ELSEVIER

Catalysis Today 56 (2000) 53–64

CATALYSIS TODAY

www.elsevier.com/locate/cattod

An analysis of the performance of membrane reactors for the water–gas shift reaction using gas feed mixtures

A. Criscuoli [a,*], A. Basile [b], E. Drioli [a,b]

[a] *Department of Chemical Engineering and Materials, University of Calabria, I-87030 Arcavacata di Rende (CS), Italy*

[b] *Research Institute on Membrane and Modelling of Chemical Reactors, CNR-IRMERC, I-87030 Arcavacata di Rende (CS), Italy*

Abstract

The water–gas shift (WGS) reaction in membrane reactors has been widely studied by several authors. From these works, the increase of the CO conversion above the equilibrium values appears to be possible when hydrogen is removed through the membrane.

However, to date, this feasibility has been verified mostly when feeding pure reagents to the reactor, although in an industrial context the feed normally contains several other compounds.

The objective of this work has been to analyse the effect of the feed composition on the membrane reactor efficiency in order to determine the best conditions in terms of CO conversion. At this purpose, experimental tests with mixtures of different compositions have been carried out in three different systems of reaction: (1) traditional fixed-bed reactor; (2) membrane reactor with mesoporous ceramic membrane; (3) membrane reactor with palladium membrane.

The experiments included permeation (for the membrane reactors) and reaction tests.

The experimental results obtained with the various systems of reaction have been compared.

A mathematical model has been also formulated for the different type of reactors used in order to verify the experimental results obtained.

From the work carried out it can be concluded that by using the palladium membrane reactor it is possible to overcome the equilibrium conversion. Moreover, a complete conversion has been achieved for one of the mixtures fed to the reactor.

Keywords: Water–gas shift reaction; Catalytic membrane reactors; Mixture gases feed

1. Introduction

The water–gas shift (WGS) reaction is present in several industrial processes, such as catalytic steam reforming of hydrocarbons, coal gasification, production of ammonia. Generally, in all these processes, the stream which is fed to the water–gas shift reactor comes from a previous step and consists of different compounds depending on the process considered. For example, in the catalytic steam reforming of hydrocarbons, the gas which leaves the primary reformer and which is fed to the WGS reactor is ca. 76% H_2, 12% CO, 10% CO_2, 1.3% CH_4 on dry basis; when the WGS is applied to the hydrogen production in coal gasification plants, the typical feed composition consists of 48.6% H_2, 21% CO_2, 17.3% CO and 13.1% N_2 [1].

It has already been showed [2,3,4,5] that, by carrying out the WGS reaction in a membrane reactor, where hydrogen is selectively removed through the membrane, it is possible to reach complete conversion,

* Corresponding author. Tel.: +39-984-492014; fax:+39-984-402103.
E-mail address: a.criscuoli@irmerc.cs.cnr.it (A. Criscuoli).

0920-5861/00/$ – see front matter
PII: S0920-5861(99)00262-X

overcoming the thermodynamic constraints. However, to date, this feasibility has been verified mostly when feeding only reagents to the reactor. Few are, in fact, the works appeared in literature relatively to studies on the performance of membrane reactors for the WGS reaction when reagents in mixture with other compounds are used as feed and they are essentially theoreticals. For example, Damle et al. [1] developed a model to simulate a catalytic membrane WGS reactor considering the typical coal gasifier exit composition; Bracht et al. [5] carried out a techno-economical feasibility study for the WGS membrane reactor applied to a CO_2 control in IGCC systems. From a first experimental study carried out by Basile et al. [3] in which reagents were in mixture with products and nitrogen, the CO conversion obtained has never been higher than the equilibrium one. This result has been attributed to the low selectivity of the membrane used: the presence of nitrogen in the gases mixture (53%) reduced, by competition, the hydrogen permeation flux, and, thus, the CO conversion.

In the present work, the effect of the feed composition and membrane characteristics (selectivity and permeability) on the membrane reactor efficiency has been analysed both experimentally and theoretically, in order to determine the best conditions in terms of CO conversion.

2. Experimental section

2.1. Experimental apparatus

Three different systems of reaction have been analysed:

1. fixed-bed reactor;
2. mesoporous membrane reactor;
3. palladium membrane reactor.

All of them were in tubular shape with the membrane as inner tube. For the traditional fixed-bed reactor, the inner tube was a simple stainless-steel tube (length 21 cm, inner diameter 6.7 mm) having the same volume of reaction of the two membranes. A low-temperature shift catalyst (9.64 g) has been packed in the lumen of the membranes/tube where the feed stream is supplied. For what concerns the fixed-bed reactor and the mesoporous ceramic membrane reactor, the experimental apparatus used has been described elsewhere [2]. For the palladium membrane reactor, the same apparatus has been utilised except for the warming up of the reactor. In this case, a coil rolled up on three bars of quartz positioned on the palladium membrane, was connected to a potentiometer; by using it, we regulated and controlled the temperature of the reactor which was measured by a thermocouple positioned near by the palladium surface. The bars serve to prevent the contact between coil and palladium surface.

2.2. Mesoporous membrane reactor

The membrane used is a commercial asymmetric tubular furnished by SCT (France) alumina membrane (internal diameter 6.7 mm, external diameter 10.2 mm, length 25 cm). The inner layer is 4 μm thick γ-alumina with an average pore diameter of 4 nm. The other layers in α-alumina have larger pores dimensions (0.2–12 μm) and are thicker. The reactor is 27 cm long with an inner diameter of the outer tube of 20 mm. The permeation occurs for 21 cm, being the ends of the membrane sealed. The catalyst is packed for this length. The volume of reaction is 7.4 cm^3.

2.3. Palladium membrane reactor

The palladium membrane has been obtained by folding into a cylindrical shape a palladium foil 70–75 μm thick; length of the membrane tube: 15 cm. To prevent the direct contact between catalyst and the palladium surface, a commercial porous alumina membrane has been positioned in between. The Pd membrane is not sealed over the ceramic one and the distance between the two membranes is of 20 μm. The reactor is 28 cm long with an inner diameter of the outer tube of 40 mm. The catalyst is packed only in the inner of the palladium membrane. Two stainless-steel tubes (each 5 cm long) are jointed at the ends of the palladium membrane and are sealed to the shell by an O-ring system to prevent leakage between lumen and shell. The effective lumen diameter is 8 mm and the volume of reaction is 7.5 cm^3.

Although the length of the two membranes used is different, the two membrane reactors present the same volume of reaction.

3. Model description

The mathematical model developed to simulate the behaviour of the three systems of reaction is based on the formulation of differential mass balances at steady state. The flux of species through the membrane is obtained by considering:

3.1. Mesoporous membrane

Two mass transfer resistances in series:
- the resistance through the film at the interface between the inside membrane wall and the gas mixture;
- the resistance through the ceramic membrane.

3.2. Palladium membrane

Three mass transfer resistances in series:
- the resistance through the film at the interface between the inside membrane wall and the gas mixture;
- the resistance through the ceramic membrane;
- the resistance through the palladium layer.

Some hypothesis made in order to simplify the calculations are:
- isothermal and isobaric conditions (experimentally verified);
- negligible effect of competitive reactions (experimentally verified);
- plug flow fluid dynamic regime;
- ideal gas behaviour;
- negligible effect of the catalyst pellets on the evaluation of the resistance of the interface film between the composite palladium membrane and the gas.

From previous theoretical results [6], it appeared that the kinetic for membrane reactors can be different from the kinetic studied in a traditional reactor because of the changes of the type of contact between catalyst and reactants, contact time and of the concentration of species.

For that reason, in the simulation program both kinetic expressions used in the previous work continue to be considered:

Langmuir–Hinshelwood's kinetic expression [7]

$$r = k\ K_{CO} K_{H_2O} (P_{CO} P_{H_2O} - P_{CO_2} P_{H_2} / K_{eq}) (1 + K_{CO} P_{CO} + K_{H_2O} P_{H_2O} + K_{CO_2} P_{CO_2})^{-2} \rho_{cat}/60 \quad (\mathrm{mol/cm^3\,s})$$

Temkin's kinetic expression [8]:

$$r = k(P_{H_2O} P_{CO} - P_{H_2} P_{CO_2} / K_{eq})(A P_{H_2O} + P_{CO_2})^{-1} \quad (\mathrm{s^{-1}})$$

The values of the parameters present in the above equations have been taken from literature [7,8] and are reported in Appendix A.

All the theoretical calculations related to the determination of the CO conversion have been made by using the experimental permeability and separation factor values.

4. Permeation tests

To determine the permeability and the separation factors of the membranes used, a series of experiments has been carried out.

It has been already shown [9] that the separation of species through membranes can be different depending on the way of feeding: single gas feed or mixed gas feed. In particular, when gases are fed singularly, the selectivities are higher than in the other case. This is due to the fact that, by using mixed gas feeds the fluxes values are influenced by the multicomponent interactions which strongly impact the overall behaviour.

On the basis of these results, to realistically simulate the process, the permeabilities and separation factors of the membranes have been determined by feeding to the reactor a mixture of gases containing all the species present during the reaction. To obtain a 'true' separation factor, some inert glass pellets have been packed in the lumen of the membrane at the feed side. The mixture has been fed to the lumen side; the pressure difference has been fixed by controlling the pressures at the lumen and shell side. All experiments have been made at the reaction temperature (325°C).

During the permeation tests, the hydrogen permeation rates through the membranes have been determined by measuring the permeate flow rate by using a bubble flow meter and analysing the stream composition by a gas chromatograph (GC). The uncertainties in the determination are related to the GC error (ca. 3%). The measures were repeated until the obtained

value was reproduced for at least three times. The same procedure has been followed during reaction tests.

5. Reaction tests

Three mixtures of different composition have been used for reaction tests: mix1: CO 32%, CO_2 12%, H_2 4%, N_2 52% on dry basis; mix2: CO 12.27%, CO_2 11.49%, H_2 75%, CH_4 1.24% on dry basis; mix3: CO 27%, H_2 73% on dry basis (see Table 1). The operating conditions varied during the experiments have been:

Fixed-bed reactor:
- time factor
- temperature

Mesoporous membrane reactor:
- time factor
- sweep gas flow rate.

Palladium membrane reactor:
- time factor
- lumen pressure (P_{lumen})
- sweep gas flow rate
- feed molar ratio.

The sweep gas has been fed always in co-current mode with respect to the feed stream. The shell pressure (P_{shell}) has been always 1 atm. The CO conversion has been calculated by a balance on CO. From a carbon balance no carbon formation occurred during all the reaction tests and for all mixtures used due to the high selectivity of the catalyst utilised. Same result has been achieved in previous works on WGS reaction by Basile et al. [3,10].The methane did not react being the flow rate of methane at the exit equals to the feed value.

6. Results and discussion

6.1. Permeation results

6.1.1. Mesoporous membrane

The separation factors obtained are in agreement with the ones presented by Basile et al. [3] and Damle et al. [1], and are reported in Table 2. Their values are lower than the Knudsen ones because of the presence of viscous flow.

A permeance of hydrogen of 3.8×10^{-6} mol/m^2 s Pa has been found at 595 K. This value is in agreement with literature data [11].

6.1.2. Palladium membrane

The permeation tests pointed out a very excellent performance of the palladium membrane, being only hydrogen the specie which passed through it. The experiments have been carried out at several temperatures (320–350°C) and lumen pressures (130–150 kPa). The shell pressure was always equal to 101.3 kPa. From them, it results that both the Sievert's law and the Arrhenius's law are followed.

The permeability of hydrogen through the palladium is [12]

$$Pe = 2.95 \times 10^{-4} \exp(-5833.5/T) \ (\text{mol m}/\text{m}^2\ \text{s Pa}^{0.5})$$

At 325°C, the permeability of hydrogen is 1.63×10^{-8} mol m/m^2 s Pa$^{0.5}$, in agreement with the value found by Itoh et al. [13] (7.75×10^{-9} mol m/m^2 s Pa$^{0.5}$) calculated at the same temperature.

6.2. Reaction results

The obtained results are shown in Figs. 1–11.

In Fig. 1 is reported the CO conversion versus temperatures for the three mixtures in the fixed-bed reactor. A maximum is observed around 595 K: the same behaviour has been found by Basile et al. [3] when using a composite Pd/ceramic membrane with selectivities of the order of 8.24. This result represents a compromise between kinetic rate (which is higher at higher temperatures) and the thermodynamic (for which lower temperatures give higher conversions) and has been confirmed also theoretically by Violante

Table 1
Composition of the mixtures used as feed

Mixture composition on a dry basis	CO	CO_2	H_2	N_2	CH_4
Mix1	32%	12%	4%	52%	–
Mix2	12.27%	11.49%	75%	–	1.24%
Mix3	27%	–	73%	–	–

Table 2
Separation factors for the mesoporous membrane, $T = 595$ K

	Knudsen values	Experimental values
H_2/N_2	3.74	1.38
H_2/CO	3.74	1.38
H_2/H_2O	3	1.11
H_2/CO_2	4.69	1.46
H_2/CH_4	2.83	1.047

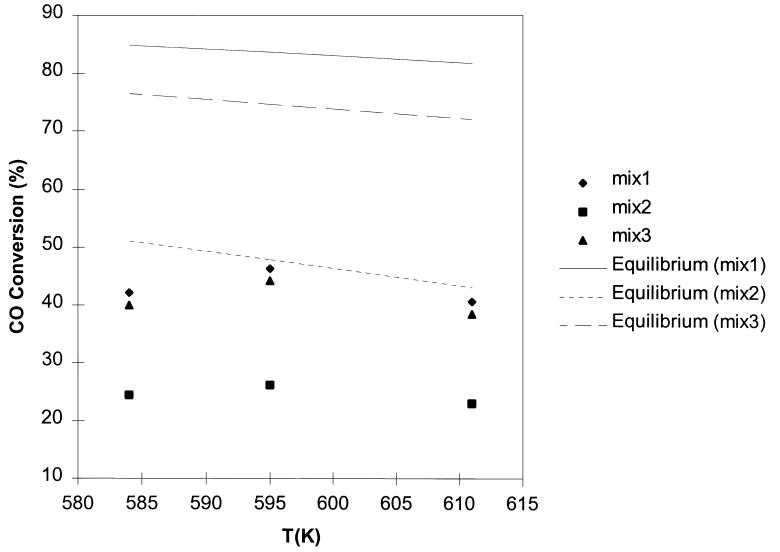

Fig. 1. CO conversion versus temperature for the three mixtures in the fixed-bed reactor. $H_2O/CO = 1.1$; $P = 1$ atm; time factor $= 15.45 \times 10^3$ g-cat min $(CO\ mol)^{-1}$.

et al. [14] for the WGS reaction carried out in a composite membrane configuration. From this figure, higher conversions are achieved for the mixed feed gas compositions thermodynamically more favourable for CO conversion.

Figs. 2–4 show the effect of the time factor on the CO conversion for the three reaction systems and the three mixtures used. As expected, by using membranes it is possible to reach higher conversions than the traditional reactor. In particular, the equilibrium value

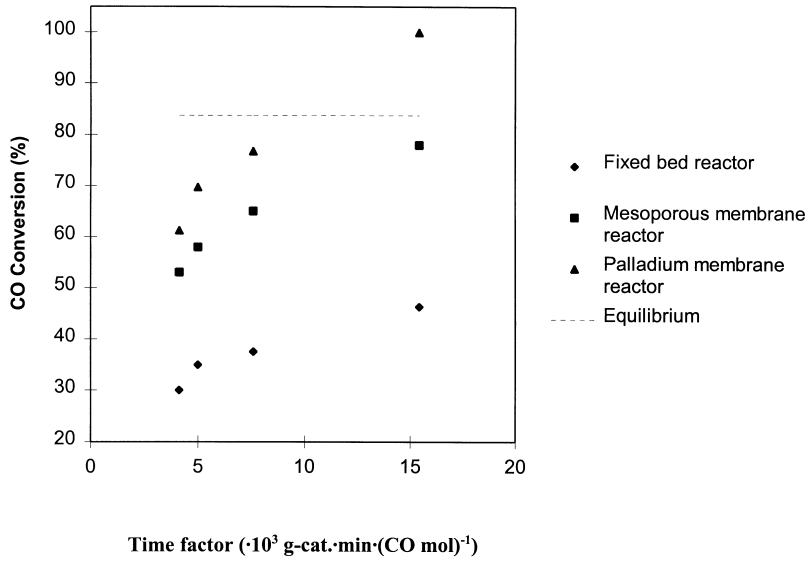

Fig. 2. Effect of the time factor on the CO conversion for the three reaction systems and mix1. $T = 595$ K; $H_2O/CO = 1.1$; fixed-bed reactor: $P = 1$ atm; mesoporous membrane reactor: $P_{lumen} = P_{shell} = 1$ atm; no sweep gas; palladium membrane reactor: $P_{lumen} = P_{shell} = 1$ atm; sweep gas flow rate = 43.6 ml/min.

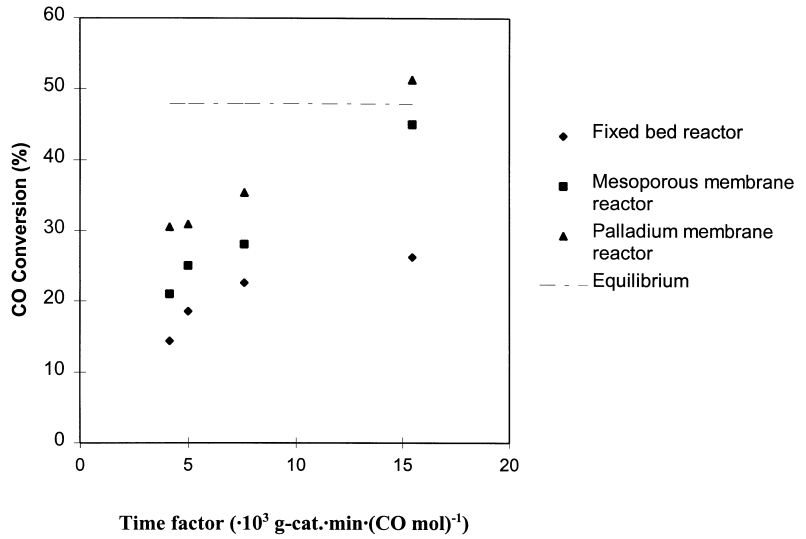

Fig. 3. Effect of the time factor on the CO conversion for the three reaction systems and mix2. $T = 595$ K; $H_2O/CO = 1.1$; fixed-bed reactor: $P = 1$ atm; mesoporous membrane reactor: $P_{lumen} = P_{shell} = 1$ atm; no sweep gas; palladium membrane reactor: $P_{lumen} = P_{shell} = 1$ atm; sweep gas flow rate = 43.6 ml/min.

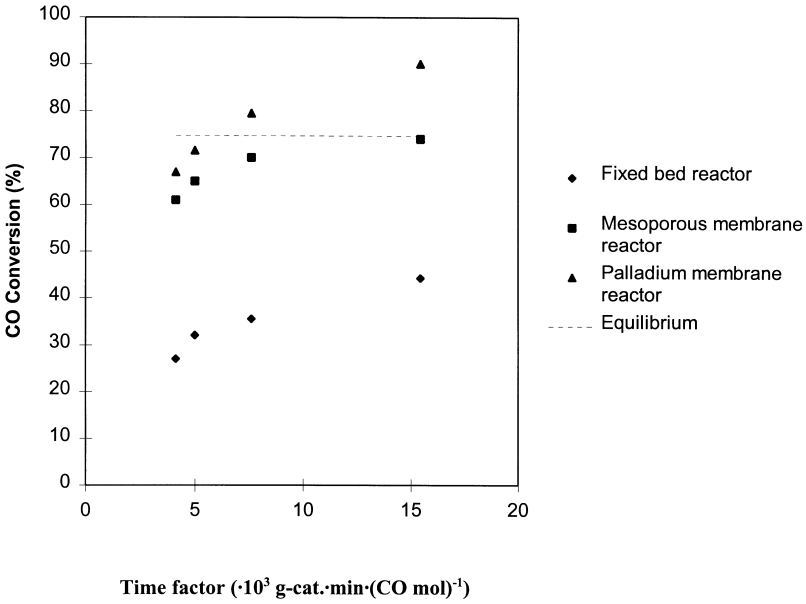

Fig. 4. Effect of the time factor on the CO conversion for the three reaction systems and mix3. $T = 595$ K; $H_2O/CO = 1.1$; fixed-bed reactor: $P = 1$ atm; mesoporous membrane reactor: $P_{lumen} = P_{shell} = 1$ atm; no sweep gas; palladium membrane reactor: $P_{lumen} = P_{shell} = 1$ atm; sweep gas flow rate = 436 ml/min.

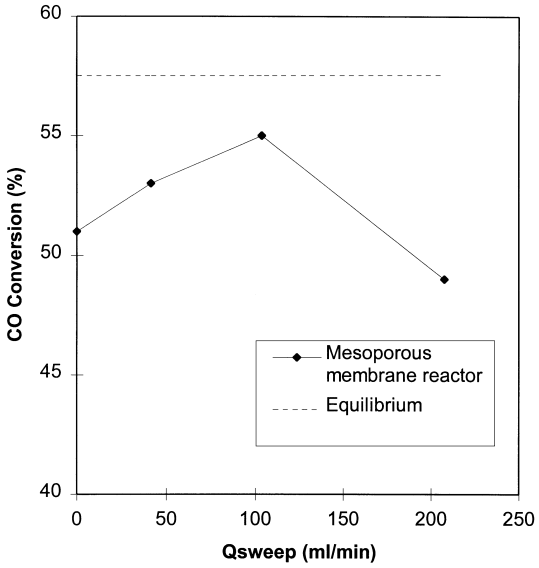

Fig. 5. CO conversion against the sweep gas flow rate for the mesoporous membrane and mix3. $H_2O/CO = 0.73$; $T = 595\,K$; $P_{lumen} = P_{shell} = 1\,atm$; $Q_{feed} = 14.1 \times 10^{-5}\,mol/s$; co-current flow mode.

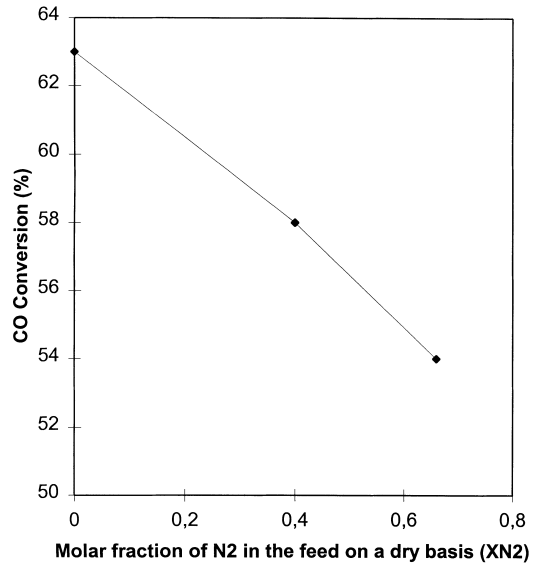

Fig. 6. Effect of nitrogen in the feed stream on the CO conversion for the mesoporous membrane; no sweep gas; $T = 595\,K$; $H_2O/CO = 1.1$; $Q_{feed} = 8.78 \times 10^{-5}\,mol/s$.

can be overcome only by palladium membrane reactor, in which just the hydrogen permeates, operating at high time factors. The fact that very highly selective membranes have to be used in order to overcome the equilibrium conversion is also confirmed by data found by Basile et al. [3]: the equilibrium conversion has never been reached when feeding a mixture of gases to the reactor, although a membrane with selectivities ($H_2/N_2 = 8.24$) higher than the mesoporous one has been used.

Also, in membrane reactors the highest conversion is obtained as the composition of the mixtures tends to the more thermodynamically favourable ones. At the highest time factor (15.45×10^3 g-cat min $(CO\,mol)^{-1}$) the following conversion values have been obtained:

Palladium membrane reactor	Mesoporous membrane reactor	Fixed-bed reactor
mix1: 100%	mix1: 78%	mix1: 46.31%
mix2: 51.3%	mix2: 45%	mix2: 29.17%
mix3: 90.1%	mix3: 74%	mix3: 44.21%

Complete conversion has been obtained for mix1 at the highest time factor. By working at the right operating conditions it is, thus, possible to convert all the CO fed to the reactor. Complete conversions for the WGS reaction have also been reported by Basile et al. [10], Violante et al. [14] and Uemiya et al. [15].

It is interesting to note that also if the trend is the same for the three mixtures analysed, some differences can be noted.

For example, for mix1 (see Fig. 2) the equilibrium conversion is reached at time factors of the order of 10 (10^3 g-cat min $(CO\,mol)^{-1}$) when using palladium membrane reactor while with mesoporous membrane the conversion value closer to the equilibrium is obtained for time factors around 15. The difference, at each time factor, in conversion values obtained by the three systems of reaction remains the same (higher between the mesoporous membrane reactor and fixed-bed reactor), with exception for time factor of 15 at which the range between points obtained by membrane reactors becomes larger (Pd membrane reactor: 100%; mesoporous membrane reactor: 78%).

For mix2 (see Fig. 3), the equilibrium conversion is achieved at time factors around 12 for the palladium membrane reactor. Also, in this case, the difference

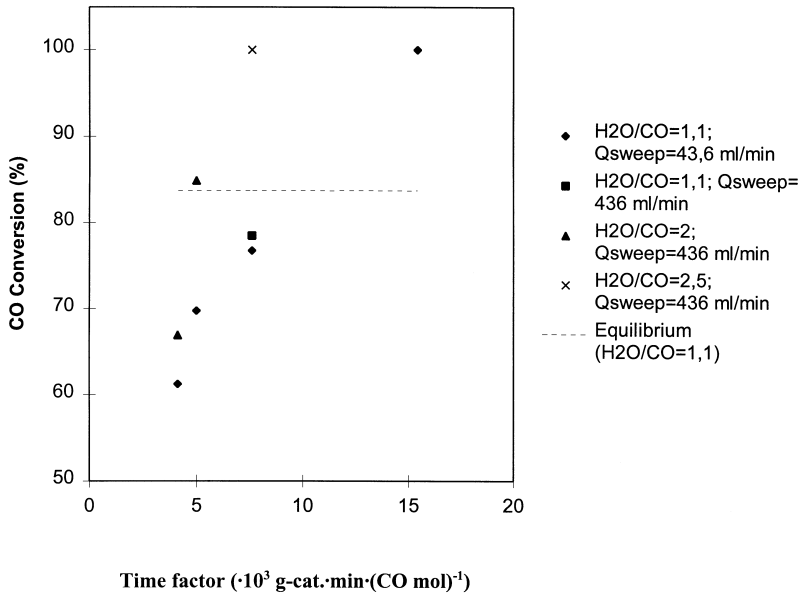

Fig. 7. CO conversion versus the time factor for mix1 in the palladium membrane reactor. $T = 595\,\text{K}$; $P_{\text{lumen}} = P_{\text{shell}} = 1\,\text{atm}$; co-current flow mode.

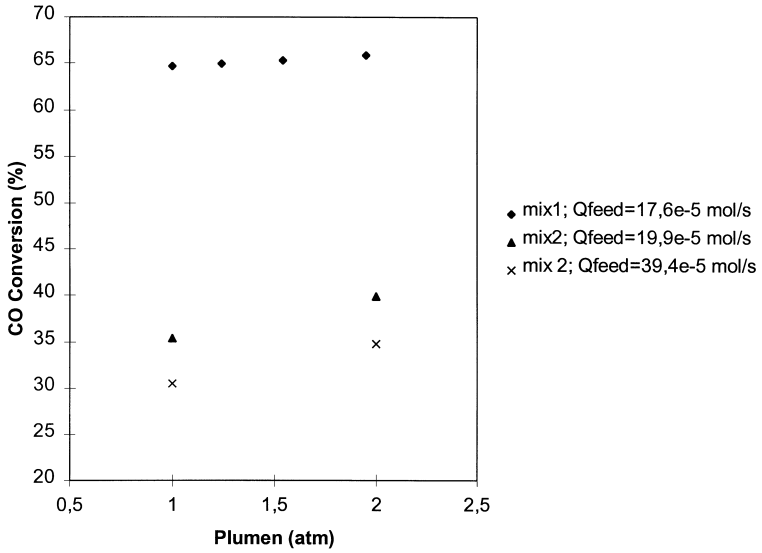

Fig. 8. Effect of the lumen pressure on the CO conversion for the palladium membrane for mix1 and mix2. $H_2O/CO = 1.1$; $T = 595\,\text{K}$; $P_{\text{shell}} = 1\,\text{atm}$; $Q_{\text{sweep}} = 436\,\text{ml/min}$.

in conversion values obtained by the three reactors is higher at higher time factors, but now it is relative to the mesoporous membrane reactor and fixed-bed reactor. The gain in conversion achieved by palladium membrane with respect to the mesoporous one is now lower (Pd membrane reactor: 51.3%; mesoporous membrane reactor: 45%).

For mix3 (see Fig. 4), equilibrium conversion is reached at time factor of the order of 5 for the palladium membrane. At time factor equal to 15 also the

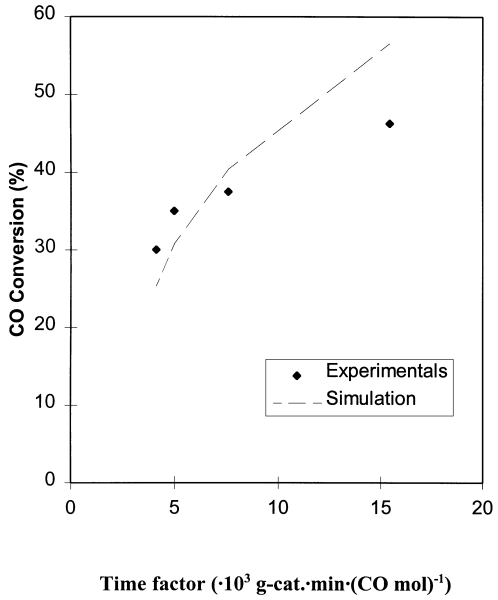

Fig. 9. A comparison between experimental and simulation results for the fixed-bed reactor and mix1. $T = 595$ K; $P = 1$ atm; $H_2O/CO = 1.1$; Langmuir–Hinshelwood's kinetic expression.

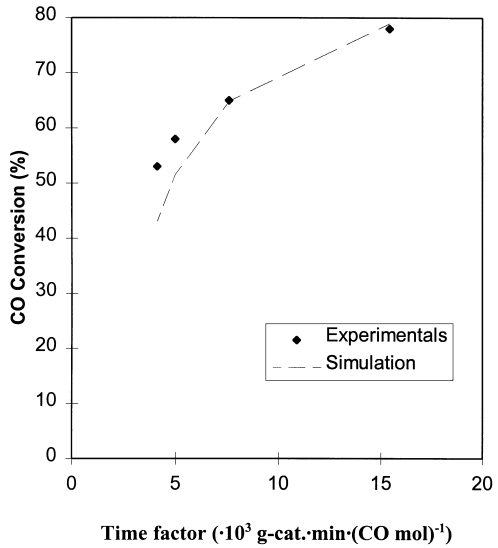

Fig. 10. A comparison between experimental and simulation results for the mesoporous membrane reactor and mix1. $T = 595$ K; $P_{lumen} = P_{shell} = 1$ atm; $H_2O/CO = 1.1$; no sweep gas. Temkin's kinetic expression.

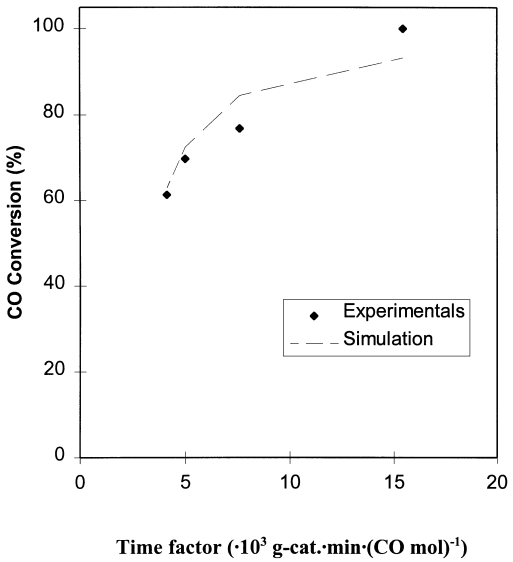

Fig. 11. A comparison between experimental and simulation results for the palladium membrane reactor and mix1. $T = 595$ K; $P_{lumen} = P_{shell} = 1$ atm; $H_2O/CO = 1.1$; $Q_{sweep} = 43.6$ ml/min. Temkin's kinetic expression.

mesoporous membrane lead to the equilibrium value. The difference at each time factor in conversion values remains the same for all time factors investigated, becoming larger for membrane reactors at time factor equal to 15 (Pd membrane reactor: 90.1%; mesoporous membrane reactor: 74%).

The CO conversion difference between membrane reactors, for all mixtures, is low at low time factors due to the fact that lower time factors correspond to higher feed flow rates and, thus, lower time for permeation through the membrane.

For mix2, the difference between mesoporous membrane reactor and fixed bed is the lowest one due to the fact that with respect to the other two mixtures, the same time factors are achieved at higher feed flow rates (e.g. time factor = 4.14 (10^3 g-cat min (CO mol)$^{-1}$); mix1: $Q_{feed} = 17.6 \times 10^{-5}$ mol/s, mix2: $Q_{feed} = 39.4 \times 10^{-5}$ mol/s, mix3: $Q_{feed} = 20 \times 10^{-5}$ mol/s) which give lower time for permeation through the membrane.

The advantage of using membrane reactors is more evident if these results are compared with those industrially obtained. For example, Moe [16] reported that, by feeding the following composition: CO 11.85 mol, H_2 75.44 mol, CO_2 9.98 mol on a dry basis, to two

fixed-bed reactors (high and low temperature) with a feed molar ratio of 10.55, a CO conversion equals to 91.14% is achieved. At 595 K for that feed composition the equilibrium conversion is 95.29%. On the basis of the results obtained in this work, with the palladium membrane reactor it is possible to overcome the equilibrium conversion, thus, achieving conversion values higher than the industrial ones. Furthermore, with membrane reactor, the operating temperature might be lower (with consequently energy consumption reduction) and all the processes might be carried out in a single unit.

In Fig. 5, the CO conversion is reported against the sweep gas flow rate for the mesoporous membrane and mix3.

When the sweep gas flow rate increases, two are the main effects:

– a higher quantity of nitrogen permeates from the shell to the lumen side giving a 'dilution' of the reaction zone;
– there is higher driving force through the membrane.

Both effects give higher CO conversion up to 100 ml/min sweep gas flow rates, but for higher values the 'counterdiffusion' of nitrogen from the shell to the lumen side becomes dominant and contrasts the removal of species from the reaction zone, thus leading to a decrease in CO conversion.

Fig. 6 shows the effect of nitrogen in the feed stream for the mesoporous membrane. No sweep gas is used. Tests have been done by feeding at the same flow rate mixtures of different composition. In particular, the CO conversion has been calculated by feeding only CO and water vapour ($X_{N_2} = 0$) and CO and water vapour in mixture with nitrogen ($X_{N_2} = 0.4$ on a dry basis; $X_{N_2} = 0.66$ on a dry basis). The higher is the quantity of nitrogen in the feed stream, the lower is the CO conversion. This result is due to the fact that, being the membrane not highly selective, the presence of nitrogen reduces, by competition, the other fluxes through the membrane.

In Fig. 7 is shown the CO conversion versus the time factor parametric in sweep gas flow rate and H_2O/CO ratio for the palladium membrane and mix1. Higher molar feed ratio and sweep gas flow rates give higher conversion. In particular, at time factor of 7.61×10^3 g-cat min $(CO\,mol)^{-1}$ for $H_2O/CO = 1.1$ by increasing the sweep gas flow rate from 43.6 to 436 ml/min, the CO conversion weakly increases (from 76.74 to 78.46%). At the same time factor value, 100% of CO conversion is reached by working with $H_2O/CO = 2.5$. For lower time factors, complete conversion is not achieved even increasing the feed molar ratio up to 2.

Table 3
CO conversion for different membrane reactors (with the same dimensions) calculated by using the Temkin's reaction rate (theoretical results)[a]

Membrane reactor	CO conversion (%)
Palladium (thickness $= 75 \times 10^{-5}$ m)	83.93
Palladium (thickness $= 75 \times 10^{-6}$ m)	93.23
Mesoporous	82.26

[a] Mix1; $Q_{feed} = 4.56 \times 10^{-5}$ mol/s; $H_2O/CO = 1.1$; $T = 595$ K; $P_{lumen} = P_{shell} = 1$ atm; palladium membrane reactor: $Q_{sweep} = 43.6$ ml/min; mesoporous membrane reactor: no sweep gas.

By increasing the sweep gas flow rate from 43.6 to 436 ml/min, the CO conversion passes from 61.25 to 64.66% (mix1, $T = 595$ K, $P_{lumen} = 1$ atm, $P_{shell} = 1$ atm, $H_2O/CO = 1.1$, time factor $= 4.14 \times 10^3$ g-cat min $(CO\,mol)^{-1}$, palladium membrane reactor).

Fig. 8 shows the effect of the lumen pressure on the CO conversion for the palladium membrane for mix1

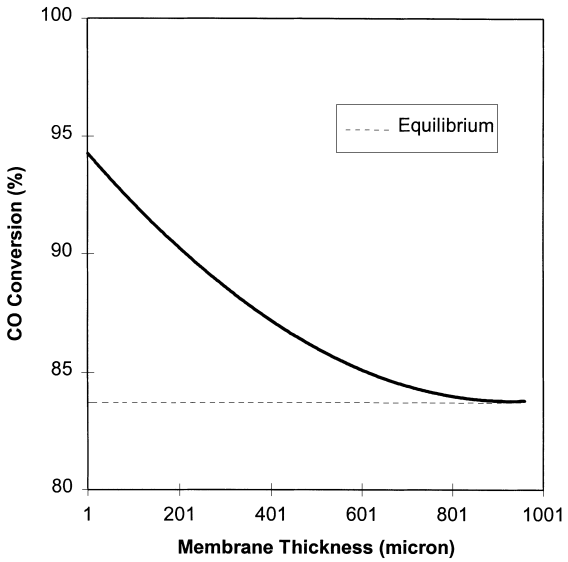

Fig. 12. Effect of membrane thickness on palladium reactor performance obtained by using the Temkin's reaction rate (theoretical results). Mix1; $Q_{feed} = 4.56 \times 10^{-5}$ mol/s; $H_2O/CO = 1.1$; $T = 595$ K; $P_{lumen} = P_{shell} = 1$ atm; $Q_{sweep} = 43.6$ ml/min.

and mix2. Higher lumen pressures give higher conversion values (due to the higher driving force through membrane) but their influence, as the sweep gas flow rate effect, is very weak, the key parameter being the time factor. Same results have been found by Basile et al. [3].

Figs. 9–11 present a comparison between experimental and simulation results. The model fits well the experimental points, confirming the previous considerations. It is interesting to note that for a fixed-bed reactor the kinetic which is in better agreement with the experimental data is the Langmuir–Hinshelwood one, whereas when a membrane reactor is used, the Temkin model is much more close to them. This result confirms that the removal of species from the reaction zone influences the kinetic in the reactor [6].

From the obtained results, it becomes clear that to reach conversion values higher than equilibrium ones when mixture gases are used as feed, it is necessary to use a membrane with very high selectivity. However, it is interesting to observe that the better performance of the palladium membrane with respect to the ceramic one is due not only to the selectivity but also to the hydrogen permeation rate. It is necessary, in fact, for the palladium membrane, to guarantee that a 'minimum' flux of hydrogen is removed from the reaction zone in order to have a significant shift of the reaction. This aspect has been theoretically verified as it is shown in Table 3 and Fig. 12.

Fig. 12 shows the effect of membrane thickness on the palladium reactor performance. By increasing the membrane thickness the hydrogen permeation rate decreases and lower conversions of carbon monoxide are achieved. For membrane thickness values above 750 μm the equilibrium conversion is reached.

7. Conclusions

In the present work, some interesting results have been achieved:

1. The composition of the mixture gas fed to the WGS reactor influences, in terms of CO conversion, both the traditional reactor and the membrane reactors in the same way. In particular, the highest conversion is obtained when the composition approaches to the thermodynamically more favourable one.
2. The time factor is, for the systems of reaction used in this work, the key parameter for obtaining high CO conversion values.
3. By using membranes with infinite selectivity, it is possible to overcome the equilibrium conversion also when mixture gas are fed to the reactor.
4. The better performance of the palladium membrane with respect to the ceramic one is due not only to the selectivity but also to the hydrogen permeation rate.
5. The fact that different kinetic expressions have to be used to describe the fixed-bed reactor and membrane reactors confirms that in membrane reactors the kinetic mechanism might be different than in a traditional system.

8. List of symbols

A	constant
k	rate constant (mol/(g-cat min) [7]; (s/atm) [8])
K_{eq}	equilibrium constant
K_i	adsorption equilibrium constant of component i $(atm)^{-1}$
Pe	hydrogen permeability through the palladium membrane (mol m/m^2 s $Pa^{0.5}$)
P_i	pressure of component i (atm)
P_{lumen}	pressure at the lumen side (atm)
P_{shell}	pressure at the shell side (atm)
Q_{feed}	total feed flow rate (mol/s)
Q_{sweep}	sweep gas flow rate (ml/min)
r	reaction rate (mol/cm^3 s [7]; s^{-1}[8])
ρ_{cat}	density of catalyst (2.4 g/cm^3)
T	temperature (K)
X_{N_2}	molar fraction of nitrogen

Acknowledgements

Authors are grateful to Dr. Violante and Dr. Tosti (Enea, Rome, Italy) for the palladium reactor supply and to Dr. P. Thygesen and Dr. N. Nielsen (Haldor Topsoe A/S, Copenhagen, Denmark) for providing the catalyst for the water–gas shift reaction.

Appendix A

Values of the parameters present in the Langmuir–Hinshelwood's kinetic expression

$$K_{eq} = \exp(4577.8/T - 4.33)$$

$$k = \exp(-29364/(1.987T) + 40.32/1.987)$$

$$K_{CO} = \exp(3064/(1.987T) - 6.74/1.987)$$

$$K_{H_2O} = \exp(-6216/(1.987T) + 12.77/1.987)$$

$$K_{CO_2} = \exp(12542/(1.987T) - 18.45/1.987)$$

Values of the parameters present in the Temkin's kinetic expression

$$K_{eq} = \exp(4577.8/T - 4.33)$$

$$k = 6 \times 10^{11} \exp(-26800/(1.987T))$$

$$k = 2.5 \times 10^{9} \exp(-21500/(1.987T))$$

References

[1] A.S. Damle, S.K. Gangwal, V.K. Venkataraman, Gas Sep. Purif. 8 (2) (1994) 101–106.
[2] A. Basile, E. Drioli, F. Santella, V. Violante, G. Capannelli, G. Vitulli, Gas Sep. Purif. 10 (1) (1996) 53–61.
[3] A. Basile, A. Criscuoli, F. Santella, E. Drioli, Gas Sep. Purif. 10 (4) (1996) 243–254.
[4] E. Xue, M. O'Keeffe, J.R.H. Ross, Catal. Today 30 (1996) 107–118.
[5] M. Bracht, P.T. Alderleisten, R. Kloster, R. Pruschek, G. Haupt, E. Xue, J.R.H. Ross, M.K. Koukou, N. Papayannakos, Energy Convers. Mgmt. 38 (1997) S159–S164.
[6] A. Criscuoli, A. Basile, E. Drioli, AIDIC Conferences Series ECCE-1 Young Researchers Forum, Eris C.T. S.r.l. Milano 3 (1997) 1–7.
[7] W.F. Podolski, Y.G. Kim, Ind. Eng. Chem. 13 (4) (1974) 414–421.
[8] D.S. Newsome, P. Kellog, Catal. Rev.-Sci. Eng. 21 (2) (1980) 275–318.
[9] H. Weyten, K. Keizer, A. Kinoo, J. Luyten, R. Leysen, AIChE J. 43 (7) (1997) 1819–1827.
[10] A. Basile, V. Violante, E. Drioli, Catal. Today 2 (1995) 321–326.
[11] D. Uzio, J. Peureux, A. Giroir-Fendler, M. Torres, J. Ramsay, J.-A. Dalmon, Appl. Catal. 96 (1993) 83–97.
[12] A. Basile, unpublished results, 1998.
[13] N. Itoh, W.-C. Xu, K. Hakara, J. Membr. Sci. 66 (1992) 149–155.
[14] V. Violante, A. Basile, E. Drioli, Fusion Eng. Design 30 (1995) 217–223.
[15] S. Uemiya, N. sato, H. Ando, E. Kikuchi, Ind. Eng. Chem. Res. 30 (1991) 585–589.
[16] J.M. Moe, Chem. Eng. Prog. 58 (3) (1962) 33–36.