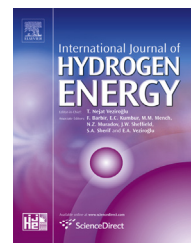




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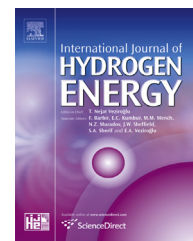
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Highlights

- Application of membrane gas separation for biohydrogen enrichment.
- Study on the significant parameters affecting membrane performance by experimental design.
- Discussion on the impacts of the statistically important process variables.

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Biohydrogen purification using a commercial polyimide membrane module: Studying the effects of some process variables

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ABSTRACT

In this work the purification of biohydrogen was attempted in mixed gas measurements using a commercial polyimide membrane module. The impact of several process variables (gas composition, temperature, ratio of retentate and feed flows) on the real separation efficiency was statistically studied applying a 3-level full-factorial experimental design. The results showed that all the factors examined could significantly affect the achievable selectivity and it was observed that the theoretical and real separation factors were remarkably different. It was also found that – in comparison with other commercially available membranes – the module reflected potential for hydrogen enrichment. Considering the design boundaries, the highest H₂/CO₂ gas selectivity (1.62) could be achieved at feed pressure, separation temperature and recovery value of ~2.2 bar, 55 °C and 0.6, respectively, using a 65 vol% hydrogen/35 vol% carbon dioxide binary mixture.

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1. Introduction

The research on environmental-friendly and renewable energy sources has gained considerable attention in the recent decades [1]. Among possible alternatives, hydrogen is highly promising and can play a key role in sustainable economical growth due to its carbon neutral characteristic. Moreover, it has the highest energy content (122 MJ/kg) of all the known fuels – excluding nuclear energy carriers – on gravimetric base. However, the annual hydrogen consumption is presently being satisfied through the conversion of traditional, fossil-based chemical substances such as methane [2]. Therefore, H₂ generation needs green technologies to be developed in order to

make it an attractive option. In recent years, enormous efforts have been done to achieve the aforementioned aim and the biological production ways – providing biohydrogen – are in the spotlight of the research [3–5]. These methods can help to accomplish the dual goal of simultaneous organic waste management and energy production. The bioH₂ produced can be fed into highly energy-efficient fuel cells or internal combustion engines [6,7]. However, these applications require purified hydrogen and therefore its separation from the different gaseous by-products – mainly CO₂ – formed during the fermentation is an essential task.

A broad range of processes e.g. chemical absorption, cryogenic distillation, adsorption and membrane separation

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are available and compete with each other for biohydrogen upgrading purposes [8–10]. Recently, significant improvements have been realized in membrane technology, hence it is being considered as an energy- and cost-effective, environmental-gentle method [11,12]. Furthermore, a main benefit of membranes is that they can easily be attached to hydrogen producing bioreactors leading to the chance of integrated production and purification.

Among the various membrane-based purification systems, membrane contactors, supported liquid membranes and gas separation membranes show potential for biohydrogen enrichment.

Independent research reports on the applicability of membrane contactors for biohydrogen concentration demonstrated that this technique was sufficient to remove carbon-dioxide from hydrogen containing gaseous mixtures [13,14]. However, this technology suffers from the drawback that various chemicals must be used in the process for CO₂ absorption taking place within the membrane contactor itself.

Beside membrane contactors, supported liquid membranes employing different room temperature ionic liquids are also potential candidates for biohydrogen separation [15,16]. However, this approach is still under intense research and development. Thus, more time and experience is needed to make it feasible at larger scale [17].

Nevertheless, membrane gas separation is a mature option and has already been commercialized. Therefore, its viability is more realistic compared to the other above-mentioned procedures. In addition, it has some advantages e.g. no need of extra chemicals during operation, ease of processing, robustness and moderate operating requirements in case they are manufactured from synthetic polymers e.g. polyimide [18]. However, membranes for H₂ purification also face several issues. For example, the progress in their development needs to be further continued in order to engineer ones with both reliable permeation and selectivity features [19]. Moreover, the membranes have mainly been studied in pure gas experiments [20] and gaseous mixtures have much less frequently been used [21–23] although it is crucial for industrial spread. Therefore, expanding the knowledge about the membranes behavior during mixed gas measurements is recommended [24].

Hence, in this work we aimed to test a commercially available polyimide membrane module – product of UBE Industries Ltd. – for H₂/CO₂ separation employing binary mixed gases differing in composition. Furthermore, the impacts of other important process parameters such as temperature and the ratio of retentate and feed flow on the performance of the membrane were statistically investigated applying a 3-level full-factorial experimental design.

2. Theoretical background

2.1. Membrane separation

The gas transport through dense, non-porous polymers can be described by Eq. (1) [25]:

$$J_i = D_i S_i (p_i^F - p_i^P) / l \quad (1)$$

where J_i is the flux of gas component “i”, p_i^F and p_i^P are the partial pressures of the component “i” in the feed and permeate fractions, respectively. l is the thickness of the membrane, D_i and S_i are the diffusion and solubility coefficients, respectively. Usually, the $D_i S_i$ is given as P_i (called the permeability coefficient) that shows the permeation ability of gas component “i” through the membrane. The theoretical selectivity (separation efficiency) of the membrane – used in pure gas experiments – can be given by Eq. (2):

$$\alpha_{i/j} = P_i / P_j = (D_i / D_j) / (S_i / S_j) \quad (2)$$

where the D_i / D_j is called as diffusive selectivity, meanwhile S_i / S_j is known as the solubility selectivity. The former reflects the different sizes of the molecule “i” and “j”, while the latter shows the relative condensabilities of the “i” and “j” gas components, respectively.

On the other hand, for gaseous mixtures the real (composition) selectivity ($\alpha_{i/j}$) can be calculated according to the Eq. (3):

$$\alpha_{i/j} = (x_i^P / x_j^P) / (y_i^F / y_j^F) \quad (3)$$

where x_i^P and x_j^P are the volumetric fractions of compound “i” and “j” in the permeate, meanwhile y_i^F and y_j^F are the volumetric fractions in the feed of the same components.

3. Materials and methods

3.1. Experimental design

A 3-level full-factorial experimental design was selected to study the effects of some process variables on biohydrogen enrichment. The advantages of statistical procedures over the most common “one-factor-at-a-time” method are their robustness, time-saving and cost-effective traits [26].

Moreover, experimental designs could explore the mutual interactions between the variables, if there is any. In a series of experiments the independent factors are purposely changed in a predetermined range in order to get their influences on the dependent variable. The design of experiments is an attractive technique to plan a set of experiments and the data measured can statistically be analyzed, providing reliable and objective conclusions [27]. A properly-chosen experimental design is able to extract the maximum amount of information for a given amount of experimental work.

3.2. Hydrogen purification experiments

In this work, H₂ separation experiments were carried out by using a composite polyimide membrane in hollow-fiber configuration (UBE Industries Ltd., product name: NM-B01A). Certain technical specifications such as the effective transport surface and the thickness of the membrane capillaries are unknown since these data are not provided by the producer. The lab-scale module is primarily suggested for the separation of nitrogen from air. At first glance, the reader might wonder why a membrane with originally different purpose was chosen for hydrogen enrichment. The reason for this possible contradiction is that although specific

membranes have been designed for hydrogen concentration [20], they are usually not commercialized [24]. Therefore, the number of available polymers for the intended separation is limited, among which polyimides are the largest group by far with confirmed potential for various gas (e.g. H_2) separation applications [18,22].

The hydrogen purification measurements were conducted in a lab-size membrane testing apparatus developed for working with both pure and mixed gases. The scheme of the set-up indicating the coupled equipment is demonstrated in Fig. 1. The flow rates were followed by digital mass flow meters (Bronkhorst El-Flow® Select) and the data were recorded by Labview 8.5 software. The hydrogen concentrations of the feed, permeate and retentate streams were real-time monitored using H_2 analyzer (BlueSens Gas Sensor GmbH). The displayed signal of the sensor gives the precise value of H_2 content in the respective membrane fractions. The device is capable to measure hydrogen in the range of 0–100 vol% with the minimum response time of 20 s. More specific and detailed information are available on the supplier's website (www.bluesens.com).

The feed pressures – indicated by Honeywell ST2000 transmitter – in all the cases were maintained below 3 bar due to process economical considerations and were dependent on the ratio of retentate and feed flows. The permeate side was kept under ambient conditions (~ 1 bar). According to the data collected, the pressure-loss on the hollow-fiber module between the feed and the retentate sides was negligible and subsequently no significant lengthwise (axial) pressure gradient was developed. Therefore, the differential pressure or in other words the effective driving force along the membrane can easily be calculated by deducting the permeate side pressure from the pressure value on the gas delivery side.

The separation efficiency of the polyimide membrane module for H_2 and CO_2 separation was studied tentatively employing the apparatus shown in Fig. 1. The influences of three process variables on hydrogen purification were determined using 3-level full-factorial experimental design presented in Table 1. The data evaluation was carried out by using Statistica 8 software and the results can be seen in Table 2.

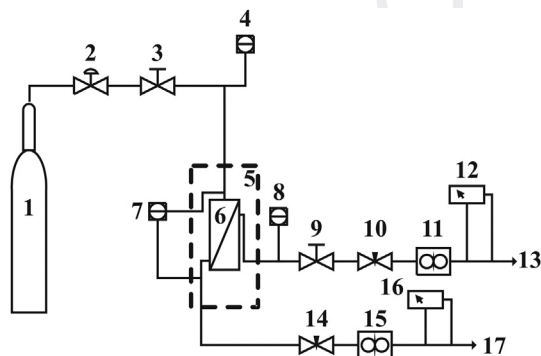


Fig. 1 – Experimental membrane test rig. 1; gas cylinder, 2; pressure reducer, 3; feed valve, 4; feed pressure indicator, 5; thermostat, 6; membrane module, 7; differential pressure indicator, 8; permeate pressure indicator, 9,10; permeate valves, 11,15; digital gasflow meter, 12,16; H_2 sensors, 13; permeate fraction, 14; retentate valve, 17; retentate fraction.

The experimental runs were randomly conducted. The design boundaries for temperature were selected in the range of 37–55 °C since biotechnological hydrogen production processes are usually carried out under mesophilic (~ 37 °C) and thermophilic (~ 55 °C) circumstances. To investigate the effect of hydrogen content on the membrane selectivity various binary gaseous mixtures (H_2/CO_2 (vol%/vol%): 30/70 \pm 0.5; 41/59 \pm 0.5; 65/35 \pm 0.8) were prepared in a single gas cylinders and afterwards introduced to the membrane module, meaning that no separate feed tanks of individual gases were applied to obtain the desired combinations. This range covers the possible hydrogen concentrations could be found in steady-state bioreactors as a result of the metabolic activity of hydrogen-evolver strains.

Beyond temperature and gas composition, the ratio of retentate and total feed flows (V_R/V_F) can also impact the separability of multi-component gaseous mixtures (e.g. H_2/CO_2) since the purity of both the concentrate and permeate are dependent on the relative extent of these main fractions. As an example, the measured and calculated values are presented in Table 3.

For each case, the mixed gas selectivities corresponding to the $V_R/V_F = 0.2, 0.4, 0.6$ values used in the statistical evaluation were calculated by interpolation method employing the curves that were fitted to V_R/V_F vs. selectivity data. Since gas

Table 1 – The 3-level full-factorial design with the real mixed gas selectivity data.

Run	Feed H_2 conc. (vol%)	Temperature (°C)	V_R/V_F	Real selectivity
1	30	37	0.2	1.22
2	30	37	0.4	1.30
3	30	37	0.6	1.34
4	30	46	0.2	1.26
5	30	46	0.4	1.35
6	30	46	0.6	1.37
7	30	55	0.2	1.28
8	30	55	0.4	1.37
9	30	55	0.6	1.45
10	41	37	0.2	1.35
11	41	37	0.4	1.45
12	41	37	0.6	1.61
13	41	46	0.2	1.37
14	41	46	0.4	1.51
15	41	46	0.6	1.58
16	41	55	0.2	1.37
17	41	55	0.4	1.50
18	41	55	0.6	1.58
19	65	37	0.2	1.41
20	65	37	0.4	1.49
21	65	37	0.6	1.57
22	65	46	0.2	1.46
23	65	46	0.4	1.55
24	65	46	0.6	1.61
25	65	55	0.2	1.43
26	65	55	0.4	1.54
27	65	55	0.6	1.62

Symbols: P^F – Feed pressure; V^F – Feed flow rate; V^P – Permeate flow rate; V^R – Retentate flow rate; H_2^F – H_2 concentration in the permeate; H_2^R – H_2 concentration in the retentate; V_R/V_F – Ratio of retentate and feed flow rate (recovery).

Table 2 – The evaluation of the 3³ statistical experimental design employed.

Factor	SS	df	MS	F	p
(1) H ₂ concentration (L + Q)	0.1897	2	0.0948	99.2251	<0.0001
(2) Temperature (L + Q)	0.0088	2	0.0044	4.608	0.0251
(3) V _R /V _F (L + Q)	0.1416	2	0.0708	76.0661	<0.0001
1 by 2	0.0005	1	0.0005	0.5719	0.4598
1 by 3	0.0002	1	0.0002	0.2236	0.6423
2 by 3	<0.0001	1	<0.0001	0.0348	0.8541
Error	0.0162	17	0.0009		
Total SS	0.3595	26			

Symbols: SS – Sum of Squares; df – Degree of Freedom; MS – Mean Square; F – F-test value; p – Significance value; L: linear effect; Q: Quadratic effect.

concentrations determine the separation efficiency according to Eq. (3), only the data collected at steady-state conditions – when no further change in the retentate and permeate flows and in their compositions could be observed – were utilized to get the mixed gas selectivities.

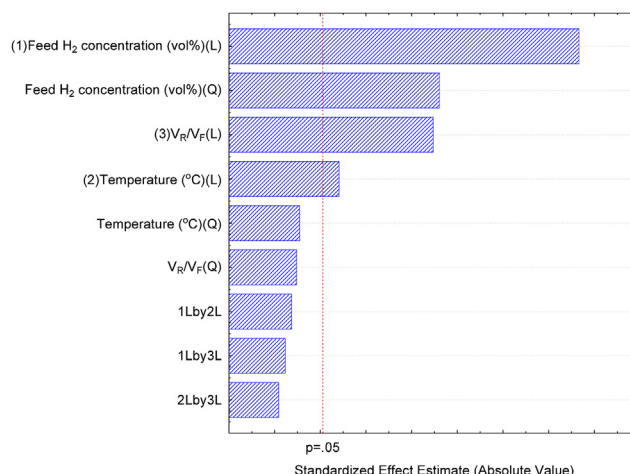
4. Results and discussion

As it could be observed that hydrogen was enriched in the permeate meaning that this component was the more permeable one, representing the H₂-selective characteristic of the membrane [28]. The mixed gas selectivities were calculated based on Eq. (3).

Analysis of variance (ANOVA) was performed to evaluate the experimental design and the results obtained are listed in Table 2. Based on ANOVA, the factors with significance value (*p*) less than 0.05 could be considered as statistically important process parameters affecting the real selectivity. The results of the ANOVA are graphically plotted on the Pareto chart (Fig. 2). According to the statistical results in Table 2, feed H₂ concentration, temperature and V_R/V_F were found to be significant process variables meanwhile none of their interactions could be assigned to statistically important ones. The impacts and the roles of the major separation factors are outlined and discussed in the following sections. The response surfaces demonstrating the input variables' effects on the real selectivity are illustrated in Figs. 3–5.

4.1. Effect of temperature

As it is seen in Fig. 3 the achievable selectivity was increased at higher temperatures. This is presumably due to the fact that

**Fig. 2 – The Pareto-chart of standardized effects.**

increasing temperature has reverse effects on the crucial parameters of the separation (solubility and diffusion). In general, solubility decreases, meanwhile diffusion increases at elevated temperatures. Moreover, H₂ and CO₂ have completely distinct diffusion and solubility properties in glassy (H₂-selective) membrane materials such as polyimide. CO₂ can be described by a relatively higher solubility compared to hydrogen which is in turn more mobile and can be characterized by faster diffusion capability. This is attributed to the fact that the diffusion coefficient of the gases decreases with increasing molecular size since larger compounds are able to interact with more segments of the polymer matrix [29]. Furthermore, the main objective in the development of H₂-selective membranes – such as polyimide – is to enhance the diffusive selectivity ($\uparrow D_{H_2}/D_{CO_2}$) and in parallel restrict the solubility selectivity ($\downarrow S_{CO_2}/S_{H_2}$) [20].

Therefore, applying such materials the impact of diffusive selectivity is more pronounced and particularly contributes to the separation efficiency. Consequently, the increment in the permeation of carbon-dioxide with ascendant temperature was lower than that of hydrogen and thus, the real separation efficiency of H₂/CO₂ has increased with raising temperature. Regarding the temperature effect similar finding were obtained by David et al. using a Matrimide® membrane [22]. Even though it seems that elevating the temperature could help to attain better separation performance, the temperature sensitivity of the membrane limits this opportunity. Furthermore, heating the membrane unit to higher temperature ranges (e.g. above the values where biohydrogen fermentation is performed) might cut down the process economy.

Table 3 – Separation of H₂/CO₂ gas mixture at 46 °C containing 65 vol% H₂.

P _F (bar)	V _F (STP L min ⁻¹)	V _P (STP L min ⁻¹)	V _R (STP L min ⁻¹)	H ₂ ^P (vol%)	H ₂ ^R (vol%)	V _R /V _F	Selectivity
2.65	13.70	12.78	0.92	71.44	39.24	0.07	1.30
2.63	24.57	20.30	4.27	73.28	53.32	0.17	1.42
2.58	29.25	18.48	10.76	74.70	60.60	0.37	1.53
2.35	44.90	15.95	28.94	75.87	63.95	0.64	1.63

Measured: P_F, V_F, V_P, V_R, H₂^P, H₂^R; Calculated: V_R/V_F, Selectivity; STP: Standard Temperature and Pressure.

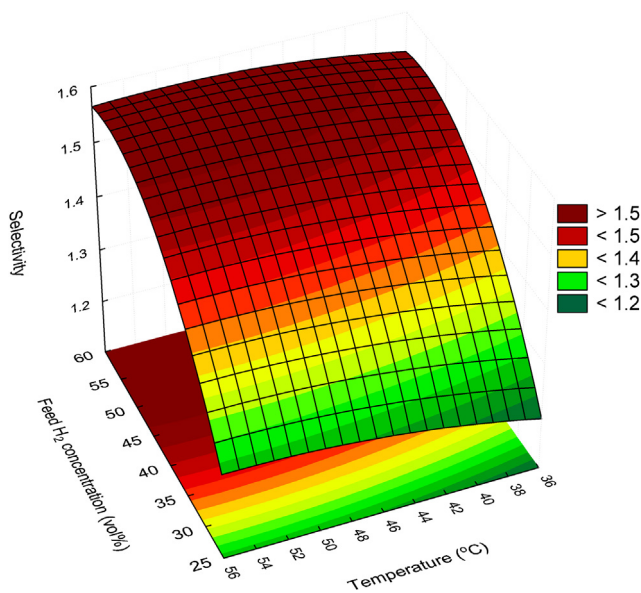


Fig. 3 – The effect of temperature and H₂ concentration on real selectivity ($V_R/V_F = 0.4$).

4.2. Effect of gas composition

Beside temperature, the composition of the gas to be separated is another factor that affects the overall performance of the membrane. The separation efficiencies of the membranes reported in the literature are generally determined in pure gas experiments (Table 4). However, this ideal value can considerably differ from the real selectivity that reflects the membrane performance under practical (mixed gas) conditions. Only in cases when the components of a gaseous mixture do not significantly interact with the membrane material the theoretical and real selectivities remain the same [24,29]. Nevertheless, in numerous cases including CO₂ and H₂

separation, the carbon-dioxide can fairly be dissolved in the membrane. This phenomena can significantly influence the permeation of the other gas e.g. hydrogen and hence the performance of the whole separation process. Therefore, it is highly recommended to test the membranes under real conditions in order to get reliable data about the applicability of the membrane for a certain task. For the above-mentioned reasons, H₂/CO₂ binary gas experiments were performed by applying three different gas compositions.

According to the experimental results, it can be stated that higher hydrogen concentration could be achieved in the permeate by introducing H₂/CO₂ mixture with higher initial hydrogen content. The experiments implied that the growing amount of carbon-dioxide presented in the feed gas caused difficulties in the whole separation process. This was probably due to the fact that CO₂ could affect the permeation of H₂ through the membrane. As CO₂ concentration decreased, the less residual impurity content resulted in enhanced separation efficiency. The outcomes suggest that it is beneficial to optimize bioreactor performance which could influence the hydrogen content of biological gas generated during the process. It means that the fermentation conditions must be chosen properly in order to limit carbon-dioxide formation as much as possible and thus, aid the final separation step. It suggests well that a proper design of the upstream (“product formation”) step highly affects the effectiveness of the downstream (“product purification”). If comparing the result to the previously determined theoretical values of the membrane module at different temperatures [30], it would appear that the real separation factors have declined in a remarkable degree. Similar observations were reported in other studies, as well [22,31].

4.3. Effect of retentate/feed flow ratio

Based on the statistical analysis the so-called recovery factor (V_R/V_F) is also an important parameter to be taken into account during the purification. In general, membranes are able

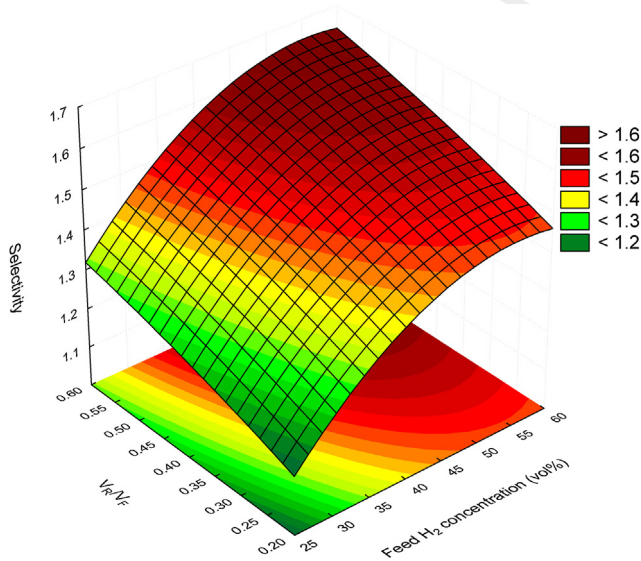


Fig. 4 – The effect of V_R/V_F and H₂ content on real selectivity (Temperature = 46 °C).

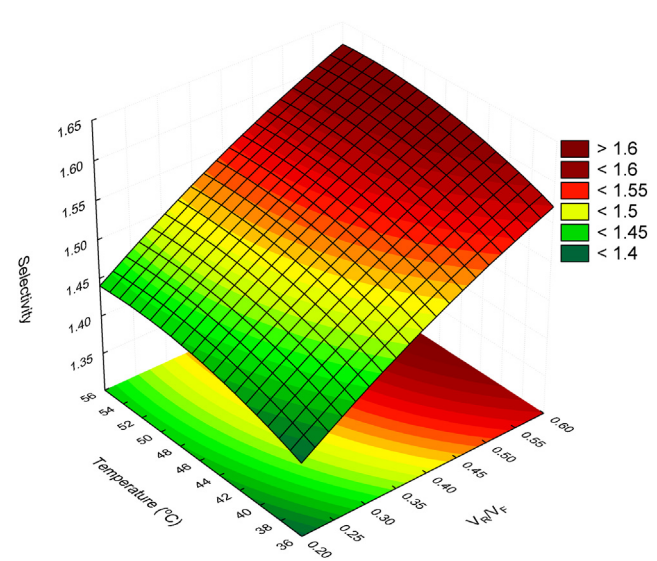


Fig. 5 – The effect of V_R/V_F and temperature on real selectivity (H₂ content = 45 vol%).

Table 4 – Separation of H₂/CO₂ gas mixture at 37 °C containing 30 vol% H₂.

P _F (bar)	V _F (STP L min ⁻¹)	V _P (STP L min ⁻¹)	V _R (STP L min ⁻¹)	H ₂ ^P (vol%)	H ₂ ^R (vol%)	V _R /V _F	Selectivity
2.63	6.40	6.06	0.34	32.83	0.39	0.05	1.12
2.48	11.26	9.34	1.92	34.58	16.20	0.17	1.21
2.42	16.19	10.01	6.18	36.18	23.87	0.38	1.30
2.16	31.61	9.81	21.80	37.20	28.26	0.69	1.36

Measured: P_F, V_F, V_P, V_R, H₂^P, H₂^R; Calculated: V_R/V_F, Selectivity; STP: Standard Temperature and Pressure.

to ensure retentate fractions enriching the slowly permeating component (in our case CO₂ as discussed above) however, only when low recovery values are applied [29]. In Fig. 6 it is plotted that hydrogen concentration in the retentate was significantly decreased at lower recovery values, suggesting that CO₂ was favorably retained in the concentrate fraction by the membrane. At certain extremely low retentate flows (V_R/V_F values) – when the vast majority of the gas introduced to the membrane module was forced to the permeate – it was possible to obtain almost pure (>99 vol%) CO₂ in that fraction (Table 4). This implies that the enrichment degree of the slower gas compound – here carbon-dioxide – was more considerably dependent on the amount of retentate taken away and the membranes selectivity had somewhat smaller impact.

On the other hand, in Fig. 6 it can also be observed that the purification of the more rapidly permeating component is determined by the membrane's selectivity, since H₂ concentration was poorly growing in the permeate when V_R/V_F was increased. Therefore, a membrane without sufficiently high selectivity yields only a slightly concentrated permeate stream. As a consequence it can be concluded that if hydrogen is to be obtained with high purity in the permeate fraction, membranes with improved selectivities need to be engineered or cascade systems have to be constructed [24,29]. Furthermore, the change in the V_R/V_F value – as intimated above – alters the amount of permeate obtained. The higher recovery value is coupled with the less amount of permeate. The total feed flow and the surface velocities should also be considered

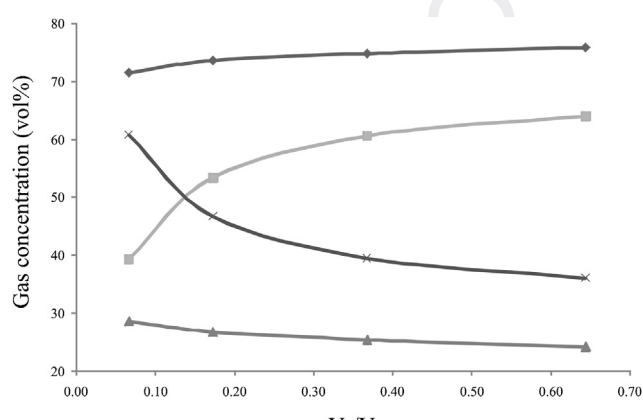


Fig. 6 – The change in the composition of permeate and retentate streams as the function of V_R/V_F (measurement conditions are given in Table 3). Symbols: ◆; H₂ permeate, ■; H₂ retentate, ▲; CO₂ permeate, ×; CO₂ retentate.

because it could be a crucial factor during gas separation due to the incidental threat of concentration polarization phenomena. As it has been reported, the application of low stage-cut values – defined as the permeate flow/feed flow – are preferable in order to maintain more efficient membrane performance [32–34]. This might be an explanation for the observed increase in selectivity with the increased recoveries (higher total- and lower permeate flows with accompanying decreased stage-cut).

Nevertheless, it would appear that the UBE polyimide membrane reflects good permeabilities and moreover, in comparison with other commercially available polymeric membranes tested in the literature it possesses sufficient and useful selectivity (Table 5) even at low transmembrane pressures (<3 bar).

5. Conclusions

In this research work it was demonstrated that the polyimide membrane module exhibited potential for the processing of hydrogen containing biogas mixture. However, it is necessary to acknowledge that the selectivity is not high enough for the one-step, complete removal of fermentation side-product carbon-dioxide. Nevertheless, it is somewhat typical for membrane processes. Generally, they cannot produce gases at the required purity in a single step. Often pre- or post-

Table 5 – H₂/CO₂ selectivities of several commercial polymer membranes.

Polymer	Selectivity (H ₂ /CO ₂)	Reference
Polyimide (Matrimide [®]) ^d	2.93	[22]
Polyethersulfone ^a	2.65	[35]
Polysulfone ^b	2.5	[18]
Polyimide ^c	2.36	[30]
Polystyrene ^b	2.3	[18]
Poly(vinylidene fluoride) ^b	2.0	[36]
Polyimide ^e	1.62	This work
Polyphenyleneoxide ^b	1.49	[18]
Polymethylpentene ^b	1.48	[18]

^a Theoretical selectivity values measured at 35 °C

^b Theoretical selectivity values measured at 30 °C.

^c Theoretical selectivity values measured at 37 °C.

^d Mixed gas selectivities. Feed pressure: 4–6 bar, temperature: 30 °C, mixture composition (H₂/CO₂): 10 vol%/90 vol%.

^e Mixed gas selectivities. Feed pressure: 2.2 bar, temperature: 55 °C, mixture composition (H₂/CO₂): 65 vol%/35 vol%.

treatment or multiple-stage processes are used. For instance, the concentration of hydrogen can be performed by a first membrane and the removal of the last traces of CO₂ by a second membrane or vice versa. Alternatively, get rid of the majority of carbon-dioxide by a membrane followed by a classical sorption process to remove the residual traces of CO₂. In addition to carbon-dioxide, some minor contaminants of the biological gas such as water vapor and hydrogen-sulfide can also play an important role in the separation but revealing their effects was beyond the scope of the present study. Nevertheless, it could definitely represent a direction for future research [24].

The results showed that process variables such as gas composition, temperature and the ratio of retentate and feed flow were important in hydrogen separation and could affect the achievable separation efficiency. Therefore, these parameters have to be taken into account when designing a proper enrichment process. Depending on the choice of the experimental design, the optimum setpoints of the input parameters may be determined especially when response surface methodology is applied. In the case of the present study, it would require the prediction of most the adequate temperature, feed gas composition and the recovery (V_R/V_F) factor values for effective separation. However, it cannot be accomplished due to the nature of the variables studied. Nevertheless, as it has been revealed, increasing the feed hydrogen concentration as well as the temperature and the V_R/V_F value within the design boundaries provided a more enriched permeate and greater H₂/CO₂ mixed gas selectivity.

Moreover, it has turned out that testing of the membrane with gaseous mixtures was required since considering only theoretical values the overall membrane performance could be strongly overestimated and hence, false conclusions may be drawn. In the future, investigation of membrane gas separation and hydrogen fermentation in a coupled system is aimed to be performed in order to obtain concentrated biohydrogen in an integrated system.

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