# Simulation of $CO_2$ hydrogenation with $CH_3OH$ removal in a zeolite membrane reactor

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## Abstract

A thermodynamic analysis of the $CO_2$ hydrogenation to methanol where competitive reactions take place is presented for a membrane reactor (MR) where methanol was selectively removed. A non-isothermal mathematical model was written to simulate a micro-porous MR. Zeolite membranes with different values of the $CH_3OH$ and $H_2O$ permeances were considered in the MR modelling. The effect of temperature, pressure and species permeation on the conversion, selectivity and yield was analysed. A higher $CO_2$ conversion and $CH_3OH$ selectivity can be reached by the use of an MR. An increased $CH_3OH$ yield allows to reduce the consumption of reactant and also to operate at lower pressures and higher temperatures, a fact, which favours the kinetics reducing the residence time and the reactor volume. The MR with the highest $CH_3OH/H_2O$ permeance ratio resulted in better selectivity and yield of $CH_3OH$ with respect to the other MR characterised by a higher conversion. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* $CO_2$ hydrogenation; Methanol; Micro-porous membrane reactor; Separation; Yield

## 1. Introduction

The industrial process of methanol production at low temperature from syngas is carried out around the methanol critical temperature (240 °C) and at pressures of the order of 50–100 bar, giving conversions between 5 and 15% at each recycle step, in a fixed bed (cupric and zinc oxide/alumina catalyst, ICI process). Methanol synthesis on copper-containing catalysts [1] occurs not from CO but only via $CO_2$ hydrogenation.

The activity of the catalyst for the hydrogenation of $CO_2$ was measured on several Cu based catalyst mixtures [2–4]. Temperature range was 200–300 °C and pressure was changed from 1 to 10 bar. The catalyst mixture CuO/ZnO/γ-alumina (34.6/35.4/30.0 wt.%) showed the highest reaction rate for methanol production. This catalyst also showed the lowest reaction rate for the by-product CO, which is undesired because it compromises the overall efficiency of the process. In addition, a basic study [5] with reactants labelled with ^{13}C clearly showed that, when $CO_2$

was fed instead of CO, the methanol formation occurred directly via $CO_2$ hydrogenation, with no intermediate step involving CO.

The reactions that occur during the hydrogenation of $CO_2$ are the following.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad -49.4\,kJ/mol\ (\Delta H) \quad (1)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \quad 41.5\,kJ/mol\ (\Delta H) \quad (2)$$

$$CO + 2H_2 \rightarrow CH_3OH \quad -90.9\,kJ/mol\ (\Delta H) \quad (3)$$

The reaction rates for $CO_2$ hydrogenation to methanol (reaction (1) above) and for the reverse of the water gas shift reaction (reaction (2) above) were reported in [2]. The reaction rate for methanol production shows a maximum at 250 °C, whereas the reaction rate of the reaction (2) is an increasing function of the temperature. However, it is lower than the reaction rate of reaction (1) up to about 255 °C, where the reaction rates are equal. Also, the selectivity to methanol has a maximum (65%) at a temperature corresponding to the maximum of the first reaction rate.

The use of a membrane reactor (MR), as substitution for traditional reactors (TRs), is aimed at increasing productivity by pushing the conversion due to selective separation of the products. Zeolite membranes have a promising future for applications in catalytic reactor [6,7] due to their

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selectivity and satisfactory permeability. As an example, a zeolite membrane was employed to selectively remove water during the gas-phase synthesis of MTBE obtaining higher performances than in a TR [8].

Several modelling works of MRs appeared in the literature. Studies on methylcyclohexane [9] and 1-butene [10] dehydrogenation and on a consecutive reaction scheme [11] in an MR were proposed. Becker et al. [12] formulated a two-dimensional mathematical model for catalytic dehydrogenation of ethylbenzene in a parallel-flow MR. Hara et al. [13] studied the effect of hydrogen removal on methanol decomposition. Methane steam reforming was modelled by Oklany et al. [14] comparing dense and microporous MRs. Barbieri and Di Maio developed an analysis of an MR with retentate and permeation streams in parallel or counter-current flows [15].

Recently, simulation and experimental studies on the MFI-zeolite membrane were performed for hydrogen/isobutane separation by Ciavarella et al. [16]. A model for the simulation of an inert MR for the oxidative dehydrogenation of butane was developed by Téllez et al. [17].

In the present work thermodynamic and simulation study of the $CO_2$ hydrogenation reaction allows to evaluate the optimal performances in an MR: the highest conversion and selectivity to the desired products with different operating conditions and different membrane selectivity. The selective removal of products reduces the rate of the reverse reaction of methanol formation. In addition, since condensable (methanol and water) species desorption is a rate determining step for the catalytic mechanism, their selective removal is expected to improve further the overall reaction rate.

## 2. Thermodynamic analysis

Reaction (1) is of interest for the methanol production from $CO_2$. Reaction (2) is competitive with this for the $CO_2$ conversion and it produces undesired CO, reducing the overall effectiveness of the process. Therefore, it is important to study the conversion of $CO_2$ and the methanol/CO selectivity. A high temperature favours the endothermic reaction (2), whereas a high pressure favours reaction (1). The use of a membrane able to remove methanol as soon as it forms would improve significantly the conversion and the selectivity, thereby, reducing the wasteful production of CO and the recycle ratio of unconverted reactants.

Reaction (3), methanol from CO, is considered for the possible presence of carbon monoxide, however, it is not necessary for the thermodynamic analysis because it is a linear combination of the first two reactions. Mechanistic studies [2,3] show that, in the methanol formation from syngas, CO is converted first to $CO_2$ before it may transform into methanol.

Equilibrium conditions for the TR and the equilibrium shift by selective removing of the reaction products in an MR were calculated. Equilibrium conversion of $CO_2$ was evaluated in the following operating conditions: temperature between 150 and 300 °C and pressure in the range 1–100 bar. MR conversion was calculated extending the "reactor in series" method [18] to a reacting and permeating system.

The conversion increase is a function of the ratio between the amount of separated products from the reaction environment and the total produced amount. When the selective separation of methanol is taken into account, a methanol separation factor, SF, has been defined as follows:

$$SF = \frac{F_{CH_3OH}^{Permeate}}{F_{CH_3OH}^{Permeate} + F_{CH_3OH}^{Retentate}}$$

where $F_{CH_3OH}^{Retentate}$ (see Fig. 1) is the flow rate of methanol leaving the block of "reactors in series" and it is in equilibrium with respect to the reaction volume. $F_{CH_3OH}^{Permeate}$ is the molar flow rate of methanol on the permeate side. The new equilibrium of the MR, as function of SF, was calculated according to the scheme reported in Fig. 1.

After the attainment of the equilibrium in a TR, determined with the reactor series method ("SofTR" block), the flow $TR^0$ was divided by the separator "S" into two streams: the permeate $F_{CH_3OH}^{Permeate}$ and the non-permeate streams. The non-permeate stream was sent to a new "SofTR" block in order to reach a new equilibrium position (flow $MR_{SF}$). The
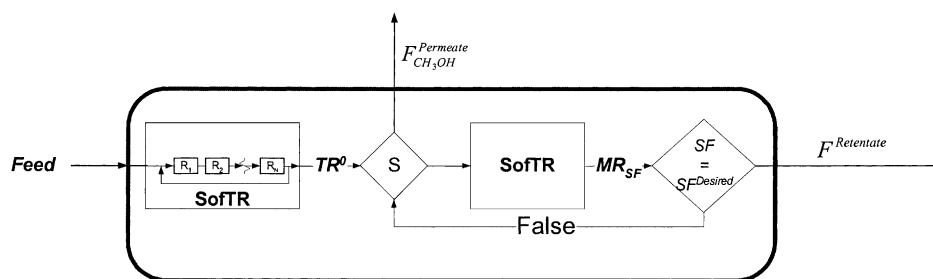
Fig. 1. Flow sheet of the method used to calculate the conversion when a SF was set. S: split point; $TR^0$: TR equilibrium; $MR_{SF}$: equilibrium in the reaction volume after removal of the methanol at the generic iteration; $F^{Retentate}$: equilibrium in the reaction volume after removal of a set percentage of methanol.

flow $F_{CH_3OH}^{Permeate}$ was varied until SF assumes the set value $SF^{Desired}$. The $F^{Retentate}$ corresponding to $SF^{Desired}$ represents retentate flow of an MR at equilibrium with respect to all reactions.

## 3. Mathematical model

A mathematical model [19,20] written to describe the behaviour of a non-isothermal Pd-MR in the stationary state was extended to simulate the behaviour of a porous MR. The model considers the following hypothesis: plug flow and isobaric conditions on reaction and permeation sides; ideal gas behaviour; the permeation flux as a linear function of the species partial pressure. The same assumption was reported in the model Moon and Park [21], they proposed a modelling analysis in terms of permeation and reaction rates and selectivity on the conversion of an isothermal MR. Modelling equations (Table 1) take into accounts the reaction and permeation through the porous membrane. The kinetics was described by assuming the rate equations proposed by Takagawa and Ohsugi [22].

Table 2
Geometric parameters of the MR[a]

| Membrane length | 20 |
| ID tube | 0.67 |
| OD tube | 1 |
| ID shell | 2 |

[a] Values of the parameters are given in cm.

The enthalpy variation, due to the mixing of the permeating species in the receiving stream, was considered in the model in addition to the conductive heat transfer. The stream temperatures undergo some variations depending on the permeate fluxes.

Table 2 reports the geometric parameters used in the calculations. The TR simulations were performed with the same computer code, setting to zero both the permeating term and the overall heat transfer coefficient ($U^{Tube}$) between the reaction and the permeate sides.

Thermodynamic properties used in the simulation were reported by Kee et al. [23] in the "Chemkin Thermodynamic Database". The values for $U^{Shell}$, $U^{Tube}$ are 227 and $2.4\,W/m^2\,K$, respectively [20].

Table 1
Mass and energy balance equations

**Mass**

Reaction side
$$\frac{dN_i}{dz} = \sum_{j=1}^{N^{Reactions}} \nu_{i,j} r_j - \frac{A^{Membrane}}{V^{Reaction}} J_i$$

Permeation side
$$\frac{dN_i}{dz} = \frac{A^{Membrane}}{V^{Permeation}} J_i$$

**Energy**

Reaction side
$$\sum_{i=1}^{N^{Species}} N_i C_{p_i} \frac{dT^{Reaction}}{dz} = \frac{U^{Shell} A^{Shell}}{V^{Reaction}} (T^{Oven} - T^{Reaction}) - \frac{U^{Tube} A^{Membrane}}{V^{Reaction}} (T^{Reaction} - T^{Permeation})$$
$$+ \sum_{j=1}^{N^{Reactions}} r_j(-\Delta H_j) + \frac{A^{Membrane}}{V^{Reaction}} \sum_{i=1}^{N^{Species}} J_i (h_i^{T^{Reaction}} - h_i^{T^{Ref}})$$

Permeation side
$$\sum_{i=1}^{N^{Species}} N_i C_{p_i} \frac{dT^{Permeation}}{dz} = \frac{U^{Tube} A^{Membrane}}{V^{Permeation}} (T^{Reaction} - T^{Permeation}) - \frac{A^{Membrane}}{V^{Permeation}} \sum_{i=1}^{N^{Species}} J_i (h_i^{T^{Permeation}} - h_i^{T^{Ref}})$$

Permeation flux through the porous membrane
$$J_i = permeance_i (P_i^{Reaction} - P_i^{Permeation})$$

$T^{Ref} = T^{Reaction} \quad \forall J_i > 0$ (trans-membrane flux from reaction side to permeation side); $T^{Ref} = T^{Permeation} \quad \forall J_i < 0$
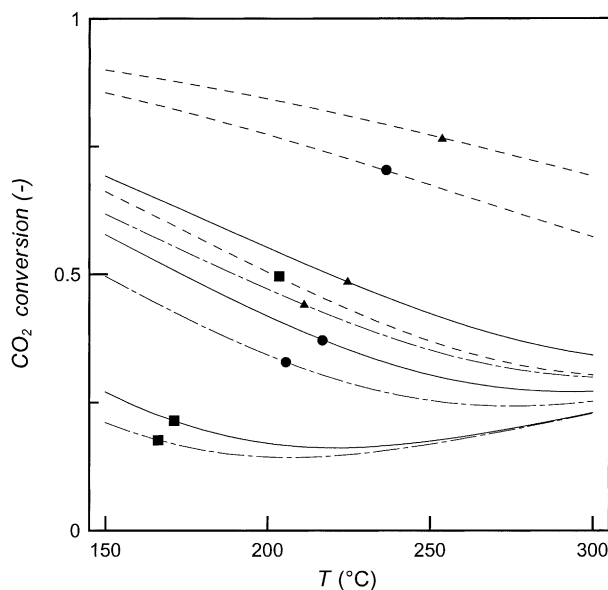
Fig. 2. $CO_2$ equilibrium conversion shifted by means of $CH_3OH$ removal vs. temperature. SF = 0 (dash-dot lines), SF = 0.5 (solid lines), SF = 0.99 (dashed lines). (■), $P = 10$ bar; (●), $P = 50$ bar; (▲), $P = 100$ bar. $H_2/CO_2$ initial molar ratio = 3.
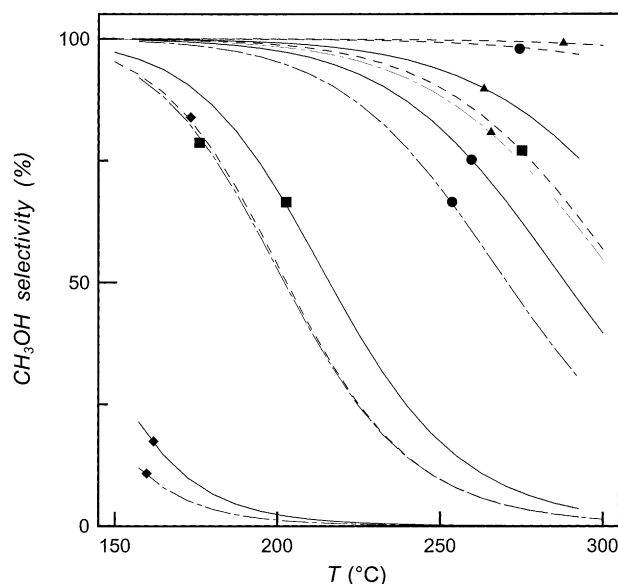


Fig. 3. Methanol selectivity improved by means of $CH_3OH$ removal vs. temperature. SF = 0 (dash-dot lines), SF = 0.5 (solid lines), SF = 0.99 (dashed lines). (◆), $P = 1$ bar; (■), $P = 10$ bar; (●), $P = 50$ bar; (▲), $P = 100$ bar. $H_2/CO_2$ initial molar ratio = 3.

## 4. Results and discussion

Methanol was considered the only permeating species in the performed thermodynamic analysis. Fig. 2 reports the $CO_2$ conversion vs. the temperature at different operating pressures for a TR and an MR at several SFs.

The conversion difference between an MR and a TR is higher at low temperature because a higher methanol partial pressure on the reaction side allows a better permeation. Reaction (1) (methanol formation) is favoured with respect to reaction (2) (CO production) by low temperatures. The methanol selective separation favours a higher production of the methanol itself and, as a consequence, also a higher $CO_2$ conversion is obtained. $CO_2$ conversion shows a minimum due to the competitiveness between reactions (1) and (2); this minimum is shifted at higher temperature by the increase of pressure and SF. The conversion behaviour resembles typical exothermic reaction at high pressures and SFs and the minimum is at beyond 300 °C. At a lower pressure the behaviour is typical of an endothermic reaction and the minimum is located at low temperature. The advantages of the use of an MR are less evident at low pressure also due to the low conversion and consequently the low methanol concentration. A higher pressure has a double effect on the desired reaction: it is favoured by the reduction in the mole number of gas, and the permeation is also increased. In an MR, high pressures and SFs promote a high conversion also at a high temperature.

An analysis of the selectivity as a function of the temperature (Fig. 3) shows that both the shifting of the minimum of equilibrium conversion and the variation of the concavity of $CO_2$ conversion curves are due to an increase of the selectivity toward methanol. The selectivity is defined by the ratio between the produced moles of the species of interest and reacted moles of reference species. For a TR, the expression of the selectivity is the following:

$$S_{CH_3OH} = \frac{F_{CH_3OH}^{Produced}}{X_{CO_2} F_{CO_2}^{Feed}}$$

whereas, for an MR, it is also a function of the methanol SF:

$$S_{CH_3OH} = \frac{F_{CH_3OH}^{Permeate} + F_{CH_3OH}^{Retentate}}{X_{CO_2} F_{CO_2}^{Feed}} = \frac{1}{1 - SF} \frac{F_{CH_3OH}^{Retentate}}{X_{CO_2} F_{CO_2}^{Feed}}$$

where $F$s are the molar flow rates.

In a TR, only 18% of the $CO_2$ reacted is converted in methanol at 1 bar and 150 °C. The selectivity decreases with temperature and at 200 °C it is quite null. The selectivity increases with the pressure and decreases with the temperature. Thus, $CO_2$ produces only CO at low pressures and high temperature. In fact, it is necessary to work at a pressure of 100 bar when the temperature is 300 °C, in order to obtain a selectivity to methanol of about 50%.

The use of MR shows some advantages also from the selectivity point of view. With two competitive reactions (1) and (2), the selective separation of methanol increases the conversion and also the selectivity to the desired product.

The methanol/CO selectivity decreases when temperature increases due to the higher impact of the competitive reaction (2). At low temperature (150 °C) the selectivity is about 100% for all the SFs. Increasing the temperature (240, 300 °C) the selectivity decreases, however, at a high SF the
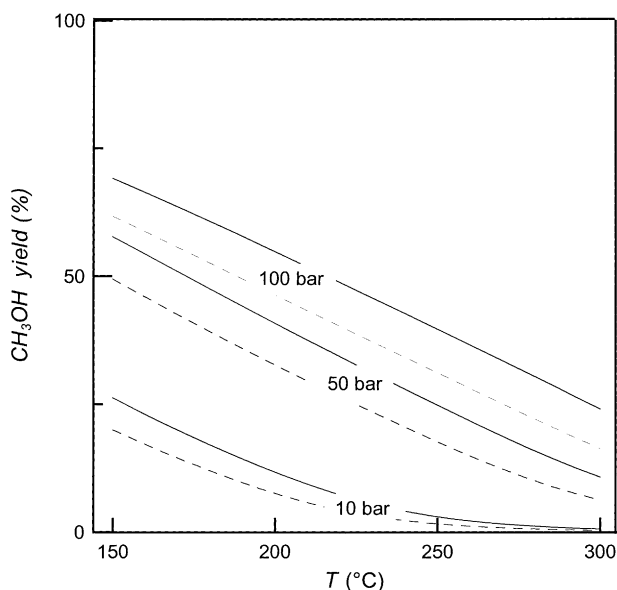
Fig. 4. Methanol yield shift following $CH_3OH$ removal vs. temperature. SF = 0 (dashed lines), SF = 0.5 (solid lines). $H_2/CO_2$ initial molar ratio = 3.

Table 3
Species permeances

| Species | Permeance ($\mu mol/cm^2\,s\,bar$) | |
|---|---|---|
| | Membrane A | Membrane B |
| $CH_3OH$ | 2.87 | 1.05[a] |
| $H_2O$ | 1.05 | 2.87[a] |
| $H_2$ | 0.105 | 0.105 |
| CO | 0.105 | 0.105 |
| $CO_2$ | 0.105 | 0.105 |
| Sweep gas | 0.105 | 0.105 |

[a] Piera et al. [24].

selectivity is near to 100%. At 240 °C the selectivity of a TR is about 75%; it increases at 100% when the SF is 99%. Also for the highest temperature the selectivity increases with SF, in fact, it increases from 25 to 95% when the SF increases from 0 to 99%.

The yield of the methanol synthesis process, defined by the molar ratio between the produced methanol and the feed $CO_2$, has a significant importance in order to evaluate the global efficiency of the system. The yield of an MR with SF = 0.5 decreases with a temperature increase (Fig. 4), however, it is always higher than that of a TR. A higher yield is obtained at a high pressure and a low temperature; at a pressure equal to 100 bar the yield exceeds 50%. The thermodynamic analysis shows the advantages of the MR use on the conversion and selectivity in the $CO_2$ hydrogenation when the methanol is removed selectively.

The MR performance depends also on the kinetics, on the permeating properties of the membrane, on the flow conditions, on the heat exchange, etc. Therefore, in addition to the thermodynamic analysis, some simulations of an MR were performed.

Thermodynamic analysis was developed considering an ideal separation of methanol. Zeolite membranes, even if they have a good selectivity, are characterised by a non-ideal methanol separation. Thus, two set of permeances for all species involved in the reaction were assumed (Table 3) in order to analyse the MR performance as a function of the $CH_3OH/H_2O$ selectivity. In particular, the choice was to consider an organophilic membrane (e.g. a silicalite(I) membrane) with $CH_3OH/H_2O$ selectivity of about 3 (membrane A) and a hydrophilic membrane (e.g. the

MOR/ZSM-5/chabazite membrane [13]) with $CH_3OH/H_2O$ selectivity of about 1/3 (membrane B). The permeance of the other species were assumed ten fold lower with respect to $CH_3OH$ and $H_2O$ for both cases in order to have an effective separation of the main products and an improved performance of the MRs. Piera et al. [24] reported for a permanent gas, such as oxygen, through a MOR/ZSM-5/chabazite hydorphilic membrane, a permeance value near that of methanol. However, this value was measured at very low partial pressure of $CH_3OH$ and $H_2O$ and a higher condensable/permanent gas selectivity is reasonably expected at higher $CH_3OH$ and $H_2O$ concentration.

$CO_2$ conversion (Fig. 5) of an MR-B (hydrophilic) is higher than that of an MR-A (organophilic) because the selective $H_2O$ removal shifts both reactions (1) and (2). Conversion of both MRs is higher than that of a TR overcoming the negative effect that the sweep gas back-permeation has on the reaction (1). The conversion of the MR-B is equal to
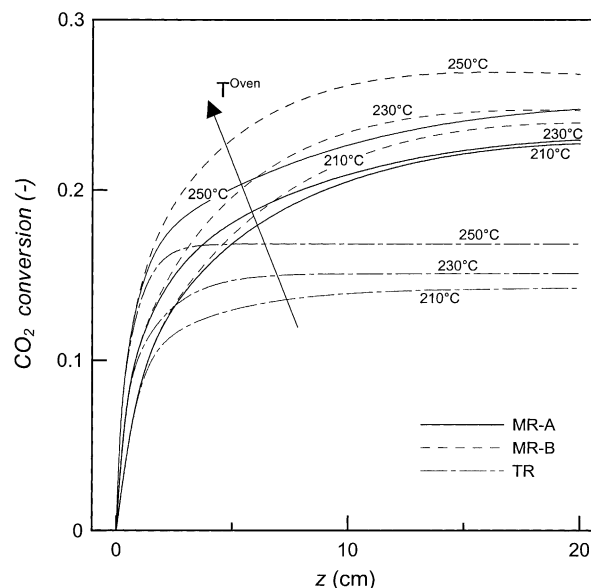


Fig. 5. $CO_2$ conversion profiles for MR and TR at oven temperatures of 210, 230, 250 °C. Feed flow rate 400 $cm^3$ (STP)/min, sweep gas flow rate = 1000 $cm^3$ (STP)/min, $H_2/CO_2$ feed molar ratio = 3, $P^{Reaction} = P^{Permeation} = 10\,bar$.
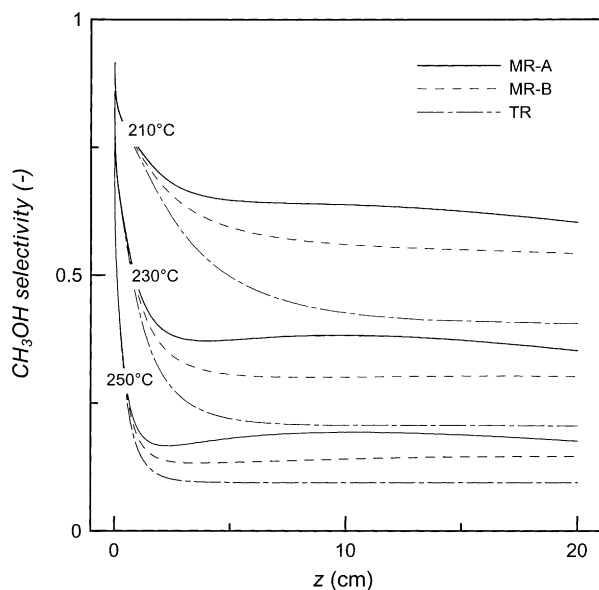
Fig. 6. $CH_3OH$ selectivity profiles for MR and TR at oven temperatures of 210, 230, 250 °C. Feed flow rate 400 $cm^3$ (STP)/min, sweep gas flow rate = 1000 $cm^3$ (STP)/min, $H_2/CO_2$ feed molar ratio = 3, $P^{Reaction} = P^{Permeation} = 10$ bar.



Fig. 7. $CH_3OH$ yield profiles for MR and TR at oven temperature of 210, 230, 250 °C. Feed flow rate 400 $cm^3$ (STP)/min, sweep gas flow rate = 1000 $cm^3$ (STP)/min, $H_2/CO_2$ feed molar ratio = 3, $P^{Reaction} = P^{Permeation} = 10$ bar.

27% at 250 °C, the highest considered temperature, and it reduces at 25% for the MR-A and even at 17% for the TR. The realised methanol SF was equal to 75% for the MR-A and 70% for the MR-B.

The process was almost isothermal: the heat flux required from the system was relatively low due to the different (exothermic and endothermic) reaction nature and the low reaction rates. In addition, the good heat exchange, between the reaction side and the energy source, supplied quickly the energy required. Only, the inlet part of the MR undergone some temperature variations, in any case, these variations were limited and contained in ±2 °C in the worst case (250 °C).

The temperature increased at the reactor inlet because the rate of the exothermic reaction (1) was higher than that of the endothermic reaction (2). A limited (±2 °C) oscillation happened due to a change in the weight of the reactions (1) and (2).

The axial profile of methanol selectivity is reported in Fig. 6 for the three considered reactors at three different temperatures. The MR-A has the highest selectivity, at any considered temperature, followed by MR-B and TR. The selectivity values decrease rapidly with the temperature, e.g. for the MR-A it passes from 60% at 210 °C to 18% at a lower temperature of only lower of 40 °C.

A minimum is present in the selectivity profile of the MR-A at 230 and 250 °C; it is due to the competitiveness between the reactions (1) and (2) and to their different rates. The selectivity decreases until a minimum because the higher CO production with respect to methanol, then it increases due to the methanol selective permeation. After, the
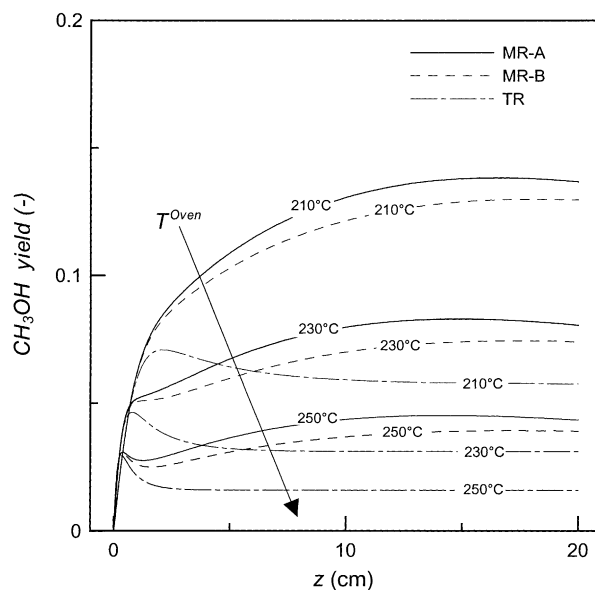
selectivity decreases again due to the CO permeation and back-permeation of the sweep gas, which has a negative effect on the methanol production.

The $CH_3OH/CO$ selectivity given from the equilibrium at 230 °C, e.g. for a TR, is higher than that at 250 °C; therefore, the difference between maximum and minimum values in the MR-A profile is reduced and at 210 °C it disappears.

The MR-B profiles are monotonic because $H_2O$ is considered the more permeable species and it shifts both the methanol and the CO productions.

It is interesting to have information on the methanol yield because the MR-B has a higher conversion but lower selectivity of the MR-A. Fig. 7 shows that the methanol yield of MR-A is higher than that of MR-B, and the latest has a better yield than a TR. Also the yield shows that the major advantages are given at 210 °C the lowest considered temperature. At this temperature the yield of MR-A is about 2.5 times higher than at 250 °C.

## 5. Conclusions

The thermodynamic analysis of an MR, considering an ideal methanol separation, shows that the reaction (1) of methanol formation from $CO_2$ is favoured with respect to reaction (2) (CO production) when the methanol SF was increased. Higher conversion, selectivity and yield were obtained in an MR; thus, the consumption of reactant was limited. An MR can operate at lower pressure and higher temperature, with respect to a TR, achieving 40–50% conversion and a higher selectivity, near 100%. The possibility

Table 4
CO$_2$ conversion, methanol selectivity and yield of the outlet streams from
MR-A, MR-B and TR at 210 °C, 10 bar

|  | MR-A (%) | MR-B (%) | TR (%) |
|---|---|---|---|
| CO$_2$ conversion | 22.7 | 23.9 | 14.2 |
| CH$_3$OH selectivity | 60.2 | 54.2 | 40.5 |
| CH$_3$OH yield | 13.7 | 13.0 | 5.8 |

to operate at a higher temperature, without losing performance with respect to TRs, increases the reaction rate; as a consequence a lower residence time is necessary and also the reaction volume could be reduced.

Reactor simulations were performed considering a non-ideal methanol separation in order to approach the behaviour of real membranes. In particular, an organophilic (A) and hydrophilic (B) membranes were considered with modest permeances of permanent gases. Thus, conversion, selectivity and yield of two MRs were studied and compared with those obtained in a TR. The MR-B reaches a higher conversion for all considered temperatures with respect to the MR-A. However, the MR-A selectivity is always higher than that of the MR-B due to a better methanol permeation; thus, the MR-A is characterised by a higher yield when compared with the other MR. Both MRs have better performance of that of the TR. A comparison of the performance of all reactors is reported in Table 4 for an oven temperature of 210 °C and a rather low pressure of 10 bar. A comparison of the performance of the MR-A at 230 °C and the TR at 210 °C shows that the TR has a higher selectivity but the MR-A has a higher conversion but above all it has a higher methanol yield.

## Acknowledgements

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