



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



P. Bakonyi^{a,*}, F. Bogdán^b, V. Kocsi^b, N. Nemestóthy^b, K. Bélafi-Bakó^b, G. Buitrón^a

^aLaboratory for Research on Advanced Processes for Water Treatment, Instituto de Ingeniería, Unidad Académica Juriquilla, Universidad Nacional Autónoma de México, Blvd. Juriquilla 3001, Querétaro 76230, Mexico

^bResearch Institute on Bioengineering, Membrane Technology and Energetics, University of Pannonia, Egyetem ut 10, 8200 Veszprém, Hungary

ARTICLE INFO

Article history:

Received 25 September 2015

Received in revised form 11 November 2015

Accepted 12 November 2015

Available online 14 November 2015

Keywords:

Biohydrogen

Purification

PDMS

Membrane

Gas separation

Hydrogen sulfide

ABSTRACT

This work reports on the separation of biohydrogen using a hollow-fiber PDMS membrane. The performance of the module was evaluated using binary CO₂/H₂ (35–65 vol.% H₂ content) and ternary CO₂/H₂/H₂S mixtures (50 vol.% H₂, 50 vol.% CO₂, 25–175 ppm H₂S) and the effect of recovery and gas composition (with special focus on hydrogen sulfide content) was revealed. H₂S is a potential impurity of the raw gas coming from steady-state, dark fermentative hydrogen producing bioreactors. The results indicated that H₂S could have a concentration-dependent impact on membrane behavior and affected the obtainable CO₂/H₂ 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.

© 2015 Elsevier B.V. All rights reserved.

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 H₂-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 H₂ may be obtained separately, in classical dark fermentation H₂ is formed in a complex gaseous mixture and therefore is accompanied by certain major (e.g. CO₂) and minor impurities (e.g. H₂S, N₂, water vapor, etc.) [13]. Hence, the fermenter off-gas, which can comprise roughly of 35–65 vol.% H₂ [14] has to be upgraded for efficient utilization e.g. in PEM fuel cells.

* Corresponding author.

E-mail addresses: bakonyipeter85@gmail.com, PBakonyi@iingen.unam.mx (P. Bakonyi).

To accomplish the enrichment of H₂ 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

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 CO₂ through such membrane exceeds that of less condensable, light compounds such as H₂ [25,26]. Thus, PDMS is characterized with a remarkable permeability for CO₂ and a moderate CO₂/H₂ selectivity [22,27]. Lately, the properties of a commercial PDMS membrane module were determined for H₂ enrichment using real fermentation gas mixture coming from a steady-state fermenter unit [22]. It has turned out that PDMS reflected decent CO₂/H₂ 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 H₂, CO₂ 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, H₂S is a potential contaminant with a concentration that normally does not exceed several ten to hundred ppm [29–31]. H₂S 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 H₂S removal and/or H₂ 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 H₂S with various concentrations.

Therefore, in this work, the influence of H₂S on the performance of a commercially available poly(dimethylsiloxane) membrane during H₂/CO₂ permeation was experimentally assessed. Firstly, a commercial PDMS hollow-fiber membrane was exposed to binary H₂/CO₂ mixtures with three different compositions. Afterward, ternary gases were used containing various H₂S 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. H₂S) applying membrane separation technology can be of practical importance [13,51], such experimental studies in the area of fermentatively produced biohydrogen purification are scantily 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 cm².

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 H₂/CO₂ mixtures (35, 50, 65 vol.% CO₂ content), H₂ (99.9%) and CO₂ (industrial grade)

were applied. H₂ and CO₂ 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 H₂S (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 CO₂. Thereafter, the gas bag was attached to a Kipp generator, in which pure H₂S was evolved by reacting solid FeS with HCl solution. After finishing the addition of H₂S to CO₂, the mixture was homogenized and actual H₂S concentration in the CO₂/H₂S mixture was checked by Dräger X-am[®] 7000 device (Drägerwerk AG & Co. KGaA, measuring range for hydrogen sulfide: 0–1000 ppm). If H₂S concentration was still higher than required, further amount of CO₂ was supplemented and H₂S content was rechecked. These steps were repeated until the pre-calculated concentration of H₂S – taking into account the diluting impact of H₂ in the next stage – has been achieved. Thereafter, the mixture of CO₂ and H₂S was complemented with H₂ gas in a several consecutive steps in order to carefully attain the proper H₂/CO₂ ratio as well as desired H₂S concentration for the measurements. The final H₂ and CO₂ contents of the mixture were determined by gas chromatography method as referred in our earlier work [9]. The mixing accuracy for H₂ and CO₂ was ±1 vol.%, while for H₂S it has not exceeded ±5 ppm. The necessity of this multiple-step, mixing-diluting approach to deliver H₂/CO₂/H₂S mixtures was attributed to the sensitivity of electrochemical H₂S sensor in Dräger X-am[®] 7000 to the presence of molecular H₂ gas. In other words, H₂S concentration was possible to measure and precisely adjust only before CO₂/H₂S binary gas was complemented with H₂.

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 H₂ and CO₂ permeabilities in Barrer (1 Barrer equals to 10⁻¹⁰ cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹) as well as CO₂/H₂ selectivity values presented thoroughly in this study were calculated as

Download English Version:

<https://daneshyari.com/en/article/640261>

Download Persian Version:

<https://daneshyari.com/article/640261>

[Daneshyari.com](https://daneshyari.com)