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Membrane processes for effective methanol synthesis in the forest based biorefinery

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ABSTRACT

ZSM-5 membranes were prepared and their performance for methanol separations from synthesis gas was evaluated. The experimentally observed permeances at room temperature for the ZSM-5 membranes were 0.3, 1, 12 and 18×10^{-7} mol m^{-2} s^{-1} Pa^{-1} for H_2, CO_2, CH_3OH and H_2O, respectively, which resulted in a separation factor α methanol/H_2 of about 30. For a stoichiometric feed, the one pass CO_x-conversion for a traditional methanol process is about 26% per pass, which requires a recirculation loop with the associated disadvantages. By assuming that the same membrane performance could be obtained at industrial conditions, it was shown by mathematical modeling that a ZSM-5 membrane reactor could reach 97% CO_x-conversion per pass, while a ZSM-5 membrane module process could reach 81% conversion per pass for a stoichiometric feed. As a result of the high conversion per pass for the membrane processes, one pass design with the associated advantages is possible for these processes. A membrane module based system is preferable over a membrane reactor of practical reasons. However, similar performance to the membrane processes can of course be achieved with a one pass process comprised of a series of methanol reactors, reactor effluent heat exchangers, coolers and condensers.

1. Introduction

Black liquor is an internal biomass stream in pulp mills, which contains dissolved lignin and cooking chemicals. The only demonstration plant for pressurized black liquor gasification is operated at a large mill in Piteå, Sweden. It is unlikely that the recovery boiler in existing plants can be replaced by gasification plants in the first step, since a recovery boiler represents a very large investment. However, the recovery boiler is often the bottleneck in a pulp plant and if as much as 25% of the black liquor produced in a large pulp mill is gasified in order to increase the pulp production capacity, about 70,000 ton of methanol can be produced per year. Due to the complexity of the processes and in order to arrive at favorable economy, the production capacity in new plants for production of methanol from fossil fuels exceeds 1000,000 ton of methanol per year. The production capacity of bio-fuels in the example of a forest based biorefinery described above is thus <7% of the capacity of plants utilizing fossil fuels, which calls for development of more cost effective processes such as membrane processes.

It has been shown earlier [1,2] that the use of membrane reactors could increase the productivity of a conventional methanol synthesis process by increasing the one pass conversion of a hydrogen rich synthesis gas. However, there are a number of possible designs for this process and these have not been evaluated and compared as will be done in the present work. Also, the advantages of membrane processes are greatest for stoichiometric feeds rather than for hydrogen rich synthesis gas. Furthermore, previous works mostly consider hypothetical membranes, while the present work is based on permeation data for a real ZSM-5 membrane.

2. Experimental

Porous graded α-alumina discs (Inocermic GmbH, Germany) were used as membrane supports. The supports were masked and seeded as described previously [3] and were subsequently hydrothermally treated in a hydrolyzed synthesis solution at 100 °C for 27 h, under atmospheric pressure and reflux. The molar composition of the synthesis mixture was 3 TPAOH:0.25 Al_2O_3:Na_2O:25 SiO_2:1600 H_2O:100 EtOH. After synthesis, the membranes were rinsed in a 0.1 M NH_3 solution for 24 h, and calcined at 500 °C for 6 h. The heating and cooling rates for calcination were 0.2 and 0.3 °C/min, respectively.

A Wicke–Kallenbach setup was used for the separation experiments. The membranes were mounted in a stainless steel cell with graphite gaskets. In order to remove adsorbed species, the membranes were heated overnight at 300 °C in a flow of pure helium. The separation experiments were performed at 25 °C. Three mass flow controllers and two saturators in thermostat baths were used

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Table 1
Catalyst, feed, reactor and membrane specifications.

Parameter	Value	Parameter	Value
Catalyst		*Reactor*	
Catalyst density	1775 kg/m^3	Tot. reactor length	16 m
Catalyst pellet diameter	0.0042 m	Reactor tube I.D.	0.0254 m
Void fraction of bed	0.4	*Membrane*	
		Tot. memb. area	450 m^2
Feed[a]		Memb. tube O.D.	0.01 m
Stoichiometric number of feed	2	Membrane module length	4 m
CO/CO$_2$ ratio in feed	2.75	*Sweep gas and Cooling*	
Concentration of inert in feed	2%	Sweep gas per MRP tube	1.200 mol/s
Inlet temperature of feed	513 K	Sweep gas per MMP tube	0.450 mol/s
Inlet pressure of feed	80 bar	Sweep gas pressure	70 bar
Fresh feed to each TRP tube	0.170 mol/s	C.W. temp. TRP	533 K
Feed to each MRP tube	0.270 mol/s	C.W. temp. MRP	513 K
Feed to each MMP tube	0.390 mol/s	C.W. temp. MMP	513, 523, 533 K

[a] No water in the feed.

to achieve a feed gas composition of 5.8 kPa methanol, 40 kPa H$_2$, 10 kPa CO$_2$ and 0.6 kPa H$_2$O, with helium balance to atmospheric pressure. Except for the absence of CO and the helium balance, this feed mixture is similar in composition to a methanol reactor effluent. The feed flow rate was 1000 ml/min and the sweep gas (helium) flow rate was 150 ml/min. Quantitative analysis of the gas compositions was performed online using a Varian 3800 GC equipped with a thermal conductivity detector.

3. Process and model description

The mathematical model for simulating the processes considered in the present work was developed using the following assumptions: one dimensional plug flow in the reactors and membrane modules, ideal gas, no radial diffusion resistance in the catalyst pellets, no axial dispersion of heat along the reactors. In the overall systems, the energy balances were neglected. In all reactors, the catalyst was diluted 35% compared to a conventional reactor [4] in the first 4 m of the reactors due to the large heat development associated with a stoichiometric feed and product removal in the membrane processes. Also, the activity of the catalyst was assumed to be 70% of that of a fresh catalyst [4]. The tube diameter is 38 mm in the Lurgi process [5] and a smaller diameter (25 mm) was used here for all three processes for better temperature control. The main implication of diluted catalyst and reduced tube diameter is better temperature control in all processes. Better temperature control was only needed in the membrane processes, but to allow straightforward comparisons, the same dilution and tube diameter was applied in the simulations of all processes.

The traditional reactor process (TRP), represented here by the Lurgi low-pressure process [5], see Fig. 1a, consists of a water-cooled tubular reactor in which the feed-effluent heat exchanger preheats the recycled synthesis gas to the reactor inlet. Crude methanol, i.e. a mixture of methanol and water, is condensed and separated from the reactor effluent in a condenser, while unreacted synthesis gas is compressed and recycled to the reactor. The recycle ratio is 3.8, which is suitable for the stoichiometric feed considered here and 2% of the recycled gas is purged, in order to not accumulate too much inert components in the TRP.

The traditional reactor is 16 m long and consists of 1460 steel tubes, which are filled with spherical pellets with a diameter of 4.2 mm consisting of Cu/ZnO/Al$_2$O$_3$ catalyst. The total mass of catalyst in the reactor is 11 ton. The reactor tubes are cooled with boiling water at 533 K from a steam drum (not shown in the flow sheets) generating medium pressure steam. Parameters for the TRP are summarized in Tables 1 and 3.

The mass and energy balance and the Ergun equation for the water-cooled tubular reactor are:

$$\frac{dF_i}{dz} = r_i \rho_b \tag{1}$$

$$\frac{dT}{dz} = \frac{1}{\sum_{i=1}^{n_c} F_i C_{pi}} \left(aU(T_a - T) + \sum_{i=1}^{n_r} r_i \left(-\Delta H_i^{rx}\right) \rho_b \right) \tag{2}$$

$$\frac{dP}{dz} = \frac{G_0^2}{\rho_G D_P} \frac{(1-\phi)}{\phi^3} \left(\frac{150}{Re} + 1.75 \right) \times 10^{-5} \tag{3}$$

The boundary conditions for the water-cooled tubular reactor are:

$$P\big|_{z=0} = P_0, \quad F_i\big|_{z=0} = F_{i0}, \quad T\big|_{z=0} = T_0 \tag{4}$$

The overall heat transfer coefficient, U, between the circulating boiling water on the shell side and the gas flow on the reaction side was estimated from:

$$\frac{1}{U} = \frac{1}{h_i} + \frac{(D_o - D_i)}{(D_o + D_i)} \frac{D_i}{k_s} + \frac{D_i}{D_o} \frac{1}{h_o} \tag{5}$$

where h_i is the heat transfer coefficient between the packed bed and the tubular wall of the reactor and h_o is the heat transfer coefficient between the tubular wall on the outer side and the cooling water,

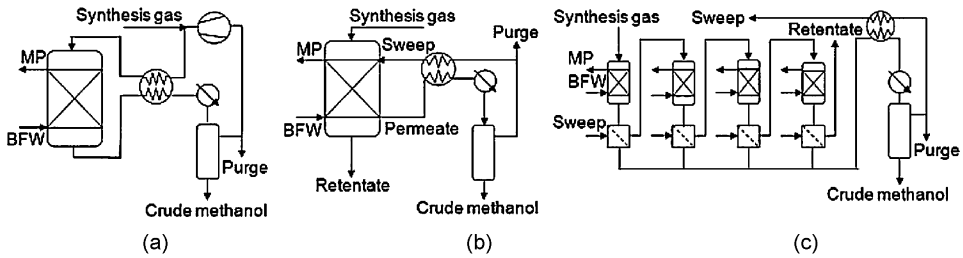

Fig. 1. Traditional reactor process (a), membrane reactor process (b) and membrane module process (c) for methanol synthesis considered in this work.

which is obtained by the correlations [6,7]:

$$h_i = \frac{2.06\rho_G V_0}{\phi C_{pG}} \left(\frac{V_0 D_P \rho_G}{\mu_G}\right)^{-0.575} \left(\frac{C_{pG}\mu_G}{k_G}\right)^{-2/3} \tag{6}$$

$$h_o = \frac{0.020 k_w}{D_o} \left(\frac{V_T D_H}{\mu_w}\right)^{0.8} \left(\frac{C_{pw}\mu_G}{k_w}\right)^{1/3} \left(\frac{D_T}{D_o}\right)^{0.53} \tag{7}$$

In the membrane reactor process (MRP) considered here, see Fig. 1b, the synthesis gas is not recycled as in the TRP. The synthesis gas is fed to the reactor and permeate from the membrane is sent to a condenser, and raw methanol is separated from the permeate by condensation. The permeate leaving the separator is then used as sweep gas. The retentate from the reactor is purged. The membrane reactor consists of 900 steel tubes, which are filled with catalyst. The dimensions of the steel tubes and catalyst particles in the MRP are identical to the TRP. A ZSM-5 zeolite membrane supported on the outer side of an alumina tube is placed in the centre of each steel tube in the reactor. The outer diameter of the alumina tubes is 10 mm and the total membrane area is 450 m^2. The catalyst is thus surrounding the membrane and the total mass of catalyst is 5.9 ton. The reactor is cooled with boiling water with a temperature of 513 K on the outer side of the steel tubes generating medium pressure steam from a steam drum (not shown in the flow sheets). Parameters for the MRP are listed in Tables 1 and 3.

The mass and energy balance for the membrane reactor are:

$$\frac{dF_i}{dz} = r_i \rho_b - f_i \Delta P_i a_m \rho_b \tag{8}$$

$$\frac{dF_{si}}{dz} = f_i \Delta P_i a_m \rho_b \tag{9}$$

$$\frac{dT}{dz} = \frac{1}{\sum_{i=1}^{n_c} F_i C_{pi}} \left(aU(T_a - T) + a_m U_S (T_s - T) + \sum_{i=1}^{n_r} r_i \left(-\Delta H_i^{rx}\right) \rho_b \right) \tag{10}$$

$$\frac{dT_s}{dz} = \frac{a_m U_S (T_s - T)}{\sum_{i=1}^{n_c} F_{si} C_{pi}} \tag{11}$$

The boundary conditions for the membrane reactor are:

$$P\big|_{z=0} = P_0, \quad F_i\big|_{z=0} = F_{i0}, \quad T\big|_{z=0} = T_0, \quad F_{si}\big|_{z=0} = F_{si0}, \quad T_s\big|_{z=0} = T_{s0} \tag{12}$$

The overall heat transfer coefficient, U_S, between the gas flow on the reaction side and the sweep gas flow on the inside of the membrane tube was estimated in the same way as in Eq. (5), where the heat transfer coefficient between the sweep gas and the membrane with support was obtained by the correlation [7]:

$$h_m = 3.66 \frac{k_G}{D_m} \tag{13}$$

The membrane module process (MMP) evaluated in the present work, see Fig. 1c, consist of four sections with 4 m long water-cooled tubular reactors in each section. The inner diameter of the reactor tubes is the same as in the other reactors and the number of reactor tubes in each reactor is 755 and the total number of tubes in the four reactors is thus 3020. The total catalyst mass is the same as in the MRP (5.9 ton). The four reactors are placed in series with membrane modules after each reactor and the total membrane area is 450 m^2. The membrane modules consist of 895 ZSM-5 zeolite membrane tubes with an outer diameter of 10 mm that separate methanol and water from the synthesis gas at reaction temperature. The zeolite film is positioned on the outer side of each tube. Crude methanol is separated from the membrane permeate streams by condensation in a condenser and the retentate from the last membrane module is purged. Synthesis gas from the condenser is used as sweep gas in the membrane modules. The sweep gas is fed co-currently in the module while the synthesis gas from the reactor is fed to the centre of each membrane tube. The module tubes consist of 6 equally large sections in which the sweep gas is fresh for each section, while the retentate from each section is sent to the next section. The permeate from each module is sent to the condenser. In each reactor in the MMP, the cooling water temperature is set independently. The cooling water is fed from four steam drums (not shown in the flow sheets). Parameters for the MMP are listed in Tables 1 and 3.

Table 2
Kinetic and equilibrium constants [4].

$k = A\exp(B/RT)$	A	B
k_A [$bar^{-1/2}$]	0.499	17,197
k_B [bar^{-1}]	6.62e−11	124,199
k_C [–]	3 453.38	–
k_D [$mol\,kg^{-1}\,s^{-1}\,bar^{-2}$][a]	1.07	36,696
k_E [$mol\,kg^{-1}\,s^{-1}\,bar^{-1}$][a]	1.22e10	−94,765
$K_{eq} = 10^{(A/T-B)}$	A	B
$K_{eq}{}^1$ [bar^{-2}]	3066	10.592
$K_{eq}{}^2$ [–]	2073	2.029

[a] The rate constants k_D and k_E are multiplied with 0.7 in the model to reflect the activity of a used catalyst.

The mass balance with boundary conditions for the membrane modules are:

$$\frac{dF_i}{dz} = -f_i \Delta P_i a_m \rho_B \tag{14}$$

$$\frac{dF_{si}}{dz} = f_i \Delta P_i a_m \rho_B \tag{15}$$

$$F_i\big|_{z=0} = F_{i0}, \quad F_{si}\big|_{z=0} = F_{si0} \tag{16}$$

Methanol formation occurs through two independent reactions, i.e. hydrogenation of carbon dioxide and the reverse water–gas shift reaction Here, the kinetics for these reactions are described by a Langmuir–Hinselwood Hougen–Watson model [4] by the following equations with constants as in Table 2:

$$r_{CH_3OH} = \frac{k_D p_{CO_2} p_{H_2} [1 - (p_{H_2O} p_{CH_3OH} / p_{H_2}^3 p_{CO_2} K_{eq}^1)]}{M^3} \tag{17}$$

$$r_{RWGS} = \frac{k_E p_{CO_2} [1 - (p_{H_2O} p_{CO} / p_{CO_2} p_{H_2} K_{eq}^2)]}{M} \tag{18}$$

$$M = 1 + k_C \left(\frac{p_{H_2O}}{p_{H_2}}\right) + k_A \sqrt{p_{H_2}} + k_B p_{H_2O} \tag{19}$$

To solve the ordinary differential equations above an implicit Runge–Knutta method was used. Permeation rates depend on the partial pressures, and the composition of the feed to reactor depends on the recycled flow. An iterative method was thus used to determine these variables and MATLAB R2008b (MathWorks, Inc.) was used for numerical solution.

4. Results and discussion

The prepared ZSM-5 membranes, shown in Fig. 2, are comprised of well intergrown crystals and the film thickness is about 500 nm.

The observed permeances for the ZSM-5 membranes in mixture separation experiments at room temperature were 0.3, 1, 12 and $18 \times 10^{-7}\ mol\,m^{-2}\,s^{-1}\,Pa^{-1}$ for H_2, CO_2, CH_3OH and H_2O, respectively. The methanol permeance is five times higher than for previously reported zeolite membranes [8,9]. The resulting separation factor α methanol/H_2 was about 30, and α methanol/CO_2 was

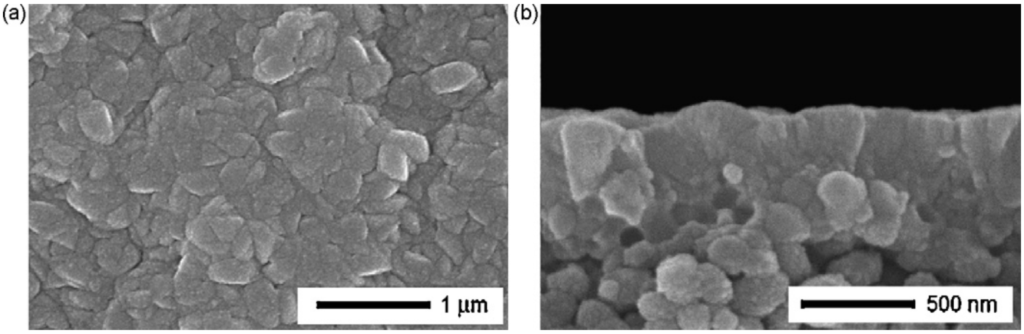

Fig. 2. SEM images of (a) the surface and (b) the cross-section of a ZSM-5 membrane.

about 9. In the present work, it was assumed that the same membrane performance would be obtained at reaction conditions as that experimentally observed at room temperature and atmospheric pressure. The selectivity of the ZSM-5 membrane is adsorption governed. In any adsorption governed separation processes, separation is achieved at conditions when there is a large difference in adsorption between the components. If both temperature and pressure is increased, these favorable conditions may be maintained. The separation in the ZSM-5 membrane is caused by strong adsorption of methanol and water and only weak adsorption of hydrogen and CO_2 in the pores. The permeances of CO_2 and H_2 are very high when no water or methanol is present in the feed. Selectivity would be lost when only temperature is increased since adsorption of water and methanol, that block the pores for transport of CO_2 and H_2 is reduced when the temperature is increased. It is possible that this pore blocking effect, which leads to selective membranes, also would be observed at reaction conditions. At reaction conditions, the pressure of methanol and water is much higher than in our separation experiments, which may lead to pore blocking and selective membranes also at the higher temperatures at reaction conditions. The permeances may also be similar at the process conditions considered in the present work. The higher pressure gradient applied in the considered process than in the experiments may lead to a reduced permeance. However, this reduction may be counteracted by a lower relative mass transfer resistance in the support at higher pressures since the transport by Poiseuille flow in the support is improved at high pressure [10]. It was also assumed that the CO and N_2 permeances were identical to the H_2 permeance.

Based on the experimental data for membrane performance and literature data for catalyst performance, the processes described in Fig. 1 were evaluated, for a production of 70,000 ton methanol per year using a stoichiometric feed with 2% inert (N_2) and a feed pressure of 80 bar. Benchmarking against published data on a traditional reactor process (Lurgi low-pressure process) showed that the model prediction was satisfactional [5].

Table 3 shows results from simulations of the modeled processes. The total flow to the condensers is quite high in all processes and somewhat higher for the MMP and MRP compared to the TRP. The flow to the condenser is high in the TRP due to the recycle of synthesis gas in this system. The flow to the condensers is also high in the membrane processes due to the high flow of sweep gas used. In principle, the sweep gas flow rate can be reduced to minimize the flow to the condensers in the membrane processes. However, for an effective membrane process, the sweep gas flowrate must be sufficiently high, to maintain sufficient driving force for transport through the membrane. For more selective membranes, the flow to the condensers could be reduced further.

The membrane processes require about half the catalyst mass of the TRP due to the selective removal of products, which increases the reaction rate, and due to that no recirculation, which leads to accumulation of inert (see Table 3), is applied. The hydrogen loss is highest in the MMP due to the lower overall conversion in this process, which will be discussed below. Some reactants thus leave the processes with the retentate from the last membrane module and also with the purge. However, the energy in these streams could be recovered in a boiler. Obviously, with a more selective ZSM-5 membrane, the maximum CO_x-conversion would increase and the hydrogen loss would be reduced for the MMP.

The pressure drop is quite high in the TRP due to the high flow rate in this reactor, which is caused by the recirculation of synthesis gas, while the pressure drop is almost insignificant in the membrane processes. In addition, a compressor is needed in the TRP to recompress the recycled gas, which is not needed in the membrane processes (MMP and MRP) due to the one pass design.

Fig. 3a shows the temperature along the reactor length for the three processes. The temperature reaches the catalyst sintering temperature after about 1 m in the TRP and levels out at the cooling water temperature (533 K) in the last part of this reactor. In the membrane processes, the reaction rate is higher due to a more concentrated feed with less inert and the removal of products, which results in more uneven temperature profiles. Due to the high reaction rate in the membrane processes, it was necessary to reduce the catalyst tube diameter from 38 mm as in the Lurgi process, to 25 mm, and to dilute the catalyst 35% in the first 4 m of the reactors to limit the maximum catalyst temperature below the sintering temperature. For the sake of simplicity and to facilitate direct comparisons between the processes, this reactor tube diameter and catalyst dilution was used in all cases. It was further necessary to also reduce the cooling water temperature 20–513 K in the MRP to reduce the maximum catalyst temperature below the sintering temperature. In the MMP, the cooling water temperature was reduced with 20–513 K in the first two reactors to reduce the maximum catalyst temperature below the sintering temperature. The cooling water temperature was then set 10 and 20 K higher for reactor three and four, respectively, in order to compensate for the decreased reaction rate in these reactors due to the increased

Table 3
Comparative data for the different processes.

Specification	TRP	MRP	MMP
Flow to condenser [kmol/h]	3810	4200	5230
Catalyst mass [ton]	11.3	5.9	5.9
Hydrogen loss [kmol/h]	38.0	21.5	178.4
Pressure drop [%]	17.3	1.3	1.0
Recycle ratio [–]	3.8	0	0
Inert concentration[a] [%]	21–23	2–17	2–8
Number of reactor tubes	1460	900	3020
Number of membrane tubes	0	900	3580
Length of membrane tubes [m]	0	16	4
CO_x-conversion per pass [%]	26	97	81
CO_x-conversion overall [%]	98	97	81

[a] Reactor entrance−reactor exit.

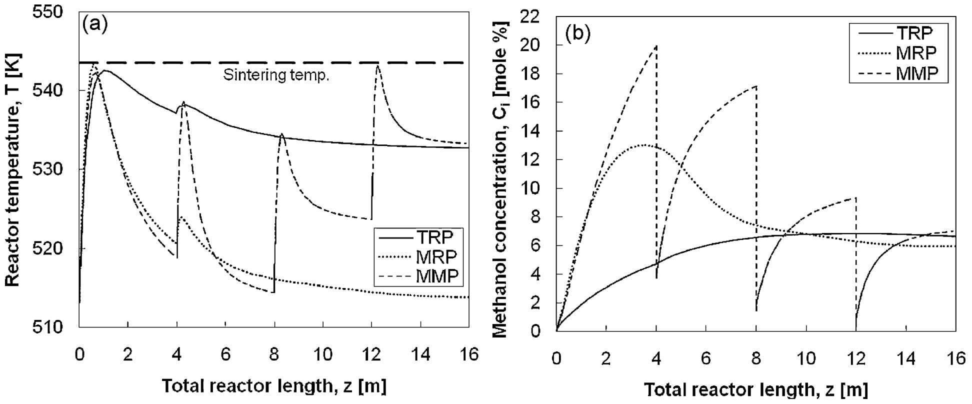

Fig. 3. Temperature (a) and methanol concentration (b) as a function of reactor length for the three processes.

concentration of inert. The temperature in the MRP reaches its maximum after about 1 m and is then quickly approaching the cooling water temperature, except for a little excursion after 4 m of reactor length, when the catalyst is no longer diluted. The temperature in the MMP varies more due to the modular design of this process and the different cooling water temperatures.

Fig. 3b shows the methanol concentration along the reactor length of the three processes. The highest methanol concentration is observed for the MMP, which is explained by the more concentrated feed with less inert compared to the TRP and that methanol is not continuously removed as for the MRP. The MMP could be optimized by a more suitable distribution of membrane area in the four membrane modules (larger area in the first module), which may allow complete removal of methanol between each reactor in the MMP. The MMP could also be optimized with respect to the reactor length, since a large part of the catalyst mass operates close to equilibrium in the last two reactors in the design considered here. For the sake of simplicity, in this work, the membrane area in each module was set to 1/4 of the total membrane area, and the length of each reactor was set to 1/4 of the total reactor length, which is not optimal for the MMP. As opposed to the MRP, the degrees of freedom are quite large in the MMP process, which opens up for further optimization of this system.

As illustrated by Fig. 4, it is possible to reach about 97%, 81% and 26% CO_x-conversion per pass, for a MRP, MMP and TRP, respectively. However, the overall CO_x-conversion is equal the one pass conversion for the membrane processes but for the TRP it is as high as 98% due to the recycle of synthesis gas. Due to CO_x and H_2 loss through the membranes, it is not possible to reach 100% CO_x-conversion using the membrane processes. However, with a more selective ZSM-5 membrane, higher conversion could be achieved using the membrane processes.

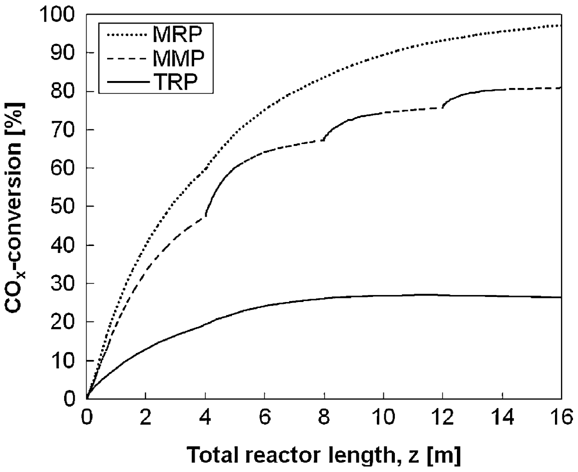

Fig. 4. CO_x-conversion for the three processes.

5. Conclusions

Provided that the same performance as observed at room temperature and atmospheric pressure is obtained at reaction conditions, the performance of our current ZSM-5 membranes seems sufficient in order to improve the methanol synthesis process. This work shows that the MRP is the best alternative with the highest conversion per pass enabling one pass operation for a stoichiometric feed in commencing biorefineries, and even more selective membranes would of course improve the membrane processes (MRP and MMP) even further. A membrane module configuration (MMP) is better from a practical point of view since catalyst and membrane is separated and by adding more membrane units, the performance of the MMP will approach the MRP. Also, a MMP has more degrees of freedom compared to a MRP wich allows further optimization of the MMP. However, a similar system to the MMP could be designed by replacing each membrane module by a reactor effluent heat exchanger, a cooler and a condenser. A disadvantage with the latter process would be a higher complexity of the processes compared to the currently used TRP. Membrane processes would be more preferable in systems that not only are limited by thermodynamic equilibrium, but also have selectivity issues, such as in the synthesis of higher alcohols from synthesis gas.

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References

[1] G. Barbieri, G. Marigliano, G. Golemme, E. Drioli, Simulation of CO_2 hydrogenation with CH_3OH removal in a zeolite membrane reactor, Chem. Eng. J. 85 (2002) 53–59.
[2] F. Gallucci, L. Paturzo, A. Basile, An experimental study of CO_2 hydrogenation into methanol involving a zeolite membrane reactor, Chem. Eng. Proc. 43 (2004) 1029–1036.
[3] J. Hedlund, J. Sterte, M. Anthonis, A.J. Bons, B. Carstensen, N. Corcoran, D. Cox, H. Deckman, W. De Gijnst, P.P. de Moor, F. Lai, J. McHenry, W. Mortier, J. Reinoso, High-flux MFI membranes, Micropor. Mesopor. Mater. 52 (2002) 179–189.
[4] K.M. Vanden Bussche, G.F. Froment, A steady-state kinetic model for methanol synthesis and the water gas shift reaction on a commercial $Cu/ZnO/Al_2O_3$ catalyst, J. Catal. 161 (2006) 1–10.
[5] F. Harting, F.J. Keil, Large-scale spherical fixed bed reactors: modeling and optimization, J. Ind. Eng. Chem. Res. 32 (1993) 424–437.

[6] R.H. Perry, D.W. Green, Perry's Chemcial Engineers' Handbook, McGraw-Hill, New York, 1997.
[7] F.P. Incropera, D.P. DeWitt, Fundamentals of Heat and Mass Transfer, Wiley, New York, 2007.
[8] M.D. Jia, B. Chen, R.D. Noble, J.L. Falconer, Ceramic–zeolite composite membranes and their application for separation of vapor/gas mixtures, J. Membr. Sci. 90 (1994) 1–10.
[9] K. Sato, K. Sugimoto, Y. Sekine, M. Takada, M. Matsukata, T. Nakane, Application of FAU-type zeolite membranes to vapor/gas separation under high pressure and high temperature up to 5 MPa and 180 °C, Micropor. Mesopor. Mater. 101 (2007) 312–318.
[10] F. Jareman, J. Hedlund, Single gas permeance ratios in MFI membranes: effects of material properties and experimental conditions, Micropor. Mesopor. Mater. 82 (2005) 201–207.