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Foreword

A significant increase of interest in membrane reactors in recent years together with several research programs which are in progress nowadays has pushed the authors to consolidate their experiences into this book focusing on the more attracting and promising processes. Few authors have been working together in an R&D project started in 2006. The goal of this project was the development of a new scheme for hydrogen production through stream reforming based on integrating chemical reaction and membrane separation.

One of the main objectives of the project was to build a pilot plant with industrial-size components. Today the pilot plant (see figure below) is running and the experimental campaigns are allowing to verify the reliability of the novel scheme and at the same time useful information is generated to assess the plant operation and for scaling-up the design to future industrial size units.Semi-industrial membrane-based steam reformer installed in Chieti Scalo (Italy)

The R&D project was financially supported by the Italian Research Ministry, and managed by the Chemical Engineering Department of the University of L'Aquila.

In the next year the experimental program will be oriented both to the theoretical aspects of the process and to the technological ones, focusing on the reliability and on the scaling-up criteria for process design of industrial plants.

The research project allowed to compare two different ways of integrating catalytic reaction and hydrogen separation: one in which the membranes are set inside the reaction environment (e.g. the membranes constitute the catalytic tube walls) and another one in which the catalytic module is separated from the hydrogen permeation one.

With reference to the book content, the authors divided it into 11 chapters. The book starts with an overview on membrane selective membranes integrated in the chemical reaction environment. The thermodynamics and kinetics of membrane reactors are also formulated and assessed for different membrane reactor architectures.

The rest of the book is divided into three parts. The first part deals with the membranes, membranes manufacturing and mathematical modeling. The second

Semi-industrial membrane-based steam reformer installed in Chieti Scalo (Italy)

reviews the most attracting application from an industrial point of view. The third is dedicated to the description of the pilot plant where the novel configuration was implemented at a semi-industrial scale.

In Chap. 2, an extensive overview concerning palladium-based membranes is presented. In particular, an assessment of the problems associated with palladium membranes is given followed by a description of the preparation methods. Chapter 3 focuses on a proper membrane manufacturing strategy to improve their industrial competitiveness by lowering production costs. In Chap. 4, the mathematical modeling strategies focused on the simulations of membrane reactors (MR) and reactor membrane modules (RMM) are presented. In Chap. 5, the membrane reactor application to natural gas steam reforming is presented and assessed in the MR and in the RMM configuration. Chapter 6 is dedicated to the autothermal reforming reaction (ATR) for syngas production. An higher efficiency can be achieved integrating in the reactor an H_2 permselective membrane. In Chap. 7, the water–gas shift reaction is studied. The integration of membranes inside or outside the shift environment is also analyzed. A techno-economic analysis is dedicated to the shift reactor integrated with the membrane module

compared to the conventional process. In Chap. 8 the H_2S catalytic cracking process is analyzed. Also in this case the benefits derived by coupling the Claus reaction and the hydrogen module separation are examined with reference to different process configurations. In particular, the high Claus reaction temperature (900°C) and the low working temperature of ceramic membrane modules (600°C) are taken into account in the definition of process multi-staged configuration. Chapter 9 deals with alkanes dehydrogenation. Olefins production by catalytic dehydrogenation of light alkanes might be an alternative to conventional heavy hydrocarbons cracking. Also in this case the catalytic membrane reactor might improve the process yield. In particular is studied the coupling of the Pd–Ag membrane and catalysts usually used in the dehydrogenation process that need to operate at low H_2 partial pressures. In Chap. 10 the characteristics of the pilot plant discussed at the beginning of this foreword are shown in more detail referred to the process design and to the first positive experimental results.

Each chapter was developed as a whole that can be read without reference to the others.

Professor Diego Barba
Scientific Director

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Chapter 1
Integration of Selective Membranes in Chemical Processes: Benefits and Examples

Luigi Marrelli, Marcello De Falco and Gaetano Iaquaniello

1.1 Introduction

Integration of reaction and separation in a single unit is a powerful tool to increase efficiency and economic advantages of many chemical processes. Reactive distillation, extraction, and adsorption are well-known examples of this technological resource. Recently, a very promising solution is offered by membrane reactors (MRs).

A MR is a system coupling reaction and separation of one or more products, with the separation operation performed by a selective membrane. Although not yet very used at industrial scale, MRs are attracting the attention of scientists and engineers in the last two decades, and many interesting articles have appeared in the literature on their performance and possible application in many fields of chemical and biochemical industries. An excellent review about these topics has appeared in 2002 by Sanchez Marcano and Tsotsis [1].

For biotechnological applications, synthetic membranes entrapping enzymes, bacteria, or animal cells are used in membrane bioreactors disclosing new important developments mainly due to the increased stability of immobilized enzymes, the possibility of their continuous reuse and the absence of pollution of the products. Membrane bioreactors are of great interest as well for the possibility of continuously removing metabolites whose presence in the reaction environment could reduce the productivity of the reactor.

In the field of inorganic heterogeneous catalysis, metallic or ceramic membranes are used to bear the generally more severe thermal conditions. Both dense and

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porous, inert and catalytically active membranes have been used in the different processes analyzed in the scientific or technical literature. Dense Pd-based membranes or almost dense SiO_2 membranes offer very good selectivity and permeability features in all reactions involving generation or consumption of hydrogen [2]. Composite membranes made of a dense selective layer supported on a porous material can represent a technical solution when strong mechanical stresses are imposed to the membrane. Palladium and its alloy membranes were prepared on stainless steel supports by the electroless plating technique and on alumina supports by sputtering or by metal–organic chemical vapor deposition [3–6].

Two main advantages are offered by MRs. If the membrane is very selective with regard to a specific product, then it is possible to obtain a very pure compound in the same equipment used to produce it. Furthermore, in the case of reversible reactions, removing one or more reaction products as they are generated allows conversions higher than equilibrium values to be reached.

The use of inorganic MRs has been investigated for a number of reactions.

Pd-based membranes, mainly Pd–Ag (23%wt), have been extensively tested for natural gas steam reforming, which is the main process to produce large amount of hydrogen. Many experimental works are reported in the literature [7–11], attesting the good performance in terms of natural gas conversion at much lower operating temperature than traditional process (methane conversions up to 90–95% at 450–550 vs. 850–1000°C).

The dehydrogenation of cyclohexane to benzene [12] and of ethylbenzene to styrene [13, 14] have been studied in MRs using glass or alumina membranes. Even if a conversion increase beyond the equilibrium value has been observed in all the cases, compared with Pd-based membranes, which are much more selective with respect to hydrogen, porous membranes are less efficient in improving the conversion. For example, the conversion of cyclohexane to benzene at 200°C and 1 atm (equilibrium conversion 19%) is 45% in a Vycor glass MR whereas it becomes 99.7% in a Pd–Ag MR.

A growing interest in the membrane assisted Water–Gas Shift reaction (WGSR) is manifested by a substantial volume of the published pertinent literature that could be grouped around the two most popular hydrogen permselective membranes, based either on palladium [15–19] or silica [20–22]. Among them, Basile et al. [15] studied the WGSR in a palladium MR and showed the importance of the membrane preparation method in obtaining high-quality membrane materials. The best membrane increased CO conversion up to 99.89% at about 330°C with a performance claimed stable for more than 2 months [16].

The most recent application of a silica membrane—prepared by counter-diffusion CVD of TMOS (TetraMethylOrthoSilicate) and oxygen—to H_2S decomposition was reported by Akamatsu et al. [23]. It was claimed that using this membrane and a commercial desulphurization catalyst at 600°C, about 70% H_2S diluted in 99% nitrogen was converted in a relatively short residence time of 7 s. A similar application but with a different process architecture was proposed by Galuzka et al. [24] and is reported in Chap. 8.

In general, membrane integration inside the reaction environment involves the following main benefits:

1. The ability of such a reactor to circumvent thermodynamic limitation of an equilibrium-controlled process allows the same reactants conversion to be obtained at a lower temperature or a higher conversion to be reached at the same temperature.
2. Operating at lower reaction temperatures, new heat integration strategies to supply heat duty to reactors can be proposed. The use of gas exhausts from a gas turbine as suggested by [25] or solar heated molten salts [26] could become applicable and reliable industrial solutions.
3. Lower operating temperatures reduce materials cost as well as increase operation safety.
4. The expected significant process simplification and intensification would capitalize on a new industrial paradigm offered by equipments combining reaction and separation in one step. New reactors and overall plant design strategy have to be defined.

In this chapter, a theoretical demonstration of operating benefits for chemical processes in integrating selective membrane is given to the readers. For practical cases refer to the following chapters.

1.2 Thermodynamics and Kinetics Background

Reversible reactions are thermodynamically limited since equilibrium conditions cannot be overcome in the reacting mixture. From a thermodynamic point of view, equilibrium is represented by a constraint (equilibrium constant) on mole fractions (or concentrations), temperature, and pressure; this constrain derives from the second principle of thermodynamics. At equilibrium conditions, no net change in state variables is observed.

From a kinetic point of view this means that at equilibrium the reaction rate of the direct reaction is equal to the reaction rate of the inverse reaction. As known, the reaction rates of the direct and of the inverse reactions generally increase with the reactant and the product concentrations, respectively. Only when product concentrations are high enough and reactant concentrations are low enough, i.e., when the conversion of a key reactant is high enough, the equilibrium is reached. Some kinds of reactions (irreversible reactions) require very high conversions to reach equilibrium conditions at a given temperature, whereas for other reactions a quite low value of the conversion corresponds to equilibrium. These latter reactions are named reversible reactions according to the thermodynamic statement that each transformation close to equilibrium is a reversible transformation. In the case of reversible reactions, the thermodynamic limit can prevent acceptable conversions to be obtained.

The equilibrium composition depends on temperature and pressure of the system as well as on the composition of the charge or feed.

A very simple numerical example can be useful to illustrate these subjects.

Let's consider the following synthesis reaction in gas phase:

$$\mathrm{A} + \mathrm{B} \Leftrightarrow \mathrm{R}$$

Let be $K = 1.5$ the equilibrium constant, at a given temperature T. At a not too high pressure P, the equilibrium composition in terms of mole fraction is easily obtained from the definition of K:

$$K = \frac{y_R}{y_\mathrm{A} \cdot y_\mathrm{B}} \cdot P^{-1} \tag{1.1}$$

If the charge is composed of $n_\mathrm{A}^0 = 5$ mol of A and $n_\mathrm{B}^0 = 5$ mol of B, equilibrium conversion of A at $P = 1$ atm, is $X_\mathrm{A} = 0.367$.

This conversion depends on the charge composition. For example, with $n_\mathrm{A}^0 = 5$ and $n_\mathrm{B}^0 = 3$, at the same temperature and pressure, we get $X_\mathrm{A} = 0.274$ at equilibrium, whereas with $n_\mathrm{A}^0 = 3$ and $n_\mathrm{B}^0 = 5$ we get $X_\mathrm{A} = 0.399$.

The effect of the pressure depends on the phase of reacting system and on the stoichiometry of the reaction. In the present case of reaction in gas phase with a negative sum of stoichiometric coefficients, high values of P promote the conversion.

In any case, higher values of equilibrium conversion can be obtained with a higher value of the equilibrium constant. For example, with $K = 1.5$, $P = 15$ atm and $n_\mathrm{A}^0 = n_\mathrm{B}^0 = 5$ we get $X_\mathrm{A} = 0.75$.

Since the equilibrium constant K depends on the temperature, a way to change its value is to change T. In particular, K increases with T for endothermic reactions and decreases for exothermic reactions according the well-known Van't Hoff equation:

$$\frac{\mathrm{d} \ln K}{\mathrm{d}T} = \frac{\Delta H}{R \cdot T^2} \tag{1.2}$$

with $\Delta H > 0$ for endothermic reactions and $\Delta H < 0$ for exothermic reactions.

In the case of exothermic reactions, low temperatures should be required to get acceptable equilibrium conversions but the corresponding slow reaction rates should require very high residence time in the reactor.

On the contrary, in the case of endothermic reactions, suitable values of K are often obtained only at very high temperatures with corresponding unacceptable heat duties, quick deactivation of catalysts, and technical and economic problems in construction materials.

These shortcomings can be overcome by removing one or more products from the reaction environment to prevent the equilibrium composition can be reached, i.e. maintaining y_R in Eq. 1.1. at lower values than equilibrium.

1.2.1 Thermodynamics of Reacting Systems

It is well known that a way to express equilibrium condition in a closed system is to set Gibbs free energy at its minimum value at constant P and T.

$$\mathrm{d}G = 0 \quad [P, T] \tag{1.3}$$

Equation 1.3, that is a consequence of the second Principle of Thermodynamics, states that any change from the equilibrium state at constant T and P involves an increase of G.

If the system is a multi-component reacting system, Eq. 1.3 can be expressed in the following form:

$$\sum_{i=1}^{c} \alpha_i \mu_i = 0 \tag{1.4}$$

where α_i are the stoichiometric coefficients of the components (assumed to be positive for products and negative for reactants) and μ_i are the chemical potentials defined as:

$$\left(\frac{\partial G}{\partial n_i}\right)_{P,T,nj\neq i} = \mu_i \tag{1.5}$$

If chemical potentials at system conditions are expressed in terms of fugacities f_i, and components are assumed to be pure in the reference state, Eq. 1.4 becomes:

$$-\frac{\Delta g^0}{R \cdot T} = \ln \prod \left(\frac{\bar{f}_i(P, T, z_i^{\mathrm{eq}})}{f_i^0(P^{\oplus}, T)}\right)^{\alpha i} \tag{1.6}$$

where $\Delta g^0 = \sum \alpha_i \cdot g_i^0$, g_i^0 are the molar free energies of pure components and z_i^{eq} are the mole fractions at equilibrium conditions.

The product at the r.h.s. of Eq. 1.6 is the thermodynamic constant K of the reaction.

$$K(P^{\oplus}, T) = \prod \left(\frac{\bar{f}_i(P, T, z_i^{\mathrm{eq}})}{f_i^0(P^{\oplus}, T)}\right)^{\alpha i} \tag{1.7}$$

Therefore, Eq. 1.6 can be written in the following form:

$$\ln K(P^{\oplus}, T) = -\frac{\Delta g^0}{R \cdot T} \tag{1.8}$$

The value of K depends on the temperature and on the pressure and composition conditions assumed as reference state. Once pressure and composition are fixed, equilibrium constant depends on the temperature only.

1.2.2 Affinity and Evolution of Reacting Systems

If a closed system is not at equilibrium, a change of its state variables is observed. The direction of the system evolution is stated by the second Principle of Thermodynamics and corresponds to a positive production of entropy $\mathrm{d}_i S > 0$:

$$\mathrm{d}_i S = -\sum_{j=1}^{c} \frac{\mu_j}{T} \mathrm{d}n_j \geq 0 \tag{1.9}$$

where the equality holds at equilibrium conditions. The presence of chemical reactions in a closed system causes changes in the mole number of reactants and products which are not independent each other since the stoichiometry of reactions imposes some constraints.

In the case of r simultaneous reactions and c components, we have:

$$\mathrm{d}n_j = \sum_{k=1}^{r} \alpha_{j,k} \cdot \mathrm{d}\xi_k \qquad j = 1 \ldots c \tag{1.10}$$

where ξ_k is the degree of advancement of reaction k and $\alpha_{j,k}$ indicates the stoichiometric coefficient of component j in reaction k.

Using conditions 1.10 in Eq. 1.9 we get:

$$\mathrm{d}_i S = \frac{1}{T} \sum_{k=1}^{nr} A_k \mathrm{d}\xi_k \geq 0 \tag{1.11}$$

or in terms of entropy production rate:

$$\frac{\mathrm{d}_i S}{\mathrm{d}t} = \frac{1}{T} \sum_{k=1}^{nr} A_k \frac{\mathrm{d}\xi_k}{\mathrm{d}t} \geq 0 \tag{1.12}$$

In Eqs. 1.11 and 1.12, A_k is the affinity of reaction k defined as follows:

$$A_k = -\sum_{j=1}^{c} \alpha_{jk} \cdot \mu_j \tag{1.13}$$

In the case of a single reaction, Eq. 1.12 states that the reaction proceeds in the direction of increasing ξ when the affinity is positive while ξ decreases for $A < 0$. At equilibrium, the affinity of the reaction is zero:

$$A = -\sum_{j=1}^{c} \alpha_j \mu_j = 0 \qquad \text{Equilibrium condition} \tag{1.14}$$

In the case of multiple reactions, Eq. 1.12 is satisfied even with some terms $A_k \mathrm{d}\xi_k < 0$ if the summation is greater than 0. Obviously, at equilibrium conditions,

since d_iS must be zero for every infinitesimal variation of degrees of advancement, the affinity of each reaction has to be zero:

$$A_1 = A_2 = \cdots A_{nr} = 0 \tag{1.15}$$

At non-equilibrium conditions, the reaction proceeds from left to right ($d\xi > 0$) only if $A > 0$.

This means (Eqs. 1.6 and 1.13):

$$\begin{aligned} \left[\Delta\mu^{\oplus} + R \cdot T \cdot \ln \hat{K}\right] &< 0 \\ R \cdot T \cdot \left[\ln \hat{K} - \ln K\right] &< 0 \end{aligned} \tag{1.16}$$

where:

$$\hat{K} = \prod \left(\frac{\bar{f}_i(P, T, z_i)}{f_i^{\oplus}(P^{\oplus}, T)}\right)^{\alpha i} \tag{1.17}$$

In other terms, if $\hat{K} < K$ mole fractions of products are lower than equilibrium values and mole fractions of reactants are higher than equilibrium values and the reaction evolves from left to right.

Vice versa, if $\hat{K} > K$ the evolution is from right to left. Finally, if $\hat{K} = K$, the reaction is at equilibrium and its evolution stops.

In each case, outside equilibrium condition, the reaction evolves in the direction corresponding to a decrease of free energy G of the system.

Selective membrane application allows products mole fraction to be reduced and consequently the condition $\hat{K} < K$, i.e., mole fractions of products lower than equilibrium values, is verified, promoting continuously the reaction from left to right.

1.2.3 Kinetics of Reversible Reactions

The reaction rate of a reversible reaction is the result of two contributions: the forward reaction that generates the products (chemical species at the right of the stoichiometric equation) from the reactants (chemical species at the left of the stoichiometric equation) and the reverse reaction that proceeds in the opposite direction.

For instance, in the case of a general reaction:

$$\alpha_1 A_1 + \alpha_2 A_2 \Leftrightarrow \alpha_3 A_3 + \alpha_4 A_4 \tag{1.18}$$

the net disappearance rate of A_1 is given by:

$$-r_1 = r_{1,\text{forward}} - r_{1,\text{reverse}} \tag{1.19}$$

where the forward reaction rate generally increases with the concentration of reactants A_1 and A_2 whereas the reaction rate of the reverse reaction generally increases with the concentration of the products A_3 and A_4.

If the concentrations of the reactants and of the products are such as the forward reaction rate is higher than the reverse reaction rate, the reaction evolves from left to right; vice versa the direction of the reaction is from "products" to "reactants" when the product and reactant concentrations make the reverse reaction faster than the forward reaction.

At equilibrium, no net change is observed in the reaction mixture so that forward and reverse reaction rates are equal.

Removing a product from the reaction environment usually reduces the reaction rate of the reverse reaction allowing the reaction to evolve further from left to right.

1.3 Membrane Reactors

Thermodynamics and kinetics conclusions reported in the previous sections show that removing one or more products from the reaction environment allows the reaction to proceed without reaching equilibrium conditions.

A technical way to fulfill this plan is to surround the reacting mixture by a membrane selectively permeable to one of the products at least (Integrated Membrane Reactor). As a result, the reaction rate of the reverse reaction is lower than that of the forward reaction and the conversion increases theoretically to the value corresponding to the complete depletion of the limiting reactant.

A tubular MR is simply composed of two co-axial tubes with the inner one made of a material selectively permeable to a product of the reaction.

The reacting stream can be fed to the annular region or to the inner tube. The region where the reactants are fed and the reaction takes place is called *reaction* or *retentate* region whereas the part of the reactor where the products permeated through the membrane are collected is the *permeate* chamber.

In the permeate region, the products are usually swept by a gas easily separable from them (often water vapor). The sweep gas can move co-currently or counter-currently with respect to the reacting mixture. Each of these schemes has advantages and drawbacks.

A schematic representation of these two possibilities is shown in Fig. 1.1. The reaction chamber is the inner tube where a fixed bed of catalyst is assumed to be present. The permeate chamber is the annular region between the inner tube and the shell. In the permeate region, the sweep gas flows in co-current mode in the case (a) and in counter-current mode in the case (b). One or more products of the reaction are shown to flow through the membrane from the catalytic-fixed bed toward the permeate region. However, in co-current scheme an inversion of the flux is theoretically possible at some distance from the inlet section since the flux

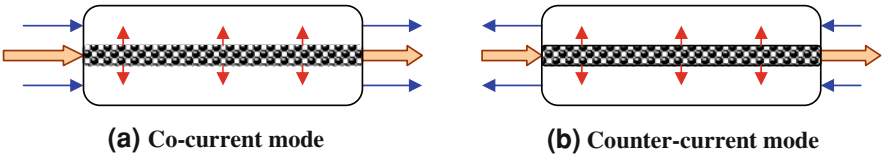

Fig. 1.1 Schemes of feed and sweep gas motion

of a compound occurs from regions with high partial pressures toward those with lower partial pressures. In co-current mode, both reacting mixture and sweep gas are relatively poor of products in the inlet section so that some compounds generated by the reaction can diffuse from the reactor to the permeate chamber; but, along the axis of the reactor the sweep gas is more and more rich of these compounds where their partial pressure in the reacting mixture decreases due to the transport through the membrane, the slowing of the reaction rate and the pressure drop along the catalytic bed. When partial pressures have the same value in the reaction and permeate chambers, the flux stops. In the next sections of the reactor, an inverse transport from permeate to the reaction region could occur if the effect of pressure drop is prevailing on the generating rate due to the reaction.

This anomalous behavior is to be taken into account, but it is usually only a theoretical oddness.

Obviously, this anomaly is not generally allowed in counter-current mode where the end section of the reactor is characterized by low pressures of removable compounds in the reacting region but by a practically pure sweep gas entering into the permeate region.

In Fig. 1.2, a draft of a reactor for methane steam reforming with multiple membrane tubes for hydrogen separation, operating in co-current mode, is shown.

Unfortunately, the integrated solution of MRs, although very intriguing for the compactness of the equipments, presents some technical problems.

Some membranes are sensitive to high temperatures so that they could be incompatible with the reactor temperature. Furthermore, in an integrated MR, damage to the membrane needs to stop the system, to unload the catalyst (if present), to substitute the membrane, and a new start-up of the system.

Due to these main reasons, new configurations called Staged Membrane Reactor (SMR) or Reformer and Membrane Modules (RMMs) have been proposed in the technical literature [25–29].

A SMR is a series of modules (RMM) each composed of a traditional reactor followed by a membrane separation unit. The stream flowing out of the reactor, rich of reaction products, enters into the separation unit where the selective membrane removes one of the products. The retentate of the membrane unit is then fed to the subsequent module. A system of heat exchangers can be present between each unit and the following one. A system composed of two modules is shown in Fig. 1.3.

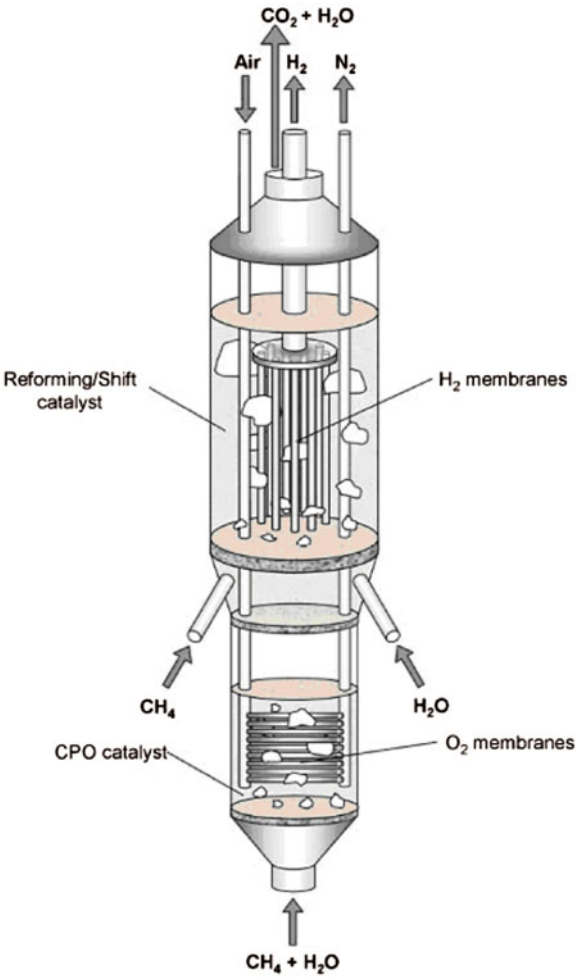

Fig. 1.2 Multiple membranes reactor for methane steam reforming (http://fcre.tnw.utwente.nl/)

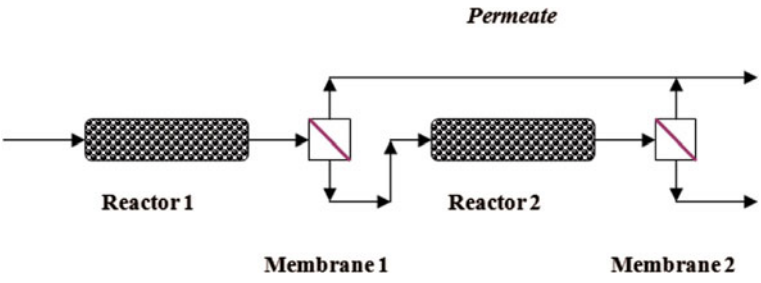

Fig. 1.3 Staged membrane reactor with two modules

A SMR is not strictly a single equipment but each module and the whole system offer "enhanced performance in terms of separation, selectivity, and yield" [1].

An optimized design of a SMR requires the evaluation of a number of parameters such as number of modules, conversion to be achieved in each reactor, degree of product removal in each membrane unit, temperature distribution etc.

It is easy to realize that a system composed of an infinite number of modules approaches the behavior of an integrated MR if the reaction volume and the product removal degree are infinitesimal in each module.

Figure 1.4 shows the RMM test plant having the capacity of 20 Nm^3/h of pure hydrogen, developed and fabricated by Tecnimont KT and deeply described in Chap. 10. The plant, composed by a two-stages natural gas steam reformer + Pd-based separation modules, has demonstrated the feasibility of SMR configuration.

Fig. 1.4 20 Nm^3/h of pure H2 capacity RMM plant (Courtesy from Tecnimont KT)

1.4 Theoretical Study of Staged Membrane Reactor Performance

The following very simple reversible reaction in gaseous phase can be used to show the effect of separation units on the attainable conversion:

$$A \Leftrightarrow B \qquad (-r_A) = k_1 \cdot P_A - k_2 \cdot P_B \tag{1.20}$$

If the equilibrium constant K_P at a certain temperature T is assumed to be $K_P = 0.4$, the equilibrium conversion is:

$$X_A^{eq} = \frac{K_P}{K_P + 1} = 0.8$$

This is the maximum value of conversion attainable in an isothermal reactor operating at the temperature T. It is easy to show that the reaction volume needed to achieve a conversion X_A in an isobaric and isothermal plug flow reactor is:

$$V(X_A) = \frac{F_A^0}{k_1 \cdot P} \cdot X_A \cdot \ln\left(\frac{X_A^{eq}}{X_A^{eq} - X_A}\right) \tag{1.21}$$

In order to achieve the equilibrium conversion an infinite volume V of reactor is required since forward and reverse reaction rates tend to become equal as equilibrium is approached.

However, if the scheme of Fig. 1.3 is adopted and a membrane unit (Membrane 1) is used to remove a fraction γ of the product B generated in the first reactor of finite volume V_1, the reaction can proceed in the second reactor and a conversion even higher than the equilibrium value can be reached in a finite reaction volume given by the sum of the two reactor volumes, V_1 and V_2.

In Fig. 1.5, the reaction volume required to achieve a conversion X_A is shown for three values of removal fraction γ.

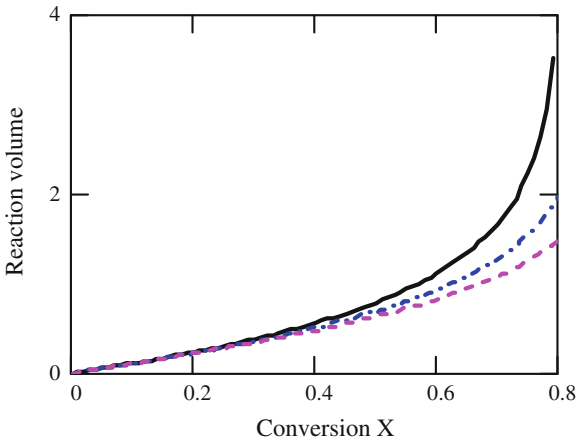

Fig. 1.5 Reaction volume versus conversion: $\gamma = 0$ *solid line*; $\gamma = 0.3$ *dash and dot line*; $\gamma = 0.5$ *dash line* (parameters used in this simulation: $k_1 = 1$ mol/(m^3 min atm); $P_1 = P_2 = 5$ atm; $F_A^0 = 5$ mol/min.)

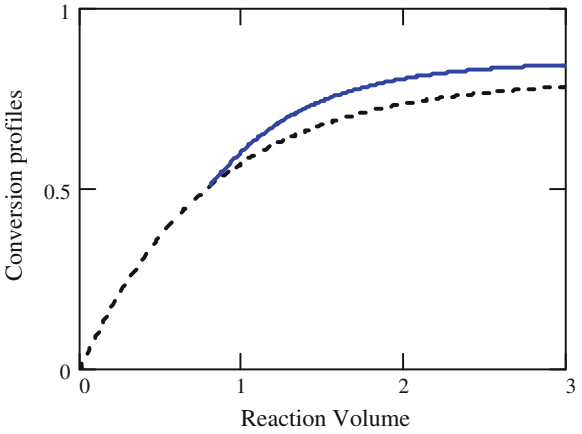

Fig. 1.6 Conversion profiles along the reactors. *Dash line*: only a reactor without product removal; *solid line*: 50% product removal at $V_1 = 0.8$

An infinite volume is required to get $X_A = 0.8$ if no product removal is implemented, whereas the same conversion can be obtained by very lower volumes (about $V = 2$ and $V = 1.5$) when removal ratios ($\gamma = 0.3$ and 0.5, respectively) are used.

Likewise, in a reaction volume of 1, a conversion $X_A = 0.572$ is achieved when no product removal is carried out, while conversions $X_A = 0.625$ and $X_A = 0.674$ are obtained with removal fractions $\gamma = 0.3$ and $\gamma = 0.5$, respectively.

Figure 1.6 shows the effect of product removal on conversion profiles along the first and the second reactor (see Fig. 1.3).

A removal ratio $\gamma = 0.5$ used in the first membrane unit (Fig. 1.3) located at the outlet of a reactor with a volume $V_1 = 0.8$ allows the conversion profile in the second reactor to be higher than in the case of absence of membrane unit.

1.5 Recycle of Retentate

The fluid not permeated at the end of the set of modules contains reaction products as well as un-reacted compounds which could be a valuable material. This mixture undergoes different treatments depending on the nature of the material and the kind of the process. In some cases, a further separation and purification operation are used after the reaction step to recover useful compounds. For example, in the case of steam reforming of light hydrocarbons for producing hydrogen, a pressure swing adsorption (PSA) step could be used for recovering pure hydrogen not permeated through the membrane of the reaction system.

An interesting solution is used in cogeneration processes when the retentate gas has a high energetic content. In this case, a part of the exiting gas is burned to give power to an electric generator whereas the residual part is recycled to the reaction system to convert the un-reacted compounds. A simple scheme of the recycle system is shown in the Fig. 1.7, while a complete process scheme of a two steps

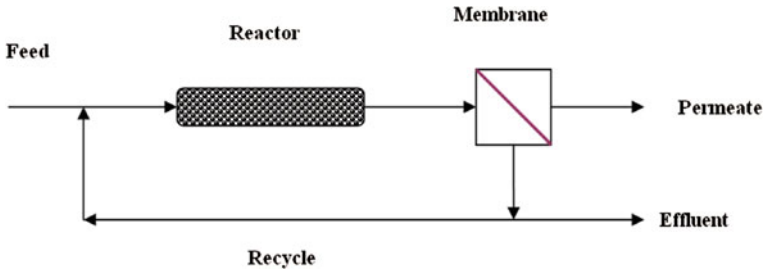

Fig. 1.7 Membrane system with recycle

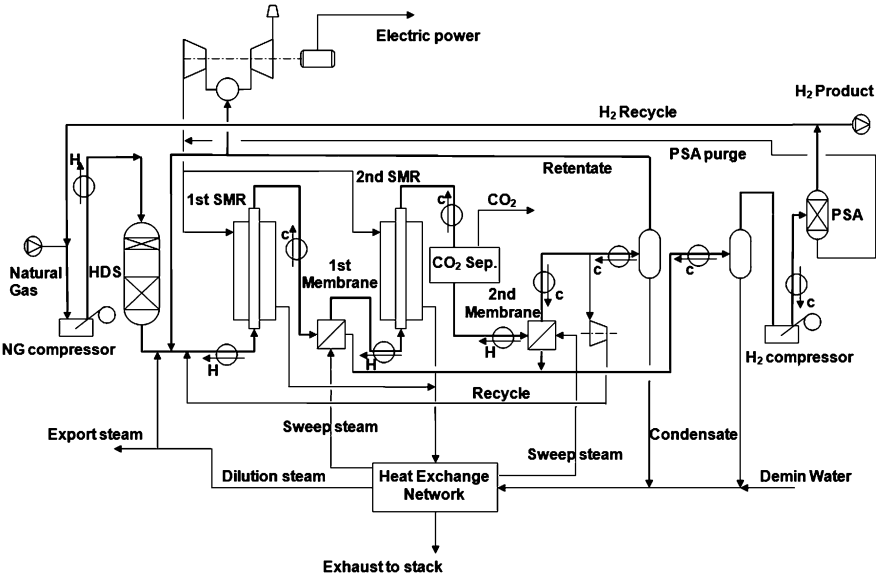

Fig. 1.8 Two-steps RMM natural gas steam reforming process with electric power production and recycle layout [25, 29]

RMM plant with a recycle stream and electricity power production by retentate gas is reported in Fig. 1.8 (refer to [25, 29] for a complete description and assessment of the plant).

It is known that, in a traditional tubular reactor, the recycle of a portion of the exiting stream makes worse the performance of the reactor; however, the case of MRs is very different due to the removal of a product and considerable improvements can be achieved.

Figure 1.9 shows the effect of recycle ratio R on the conversion.

The conversion X_A is defined as the reacted fraction of A in the feed leaving the system with the effluent. The removal percentage ρ is the ratio between the flow rate of B in permeate and the flow rate of this product entering the membrane module.