaluated, and strategies to decrease (or avoid) these limitations have been proposed.

2. Reactor configurations
Fluidized bed membrane reactor concept
A schematic representation of the considered fluidized bed membrane reactor configuration is reported in Fig. 1. Pure hydrogen is recovered via Pd-based membranes inserted into the fluidized bed. With the fluidized bed membrane reactor a virtually isothermal condition can be achieved and bed-to-membrane mass transfer limitations are largely
avoided. On the other hand, bubble-to-emulsion phase mass transfer limitations and the extent of gas back-mixing could deteriorate its performance. In particular, the use of membranes inside the reactor could decrease the extent of back-mixing and can also help decreasing the bubble diameter, enhancing the bubble-to-emulsion phase mass transfer. With the help of a two-phase phenomenological reactor model, the effect of bubble-to-emulsion phase mass transfer limitations and gas back-mixing have been quantified.

**Fig. 1** Scheme of the fluidized bed membrane reactor

**Packed bed membrane reactor concept**
The typical tube-in-tube packed bed membrane reactor configuration was considered (see Fig. 2). The reactor has been studied with both a 1D model and a detailed 2D model in order to identify the extent of wall-to-bed heat transfer limitations and the bed-to-membrane mass transfer limitations (concentration polarization) and their effect on the temperature profiles and reactor performance. The influence of the reactor and particle dimensions has been investigated.

**3. Reactor models**
In both reactor concepts the reactions considered are the following:

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3\text{H}_2 \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2
\end{align*}
\] (1) (2)

Where the rate expressions are taken from Numaguchi 1988. The hydrogen permeation rate through the palladium membranes follows the Richardson’s equation, where the values of the apparent activation energy \(E_a\) and pre-exponential factor \(P_0^0\) are 12540 J mol\(^{-1}\) and \(2.21 \times 10^{-03}\) mol s\(^{-1}\)m\(^{-2}\)Pa\(^{-0.5}\), respectively.

**Fig. 2** Scheme of the packed bed membrane reactor

**Fluidized bed membrane reactor model**
A typical one-dimensional two-phase model for a membrane assisted fluidised bed reactor has been used for simulating the fluidized bed membrane reactor. The model assumptions are as follows:
- Dead-end hydrogen perm-selective membranes are integrated in the reactor.
- The reactor consists of two phases, viz. the bubble and emulsion phase.
- The gas flowing through the emulsion phase is considered to be completely mixed in each section and at incipient fluidization conditions.
- The bubble phase gas is assumed to be in plug flow (i.e., large number of CSTRs), where the bubble size and the bubble rise velocity changes for each section.
- The heterogeneous reactions (methane steam reforming and water gas shift reactions) take place only in the emulsion phase, assuming that the bubble phase is free of catalyst particles. (Note that it has been experimentally verified that the contribution by homogeneous gas phase reactions can be neglected).
- Gas removed from the fluidised bed via membranes is assumed to be extracted from both the emulsion phase and bubble phase, distributed according to the local bubble fraction. The gas extracted from the emulsion phase is subsequently instantaneously replenished via exchange
from the bubble phase (to maintain the emulsion phase at minimum fluidization conditions) (following Deshmukh et al. 2005a,b).

- A uniform temperature is assumed throughout an entire section of the fluidized bed, assuming no heat losses to the surroundings (adiabatic conditions) and no heat transfer limitations between the bubble and emulsion phase (Deshmukh et al. 2005c and Patil et al. 2006).

The mass and heat balance equations are reported elsewhere (Gallucci 2008b).

Packed bed membrane reactor 1D and 2D models.

The axial temperature and concentration profiles in both reaction and permeation compartments were modeled with a one-dimensional reactor model using the following general assumptions:

- Radial temperature and concentration gradients in the compartments were ignored.
- The gas phase was assumed to be in pseudo stationary-state because of the small gas residence time compared to the switching times, i.e., the accumulation terms in the species conservation equations and switching losses were neglected.

The other correlations needed for the model are summarised elsewhere (see Smit et al. 2005). The 2D model consists of a pseudo-homogeneous, two-dimensional reactor model consisting of the total gas-phase continuity and Navier–Stokes equations augmented with gas-phase component mass balances and the overall energy balance (see e.g. Tiemersma 2006). The model is based on standard dispersion model which describes the gas phase mass and energy transport as convective flow with superimposed radial and axial dispersion.

The following assumptions have been made in this model:

- The particle size is sufficiently small so that both intra-particle mass and heat transfer limitations and external mass and heat transfer limitations from the gas bulk to the catalyst surface can be neglected.
- Homogeneous gas phase reactions are neglected in view of the relatively low temperatures.
- The gas bulk can be described as an ideal Newtonian fluid.

4. Results and discussion

A first comparison has been made between the fluidized bed membrane reactor model and the 1D packed bed reactor model in ideal conditions (i.e. isothermal conditions and absence of mass and heat transfer limitations, number of grid cells of 1D model equal to number of CSTRs in MAFB model). The results show that in these conditions the two reactors give identical performance in terms of membrane area required for a given conversion. In this way it has been verified that the two models are working properly. The following simulations have been performed with a heat flux through the reactor walls. The main difference between the fluidized bed and the packed bed membrane reactors can be seen in the heat management. In fact, for the fluidized bed membrane reactor it is well known that a virtually isothermal condition can be achieved while for the packed bed membrane reactor a temperature drop in the first part of the reactor is always observed no matter the profile of temperature at the reactor wall. The results show a temperature drop of 80-100K in the first part of the reactor (Fig. 3) which can give stability and sealing problems for the membrane. In fact, the membrane material should stand at a great axial temperature gradient which can cause the detachment of the Pd-based layer from the support with consequent loss in perm-selectivity.

![Fig. 3. Temperature profile in a packed bed membrane reactor.](image-url)
The decrease of temperature at the beginning of the reactor also gives a decrease of the reaction rate. The result is an increase of the membrane area needed for the required conversion. In particular, the membrane area increased by around 21% if compared with an isothermal operation (which is only possible in a fluidized bed membrane reactor). The effect of the particle size on the temperature profile is quite negligible as also indicated in the same figure (Fig. 4).

In these conditions the increase of membrane area with respect to an ideal fluidized bed membrane reactor is 13%. Another difference that can occur between a packed bed and a fluidized bed is the mass transfer limitations between the bed and the membrane wall which are present in the packed bed but not in the fluidized bed. As it can be seen in Fig. 6, H$_2$ radial profiles are present but not really pronounced. It can be concluded that for the present membranes and for small membrane diameters, the bed-to-wall mass transfer limitations have a negligible influence on the membrane area. In view of further developments and optimization of the Pd-based membranes, higher membrane fluxes will become possible in near future.

A way to overcome the problem of the temperature drop is the use of a pre-reforming zone (in our case of 20-25 cm) where membrane is not used (Fig. 5). In this case (pre-reforming 25 cm) the membrane is used at an almost constant temperature (maximum temperature difference 28K) so that the stability problems are prevented and the membrane is effectively used resulting in a lower membrane area needed for a given conversion (i.e. slightly longer packed bed, but smaller membrane area).
The results reported in the figure 8 show that at higher membrane permeabilities mass transport limitations to the membrane wall will negatively affect the reactor performance resulting in an increased H₂ slip through the reactor exhaust. Concerning the fluidized bed membrane reactor, an important transfer limitation affecting its performance is the mass transfer limitation between the bubble phase and the emulsion phase. In our fluidized bed membrane reactor model the bubble-to-emulsion phases mass transfer coefficient is calculated with the equations derived for a fluidized bed without internals. For a fair comparison with the packed bed membrane reactor, the fluidized bed has been simulated with the same membrane area but also with the same bed length. As a matter of fact, the bubble-to-emulsion phase mass transfer limitation increases with increasing bubble diameter, which itself increases by increasing the reactor length. As a result of this bubble increase, the methane conversion decreases as indicated in the following figure.

To achieve the same conversion degree of a fluidized bed membrane reactor without mass transfer limitations the membrane area used need to be increased as indicated in the following figure. The membrane area needed increases 2.4 times with respect the case without limitations. However, it has to be pointed out that the use of membranes inside the bed leads to a decrease of the bubble size and a consequent decrease of the mass transfer limitations.

On the other hand, even considering the worst case (bubble to emulsion phase mass transfer coefficient equal to a fluidised bed without internals) the mass transfer problem in the fluidized bed can be easily circumvented. In fact, the mass transfer resistance is higher when the bubble diameter becomes larger. As already said, the bubble diameter increases with the increasing of the bed height. However, we can reduce the bubble diameter by inserting other distribution plates at different reactor height (i.e. staging the fluidised bed reactor).

Simulations show that the conversion required can be achieved already with 3-4 stages. Thus, dividing the reactor in different stages completely circumvents the problems of mass transfer limitation for the fluidized bed membrane reactor.

A direct comparison between the performances of a fluidized bed and a packed bed is reported in the following table (for a 50 Nm³/h hydrogen production):

<table>
<thead>
<tr>
<th>T</th>
<th>P</th>
<th>Fluidized bed (5 stages)</th>
<th>Packed bed</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>20</td>
<td>3.24</td>
<td>3.94</td>
</tr>
</tbody>
</table>

The packed bed membrane reactor needs around 22% larger membrane area if compared with a staged fluidized bed membrane reactor. Finally, we can state that the more evident advantages of a fluidized bed reactor with respect a packed bed reactor are: constant temperature along the reactor and better heat integration (see Gallucci 2008a,b), no mass
transfer limitation between the fluidized bed and the membrane surface. The selection between the two concepts could be done on the basis of the heat management. In fluidised bed the heat management is quite simpler since the heat can be supplied via oxidation of methane with oxygen (Patil 2007 Gallucci 2008a) or with air inside the reactor without problems of temperature peaks. In this case an increase of membrane area required in the order of 25% should be considered due to the dilution. The heat can be also supplied by heating tubes inside the reactor also in this case without problem of excessive temperature gradients inside the bed. On the other hand, for a packed bed membrane reactor is not possible to perform the partial oxidation along with the steam reforming in the same reaction compartment due to the temperature peak at the beginning of the reactor (Tiemersma 2006). The heat should then be supplied via the reactor wall. A solution can be the catalytic oxidation of methane outside the reactor tube, but also in this case the temperature peak at the beginning of the reactor can be a problem as reported in the following figure. The way to solve it is to use a very high flow rate in the oxidation compartment with consequent increase of pressure drop in this compartment.

5. Conclusions
In this work, two different membrane reactor concepts have been compared via detailed models. It has been pointed out that both concepts suffer from mass transfer limitations, but in each case, these limitations can be circumvented and do not really influence the membrane area required for a given operation. On the other hand, the selection between the two concepts could be done on the basis of the heat management. In fact the heat supply is much easier in a fluidized bed membrane reactor than in a packed bed membrane reactor.

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