

# WATER GAS SHIFT MEMBRANE REACTOR

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## Abstract

A water gas shift ceramic membrane reactor is being investigated. The reactor can be applied to control CO<sub>2</sub> emission from a coal based power plant. Ceramic membranes with a permselectivity of at least 15 at 325°C for H<sub>2</sub>-CO<sub>2</sub> have been prepared. Through model calculations it has been shown that these membranes can enhance the conversion of the reaction and realize an acceptable separation in H<sub>2</sub> and CO<sub>2</sub> for this application. When the membrane selectivity can be increased, it does not seem to be necessary to surpass approximately 40 because then the gain in reactor performance is marginal. Bench scale membrane reactor experiments at elevated temperatures and pressures will be conducted in order to proof the principle on a considerable scale. Therefore, tubular shaped membranes with a length up to 70 cm and special dedicated catalysts are being fabricated. Development of this process shows that full scale implementation aspects have to be considered in an early stage.

## Keywords

Membrane reactor  
Water gas shift reaction  
Modelling

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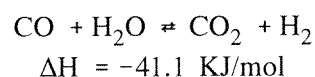
# 1. INTRODUCTION

In future energy supply coal will play a role as a very important source of energy. In a no regret scenario it might be necessary to prevent CO<sub>2</sub> being released to the atmosphere. Therefore it has to be separated from the system it is converted in. Currently, integrated coal gasification combined cycle (IGCC) power plants seem to have the highest efficiency when coals are converted into electricity. In an IGCC coal is gasified to a fuel gas mixture (mainly H<sub>2</sub>+CO) which is burnt in a gasturbine for power production. With heat from the system steam is generated, which is fed to a steamturbine also for power production. Several demonstration projects around the world have shown the IGCC's feasibility and its high efficiency already.

Various possible process flow schemes have been proposed for CO<sub>2</sub> removal from coal gas (Riemer 1993). Conventional approaches generally consist of a separate multistage water gas shift (WGS) conversion of the fuel gas (see table 1), followed by a low temperature CO<sub>2</sub> removal process. Hydrogen is the only fuel component left after the WGS conversion and is fed to the gasturbine to convert only to water. However, the conversion of the WGS reaction is limited by its chemical equilibrium and the low temperature CO<sub>2</sub> removal makes an additional cooling step necessary.

A promising approach now lies in the combination of the water gas shift reaction with continuous hydrogen separation from the reaction mixture using ceramic membranes selectively permeable to hydrogen. This so-called membrane reactor can enhance the equilibrium production of H<sub>2</sub> from fuel gas

Table 1. Water gas shift



and establish a separation between H<sub>2</sub> and CO<sub>2</sub> at an elevated temperature. In figure 1 the layout of an IGCC with CO<sub>2</sub> emission control is shown. The layout is similar to an ordinary IGCC except that the gas leaving the gas cleaning section is now fed to the membrane reactor. Nitrogen from the air separation unit is available as sweep gas for the reactor. Unconverted CO and unseparated hydrogen are catalytically burnt and the heat is utilized in the steam turbine. In this scheme CO<sub>2</sub> is recovered separately from the other components and is ready available for disposal or re-use. The availability of sweep gas as well as the high pressure of the feed gas leaving the 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. Thus, the process efficiency will increase when the hydrogen production (CO conversion) and recovery (on the permeate side) from the membrane reactor is raised. CO<sub>2</sub> 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.

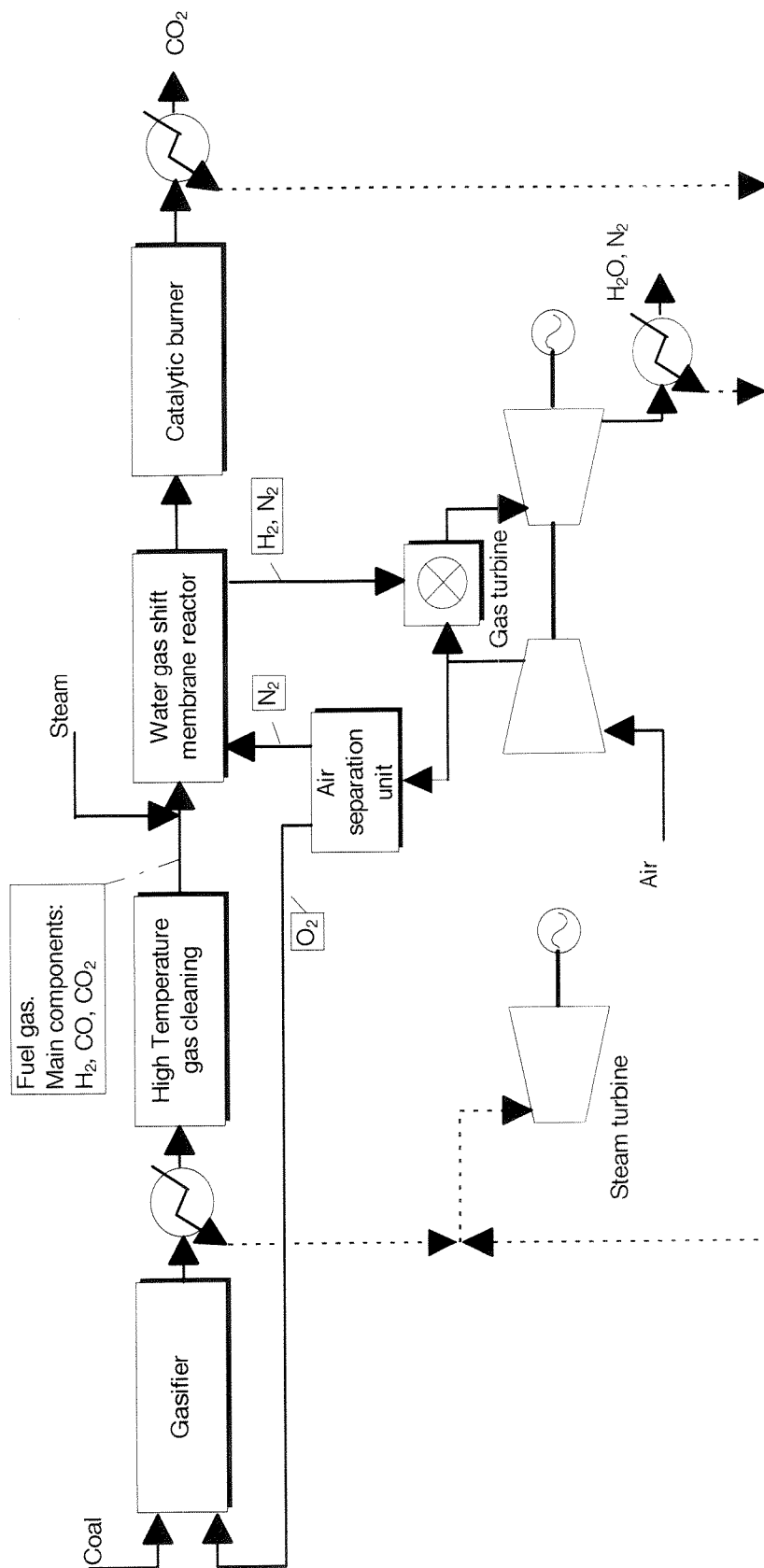


Figure 1 Layout of an IGCC with CO<sub>2</sub> emission control.

## 2. HIGH-SELECTIVE INORGANIC MEMBRANES

For this study microporous silica membranes have been prepared. The silica membrane layer was applied to a 4-layer tubular Knudsen diffusion type alumina support (Bonekamp 1995) by slipcasting of a silica sol. After sintering a microporous silica layer was formed with pores smaller than 1 nm. Permeation measurements for hydrogen and carbon dioxide have been performed on these membranes and the ratio of the permeability (permselectivity) is plotted in figure 2. The permselectivity rises with the temperature and reaches nearly 15 at 325°C. The hydrogen permeability at this temperature is as high as  $2.2 \cdot 10^{-6} \text{ mol/m}^2\text{sPa}$ . The membrane fabrication technology is being scaled up and currently membrane tubes with a length up to 70 cm can be produced.

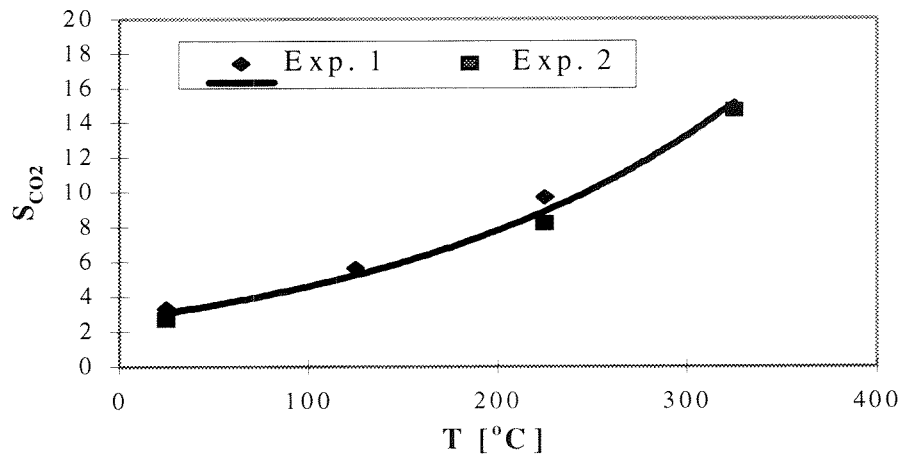


Figure 2 Permselectivity  $H_2/CO_2$  vs temperature

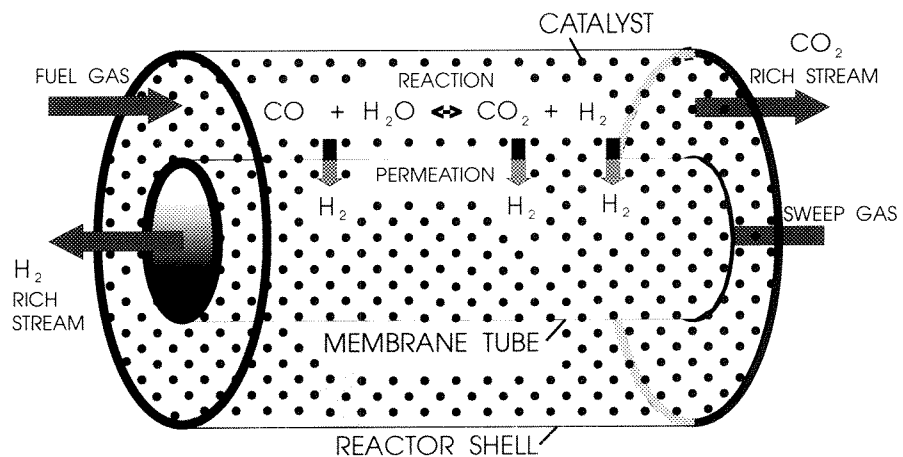


Figure 3 Schematic of the water gas shift membrane reactor.





### 3. MEMBRANE REACTOR MODEL

The possibilities of the membrane reactor were explored in first instance using a reactomodel. Different flow modes can be distinguished, but in this study only counter current flow mode for the reactor was considered, because this flow mode is known to have the best performance in separation problems. Figure 3 depicts schematically the processes in a membrane reactor under counter current flow condition. Specific assumptions were made for the model:

- isothermal operation
- steady state
- ideal gas law is obeyed
- no pressure drop in flow direction
- no catalyst/membrane mass transfer limitation

Table 2 Model mass balances.

$\text{Feed side : } \frac{dN_i^f}{dy} = -J_i \frac{S^m}{S^f L} + r_i$ $\text{Permeate side : } \frac{dN_i^p}{dy} = J_i \frac{S^m}{S^p L}$
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The basis of this model are ordinary differential mass balances for each component on either side of the membrane tube (table 2). The mechanisms for reaction and permeation are substituted in the mass balances. Permeation through the membrane has been assumed to occur only via diffusion which obeys Fick's law. The kinetic expression for reaction is of the power law type and has been taken from literature (Keiski 1992) The equations have been made dimensionless similar to the way this is done by (Lund 1993). In this process the model parameters are grouped together and a few dimensionless groups that control the solution of the equations appear.

- Feed side:

$$\frac{dF_i^f}{d\zeta} = -\frac{1}{S_i Pe} \left( \left( \frac{F_i^f}{F_{tot}^f} \right) - \phi \left( \frac{F_i^p}{F_{tot}^p} \right) \right) + v_i Da \left( \left( \frac{F_{CO}^f}{F_{tot}^f} \right)^a \left( \frac{F_{H_2O}^f}{F_{tot}^f} \right)^b \left( \frac{F_{CO_2}^f}{F_{tot}^f} \right)^c \left( \frac{F_{H_2}^f}{F_{tot}^f} \right)^d (1-\beta) \right)$$

- Permeate side:

$$\frac{dF_i^p}{d\zeta} = \frac{\psi}{S_i Pe} \left( \left( \frac{F_i^f}{F_{tot}^f} \right) - \phi \left( \frac{F_i^p}{F_{tot}^p} \right) \right)$$

By definition:  $v_i$  is negative for reactants and positive for products of a chemical reaction ( $v_i$  is zero for inert components). Counter current flow boundary conditions are shown in table 3. The definitions and meanings of the dimensionless numbers are shown in table 4.

Table 3 Counter current boundary conditions.

$\zeta=0 \Rightarrow F_i^f = (F_i^f)^0$ $\zeta=1 \Rightarrow F_i^p = (F_i^p)^0$
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Table 4 *Dimensionless numbers and their meaning.*

Parameter	Meaning	Definition
Peclet number	Ratio of total feed rate and maximum possible transmembrane flow rate	$Pe = \frac{(N_{tot}^f)^0}{Q_{H_2} P^f X}$
Danköehler number	Ratio of maximum conversion and the total feed rate	$Da = \frac{L(P^f)^\alpha k}{(N_{tot}^f)^0 (RT)^\alpha}$
$S_i$	Ratio of permeability of $H_2$ and component $i$ (permselectivity)	$S_i = \frac{Q_{H_2}}{Q_i}$
$\phi$	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	$Y = \frac{(N_{tot}^s)^0}{\Psi(N_{tot}^f)^0}$

## 4. RESULTS AND DISCUSSION

The parameters used for the model calculations are shown in table 5. In figure 4 the conversion in the reactor is plotted 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.

The influence of the Peclet number is shown in figure 5. 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.

Table 5 *Simulation parameters.*

T	=	623 K
P <sup>f</sup>	=	36 bar
P <sup>p</sup>	=	21 bar
Y	=	1.035
H <sub>2</sub> O/CO	=	1.5 (after steam injection)

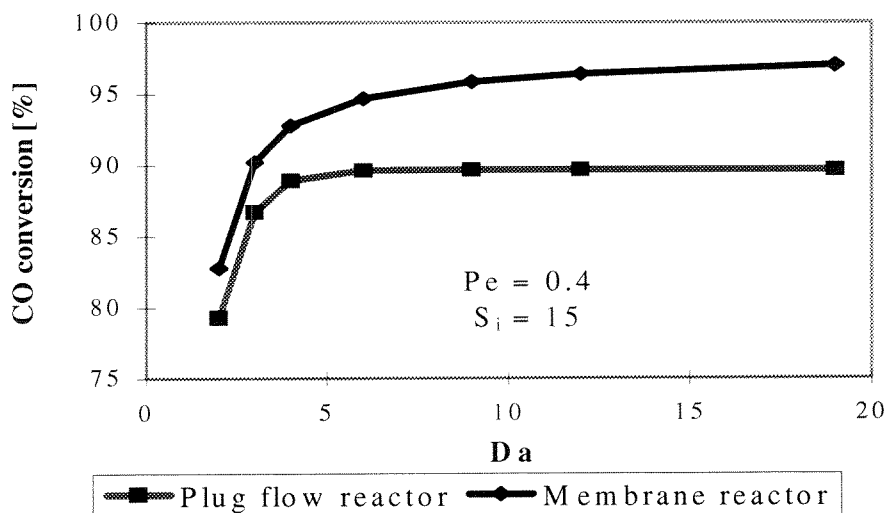


Figure 4 *Conversion vs Da.*

The influence of the membrane selectivity on the performance of the reactor is shown in figure 6. CO conversion and C recovery increase with rising 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. Currently the measured pemselectivity is 15 which gives a very acceptable reactor performance for the chosen application. The gain in performance is marginal when the selectivity surpasses 40.

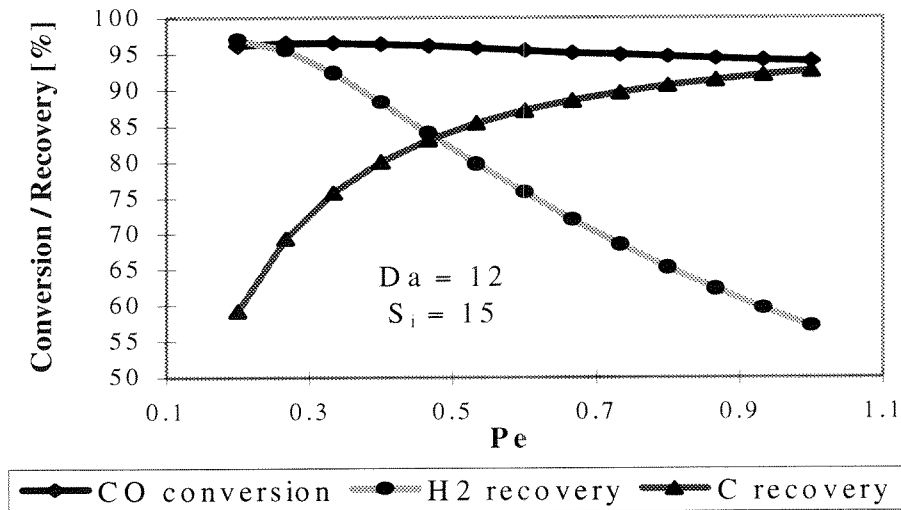


Figure 5 Conversion and recovery vs Pe.

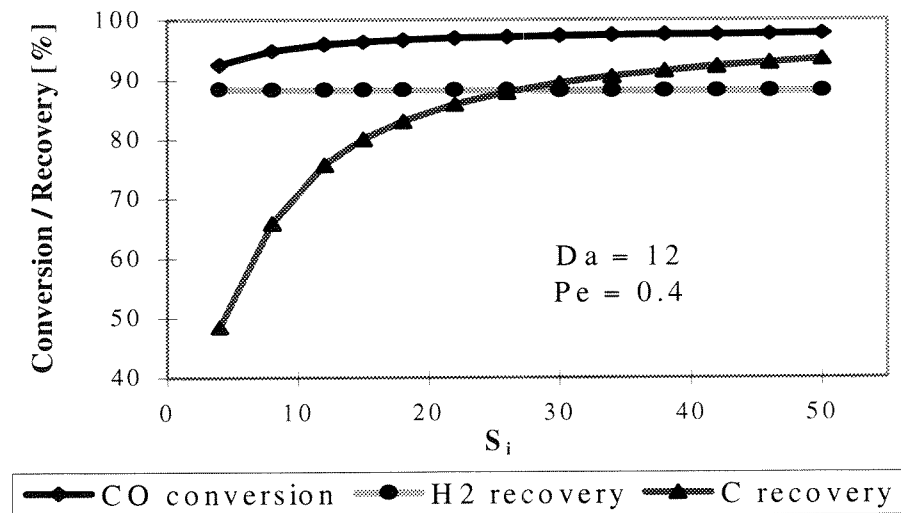


Figure 6 Conversion, recovery vs selectivity.

## 5. FURTHER DEVELOPMENT

Currently bench scale tests are being conducted under realistic conditions for this application. High pressure high temperature membrane sealing plays a vital role and this hurdle has been taken for laboratory and bench scale. 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.

The challenge for catalyst development will be to develop a catalyst that is stable under the process conditions (temperature, pressure, gas composition, presence of contaminants) and allows a lower steam over CO ratio without having coke formation.

At this point it is also very useful to consider engineering aspects of the full scale application. When the membranes will be used on an industrial scale, a considerable amount of surface area will be necessary to process the gas stream involved, even with the high permeability as shown above. A typical surface area necessary is 1500 m<sup>2</sup> for a 300 MW<sub>e</sub> 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 permeability 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. Dead end tube configuration (Saracco 1994) 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 realize for which application the membranes are being developed and to consider scaling up in an early stage.



## 6. CONCLUSION

Ceramic gas separation membranes for the application in a water gas shift membrane reactor are being investigated. Membranes with a permselectivity of at least 15 for  $H_2$ - $CO_2$  have been prepared. Through model calculation it has been shown that these membranes can enhance the conversion of the reactor and concurrently realize an acceptable separation for this application. When selectivity can be increased, it does not seem to be necessary to surpass approximately 40, because the gain in reactor performance seems marginal. Enlargement of the permeability 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 very important in the development of membrane material too.





## 7. REFERENCES

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## 8. LIST OF SYMBOLS

<i>Symbol:</i>	<i>Meaning:</i>	<i>Dimension:</i>
$\alpha$	Sum of powers in power law exp.	-
$\beta$	Reversibility factor	-
$\zeta$	Dimensionless coordinate	-
$\nu_i$	Stoichiometric coeff. of comp. i	-
$\phi$	Pressure ratio pem. and feed side	-
$\psi$	f. and p. surface area ratio= $S^f/S^p$	-
a,b,c,d	exponents in power law	-
Da	Damköhler number	-
F	Dimensionless flux	-
J	Flux through the membr.	$\text{mol/m}^2\text{s}$
k	React. rate coeff.	$(\text{mol/m}^3)^{1-\alpha}(1/\text{s})$
L	Length reactor	m
N	Flux	$\text{mol/m}^2\text{s}$
Pe	Peclet number	-
P	Pressure	Pa
$Q_i$	Membr. permeability	$\text{mol/m}^2 \text{Pa s}$
$r_i$	Reaction rate component i	$\text{mol/m}^3\text{s}$
R	Gas constant	J/mol K
S	Surface area	$\text{m}^2$
$S_i$	Pemselectivity $H_2/i$	-
T	Temperature	K
X	f. and m. surface area ratio= $S^m/S^f$	-
Y	Sweep ratio	-
y	Length coordinate	m

### Superscripts

f	Feed
m	Membrane
p	Pemate
s	Sweep
( ) <sup>0</sup>	At the entrance

### Subscripts

i	Component i
tot	Total

## 9. ACKNOWLEDGEMENT

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