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TWO-STAGE MEMBRANE SEPARATION PROCESS FOR BIOHYDROGEN RECOVERY

Porous and non-porous gas separation membranes were used for concentration of biohydrogen produced by a heterotrophic hyper-thermophilic, anaerobic micro-organisms. A laboratory-scale integrated system was designed and built based on a liquid seal system and more than 70% hydrogen concentration was achieved from the initial gaseous mixture containing hydrogen, carbon dioxide and nitrogen. Liquid absorption and desorption of the carbon dioxide were also studied.

Keywords: *gas separation, adsorption, porous membranes, integrated system*

1. INTRODUCTION

Hydrogen is a promising environmentally safe alternative energy source, which has high energy density and only water steam is produced when it burns. The fuel cells are considered to be its most important application. Fuel cells are electrochemical devices that create an electron flow of charged ions. A variety of different fuel-cell systems have been developed. They differ in the type of electrolyte used but hydrogen is a suitable fuel for all types [1].

Currently, hydrogen is produced, almost exclusively, by electrolysis of water or by steam reformation of methane. However, there is an extensive research to produce hydrogen in micro-organic way (biohydrogen).

There are two main routes to produce biohydrogen: water shift by biophotolysis (by sunlight) and dark fermentation [2], [3]. Since the micro-organisms by dark fermentation produce two orders of magnitude more hydrogen, a heterotrophic, hyper-thermophilic (growing optimally at 85 °C), anaerobic bacteria were studied. They

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eliminate excessive electrons formed at the end of a multi-step degradation process with hydrogenase enzyme in a form of hydrogen [4] (figure 1).

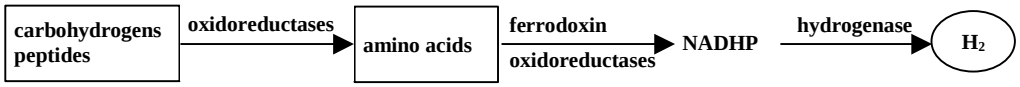

Fig. 1. Biochemical pathway of hydrogen production [3]

The primary end-products of the fermentative metabolism are carbon dioxide and hydrogen. There is also nitrogen present, assuring inert atmosphere in the bioreactor. The composition of the gas in the fermentor – without water vapour – is approximately as follows: 25–35% of H_2, 20% of CO_2 and 45–55% of N_2. The utilisation of the hydrogen in fuel cells needs, however, its higher purity, therefore the hydrogen must be separated from the other gases. Among the existing separation techniques gas separation by polymeric membranes seems to be the best choice. In traditional systems for gas separation, generally compressors and vacuum pumps are used to produce high pressure [5], [6]. To operate these systems a minimum volume rate of 1–2 dm^3/min is needed, which is far beyond a laboratory scale of hydrogen-producing system. (The volume of a headspace in a 1–20 dm^3 fermentor is altogether 0.1–10 dm^3). Thus a completely new system had to be designed and built for the adjusting/controlling the pressure; moreover, for delivery, controlling and collecting the gaseous mixtures. The objective of this work was to develop a suitable and sustainable system based on liquid seals.

2. MATERIALS AND METHODS

The experimental set-up consisting of integrated membrane separation system based on liquid seal system used is similar to that presented in [7]. Samples from gas mixtures were taken by a gastight syringe (Hamilton, 1000 cm^3) and were analysed with a gas chromatograp (Hewlett Packard 5890 Series II) equipped with a carbonplot column and an integrator (Hewlett Packard 3394 A). The operation parameters of the gas chromatography were as follows:

- temperature of column: 50 °C,
- injection temperature: 60 °C,
- temperature of detector: 150 °C,
- split: 60 kPa.

Extended experiments were performed with porous membranes to select the membrane of the best separation properties. It was found that the high-density polyethylene (HDPE) membrane with the pore diameter of 0.7 μm had relatively high value of selectivity coefficient and the flux was also acceptable, so it was used for further experiments.

Non-porous polyethersulphone-polyimide (PES-PI) membrane (from University of Twente, the Netherlands) was applied to separate gaseous nitrogen and hydrogen.

Liquid absorption test measurements were carried out in a separately constructed apparatus (figure 2).

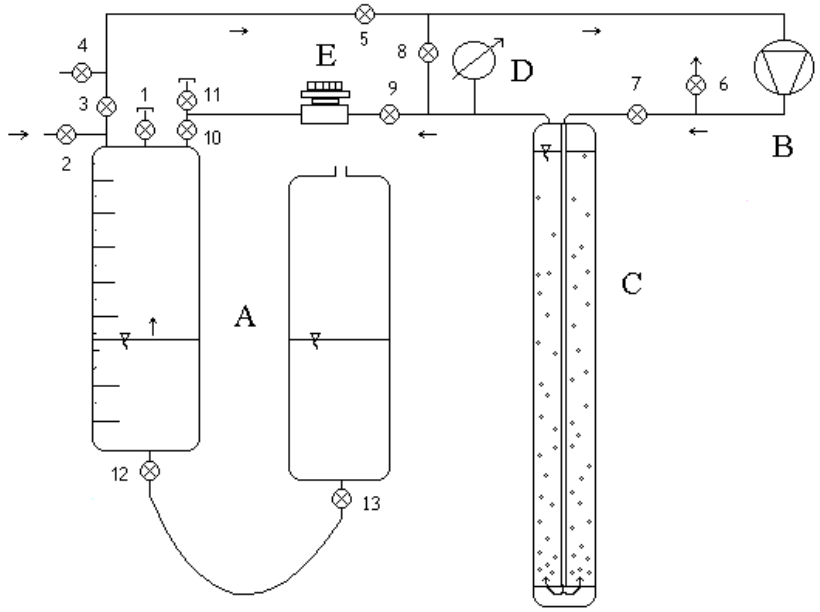

Fig. 2. Scheme of the gas absorption equipment:
gas burette with liquid sealing (A), peristaltic pump (B), absorption vessel (C),
vacomanometer (D), reductor (E), valves (1–12)

The feed gaseous mixture (nitrogen, hydrogen, and carbon dioxide) is in the gas burette with a liquid sealing. The sysytem is supplied with pure gases from a balloon through valve 2. Samples are taken through a septum at valve 1. Copper tubes are used in construction of the system. A total volume of absorption vessel is 270 cm^3; absorption liquid could be distilled water, solution of ethanol amine or potassium carbonate. The mass transfer of components is improved by a glass frit. Gaseous mixtures were circulated by a peristaltic pump. The overpressure was adjusted by a reductor and checked by vacomanometer. In the vessel "A" the pressure is kept on atmospheric level and the volume decrease can be read on the scale.

3. RESULTS AND DISCUSSION

An integrated process based on a liquid seal system was designed and built for re-

covery and concentration of biohydrogen from the fermentor (figure 3). Since the feed gaseous mixture contained hydrogen, carbon dioxide and nitrogen, a two-stage membrane process (not shown in details) and biological system were integrated. When the gaseous mixture is regularly taken out of the headspace of the fermentor by an elastic-wall vessel, in the first step a porous membrane is used for separation of CO_2 and H_2 and then in the second step its permeate is directed to a non-porous membrane, where hydrogen is concentrated. Thus the integrated system allows obtaining a hydrogen-rich gaseous mixture (up to 70% or higher hydrogen concentration [7]), which is suitable for, e.g. fuel cell applications.

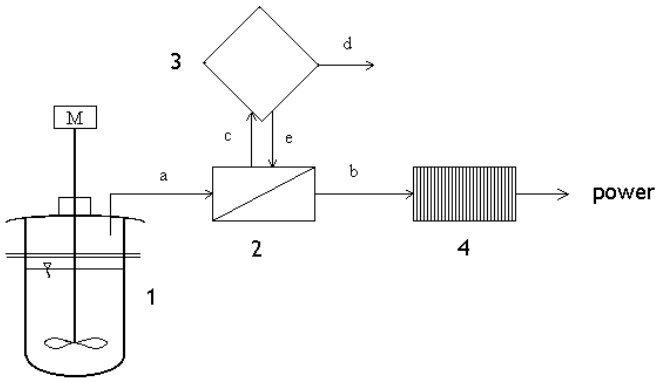

Fig. 3. Separation techniques combined with biological system:
1 – fermentor, 2 – gas separation processes, 3 – liquid absorption, 4 – fuel cell

As non-porous membrane a polyimide-polyethersulphone hollow-fiber membrane module was applied. It was developed specially for separation of N_2/H_2 [8], [9] and its selectivity factor of 42 was high enough to achieve a hydrogen-rich gas stream.

Porous membranes were used to separate CO_2 from H_2 based on the Knudsen mechanism. In such a case, the membrane selectivity depends only on the differences in their molecular weights. The separation factor in the case of CO_2 and H_2 is: $44^{0.5}/2^{0.5} = 4.7$, i.e. it is high enough to make the hydrogen purification possible.

During the separation process, however, CO_2 was gradually accumulated in the retentate of the porous membrane module, decreasing the efficiency of the membrane process. Therefore another separation step was considered: absorption of CO_2 by a liquid and then its desorption.

Absorption experiments were carried out in the equipment depicted to select the most suitable liquid for a particular purpose. Aqueous solutions of monoethanol amine were found to be the most effective liquid absorber, however, the desorption of CO_2 seems too difficult (it proceeds at over 130 °C). Potassium carbonate and distilled water have somewhat better desorption properties, but their absorption capacities are much less than those of ethanol amine solutions. Thus it seems that a compromise

should be reached.

Based on our results we have revealed that biohydrogen can be recovered and concentrated by integrated membrane processes, using porous and non-porous membranes. However, it is sensible to complete these techniques with an absorption step, which allows separation of CO_2.

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