MODELING OF METHANE STEAM REFORMING IN A PALLADIUM MEMBRANE REACTOR

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Abstract — **A mathematical model of a membrane reactor used for methane steam reforming was developed to simulate and compare the maximum yields and operating conditions in the reactor with that in a conventional fixed bed reactor. The methane steam reforming reaction has been investigated from a modeling viewpoint, considering the effect of different parameters on methane conversion and H_2/CO ratio. Results show that the membrane reactor presents higher methane conversion yield and can be operated at milder conditions than the fixed bed reactor. Control of the H_2/CO ratio is possible in the membrane reactor making the technology more suitable to be used in connection to gas-to-liquid processes (GTL).**

Keywords — **Steam Reforming, Methane, Membrane Reactors**

I. INTRODUCTION

Methane steam reforming is one of the most important chemical processes for the production of syngas and hydrogen. In recent years, the abundant availability of natural gas and the increasing demand of hydrogen have led to high interest to further develop this process increasing the yield of syngas (Shu *et al.*, 1994; Rostrup-Nielsen, 1984).

Methane syngas reforming involves two reversible reactions: reforming and water gas shift. The first is endothermic and limited by thermodynamic equilibrium. Therefore, the development of a membrane-based separation process can open-up the possibility of increasing the conversion of the reforming process. As hydrogen is selectively removed from the reactor, the chemical equilibrium of the reactions is shifted towards the products, resulting in an increase in the conversion of methane to hydrogen and carbon monoxide. As an additional advantage, the membrane reactor offers the possibility of supplying hydrogen with the same conversion degree in higher purity, than that supplied by the conventional reactor, under less severe operational conditions. Methane stream reforming in a membrane reactor becomes a transfer-limited reaction related with membrane porosity and diffusivity, rather than an equilibrium-limited reaction (Assaf *et al.*, 1998).

The development of palladium-based membrane separation process has opened up a new possibility to enhance membrane steam reforming conversion. Some researchers have reported methane conversions as high as 96% with Pd-membranes in isothermal operation (Shu *et al.*, 1994; Oertel *et al.*, 1987; Adris *et al.*, 1991; Lin *et al.*, 2003). New improvements are been done in membrane materials and structures, which supports the selective metal in porous glass and porous alumina ceramic substrate, and in nanostructured carbides.

This work presents the mathematical modeling of a one-dimensional, non-isothermal membrane reactor operating at steady-state, comparing and discussing reactor and yield improvements with results from a conventional fixed bed reactor.

II. MEMBRANE REACTOR

In methane steam reforming, the catalytic fixed-bed reactor is fed with a gas mixture of CH_4 and H_2O in a molar ratio from 1:3 to 1:4. Commercial catalyst is composed of nickel supported in alumina and the reactor is composed of vertical tubes (between 10 and 900 tubes inside the reactor) with internal diameters from 7 to 16 cm and lengths from 6 to 12 m, inserted in a radiant furnace chamber. The feed conditions are about 600°C and from 1.5 to 3.0 MPa. The maximum temperature that the reactor can support is limited by the metallurgical limitations of the tubes, since at higher temperatures the metal tubes can creep under stress.

The membrane reactor configuration is quite simple and consists of an external steel tube (shell) with an inner membrane wall tube were the sweep gas flows (permeation zone). Methane and steam are continuously fed into the catalytic zone, and a sweep gas, usually nitrogen is introduced on the permeate zone to drag the permeated hydrogen. A scheme of the reactor is shown in Fig. 1.
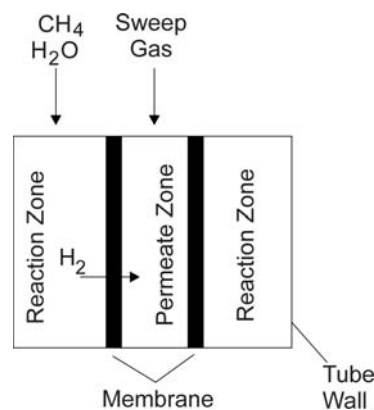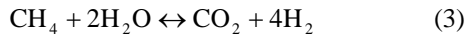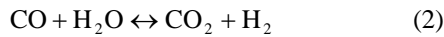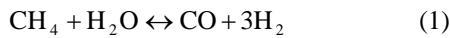

Fig. 1. Scheme of the membrane reactor.

III. MATHEMATICAL MODEL

The basic assumptions made for the membrane reactor were:

- Steady-state operation
- Non-isothermal conditions
- Plug-flow on both reaction and permeation zones
- Intrinsic kinetics for methane steam reforming and water gas shift reactions
- No boundary layer on membrane surfaces.

Methane steam reforming involves two reversible reactions, which were thoroughly studied by Xu and Froment (1989). Equation 1 is known as the methane steam reforming reaction and equation 3 is known as the water gas shift reaction. Equation 2 is known as the carbon dioxide reforming and it is a linear combination of equations 1 and 3.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{2}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \tag{3}$$

The kinetic model for the reaction on a $Ni/MgAl_2O_4$ catalyst is based on a Langmuir-Hinshelwood reaction mechanism which rate expressions for reactions (1) to (3) are given by (Xu and Froment, 1989):

$$R_1 = \frac{\frac{k_1}{P_{H2}^{2.5}} \cdot \left[P_{CH4} \cdot P_{H2O} - \frac{P_{H2}^3 \cdot P_{CO}}{K_1} \right]}{DEN^2} \tag{4}$$

$$R_2 = \frac{\frac{k_2}{P_{H2}} \cdot \left[P_{CO} \cdot P_{H2O} - \frac{P_{H2} \cdot P_{CO2}}{K_2} \right]}{DEN^2} \tag{5}$$

$$R_3 = \frac{\frac{k_3}{P_{H2}^{3.5}} \cdot \left[P_{CH4} \cdot P_{H2O}^2 - \frac{P_{H2}^4 \cdot P_{CO2}}{K_3} \right]}{DEN^2} \tag{6}$$

$$DEN = 1 + K_{CH4} \cdot P_{CH4} + K_{CO} \cdot P_{CO} + K_{H2} \cdot P_{H2} + \frac{K_{H2O} \cdot P_{H2O}}{P_{H2}} \tag{7}$$

Partial pressures for each component are given by:

$$P_{CH4} = (1 - X_{CH4}) \cdot \sigma \tag{8}$$

$$P_{H2O} = \left(\frac{F_{H2O}}{F_{CH4}} - X_{H2O} \right) \cdot \sigma \tag{9}$$

$$P_{H2} = \left(\frac{F_{H2}^0}{F_{CH4}^0} - X_{H2} \right) \cdot \sigma \tag{10}$$

$$P_{CO} = X_{CO} \cdot \sigma \tag{11}$$

$$P_{CO2} = X_{CO2} \cdot \sigma \tag{12}$$

$$\sigma = \frac{P_T}{\left(1 + \frac{F_{H2O}}{F_{CH4}} + \frac{F_{H2}^0}{F_{CH4}^0} + X_{H2} - X_{CH4} - X_{H2O} + X_{CO} + X_{CO2} \right)} \tag{13}$$

The dimensionless flow rates of component i relative to initial flow rate of methane in the reaction side are given by:

$$X_{CH4} = 1 - \frac{F_{CH4}}{F_{CH4}^0} \tag{14}$$

$$X_{H2O} = 1 - \frac{F_{H2O}}{F_{CH4}^0} \tag{15}$$

$$X_{H2} = \frac{F_{H2}}{F_{CH4}^0} \tag{16}$$

$$X_{CO} = \frac{F_{CO}}{F_{CH4}^0} \tag{17}$$

$$X_{CO2} = \frac{F_{CO2}}{F_{CH4}^0} \tag{18}$$

The dimensionless flow rate of hydrogen in the permeate side relative to initial flow rate of methane is given by:

$$Y_{H2} = \frac{F_{H2}^{PS}}{F_{CH4}^0} \tag{19}$$

The changes of each component along the reactor length are given by:

$$\frac{dX_{CH4}}{dz} = \frac{\rho_b \cdot V}{F_{CH4}^0} \cdot (R_1 + R_3) \tag{20}$$

$$\frac{dX_{H2O}}{dz} = \frac{\rho_b \cdot V}{F_{CH4}^0} \cdot (R_1 + R_2 + 2R_3) \tag{21}$$

$$\frac{dX_{H2}}{dz} = \frac{\rho_b \cdot V}{F_{CH4}^0} \cdot (3R_1 + R_2 + 4R_3) - \frac{dY_{H2}}{dz} \tag{22}$$

$$\frac{dX_{CO}}{dz} = \frac{\rho_b \cdot V}{F_{CH4}^0} \cdot (R_1 - R_2) \tag{23}$$

$$\frac{dX_{CO2}}{dz} = \frac{\rho_b \cdot V}{F_{CH4}^0} \cdot (R_2 + R_3) \tag{24}$$

$$\frac{dY_{H2}}{dz} = \frac{2\pi \cdot R_m \cdot L \cdot \beta}{\delta \cdot F_{CH4}^0} \cdot (P_{H2}^{0.5} - P_p^{0.5}) \tag{25}$$

The changes in the temperature throughout the reactor length is given by:

$$\frac{dT}{dz} = \frac{2 \cdot k_T \cdot (T_W - T) + \sum_i R_i \cdot (-\Delta H_i) \cdot \rho_b}{C_P \cdot \rho_g \cdot u_S} \tag{26}$$

The kinetic parameters for the reaction are presented in Table 1. The equilibrium constants and membrane permeance are presented in Table 2, and the simulated operating conditions are presented in Table 3.

Up to this moment no industrial membrane reactor for steam reforming has been built so it is difficult to estimate apparent rates for the reactions. Conventional steam reformers have apparent rates ranging from 0.8 to 0.05 depending on the conditions and catalyst applied when compared to the kinetic rates published by Xu and Froment (1989). Herein we have intended to be conser-

vative with the amount of hydrogen that permeates through the membrane. As such we have adopted an effectiveness factor of 1.0 so the conversion of methane into carbon monoxide and hydrogen would be higher, case in which relative amount of hydrogen that permeates is lower (as will be shown in Figure 5c of the Result section). If a lower effectiveness factor were used, the conversion of methane would be lower for the same operating conditions and reactor length, leading to a greater removal of hydrogen from the reaction zone and thus, an even higher difference in performance between the conventional reactor and membrane reactor would be obtained.

A numerical problem can arise from the initial value of hydrogen in the feedstock, which if zero (hydrogen-free feedstock), will generate a division by zero in the reaction rate equations. This problem is overcome by setting a very small value for hydrogen partial pressure at the inlet of the reactor. The solution of the differential Eqs. 19-25 was solved numerically by a 5th order Runge-Kutta-Gill method.

Table 1. Kinetic parameters for methane steam reforming.

Parameter	Pre-Exponential Factor	Ea or ΔH [J/mol]
k_1	4.2248×10^{15} [mol.atm$^{0.5}$/g.h]	240.1
k_2	1.955×10^{6} [mol/g.h]	67.13
k_3	1.0202×10^{15} [mol.atm$^{0.5}$/g.h]	243.9
K_{CH4}	6.65×10^{-4} [atm^{-1}]	-38280
K_{H2O}	1.77×10^{5}	88680
K_{H2}	6.12×10^{-9} [atm^{-1}]	-82900
K_{CO}	8.23×10^{-5} [atm^{-1}]	-70650

Table 2. Equilibrium constants and permeance of Pd membrane.

Parameter	Pre-Exponential Factor	Ea or ΔH [J/mol]
K_1	7.846×10^{12} [atm^2]	220200
K_2	1.412×10^{-2}	-37720
K_3	1.11×10^{11} [atm^2]	182400
β	2.889×10^{-1} [mol/m.h.atm$^{0.5}$]	12540

Table 3. Operating conditions and reactor parameters.

Methane flow rate [mol/h]	5200.0
Water/Methane ratio	3.358
CO_2/Methane ratio	0.056
Hydrogen/Methane ratio	0.122
Nitrogen/Methane ratio	0.164
Total Pressure [atm]	29.0
Catalyst Density [g$_{cat}$/m^3]	2355.2
Reactor Length [m]	20.0
Tube internal radius [m]	0.1016
Tube external radius [m]	0.1322
Membrane radius [m]	0.0203
Membrane thickness [m]	2.0×10^{-5}

IV. RESULTS AND DISCUSSION

The major advantage of the membrane reactor is the conversion enhancement of the equilibrium-limited reaction by selective hydrogen removal. As observed in Figs. 2 and 3 the utile reactor length for a conventional reactor is about 10 to 12 meters where after that the reaction reaches equilibrium. In membrane reactors the utile reactor length can be over 20 meters since the equilibrium is dislocated by hydrogen removal.

Figures 2 and 3 show a lower partial pressure of hydrogen throughout the membrane reactor compared to the conventional reactor, indicating hydrogen removal from the reaction zone and thus, the shift of the reaction towards the products. The figures also show an increase in CO and CO_2 partial pressures. Methane conversion is boosted in the membrane reactor presenting a significant enhancement at mild temperatures (Fig. 4a), and H_2/CO ratio is lower than for conventional reactors, which can be interesting when controlling this parameter is important for the process (Fig. 4b).

A. Influence of Temperature

Temperature plays an important role in methane steam reforming, especially at middle temperatures (from 800 to 900K) where the membrane reactor displays a greater conversion of methane compared to the conventional reactor (Fig. 5a). At 850 K, there is an additional conversion of 22.8% if compared to the conventional reactor. At temperatures below 800K the conversion is low, but the difference among reactors is increased and the
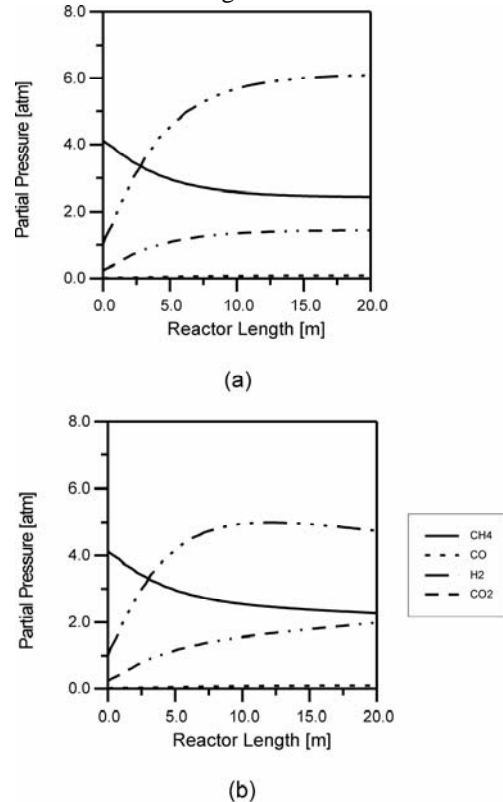

(a)

(b)

Fig. 2. Partial pressures for (a) conventional reactor and (b) membrane reactor operating at isothermal conditions (T = 793 K, P = 29 atm).
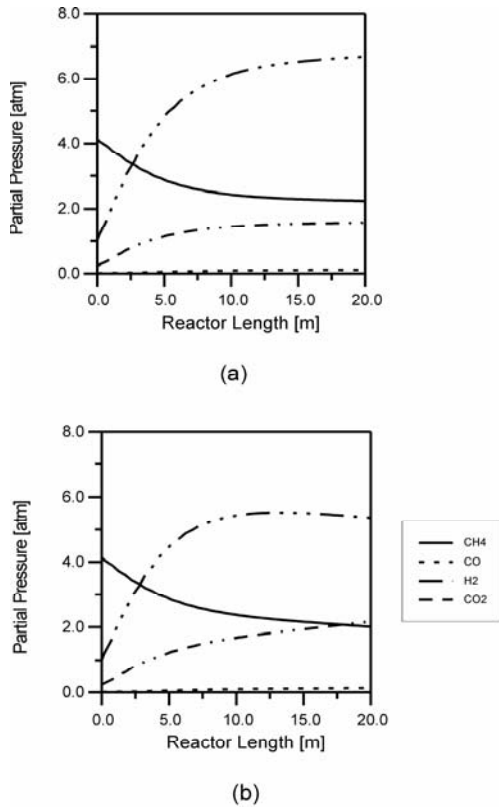
Fig. 3. Partial pressures for (a) conventional reactor and (b) membrane reactor operating at non-isothermal conditions ($T_0 = 753$ K, $T_W = 793$ K, $P = 29$ atm).
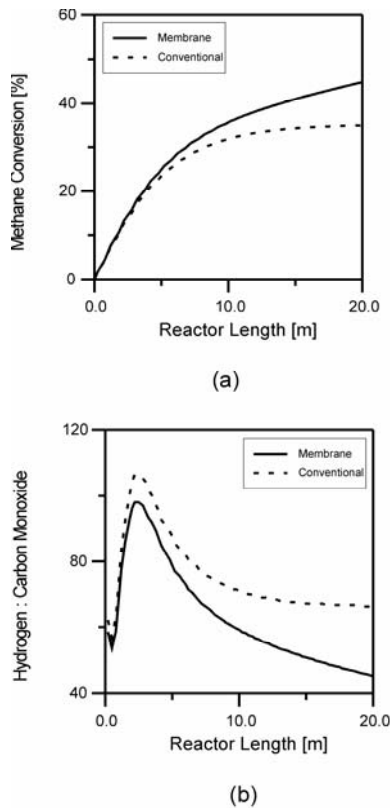

Fig. 4. Methane conversion (a) and H_2/CO ratio (b) for conventional and membrane reactor ($T = 793$ K, $P = 29$ atm).

membrane is responsible for an increase of 28.2% on the conversion. At temperatures higher than 950K the conversion on both reactors is high enough so the membrane only increases the conversion in 3.1%.

Considering the hydrogen/carbon monoxide ratio, higher temperatures lower the H_2/CO ratio benefiting the use of the syngas with GTL (gas to liquid) processes, which requires H_2/CO ratios near 2:1 (Fig. 5b). Anyway, the H_2/CO ratio for Pb-membranes with a thickness of 2.0 μm is higher than 10:1, and pos processing of the syngas is required in order to remove the hydrogen in excess.

Figure 5c shows the fraction of hydrogen that is removed from the reaction zone at different temperatures. Lower temperatures favor the permeance of hydrogen, which easily permeates through the membrane leading to a high fraction of hydrogen in the permeation zone.
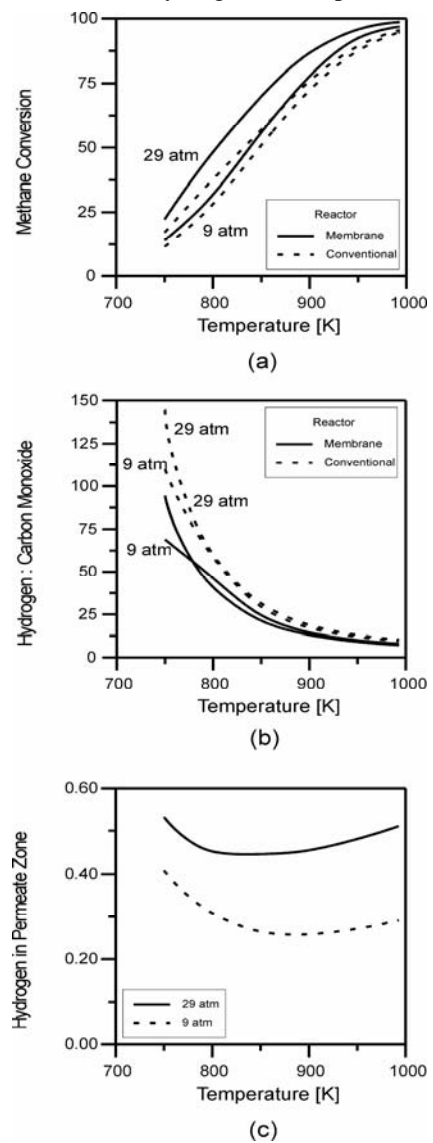

Fig. 5. Influence of temperature in the reactor performance. (a) methane conversion, (b) H_2/CO ratio and (c) fraction of produced hydrogen that goes to the permeate zone.

However, there is a limit for the permeation of hydrogen through the membrane, which reaches a saturation point below 750 K and in this case more hydrogen can only be removed if the surface area of the membrane is increased.

The removal of hydrogen from the reaction side decreases with the increase in temperature. From 750 K to 850 K (middle temperatures), a decrease in the hydrogen content in the permeate zone is observed due to the lower capacity of the membrane in removing hydrogen from the reaction side. Above 850 K a new increase in the hydrogen content in the permeate zone is observed. This increase is mainly due to the higher reaction rate that increases the partial pressure of hydrogen in the reaction side leading to a larger hydrogen partial pressure gradient between the reaction and the permeate zones, which causes a higher hydrogen removal rate despite the lower permeance.

B. Influence of H_2O/CH_4 ratio

Methane steam reforming usually proceeds in the presence of an excess of steam to prevent carbon deposition over the catalyst surface and to enhance steam reforming. The effect of molar steam-to-methane (H_2O/CH_4) ratio was examined by varying this ratio from 1.5 to 4.5. Results for two different temperatures are shown in Fig. 6.

The higher water/methane ratio in the feedstock favors higher conversions, but at the expense of increasing the H_2/CO ratio, which increases considerably at low temperatures (Fig. 6b). If hydrogen in excess if undesirable, such as for GTL processes, the reactor should be run preferably at low water: methane ratios, which can result in the formation of free carbon. Free carbon deactivates the catalyst and therefore is undesirable, but free carbon formation can be avoided by recycling part of the hydrogen steam from the permeate zone to the entrance of the reactor. This additional hydrogen feed contributes to avoiding conditions favorable to solid carbon formation.

C. Influence of Pressure

Higher pressure and thus, increase of hydrogen partial pressure on the reaction side increases the driving force for hydrogen permeation, resulting in an enhancement of the methane conversion. As shown in Fig. 1, higher pressures contribute to an increase in the hydrogen mass transfer from the reaction zone to the permeate zone. Low operating pressures (below 10 atm) do not offer great advantages and the membrane reactor performs much like the conventional reactor.

D. Influence of Membrane Thickness

Membrane thickness plays a major role both in methane conversion and H_2/CO ratio control. Thin membranes (less than 1 μm) can increase conversion even at moderate temperatures (Fig. 7a), so the reactor can operate at milder temperatures with high conversion rates. The H_2/CO ratio (Fig. 7b) is favored towards the application of GTL processes and depending on the condition ap-

plied, the syngas can be directly sent to a GTL reactor after water and CO_2 removal.
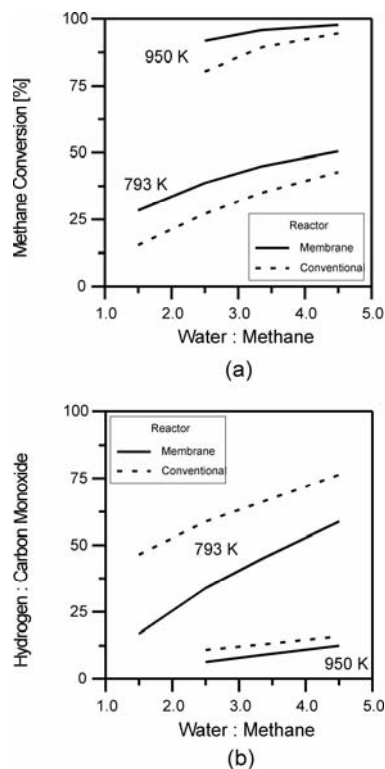

Fig. 6. Influence of water:methane ratio in the reactor performance. (a) methane conversion and (b) H_2/CO ratio (P = 29 atm).
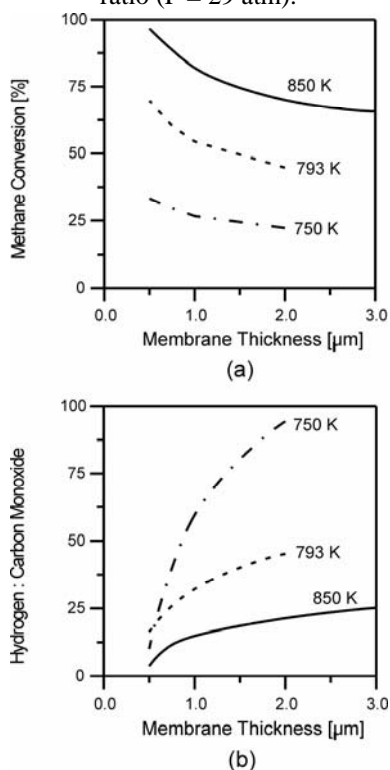

Fig. 7. Influence of membrane thickness in reactor performance. (a) methane conversion and (b) H_2/CO ratio (P = 29 atm).

The best membrane is the one that is thinner as possible in order to increase conversion at mild temperatures, to reduce the H_2/CO ratio and at the same time to resist pressure without breaking or letting the permeation of other gases. Research and development of nano-membranes would benefit enormously reforming reactors.

E. Influence of the Membrane Diameter
The diameter of the membrane tube in relation to the diameter of the tube does not have a significant influence in the reactor performance for highly permeable membranes (Fig. 8). So membranes with smaller diameters are favored since they are less expensive to build reducing capital costs. If membranes with low permeance are used, then membrane diameter will be important and a bigger surface area will be needed to compensate for the low permeance. This is a problem that can lead to a smaller reaction zone space and lower methane processing capability. Low membrane permeances are a critical factor to the performance and economics of process since reduces the amount of hydrogen that is removed from the reaction zone, thus making the membrane reactor operating much like a conventional reactor, which should be avoided.

F. Controlling the H_2/CO Ratio
Controlling the H_2/CO ratio is important, especially to GTL processes where the optimum ratio varies from 0.7 up to 3.0, and influences hydrocarbon product distribution. In membrane reactors, part of the hydrogen produced leaves through the membrane, lowering the H_2/CO ratio and producing an H_2 stream. In order to lower the H_2/CO ratio down to the GTL feed range a good alternative is to use a thin membrane at mild temperatures so no further correction is necessary.

This will not be always the case; so further processing may be required to control the H_2/CO ratio. An option is to pass the crude syngas through a membrane absorption unit so more hydrogen can permeate through the membrane correcting the H_2/CO ratio to the desired level (Fig. 9).

The membrane absorption unit can be shaped as a multitube heat exchanger where the syngas passes through the inner or outer side of the membrane tubes. Hydrogen permeates from the syngas towards the hydrogen-poor sweep gas adjusting the H_2/CO ratio to a desired value.

V. CONCLUSIONS
The methane steam reforming was studied from a modeling point of view in a membrane reactor and a conventional reactor. Simulation results show that different parameters affect methane conversion and H_2/CO ratio, such as temperature, operating pressure, and membrane parameters such as membrane thickness, membrane permeance and membrane tube diameter. In a conventional system an increase in the operating pressure causes a decrease in methane conversion, but in a membrane reactor an increase in the operating pressure corresponds to an increase in methane conversion, since allows for a greater partial pressure gradient between the reaction and permeate zone, thus contributing to shift the equilibrium towards the products.

As such, the membrane reactors are a good alternative to produce syngas for GTL processes or pure hydrogen. Operating conditions can be set to control the H_2/CO ratio to a desired value, removing H_2 through the membrane. High conversions at mild temperatures can be achieved reducing capital and operational costs.
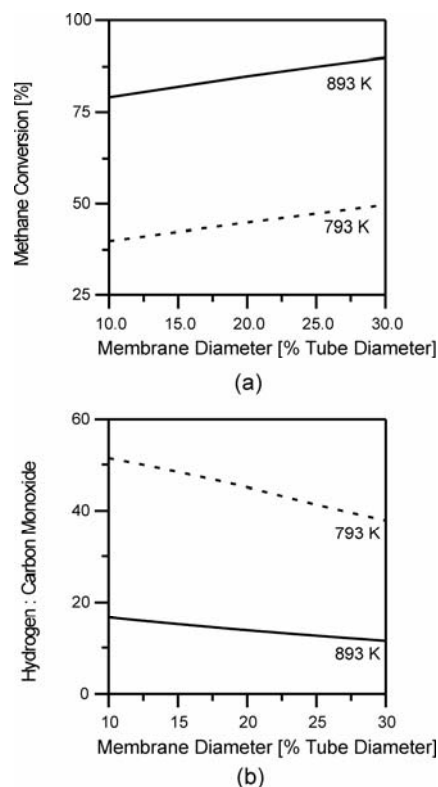
Fig. 8. Influence of membrane thickness in reactor performance. (a) methane conversion, (b) H_2/CO ratio and (c) fraction of produced hydrogen that goes to the permeate zone (P = 29 atm).
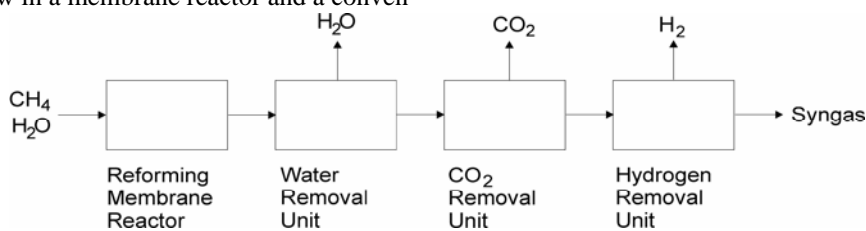
Fig. 9. Flowchart of syngas production units.

ACKNOWLEDGMENT

NOMENCLATURE

C_P heat capacity [J/g.K]

F_i flow rate of component i [mol/h]

F_i^0 flow rate of component i in the feedstock [mol/h]

F_i^{PS} flow rate of component i in the permeate side [mol/h]

k_i rate constant of reaction i

K_i equilibrium constant of reaction i or adsorption coefficient of component i

k_T heat transfer coefficient [J/h.m^2.K]

L membrane tube length [m]

P_i partial pressure in the reaction zone [atm]

P_p hydrogen partial pressure in the permeate zone [atm]

P_T total pressure in the reaction zone [atm]

R_i rate of reaction i [mol/h.g$_{cat}$]

R_m radius of the membrane [m]

T temperature [K]

T_W wall temperature [K]

u_S superficial velocity [m/h]

V reactor volume [m^3]

X_i conversion of component i or dimensionless flow rate of component i relative to initial flow rate of methane

Y_{H2} dimensionless flow rate of hydrogen in the permeate zone relative to initial flow rate of methane in reaction zone

z dimensionless reaction tube length

β permeance of the membrane [mol/m.h.atm$^{0.5}$]

δ membrane thickness [m]

σ corrected pressure [atm]

ΔH heat of reaction [J/mol]

ρ_b catalyst density [g/m^3]

ρ_g gas density [g/m^3]

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