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Review

Enhancement of dark fermentative H_2 production by gas separation membranes: A review

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ABSTRACT

Biohydrogen production via dark fermentation is currently the most developed method considering its practical readiness for scale-up. However, technological issues to be resolved are still identifiable and should be of concern, particularly in terms of internal mass transfer. If sufficient liquid-to-gas H_2 mass transfer rates are not ensured, serious problems associated with the recovery of biohydrogen and consequent inhibition of the process can occur. Therefore, the continuous and effective removal of H_2 gas is required, which can be performed using gas separation membranes. In this review, we aim to analyze the literature experiences and knowledge regarding mass transfer enhancement approaches and show how membranes may contribute to this task by simultaneously processing the internal (headspace) gas, consisting mainly of H_2 and CO_2. Promising strategies related to biogas recirculation and integrated schemes using membranes will be presented and discussed to detect potential future research directions for improving biohydrogen technology.

1. Introduction

Biohydrogen, a promising energy carrier, can be produced by microbial catalysis in several pathways, either in the presence or absence of light sources (Azwar et al., 2014; Show et al., 2019). In the former case, photo-fermentation and biophotolysis are mainly considered (Eroglu and Melis, 2011; Mishra et al., 2019) while in the latter, dark fermentation (DF) has been used as the most traditional approach (Banu et al., 2020; Ghimire et al., 2015). DF can be coupled to other processes such as microbial fuel- and electrolysis cells, anaerobic digestion to improve the energy recovery (Bakonyi et al., 2018a; 2019; Pandey et al., 2016) or microalgal biorefinery to obtain value-added chemicals (Nagarajan et al., 2017; Venkata Mohan et al., 2020). The fundamentals and traits for both of these light-dependent and independent methods are well-described in the already published literature (Mathews and Wang, 2009; Sinha and Pandey, 2011; Das and Veziroglu, 2001). Accordingly, from application and practical viewpoints, considering a wide range of operating settings (e.g. temperature, bioreactor type, culture composition, etc.) dark fermentative hydrogen production seems to be a more favorable avenue thanks to its significantly higher gas production capacities (Table 1), meaning a demand for remarkably smaller volume reactors and lower financial investments (Hallenbeck, 2009; Krupp and Widmann, 2009). Moreover, DF has successfully been demonstrated at larger-scale (Ren et al., 2011; Tapia-Venegas et al., 2015) and is therefore the technology nearest to commercialization (Das, 2019; Lai et al., 2011). Although DF has gone through considerable development, it is rather maturing than mature (McPherson et al., 2018). In fact, challenges to be addressed and scientific problems needing solutions are still there, particularly in terms of the biotic and abiotic factors as well as adequate process design, which are responsible for enhancing the biohydrogen formation efficiency (Fig. 1).

The biotic parameters, as the following examples demonstrate, are associated with the screening/selection/isolation (Marone et al., 2014; Ren et al., 2010), enrichment (Sivagurunathan et al., 2014; Wang and Yin, 2017), optional metabolic engineering (Jones, 2008; Oh et al., 2011) and deployment of highly productive H_2-fermenting strains (Bakonyi et al., 2014; Hung et al., 2011). In contrast, the abiotic factors relate to the proper operating settings of the bioreactor unit (covering the formulation, adjustment of media composition and availability of nutrients) that are important for sustaining cell reproduction and metabolism linked to hydrogen gas evolution (Aslam et al., 2018; Palomo-Briones et al., 2017; Show et al., 2011). Furthermore, as the “third piece of the puzzle” on the left hand side of Fig. 1, process design, dealing with the delivery and engineering of innovative H_2-fermentation system layouts, schemes and combinations should be taken into consideration to surpass limitations (Boboescu et al., 2016; Sivagurunathan et al., 2018). In that regard, one of the main concerns is about the development of contemporary approaches enabling the continuous and

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Table 1
Efficiency of various biohydrogen production methods. Adopted with changes from Krupp and Widmann (2009).

	Volume of bioreactor (m^3) needed for powering a PEM fuel cell of:	
H_2 Production Method	1000 W	5000 W
Biophotolysis	67	1710
Photo-fermentation	149	758
Dark fermentation	min. 0.2	max. 14.6

sufficient recovery of biohydrogen.

This, as elaborated later on, is essential to sustain the bioreactor performance by overcoming process inhibition. In the present work, it will be assessed why the insufficient mass transfer conditions in the H_2 fermenter may cause the loss of gas production capacity and what options could be exploited to circumvent this problem. In particular, it will be highlighted how H_2 can be removed and purified by membrane technology and what promising integrated constructions (where the fermenter is combined with the membrane) seem to be helpful for adequate recovery of H_2, such as via recycling of internal biogas and adjusting its quality (right hand side of Fig. 1). To the best knowledge of the authors, this topic has not undergone in-depth examination and therefore, the paper can provide insights of added-value and contribute to the enrichment of the literature. As it will be seen, the paper focuses on the presentation of general tendencies to be concluded from research findings and tries therefore guiding the readers through the most important cornerstones of this specific area.

2. Mass transfer in the H_2 fermenter and related issues to be tackled

As a matter of fact, in acidogenic fermentation of biohydrogen, the headspace gas composition has a large effect (Bastidas-Oyanedel et al., 2012). Particularly, if H_2 gas is not well-removed and builds hence an increased concentration and partial pressure in the reactor ($> 10^{-3}$ atm), the inhibition of the hydrogen formation reaction may occur due to thermodynamic restrictions (Noblecourt et al., 2017), depending somewhat on the type and properties of applied microorganisms (Nath and Das, 2004; Wang et al., 2007). Generally, factors such as the inner hydrodynamics of the bioreactor – where parameters such as the viscosity of the broth play notable roles – can determine how efficiently the gas is actually transferred through the gas-liquid interface. Even though hydrogen gas is characterized by a strongly limited physical solubility in aqueous solutions (0.0016 g H_2/kg H_2O at 1 atm and 293 K) such as the broth employed in biohydrogen fermenters, oversaturation – ascribed to insufficient mass transfer between the liquid and gaseous phases of the reactor – can take place (Beckers et al., 2015; Kraemer and Bagley, 2006; Zhang et al., 2012). In these cases, when the interphase gas exchange (desorption) is not fast enough (Frigon and Guiot, 1995; Maluta et al., 2019), higher amount of H_2 is present in dissolved state (and proportionally less appears in the gaseous phase) than expected under the given equilibrium conditions calculated from Henry's law (Eq. (1)).

$$K_H^i = \frac{p_i^G}{C_i^F} \tag{1}$$

where K_H^i is the Henry-coefficient of gas species i, p_i^G is the partial pressure of i in the gaseous phase, while C_i^F is the concentration of (dissolved) i in the liquid phase.

This may provoke metabolic and/or microbial population shifts and consequently, H_2 might be converted into certain side-products, for instance acetic acid via homoacetogenesis (Saady, 2013). Eventually, it could lead to the considerable loss of experimental hydrogen rate and yield. For instance, Dreschke et al. (2019a) have recently shown the inverse, non-linear decline of biohydrogen productivity at increasing amounts of dissolved H_2. To mitigate the probability of this threat, H_2 should leave the fermenter instantly/in-situ. This step could be assisted by enhanced mass transfer conditions (Fig. 1). To describe the mass transfer and reveal its impact on H_2 generation performance, the mass transfer coefficient (k_La) can be a useful tool (Beckers et al., 2015; Palomo-Briones et al., 2019).

Additionally, the extent of H_2 gas accumulation in the liquid phase can be evaluated via mass balance calculations, which are based on the stoichiometric reactions taking into consideration H_2 gas formation, substrate consumption and generation of soluble metabolic products (including acetic acid, butyric acid, propionic acid, ethanol, etc.) (Bakonyi et al., 2017; Dessi et al., 2018; Palomo-Briones et al., 2019). By this approach, measured quantities of H_2 are compared with theoretical values, resulting in a so-called discrepancy factor (Tapia-Venegas et al., 2013). Values of discrepancy convergent to zero indicate nice recovery of hydrogen gas, while marked divergences would suggest accumulation inside the bioreactor. When a remarkable portion of the gaseous product passes to the liquid phase, its eventual loss with the effluent leaving the bioreactor can be expected. This issue has been reported not only for biohydrogen production, but analogously for other types of anaerobic bioprocesses, such as biogas fermentation. In this regard, according to the assessment of Liu et al. (2014), losses of methane during anaerobic digestion can even be 50% and Cookney et al. (2012) calculated the CH_4 content in the effluent to be as high as 25 g/m^3. Though losses of biohydrogen with the fermentation liquor are best avoided, one possibility to take action for turning these amounts of hydrogen gas contained in the effluent into a useful product may be offered by biogas fermentation where hydrogenotrophic strains are present (Ojeda et al., 2017, Szuhaj et al., 2016). Consequently, although both biohydrogen fermentation and anaerobic digestion can be operated as single-stage technologies, the design of integrated systems where they are properly attached together may be seen as a way forward to resolve problems and improve the net energy yield (Bakonyi et al., 2019).

To positively influence mass transfer conditions and facilitate the desorption of H_2, favorable hydrodynamics (such as turbulent instead of laminar flow regimes) should be adjusted in the fermentation liquor where via adequate mixing (Chezeau et al., 2019; Chou et al., 2008; Ding et al., 2010; Nino-Navarro et al., 2016; Trad et al., 2016). This shows that biohydrogen fermentation, on the top of microbiological phenomenon, depends heavily on physical processes taking place in the broth between suspended solids, particulates and dissolved substances, as underlined by Trad et al. (2015). Besides stirring, reduced pressure operation (Kisielewska et al., 2015; Lee et al., 2012; Sonnleitner et al., 2012), recycling of the liquid effluent (Lima and Zaiat, 2012), cavitation-governed degassing (Cho et al., 2018) and submerged membrane extraction (Singer et al., 2018) are among the approaches that have been applied to improve the liquid-to-gas mass transfer rate. Moreover, bioreactor stripping using a gas flow is an effective alternative (Kim et al., 2006; Kraemer and Bagley, 2007; Mizuno et al., 2000). In this aspect, the most common techniques rely on the application of an externally-supplied gas, such as nitrogen. However, this solution is economically not feasible for economic reasons and in fact, complicates the H_2 downstream. Therefore, it seems to be a more viable way to utilize the internal biogas (comprised mainly of H_2 and CO_2) of the fermenter unit, which is inexpensive, renews itself and is available on-site in the required quantity (Bakonyi et al., 2017; Clark et al., 2012).

To sum up and conclude, improved biohydrogen production can be expected when the liquid-to-gas mass transfer is intensified and the H_2 is separated from the fermenter. For the latter purpose, it has lately been a hot topic to deploy membranes and in the next section, it will be assessed what experiences and results with various membrane-assisted strategies were obtained.

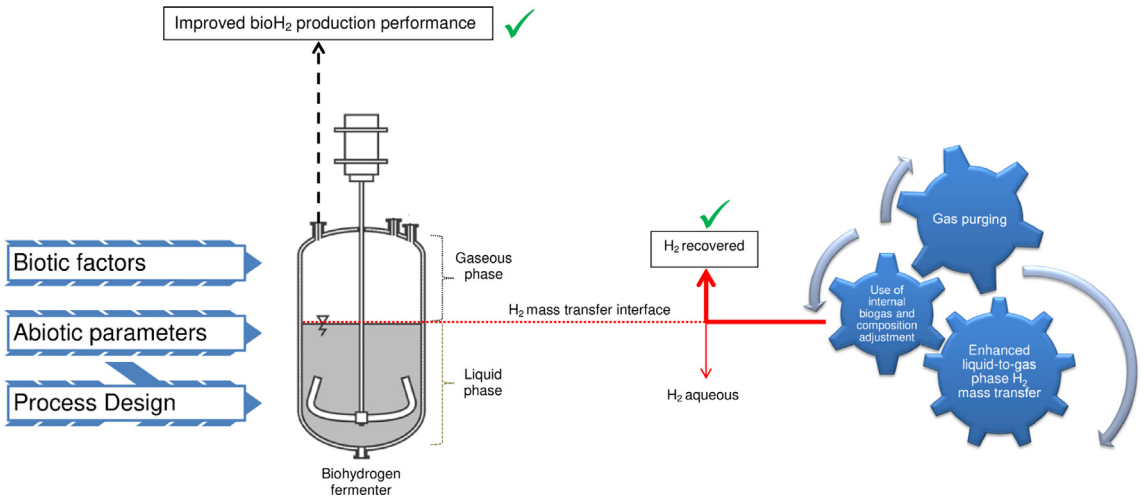

Fig. 1. Factors affecting practical biohydrogen fermentation performance and the importance of sufficient H_2 recovery for process enhancement.

3. The role of membranes in the separation and purification of biohydrogen, opportunities for process integration

To take hydrogen gas out of the bioreactor off-gas, membrane-based bioreactor technologies have been emerging because of their gentle operating requirements resulting in lower energy demand and suitable permeation features, required for completing the task in a relatively selective and rapid manner (Bélafi-Bakó et al., 2006; Ramírez-Morales et al., 2015, 2013). However, the achievable separation efficiency with a given membrane module, besides the operating settings (Nemestóthy et al., 2018), is significantly influenced by the gas composition. Actually, the raw fermentation gas mixture contains typically a notable quantity of carbon dioxide as well as other compounds to lower extent (usually up to a few percent) such as nitrogen, hydrogen sulfide, water vapor, methane if methanogenic archaea are not well-eliminated from the underlying microbial consortia, etc. (Bakonyi et al., 2016, 2013a; Shalygin et al., 2015).

The separation of gases (e.g. H_2/CO_2) by membranes is mostly carried out on non-porous materials made of polymers. The efficiency of the process is commonly described by (the rate of gas permeation implicitly expressed in) the permeability (P_i) and the selectivity ($\alpha_{i/j}$ for a gas pair of i and j) according to Eqs. (2) and (3), respectively (Freeman, 1999; Liang et al., 2019; Robeson, 1991).

$$P_i = \frac{Q_i L}{\Delta p_i A} \tag{2}$$

where Q_i, L, Δp_i and A are the flow rate of gas i, the membrane thickness, the partial pressure difference of component i across the membrane (driving force) and the active membrane permeation area, respectively.

$$\alpha_{i/j} = \frac{P_i}{P_j} \tag{3}$$

where i, compared to j, is the more rapidly permeating component. In case the criteria of Robeson (1991) are followed, a widely-accepted form of representing membrane material performance in gas separation studies can be obtained by the upper-bound chart (UBC). In UBC, the selectivity of the membrane for a gas pair (delivered from single-gas experiments) is plotted against the permeability of the faster gas compound, for instance as illustrated by a generalized form of the relationship in Fig. 2.

Related to the use of gas membrane technology in anaerobic fermentation systems, at least two principally different options are distinguished. One type is the bioreactors coupled with a membrane contactor (operated in gas-liquid extraction mode) that can facilitate the fermentation media degassing (recovery of dissolved gases). As commented earlier in Section 2, both biohydrogen and biogas, as anaerobic fermentations can face similar issues linked to incomplete recovery of products (H_2 and CH_4, respectively). In fact, gas-liquid membrane contactor technology has been routinely practiced for the removal of methane from effluents and proven be highly efficient (Heile et al., 2017). The other type applies membrane contactors or gas separation membranes to assist the purification/separation of the gas recovered in the gaseous phase (i.e. the headspace of the bioreactor). The operations of such gas permeation systems installed with H_2/CO_2 separation membranes have been already demonstrated (Bakonyi et al., 2013b; Modigell et al., 2008; Shalygin et al., 2015), even when coupled with the fermenter to form an integrated bioprocess (Bakonyi et al., 2017, 2015; Ramírez-Morales et al., 2019; Teplyakov et al., 2002). Data of literature examples reporting on membrane-based systems suitable for biohydrogen separation are listed in Table 2. As it can be seen in Table 2, the membranes tested for this objective were mainly made of Polydimethylsiloxane (PDMS), Polyimide (PI) and Polysulfone (PS), which are among the several commercial materials available to cast and fabricate gas separation membranes (Li et al., 2015; Perry et al., 2006; Shao et al., 2009). As highlighted by the circled area in Fig. 3, researchers have experimented with feed gas compositions in a wider-scale, but 40–70 vol% of H_2 seems to be the most common since this range is more frequently experienced in steady-state fermenters (Bakonyi et al., 2014). To compare the membranes in Table 2, particularly those for which more (4–5) data are available (Polysulfone, PDMS, Polyimide), a H_2 enrichment factor (the ratio of H_2 concentrations in the product and feed gases) can be defined. From this analysis, as highlighted in Fig. 4, it would appear that similar efficiencies were attainable with all this three membranes. However, in some cases fluctuations could be noticed, even for the same material, such as seen in Fig. 4 for the dataset of Polysulfone. The variation in the performance of membrane materials is strongly ascribed to the divergence in the experimental separation conditions (e.g. feed pressure, temperature, stage-cut, inlet gas composition). Although the selection of these parameters is subject to the actual case – e.g. the temperature optimum with rubbery- and glassy-polymers is different, elevated pressures may lead to the plasticization of a given material especially when higher-quantities of CO_2 are present, etc. – certain standardization of the measurements would be needed to ensure the more direct comparison of results regarding the efficiency of materials, modules and support therefore decisions. Besides, the global feasibility of the process could be estimated by considering how the quality and recovery of the product by the membrane module meets the desired targets and how the achievements relate with the monetary investments (e.g. how much it

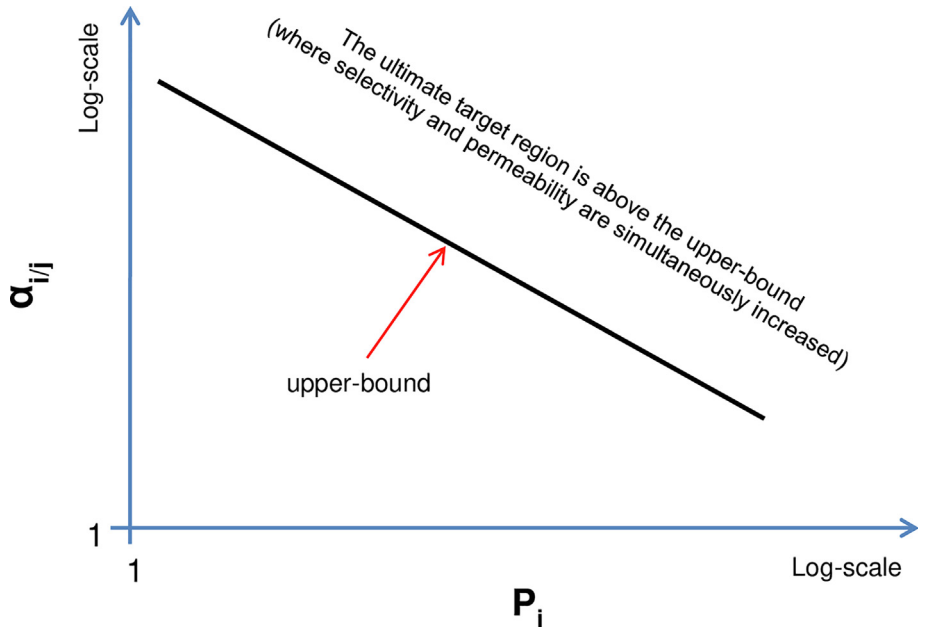

Fig. 2. A generalized presentation of the Robeson's upper-bound relationship.

costs to remove impurities and enhance the purity of H_2).

In agreement with the above, the feed gas composition plays a key-role in the effectiveness of the actual membrane system. Actually, apart from the gaseous components, the fermenter headspace may contain particulates (onto which microbes can get attached) and moisture up to saturation level that may have a negative effect on the separation efficiency and stability. Suggestions to address technological challenges e.g. the necessity of gas treatment prior to feeding into the membrane module and experiences related with plausible technical designs were outlined and assessed in previous articles (Bakonyi et al., 2018b, 2017, 2013a; Ramírez-Morales et al., 2019, 2015, 2013) It is worthy to keep in mind that even in stabilized bioreactors, the quality and quantity of the raw biogas can fluctuate due to microbiological reasons and process perturbations likely occurring in practice (Monroy et al., 2018). Taken these all into consideration, integrated systems such as gas separation membrane bioreactors may be designed with an adequate capacity intermittent gas storage (buffer) tank between the fermenter and the membrane in order to steadily supply the feed gas of balanced composition to the membrane module and make the H_2/CO_2 separation performance more predictable, as illustrated in Fig. 5 (Bakonyi et al., 2015). However, even if membrane-based systems can work well, they could be in the need of support when the actual H_2 purity requirement is high e.g. higher than those achievable in a single-stage. For further purification, various methods such as absorption or adsorption could be suggested (Bakonyi et al., 2013b; Ohs et al., 2019, 2018; Shalygin et al., 2015). In these cases, for instance, the membrane can do a pre-concentration of the bulk received and subsequently, the separation is finished by the other connecting technology (Ohs et al., 2019). Alternatively, multi-stage membrane processes might be applied to attain the sequential, step-wise concentration of hydrogen gas (Lassmann et al., 2016; Ramírez-Morales et al., 2019).

The membrane unit installed to the H_2 fermenter, based on the principles of cross-flow membrane separation and in agreement with Fig. 5, provides two fractions: one enriched in H_2 (considered as the product flow) and another containing higher amount of carbon dioxide (considered as a secondary, H_2-lean flow) (Bakonyi et al., 2018b). The fate of the former is clear e.g. by ending up in fuel cell to generate electricity, however, for the latter (without any backflow to the fermentative H_2 reactor), a field of application should be found. On that matter, promising biotechnological opportunities are offered by

Table 2
Literature achievement regarding biohydrogen separation using gas membrane technology.

Membrane	Feed gas composition (vol.%)		Product gas composition (vol.%)		H_2 enrichment factor (1)	Reference
	H_2	CO_2	H_2	CO_2		
Polysulfone	18	82	68	32	3.77	Mohamad et al. (2016)
	27	73	71	29	2.63	
	62	38	77	23	1.24	
	50	50	78	22	1.56	
Polyimide	66.4	34.6	79.9	20.1	1.20	Lassmann et al. (2016)
PDMS	51.3	47	67.3	32.7	1.31	Bakonyi et al. (2015)
PDMS	65	35	73.7	26.3	1.13	Bakonyi et al. (2016)
PDMS	10	90	14.7	85.3	1.47	Ramírez-Morales et al. (2013)
Polyimide	65	35	75.8	24.2	1.16	Bakonyi et al. (2013b)
	30	70	37.2	62.8	1.24	
PDMS	60	40	80	20	1.33	Koroglu et al. (2019)
PDMS	55	45	68	32	1.24	Ramírez-Morales et al. (2019)
PVDF/PBI	40	60	80	20	2.00	Ahmad et al. (2016)
Polysulfone	50	50	91	9	1.82	Hamid et al. (2019)
Polysulfone/Polyimide	50	50	80	20	1.60	
Polyimide	50	50	63	37	1.26	

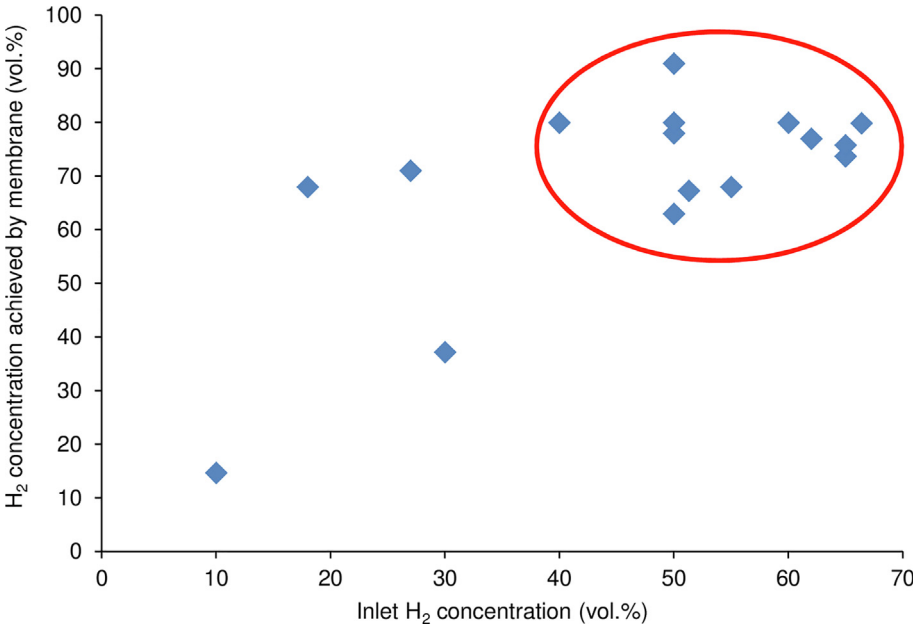

Fig. 3. The correlation of product gas composition with the H_2/CO_2 content of the feed in the membrane gas separation process. Data are taken from Table 2.

biomethane production, cultivation of algae and synthesis of chemicals in microbial electrochemical cells (Bakonyi et al., 2020).

Nonetheless, another, plausible avenue can be taken into account for its direct utilization in the biohydrogen-producing reactor itself, as follows. The gaseous mixture present in-situ in the biohydrogen fermenter could be a more suitable source of gas for bioreactor stripping than external ones to increase the liquid-to-gas phase mass transport and concomitantly the recovery of H_2, as noted in Section 2. Lately, it has been shown by Dreschke et al. (2019a,b) that recirculating a portion from the biohydrogen fermenter's own atmosphere could act effectively against H_2 supersaturation and aid hydrogen gas recovery. Similar improvement of the biohydrogen process was observed by Buitrón et al. (2019), where the gas upflow recirculation helped the release of H_2 from the liquid phase and resulted in a 2.8-fold enhancement of productivity. Furthermore, the positive effect of lower H_2-content/higher CO_2-content in the recycled biogas was noted by Bakonyi et al. (2017) (Fig. 6A and B).

4. Outlook and perspectives

It can be deduced from the results of Dreschke et al. (2019a,b), Buitrón et al. (2019) and Bakonyi et al. (2017) that the recirculation of biogas can be a beneficial strategy to enhance the biohydrogen production and besides factors such as the purging intensity (indicating how much biogas is loaded per unit of bioreactor working volume and unit of time, e.g. $L_{biogas}/L_{bioreactor} - h$), the composition of this biogas may count (Fig. 6A and B). In this latter aspect, the ratio of H_2 and CO_2 in such biogas streams can be set by the membrane attached to the process (primarily for biohydrogen purification). According to the concept displayed in Fig. 6B, the CO_2 concentration in the gas returned into the bioreactor can be adjusted through the membrane (Bakonyi et al., 2017, 2018b). From fundamental investigations, it turned on the one hand out that CO_2 stripping could lead to advantages in the biohydrogen fermentation process thanks to the substitution (dilution) of H_2 by CO_2 in the biogas and higher buffer capacity of the media, respectively (Devi et al., 2010; Kim et al., 2012, 2006). On the other hand, it was shown that the presence of carbon dioxide can be decisive

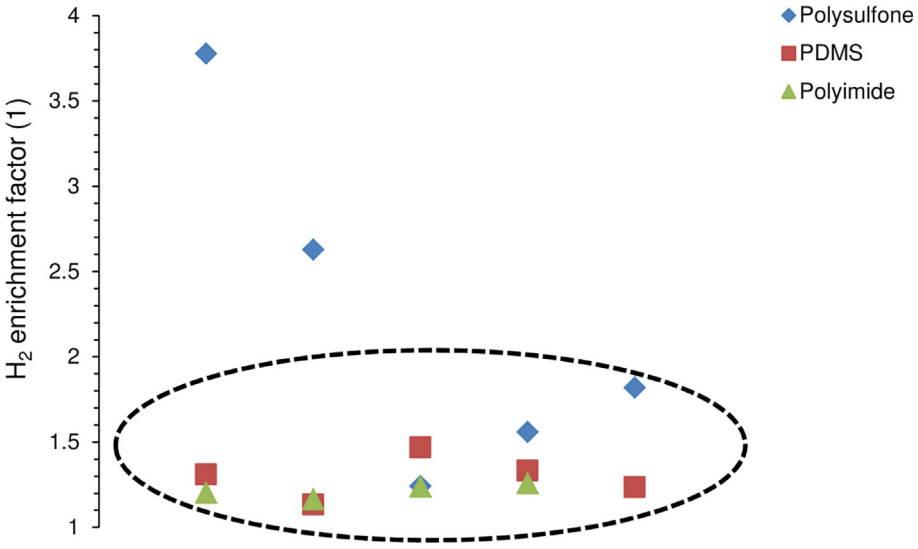

Fig. 4. A comparison of various gas separation membranes for H_2 enrichment.

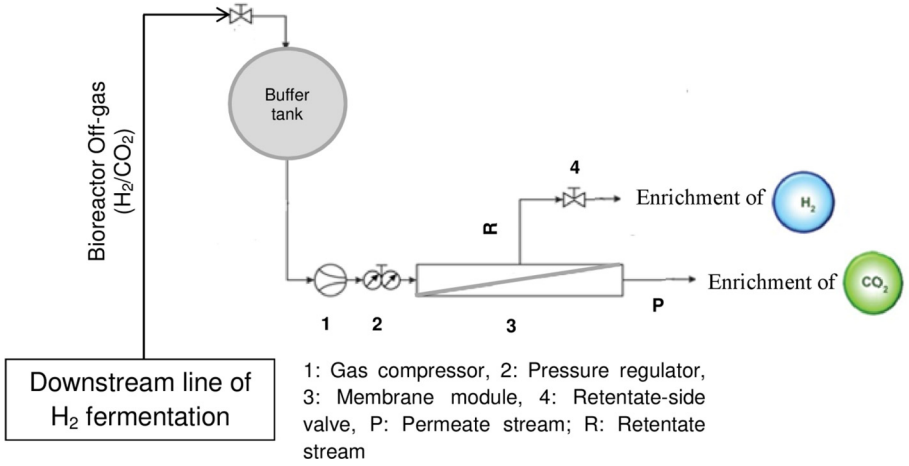

Fig. 5. A proposed design to integrate the biohydrogen fermenter with a membrane-based downstream process and separate H_2/CO_2 in-place. Adopted with changes from Bakonyi et al. (2015).

for actual H_2 yields since CO_2 can be used together with NADH to form components such as succinate and formate. If less NADH is available, less H_2 can be liberated from its enzymatic re-oxidation, as summarized by Nath and Das (2004). This mechanism was considered by Wang et al. (2007) to explain why bubbling the pure culture H_2 fermenter with CO_2 depressed the productivity, though the authors suggested more investigation to clearly understand the observed inhibition. Interestingly, it has been found by Buitrón et al. (2019) that recycling of biogas enriched the H_2-producing microorganisms and simultaneously suppressed the H_2-scavenging bacteria, allowing a better control over homoacetogenesis. In addition, the results of Bakonyi et al. (2017) indicated that although the various gas recycling strategies considerably affected the microbial community dynamics for a longer period, switching back to non-sparged operation more or less restored the original H_2 production performance.

Overall, these examples show that the effect of CO_2 on bioreactor behavior is rather complex and should be evaluated systematically both at mass transfer- and microbiological-levels.

5. Conclusions

In this review, challenges of dark fermentative biohydrogen production due to inadequate mass transfer between the gaseous and liquid phases and the accumulation of H_2 were presented and discussed. It was demonstrated through our analysis how membrane technology can serve to overcome this problem by assisting the recovery and separation of biohydrogen from the fermenter unit. The features of various process schemes with the involvement of membranes were assessed, including the opportunities and advantages of (CO_2-enriched) internal biogas recycling to realize enhanced mass transfer via bioreactor sparing. Finally, perspectives and potential expansion of this research line were considered.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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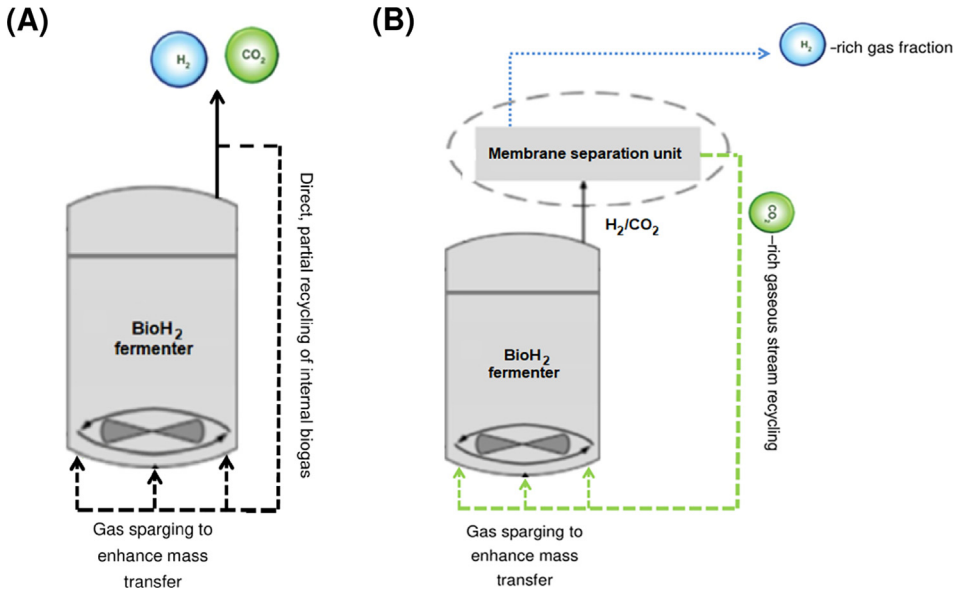

Fig. 6. Possible H_2 fermentation designs for recycling of internal biogas (A) without and (B) with composition adjustment.

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