

## FEASIBILITY STUDY OF GAS SEPARATION MEMBRANES FOR BIOHYDROGEN SEPARATION

P. BAKONYI<sup>1,✉</sup>, N. NEMESTÓTHY<sup>1</sup>, J. RAMIREZ<sup>2</sup>, G. RUIZ-FILIPPI<sup>2</sup>, K. BÉLAFI-BAKÓ<sup>1</sup>

<sup>1</sup>University of Pannonia, Research Institute on Bioengineering, Membrane Technology and Energetics  
Egyetem út 10, 8200 Veszprém, HUNGARY

✉E-mail: bakonyip@almos.uni-pannon.hu

<sup>2</sup>Pontificia Universidad Católica de Valparaíso, Escuela de Ingeniería Bioquímica,  
General Cruz 34, Valparaíso, CHILE

Hydrogen is considered as a promising clean energy carrier that could replace fossil fuels. It can be produced by several ways including biological processes which are definitely environmental-safe methods. Unfortunately, the concentration of hydrogen in the gas mixture obtained during the fermentation process is not high enough for direct utilization (e.g. in fuel cells) since there are other gases (mainly carbon-dioxide) present as a result of the microbial activity. In this work concentration of biohydrogen by gas separation membranes were aimed to study. Two different membrane modules were tested in order to obtain pure hydrogen. The permeabilities and selectivities for both membranes were determined by single gas experiments and the feasibility of the membranes for biohydrogen separation was discussed.

**Keywords:** separation, membranes, biohydrogen

### Introduction

In most cases removal of hydrogen from the headspace of the bioreactor is required in continuous hydrogen producing biosystems [1], mainly due to the high partial pressure of hydrogen formed during the fermentation since it could significantly reduce gas production rates and yields [2]. Therefore, separation and enrichment of biohydrogen is desirable in order to ensure optimal conditions for sustainable microbial hydrogen production and the appropriate concentration of hydrogen for its end-use e.g. in fuel cells [3, 4]. Biohydrogen producing processes are carried out in gas tight bioreactors where anaerobic circumstances are always essential [5]. Usually, anaerobic conditions at start-up phase are provided by inert gas sparging (e.g. nitrogen) in the liquid and gas phase within the fermenter [6]. The elimination of the redundant impurities from hydrogen is obviously needed. There are different methods for hydrogen separation and concentration including the membrane processes such as membrane gas separation [7, 8] which is considered extremely attractive from environmental point of view [9]. Gas separation is one of the most widely applied membrane techniques which is basically a pressure driven procedure where the initial gas mixture is divided into two fractions (the permeate and the retentate) by the membrane [10]. These membranes can be characterized by different parameters but permeability and selectivity

are considered the most important. Among available polymers, membranes made of aromatic polysulfones [11], polycarbonates [12], polyarylates [13], polyaryl ketones [14], polyarylene ethers [15] and polyimides [16-18] have demonstrated appropriate potential for gas separation due to their favorable properties. In addition, porous membranes could also be used for gas separation (based on Knudsen-diffusion) when the permeabilities and selectivities are determined by molecular weights of the gas compounds [10]. During gas separation the pressure issue is one of the most crucial limiting factors, therefore pressure difference must be maintained between the feed and the permeate side of the membrane in order to achieve high permeabilities and selectivities. At laboratory scale, high pressure ratio is generally provided by using compressors at the primary side (high feed pressure) while vacuum pumps are often used at the permeate side (low pressure) [10]. In present work two different gas separation membrane modules were aimed to study. Single gas experiments with pure H<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub> were carried out to determine the permeabilities and theoretical selectivities (the ratios of the fluxes). Afterwards, the feasibility of the membranes for hydrogen separation were performed based on the obtained experimental result. Our final goal is to construct a continuous integrated system where biohydrogen fermentation and membrane gas separation could be coupled in order to produce purified hydrogen to be used in fuel cells.

## Materials and methods

Both membranes (ME1 and ME2) tested in dead-end experiments were non porous, hollow fibre, composite polymers which were manufactured at the University of Twente. The ME1 hollow fibres were made of Matrimid 5218 polyimid. The polyimid is consisted of 3,3',4,4'-benzophenon tetracarboxyl-dianhydrid and diamino-phenilidene, while ME2 was a PPO (poly(2,6-dimethyl-1,4-phenylene oxide)) supported hollow fibre membrane which were dipped and two times coated with Pebax 1657 (polyether-polyamide or polyether block amide) 1% wt. The membranes were built in a high pressure stainless steel tube (Fig. 1). The active transfer surface area of ME1 and ME2 were 12 cm<sup>2</sup> and 25 cm<sup>2</sup>, respectively. The hydrogen, nitrogen and carbon-dioxide gases in cylinders were the products of Messer Hungarogas (Hungary) with a purity higher than 99.9 vol%. The membrane modules were tested using single gases, and the permeation rates were determined. The feed gases were delivered on the shell side of the modules at ~2 bar pressure from a buffer vessel (approx. 2.4 l), while permeate was collected from the inner side of the fibres. The temperature was maintained at 40 °C.



Figure 1: The capillary membrane module

## Results and Discussion

Gas separation measurements were performed using pure, single gases: hydrogen, nitrogen and carbon dioxide where the decreasing pressure of the feed gas with time was followed. The measured and evaluated data for ME1 and ME2 membranes are demonstrated in Fig. 2 and Fig. 3, respectively.

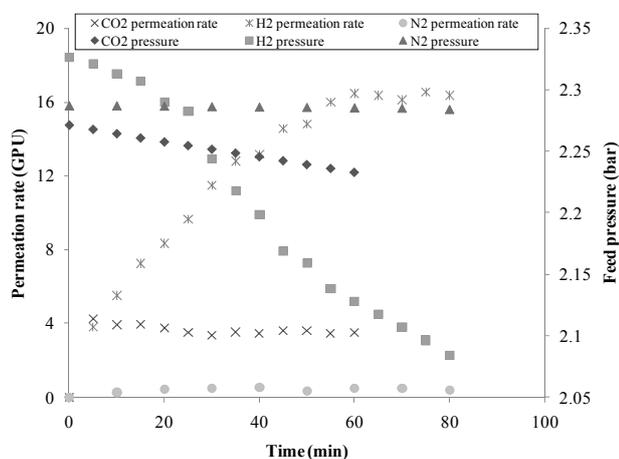


Figure 2: The permeation data for ME1

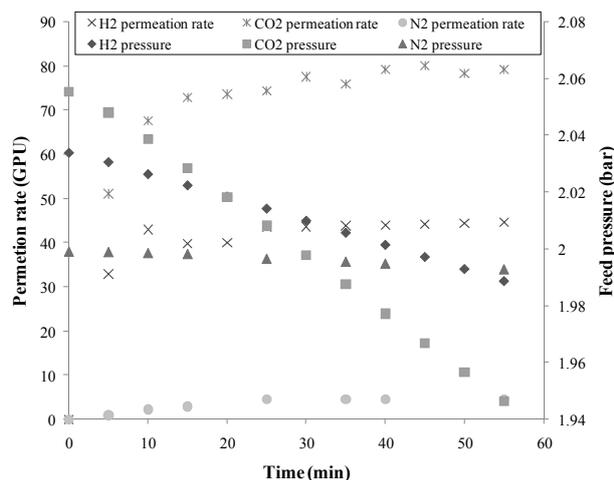


Figure 3: The permeation data for ME2

It seems that pressure decreased rather quickly due to the high gas permeation through the membrane thus the experiments were conducted in a narrow range of pressure. The permeabilities were determined when steady-state occurred.

Based on the determined permeabilities the theoretical selectivities were calculated as a ratio of the permeation rates of the various gases and the results for ME1 and ME2 modules are listed in Table 1.

Table 1: The theoretical selectivities for ME1 and ME2

|                                 | Selectivity (40 °C) |      |
|---------------------------------|---------------------|------|
|                                 | ME1                 | ME2  |
| H <sub>2</sub> /N <sub>2</sub>  | 21.2                | 9.8  |
| H <sub>2</sub> /CO <sub>2</sub> | 4.5                 | 0.5  |
| CO <sub>2</sub> /N <sub>2</sub> | 4.7                 | 18.1 |

Experimental results indicated that ME1 and ME2 gas separation membranes have advantageous properties regarding the selectivities and permeabilities (not shown). The H<sub>2</sub>/N<sub>2</sub> selectivity is remarkably high for both membranes, while the H<sub>2</sub>/CO<sub>2</sub> selectivity of ME1 and CO<sub>2</sub>/N<sub>2</sub> of ME2 would appear to meet the requirements of carbon-dioxide separation. It can be pointed out that membranes tested are attractive for H<sub>2</sub> recovery and these membrane materials have high potential for practical applications but it is important to consider that the industrial applicability of the modules requires extended research with binary and ternary model gas mixtures and long-term experiments using raw gas directly from the fermenter are particularly important, as well.

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