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Methane Steam Reforming in a Staged Membrane Reactor: Influence of the Number of Stages and Amount of Catalyst

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In this work, the performances of a tube-shell staged membrane reactor (SMR) for methane steam reforming are analyzed by computer modelling in terms of methane conversion, hydrogen recovery factor and hydrogen recovery yield. The internal tube (the permeate side) is represented by the Pd-alloy membrane, whereas the reaction occurs in the packed bed retentate side. The staged membrane reactor is composed of several reactive and inert stages laid out in alternative series and filled with catalytic and inert pellets, respectively. For this analysis, a 1-D model including momentum, energy and mass transfer is used. Its validation was already performed by means of experimental data taken from literature (Caravella et al., 2008). In particular, the specific topic of the investigation is the role of the number of reactive and inert stages and of the amount of catalyst, comparing the obtained results with those of the conventional membrane reactor (MR). A very significant result of the analysis is that an SMR with a sufficiently high number of stages can reach performances very close to those of the MR with a significantly smaller amount of catalyst (up to 70% lower) for all the temperatures considered. As a consequence, the amount of saved catalyst can be evaluated, relating it to the performance losses with respect to the conventional MR and providing a qualitative and quantitative rule to exploit efficiently the catalyst.

1. Introduction

The process considered here is one of the most important for hydrogen production: methane steam reforming. Many simulative and/or experimental works of literature have dealt with the study of the performance of this process in membrane reactor by analyzing the role of several design parameters to maximize their performances. In this study, the influence of two variables is investigated in a specific Staged Membrane Reactor (SMR): the number of stages and the catalyst amount. In literature, several simulation studies have been carried out on staged membrane reactors (Birdsell and Willms, 1998; Asen and Andersen, 2002; Lund, 2002), but in all the cases the number of stages and catalyst amount were set as constant. In their simulation work concerning the possibility to integrate a hydrogen selective membrane technology, Jordal et al.

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(2004) considered five conventional reformers in series with five Pd-based membrane permeators, selecting the number of equipments in accord with some computational conveniences. Very recently two modelling studies about the efficient exploitation of the membrane area in two different Pd-based membrane reactors for methane steam reforming were conducted by Li et al. (2008) and Caravella et al. (2008). The first ones analyzed the performances of a staged reactor with two reactive and two separative stages placed, respectively, in two different furnaces, each of which with its own temperature. In particular, they performed an investigation on the effect of the membrane area in the separative stages and the influence of other operating conditions. On the other hand, Caravella *et al.* (2008) analyzed a staged Pd-based membrane reactor with five reactive stages (no permeation) and four separative ones (no reaction), all placed in the same furnace. In this case, the optimal membrane area and catalyst axial distributions were evaluated by maximizing two objective functions one at a time. Nevertheless, in these investigations the possibility of studying the role of the number of stages and amount of catalyst on the process performances was not taken into consideration. Hence, throughout this work, the effect of these two design variables will be shown to be relevant to improve significantly the reactor performances.

2. Description of the system

Figure 1 shows the Staged Membrane Reactor (SMR) considered in this analysis. It is composed of several reactive and inert stages laid out alternatively to each other and placed in the shell side. Methane steam reforming occurs in the reactive stages only, whereas the selective hydrogen permeation through a Pd-based membrane regards the whole reactor length. For simplicity of assembling, the inert stages are considered to be filled with inert pellets, having the same characteristics of the catalytic ones.

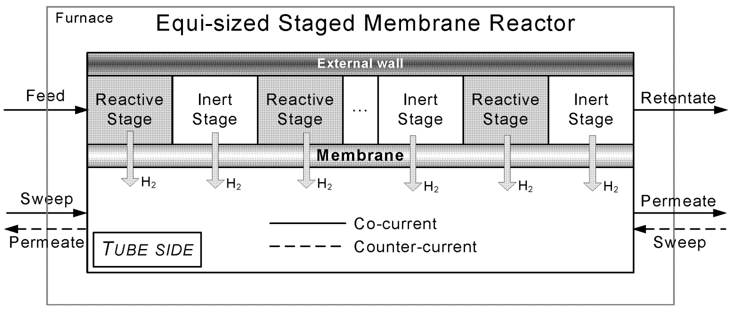

Figure 1. Sketch of the considered Staged Membrane Reactor (SMR).

The properties of the Pd-based membrane used in this study are taken from literature (Tong et al., 2005) and the works of Xu and Froment (1989) is used for the mechanism of methane steam reforming. For performing the simulation of the reactor, a 1-D model has been developed in steady state, accounting for non-isothermal and non-isobaric conditions and handling both co- and counter-current flow configurations. The model validation has been already performed in another work (Caravella et al., 2008). In order to measure the reactor performances, the indices defined in Table 1 are used.

Table 1. Definition of the performance indices considered.

Index	Meaning	Formal Definition	Mathematical Definition
x	CH_4 Conversion	$\frac{CH_4 \text{ Converted}}{CH_4 \text{ Fed}}$	$1-\frac{F_{CH_4}}{F^0_{CH_4}}$
RF	H_2 Recovery Factor	$\frac{H_2 \text{ Recovered in Permeate}}{H_2 \text{ Produced}}$	$\frac{F^{Perm}_{H_2}}{F^{Ret}_{H_2}+F^{Perm}_{H_2}}$
RY	H_2 Recovery Yield	$\frac{H_2 \text{ Recovered in Permeate}}{\text{Maximum } H_2 \text{ Produced}}$	$\frac{F^{Perm}_{H_2}}{4F^0_{CH_4}}$

Table 2. Reactor operating conditions.

Side	Pressure, kPa						Total flow rate mmol/s
	H_2	CH_4	CO_2	H_2O	CO	Total	
Feed	-	125	-	375	-	500	8
Sweep	-	-	-	120	-	120	8
$T^{Furnace}$ = {500, 600}°C							

The letter "F" in Table 1 indicates the molar flow rate, whereas the superscripts "0", "Ret" and "$Perm$" indicate the reactor inlet, retentate and permeate, respectively. Both the effects of catalyst amount (expressed as a fraction y_{Cat} of the total volume of pellets) and total number of stages (n^{Stages}) are investigated, comparing the results of the SMR to the ones of the conventional Membrane Reactor (MR), having the same membrane area as the SMR but completely filled with catalyst (y_{Cat} = 100%). The expressions relating the topic design variables are reported in Eq.1-4, where l and n are the stage length and the number of stages, whereas "R" and "I" indicate the reactive and inert stages, respectively. The operating conditions of the SMR are reported in Table 2, where it is shown that a typical value of molar feed ratio H_2O/CH_4 (= 3) is considered.

$$l^R = \frac{y_{Cat} \cdot l^{Mem}}{n^R}, \; l^I = \frac{(1-y_{Cat}) \cdot l^{Mem}}{n^I}, \; \frac{l^R}{l^I} = \frac{y_{Cat}}{1-y_{Cat}}, \; n^R = n^I = \frac{n^{Stages}}{2} \qquad (1\text{-}4)$$

3. Results and discussion

In Figure 2 some conversion and recovery yield profiles are reported for different number of stages n^{Stages} at a catalyst amount y_{Cat} of 30% in counter-current. The significant effect of n^{Stages} is clear for both the performance indices considered. As regards the conversion, a high n^{Stages} allows the system to exploit the catalyst in a better way by reducing progressively the low-efficiency zones. An analogous fact occurs for the recovery yield, whose shape appears less segmented as the hydrogen recovery is performed in both reactive and inert stages, whilst the conversion increases only in the reactive stages. The system behaviour as function of n^{Stages} is better shown in Figure 3, where the functionality of the performance indices with the catalyst amount is also reported. The most important peculiarity of this plot is the plateau reached by the curves, which present the highest variations at the beginning of the profiles (n^{Stages} <50% ca. and y_{Cat} <25% ca.).

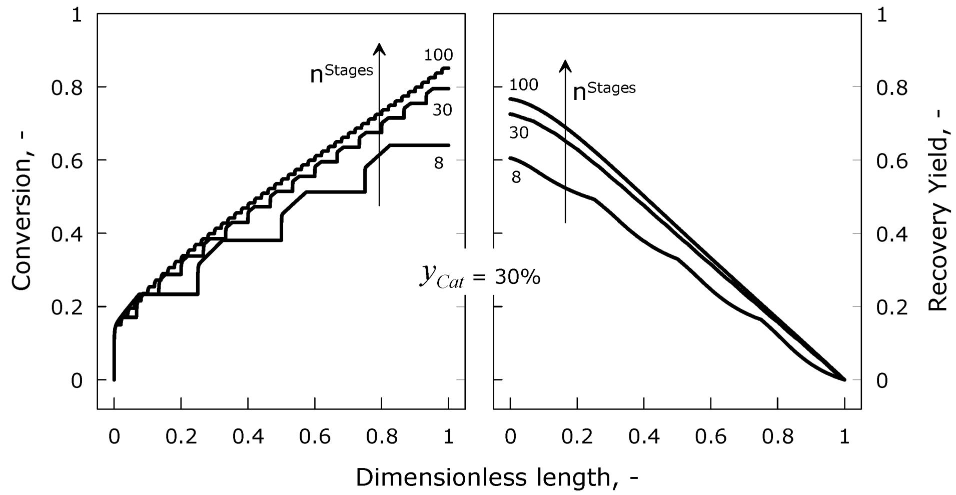

Figure 2. Axial profiles of the methane conversion (left) and hydrogen recovery yield (right) at y_{Cat} of 30% for several numbers of stages in counter-current flow.

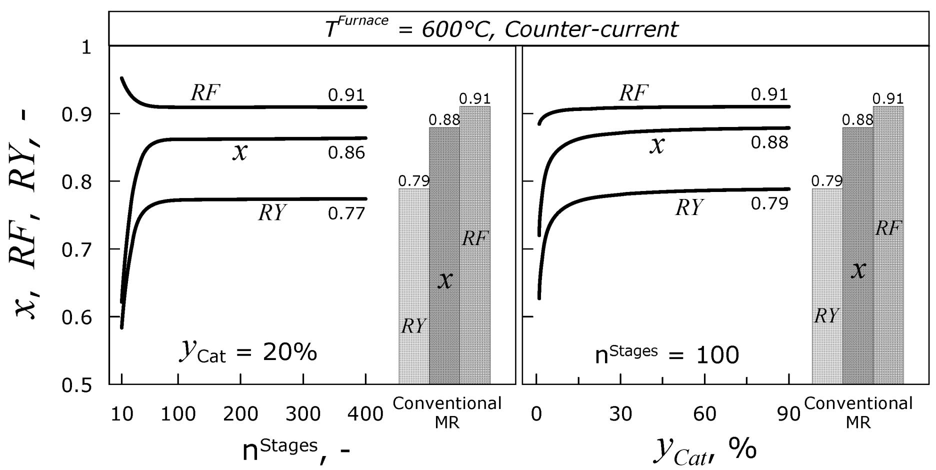

Figure 3. Performance indices as functions of the number of stages (left) and amount of catalyst (right) at 600°C in counter-current flow

This means that it is useless for the reactor to work in conditions above these limit values, which are very close to the ones of the conventional MR, even for a significantly lower amount of catalyst (20%). Analogous considerations can be made for co-current flow and other temperatures, whose plots are not reported. Therefore, Figure 3 provides a method to evaluate quantitatively the advantage in using a high number of stages in terms of less amount of catalyst to use (Figure 4) with respect to MR and in terms of reduced furnace temperature with respect to a reference case at lower n^{Stages} (Figure 5). The grey-coloured areas in the following plots indicate their generality, being valid for co-current, counter-current, conversion and recovery yield.

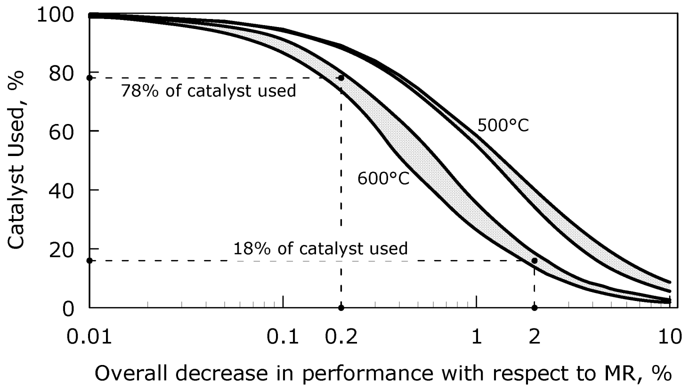

Figure 4. Amount of catalyst used as a function of the decrease of conversion and/or recovery yield) with respect to the conventional MR at different furnace temperatures.

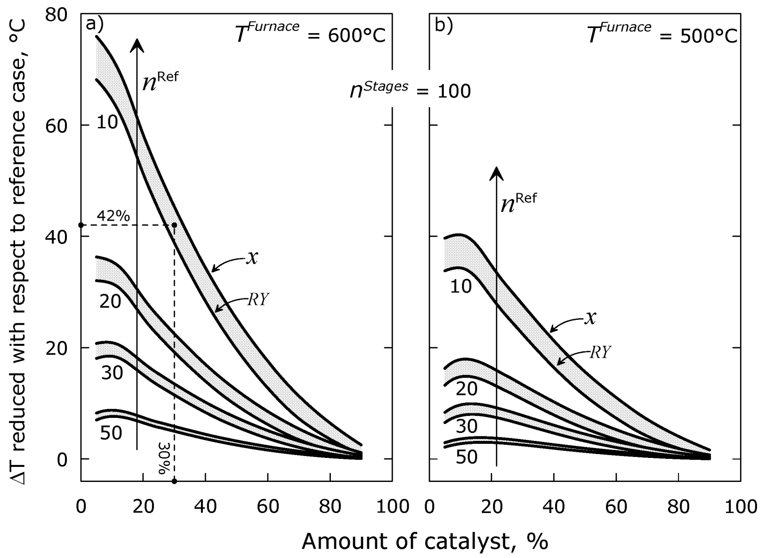

Figure 5. Reduction of $T^{Furnace}$ as a function of the amount of catalyst used for different reference conditions and temperatures. The plot is valid for co- and counter-current.

In particular, Figure 4 indicates that, if a high n^{Stages} are adopted (>100 ca.), it is possible to use 18% of the catalyst of the fully filled conventional MR only renouncing to 2% of conversion or recovery yield of MR. As an example, if MR reaches a conversion of 88%, an SMR with high n^{Stages} provides a conversion of about 86% with 18% of catalyst, corresponding to 82% of catalyst saved.
In Figure 5 the reduced furnace temperature being possible to adopt at high n^{Stages} is calculated for different reference cases at 500 and 600°C. For example, if a reference case of 600°C and 10 stages (=n^{Ref} in figure) is chosen (Figure 5a), the same conversion or recovery yield can be obtained with 558°C and 100 stages. Naturally, as the number of stages of the reference case increases, the advantage is progressively reduced. An analogous fact holds for 500°C (Figure 5b).

4. Conclusions

In this study, the effect of the number of stages and catalyst amount in a Staged Membrane Reactor (SMR) was analyzed in several different operating conditions. Firstly, it was demonstrated that, at sufficiently high number of stages (>100 ca.) and catalyst amount (>30% ca.), the SMR performances reach a plateau. Then, from these results it was possible to quantify the advantage in using an SMR with a high number of stages in terms of 1) catalyst saved and 2) reduced furnace temperature, showing the importance of considering the catalyst distribution as a design variable.

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