

FEASIBILITY OF THE APPLICATION OF POROUS INORGANIC GAS SEPARATION MEMBRANES IN SOME LARGE-SCALE CHEMICAL PROCESSES

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This document will be published as chapter 14 of the book
“Fundamentals of inorganic membrane science and technology”
Editors: A.J. Bruggraaf and L. Cot, Elsevier, 1996

JUSTIFICATION

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1. INTRODUCTION

During the last decade there has been an intensified activity in research and development of ceramic membranes for gas separation applications. In several studies it is said that the market for these membranes will expand very rapidly in the near future [1, 2, 3]. This market growth will be due to advantages such as high permeation and membrane stability as compared with other membrane separation technologies.

During the first years of inorganic membrane development, R&D was mainly focused on the membrane as the product, and research was driven by material development and material scientists. Research was carried out by universities, while research institutes and especially (end-user) industry were hardly involved. Main reason for this was that a lot of fundamental knowledge was needed before these membranes could be implemented in the foreseen market.

Nowadays somewhat more attention is paid towards applications and use of these membranes in processes and under process conditions. Industry is now getting more involved in R&D. In several review articles, membrane development and possibilities of inorganic membranes in gas separation applications [4 – 8] and especially in membrane reactor applications [9 – 16] have been summarised. In most of the literature the use of inorganic membranes for gas separation and reactor applications are considered to be very promising. However, research is still strongly focused on the membrane as a material and much less on the membrane process. As a result insufficient data, especially on testing under realistic circumstances, are available on the real possibilities of inorganic membranes in large-scale processes. There is a need for these data and extensive technical and economic evaluations of membranes in different possible applications should be made, preferably using a multidisciplinary approach. Aspects such as chemical engineering and mechanical engineering are as important as materials engineering to introduce inorganic gas separation membranes into commercial processes. Furthermore, in order to introduce these membranes into the market successfully all aspects starting from fundamental material development to marketing strategies must be considered, depending, of course on the state of development. If these aspects are taken into account it will become clear that the introduction of inorganic membranes in petrochemical and energy production processes is more difficult than first expected.

The aim of this chapter is to show that a multidisciplinary approach, focusing on materials, processes and modelling, as depicted in figure 1, is needed to judge the techno-economic feasibility of inorganic membranes in large-scale processes. This will be done by discussing examples of the potential use of porous inorganic membranes in three different membrane reactor applications. In all three, hydrogen separation will take place: the dehydrogenation of propane to propylene, the dehydrogenation of ethylbenzene to styrene, and the water-gas shift reaction.

Membrane characteristics such as permeation, selectivity and separation factor are given throughout this chapter. The definitions for these characteristics are given in the appendix.

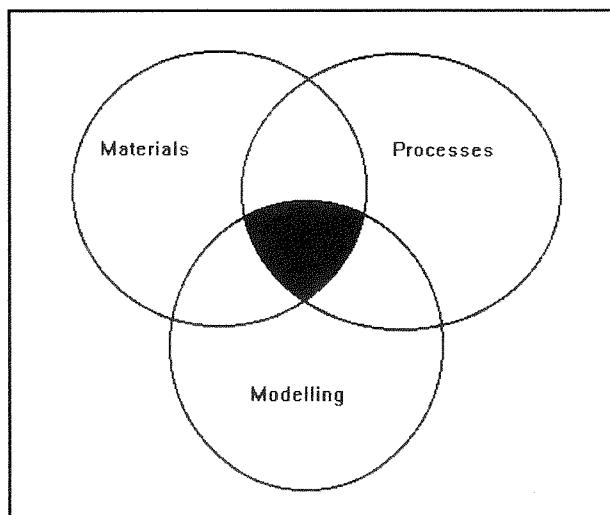


Figure 1 *Disciplines to be considered.*

2. BACKGROUND INFORMATION

2.1 Materials

Hydrogen selective inorganic membranes can be mesoporous (2 nm < porediameter < 50 nm; ceramic, glass or carbon) microporous (porediameter < 2 nm; ceramic, carbon or zeolite) or dense (ceramic or metal). These membranes can be used from ambient temperatures up to about 600°C for mesoporous materials, up to about 500 C for microporous inorganic membranes and up to about 800°C for dense inorganic membranes [14, 15, 16]. These temperatures are only a rough indication, because of the different materials which can be used and the test conditions at which the membranes have to operate.

Typical characteristics of both porous and dense inorganic membranes are given in table 1. Only applications with porous ceramic membranes will be dealt with in this chapter.

Inorganic gas separation membranes normally consist of a substrate, on which one or more intermediate layers and a toplayer or gas separation layer having Knudsen diffusion selectivity (pores of about 4 nm in diameter) is applied. These membranes were developed during the last ten years in mainly flat and tubular configuration and by using alumina as the base material. They are now available on a semi-commercial scale. Because of the low price of organic membranes and the rather low selectivity of inorganic Knudsen diffusion membranes it will be hard to find commercial applications for these membranes, unless they can be used under conditions where organic membranes would not be able to operate, e.g. high temperature or chemically harsh applications.

The Knudsen diffusion gas separation layer can be modified by e.g. sol-gel, cvd, or crystallisation techniques to enhance the selectivity, but this decreases the permeation. Silica is the material mainly used for modification. However, data on reproducibility and stability are still scarce. The large scale use of high selective inorganic membranes and these membranes at high temperatures, up to at least 600°C, will probably last another 5–10 years. On a laboratory-scale (maximum membrane surface area of about 50 cm²) these high selective membranes are now available, although stability can be a problem in certain atmospheres.

Only a few years ago it was recognised that research and development should also be focused on high temperature gas tight sealing, membrane systems/modules and decreasing of costs by e.g. the increase of membrane surface area to volume ratio. On a laboratory-scale membrane sealing technology is now available up to temperatures of about 600°C [28, 29]. Some work has been reported on the increase of membrane surface area to volume ratio for ceramic gas separation membrane systems [30]. However, difficulties are foreseen in scaling up and controlling this technology [30, 31].

Table 1 Typical characteristics of inorganic gas separation membranes.

Membrane system	porediam. + (thickness)	Temp [°C]	gasmixture ¹	permeation ² [mol/m ² sPa]	perm- selectivity ³
Mesoporous alumina [17]	4 nm (3 μm)	25	H ₂ /C ₃ H ₈	6 * 10 ⁻⁵	3.0
		250		4 * 10 ⁻⁵	3.7
		475		3 * 10 ⁻⁵	4.0
Mesoporous glass: Vycor™ (Toshiba) [18]	4,5 nm (300 μm)	20	H ₂ /N ₂ and H ₂ /CO ₂	7.4 * 10 ⁻⁸	Knudsen
Mesoporous carbon [19]	several nm (12–18 μm)	400	H ₂ /CO– CO ₂ –H ₂ S	2 * 10 ⁻⁶	3.5:CO*) 4.5:CO ₂ *)
Microporous SiO ₂ on Al ₂ O ₃ by poly- meric sols [20]	appr.10 Å (100 nm)	25	H ₂ /C ₃ H ₆	7 * 10 ⁻⁷	14
		100		10 * 10 ⁻⁷	62
		200		11 * 10 ⁻⁷	156
Microporous SiO ₂ on Al ₂ O ₃ by polymeric sols + CVD [21]	appr.1 nm (5 μm)	50	H ₂ /N ₂ H ₂ /N ₂	1.8 * 10 ⁻⁸	44
		250		5.4 * 10 ⁻⁸	200
Hollow fibre microporous glass (PPG) [22]	4 – 8 Å (5 μm)	204	H ₂ /CO	8.7 * 10 ⁻⁹	325 *)
		260	H ₂ /CO	11.0 * 10 ⁻⁹	205 *)
		316	H ₂ /CO	10.9 * 10 ⁻⁹	147 *)
		371	H ₂ /CO	10.2 * 10 ⁻⁹	101 *)
Microporous carbon molsieve; hollow fibre [23]	appr.5 Å (6 μm)	20	O ₂ /N ₂	6 * 10 ⁻⁸	8
		20	He/N ₂	3 * 10 ⁻⁷	20
		200	H ₂ /CH ₄	1.07 * 10 ⁻⁷	57 *)
		500	H ₂ /CH ₄	1.16 * 10 ⁻⁷	35 *)
Silicalite on ceramic disc [24]	appr.4.5 Å (5 μm)	20	H ₂ /N ₂	2.3 * 10 ⁻⁷	3.1
		20	H ₂ /n–C ₄ H ₁₀	2.3 * 10 ⁻⁷	146
		20	N ₂ /n–C ₄ H ₁₀	2 * 10 ⁻⁷	15
		20	N ₂ /i–C ₄ H ₁₀	2 * 10 ⁻⁷	55
Dense SiO ₂ by CVD modification of microporous silica on alumina [25]	dense (5 μm)	50	H ₂ /N ₂	3 * 10 ⁻⁹	26
		250	H ₂ /N ₂	2.2 * 10 ⁻⁸	250
		50	H ₂ /CH ₄	3 * 10 ⁻⁹	17.5
		250	H ₂ /CH ₄	2.2 * 10 ⁻⁸	166
		270	H ₂ /N ₂		47 *)
Metal: Pd alloy on ceramic [26]	dense (6–8 μm)	440	H ₂ /N ₂	1.6 * 10 ⁻⁶	> 1000
Metal: Pt/Pd (80/20) on alumina [27]	dense (?)	100	H ₂ /N ₂	1.2 * 10 ⁻⁷	5.6
		200		3.6 * 10 ⁻⁷	37
		300		7.5 * 10 ⁻⁷	200

¹ The fastest permeating compound is mentioned first.

² Permeation of fastest permeating compound.

³ If marked with *) then these figures are real separation factors.

*) Separation factor is a function of the process variables and process circumstances.

2.2 Membrane reactors

Besides the application of inorganic membranes in stand-alone gas separation units, attention is focused on more process-integrated applications. In such configurations the separation function of the membrane can be used to shift the equilibrium of a chemical reaction by selective removal of one or more components on the product side of the reaction in a so-called membrane reactor.

Four basic catalytic membrane reactor configurations, when the membrane and reactor are in the same physical unit, can be distinguished [32]:

- a catalytic membrane reactor (CMR), in which the membrane is permselective to one or more components and is catalytically active;
- a catalytic non-permselective membrane reactor, where the membrane acts as the catalyst, but is not selective to any of the components;
- a packed bed or fluidized bed membrane reactor (PBMR or FBMR), in which the selective membrane is surrounded by a packed bed or fluidized bed of catalyst particles;
- a packed bed or fluidized bed catalytic membrane reactor (PBCMR or FBCMR), in which the selective and catalytic active membrane is also surrounded by a packed bed or fluidized bed of catalyst particles.

A schematic of a PBMR, in this case for the water-gas shift reaction, is given in figure 2.

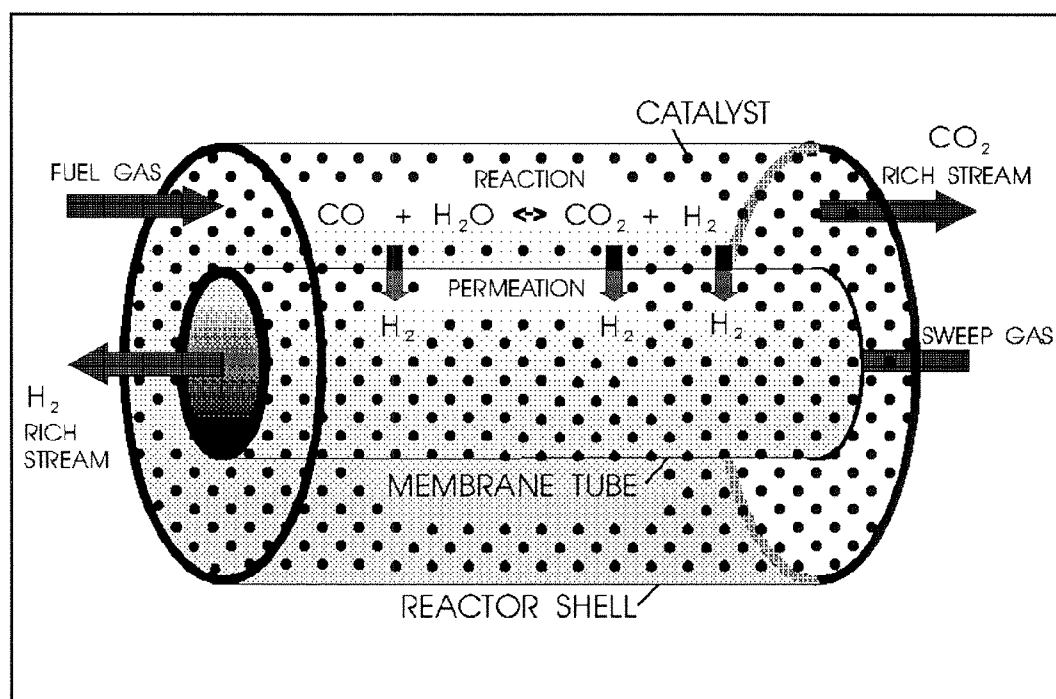


Figure 2 Schematic of the water gas shift membrane reactor.

Of course the catalytic reactor and the membrane unit can also be separated from each other, but can still be used to enhance the yield of a catalytic process, as will be shown in section 3, see also figure 5.

2.3 Membrane process modelling

In the various feasibility studies presented in this chapter, models of membrane separation and membrane reactor systems play an important role. Models are being used for various reasons: not only because there is a lack of experimental data, or the calculations concern non-existing, fictive membranes, they are also used to conveniently represent available data. In the various studies, different types of models have been used. However, the basis of all the models used is the same and will be discussed here.

In a membrane permeator unit two important phenomena are encountered:

- Transmembrane transport
- Flow around the membrane.

In a membrane reactor a third phenomenon is of importance:

- Chemical reaction

In the feasibility studies relatively simple models have been used because these concern mostly a rough estimate of the possibilities. For high selective and microporous types of membranes, permeation through the membrane is assumed to occur only via diffusion which obeys Fick's law. In the case of the Knudsen diffusion membranes the contribution of the non-separating viscous flow through the membrane is also accounted for.

The basis of the flow models are ordinary differential mass balances for each component on either side of the membrane. The mechanism for permeation is substituted in the mass balances. When reaction occurs the kinetic expression is also added to the balances. The chemical reaction is assumed to take place in close proximity of the membrane surface (passive membrane reactor system), and not in the membrane pore itself (active membrane reactor system). The latter case will lead to a completely different and more complicated description of the phenomena. Further steady-state conditions are assumed, so the parameters are time-independent. The model as used here is treated extensively in [57, 29]. Furthermore information can be found in [61, 68 - 71].

In the membrane reactor many parameters influence the performance of the system. By making the model equations (mass balances) dimensionless [61], parameters are grouped so that a few dimensionless groups appear which describe the process. The physical meaning and their definitions are given in table 2. A kinetic expression of the power law type for the reaction rate is assumed.

The Peclet number is an important parameter which has an influence on the performance of the membrane process. Permeation and surface area are coupled via the Pe number. In the equation Q_{H_2} is the permeation of the fastest permeating component (usually H_2 in this study). In membrane gas separation processes Pe is usually between 0.1 and 1.0. For new applications $Pe = 0.5$ can be taken as a first guess. The actual performance of the systems depends on many more parameters than the Pe number only, i.e. membrane selectivity, pressure drop, sweep gas flow to feed gas flow ratio, composition of the feed.

Table 2 *Dimensionless numbers and their meaning.*

Parameter	Meaning	Definition
Peclet number	Ratio of total feed rate and maximum possible transmembrane flow rate	$Pe = \frac{F_{tot}^f}{A Q_{m-H_2} P^f}$
Damköhler number	Ratio of maximum conversion and the total feed rate (dimensionless residence time)	$Da = \frac{V(P^f)^{\alpha} k}{F_{tot}^f (RT)^{\alpha}}$
S_i	Ratio of permeation of H_2 and component i (permselectivity)	$S_i = \frac{Q_{H_2}}{Q_i}$
ϕ	Ratio of permeate and feed side pressure	$\phi = \frac{P^p}{P^f}$
Y	Molar ratio of total sweep gas flow and total feed flow	$Y = \frac{F_{tot}^s}{F_{tot}^f}$

For the purpose of two of the studies described in this chapter a membrane separation model based on the characteristics given above has been implemented in the flow sheeting package ASPEN PLUS™. This package allows the use of self-made user sub-routines and is therefore suitable for the implementation of the membrane model. The advantage of the use of the flow sheeting package is that the sensitivity of the total system performance to changes in membrane parameters can be determined quickly and that optimum process configurations can be found more easily.

3. GAS SEPARATION APPLICATIONS FOR INORGANIC MEMBRANES

In this section some examples of inorganic gas separation membranes in membrane reactor applications will be discussed. A first indication of the technical and economic feasibility of these membranes in dehydrogenation reactions and in the water-gas shift reaction will be given.

3.1 Dehydrogenation of propane

This section is written in close cooperation with Kinetics Technology International B.V. in Zoetermeer and Holland Industrial Ceramics in Velsen-Noord, the Netherlands [33].

3.1.1 Introduction

Steam cracker plants based on naphtha and/or gasoil feedstocks are the major source of locally produced propylene in Europe and the Far East. In the United States approximately 90% of propylene comes from steam crackers and refinery operations. The balance comes from catalytic dehydrogenation units. The growth rate of propylene use is expected to be 3-4% worldwide. With the more conventional sources of propylene such as steam cracker operations and refinery operations it is not possible to supply sufficient propylene for this growing demand. However, at the price levels of mid 1993 the economics of propane dehydrogenation are not very attractive.

In recent decades various processes have been developed for catalytic dehydrogenation of propane to propylene [34 - 37]. These processes can be divided into two groups:

- processes with an adiabatic reactor concept, and
- processes with an isothermal reactor concept.

Current commercial processes for catalytic dehydrogenation of propane to propylene are based on adiabatic reactor systems. Typical examples are:

- the Catofin process (Lummus/Air Products);
- the Oleflex process (UOP);
- Fluidized Bed Dehydrogenation Process (FBD) (Snamprogetti/Yarsintez).

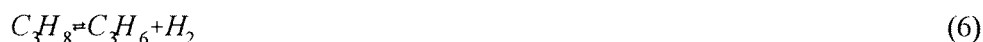
Recent developments in catalytic dehydrogenation have lead to nearly commercial processes, using an isothermal reactor concept. Examples are:

- the STAR process (Phillips) [35, 37];
- the LINDE process (Linde/BASF) [36].

The potential benefits which can be achieved by using ceramic membranes in comparison to conventional propane dehydrogenation processes such as Oleflex and Catofin will be discussed here.

3.1.2 Thermodynamics of propane dehydrogenation

Besides several side reactions, the following main endothermic reactions are of importance in the dehydrogenation of propane to propylene:



By selectively removing hydrogen from the reaction mixture, the reaction can be shifted beyond the original thermodynamic equilibrium. In this way reaction limitations can be overcome and the propylene yield enhanced.

In figure 3 the equilibrium conversion for these two reactions as a function of temperature is given. From this figure it is concluded that: reaction (7) is more favoured from a thermodynamic point of view, and for high propylene yields a high temperature is needed.

Another important reaction which can take place at high temperatures is thermal cracking, which sets an upper limit to the reaction temperature. Therefore, a high-selective catalyst is necessary which only promotes the dehydrogenation and not the cracking reaction. The upper limit temperature of the cracking reaction has been determined by thermodynamic calculations using the programme SPYRO[®]. The results are given in figure 4.

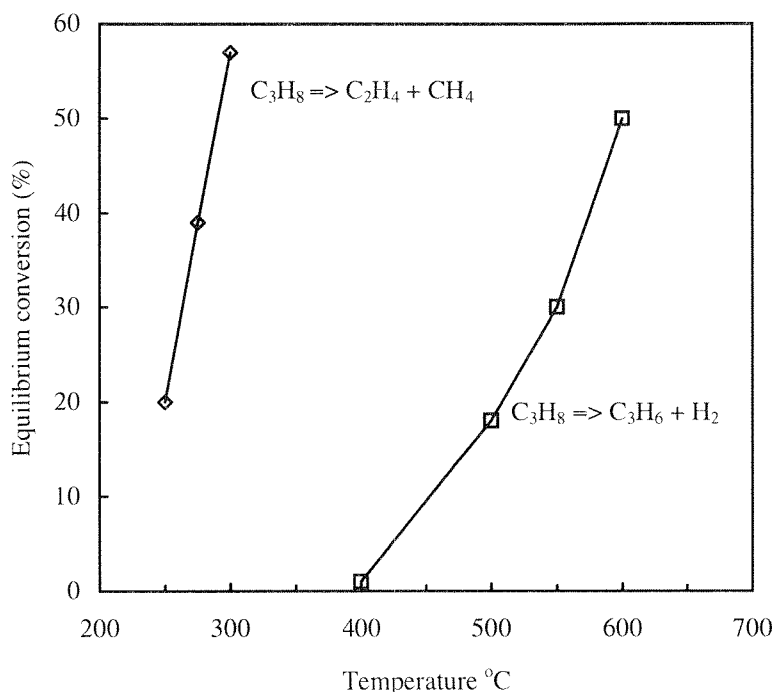


Figure 3 Thermodynamic equilibrium at 1 bar.

Figure 4 shows that a temperature above 625–650°C leads to important thermal cracking reactions, which reduces the selectivity towards propylene, but also leads to increased coke formation, which deactivates the catalyst.

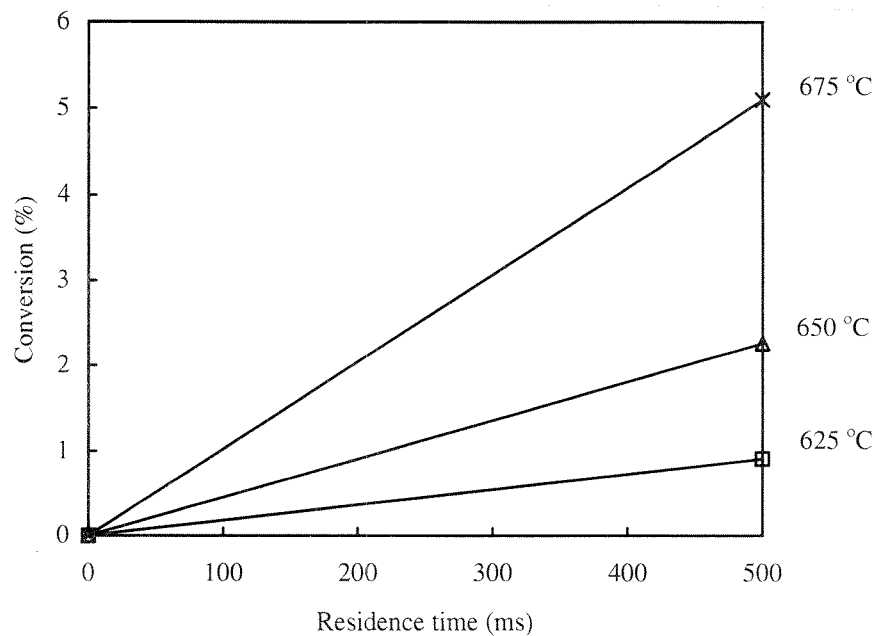


Figure 4 Influence of temperature on thermal cracking.

3.1.3 Adiabatic reactor concepts; reactor modelling evaluation

In this modelling study only a packed bed membrane reactor has been dealt with, because the regeneration of the catalyst and membrane can be done separately, and also it will be easier to match the catalyst and membrane surface necessary.

Both Catofin and Oleflex use an adiabatic reactor concept. The Oleflex process uses 4 reactor beds in series, which as such is more suitable for addition of a ceramic membrane separation unit than the Catofin process which uses a parallel reactor system. A comparison between the Oleflex process as a base case and an Oleflex process equipped with ceramic membranes is made for the following cases:

1. A 'Knudsen diffusion selective' membrane after the first, second and third reactor, see figure 5. The permeation of the pure gases is inversely proportional to the square root of the molecular masses.
2. A 'Knudsen diffusion selective' membrane after the third reactor only.
3. 'Ideal' membranes, which remove all the hydrogen formed in the reaction, after the first, second and third reactor.
4. 'Ideal' membranes, which remove all the hydrogen formed in the reaction, after the first, second and third reactor and with increased outlet temperature.

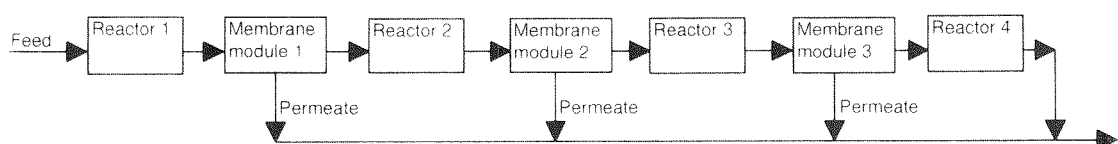


Figure 5 Process flow diagram including a membrane module after each reactor.

In cases 1 to 4 part of the reactor effluent is split off by the membrane as permeate. The retentate stream, depleted in hydrogen, is then fed to the next reactor. After the fourth reactor membrane permeate and reactor effluent are mixed again to be treated further in the downstream section of the process.

Permeation characteristics of 'Knudsen diffusion' membranes, consisting of a support and two consecutive layers, have been used to calculate the performance of the ceramic membrane reactor, see also section 2.1 [17, 31]. The pore size of the separation layer of these membranes is 4 nm in diameter [31, 38]. Ideal membranes which remove all the hydrogen formed do not exist (maybe Pd based membranes will come close to the desired characteristics), but are used as a basis for calculating the maximum possible increase in conversion and selectivity.

Two semi-quantitative models describing the reactor and membrane performance were used to evaluate the overall performance. The reactor was modelled using the flow-sheeting package PRO II. A membrane model was used which describes both the transport through the membranes and transport along the membrane. These models are described in [33]. Based on the Oleflex process the following boundary conditions were chosen for the calculations:

Plant capacity:	150,000 t/yr propylene
Pressure after first reactor:	1.7 bar
Pressure after second reactor:	1.5 bar
Pressure after third reactor:	1.3 bar
Permeate pressure:	1.1 bar
Residence time in reactor:	0.5 seconds
Permeate flow:	10% of feed flow

The results of the calculations are given in table 3.

Table 3 *Adiabatic Oleflex based reactor performance (all figures on weight bases).*

	Base Case	Case 1 Knudsen + reactors 1,2,3	Case 2 Knudsen + reactor 3	Case 3 Ideal + reactors 1,2,3, constant T	Case 4 Ideal + reactors 1,2,3, higherTemp
Conversion (%)	47.0	42.2	46.1	49.4	54.0
Selectivity (%)	73.9	74.0	74.0	75.7	74.5
Yield (%)	34.7	31.2	34.2	37.4	40.3
T _{in} °C	650	650	650	650	685
T _{out} °C	595	594	595	583	595
Membrane area (m ²)	-	475	313	- *)	- *)

*) Membrane area not calculated because no estimation of the permeation for ideal membranes has been made.

From table 3 it is clear that in process configurations with Knudsen diffusion selective membranes a drop in yield is obtained, as compared with the base case. Apparently, the use of Knudsen diffusion membranes under the chosen conditions in these configurations is not attractive due to the relatively large amount of propane permeating through the membrane.

With 'ideal' membranes (case 3 and 4) positive effects are observed. In case 3, with the same heat input as in the base case, the increase in yield is limited. However, in case 4, with a higher inlet temperature, higher yields are obtained and maximum profit of the membrane is made.

From this we can conclude that:

- membranes with a selectivity higher than Knudsen diffusion are needed
- the process conditions should be changed in order to increase the membrane separation performance, and
- the dehydrogenation reaction kinetics seem fast enough to react on the hydrogen removal, at the chosen residence time of 0.5 seconds.

In order to increase the membrane separation performance there are two possibilities:

- 1) increase the membrane permselectivity, to values higher than for Knudsen diffusion;
- 2) increase the driving force for separation across the membrane (a higher driving force for separation means a membrane process with higher separation factors, at the same membrane permselectivity) by:
 - increasing the feed pressure;
 - increasing the amount of hydrogen in the feed;
 - using a sweep gas at the permeate side;
 - reducing the permeate pressure.

Since the driving force for hydrogen transport is low, a moderate increase in membrane selectivity (to a permselectivity of 10 for H_2 vs C_3H_8 and C_3H_6) has shown to have hardly any influence on the performance. Furthermore, the membrane surface needed will increase because it is assumed that the increase in selectivity is obtained by a decrease in permeability of all the components, except hydrogen whose permeability is constant. An increase in membrane surface means an increase in costs. An increase in feed gas pressure is not attractive since the reaction conversion drops significantly with an increase in the feed gas pressure. As can be expected, the use of extra hydrogen in the feed has a negative effect on the conversion. Potential sweep gas candidates are steam and propane. Unfortunately steam will permeate in reverse through the membrane (when the membrane has a rather low selectivity) and deactivate the catalyst in the next reactor. Propane as a sweep leads to a significant change in the hydrogen and propane quantities in the retentate. The propane recycle which is required to use propane as a sweep gas, leads to a significant increase in utility consumption.

Finally, we have calculated the effect of permeate pressure reduction. In table 4 the results for the base case and case 2 are compared with a new case 5, in which Knudsen diffusion membranes have been used only after the third reactor and in a process having a permeate pressure of 0.3 bar.

Table 4 *Adiabatic Oleflex based reactor performance (all figures on weight bases).*

	Base Case	Case 2 Knudsen + reactor 3	Case 5 Knudsen + reactor 3
Conversion (%)	47.0	46.1	46.6
Selectivity (%)	73.9	74.0	74.0
Yield (%)	34.7	34.2	34.5
T _{in} °C	650	650	650
T _{out} °C	595	595	593
Membrane area (m ²)	–	313	60
Feed pressure (bar)	–	1.3	1.3
Perm. pressure (bar)	–	1.1	0.3

Permeate pressure reduction leads only to a marginal improvement in yield. The only possibility to use inorganic membranes in an adiabatic reactor concept for dehydrogenation of propane is to use membranes with a selectivity much higher than Knudsen diffusion, in combination with a reduced permeate pressure. In this case, hardly any reactant will be lost through the membrane and the driving force for hydrogen transport will be high enough. Results of calculations for this combination will be reported in future.

Possibilities of the use of inorganic membranes in an isothermal concept may lead more easily to a technically feasible process, because extra heat for propane conversion is available. Detailed flow sheeting calculations for the integrated process are not yet available. However, to obtain a first indication of the economic feasibility of this concept, laboratory-scale (membrane) data are being used for performance estimation, see section 3.1.4.

In general, membranes to be applied should be stable under the working conditions. Also, coke formation on the membranes should not lead to dramatic reduction of permeation and selectivity and regeneration with steam should not be a problem [39]. Another technical constraint can be the connection of membranes to the metal housing.

3.1.4 Isothermal reactor concepts; economic evaluation

An isothermal reactor concept incorporating a ceramic membrane is more attractive compared to an adiabatic reactor concept from a thermodynamic point of view. In this concept we assumed a reactor with reactor tubes located in a direct-fired heater and operated in a cyclic way to remove coke formed on the catalyst. Parallel bed and heaters have been assumed [35 – 37].

On behalf of KTI an experimental programme on these reactor concepts has been started at the University of Southern California (USC). Some of the experimental results, concerning the use of Knudsen diffusion membranes are available in the literature [32, 40]. These data have been used to calculate the economics of an isothermal propane dehydrogenation membrane reactor concept and are compared with the commercial Oleflex and Catofin processes, based on an adiabatic concept. The experimental

circumstances of these lab-scale experiments, especially residence time, pressures and gas composition are not the same as in commercial, large-scale processes. However, we do not expect these differences to have a great influence on the results of the work presented here.

Two process flow diagrams have been developed for a ceramic membrane reactor process:

- the CMRL process: a process based on the commercial Oleflex process with a low propane conversion and Knudsen diffusion membranes
- the CMRH process: a process based on the commercial Catofin process with a high propane conversion and Knudsen diffusion membranes

The operating characteristics of these processes are given in table 5.

Table 5 *Operating characteristics.*

	Oleflex [34]	Catofin	CMRL [32,33,40]	CMRH [32,33,40]
Reactor type	adiabatic	adiabatic	isothermal	isothermal
Conversion (%)	35.0	54.9	38.0	53.4
Selectivity (wt%)	77.0	69.4	89.0	78.6
H ₂ /feed ratio	0.8	0.0	0.2	0.2
Pressure (bar)	1.6-1.1	0.5	1.15	1.15
Inlet temp. (°C)	625	650	560	580
Outlet temp. (°C)	520-580	520-600	560	580
LHSV (h ⁻¹)	2.5	1.2	2.5	2.5
Reactor volume (m ³)	55.7	82.0	44.4	36.1

The design capacity of the plant is 150,000 MT/yr polymer grade propylene, which is equivalent to a production of 18,750 kg/hr (8,000 hr/yr).

The basis of the economic evaluation is the comparison of operating and investment costs for a membrane reactor with those for a conventional dehydrogenation plant. The Return On Investment (ROI) and the propylene production costs of the different processes have been calculated. The results are summarised in table 6. Details of the calculations are reported in [33]. In the calculations a propane price of 130 \$/tonne and a propylene price of 330 \$/tonne has been assumed [33].

Table 6 *Production cost breakdown (figures in US\$).*

	Catofin	Oleflex	CMRL	CMRH
Propane feed	203	183.0	171.6	177.9
Co-product credit	-55.8	-47.3	-28.8	-44.3
Utilities, catalyst, chemicals	60.3	66.8	67.1	59.3
Fixed expenses	41.1	42.7	37.6	37.2
Full production costs	248.7	245.2	247.5	230.1
Depreciation	66.2	69.2	59.8	59.0
Accounting production costs	314.9	314.4	307.3	289.1
Selling price	330	330	330	330
Overall margin	15.1	15.6	22.7	40.9
ROI resulting from overall margin (%)	1.5	1.4	2.4	4.4

From table 6 it can be seen that Catofin and Oleflex give about the same ROI. This ROI is not very attractive. The CMRL gives an ROI of about 2.4 %. The CMRH case gives an absolute increase in ROI of 3% points compared to commercial adiabatic processes. A sensitivity analysis of the ROI on both the feed costs and the product values is performed. For the Oleflex and CMRH case these results are summarised in figures 6 and 7 which indicate that the ROI of such a propane dehydrogenation unit is not attractive when the price difference between propane and propylene is less than about 250–300 \$/tonne. At mid 1993, price levels of 330 \$/tonne propylene and 130 \$/tonne propane, the process is not economically viable. Historical price levels show that a price difference of 300 \$/tonne has not been encountered during the last 3 years.

It is concluded that a ceramic membrane reactor based on Knudsen diffusion membranes can give improvements in an isothermal reactor concept although the difference in price level between feedstock and product is too small to give an economically viable process.

Following the results of the adiabatic reactor concept it is expected that high selective membranes will further improve the economics. However, it should be recognised that the process conditions in an isothermal concept are more severe than in an adiabatic concept. In particular, decoking conditions can be a problem in using high selective membranes. Detailed calculations on the isothermal membrane reactor concept are being performed and will be reported in future.

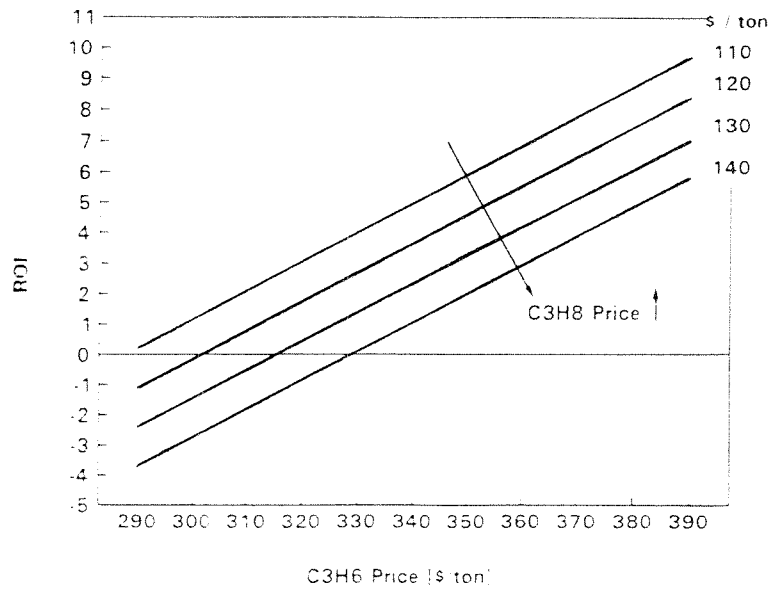


Figure 6 Influence of propane/propylene price on Oleflex ROI.

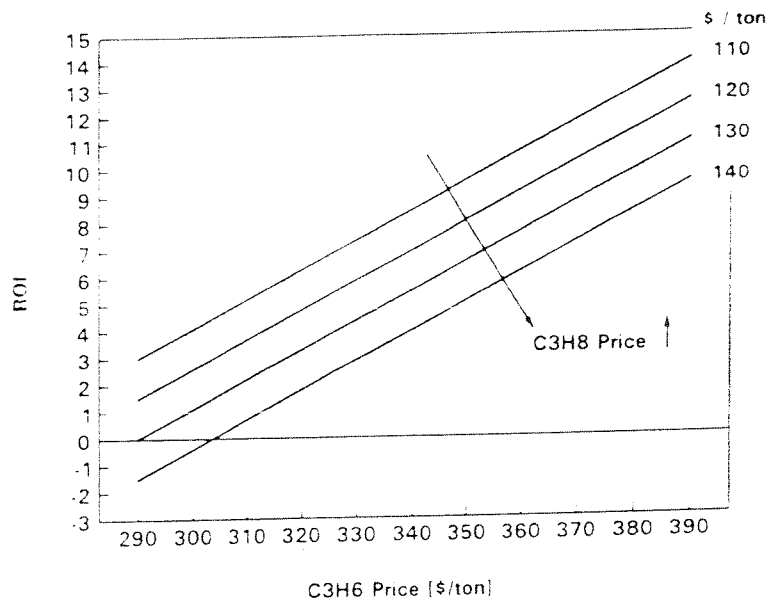


Figure 7 Influence of propane/propylene price on CMRH ROI.

3.1.5 General conclusions propane dehydrogenation

The selectivity of Knudsen diffusion membranes is not high enough to give a technical and economically feasible ceramic membrane reactor process for the dehydrogenation of propane to propylene based upon an adiabatic reactor concept. Measures such as an increased driving force or a moderately increased selectivity do not lead to positive results, because the driving force for hydrogen separation under the chosen process conditions is not high enough.

Probably the only possibility is the combination of a high driving force (sweep gas or low permeate pressure) and a very high selective membrane. The use of ceramic membranes in an isothermal reactor concept shows better prospects. This process, in combination with high selective membranes and the necessary membrane boundary conditions are being studied, and the results will be reported in future.

Propane and propylene prices are the main actors in the introduction of a dehydrogenation process in general, thus also for processes based upon membrane reactors. At a price difference (propylene - propane) of 300 \$/tonne or less membrane based dehydrogenation processes will hardly be economic feasible.

3.2 Dehydrogenation of ethylbenzene to styrene

3.2.1 Introduction

Next to ethylene, propylene and vinylchloride, styrene is one of the most important monomers for the production of plastics. The worldwide demand for styrene in 1992 was 18.2 million tonnes and is expected to grow annually with 3-5 % to 23.9 million tons in 2000 [42]. Recent production statistics show an annual production of about 1.3 million tons of styrene in the Netherlands. Approximately 75 % of this is produced at DOW Benelux in Terneuzen by catalytic adiabatic dehydrogenation of ethylbenzene [42].

The conversion of the endothermic reaction by which styrene is produced from ethylbenzene is mainly limited by temperature and thermodynamic equilibrium. The conversion to styrene increases with temperature, decreases with pressure and with dilution of an inert component like steam.

When producing styrene from ethylbenzene several reactions besides the main reaction take place. Six reactions are of importance; these include the production of toluene, benzene, ethylene and methane and the thermal cracking of ethylbenzene (coking) [43]. This last reaction is the main reason for the upper temperature limit of 630°C. On the other hand, high temperatures favour the dehydrogenation reaction, so the process takes place between approximately 570°C and 630°C. The dehydrogenation reaction is presented in figure 8.

As with the dehydrogenation of propane, removing hydrogen from the reaction mixture may shift the conversion beyond the reaction equilibrium to the product side, obtaining higher selectivities to and yields of styrene.

Figure 8 *The dehydrogenation of ethylbenzene to styrene.*

In the literature several experiments and some modelling results are presented about the possibilities of membrane reactors in the dehydrogenation of ethylbenzene. The results vary from a small increase in yield and selectivity [39, 44] to very large increases in yield up to 20 % [45 – 49].

In this study the feasibility of implementing ceramic membranes on an industrial scale in the styrene production process is treated. Therefore, a model has been set up in the flowsheeting package ASPEN PLUS™, which describes a styrene process production plant. Some modelling has been done with different types of membrane reactors in different reactor section configurations to investigate the influence on the performance of the production of styrene.

3.2.2 Conventional process description

This work focuses on the reactor section of the styrene production process because it is the most promising part for the implementation of membranes. The reactor section of this process is shown in figure 9 [50].

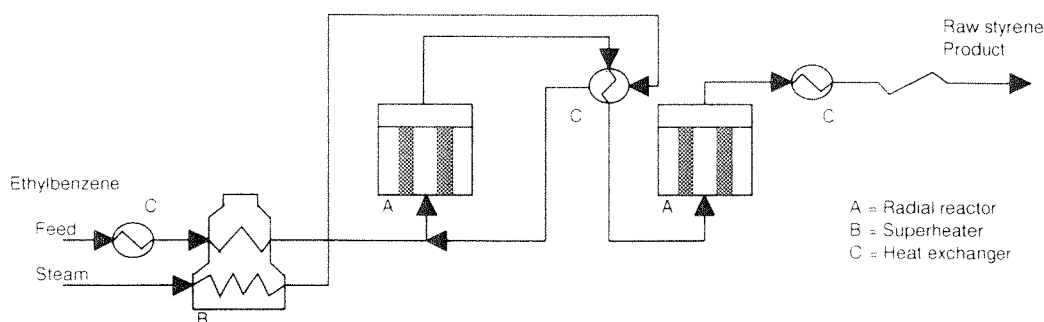


Figure 9 *Reactor section of the styrene production process.*

The process uses two radial reactors in series with one preheater and one interstage heater. Steam is used as an energy carrier (adiabatic reactor) and diluent [43, 50, 51]. Reactor temperatures and pressures are 570–630°C and 1.5 bar, respectively. Total hydrocarbon massflow (96 wt% ethylbenzene) is 95,000 kg/hr. The steam/hydrocarbon ratio is 2. Typical conversion, selectivity and yield numbers are 71, 92 and 66 %, respectively.

respectively. Definitions are given in the appendix. Reaction equations and kinetics are taken from literature [43, 51].

3.2.3 Implementation of membranes

The packed bed ceramic membrane reactor configuration (PBMR) has been chosen as the reactor set-up, see section 2.2. In the PBMR configuration three possible sub-configurations can be envisioned for a specific sweep gas in combination with a hydrogen or oxygen selective membrane for the dehydrogenation of ethylbenzene. These sub-configurations are shown in figure 10:

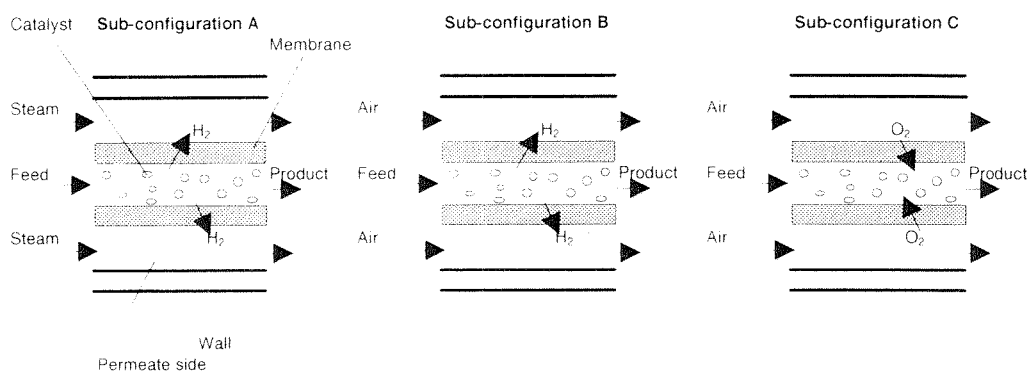


Figure 10 *Membrane reactor sub-configurations.*

In sub-configuration A hydrogen will permeate through the hydrogen selective membrane tube under the influence of a pressure difference over the membrane and it will be carried away with an inert sweep gas (steam). The partial pressure of hydrogen in the reaction mixture will decrease and the equilibrium will shift to the product side.

In sub-configuration B the permeated hydrogen will be swept away with air. Hydrogen will be burned and the heat generated by this exothermic reaction flows through the membrane to the reaction mixture. In this way the reactor will get an isothermic character and therefore higher conversions.

The third sub-configuration C uses oxygen permeable membranes instead of hydrogen permeable membranes. Again air is used as an oxygen source in the annular space of the reactor. Now oxygen will permeate through the membrane into the reaction mixture where it will burn the hydrogen formed. In this way there will be less loss of heat compared to the second case. Sub-configuration C is a principally different process: oxidative dehydrogenation.

The most important disadvantage of the last two configurations is that not only hydrogen will be burned, but also hydrocarbons such as styrene and ethylbenzene. It is assumed that in sub-configuration B the membranes do not have an infinite hydrogen selectivity. For this reason we have chosen to focus our investigation on the first reactor sub-configuration A. Although, especially sub-configuration C, the oxidative dehydrogenation process seems very promising if a catalyst active only for H_2 oxidation (and not C_xH_y oxidation) is developed.

By implementing the membrane reactor in the process according to sub-configuration A, the conventional process is changed as little as possible. Again several configurations for the reactor section are possible. The first is to implement membranes in the first reactor (see figure 9) and leave the rest of the process intact. The second possibility is to implement the membranes in the second reactor and leave the first intact. Another option

is to leave both reactors intact and to implement membranes between the two reactors. Because of the expected high costs of ceramic membranes, implementation in both reactors will probably be too expensive in relation to the possible advantages.

For modelling the styrene-process in ASPEN PLUS™, several assumptions have been made:

- the radial flow reactors are estimated by plug flow reactors;
- all reactions are catalytic and only the main reaction is reversible;
- under these conditions coking is negligible;
- the pressure drop in the reactors is negligible;
- heat transfer through the membrane is posed ideal;
- the sweep gas flows cocurrently with the reactant gas;
- a small part of the steam which is originally used as carrier gas and heat carrier, is now used as sweep gas. The total amount of steam used, stays the same;
- the standard pressure at the permeate side of the membrane reactor is 0.1 bar.

In modelling we used (if possible) permeations and selectivities based upon real measurements on different types of membranes [17, 26, 27, 29, 31, 38], see also section 2.1. These membranes are:

- Knudsen diffusion membranes; as developed by ECN;
- microporous, highly selective membranes; as developed by ECN; and
- palladium membranes [26, 27].

We also formulated a non-existing, hypothetical membrane to see what would be ultimately possible. The performance of these membranes is in principle the same as of microporous membranes. The only difference is that the permselectivity of hydrogen in relation to the other components is ten times higher. The permeation of hydrogen however, remains the same [29, 31]. In table 7 the permeations and permselectivities are given for the chosen membrane types. These data have been used to perform the modelling.

Table 7 *Permeations and permselectivities of the used membranes.*

	Knudsen		Microporous		Palladium		Hypothetical	
	Q *	S*	Q *	S*	Q *	S*	Q *	S*
H ₂	13·10 ⁻⁶	1	1·10 ⁻⁶	1	0.8·10 ⁻⁶	1	1·10 ⁻⁶	1
Ethylbenzene	1.8·10 ⁻⁶	7	2·10 ⁻⁸	50	5·10 ⁻⁹	160	2·10 ⁻⁹	500
Styrene	1.9·10 ⁻⁶	6.9	2·10 ⁻⁸	50	5·10 ⁻⁹	160	2·10 ⁻⁹	500
Toluene	2.0·10 ⁻⁶	6.5	2·10 ⁻⁸	50	5·10 ⁻⁹	160	2·10 ⁻⁹	500
Benzene	2.2·10 ⁻⁶	5.9	2·10 ⁻⁸	50	5·10 ⁻⁹	160	2·10 ⁻⁹	500
H ₂ O	4.6·10 ⁻⁶	2.8	1·10 ⁻⁷	10	8·10 ⁻⁹	100	1·10 ⁻⁸	100

* Q = Permeation [mol/m².s.Pa] and S = permselectivities [Perm_{H₂}/Perm_X]

In this investigation $Pe = 0.5$ is taken as a standard for calculations, see section 2.3. No further optimisation towards membrane surface area has been carried out.

3.2.4 Results

With $Pe_{let} = 0.5$, it has been calculated that under the chosen conditions in all configurations of the reactor section a membrane surface area of approximately $43,000 \text{ m}^2$ is required for microporous and palladium membranes and $3,300 \text{ m}^2$ for Knudsen diffusion membranes.

Sub-configuration A

Results of the implementation of all four types of membranes in only the first reactor (PBMR) are given in table 8.

Table 8 *Results of the simulations with sub-configuration A.*

Implementation of membranes in the first reactor			
Membrane	Yield	Conversion	Selectivity
No membrane	43 %	46 %	95 %
Knudsen	38 %	40 %	94 %
Microporous	40 %	42 %	95 %
Palladium	40 %	42 %	95 %
Hypothetical	40 %	43 %	95 %

Implementation of these membranes decreases the performance of the reactor because:

- a part of the steam that is used for dilution and energy carrier in the conventional model is now used as sweep gas; less dilution and energy input has a negative effect on the dehydrogenation;
- in this early stage not much hydrogen has been formed that can be transported through the membrane; and
- the high partial pressure of ethylbenzene will enhance the permeation of this reactant through the membrane with the consequence that there is less ethylbenzene left to react to styrene.

For membranes implemented in the second reactor only the results of microporous membranes will be discussed in detail, because palladium membranes gave almost the same results and the performance is better than that of Knudsen diffusion membranes. The yield and selectivities have been calculated at different permeate pressures and are plotted in figures 11a and 11b. The results for the conventional reactor are obtained without a membrane implemented in the process.

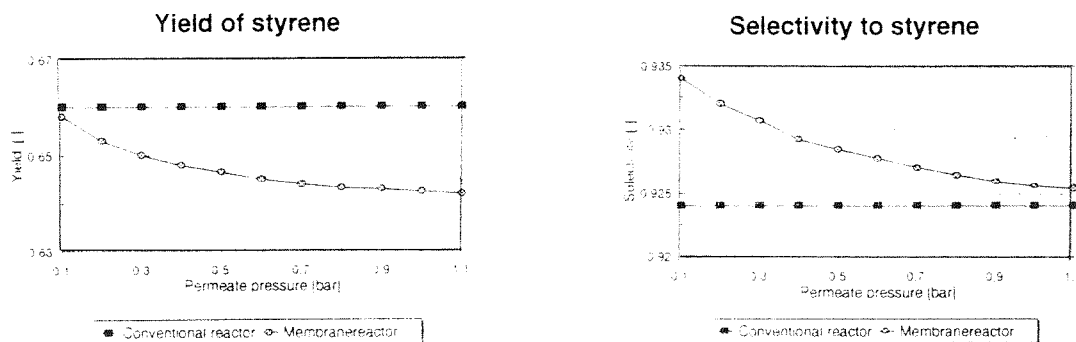


Figure 11 a,b *Yield and selectivity as a function of the permeate pressure.*

With decreasing permeate pressures, the yield increases to the same level as in the conventional reactor and the selectivity increases to a higher level. In this stage of the process the reaction approaches the equilibrium closer than in the first reactor, so the negative effect of permeating ethylbenzene is less and the positive effect of hydrogen permeation is larger. The increase in yield, with decreasing permeate pressure is due to the suppression of the hydrogenation reaction in which styrene reacts to ethylbenzene. The increase in selectivity to styrene is explained by the suppression of the side reactions to, e.g., toluene and benzene, due to the lower partial pressure of hydrogen. Thus, implementation of membranes leads to the expected effects, but these are too small to compensate the negative effect of less steam in the reactant gas (partly used in this case as sweep gas).

The results from simulations with a membrane unit placed between the two conventional reactors are comparable to the above mentioned results, because the average partial pressures are almost the same.

The simulation results are not as promising as expected at forehand and not as good as those reported in literature [45 – 49]. To find an explanation for our results, we first simulated the implementation of membranes having a permselectivity which is thousand times higher than that for microporous membranes, but which have the same hydrogen permeability. To create an even more ideal environment for extremely selective removal of hydrogen from the reactant gas, the permeate pressure has been set to 0.005 bar. Although the hydrogen partial pressure in the reactant gas was negligible (meaning that the hydrogen transport through the membrane was as large as possible), the increase in yield and selectivity was no more than 2 percentage points. However, a large increase was expected under these conditions. From this it can be concluded that application of membranes under these circumstances will not lead to an improvement in the performance of the process.

In order to explain this, the influence of the kinetics of the main reaction on the performance of the membrane reactor has been studied, for microporous membranes implemented in the second reactor. The reaction rate of the main reaction is successively multiplied by a factor 2 and 10, and as a consequence the reaction equilibrium is reached much faster. Under these circumstances increases are found in both yield and selectivity for the conventional dehydrogenation reactor without membranes. The results of the calculations are presented in table 9 in which the differences in yield and conversion are given in percentage points with respect to the conventional case.

Table 9 *Yield and selectivity in a PBMR as a function of reaction kinetics, compared to those in a conventional reactor.*

Reaction-rate	Conventional	2 times faster	10 times faster
Yield	± 0 % point	+ 5 % point	+ 12 % point
Selectivity	+ 1 % point	+ 1.5 % point	+ 2 % point

The higher yields and conversions for the PBMR compared to the conventional reactor are due to the fact that the conversion is no longer limited by the kinetics, as in the previous cases, but by the permeation of hydrogen.

It can be concluded that, if the reaction rate of the dehydrogenation process is faster than in current processes, implementation of microporous membranes will give a significant improvement in yield and selectivity. The ratio of permeation and reaction rate is very important in selecting membranes for this application. This is comparable to that reported for the cyclohexane dehydrogenation process [52].

3.2.5 Discussion

The results found in this study are less promising than those reported in literature [45 – 49]. There are several reasons for this difference. In some publications experiments have been reported in which process conditions and/or feed compositions have been used that are not realistic or feasible on an industrial scale but do have a large impact on the performance of the membrane reactor. Also, when results are reported from modelling this process, incorrect assumptions were sometimes made, e.g. side-reactions which have a large influence on the performance of this process have been neglected [47]. In other publications a very large heat input is taken, which leads to a more or less isothermal reactor, and as a consequence to higher conversions [45, 46, 48].

Even if implementation of membranes on technical basis is possible, one of the major problems of implementing ceramic membranes in this styrene production-process is the enormous membrane surface area required, which does not appear economically viable. Other membrane reactor configurations with a higher surface area to volume ratio may reduce the required module volume and simplify the installation. The biggest problem, however, is that these large membrane surface areas lead to very high costs. We assumed that in about ten years installation of one square metre of microporous gas separation membranes will cost about as much as \$ 5,700,-. In the case treated a surface area of 43,000 m² of microporous membranes is required, which will cost a total of 250 million dollars. The possible gain is 1 % in selectivity, which gives an annual profit of 4.5 million dollar. Even when the reaction rate of the main reaction is enhanced by a factor ten, the possible profit of 9 million dollars does not lead to an interesting ROI. It should be realized that extra costs for e.g. process integration are not yet included.

3.2.6 Conclusions

In the present concept of styrene dehydrogenation implementation of inorganic membranes is not feasible. Application of Knudsen diffusion membranes with a low permselectivity to hydrogen leads to a considerable permeation of ethylbenzene and thus, to lower yields. Microporous and palladium membranes give better results, but worse than a conventional case, because the conversion is limited by reaction kinetics. The ratio

of permeation rate to reaction rate is very important in selecting membranes in a membrane reactor process in which equilibrium shift is foreseen.

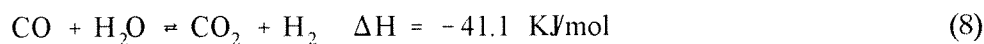
From the simulations with higher reaction rates it follows that implementation of ceramic membranes can lead to higher yields and selectivities. However, even under these conditions the profit from extra styrene yield does not compensate the costs of the membranes.

For profitable implementation of inorganic membranes, a high-selective membrane with a higher permeability than the membranes now available is necessary, in combination with higher reaction rates.

3.3 Water-gas shift membrane reactor

3.3.1 Introduction

The Water-gas shift (WGS) reaction is an important reaction in many commercial processes where hydrogen has to be generated or where CO must be converted. In the WGS reaction carbon monoxide together with steam is converted to carbon dioxide and hydrogen. The reaction is a reversible chemical reaction, usually assisted by a catalyst (see equation 8).



Hydrogen is a very important gas in many areas of industry [50, 53]. Currently, hydrocarbons are the main source for large scale production of hydrogen [42, 54]. Most of the hydrogen for industrial purposes is produced from natural gas and oil. The contribution of coal is limited at present but is expected to grow considerably in the future. In addition, biomass is expected to be a growing hydrogen source in the future. All these processes and/or feedstocks produce a gas mixture containing mainly hydrogen and carbon monoxide (syn gas). The hydrogen and carbon monoxide concentration will vary depending on the feedstock and process. The WGS process is being used to adjust the syn gas compositions for further syntheses or to enhance the hydrogen content for hydrogen production.

Coal particularly is thought to play a major role in future world energy supplies and possibly also as a feedstock supplier for the chemical industry [54]. Through integrated coal gasification combined cycle (IGCC) power plants, coal can be converted in a clean and efficient way into electricity with syn gas as intermediate product. In future IGCC options, syn gas can be partially converted into secondary gaseous products and be partially used to generate power. Hydrogen is an obvious secondary product for such a system [55].

A possible problem in future energy generation from coal is the emission of large quantities of CO₂. The rapidly increasing concentration of greenhouse gases in the atmosphere has already triggered the development of clean coal technologies for power generation worldwide. In the long term even the introduction of the highly efficient IGCC systems might not be sufficient to ensure the use of coal for power production, and further measures to decrease the emission of greenhouse gases, CO₂ in particular, might be necessary. The options to do so in an IGCC system also compare favourably to other large-scale coal-based combined cycles. Generation of hydrogen (WGS process) also plays an important role here [56, 57].

The attainable conversion with the WGS reaction depends on how the chemical equilibrium is set. The equilibrium constant K_p decreases as the temperature increases. This implies that the CO conversion decreases with increasing temperature. In many cases a high hydrogen yield is the objective of the WGS application. Increased hydrogen yield and reduced carbon monoxide content can be obtained in several ways. In principle it is desirable to carry out the reaction at low temperatures. This can be achieved by:

- 1) cooling during the reaction by heat transfer, or inert gas addition;
- 2) intercooling through execution of the reaction in several steps (reactors).

Other methods to increase the level of conversion are:

- 3) increasing of the steam to carbon monoxide ratio;
- 4) forcing equilibrium displacement to the product side; this should be achieved by continuous removal of either hydrogen or carbon dioxide directly at the place where it is formed.

Generally, in a conventional WGS system, a two-step shift is used to obtain high CO conversion rates. In the first high-temperature shift reactor the major part of the CO is converted at high activity, whereas in the second shift reactor the rest of the CO (closely up to the thermodynamic equilibrium) is converted at low temperature and also low activity. Steam to carbon monoxide ratios above the stoichiometric ratio (higher than 2) are generally being used to attain the desired carbon monoxide conversion, but also to suppress carbon formation on certain catalysts.

Different types of catalysts exhibit shift activity. Commercially available high temperature (HT) FeCr and low temperature (LT) CuZn are generally employed. Among some interesting new developments is the Co/Mo based catalyst. This type is completely insensitive to sulphur, and certain formulations are claimed to possess good activity at both high and low temperatures. The steam/carbon ratio is set by equilibrium considerations and carbon formation suppression.

Of the methods to increase the CO conversion mentioned, the first three possibilities are accompanied by severe penalties with respect to energy use, exploitation and investment costs. The fourth possibility seems less affected with such drawbacks and is therefore preferred [57].

Inorganic gas separation membranes with their unique properties can be used to selectively remove hydrogen in a membrane reactor. A schematic of the combination of membranes and the WGS reaction has already been shown in figure 2, in section 2.2. With such a PMBR reactor it is possible to enhance the CO conversion of the reaction and concurrently separate hydrogen from the reaction mixture, and furthermore have a separate CO₂ rich stream. The membrane reactor replaces two unit operations, has an enhanced hydrogen yield and will save steam, and therefore has the potential of energy efficiency improvement. The hydrogen produced can either be sold as an end-product or consumed directly as feed stock in down-stream hydrogen consuming processes, in e.g. the petrochemical industry. A first step to explore the potential of a WGS inorganic membrane reactor is to assess its technical and economic feasibility. The potential and exact lay-out of such a reactor is thought to be strongly dependent on the upstream raw gas production and gas treatment processes and the respective downstream processes. Therefore the techno-economic feasibility of the application can only be judged after a detailed investigation of the performance of the reactor against the background of the specific detailed characteristics of the process chains envisaged.

gasifier makes this process very favourable for the application of membranes as a separation technique.

Hydrogen from the membrane reactor is converted in a gasturbine with a high efficiency. The process efficiency will increase when the hydrogen production (CO conversion) and recovery (on the permeate side) from the membrane reactor is raised. CO₂ abatement increases with increasing recovery of carbon components on the retentate side of the membrane. The performance of the reactor can be measured in terms of these three parameters. The boundary conditions for the membrane reactor in the total system depends upon final performance of, amongst others, the membrane reactor itself. For an initial insight, it is desirable to carry out sensitivity analyses with the membrane reactor. For this purpose the boundary conditions around the membrane reactor will be estimated in first instance.

Ceramic membranes

Inorganic membrane development is still in progress [57], see also section 2.2. Microporous silica membranes have been developed at several universities and research institutes. Membrane selectivities of 15 and 20 for the separation of H₂ from CO₂ have been reported. Even higher selectivities for H₂ and CO, CH₄ and N₂ have been measured [57, 20]. Most measurements reported in literature have been performed on a laboratory-scale. However, it has been shown that it is possible to upscale these microporous ceramic membranes to, at least, bench scale [31, 57]. With other membranes such as noble (Pd) metal membranes and dense ceramic membranes very high and almost infinite selectivities for hydrogen are possible [58]. The permeation of these membranes is generally smaller than the permeation of microporous membranes.

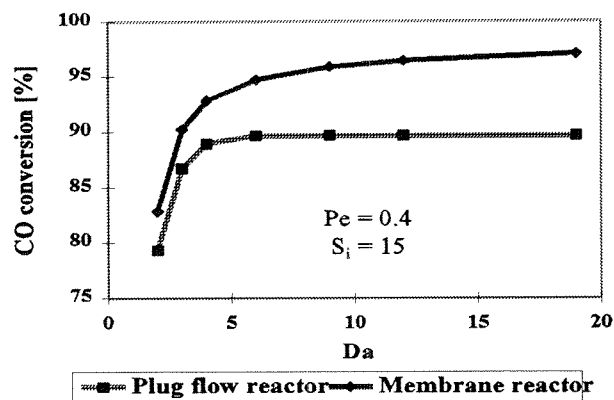
Microporous carbon membranes have been developed [59] but their possibilities in high temperature hydrogen separation is still unclear, although it is believed that there are opportunities. Scaling up of these membranes seems possible from a technical point of view. All these membrane types are potentially suitable for application in the WGS membrane reactor concept, provided their endurance is sufficient.

Results and discussion

The initial parameters used for the membrane reactor sensitivity analysis are shown in table 10. These parameters are a first guess of the boundary conditions of the total process.

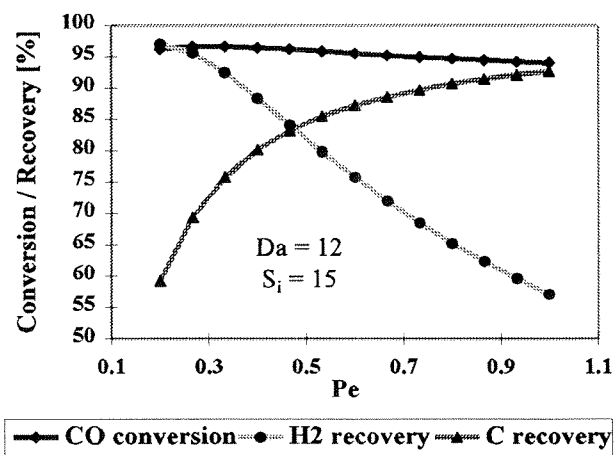
Table 10 *Initial simulation parameters.*

T _f	= 623 K
P ^f	= 36 bar
P ^p	= 21 bar
Y	= 1.035
H ₂ O/CO	= 1.5 (after steam injection)

Figure 13 Conversion vs. Da .

The conversion in the reactor is plotted in figure 13 against the Da number which can be regarded as a dimensionless residence time. From this plot it follows that the conversion in the membrane reactor equipped with high selective membranes can exceed the values possible with an ordinary plug flow reactor. From the graph it is clear that the conversion increases with increasing Da as would be expected. Conversion in an ordinary reactor reaches a certain maximum due to the establishment of the chemical equilibrium. In a membrane reactor conversion keeps increasing as a result of continuous hydrogen permeation. This is an important aspect of the membrane reactor, because the steam excess can be reduced which leads to a favourable economy of the process.

The influence of the Peclet number is shown in figure 14. Pe is reciprocally proportional to the membrane surface. Decreasing the Pe number increases hydrogen recovery and as a consequence the CO conversion. When more membrane surface is available, also more carbon dioxide and carbon monoxide permeates through the membrane and the carbon recovery decreases.

Figure 14 Conversion and recovery vs Pe .

An important question for the application of membranes is what the desired selectivity for the membranes has to be. The influence of the membrane selectivity on the performance of the reactor is shown in figure 15. CO conversion and C recovery increase with rising

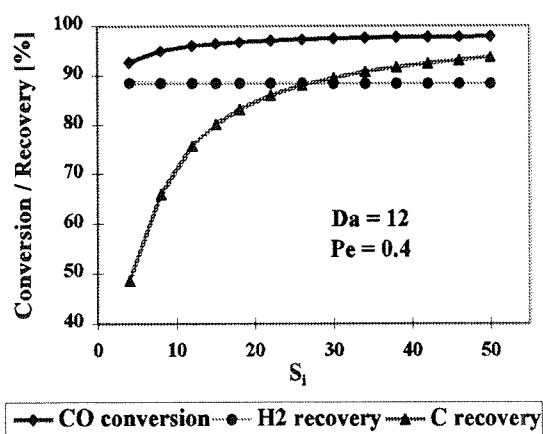


Figure 15 Conversion, recovery vs selectivity.

selectivity. The hydrogen recovery is more or less constant as a result of the Pe number that is held constant for the various simulations. CO conversion rises slightly due to the decreased losses of reactants with higher selectivity. Carbon recovery increases strongly with rising selectivity. Though the performance of the reactor increases with rising selectivity, the incremental increase in conversion and especially the C-recovery decreases with growing selectivity. The gain in performance is marginal when the selectivity surpasses 40.

The current measured H_2/CO_2 permselectivity of scaled up membranes is 15 [57]. With this value a good recovery of both H_2 and CO_2 is possible as appears from figure 15.

For a power plant including a membrane reactor with membranes with a selectivity of 15 the efficiency of the total system has been determined through flow sheet calculations. In these calculations the requirements and the demands of the membrane reactor and the rest of the system must match, so one or more iterative calculations is necessary to optimise the total system. The results of the calculations after optimisation are presented in table 11, in which three systems are compared.

Table 11 Results of power plant efficiency calculations.

Process	Process efficiency [%]
IGCC with membrane reactor for CO_2 removal	42.8
IGCC with conventional CO_2 removal	40.5
IGCC without CO_2 removal	46.7

Obviously a system without CO_2 removal exhibits the highest efficiency. However, the efficiency penalty induced is significantly lower when CO_2 is removed using the membrane reactor system instead of removal with a conventional technique. The conventional technique used here is a wet scrubbing process in which CO_2 is absorbed on a physical sorbent.

3.3.3 Full Scale Process considerations

When the membranes are used on an industrial scale, a considerable amount of surface area will be necessary to process the gas stream involved. A typical surface area necessary is 1500 m² for a 300 MW_e class power plant. For ceramic membranes this is a rather large surface area. Considering that permselectivity is already good for this application, it seems reasonable to direct research towards enlargement of the permeation or explore module concepts with a high surface area to volume ratio (e.g. monolytic systems) next to selectivity improvement.

When membranes are produced in a tubular geometry, which seems the most feasible currently, all membranes have to be sealed separately. This favours tubes with large diameters to reduce the number of seals. On the other hand, the smaller the tube diameter the higher the specific surface area attainable in a module.

High pressure, high temperature membrane sealing is an important aspect of the full scale module and this hurdle has been taken for laboratory and bench scale [16, 28, 31, 57]. The membranes can be sealed gas-tight to a stainless steel tube by a special joining technique. Experiments will be carried out initially for the so-called passive reactor concept in which a high selective membrane is surrounded by catalyst.

Dead end tube configuration, in which only one end of the membrane tube is connected and the other end is closed [14], seems favourable since it needs one ceramic to metal joint less than two-side connected tubes. A drawback of this option is the large force that will act upon the dead end side of the membrane when the process works with a considerable pressure drop as in this application. These aspects show that it is important to realise for which application the membranes are being developed and to consider scaling up in an early stage.

3.3.4 Conclusion

Through membrane reactor model calculation it has been shown that membranes can enhance the conversion of a WGS membrane reactor and concurrently separate hydrogen from carbon dioxide. This system can be used to control the release of CO₂ to the atmosphere from a IGCC power plant. Through process flow sheet calculations it has been shown that the efficiency of CO₂ control using the membrane reactor is significantly higher than when a conventional technique (i.e. wet washing with a sorbent) is applied. When selectivity of the membranes can be increased, it does not seem to be necessary to surpass approximately 40 for the process under consideration, because the gain in reactor performance seems marginal. Enlargement of the permeation is an important aspect on the other hand, so that the total surface area necessary for the full scale application can be reduced. This example shows that knowledge of the demands and requirements of the application are also very important in the development of membrane material.

4. CONCLUSIONS

Three examples of the use and feasibility of inorganic membranes in reactor applications have been discussed. Although several references give a very positive indication on the technical possibilities of the use of inorganic membranes in reactor applications, it has been shown that measurements under realistic conditions and calculations involving the complete process can show the opposite. A multidisciplinary approach is needed to study the feasibility of inorganic membranes in (membrane reactor) applications. A combination of membrane and materials know-how and insight in application opportunities and process economics is necessary to discuss the techno-economic feasibility of inorganic membranes. Furthermore, measurements and calculations should be performed on a realistic basis and scale in order to obtain reliable data on the performance of the membranes. As yet, insufficient realistic data on long term membrane stability and coke formation on the membranes are available.

In general the membrane reactor examples show that knowledge of the demands and requirements of each foreseen membrane application is very important in the choice and development of the membrane materials.

Application of ceramic membranes can improve the Return On Investment in the propane dehydrogenation process. Probably the only possibility for a technically and economically feasible propane dehydrogenation process, able to enhance the ROI enough to make the investment worthwhile, is the combination of a high driving force (sweep gas or low permeate pressure) and a very high selective membrane. The isothermal reactor concept shows better prospects than the adiabatic concept. At a price difference smaller than 300 \$/tonne between propylene and propane the propane dehydrogenation process based upon membranes will hardly be economically viable.

The present concept of implementation of ceramic membranes in the styrene process is not feasible, because:

- the permselectivity to hydrogen of Knudsen membranes is too low, which leads to a significant loss of ethylbenzene from the reaction side which can no longer take part in the reaction;
- the lower permeation of high selective microporous and palladium membranes leads to very high surface areas, which makes the application unattractive;
- the reaction rate of the dehydrogenation of ethylbenzene to styrene is too low: the kinetics and not the permeation are the limiting step in the membrane reactor.

From the simulations with higher reaction rates it has been shown that implementation of ceramic membranes can lead to higher yields. However, even under these conditions the profit from extra styrene yield does not compensate for the costs of the membranes. For profitable implementation of inorganic membranes, a high-selective membrane with a higher permeability than the membranes now available is necessary, in combination with higher reaction rates.

It has been shown that membranes can enhance the conversion of a water-gas shift membrane reactor and concurrently separate hydrogen from carbon dioxide. The efficiency of CO₂ control using the membrane reactor with a H₂/CO₂ selectivity of 15 is significantly higher compared to a conventional technique (i.e. wet washing with a sorbent). It is not necessary to exceed a selectivity of approximately 40 for H₂/CO₂ for the

process under consideration, because further increase in reactor performance seems marginal. Enlargement of the permeation is an important aspect on the other hand, so that the total surface area necessary for the full-scale application can be reduced.

In all three applications discussed, the stability of the membranes in these high temperature processes and the design of suitable modules still needs much research and development.

5. ACKNOWLEDGEMENTS

The research work described here has been funded in part by the Dutch Organization for Energy and Environment (NOVEM), the Dutch Ministry of Economic Affairs (EZ), and the Commission of the European Union.

Kinetics Technology International BV is gratefully acknowledged for their helpful discussions and calculations.

The authors would like to express their thanks to Prof. R. Pruschek, Dr. G. Oeljeklaus and R. Kloster of the University of Essen, G. Haupt of Siemens AG Power Generation (KWU), Dr. H. van den Berg of Dow Benelux BV, and Dr. L. van der Ham of the University of Twente.

K. Hemmes, G. Leendertse, and E. Delnoij are gratefully thanked for their help in modelling and setting up of the membrane models.

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LIST OF SYMBOLS AND ABBREVIATIONS

A	membrane surface area	m ²
Da	Damköhler number	-
F	flow rate	mol/s
k	reaction rate coefficient	(mol/m ³) ^{1-α} (1/s)
K _p	equilibrium constant	-
P	pressure	Pa
Pe	Peclet number	-
Q	permeation	mol/msPa
R	gas constant	J/molK
S _i	permselectivity (ratio H ₂ /component i permeation)	-
T	temperature	K
V	volume reactor	m ³
Y	molar ratio sweep flow vs. feed flow	-
α	sum of powers in power law expression	-
Φ	ratio of permeate and feed side pressure	-
superscripts		
f	feed	
m	membrane	
p	permeate	
s	sweep	
subscripts		
i	component i	
tot	total	
Abbreviations		
CMR	catalytic membrane reactor	
CMRL	catalytic membrane reactor low conversion	
CMRH	catalytic membrane reactor high conversion	
FBCMR	fluidized bed catalytic membrane reactor	
FBMR	fluidized bed membrane reactor	
HT	high temperature	
IGCC	Integrated coal Gasification Combined Cycle	
LHSV	Liquid Hourly Space Velocity.	h ⁻¹
LT	low temperature	
PBCMR	packed bed catalytic membrane reactor	
PBMR	packed bed membrane reactor	
ROI	return on investment	
WGS	water-gas shift	

APPENDIX

The permeation is defined as the (pure gas) flow (mol/s) through the membrane per surface area and per pressure difference over the membrane.

The permselectivity is defined as the ratio of the permeation of pure gases.

The separation factor is defined as:

$$\frac{y}{1-y} * \frac{1-x}{x} \quad (9)$$

in which y = concentration fastest permeating component on permeate side
 x = concentration fastest permeating component on feed side

The conversion and selectivity are given for the propane dehydrogenation reaction. For the ethylbenzene dehydrogenation and water-gas shift reaction the same definitions can be used for the respective reactants/products.

The conversion is defined as:

$$\text{conversion} = \frac{\text{mass flow propane in} - \text{mass flow propane out}}{\text{mass flow propane in}} \quad (10)$$

The selectivity can be expressed on a molar basis or mass basis:

$$\text{select. (mol)} = \frac{\text{mol flow propylene out} - \text{mol flow propylene in}}{\text{mol flow propane in} - \text{mol flow propane out}} \quad (11)$$

$$\text{select. (mass)} = \frac{\text{mass flow propylene out} - \text{mass flow propylene in}}{\text{mass flow propane in} - \text{mass flow propane out}} \quad (12)$$

The yield is defined as conversion * selectivity, on mol or mass basis.