

## INVESTIGATION OF MEMBRANE PERFORMANCE IN THE SEPARATION OF CARBON DIOXIDE

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HY2SEPS was an EU-funded project directed at the reduction of CO<sub>2</sub> emissions. The principal objective of the project was to develop a hybrid membrane-adsorptive H<sub>2</sub>/CO<sub>2</sub> separation technique that would form an integral element of the pre-combustion process. Specific tasks included the derivation of simplified mathematical models for the membrane separation of H<sub>2</sub>/CO<sub>2</sub> mixtures.

In the present study one of the developed models is discussed in detail, namely that with the countercurrent plug flow of the feed and the permeate. A number of simulations were carried out concerning the separation of binary mixtures that may appear following steam conversion of methane. The numerical results were then compared with the experimental data obtained by FORTH/ICEHT. The estimated fluxes of pure CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> are shown alongside those measured experimentally as a function of temperature and CO<sub>2</sub> partial pressure in Figs 2 – 7. It is concluded that, in general, CO<sub>2</sub> flux increases monotonically with both temperature and CO<sub>2</sub> partial pressure. It is also found that the fluxes of hydrogen, methane and nitrogen reach a minimum at a temperature slightly above 323 K. Overall, a good agreement was obtained between the simulations and experiments.

**Keywords:** CO<sub>2</sub> capture, hydrogen production, hybrid process, pressure swing adsorption, membrane processes

### 1. INTRODUCTION

An increase in atmospheric CO<sub>2</sub> emissions is largely due to the production of energy using fossil fuels. This problem has been the focus of a number of EU activities. The European Commission, through an array of instruments, stimulates measures aimed at reducing CO<sub>2</sub> emissions. One of such instruments is the financing of research within the framework programmes. The present study was done as a collaborative 6. FP EU project, within priority 6.1 (Sustainable Energy Systems). Its principal objective was to develop a hybrid membrane/adsorptive (pressure swing adsorption) system for the separation of H<sub>2</sub>/CO<sub>2</sub> mixtures (Warmuzinski et al., 2006). Such a system would form a vital part of post-combustion decarbonisation processes. The goal of the study is therefore the removal of CO<sub>2</sub> from the energy production chain before the fuel is finally converted into energy. The case study investigated in this paper is the separation of hydrogen from the synthesis gas obtained via steam reforming of methane. The hybrid process has to yield a high-purity hydrogen stream with a parallel reduction in CO<sub>2</sub> emissions (which commonly accompany the production of H<sub>2</sub> in conventional PSA processes) (Doshi, 1997; Esteves and Mota, 2002; Feng et al., 1998; Sircar et al., 1999).

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One of the crucial components of an improved hybrid system is the membrane separation unit. An enhanced performance of this unit can be achieved by the development of improved membrane materials as well as the modelling (and subsequent optimisation) of membrane separation. The study focuses on one of the membrane models developed within the project, namely that with the countercurrent plug flow on both the feed and the permeate side of a membrane module. Numerical simulations concerning the separation of CO<sub>2</sub>/H<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> will be presented and compared with the relevant experimental data.

## 2. MODELS FOR THE PERMEATION OF GASES IN THE MEMBRANE MODULE

To describe the membrane separation two alternative models were developed: the model with the countercurrent plug flow on the feed and permeate sides and the model in which the feed and permeate streams flow cocurrently. The principal assumptions for the two models are as follows:

- the feed may contain N permeating species,
- apart from the components already present in the feed, the permeate may contain an inert species used as a purge gas,
- there are no interactions between the permeating gases,
- permeation coefficients are independent of pressure,
- pressure drops are negligible on both sides of the membrane,
- the process is isothermal,
- concentration polarisation is insignificant on both the feed and the permeate sides.

A schematic diagram of the countercurrent flow case is shown in Fig.1. The balance equations and the relevant boundary conditions are given for the same flow configuration.

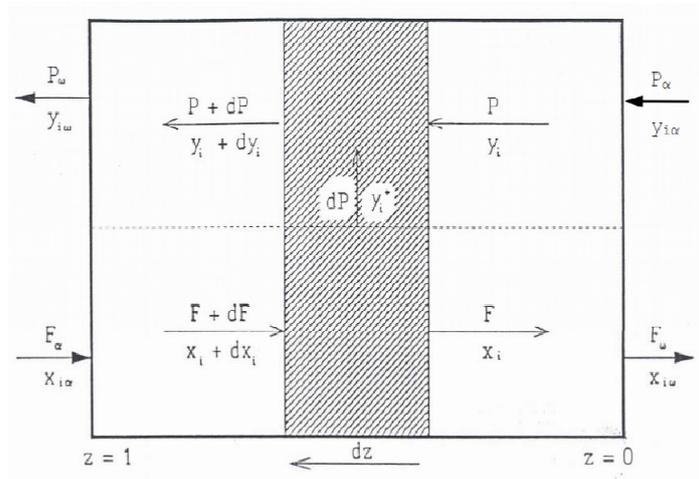


Fig. 1. Feed and permeate flow rates and concentrations

Feed gas composition is calculated from Equation (1)

$$\frac{dx_i}{dz} = R \frac{y_i - x_i}{\left(1 - \frac{P_w}{F_\alpha}\right)(y_i - x_{i_w}) - \frac{P_\alpha}{F_\alpha} x_{i_w}} \left[ \alpha_{i1}(x_i - \delta y_i) - x_i \sum_{j=1}^N \alpha_{j1}(x_j - \delta y_j) \right] \quad (1)$$

for  $i = 1, \dots, N - 1$ , and from Equation (2)

$$x_N = 1 - \sum_{i=1}^{N-1} x_i \quad (2)$$

for  $i = N$ . Equation (1) is obtained by combining the mass balance for the  $i$ -th component on the feed side with the kinetic equation for this component:

$$dPy_i^+ = RF_\alpha \alpha_{i1} (x_i - \delta y_i) dz \quad (3)$$

Upon dividing the combined equation by  $dz$  and  $F$  an expression is obtained that contains two unknown quantities,  $F_\alpha/F$  and  $dF/dz$ . The latter is determined by adding the combined balance equations and kinetic equations for all the components ( $i = 1, \dots, N$ ). The ratio  $F_\alpha/F$  is calculated using two overall mass balance equations and the mass balance for component 1. Similarly, the mole fraction of component 1 in the permeate may be derived to yield

$$\frac{dy_1}{dz} = R \frac{y_1 - x_1}{\left(1 - \frac{P_\omega}{F_\alpha}\right)(x_1 - x_{1\omega}) - \frac{P_\alpha}{F_\alpha} x_{1\omega}} \left[ (x_1 - \delta y_1) - y_1 \sum_{j=1}^N \alpha_{j1} (x_j - \delta y_j) \right] \quad (4)$$

The mole fractions of the other permeating species are given as

$$y_i = \frac{x_{i\omega}(y_1 - x_1) - x_i(y_1 - x_{1\omega}) + \frac{P_\alpha}{F_\omega} x_i y_1}{x_{1\omega} - x_1 + \frac{P_\alpha}{F_\omega} x_1} \quad (5)$$

where  $i = 2, \dots, N$ .

The mole fraction of the inert species in the permeate can be calculated from

$$y_{N+1} = 1 - \sum_{i=1}^N y_i \quad (6)$$

The relevant boundary conditions are

$$x_i = x_{i\alpha} \quad (i = 1, \dots, N) \quad \text{for } z = 1 \quad (7)$$

$$y_i = y_{i\alpha} \quad (i = 1, \dots, N+1) \quad \text{for } z = 0 \quad (8)$$

Retentate and permeate fluxes can be determined from Equations (9) and (10)

$$F_\omega = F_\alpha \frac{y_{1\omega} - x_{1\alpha}}{y_{1\omega} - x_{1\omega}} + P_\alpha \frac{y_{1\omega}}{y_{1\omega} - x_{1\omega}} \quad (9)$$

$$P_\omega = F_\alpha + P_\alpha - F_\omega \quad (10)$$

The foregoing model was translated into a computer program using the C++ code. In the countercurrent model the retentate flow rate and composition at  $z = 0$  have to be tentatively assumed to start the calculations. Permeate and feed gas compositions are calculated from the set of Equations (1) – (2), (4) – (6) and boundary conditions (7) – (8). The calculated feed composition at  $z = 1$  is compared with that tentatively assumed and, unless the difference between the two sets is below a preset limit, the procedure is repeated for different values of the retentate flow rate and composition.

### 3. SIMULATION CALCULATIONS

Based on the model described in Section 1 and the relevant program a number of simulations were performed. The simulations were focused on the separation of various binary mixtures containing gases appearing as products of methane steam reforming. Thus, the separation of CO<sub>2</sub> from the mixtures with hydrogen, nitrogen and methane in a ceramic membrane module was studied over a range of temperatures (308–363 K) and for a CO<sub>2</sub> concentration of 50 vol.%. In addition, the calculations were done at 333 K for mole fractions of carbon dioxide which varied over a range of 0.1 – 0.9.

In Table 1 the principal parameters associated with the experiments and calculations are shown. Table 2 contains all the experimental and computational runs. In the calculations permeation coefficients for pure species were used (cf. Table 3), while the estimations were based on experiments carried out by FORTH/ICEHT for CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> on a flat ceramic membrane with faujasite as an active layer (Giannakopoulos and Nikolakis, 2007).

Table 1. Basic parameters of the membrane separation process

$F_a$ , mol/s	$P_a$ , mol/s	$A$ , m <sup>2</sup>	$\delta_M$ , m	$p_P$ , kPa	$p_F$ , kPa
$3.568 \cdot 10^{-5}$	$3.866 \cdot 10^{-5}$	$6.217 \cdot 10^{-4}$	$15 \cdot 10^{-6}$	101	101

In Figs 2 and 3 the predicted and measured fluxes of carbon dioxide and hydrogen are presented vs. temperature and CO<sub>2</sub> partial pressure. The flux of carbon dioxide increases monotonically with an increase in both temperature and pressure. As regards the former parameter, the increase is quite considerable and may reach an order of magnitude. The permeate hydrogen flux decreases with an increase in the partial pressure of CO<sub>2</sub> in the feed. The H<sub>2</sub> flux in the permeate first decreases with temperature, and then tends to rise, with a minimum at about 328 K.

Similar behaviour of the CO<sub>2</sub> flux in the permeate can be observed for the two other mixtures (CO<sub>2</sub>/CH<sub>4</sub> – Figs. 4 and 5, and CO<sub>2</sub>/N<sub>2</sub> – Figs. 6 and 7). The dependence of the permeate fluxes of nitrogen and methane upon temperature is similar to that of hydrogen. Similarly, the N<sub>2</sub> and CH<sub>4</sub> fluxes decrease with an increase in CO<sub>2</sub> feed concentration.

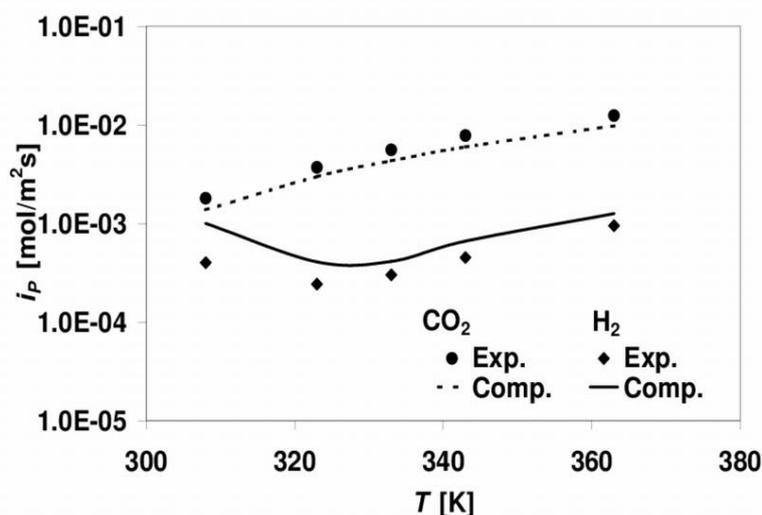


Fig. 2. Run 1. Experimental (points) and theoretical (lines) fluxes of CO<sub>2</sub> and H<sub>2</sub> vs. temperature

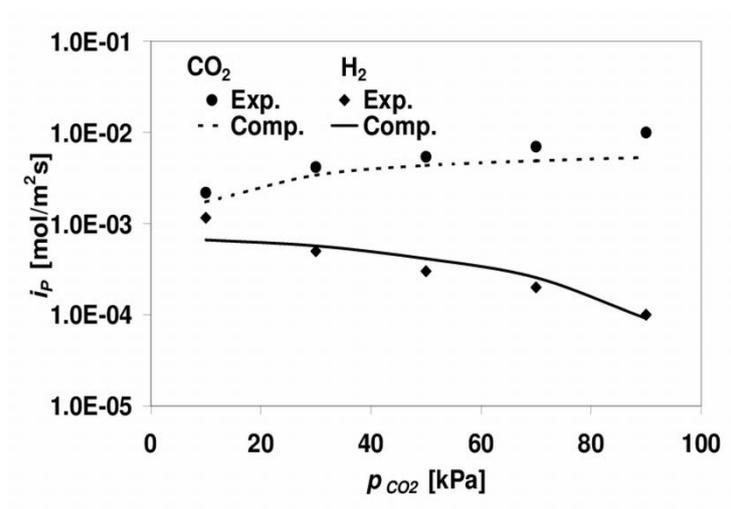


Fig. 3. Run 2. Experimental (points) and theoretical (lines) fluxes of CO<sub>2</sub> and H<sub>2</sub> vs. CO<sub>2</sub> partial pressure at 333 K

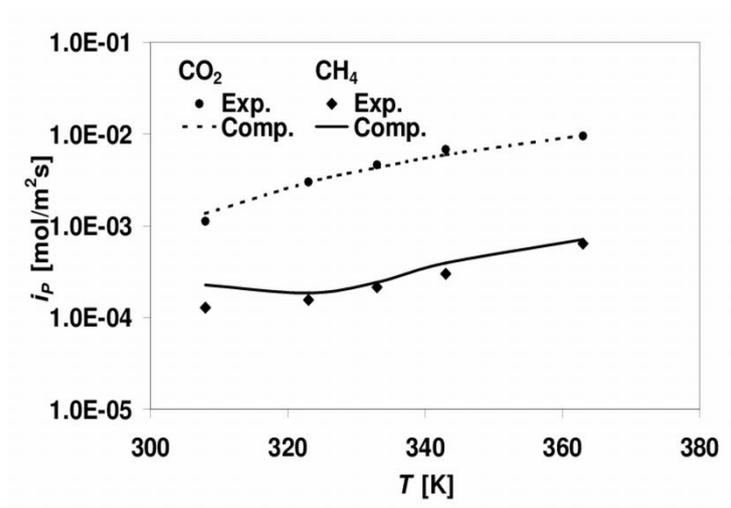


Fig. 4. Run 3. Experimental (points) and theoretical (lines) fluxes of CO<sub>2</sub> and CH<sub>4</sub> vs. temperature

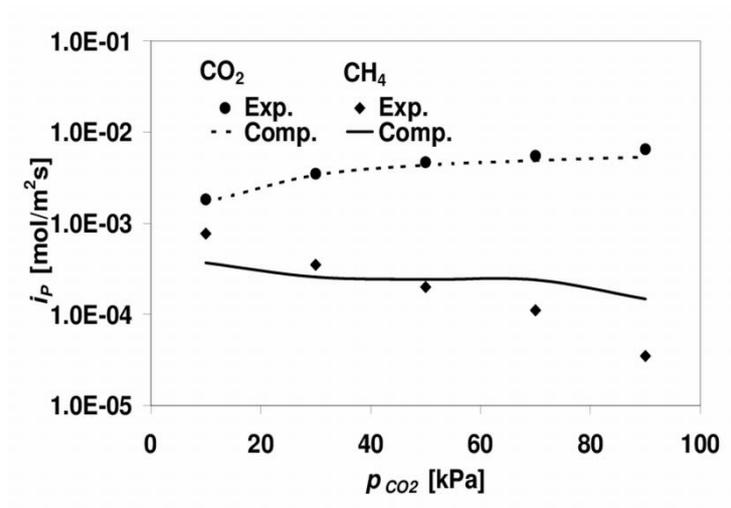


Fig. 5. Run 4. Experimental (points) and theoretical (lines) fluxes of CO<sub>2</sub> and CH<sub>4</sub> vs. CO<sub>2</sub> partial pressure at 333 K

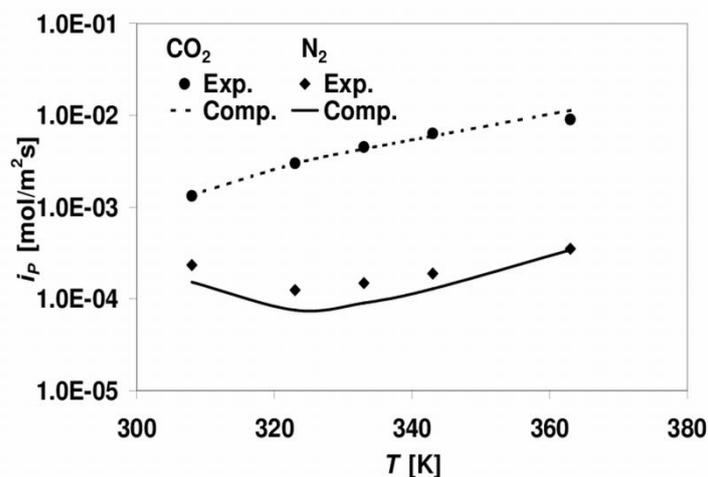


Fig. 6. Run 5. Experimental (points) and theoretical (lines) fluxes of CO<sub>2</sub> and N<sub>2</sub> vs. temperature

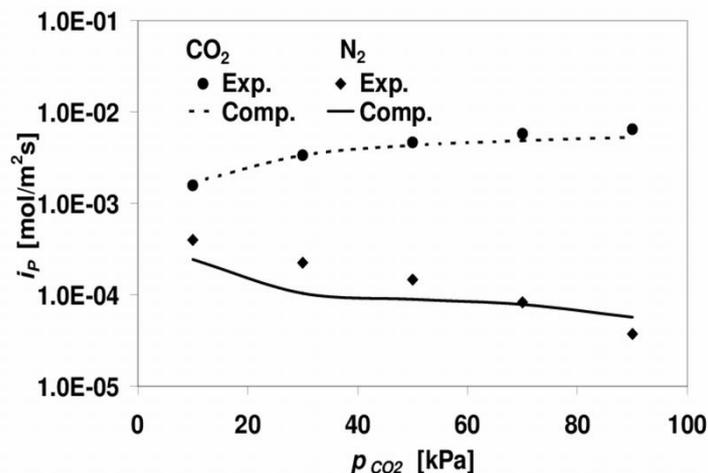


Fig. 7. Run 6. Experimental (points) and theoretical (lines) fluxes of CO<sub>2</sub> and N<sub>2</sub> vs. CO<sub>2</sub> partial pressure at 333 K

Table 2. Computational and experimental runs

No.	Feed gas composition	Fig. No.
1	$y_{CO_2(a)} = 0.5; y_{H_2(a)} = 0.5$ $T: 308 - 363 \text{ K}$	2
2	$y_{CO_2(a)}: 0.1 - 0.9$ $y_{H_2(a)}: 0.9 - 0.1$ $T = 333 \text{ K}$	3
3	$y_{CO_2(a)} = 0.5; y_{CH_4(a)} = 0.5$ $T: 308 - 363 \text{ K}$	4
4	$y_{CO_2(a)}: 0.1 - 0.9$ $y_{CH_4(a)}: 0.9 - 0.1$ $T = 333 \text{ K}$	5
5	$y_{CO_2(a)} = 0.5; y_{N_2(a)} = 0.5$ $T: 308 - 363 \text{ K}$	6
6	$y_{CO_2(a)}: 0.1 - 0.9$ $y_{N_2(a)}: 0.9 - 0.1$ $T = 333 \text{ K}$	7

Table 3. Permeabilities of pure components (active layer: FAU, support:  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>)

T, K	Q, mol/m·s·Pa			
	CO <sub>2</sub>	H <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>
308	2.41·10 <sup>-13</sup>	3.01·10 <sup>-13</sup>	6.70·10 <sup>-14</sup>	4.47·10 <sup>-14</sup>
323	5.66·10 <sup>-13</sup>	1.20·10 <sup>-13</sup>	5.39·10 <sup>-14</sup>	2.19·10 <sup>-14</sup>
333	8.64·10 <sup>-13</sup>	1.20·10 <sup>-13</sup>	7.00·10 <sup>-14</sup>	2.59·10 <sup>-14</sup>
343	1.26·10 <sup>-12</sup>	1.90·10 <sup>-13</sup>	1.12·10 <sup>-13</sup>	3.65·10 <sup>-14</sup>
363	2.31·10 <sup>-12</sup>	3.49·10 <sup>-13</sup>	1.96·10 <sup>-13</sup>	7.45·10 <sup>-14</sup>

In the case of the better permeating carbon dioxide the agreement between numerical predictions and experimental data is excellent for all the mixtures studied, both qualitatively and quantitatively. The agreement concerning the fluxes of hydrogen, nitrogen and methane is generally good. Some discrepancies may be seen for H<sub>2</sub> and CH<sub>4</sub> at low temperatures and, for methane, at high CO<sub>2</sub> partial pressures. However, two important simplifying assumptions have to be pointed out. First, the complex, adsorptive – diffusional mass transport across the membrane is described by a single global permeation coefficient. Second, permeation coefficients for pure components are used in the calculations. All these simplifications notwithstanding, the model employed is quite sufficient and will certainly serve its purpose in the design and optimisation studies.

#### 4. SUMMARY AND CONCLUSIONS

In the paper a model for membrane separation of gaseous mixtures is presented. The model was developed to describe the hybrid process for the removal of carbon dioxide from a mixture containing hydrogen, methane and nitrogen. The results of simulations are shown concerning the separation of the binary mixtures of CO<sub>2</sub>/H<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> over a range of temperatures and CO<sub>2</sub> concentrations in the feed gas. It is found that the fluxes of hydrogen, methane and nitrogen reach a minimum between 323 K and 328 K, for a CO<sub>2</sub> mole fraction of 0.5. This clearly shows the need for comprehensive optimisation of the operating parameters. Additionally, the numerical predictions were compared with the relevant experimental results. A satisfactory agreement is generally obtained, despite using a simplified model of mass transport across the membrane and employing permeation coefficients for pure species.

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#### SYMBOLS

<i>A</i>	membrane surface area, m <sup>2</sup>
<i>F</i>	flow rate on the feed side, mol/s
<i>i<sub>p</sub></i>	permeation flux, mol/m <sup>2</sup> ·s

$L$	length of the membrane module, m
$N$	number of components
$P$	flow rate on the permeate side, mol/s
$p$	pressure, Pa
$Q$	permeation coefficient, mol/m·s·Pa
$R$	permeation number ( $=AQ_i p_F / \delta_M F_a$ )
$T$	temperature, K
$x$	mole fraction on the feed side
$y$	mole fraction on the permeate side
$y^+$	local mole fraction on the permeate side
$Z$	module length coordinate, m
$z$	dimensionless length coordinate ( $=Z/L$ )

#### Greek symbols

$\alpha_{i1}$	ideal separation coefficient for component $i$ ( $=Q_i/Q_1$ )
$\delta$	pressure ratio ( $=p_P/p_F$ )
$\delta_M$	thickness of the membrane active layer, m

#### Subscripts

$F$	feed side
$i$	$i$ -th component
$P$	permeate side
$\alpha$	module inlet
$\omega$	module outlet
$1$	reference species (component with the highest permeation coefficient)

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