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Application Report

Report from

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Application of BlueSens® H_2 sensor in a gas separation study

Introduction

Biohydrogen is an emerging alternative energy carrier with high potential for sustainable development. It can be utilized in fuel cells or internal combustion engines. However, purified hydrogen should be provided for these end-use applications thus its enrichment – through getting rid of gaseous side-products especially CO_2 generated in the fermentative bioreaction – is very important.

A wide range of absorptive, adsorptive, cryogenic techniques and alternatives relying on membranes may be employed to concentrate biologically produced hydrogen. In recent decades as a result of advancements made in the field of membrane technology it is now accounted among the efficient, energy-saving and ecological-friendly opportunities. Membranes for gas separation are mature, commercially available nowadays and mostly fabricated from high-performance polymers such as polyimides. Membranes for H_2 purification, however, are featured with challenges. On one hand, membranes possess sufficiently high permeability and selectivity should be developed. On the other hand, revealing the membranes real potential under practical separation conditions e.g. with mixed gases is still of interest but such studies are not frequently conducted despite their importance.

Therefore, in this work we wanted to test a lab-scale polyimide membrane module for fermentative hydrogen recovery applying binary H_2/CO_2 gaseous mixtures.

Moreover, evaluating the influences of notable process variables, namely separation temperature and recovery factor was also aimed.

Materials and Methods

Hydrogen purification experiments using BlueSens® H_2 sensor

In the current experiments a membrane module containing polyimide hollow-fibers (UBE Industries Ltd., NM-B01A) was investigated. This polymer is considered as a highly promising material for membrane gas separation including H_2 purification, as well.

The measurements aiming the concentration of hydrogen were carried out in a laboratory-scale device schemiatically presented in in Fig. 1.

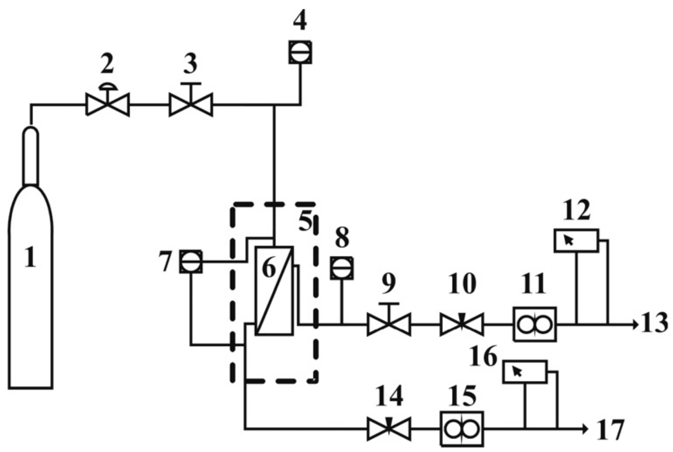


Fig. 1 – Experimental membrane testing set-up
1; gas cylinder containing binary H_2/CO_2 mixture, 2; pressure controller, 3; feed valve, 4; feed pressure indicator, 5; module thermostat, 6; membrane module, 7; differential pressure indicator, 8; permeate pressure indicator, 9,10; permeate valves, 11,15; digital gasflow meter, 12,16; BlueSens® H_2 sensor, 13; permeate fraction, 14; retentate valve, 17; retentate fraction

During the experiments, the hydrogen concentrations of the feed, permeate and retentate streams were continuously followed by using on-line BlueSens® H_2 analyzers (BlueSens Gas Sensor GmbH). The equipment is able to measure hydrogen in the range of 0-100 vol% with a quick response time of 20 seconds. The additional characteristics can be accessed by visiting the manufacturer's homepage (www.bluesens.com).
The feed gas pressures during the experiments were adjusted as low as approximately 3 bar since considering practicality, a high compression degree of biologically produced gases comprising hydrogen would consume a noticeable portion of its energy content and hence making the process economically unattractive. The permeate side of the module was kept under ambient conditions.

The influences of three process variables (temperature, feed hydrogen content and retentate/feed flow ratio referred to as recovery factor) were determined by experimental design approach using binary H_2/CO_2 mixtures.
To estimate the mixed gas selectivities ($a_{i/j}$) according to Eq. 1, only the data recorded at steady-state – when no change in the retentate and permeate flows and in their compositions occured – were considered:

$$a_{i/j} = (x_i^P/x_j^P)/(y_i^F/y_j^F) \quad (1)$$

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 their volumetric fractions in the feed mixture.

Results and discussion

Statistical analysis (ANOVA) was performed to evaluate the experimental design (Table 1). Based on ANOVA results, feed H_2 concentration, temperature and recovery factor were all identified as significant process parameters ($p<0.05$).

The response plots displaying the impacts of the independent variables mentioned can be seen in Fig. 2-Fig. 4.

Impact of gas composition

The composition of the feed gas is apparently a factor that determines the performance of the membrane module. However, the separation efficiencies of the membranes are more often than not sought only in single gas experiments. This ideal value can be notably different to those obtained under practical (mixed gas) separation circumstances. The theoretical and real selectivities would expectedly be similar only when the constituents of a gas mixture do not strongly interact with the membrane material. In the case of CO_2 and H_2 separation, however, the carbon-dioxide is easily dissolved in membrane materials such as polyimide. This phenomenon can remarkably affect the permeation of the other gases e.g. hydrogen and thus the efficiency of the overall separation process. From the tentative results, we found that higher hydrogen concentration could be attained in the permeate fraction by feeding H_2/CO_2 mixtures with higher initial hydrogen concentration. Based on the experiments it was concluded that the more amount of carbon-dioxide in the feed mixture represented a limiting factor to achieve better selectivities. This might be explained by the fact that carbon dioxide likely influences the migration of hydrogen across the membrane capillaries. As CO_2 concentration has decreased, improved separation efficiency could be observed.

ANOVA – Dependent Variable: Mixed gas selectivity; R2: 0.98

Factor	SS	df	MS	F	p
Separation Temperature	0.007200	1	0.007200	11.2941	0.02828
Feed H_2 content	0.068450	1	0.068450	107.3725	0.00049
Recovery factor	0.051200	1	0.051200	80.3137	0.00086
Error	0.002550	4	0.000637		

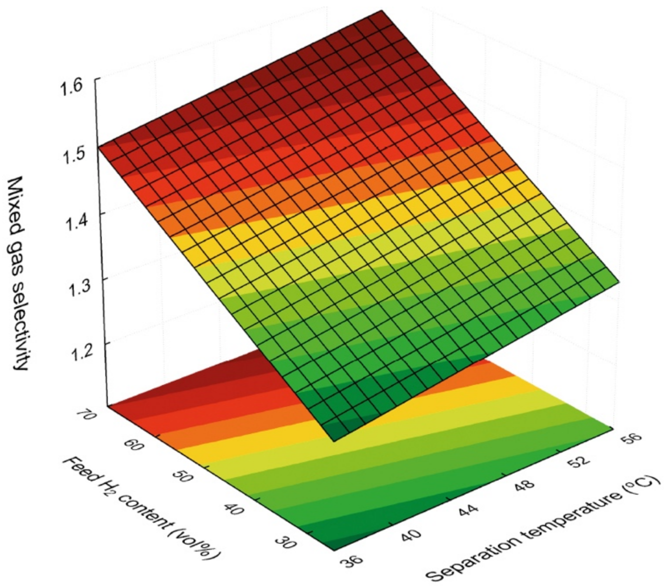


Fig. 2 – Influence of separation temperature and feed composition on mixed gas selectivity

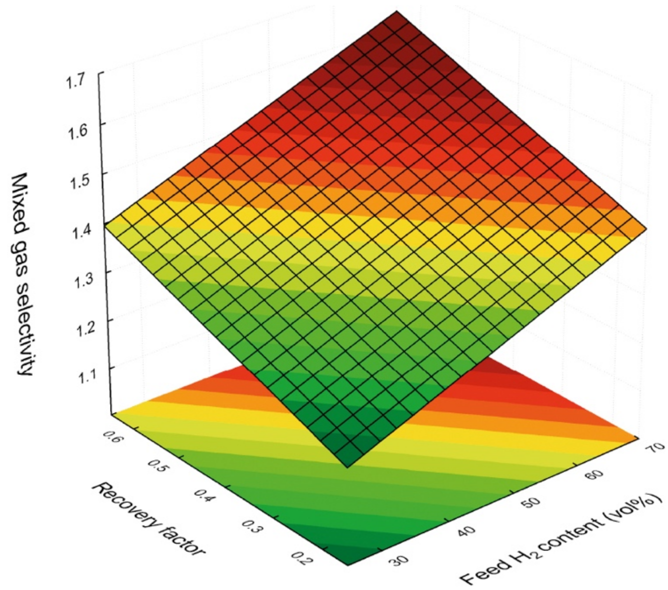


Fig. 3 – Influence of feed composition and recovery factor on mixed gas selectivity

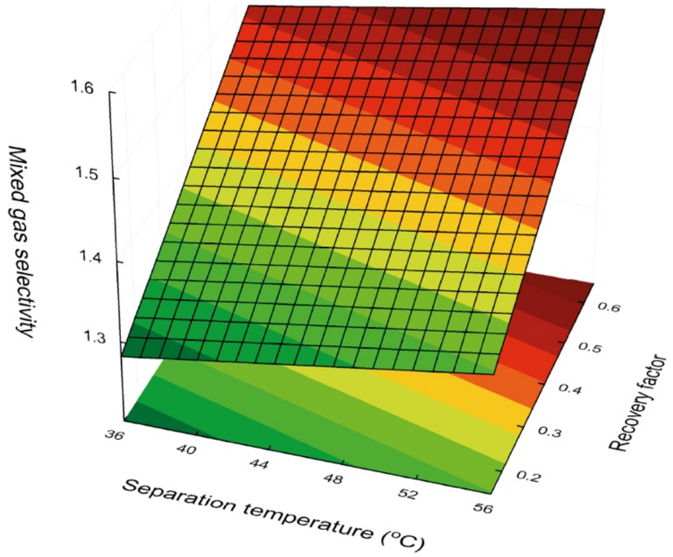


Fig. 4 – Influence of separation temperature and recovery factor on mixed gas selectivity

Influence of recovery factor

Membranes, in general, can enrich the slowly permeating compounds in the concentrate stream, however, only when low recoveries are applied. In our investigation, almost pure (>99 vol%) CO_2 could be obtained in the retentate at certain, extremely low recoveries when the vast majority of the gas introduced to the membrane module was taken at the permeate side (Table 2).

CO_2 Permeate (vol%)	CO_2 Retentae (vol%)	Recovery value	Mixed Gas Selectivity
67.17	99.61	0.05	1.12
65.42	83.8	0.17	1.21
63.82	76.13	0.38	1.3
62.8	71.74	0.69	1.36

Table 2 – Results of separating H_2/CO_2 gas mixture (Separation temperature: 37 oC; initial H_2 content: 30 vol%)

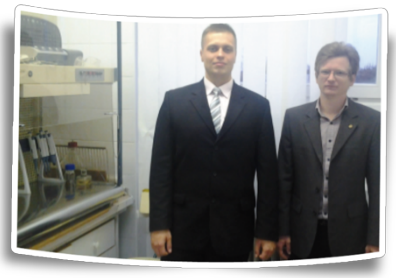
It was also observed that the separation of the faster permeating H_2 is determined by the membrane's selectivity, since H_2 concentration in the permeate was only slightly increased when recovery factor was increased. Hence, if hydrogen is to be concentrated in the permeate fraction, membranes reflecting higher selectivities need to be developed or multi-step, cascade applications should be employed. Furthermore, the change in the recovery value also changes the amount of permeate which together with the total feed flow and the surface velocities should not be neglected to avoid concentration polarization. Basically, maintaining a high recovery value is favorable so as to get a more sufficient membrane performance. This might be the reason for the increment of selectivity with increased recoveries.

Separation temperature effect

It is quite obvious from the research outcomes that the mixed gas selectivity has increased at higher temperatures. It is understandable if one keeps in mind that increasing temperature has contradictory impacts on the solubility and diffusivity of the permeating gases. In general, the former decreases, whilst the latter increases with raising temperatures. Furthermore, hydrogen and carbon dioxide have distinct characteristics from diffusion and solubility points of views in rigid, glassy polymers such as polyimide. CO_2 usually expresses a relatively higher solubility in comparison to hydrogen which is in turn more rapid and possesses faster diffusion coefficient. These properties of the gases are in correlation with molecular size, their affinity to polymers and the developing interactions with the membrane material during permeation. Polyimide, as mentioned, is a glassy polymer which basically achieves selectivity mainly on diffusivity-difference basis. Since CO_2 is a larger molecule than hydrogen, the increment in its diffusivity is less pronounced than that of hydrogen at elevated temperatures. This was assumed to be the reason for the increasing separation efficiency of H_2/CO_2 with increasing temperature.

Conclusions

In our research work we established that the polyimide membrane module had a potential to enrich hydrogen from gaseous mixtures. The results demonstrated that process variables such as gas composition, temperature and the recovery factor had remarkable influence on hydrogen separation and could affect the achievable separation efficiency. Thus, these parameters are to be considered when designing a suitable enrichment process. It has been proven that higher H_2/CO_2 mixed gas selectivity could be accomplished by increasing the feed hydrogen concentration as well as the temperature and the recovery value within the studied design boundaries.



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The main tasks of the Research Institute on Bioengineering, Membrane Technology and Energetics are:

- to teach and train students to get BSc In bioengineering
- to introduce them to a wide range of biochemical and biotechnological processes
- to introduce them to the world of membranes and their applications

Application possibilities of various membrane processes, improvements of bioprocesses and manufacture of renewable, “green” energy sources are studied at the institute involving the PhD students of the Doctoral School of Chemical Engineering and Material Sciences (University of Pannonia).