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A novel gas separation integrated membrane bioreactor to evaluate the impact of self-generated biogas recycling on continuous hydrogen fermentation

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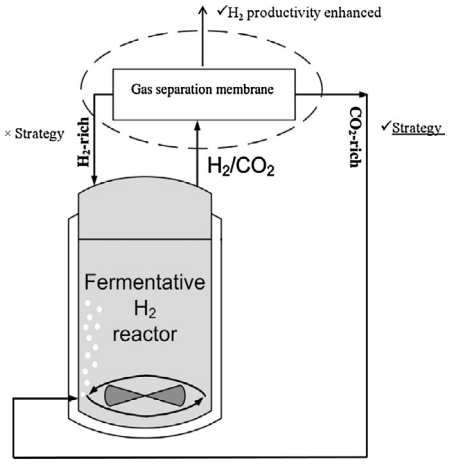
HIGHLIGHTS

- A Gas Separation Membrane Bioreactor was designed to improve H_2 production.
- Headspace gas after enrichment by PDMS membranes was used for reactor sparging.
- Stripping the bioreactor with a CO_2-enriched gas enhanced the H_2 fermentation.

GRAPHICAL ABSTRACT



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ABSTRACT

A *Gas Separation Membrane Bioreactor* (GSMBR) by integrating membrane technology with a continuous biohydrogen fermenter was designed. The feasibility of this novel configuration for the improvement of hydrogen production capacity was tested by stripping the fermentation liquor with CO_2- and H_2-enriched gases, obtained directly from the bioreactor headspace. The results indicated that sparging the bioreactor with the CO_2-concentrated fraction of the membrane separation unit (consisting of two PDMS modules) enhanced the steady-state H_2 productivity (8.9–9.2 L H_2/L-d) compared to the membrane-less control CSTR to be characterized with 6.96–7.35 L H_2/L-d values. On the other hand, purging with the H_2-rich gas strongly depressed the achievable productivity (2.7–3.03 L H_2/L-d). Microbial community structure and soluble metabolic products were monitored to assess the GSMBR behavior. The study demonstrated that stripping the bioH_2 fermenter with its own, self-generated atmosphere after adjusting its composition (to higher CO_2-content) can be a promising way to intensify dark fermentative H_2 evolution.

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1. Introduction

The development of microbiologically-driven hydrogen technology has been a leading direction of gaseous biofuel research. Biohydrogen, depending on the properties of bacterial catalysts, can be produced in a number of ways e.g. by photobiological, bioelectrochemical and dark fermentative processes [1–3]. Dark fermentation, from practical aspects, has definitive advantages such as the capability of generating H_2 from a broad range of feedstock, which include, but are not limited to municipal wastes [4], industrial by-products e.g. glycerol [5], excess activated sludge [6], food waste [7], microalgal biomass [8,9], wastewaters [10,11], lignocellulose materials [12–14]. Moreover, this production method is advanced enough to demonstrate real potential for scale-up [15]. Nevertheless, some issues with dark fermentative H_2 production still have to be managed for better sustainability and competitiveness [16,17]. Recent review articles by Sivagurunathan et al. [18], Kumar et al. [19] and Bakonyi et al. [20] have emphasized the need for process improvement for viable hydrogen fermentation systems working in continuous mode. Accordingly, research priority should be set to resolve challenges associated with areas such as (i) inoculum properties and selection, (ii) optimization of bioprocess operating parameters and (iii) bioreactor design [18–20]. In this last aspect, Jung et al. [21] overviewed the achievements of the field and it can be pointed out that the recent progress has yielded some attractive configurations such as anaerobic membrane bioreactors (AnMBRs), which can be seen as promising alternatives for the way forward. Conventional AnMBRs for hydrogen production apply porous, micro- and ultrafiltration membranes in order to accumulate and reuse the precious microbial catalysts by providing sufficiently long biomass residence time, which can be a key to achieve sufficient raw material to H_2 conversion [22].

Nonetheless, it has been shown that besides the classical membrane bioreactors, AnMBR can be designed by coupling gas separation membranes (rather than water filtration ones) to hydrogen fermenters. These systems can be called as *Gas Separation Membrane Bioreactors* (GSMBR) [23] or alternatively, *Hydrogen Extractive Membrane Bioreactors* [24], which have a vital role in facilitating the in-site purification of biohydrogen from the reactor off-gas [25]. In addition to the opportunities that GSMBRs can offer for integrated bioH_2 enrichment, these systems may possess a so far unexplored possibility for the intensification of H_2-producing biosystems. This subject will be discussed in the next section (Section 1.1) and the focused survey (based on the careful analysis of the most relevant, already published literature) shall point to key-considerations that make the GSMBR arrangement worthy for research. Subsequently, driven by the assessment in Section 1.1, the particular objectives of this paper are laid down in Section 1.2.

1.1. Possibilities of GSMBR for the biohydrogen technology

One key-driver of advanced bioreactor design for biohydrogen technology is that conventional processes e.g. those relying on CSTRs can be limited by insufficient mass transfer. For example, Tapia-Venegas et al. [26] inferred by studying hydrogen evolution in a two-stage CSTR cascade that notable amounts of H_2 can remain in the liquid phase rather than passing to the headspace. This phenomenon leads to an apparent contradiction between the theoretical and practical H_2 production performances [27] and in such a case, it is a threat that H_2 leaves the system unrecovered with the fermentation effluent.

Although H_2 has a basically poor solubility in aqueous media, Zhang et al. [28] explained that high dissolved hydrogen concentrations may be experienced as a consequence of so-called *supersaturation*, which can occur when the rate of H_2 production exceeds that of the liquid-to-gaseous phase molecular hydrogen gas transfer. As a side-effect of excessive H_2 accumulation in the fermentation liquor, structural changes in the microbial community may be induced (in terms of composition and relative abundance of species) via interspecies hydrogen transfer, which means the uptake and subsequent utilization of H_2 as a substrate in various H_2-scavenging reactions by homoacetogenic and propionic bacteria, methanogenic archaea, etc. present in mixed culture bioreactors [29]. Therefore, actions to improve H_2 desorption could result in the maintenance of favorable thermodynamic circumstances for H_2 production [30]. As a matter of fact, investigations showed that issues related to dissolved hydrogen concentrations can be mitigated by the deployment of gas stripping using N_2 [30–33]. However, it is noteworthy that the application of inert gases i.e. nitrogen for bioreactor purging brings at least two disadvantages. From an economic point of view, it brings an extra cost to the process. Moreover, technologically speaking, it dilutes the fermenter off-gas and in such a way, makes the downstream (H_2 purification and enrichment) more difficult [17,34]. To overcome these problems, use of the internal, self-generated biogas of the fermenter can be considered. As concluded by Clark et al. [35], feasible reactor stripping – especially when thinking about scale-up – should be carried out with a gas produced onsite. Results on the effect of simple biogas recycling indicated relative enhancement of H_2 formation compared to that attained under control circumstances [36,37]. However, even if the own biogas of the fermenter is applied for such a purpose, its composition can be a crucial factor to deal with.

Research studies presented that reactor sparging with CO_2 was able to promote biocatalyzed H_2 formation [37–39]. A benefit of carbon dioxide is that it is a naturally-occurring component of the atmosphere found in H_2 fermenter's headspace. Hence, it is a reasonable assumption that the production of a CO_2-enriched stream from the reactor's own, self-generated gas mixture and its subsequent employment for stripping could be a beneficial strategy. To realize CO_2-enrichment, gas separation membrane technology coupled to the bioreactors (to form a GSMBR) can be recommended as a solution (Fig. 1). In the GSMBR construction, as a result of the *in situ* separation, the headspace gas is divided to 2 gas streams (the permeate and retentate), containing higher concentrations of either H_2 or CO_2 [40]. Consecutively, at least one of the two streams (the permeate or retentate) is to be recycled to the bottom of the reactor so as to realize the intended purging of liquid phase and put the GSMBR to work (Fig. 1).

1.2. Objective and novelty of the study

Based on the above considerations in Section 1.1, the GSMBR seems to have a potential to improve the biohydrogen generation by purging the reactor with its internal biogas of modified composition (Fig. 1). However, to our best knowledge, no experimental results (proof-of-concept studies) are available to confirm this idea. Consequently, to address this existing gap of knowledge, a GSMBR was constructed – by combining laboratory-scale, PDMS gas membrane modules with a H_2-producing CSTR – in this work to examine its applicability for the enhancement of continuous hydrogen production. In the course of the measurements, several, distinct operational periods were monitored to reveal the effect of purging intensity (i.e. volumetric flow rate) and sparging gas quality (varied H_2 and CO_2 contents in the membrane permeate and retentate). The results were evaluated by establishing correlations between the system's H_2 productivity and the gas recycling conditions. Moreover, the H_2 discrepancy factor (meaning the comparison of actual and theoretical H_2 formation capacities based on mass balance using quantified soluble metabolic products) and