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Investigating the effect of hydrogen sulfide impurities on the separation of fermentatively produced hydrogen by PDMS membrane

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ABSTRACT

This work reports on the separation of biohydrogen using a hollow-fiber PDMS membrane. The performance of the module was evaluated using binary CO_2/H_2 (35–65 vol.% H_2 content) and ternary $CO_2/H_2/H_2S$ mixtures (50 vol.% H_2, 50 vol% CO_2, 25–175 ppm H_2S) and the effect of recovery and gas composition (with special focus on hydrogen sulfide content) was revealed. H_2S is a potential impurity of the raw gas coming from steady-state, dark fermentative hydrogen producing bioreactors. The results indicated that H_2S could have a concentration-dependent impact on membrane behavior and affected the obtainable CO_2/H_2 selectivity. The outcomes were thoroughly compared to other relevant gas separation reports found in the literature. Evaluating the impacts of trace-level substances present in the gaseous mixture containing biohydrogen may help to design effective purification system based on membrane technology for the hydrogen economy.

1. Introduction

The use of wastes and other biomass-derived compounds as feedstocks is a key-aspect in the development of cleaner and more environmental-friendly technologies [1]. In accordance with this concept, the microbiological conversion of organic materials e.g. lignocelluloses into gaseous biofuels, in particular hydrogen is considered as an attractive way toward a greener and more sustainable energy sector [2–5]. Biohydrogen can be formed in several ways including the practically most developed anaerobic dark fermentation [6]. In the course of this bioprocess, pure [7,8] or mixed cultures [9,10] of special H_2-generating bacteria transform basically carbohydrate-rich materials into hydrogen through their metabolic pathways in well-designed continuous bioreactors [11]. Although there are special methods such as microbial electrohydrogenesis [12] where H_2 may be obtained separately, in classical dark fermentation H_2 is formed in a complex gaseous mixture and therefore is accompanied by certain major (e.g. CO_2) and minor impurities (e.g. H_2S, N_2, water vapor, etc.) [13]. Hence, the fermenter off-gas gas, which can comprise roughly of 35–65 vol.%. H_2 [14] has to be upgraded for efficient utilization e.g. in PEM fuel cells.

To accomplish the enrichment of H_2 from multi-compound gaseous mixtures, there is a range of techniques to choose from, including membranes [15]. Among them, the ones employing liquid membranes are emerging [13,16,17], while polymeric membranes [13,18] stand as contemporary approaches.

Non-porous, polymeric membranes have been used for a long time to selectively concentrate different target gases [19]. Recently, the deployment of membranes for biohydrogen recovery and concentration has been emphasized and the concept of *hydrogen producing gas separation membrane bioreactor (which is also referred as hydrogen extractive membrane bioreactor*) was introduced [13,20,21]. In this integrated construction, the production and purification of hydrogen is carried out simultaneously, as lately demonstrated in a novel double-membrane bioreactor [22]. Furthermore, this set-up allows testing the membranes directly with untreated fermentation gases and permeation data under realistic circumstances can be attained. It could be of importance since the behavior of the membrane do can change as compared to ideal conditions [13]. Some of the membrane separation systems have been already proven to upgrade biogas [23] as well as natural gas [24] at full-scale facilities. These results indicate well that membrane gas separation may have a lot of perspectives as a downstream technique for the continuously developing (bio)hydrogen economy, as well.

Reports from the past couple of years evaluated membrane modules for fermentative hydrogen separation in different

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experimental conditions [13,14,20,21]. Among the materials that various scientific groups have dealt with, PDMS was shown as an attractive candidate. PDMS, as a reserve-selective, rubbery polymer material favors to permeate gases possessing higher condensabilities suggesting that the permeation rate of CO_2 through such membrane exceeds that of less condensable, light compounds such as H_2 [25,26]. Thus, PDMS is characterized with a remarkable permeability for CO_2 and a moderate CO_2/H_2 selectivity [22,27]. Lately, the properties of a commercial PDMS membrane module were determined for H_2 enrichment using real fermentation gas mixture coming from a steady-state fermenter unit [22]. It has turned out that PDMS reflected decent CO_2/H_2 selectivity, however, the values were rather lower as compared to those previously found with a model gas mixture [20]. These outcomes carry the message that feed gas composition is important and imply also that the trace substances present in the multi-compound gas mixture may interfere with H_2, CO_2 and/or the polymer itself and hence, take an effect on the transmembrane permeation features. Consequently, it is worthy to pay attention to the influence of these accompanying impurities [26,28] such as hydrogen sulfide, which stands in the scope of this paper.

During biological hydrogen production via dark fermentation, H_2S is a potential contaminant with a concentration that normally does not exceed several ten to hundred ppm [29–31]. H_2S is known as an aggressive gas with an acidic character and therefore it can be harmful for the technological pipeline as well as to the end-use applications e.g. fuel cells. Moreover, from membrane technological point of view, hydrogen sulfide is kept in mind as a possible plasticizer agent for polymeric membranes [32]. Although PDMS has been tested by various groups of authors for H_2S removal and/or H_2 recovery using syngas and model mixtures [20,26,33–36], not much is known about its separation qualities for (bio)hydrogen purification in the presence of H_2S with various concentrations.

Therefore, in this work, the influence of H_2S on the performance of a commercially available poly(dimethylsiloxane) membrane during H_2/CO_2 permeation was experimentally assessed. Firstly, a commercial PDMS hollow-fiber membrane was exposed to binary H_2/CO_2 mixtures with three different compositions. Afterward, ternary gases were used containing various H_2S concentrations and fixed hydrogen/carbon dioxide ratio to reveal the effect of this low concentration impurity. Besides feed gas composition, the impact of recovery ratio on the separation performance has been sought, as well. Although seeking the impact of minor gaseous by-products (e.g. H_2S) applying membrane separation technology can be of practical importance [13,51], such experimental studies in the area of fermentatively produced biohydrogen purification are scantly reported and was the aim of this work.

2. Materials and methods

2.1. Membrane module

In this study, a commercial, non-porous PDMS membrane (MedArray Inc., product reference code: PDMSXA-10) was thoroughly employed in a cross-flow experimental arrangement, as further specified in Section 2.3. The module contains 30 thin membrane fibers built-in a polycarbonate jacket. The capillaries have outer- and inner diameters of 300 μm and 190 μm, respectively. The effective surface area is 10 cm^2.

2.2. Preparation of binary and ternary gas mixtures

The feed gas mixtures with different compositions were prepared in sealable gas bag. For the binary H_2/CO_2 mixtures (35, 50, 65 vol.% CO_2 content), H_2 (99.9%) and CO_2 (industrial grade) were applied. H_2 and CO_2 were filled in the preliminary vacuumed container to get their appropriate ratios. The composition was analyzed by gas chromatography according to the method detailed in our previous work [9].

To prepare the ternary mixtures containing H_2S (25, 100, 175 ppm) next to hydrogen (50 vol.%) and carbon dioxide (50 vol.%), the following procedure was applied. First, the balloon was vacuumed and subsequently filled with CO_2. Thereafter, the gas bag was attached to a Kipp generator, in which pure H_2S was evolved by reacting solid FeS with HCl solution. After finishing the addition of H_2S to CO_2, the mixture was homogenized and actual H_2S concentration in the CO_2/H_2S mixture was checked by Dräger X-am® 7000 device (Drägerwerk AG & Co. KGaA, measuring range for hydrogen sulfide: 0–1000 ppm). If H_2S concentration was still higher than required, further amount of CO_2 was supplemented and H_2S content was rechecked. These steps were repeated until the pre-calculated concentration of H_2S – taking into account the diluting impact of H_2 in the next stage – has been achieved. Thereafter, the mixture of CO_2 and H_2S was complemented with H_2 gas in a several consecutive steps in order to carefully attain the proper H_2/CO_2 ratio as well as desired H_2S concentration for the measurements. The final H_2 and CO_2 contents of the mixture were determined by gas chromatography method as referred in our earlier work [9]. The mixing accuracy for H_2 and CO_2 was ±1 vol.%, while for H_2S it has not exceeded ±5 ppm. The necessity of this multiple-step, mixing-diluting approach to deliver $H_2/CO_2/H_2S$ mixtures was attributed to the sensitivity of electrochemical H_2S sensor in Dräger X-am® 7000 to the presence of molecular H_2 gas. In other words, H_2S concentration was possible to measure and precisely adjust only before CO_2/H_2S binary gas was complemented with H_2.

2.3. Continuous gas permeation tests

Once the gases with proper compositions were prepared as described in Section 2.2., the continuous feeding of the membrane module has begun by a controllable peristaltic pump (Masterflex®, Cole-Parmer Instrument Co.) in a constant temperature room (25 ± 1 °C). The gases were delivered into the hollow-fibers at an upstream-side pressure of 3 bar(a), which was adjusted by a pressure reductor located in between the compressor pump and the gas receiving side of membrane. Permeate was obtained at a downstream side pressure of 1 atmosphere at one of the two possible spots on the shell (near to the retentate side of the module), the other one (near to the feeding side) was closed. No sweep gas was employed. The retentate and permeate side gas fluxes were measured by individual soap bubble flow meters. The various elements of the test apparatus including the PDMS module, pressure reductor and flow meters were interconnected via glass tubes, only short parts were made of Norprene® material (Masterflex®, Cole-Parmer Instrument Co.). The scheme of the membrane system is seen in Fig. 1, where it can be noticed that a needle valve was also inserted to the set-up in order to control the recovery ratio (the retentate flow rate divided by the feed flow rate). Similar gas permeation systems (Fig. 1) were designed and used to test hollow fiber membranes by other authors, as well [37,38]. Photos about the experimental set-up can be found in Fig. 2.

Prior to conducting the measurements, leakage tests were successfully performed and the reliability of the apparatus was validated. To monitor the composition of retentate and permeate under various experimental sets, samples were taken in appropriate time intervals by gastight Hamilton® syringe (500 μL) and the already mentioned gas chromatography method [9] was used. The H_2 and CO_2 permeabilities in Barrer (1 Barrer equals to 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1}$) as well as CO_2/H_2 selectivity values presented thoroughly in this study were calculated as

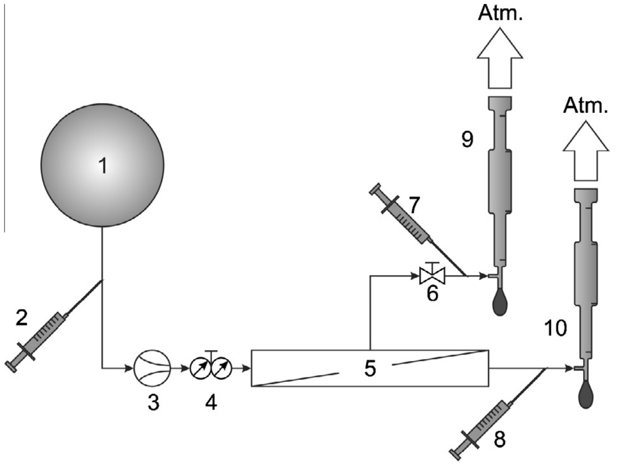

Fig. 1. The scheme of the gas separation membrane system 1: gas container, 2: feed gas sampling; 3: compressor pump, 4: pressure reductor, 5: membrane module, 6: retentate side needle valve, 7: retentate sampling, 8: permeate side sampling, 9: retentate side soap flow meter and 10: permeate side soap flow meter.

detailed in a previous work [22] and refer to steady-state permeation conditions. Steady-state – when outlet gas flow rates and compositions (H_2, CO_2) have not changed with time any longer [39] – was reached within 3–4 h for all the experimental runs. According to our recent paper [22], mass balances for H_2 and CO_2 were computed that supported the reliability of the results. Unlike for the case of H_2 and CO_2, the transmembrane migration of H_2S was not followed and thus, hydrogen sulfide permeability could not be given. The measurements (Table 1) were executed at least in duplicates and standard deviations were less than 5 %.

Table 1
The experimental boundaries of this study.

Feed H_2S (ppm)	Feed CO_2 (vol.%)	Feed H_2 (vol.%)	Recovery (*R*/*F*) value
0	35	65	0.34
0	35	65	0.84
0	50	50	0.54
0	65	35	0.34
0	65	35	0.84
25	50	50	0.34
25	50	50	0.84
100	50	50	0.54
175	50	50	0.34
175	50	50	0.84

3. Results and discussion

3.1. PDMS membrane performance with binary (H_2/CO_2) and ternary ($H_2/CO_2/H_2S$) mixtures

Dark fermentative biohydrogen is formed together with other gases among which carbon dioxide is the most particular. However, other low-concentration components e.g. H_2S can contaminate the mixture too [29–31].

In the first series of the constant pressure and temperature tests, the PDMS membrane was subjected to binary H_2/CO_2 gas mixtures encompassing 35–65 vol.% H_2. This range covers the typical and expectable gas concentrations that potentially occur in continuous, steady-state hydrogen producing bioreactors [14]. In the second series of the investigation, H_2S was added to CO_2 and H_2 to obtain ternary mixtures. Besides varying feed composition, three different recovery values were adjusted according to Table 1. Recovery was chosen to study because it has been found a critical parameter when purifying biohydrogen by membrane technology

Fig. 2. The image of the gas separation membrane system.

[14,22]. To interpret and discuss the trends regarding the impacts of feed gas composition and recovery, individual plots were created both for binary (Figs. 3 and 4) and ternary gas (Figs. 6 and 7) experiments based on the results obtained for Table 1.

Figs. 3 and 4 illustrate the CO_2/H_2 selectivities for the CO_2-selective PDMS membrane considering feed composition and recovery as independent variables, respectively. According to these graphs, higher CO_2 content in the feed and higher recovery positively affected and hence improved the binary CO_2/H_2 selectivity. This dependency pattern is similar to that found in our earlier work [14], where a H_2-selective polyimide membrane could be operated with better selectivity by increasing recovery and H_2 concentration in the gas to be separated.

Fig. 5 illustrates a comparison with regards to the separation features of the tiny PDMS module using binary H_2/CO_2 and ternary $H_2/CO_2/H_2S$ mixtures. The data of Fig. 5 were obtained under similar conditions (transmembrane pressure gradient: 2 bar(a), temperature (25 °C), recovery: 0.54 as can be seen in the 3rd and 8th lines of Table 1), the only difference was in the feed gas composition: in the first case 50 vol.% H_2/50 vol.% CO_2 without H_2S and in the second case, 50 vol.% H_2/50 vol.% CO_2 with 100 ppm H_2S. It has turned out that the addition of 100 ppm hydrogen sulfide resulted in the increase of CO_2 and H_2 permeabilities, however, by different extents (58% and 48%, respectively). Because of the relatively larger increment of CO_2 permeability, CO_2/H_2 selectivity has been enhanced by 7%. Since the change of permeabilities was higher than could have been caused by the measurement error, it is attributable to the 100 ppm H_2S content.

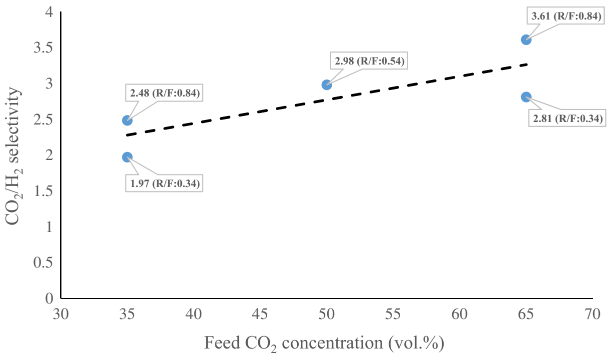

Fig. 3. Effect of feed CO_2 content on CO_2/H_2 selectivity using binary CO_2/H_2 mixture.

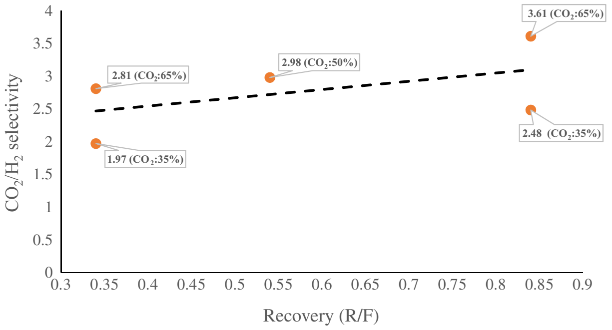

Fig. 4. Effect of recovery on CO_2/H_2 selectivity using binary CO_2/H_2 mixture.

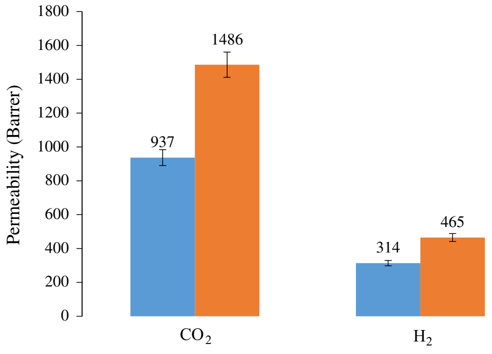

Fig. 5. PDMS membrane performance with and without H_2S under identical separation (pressure, temperature, recovery) conditions. Blue columns: 50 vol.% H_2, 50 vol.% CO_2, no H_2S; red columns: 50 vol.% H_2, 50 vol.% CO_2, 100 ppm H_2S. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

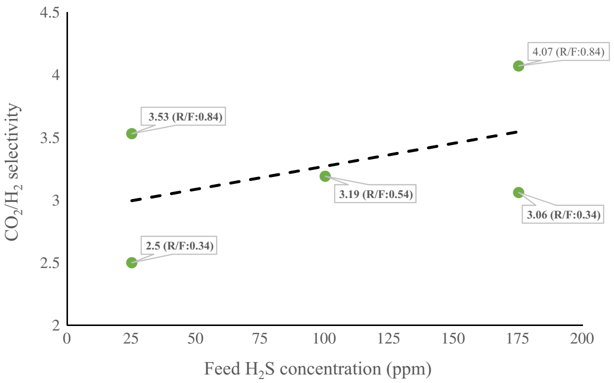

Fig. 6. Effect of feed H_2S concentration on CO_2/H_2 selectivity using ternary $CO_2/H_2/H_2S$ mixture.

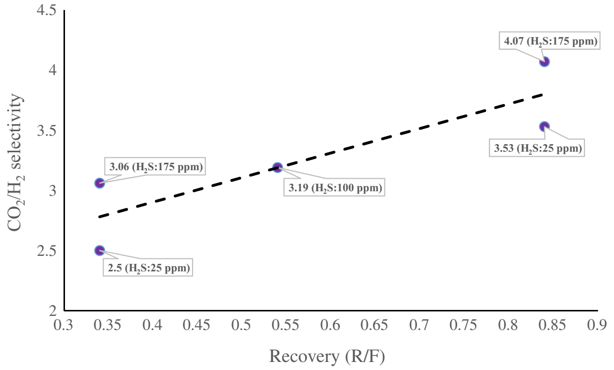

Fig. 7. Effect of recovery on CO_2/H_2 selectivity using ternary $CO_2/H_2/H_2S$ mixture.

In addition to the observation that H_2S could accelerate gas permeation relatively to that determined with binary gas mixture (Fig. 5), it is also to notice that the influence of H_2S was concentration-dependent. In Fig. 6, it is depicted that the gradually increasing H_2S content of the ternary gas (from 25 ppm to 175 ppm) led to higher CO_2/H_2 selectivity. The dependency of membrane selectivity on recovery can be characterized by a similar trend than in case of binary gases, since higher recoveries (meaning that permeate was drawn in smaller volumes) were coupled with improved CO_2/H_2 selectivity values (Fig. 7).

For comparison purposes, Fig. 8 (constructed by merging Figs. 4 and 7) indicates the CO_2/H_2 selectivity for the binary (35–65 vol.% CO_2, no H_2S added) and ternary (fixed 50 vol.% CO_2, 25–175 ppm H_2S) mixtures referring to identical recovery (R/F: 0.34, 0.54, 0.84) settings. As it can be seen in Fig. 8, the selectivity values in the latter case were tendentiously higher, which implies the contribution of hydrogen sulfide toward better performance.

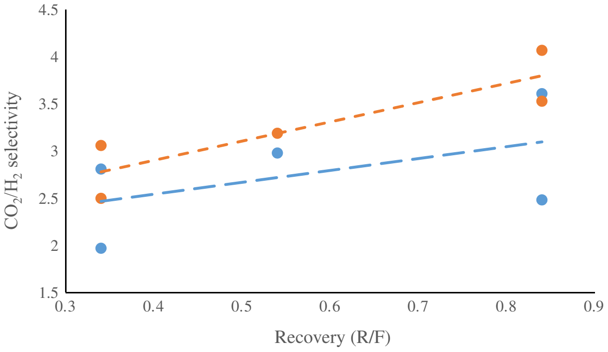

Fig. 8. Comparison of CO_2/H_2 selectivity obtained with the binary and ternary gas model mixtures under identical recovery conditions. Blue data: binary (CO_2/H_2) gases; orange data: ternary ($CO_2/H_2/H_2S$) gases. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The causes and responsible phenomenon concerning the effect of H_2S are likely associated with the changes in diffusivity and solubility properties of the permeating gases. Generally, considering non-porous, dense membrane materials such as PDMS, the permeability and selectivity are the products of diffusivities and solubilities of the individual gases. These intrinsic parameters are related with kinetic diameter and condensability (critical temperature) of the molecules [33], however, can significantly vary with gas composition due to gas–gas and gas–polymer interactions. Therefore, the overall performance of a given membrane may alter when subjected to (i) single gases and (ii) binary, ternary or even more complex mixtures [13], where the competition of permeating compounds for the sorption sites in the polymer matrix can play a key role [26]. As a summary, laboratory experiments with artificial mixtures that resemble the composition of real-case gases to be purified (e.g. biogas at an anaerobic digester; post-combustion flue gas at a power plant; gaseous biofuel (hydrogen) at up-scaled bioreactor [40]) give a more practical and accurate measure of the membrane's (expectable) performance.

Although more in-depth research will be needed to clearly unravel the effect of hydrogen sulfide on membrane behavior in this study, it may be ascribed to the swelling (plasticization) of PDMS material. Basically, swelling is induced by compounds with relatively higher condensabilities and solubilities (such as H_2S). As a result, it is accompanied by the increased permeability of the substances in the gas mixture, which has been observed for CO_2 and H_2 herewith (Fig. 5). Though plasticization many times causes the deterioration of selectivity due to the overall lowered gas transfer resistance of the membrane [13], the results of this work showed that the increase of CO_2 permeation – in the presence of H_2S – was greater than that of H_2 and thus, higher CO_2/H_2 selectivity could be attained. This outcome (pertaining the occasionally positive role of swelling) is supported by literature data where it would appear that in some cases, polymeric membrane performance for H_2 purification could be aided by plasticization [52]. Furthermore, Stern et al. [53] experienced improved CO_2/light gas (methane) separation by 6FDA-HAB and 6FDA-4,4′-PDA polyimide membranes when ternary ($CO_2/CH_4/H_2S$) gas was used instead of binary (CO_2/CH_4) one (35 °C, feed pressure: 10 atm), which is a similar behavior that was recorded in this investigation.

3.2. Assessment and comparison of the results with the literature

According to manufacturer's data, pure CO_2 and H_2 permeabilities for the PDMS membrane used in this work are 3250 Barrer and 650 Barrer, respectively. Similar values (CO_2: 3285 Barrer, H_2:569 Barrer) were found in our previous research (at 23 °C and 80 kPa transmembrane pressure difference) with a highly CO_2-dominant binary mixture (90 vol.% CO_2 and 10 vol.% H_2) [20]. As a matter of fact, these permeabilities for CO_2 are comparable to those (3800–5404 Barrer) reported in the literature by other authors [40–43]. Nonetheless, it can be deducted from the CO_2 and H_2 permeabilities obtained in this study with binary gases (Fig. 5) that the permeation through PDMS can be strongly feed composition dependent, since the permeability values (CO_2: 937 Barrer; H_2: 314 Barrer) appeared to be rather lower than those previously determined either with pure or binary gases, as given above. This observation correlates well with the results of Scholes et al. [26], who encountered a more than 50% reduction in CO_2 permeability for a PDMS membrane when a binary mixture (10 vol.% CO_2, 90 vol.% N_2) was applied instead of pure CO_2. This was associated with the competition of N_2 and CO_2 under mixed gas circumstances, causing that the free volume of the polymer matrix was notably occupied by N_2, which hindered CO_2 transport across the membrane.

As for outcomes on PDMS membrane with gas mixtures containing CO_2, H_2S and H_2, few papers can be referenced. For example, the results of Scholes et al. [26] led to the conclusion that during simultaneous H_2S and CO_2 permeation in a binary (CO_2/H_2S) mixture system, H_2S was a trigger of decreased CO_2 permeability (by an average of 8%) due to possible competitive transport, as proposed by the authors. However, these findings are in contrast with those presented in this work, where H_2S seemed to assist faster CO_2 permeation. In our opinion, this contradiction might have been caused by the differences in separation conditions, in particular (i) inlet H_2S concentration (500 ppm vs. 25–175 ppm), (ii) the complexity of the feed gas (lack/presence of H_2) and (iii) the design of the experimental apparatus (e.g. use of sweep gas, recovery/stage-cut adjusted, driving force applied). In addition, Merkel et al. [35] investigated CO_2, H_2 and H_2S permeation in PDMS membrane with model syngas mixture consisting of H_2S (1.5%), CO_2 (10.5%), H_2 (42%), and CO (46%). Based on the results, it could be concluded that the PDMS membrane was more permeable to H_2S and CO_2 than to H_2. However, it was shown that permeabilities and hence CO_2/H_2 as well as CO_2/H_2S selectivity values were quite sensitive to the separation temperature [35]. Lately, in a research by Ren et al. [44] PDMS was successfully combined with other materials (PEI, PEBA1657) to manufacture multi-layer composite membranes that had increased permeances for CO_2 and H_2S, making them potential candidates for sour gas separation that can have industrial importance.

It is interesting to compare the outcomes of current study with those recently obtained [22] using a same module and raw gas mixture from a steady-state hydrogen producing bioreactor. In the course of bioreactor-off gas permeation (composition: 51.3 vol.% H_2, 47.0 vol.% CO_2, 1.7 vol.% undetermined accompanying compounds), CO_2 and H_2 permeabilities were 1624 Barrer and 452 Barrer, respectively under test circumstances applied in this research too (temperature: 25 °C, recovery: 0.54, transmembrane pressure difference: 2 bar(a)). Under these conditions, as shown in Fig. 5, CO_2 and H_2 permeabilities were 1486 Barrer and 465 Barrer, respectively. Since (i) the measurement conditions during the present and previous [22] investigations were identical and (ii) inlet CO_2 and H_2 concentrations were almost the same, the differences in membrane behavior may be associated with the quantity and quality of minor impurities in the gases. In this study, the only added background gas was H_2S, while in case of the real bioreactor [22], a much more complex, multi-compound trace gas composition can be assumed, potentially comprising of N_2, water vapor, NH_3, H_2S, etc.

For instance, among these compounds, water vapor was found to have permeability as high as 40,000 Barrer for PDMS at 30 °C [45], which is one-two order of magnitude higher than CO_2 and

H_2 permeabilities commonly reported for this polymer. Attributed to this extreme permeation rate, moisture may induce concentration polarization [46] and due to its special characteristics it can alter the behavior of other gaseous substances in the membrane [13].

Therefore, experiments should be carried out with these low concentration substances in order to better understand the observable differences in membrane performance during the permeation of binary, ternary and raw gas mixtures containing (bio)hydrogen. Moreover, these tests ought to be conducted in long-terms to reveal the components effect on membrane integrity and durability/stability since exposure to certain aggressive substances may cause the deterioration of separation properties over time [13,47]. These practical data can be quite useful for possible future implementations and also to perform cost-benefit analysis for cases when dark fermentative hydrogen is aimed to be purified by gas separation membrane applications.

It must be noted that the commercial PDMS membrane in this work was not capable of ensuring high enough hydrogen concentration for direct utilization in fuel cells, which is just similar that was experienced with a commercialized polyimide module investigated earlier [14]. The highest steady-state H_2 concentration of the retentate in this study was 73.75 vol.% (recovery: 0.34; feed composition: 35 vol.% CO_2, 65 vol.% H_2). This implies that cascade membrane technology should be established for satisfactory purification efficiency or alternatively, membrane gas separation may be complemented with post-treatment methods e.g. classical absorption.

Recently, Lassmann et al. [48] addressed the upgrading of dark fermentative gas mixture by polymer membranes. In essence, three different, two-step gas purification systems – involving intermediary retantate or permeate recirculations as common elements of cascade gas separation using membranes [49,50] – were designed and assessed employing either H_2- or CO_2-selective membranes. The conclusion was that online gas purification was possible, but the process has depended on the stability of the fermentation. This is consistent with our results published lately [22], where a buffering tank was built-in between the fermenter and the membrane separation unit to stabilize feed gas composition and ensure a smooth process operation. Furthermore, Lassmann and colleagues [48] enlightened that the insertion of a second-stage membrane application could considerably enhance product (H_2) quality as compared to single-stage system. It was also suggested that CO_2-selective materials are favored for H_2-enrichment because of the lower specific energy requirement of the purification. According to these findings, the H_2-rejective PDMS applied in this work can be a feasible and worthy material for further research to construct more sufficient H_2-recovery technology.

4. Conclusions

In this work a commercial PDMS membrane module was evaluated for hydrogen separation with binary and ternary gas mixtures and various recovery ratios. It was demonstrated that gas composition had a significant impact on both (i) gas permeabilities and (ii) membrane CO_2/H_2 selectivity. The results indicated that the presence of trace gas, in particular H_2S in the model biohydrogen mixture notably influenced the permeability of gases as compared to those determined in binary gas experiments. The PDMS membrane investigated in this study showed modest performance (which is consistent with previous literature reports) and with further design considerations (e.g. in multi-stage arrangement) may be used to construct efficient downstream systems for biohydrogen technology.

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References

[1] J. Madarász, D. Németh, J. Bakos, L. Gubicza, P. Bakonyi, Solvent-free enzymatic process for biolubricant production in continuous microfluidic reactor, J. Clean. Prod. 93 (2015) 140–144.
[2] L. Koók, T. Rózsenberszki, N. Nemestóthy, K. Bélafi-Bakó, P. Bakonyi, Bioelectrochemical treatment of municipal waste liquor in microbial fuel cells for energy valorization, J. Clean. Prod. (2015), http://dx.doi.org/10.1016/j.jclepro.2015.06.116.
[3] G. Kumar, P. Bakonyi, S. Periyasamy, S.H. Kim, N. Nemestóthy, K. Bélafi-Bakó, Lignocellulose biohydrogen: practical challenges and recent progress, Renew. Sustain. Energy Rev. 44 (2015) 728–737.
[4] G. Kumar, P. Sivagurunathan, S.H. Kim, P. Bakonyi, C.Y. Lin, Modelling and optimization of biohydrogen production from de-oiled Jatropha using the response surface method, Arab. J. Sci. Eng. 40 (2015) 15–22.
[5] T. Rózsenberszki, L. Koók, D. Hutvágner, N. Nemestóthy, K. Bélafi-Bakó, P. Bakonyi, R. Kurdi, A. Sarkady, Comparison of anaerobic degradation processes for bioenergy generation from liquid fraction of pressed solid waste, Waste Biomass Valorization 6 (2015) 465–473.
[6] P. Bakonyi, N. Nemestóthy, V. Simon, K. Bélafi-Bakó, Fermentative hydrogen production in anaerobic membrane bioreactors: a review, Bioresour. Technol. 156 (2014) 357–363.
[7] P. Bakonyi, N. Nemestóthy, É. Lövitusz, K. Bélafi-Bakó, Application of Plackett–Burman experimental design to optimize biohydrogen fermentation by *E. coli* (XL1-BLUE), Int. J. Hydrogen Energy 36 (2011) 13949–13954.
[8] P. Bakonyi, N. Nemestóthy, J. Ramirez, G. Ruiz-Filippi, K. Bélafi-Bakó, *Escherichia coli* (XL1-BLUE) for continuous fermentation of bioH_2 and its separation by polyimide membrane, Int. J. Hydrogen Energy 37 (2012) 623–630.
[9] P. Bakonyi, B. Borza, K. Orlovits, V. Simon, N. Nemestóthy, K. Bélafi-Bakó, Fermentative hydrogen production by conventionally and unconventionally heat pretreated seed cultures: a comparative assessment, Int. J. Hydrogen Energy 39 (2014) 5589–5596.
[10] G. Kumar, P. Bakonyi, S. Periyasamy, S.H. Kim, N. Nemestóthy, K. Bélafi-Bakó, C. Y. Lin, Enhanced biohydrogen production from beverage industrial wastewater using external nitrogen sources and bioaugmentation with facultative anaerobic strains, J. Biosci. Bioeng. 120 (2015) 155–160.
[11] P. Bakonyi, N. Nemestóthy, V. Simon, K. Bélafi-Bakó, Review on the start-up experiences of continuous fermentative hydrogen producing bioreactors, Renew. Sustain. Energy Rev. 40 (2014) 806–813.
[12] I. Rivera, G. Buitrón, P. Bakonyi, N. Nemestóthy, K. Bélafi-Bakó, Hydrogen production in a microbial electrolysis cell fed with a dark fermentation effluent, J. Appl. Electrochem. 45 (2015) 1223–1229.
[13] P. Bakonyi, N. Nemestóthy, K. Bélafi-Bakó, Biohydrogen purification by membranes: an overview on the operational conditions affecting the performance of non-porous, polymeric and ionic liquid based gas separation membranes, Int. J. Hydrogen Energy 38 (2013) 9673–9687.
[14] P. Bakonyi, G. Kumar, N. Nemestóthy, C.Y. Lin, K. Bélafi-Bakó, Biohydrogen purification using a commercial polyimide membrane module: studying the effects of some process variables, Int. J. Hydrogen Energy 38 (2013) 15092–15099.
[15] P. Li, Z. Wang, Z. Qiao, Y. Liu, X. Cao, W. Li, J. Wang, S. Wang, Recent developments in membranes for efficient hydrogen purification, J. Membr. Sci. (2015), http://dx.doi.org/10.1016/j.memsci.2015.08.010.
[16] P. Cserjési, N. Nemestóthy, A. Vass, Zs. Csanádi, K. Bélafi-Bakó, Study on gas separation by supported liquid membranes applying novel ionic liquids, Desalination 245 (2009) 743–747.
[17] P. Cserjési, N. Nemestóthy, K. Bélafi-Bakó, Gas separation properties of supported liquid membranes prepared with unconventional ionic liquids, J. Membr. Sci. 349 (2010) 6–11.
[18] L. Shao, B.T. Low, T.S. Chung, A.R. Greenberg, Polymeric membranes for the hydrogen economy: contemporary approaches and prospects for the future, J. Membr. Sci. 327 (2009) 18–31.
[19] D.F. Sanders, Z.P. Smith, R. Guo, L.M. Robeson, J.E. McGrath, D.R. Paul, B.D. Freeman, Energy-efficient polymeric gas separation membranes for a sustainable future: a review, Polymer 54 (2013) 4729–4761.
[20] J.E. Ramírez-Morales, E. Tapia-Venegas, N. Nemestóthy, P. Bakonyi, K. Bélafi-Bakó, G. Ruiz-Filippi, Evaluation of two gas membrane modules for fermentative hydrogen separation, Int. J. Hydrogen Energy 38 (2013) 14042–14052.
[21] J.E. Ramírez-Morales, E. Tapia-Venegas, J. Toledo-Alarcón, G. Ruiz-Filippi, Simultaneous production and separation of biohydrogen in mixed culture systems by continuous dark fermentation, Water Sci. Technol. 71 (2015) 1271–1285.

[22] P. Bakonyi, N. Nemestóthy, J. Lankó, I. Rivera, G. Buitrón, K. Bélafi-Bakó, Simultaneous biohydrogen production and purification in a double-membrane bioreactor system, Int. J. Hydrogen Energy 40 (2015) 1690–1697.

[23] A. Makaruk, M. Miltner, M. Harasek, Membrane biogas upgrading processes for the production of natural gas substitute, Sep. Purif. Technol. 74 (2010) 83–92.

[24] K.A. Lokhandwala, I. Pinnau, Z. He, K.D. Amo, A.R. DaCosta, J.G. Wijmans, R.W. Baker, Membrane separation of nitrogen from natural gas: a case study from membrane synthesis to commercial deployment, J. Membr. Sci. 346 (2010) 270–279.

[25] C.H. Lau, P. Li, F. Li, T.S. Chung, D.R. Paul, Reverse-selective polymeric membranes for gas separations, Prog. Polym. Sci. 38 (2013) 740–766.

[26] C.A. Scholes, G.W. Stevens, S.E. Kentish, The effect of hydrogen sulfide, carbon monoxide and water on the performance of a PDMS membrane in carbon dioxide/nitrogen separation, J. Membr. Sci. 350 (2010) 189–199.

[27] S.R. Reijerkerk, M.H. Knoef, K. Nijmeijer, M. Wessling, Poly(ethylene glycol) and poly(dimethyl siloxane): combining their advantages into efficient CO_2 gas separation membranes, J. Membr. Sci. 352 (2010) 126–135.

[28] X. Wang, H. Chen, L. Zhang, R. Yu, R. Qu, L. Yang, Effects of coexistent gaseous components and fine particles in the flue gas on CO_2 separation by flat-sheet polysulfone membranes, J. Membr. Sci. 470 (2014) 237–245.

[29] D.B. Levin, R. Chahine, Challenges for renewable hydrogen production from biomass, Int. J. Hydrogen Energy 35 (2010) 4962–4969.

[30] H.S. Lee, W.F.J. Vermaas, B.E. Rittmann, Biological hydrogen production: prospects and challenges, Trends Biotechnol. 28 (2010) 262–271.

[31] C.Y. Lin, H.P. Chen, Sulfate effect on fermentative hydrogen production using anaerobic mixed microflora, Int. J. Hydrogen Energy 31 (2006) 953–960.

[32] M.W. Uddin, M.B. Hagg, Natural gas sweetening – the effect on CO_2–CH_4 separation after exposing a facilitated transport membrane to hydrogen sulfide and higher hydrocarbons, J. Membr. Sci. 423–424 (2012) 143–149.

[33] M.K. Barillas, R.M. Enick, M. O'Brien, R. Perry, D.R. Luebke, B.D. Morreale, The CO_2 permeability and mixed gas CO_2/H_2 selectivity of membranes composed of CO_2-philic polymers, J. Membr. Sci. 372 (2011) 29–39.

[34] H. Lin, H. Zhenjie, Z. Sun, J. Vu, S. Ng, M. Mohammed, J. Kniep, T.C. Merkel, T. Wu, R.C. Lambrecht, CO_2-selective membranes for hydrogen production and CO_2 capture – Part I: membrane development, J. Membr. Sci. 457 (2014) 149–161.

[35] T.C. Merkel, R.P. Gupta, B.S. Turk, B.D. Freeman, Mixed-gas permeation of syngas components in poly(dimethylsiloxane) and poly(1-trimethylsilyl-1-propyne) at elevated temperatures, J. Membr. Sci. 191 (2001) 85–94.

[36] M. Nour, K. Berean, A. Chrimes, A.S. Zoolfakar, K. Latham, C. McSweeney, M.R. Field, S. Sriram, K. Kalantar-zadeh, J.Z. Ou, Silver nanoparticle/PDMS nanocomposite catalytic membranes for H_2S gas removal, J. Membr. Sci. 470 (2014) 346–355.

[37] M.P. Chenar, H. Savoji, M. Soltanieh, T. Matsuura, S. Tabe, Removal of hydrogen sulfide from methane using commercial polyphenylene oxide and Cardo-type polyimide hollow fiber membranes, Korean J. Chem. Eng. 28 (2011) 902–913.

[38] S.C. Kumbharkar, Y. Liu, K. Li, High performance polybenzimidazole based asymmetric hollow fibre membranes for H_2/CO_2 separation, J. Membr. Sci. 375 (2011) 231–240.

[39] P. Li, Z. Wang, Y. Liu, S. Zhao, J. Wang, S. Wang, A synergistic strategy via the combination of multiple functional groups into membranes towards superior CO_2 separation performances, J. Membr. Sci. 476 (2015) 243–255.

[40] C.Y. Lin, S.Y. Wu, P.J. Lin, J.S. Chang, C.H. Hung, K.S. Lee, F.Y. Chang, C.Y. Chu, C. H. Cheng, C.H. Lay, A.C. Chang, Pilot-scale hydrogen fermentation system start-up performance, Int. J. Hydrogen Energy 35 (2010) 13452–13457.

[41] S.A. Stern, V.M. Shah, B.J. Hardy, Structure–permeability relationships in silicone polymers, J. Polym. Sci. Part B: Polym. Phys. 25 (1987) 1263–1298.

[42] M. Sadrzadeh, K. Shahidi, T. Mohammadi, Effect of operating parameters on pure and mixed gas permeation properties of a synthesized composite PDMS/PA membrane, J. Membr. Sci. 342 (2009) 327–340.

[43] T.C. Merkel, V.I. Bondar, K. Nagai, B.D. Freeman, I. Pinnau, Gas sorption, diffusion, and permeation in poly(dimethylsiloxane), J. Polym. Sci. Part B: Polym. Phys. 38 (2000) 415–434.

[44] X. Ren, J. Ren, M. Deng, Poly(amide-6-b-ethylene oxide) membranes for sour gas separation, Sep. Purif. Technol. 89 (2012) 1–8.

[45] S.J. Metz, W.J.C. van de Ven, J. Potreck, M.H.V. Mulder, M. Wessling, Transport of water vapor and inert gas mixtures through highly selective and highly permeable polymer membranes, J. Membr. Sci. 251 (2005) 29–41.

[46] G.Q. Chen, C.A. Scholes, G.G. Qiao, S.E. Kentish, Water vapor permeation in polyimide membranes, J. Membr. Sci. 379 (2011) 479–487.

[47] P. Dolejš, V. Poštulka, Z. Sedláková, V. Jandová, J. Vejražka, E. Esposito, J.C. Jansen, P. Izák, Simultaneous hydrogen sulphide and carbon dioxide removal from biogas by water–swollen reverse osmosis membrane, Sep. Purif. Technol. 131 (2014) 108–116.

[48] T. Lassmann, M. Miltner, M. Harasek, A. Makaruk, W. Wukovits, A. Friedl, The purification of fermentatively produced hydrogen using membrane technology: a simulation based on small-scale pilot plant results, Clean Technol. Environ. Policy (2015), http://dx.doi.org/10.1007/s10098-015-0997-7.

[49] R. Pathare, R. Agrawal, Design of membrane cascade for gas separation, J. Membr. Sci. 364 (2010) 263–277.

[50] J. Hao, P.A. Rice, S.A. Stern, Upgrading low-quality natural gas with H_2S- and CO_2-selective polymer membranes Part II. Process design, economics, and sensitivity study of membrane stages with recycle streams, J. Membr. Sci. 320 (2008) 108–122.

[51] C.A. Scholes, S.E. Kentish, G.W. Stevens, Effects of minor components in carbon dioxide capture using polymeric gas separation membranes, Sep. Purif. Rev. 38 (2009) 1–44.

[52] H. Lin, E.V. Wagner, B.D. Freeman, L.G. Toy, R.P. Gupta, Plasticization enhanced hydrogen purification using polymeric membranes, Science 311 (2006) 639–642.

[53] S.A. Stern, H. Kawakami, A.Y. Houde, G. Zhou, Material and process for separating carbon dioxide from methane, US Patent 5591250 A (1997).