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Possibilities for the biologically-assisted utilization of CO_2-rich gaseous waste streams generated during membrane technological separation of biohydrogen

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Abstract

In the course of dark fermentative hydrogen production, a complex gaseous mixture with significant quantity of CO_2 is formed. Hence, proper separation of H_2 and CO_2 is required for adequate utilization of hydrogen gas in fuel cell applications. Technological solutions for the removal of CO_2 can be designed by using gas separation membranes. Nevertheless, contemporary systems should be concerned with the consecutive valorization of carbon dioxide, as well. In this review article, the membrane-based technologies aiming at the effective separation of CO_2 and biohydrogen (bioH_2) will be evaluated, along with concise discussion and perspectives of integrative schemes offering alternatives for the biologically-mediated (fermentative, bioelectrochemical and algal) conversion of carbon dioxide into value-added substances, such as methane, hydrocarbons, etc. With this analysis, the objective was to bring the most important aspects of membrane-assisted biohydrogen downstream technology under one cover and give insights to recent advancement and possible future research directions.

Keywords: biohydrogen; membrane separation; CO_2 removal; CO_2 utilization; integrated CO_2 valorization

1. Introduction

Membrane-based technology exhibit large application potential over other gas-upgrading systems including overcoming the difficulties with CO_2 capturing and enhancing the hydrogen purity in various gas mixtures [1]. Benefits of membrane technology lay on the possibility to separate chemical substances without occurrence of phase change (if this is desirable) with high energetic efficiency and reliability, possibility of easy start-up as well as shutdown procedure, process design flexibility and low areal footprint. Membranes could be divided according to their morphology into symmetric/asymmetric, non-porous and porous ones. Mainly, the performance of overall membrane process is displayed by two measures, particularly the selectivity and permeability [2]. In principle, for non-porous (polymeric) membranes that are widely used for gas purification, the separation is mostly described by the solution-diffusion theory [2]. Hence, to achieve sufficient separation, differences in solubility and diffusivity for the various gases should be exploited for a particular membrane material and operating conditions. Concerning membranes, a broad range of materials are available for separation of CO_2/H_2 mixture, to be classified as (i) inorganic (such as ceramic, carbon molecular sieve, clay, glass, metal), (ii) organic (typically polymer) membranes, plus (iii) the combination of those (so called mixed-matrix membranes) [3-5].

In fact, for the enrichment of biologically-produced hydrogen gas (called biohydrogen or $bioH_2$), membrane gas separation has been demonstrated as a feasible technological choice [6]. The main target of the process is set on the efficient removal of carbon dioxide, which is the most significant secondary product found in the bioreactor off-gas [7,8]. Basically, CO_2 separation can be attempted by the proper selection of membrane material, adequate design of the module and last but not least, the optimization of operation conditions in terms of transmembrane partial pressure gradient, temperature, stage-cut, etc. [9]. However, it is generally experienced that the permeability difference of H_2 and CO_2 gases is not sufficiently high and consequently, the permselectivity for this gas pair remains relatively low for most polymeric, non-porous membranes commonly employed for the above purpose. Actually, the Robeson-upper bound plot (**Fig. 1**) is representative of this issue, illustrating that the CO_2/H_2 selectivity and permeability of carbon dioxide are often compromised [10,11]. Accordingly, further development of advanced materials and approaches is suggested to enter the attractive region where high selectivity and permeability are accomplished simultaneously. During the process, as presented in our recent publication [12] the membrane stage will split the feed into permeate and retentate streams and depending on the membrane properties, one of those will enrich H_2 while the other CO_2. This means that the latter technological flow containing larger quantity of CO_2 (and lower amount of H_2 in accordance with the separation efficacy) can be viewed as side-stream by-product to deal with.

Therefore, in this review, the paper will be structured around discussing the literature information relevant to the membrane separation part including materials design and modelling (Sections 2 and 3, respectively), followed by an overview and assessment pertain to the utilization of CO_2 refused by the gas separation membrane in the course of bioH_2 purification. On this matter, the analysis in Section 4 will cover the options ranging from hydrogenotrophic methanogenesis (Section 4.1), microbial electrosynthesis (Section 4.2) to algae-assisted electrochemical systems (Section 4.3). The ultimate goal of this work is to give an insight to downstream-associated aspects of biohydrogen technology and interpret what opportunities are available and could be considered subsequent to the upstream (production) side of biological, dark fermentative hydrogen generation, especially in relation to the utilization of CO_2 obtained after membrane separation step. To our knowledge, for now, there is no such a review-type article combining all these aforementioned fields and hence, could fill an existing gap in the scientific literature.

2. Membrane gas technology for CO_2 and H_2 separation

According to authors such as Mulder [13] and Bakonyi et al. [6], gas separation process is influenced by many important factors such as: permeabilities and separation factors of permeating gases, geometry of the membrane (flat-sheet, hollow fiber), membrane structure and morphology, separation layer thickness, membrane module design. All these variables should be taken in account when designing the whole gas separation process.

Typical membrane gas separation utilizes asymmetric membranes with non-porous top-layer made from organic polymer by phase inversion process [13].

Partial pressure difference between the feed and the permeate is the driving force for permeation of CO_2 through a membrane. They are several possibilities how to enhance the driving force. One way is to recycle part of the CO_2 permeate into the feed and thus increase the initial CO_2 concentration. Second way is to increase the feed pressure using a compressor or decrease the pressure in the permeate with a vacuum pump. Other option could be lowering CO_2 partial pressure in the permeate with a sweeping gas [6,14]. Increasing the driving force on the other hand means higher consumption/energy costs. From this reason it is always necessary to perform economical evaluation of the overall process at explicit process conditions and compare it with other options or consider using hybrid processes or other alternative separating processes to find the best solution, e.g. Bakonyi et al. [7] suggesting the need for combined membrane and chemical absorption based process.

2.1. Polymer blend and mixed matrix membranes

Thousands of polymer materials and membranes were characterized regarding gas separation properties. Robeson [11,15] pointed out on the certain trade-off between selectivity and permeability of the membranes. This trade-off, displayed by the upper-bound line in **Fig. 1**, in general shows that it is difficult to achieve high permeability and high selectivity simultaneously.

Among the approaches to overcome this trade-off, the preparation of special class of membranes incorporating components to promote the gas transport or selectivity can be mentioned. Such material could be other polymer or softener, various fillers like zeolites, layered minerals, graphene related materials, etc. Membranes containing inorganic fillers are often called mixed matrix membranes (MMMs). Special group of materials which involve combination with ionic liquids are discussed in Section 2.2.

Some promising materials surpassing the Robeson's upper-bound for CO_2/H_2 separation are presented in **Fig. 1**. According to Bakonyi et al. [6] and Rabiee et al. [16], one of the most studied polymer for CO_2/H_2 separations is polyamide and polyether copolymer under commercial name PEBAX® (there are more polymers under this brand which differ in chemical structure of PA and ether blocks). These neat polymers can have CO_2 permeability about 80 Barrers and CO_2/H_2 selectivity around 8 [12].

Regarding specific discussion of some salient accomplishments plotted in **Fig. 1**, it is worthy of mentioning the significant permeability and selectivity improvements of PEBAX® polymer achieved by Car et al. [17] thanks to combining PEBAX® MH 1657 with PEG (polyethylene glycol), which is well-known for its notable affinity toward carbon dioxide. Actually, the CO_2 permeabilities were doubled and at the same time, the CO_2/H_2 selectivities increased from the value of 9 to nearly 11. Besides that, in the paper of Reijerkerk et al. [18], the mixture of PEO and polydimethylsiloxane (PDMS) was added to PEBAX® 1657 matrix. Well-known gas separation company MTR Inc. uses its own membrane with 2000 GPU CO_2 permeance and CO_2/H_2 selectivity of 10 (at 25 ^oC) under brand name Polaris™ (**Fig. 1**).

In the work of Huang et al. [19], a range of MMM were prepared by IL-modified graphene oxide (GO) and PEBAX®. As a matter of fact, GO was modified by 1-(3-aminopropyl)-3- methylimidazolium bromide ionic liquid (IL). The GO nanosheets have high aspect ratio and when incorporated into polymer matrix, they increase tortuosity for permeating gas molecules and thus increase diffusion selectivity. Chosen ILs contain free amino groups helping to improve the interfacial compatibility between GO nanosheets and the polymer. Furthermore, IL intercalated GO nanosheets, which led to facilitated CO_2 transport through the reversible reaction, resulted in enhanced CO_2/H_2 and CO_2/N_2 selectivities surpassing the Robeson's upper bound published in 2008 [11].

2.2. Membranes containing ionic liquids (ILs)

ILs can be considered as salts consisted of the inorganic/organic anion and organic cation which have melting point below 100°C. The variety of combination of cations and anions is almost unlimited, because of large number of possible ions. Nevertheless, the properties of chosen cation and anion extensively determine the resulting IL physico-chemical properties such as hydrophobicity/hydrophilicity, viscosity, melting point, and solvatation properties. Therefore, such ILs can be tailor-made for specific applications including gas separation [6].

To utilize advantages of polymers and ILs, they are several ways how to combine them. Supported liquid membranes (SLMs) are prepared when the pores of porous asymmetric membrane are filled with single or mixture of ILs. Because of extremely low vapor pressure ILs practically don't evaporate from the membrane in comparison with other liquid membranes. On the other hand, often the capillary forces are not strong enough to keep ILs in the pores when higher pressure is applied. To minimize this problem, the common strategy is to cover the pores with top layer of highly permeable polymer such as PDMS or blend this polymer with the IL directly [20]. Other option is to use anions or cations of ILs which can be polymerized and create polymerized-IL (PIL). In the paper of Gouveia et al. [21], dense composite membranes containing pyrrolidinium-based PILs with $[C(CN)_3]^-$ or $[NTf_2]^-$ anions and various amounts of free IL ($[C_2mim][C(CN)_3]$, $[C_4mpyr][NTf_2]$ or $[C_2mim][NTf_2]$) incorporated were prepared by the solution casting method. CO_2 and H_2 permselectivities were determined at typical biohydrogen formation conditions (100 kPa of feed pressure and temperature of 308 K). PIL–IL membranes containing the $[NTf_2]^-$ anion showed the highest H_2 permeability and solubility while the PIL–IL composites having the $[C(CN)_3]^-$ anion showed the highest H_2 diffusivity and CO_2/H_2 permselectivity. Particularly, at 35 ^oC, the best result was obtained for the PIL $C(CN)_3$–60 IL $C(CN)_3$ composite membrane (permeability of CO_2 – 505 Barrer, CO_2/H_2 selectivity – 12.5), to be seen comparable with the best achievements in the literature.

2.3. Membranes with faciliated transport

Other approach to overcome the Robeson trade-off is utilizing of facilitated transport inside of the membranes. Basically, in facilitated transport a carrier should reversibly interact with the species to be separated in the mixture and leads to the formation of a transient complex molecule. Thereafter, the transfer of the targeted permeating substance is aided by the movement of the complex or the jump of the species from one carrier to another (fixed carrier). A comprehensive review on facilitated transport in separation membranes can be found in Li et al. [22].

A recent study by Cheng et al. [23] represented an approach for enhancing CO_2/H_2 gas separation by utilizing PEBAX® membrane with blended polyethylene glycol dimethyl ether (PEGDME). Several facilitated transport membranes, namely Pebax/PEGDME/[P66614][Triz], Pebax/PEGDME/MEA and Pebax/PEGDME/[P66614][2-Op] were fabricated. In fact, the last material exhibited the best CO_2 permeability of all (672.1 Barrer at temperature of 25 ^oC), while blended membrane employing MEA had the largest CO_2/H_2 selectivity with 17.8. Furthermore, all materials were coated on the α-Al_2O_3 ceramic hollow fiber support reaching permeances between 63-79 GPU.

2.4. Enzymatic gas separation membranes

Based on the fundamentals of gas separation using membranes, the gas diffusion and solubility properties in the (non-porous, polymeric) material of the membrane play key-roles and influence therefore the actual attainable selectivity [6,24,25]. Hence, approaches enabling the alteration of these features could lead to better separation efficiency. In this aspect, a promising avenue seems to be associated with the deployment of biocatalytic membranes, where the membrane is fabricated with particular enzyme(s). The advantage of enzyme deployment originates from the fact that enzymes are known to take part in and catalyze specific reactions. On these grounds, enormous potential of carbonic anhydrase (CA) has been found since this enzyme, as highlighted in **Fig. 2**, mediates the hydration transformation of CO_2 to bicarbonate [26-28] and can contribute to accelerated carbon capture [29]. Consequently, membranes containing CA are expected to achieve facilitated transport of CO_2 over other gases such as H_2 and then, the process benefits from the increased selectivity of the two gaseous compounds.

Literature examples clearly illustrate that the addition of CA to various gas separation membranes improves he CO_2 permeation rate through the membrane thanks to the facilitation of the transport [30-32] even at elevated temperatures [33], while additional studies found that membranes with immobilized CA could have pro-longed stability, considered as an important trait for a reliable technology [34,35]. Scientists such as Neves et al. [36] and Martins et al. [37] have shown that the water activity could be a notable factor to deal with in CA-containing membranes, e.g. those made with different solvents to form supported liquid membrane (SLM) due to its effect on the CO_2 solubility in the actual membrane, determining selectivity in the relation of CO_2 and other gaseous substances. As a matter of fact, it was shown by Nemestóthy et al. [31] based on the Robeson upper-bound chart that membranes lacking CA significantly underperformed those prepared with CA, which can thus be seen as a way forward in the membrane R&D progress.

Given that the gas separation process using membranes prepared with CA enzyme can produce permeate with increased CO_2 content (and thus lower H_2-contents and losses in the permeate), the utilization of this gas stream may be attempted by CO_2-consuming applications such, including either fermentative or bioelectrochemical pathways. The former involves mainly the hydrogenotrophic methanogenesis, where H_2 and CO_2 are transformed into methane [38], whilst the latter option can refer to the (electro)microbiologically-supported synthesis of chemicals, such as CH_4 or other value-added chemicals e.g. hydrocarbons, alcohols [39]. Interestingly, it was experienced by Srikanth et al. [40] that the addition of CA aided the in bioelectrocatalytic formation of formic acid applying formate dehydrogenase because of the faster dissolution and subsequently more prompt availability of substrate for the conversion.

3. Approaches to modelling of H_2 gas transport

Generally, the modeling of the membrane separation process can be performed on three levels. The first one is the membrane level, 2nd – the membrane module level, 3rd – the module arrangement level. As the membrane and the module form one unit we will concentrate only on these first two levels.

The most general are the transport equations of non-equilibrium thermodynamics which take into account the cross-effects between all the components in the membrane system. The Maxwell-Stefan equations (Eq. 2) are equivalent to those equations; they represent the balance of the driving force and the frictional forces which are proportional to differences of the velocities for moving molecules, including the membrane. Neglecting all the cross-effects the simplest transport equation is obtained relating the flux of gas i, J_i, with its pressure difference through the membrane (Eq. 1):

$$J_i = Q_i\left(p_{f,i} - p_{p,i}\right) \tag{1}$$

where Q_i is the gas permeance in the membrane, $p_{f,I}$ and $p_{p,i}$ are respectively the pressure of i in the feed and permeate sides. Because of its simplicity it is frequently used in the modeling of membrane processes [41-43].

For the solution-diffusion model Q_i is determined by the diffusion coefficient of i^{th} gas in the membrane material and its sorption factor divided by the membrane thickness [44].

3.1. Maxwell-Stefan equations

In one dimension (coordinate z) for *n*-component mixture with the membrane as the reference frame they can be written in Eq. 2 [45]:

$$-\frac{d\mu_i}{dz} = \sum_{j=1,\, j\neq i}^{n} \frac{RT}{D_{ij}} x_j \left(v_i - v_j\right) + \frac{RT}{D_i} v_i \qquad i = 1, 2, .., n \qquad (2)$$

where μ_i, v_i, x_i denote chemical potential, velocity, molar fraction of species *i*, respectively, D_{ij} – Maxwell-Stefan diffusivity representing interaction for *i* and *j*. Comparing with the frictional formalism (e.g. Spiegler [46]) RT/D_{ij} has the meaning of friction coefficient. For dense or microporous membranes D_{ij} depends not only on i-j interactions but also on interactions with the membrane. The linear velocity v_i is related to the flux J_i by the relation $v_i = J_i/c_i$, where c_i stands for the concentration of *i*th species inside the dense membrane or the membrane pores (zeolite membrane). However, the Maxwell-Stefan equations are rarely applied for polymer membranes [47]. Mostly, they are used to describe the gas transport in zeolite membranes [45,48-50]. For instance, it was possible to explain the strange behavior of permeances of H_2 and CO_2 in MFI zeolite membrane (experimental result by Sandström et al. [51]). For that membrane the permeance of hydrogen gas in the H_2-CO_2 mixture was one order below compared to pure H_2, whereas in the case of CO_2 it decreased twice. The explanation of this phenomenon given by Krishna [45] was based on the non-zero cross-coefficients D_{ij}.

3.2. Membrane as electrical circuit analog

Generally, the membranes consist of series of layers of different permeabilities. Moreover, the layers can also be heterogeneous. Such a composite membrane, including boundary diffusion layers, can be represented as the electrical circuit analog [52,53]. E.g. such a model has been applied by Peng et al. [53] to the PDMS/PS (polydimethylsiloxane /polysulfone hollow-fibre composite membrane to describe the transport of mixture H_2, N_2 and CH_4. For that system they obtained the selectivity of H_2/N_2 and H_2/CH_4 ca. 27 and 21, respectively. They assumed that the membrane consists of 3 layers – coating (PDMS, 1), dense (PS, 2), and porous support (PS) layers. The dense layer was represented by a parallel connection of the resistance of its pores containing PDMS and the resistance of PS part of that layer. Besides, the resistance for boundary layer on the feed side was also considered. The resistances of the porous support and of the boundary layer on the permeate side were negligible. The resistances of the layers that make up the entire membrane were approximated by a simple equation $R = l/(PA)$, where A, l, P are the layer area, thickness, and permeability, respectively. The resistance of the feed boundary layer was treated inversely proportional to the feed flow rate (u_f), in the nth power i.e. $R_f \propto 1/u_f^n$. The final equation for the total permeance of the system was (Eq. 3) (Eq. 21 in Peng et al. [53]):

$$\frac{J}{\Delta p}=\frac{P}{l}=\left(au_f^{-n}+\frac{l_1}{P_1}+\frac{l_2}{P_1\varepsilon+P_2(1-\varepsilon)}\right)^{-1} \qquad (3)$$

where J is the gas flux, Δp – the transmembrane pressure, ε – the surface porosity of the dense layer of PS, P_1, P_2 – permeability of PDMS, PS, respectively, a and n are experimentally determined parameters. The above equation described the experimental data satisfactory.

Grahn and Hedlund [48] applied a more sophisticated model for simulating CO_2 removal from CO_2/H_2 mixture using the tubular silicate-1 membrane in the counter-current regime. The composite membrane consisted of zeolite film and two porous support layers; the boundary diffusion layer was also taken into account. The transport was described by the following equations:

1) zeolite film - Maxwell-Stefan equations,

2) zeolite film defects – Fick's law, here the diffusional activation energy was assumed with inverse proportionality to the size of defect in third power,

3) porous layers – sum of Knudsen diffusion and viscous flow,

4) boundary diffusion layer – mass transfer coefficient was obtained by Sherwood correlation corresponding to the membrane module and Reynolds number.

The parameters of that model were evaluated on the base of literature data. The model was deployed to a hypothetical case of carbon dioxide recovery from equimolar mixture of CO_2 and H_2 in one- and two-stage layouts. A similar model (the boundary diffusion layer was neglected) was applied for the description of H_2/CO_2 separation using a disc MFI membrane [50].

3.3. First-principles modeling or molecular approach

The molecular approach to the description of membrane transport needs rather a lot of computation time and even for this reason it is not suitable for modeling the process of of membrane separation. Nevertheless, it is helpful in choosing a potentially useful membrane material for such processes. During the last decades, special attention has been dedicated to MOF membranes and the carbon materials, e.g. graphene with various defects (ideal graphene is not permeable to gases). The literature on this subject is numerous. We mention only a few examples where the selectivity H_2/CO_2 is given.

For instance, in the work of Xu et al. [54], a carbon nanopore was analyzed with respect to the gas mixtures (CO_2, H_2, and CH_4) separation both experimentally and by simulation. The tested membrane was prepared by coating the γ-alumina tube with a polyetherimide film and carbonization. The fluxes and selectivity factor (SF) were calculated for a single slit pore using nonequilibrium molecular dynamics simulations. The simulated SF for equimolar binary mixtures of H_2 and CO_2 strongly depended on the pore width (Fig. 5 in Xu et al. [54]) – for the width equal ca. $1.66\times\sigma_{CH4}$ = 0.63 nm SF(CO_2/H_2) was 1, below that value SF was going to very low values, above 0.63 nm SF could reach 20 or even higher values (not shown in that figure). However, these results were not confirmed by the experimental results. According to the BET method the pore size was in the range 0.3–1.0 nm with a sharp peak at 0.36 nm. According to the simulations for such a pore size SF (CO_2/H_2) should be below 1 whereas it was above 2.5 (Fig.10 in Grahn and Hedlund [48]).

In the paper of Qin et al. [55], the separation properties of graphene with defects were investigated basing on the ab initio quantum mechanical calculations for various gases, including H_2 and CO_2. The energetic barrier for the gas permeation was calculated for each gas, *E*. The separation factor was obtained using the Arrhenius equation (Eq. 4):

$$S_{A/B} = \frac{A_A}{A_B} \mathrm{Exp}\left(-\left(E_A - E_B\right)/kT\right) \tag{4}$$

Assuming the same prefactors (A_A, A_B) they obtained very high values of $S_{A/B}$ (Tab.2 in Qin et al. [55]): H_2/CO_2 – 10^{10}, H_2/O_2 - 3×10^9, H_2/N_2 - 2×10^{12}. Even much higher selectivities obtained from Eq. 4 were reported by Li et al. [56] for the 2D polyphenylene layer. However, the gas permeabilities in those works were not estimated; therefore, it is not possible to confirm the usefulness of such membrane materials.

CO_2, H_2, and CH_4 adsorption and self-diffusion (bio-metal organic framework (bio-MOF) with pure gases and binary mixtures) were studied by Atci et al. [57]. They applied equilibrium molecular dynamics as well as grand canonical Monte Carlo simulations assuming a rigid structure of bio-MOF-11. They found that the adsorption selectivity CO_2/H_2 exceeds 400 at the mixture composition

CO_2/H_2:10/90. They explained it by a more remarkable confinement of carbon dioxide in bio-MOF-11. On the other hand, they found that small H_2 molecules diffuse almost 1 order of magnitude faster than CH_4 and CO_2 molecules in the pores of bio-MOF-11. The permeation selectivity was calculated from Eq. 5:

$$S_{A/B} = S_{ads,A/B} \frac{D_{self,A}}{D_{self,B}} \tag{5}$$

with vacuum assumed on the permeate side. The predicted selectivity of bio-MOF-11 membrane for CO_2/H_2 mixture (composition 90/10) was from over 20 (feed gas fugacity 2 bar) to almost 70 (50 bar).

3.4. Modelling of membrane module

The number of papers dealing with the module modeling is abundant. Therefore, only some selected papers will be presented here. On a membrane module, to evaluate gas separation, three sub-models should be considered – the membrane transport model and the models describing the flows on both sides of membrane. The detailed mass, momentum, energy balance equations for hollow-fibre as well as spiral wound modules are gathered in Marriott et al. [58]. It is the most rigorous approach and the authors demonstrated its validity by testing it on the experimental examples from the gas separation, pervaporation, and reverse osmosis. Below we present basic approaches based on the mass balance equations.

A simple approach was applied by Bucsu et al. [59]. Although they used a hollow fiber membrane module they assumed perfect mixing on both sides of membrane. Their calculations applied Eq. 1 and the assumption that the molar fraction of permeate components is given by $y_i = J_i / (J_1 + J_2)$, i = 1, 2. They could roughly describe the experimental data applying that model – separation of H_2/N_2 (using a dense polyethersulphone-polyimide membrane) and H_2/CO_2 (porous hollow fibre high density polyethylene membrane). It is a question to which extent the observed deviation of the model is caused by the simple membrane transport equation or by the assumed perfect stirring on the feed and permeate sides of the membrane. The analysis of various flow arrangements: co-current flow, counter-current flow, cross flow, one-side mixing, perfect mixing (**Fig. 3**) was performed by Shindo et al. [43]. They assumed:

- the membrane transport given by Eq. 1,
- the gas permeabilities in the mixture are the same as those of pure gases and do not depend on pressure,
- negligible boundary diffusion layers,
- negligible pressure drops along the membrane on the high and low pressure sides,
- a plug flows, except the obvious situations c-e shown in **Fig. 3**
- steady state of the process, and
- isothermal conditions.

Similar flow patterns, under similar assumptions, were earlier analyzed by Walawender and Stern [60]. In both papers such as Shindo et al. [43] and Walawender and Stern [60], the advantage of the counter-current pattern is shown. On the other hand, Ji et al. [49], modeling the separation of the H_2-Ar mixture at high temperature (400 °C) in a multi-tube (cobalt oxide silica) membrane module, found that counter- and co-current flow patterns yield similar results regarding the yield, purity and recovery of H_2. The authors attribute this observation to the significant gas-through-gas diffusion in the feed domain under high temperatures. Also Aghaeinejad-Meybodi et al. [61], by applying the model from Shindo et al. [43] for the H_2 separation from CO and CO_2 (methanol steam reforming products) using the silica membrane, report that at high pressures the difference between co- and counter-current flow patterns is *not considerable*.

Regarding a hollow fiber membrane (HFM), because of small inner radius of fibers one should take into account also the drop of pressure inside such narrow capillaries. This effect was taken into account by e.g. Coker et al. [41], Thundyil and Koros [62], Ji et al. [49] by applying the Hagen-Poiseuille equation. In [41] and [62], for solving differential mass balance equations the finite-difference method was applied (called also the tank-in-series model).

Other additional assumptions used in the simulation of HFM module were [41]:

- no axial mixing of gases inside and outside the fiber in the bulk flow direction,

- the hollow fiber is comprised of a very thin separation layer and a porous support,
- the simulation results obtained for a single hollow fiber are scaled to the bundle of fibers,
- all fibers are uniform and do not deform under pressure.

The model was applied to describe the H_2 purification from light hydrocarbons and for air components separation. Peer et al. [63] applied a similar model for co- and counter-current mode as in [41] and [43]. Contrary to Coker et al. [41], they assumed the same pressure inside the fiber along its longitudinal axis. They studied the separation of hydrogen gas from carbon monoxide by a hollow fiber polyimide membrane module. It was stated that although the gas permeance depends on pressure and mixture composition their simulation results based on the constant permeance assumption differed insignificantly from the experimental results.

Katoh et al. [42] examined the impact of non-ideal mixing on the separation process using a hollow fiber module and the tank-in-series model. The general assumptions of that model were the same as that of Coker et al. [41]. The conditions of nonideal mixing was realized by increasing the number of tanks on the permeate side (inside fiber) comparing to that on the feed side (shell side). Analyzing H_2 recovery from refinery gases they found that the decrease in mixing of the feed side increases the H_2 recovery but slightly decreases the H_2 concentration in permeate.

3.5. Artificial Neural Network (ANN) approach

The ANN approach attracted also attention of some researchers; it can be applied to fit the global membrane system. Here we mention only two works where the gas mixture containing H_2 are treated [64,65]. In Peer et al. [64], the ANN technique for the description of a gas mixture separation (H_2, CO_2, CH_4 and C_2H_6) in a hollow fiber PI membrane module was applied. A good agreement of the ANN results with the experimental ones was obtained.

In Rezakazemi et al. [65], the selectivity of MMMs towards gases in particular hydrogen, carbon dioxide, methane and propane under varied conditions (input variables: feed pressure, nanofiller content and the kind of gas) was investigated. MMMs were formed by casting technique using the dispersion of zeolite 4A nanoparticles in polydimethylsiloxane (PDMS). In the experiments, a cross-flow module was tested. According to Figs. 9 and 13 in Rezakazemi et al. [65], the selectivity H_2/CO_2 for their membranes was between 0 and 0.2. The description of experimental results using the ANFIS (adaptive neuro-fuzzy inference system) model was good.

Generally, the ANN approach needs a lot of experimental data. In Peer et al. [64], among 35 data points 27 were used for training (82 %), 5 for validation and only 3 for testing (9%). Much more experimental points (216) were obtained by Rezakazemi et al. [65], randomly ordering them nto the training (151, 70%) and test (65, 30%) sets. One can notice here that for 3 input variables the full plan even on 5 levels would yield much smaller number of experiments – $5^3 = 125$.

There are two other important disadvantages of the ANN approach resulting from the fact that it is not based on any physical model and can only be treated as some kind of nonlinear fitting [66]. The 1st one is that we should not expect any reliable results beyond the range of the input data used for training (in other words: we cannot extrapolate the data) [67]. The 2nd one – it does not help us in understanding the discussed experimental process.

4. Biological processes for utilization of CO_2-rich gaseous streams generated by the membrane separation stage

4.1. Anaerobic conversion of CO_2(/H_2) to CH_4 – possible approach via methanogenesis

Biological approaches for CO_2 transformation to various value-added compounds provide a beneficial concept, since they usually can be performed without or with slight modifications of the existing reactor types and apply microbial biocatalyst with low cost and high selectivity. One of these processes is the so-called hydrogenotrophic methanogenesis (HM), which appeared mainly as a feasible technology for upgrading biogas [68,69]. The technique utilizes CO_2 and H_2 gases as feedstocks to form CH_4, according to the biological Sabatier-reaction (Eq. 6), catalyzed by hydrogenotrophic *archaea* [70] (**Tables 1 and 2**).

$$CO_2(g) + 4H_2(g) \leftrightarrow CH_4(g) + 2H_2O(l);\ \Delta G^0 = -130.7\ kJ/mol \qquad (6)$$

In theory, HM requires molar ratio of CO_2:H_2 = 1:4, although several results in literature indicated that the ratio used in real applications should compensate the utilization of substrate for biomass growth (CO_2 and H_2, as well) [71-73]. Generally, HM can be distinguished into two types: *in situ* and *ex situ* methanation. The term *in situ* methanation refers to the reduction of internally produced/obtained CO_2 by externally provided H_2 [74]. This approach can be effectively applied for product upgrading when the CO_2 is found as an undesirable by-product next to methane, such as in case of biogas fermentation technology. The so-called *ex situ* methanation, however, means the use of parallel addition of CO_2 and H_2 to a biological methanation reactor in the given ratio to perform the Sabatier-reaction [69]. When the substrate carbon dioxide is derived from technologies other than biogas fermentation, the latter method is a viable option. Moreover, in case of CO_2/H_2 separation processes (such as membrane separation), a properly designed product gas stream can be directly provided for the methanation unit.

Depending on the type of the applied biocatalyst (pure or mixed cultures), further sub-techniques can be plotted. Firstly, by using pure cultures, high selectivity can be achieved and the overall process can be well designed. Although, sustainability consideration should be also taken into account, since the methane is a low-price product. Therefore, the use of naturally occurring or industry-derived hydrogenotrophic *archaea*-containing microbe sources may be more preferable for field application. In case of such mixed consortia, the enrichment of preferred methanogenic species and the suppression of undesirable side-reactions should be carried out. For instance, in addition of Sabatier-reaction, the CO_2/H_2 mixture can be utilized through the Wood-Ljungdahl pathway (Eq. 7) to form acetic acid [75,76]:

$$2CO_2(g) + 4H_2(g) \leftrightarrow CH_3COO^-(aq) + H^+(aq) + 2H_2O(l);\ \Delta G^0 = -95\ kJ/mol \quad (7)$$

This reaction occurs and competes with HM due to homoacetogenic species being present [69]. Apparently, the homoacetogenesis means not only a reduction in the expected methane yield, but also a threat system stability due to the inhibitory effect of acid accumulation in the media, if not oxidized with appropriate rate at the same time [77]. Fortunately, if it is not inhibited in the system, the so-called acetoclastic methanogenesis (AM) may occur to further promote methane formation based on acetic acid in accordance with Eq. 8 [78]:

$$CH_3COOH(aq) \leftrightarrow CH_4(g) + CO_2(g);\ \Delta G^0 = -36\ kJ/mol \quad (8)$$

Although it is an efficient pathway to increase the methane yields and protect HM-performing microbes from acid inhibition, AM is significantly less energetically favorable than HM [79].

Another major aspect is the technological implementation of methanation. As it is generally concluded, the most significant engineering issue is the insufficient gas to liquid phase mass transfer of hydrogen gas because of its limited solubility [80,81]. It should be noted that when higher operational temperatures are set in order to stimulate the methanogen species, a counterproductive effect appears: the decrease in gas solubility at higher temperatures [82]. To enhance H_2 gas transfer to the liquid phase, the methanation in pressurized bioreactors could be highly beneficial, since the efficiency of methanogenesis, the gas solubility as well as the gas transfer coefficient (through the decrease in bubble size under pressure) can be increased by using pressure [69,83]. However, when providing H_2 externally to the system, the aspect of H_2 partial pressure should be carefully addressed and kept relatively low, since – according to several literature examples – the increase in H_2 partial pressure may have inhibitory effect on organic acid (acetate, propionate, butyrate) oxidizing microbes, thus, the acid accumulation can lead to the deterioration of methanogenesis [69,84,85,86]. Normally, the injection of hydrogen should be balanced with its consumption.

Besides the application of pressure, the H_2 distribution method and reactor type are efficient tools to control the process efficiency. Although reactor types such as anaerobic filters, bubble columns, up-flow anaerobic sludge blanket or trickle bed reactors have been developed, continuously stirred tank reactors can usually outperform them in the cost of supplied energy [69,72,81,87]. For better H_2 distribution in various reactors, distributor systems can be efficiently used in form of diffusers, sponges or even ceramic/polymeric membranes [38,88,89].

4.2. Utilization of CO_2 for Microbial Electrosynthesis

Microbial electrosynthesis (MES) is a novel technology that allows carbon dioxide valorization without the need of a chemical reductant like hydrogen gas or others, which has already been proposed within the concept of biorefinery [90,91]. In this case, the reducing power is provided by a cathode in the form of electrons, and the reduction reaction is biologically catalyzed by electrotrophic microorganisms such as *Sporomusa ovata* or *Clostridium ljundhalii,* using CO_2 as sole carbon source [92]. These special microorganisms, used as inexpensive catalyst, are able to directly exchange electrons in contact with conductive solid surfaces and incorporate them into their metabolism, together with protons, to reduce CO_2 into reduced organics such as volatile fatty acids, alcohols or methane (**Table 3**). Moreover, MES shows great potential to find new products that can be targeted, providing that the final product is strongly determined by the microbial community present in the bioelectrode, which represents an extensive field [92]. Another advantage of MES among other CO_2 or syngas valorization technologies is that MES works at ambient conditions of temperature and pressure, in contrast to high pressure and temperature required for technologies such as water/gas shift (WGS) reaction or Fischer-Tropsch (FT) synthesis [93]. Nevertheless, electric energy from an external power supply is necessary to provide the microorganisms with electrons, which makes MES a potential technology for renewable electric energy storing in the form of chemical energy.

Off-gases containing mostly CO_2 are less valuable and attractive for most CO_2 valorization technologies proposed due to the absence of a reductant, although these residual streams are largely available in heavy industries, large-scale fermentations or power plants [93]. However, pure CO_2 has already been used as feedstock in MES in several studies showing efficiency and good performance. Besides, using CO_2 has proven to be more productive than bicarbonate as feedstock, which was the first substrate proposed for inorganic carbon reduction, offering for instance a 5-fold increase in acetate productivity [94]. Nevertheless, only a few studies have dealt with real CO_2 residual streams until date. These gases have different impurities, such as O_2, N_2, NO_x, SO_x or H_2S, that are strongly dependent on the source, and can be harmful for electroactive bacteria [92,95]. Among these, oxygen is the highest threat for MES systems, as electroactive bacteria are commonly strict anaerobes [96]. The rest of usual impurities could even be removed simultaneously with CO_2 in MES systems, representing another advantage for CO_2 off-gas valorization with MES systems [95,97].

Providing that the most important energy input of MES is the external power supply to provide electrons to the biocathode, a cheap and sustainable electrical source must be found for this purpose. Renewable energy is rapidly growing in the last few years all over the world, and their variable and unpredictable nature is generating growing energy surpluses that are beginning to compromise electric grid stability. Till now, storage systems allowing for exploitation of this energy excess have been proposed as solution to this challenge [98]. MES has therefore the potential to store these energy surpluses and valorize residual CO_2 streams simultaneously, giving as a result easily storable and usable chemical energy. The unpredictable nature of renewable energy could, not only affect grid stability but also represent a potential threat to the microbial communities in the biocathode of a MES, that depend on the electrons provided by the power supply. In this sense, a few studies have already been published concluding that MES is resilient to renewable energy fluctuations, showing how the system performance and productivities can be maintained during subsequent power disconnections, and reaching titers comparable with non-disturbed systems [99,100].

Although MES has a great potential for residual CO_2 utilization and important technological advancements have been made in the last few years to make it feasible in practice, its novelty and complexity keeps it below other alternatives from an economical point of view nowadays [101]. Coupling MES with renewable energy or the use of real exhaust gases as feedstock are key steps to make MES economically viable as it has been covered above. Ion exchange membrane’s high cost, CO_2 dissolution and the use of novel metals to catalyze the counter electrode reaction are also among the main drawbacks that must be overcome. Regarding to membranes, alternative materials are already being used to lower system capital cost showing good performance [102]. Gas diffusion electrodes (GDEs) are being developed to improve inorganic carbon availability to the biocathode [103]. And the most common platinum or dimensionally stable anode counter electrodes meant for water splitting [92] are intended to be replaced by bioanodes lowering cell potential and catalyst cost [104]. It is expected that overcoming these challenges with the research efforts being carried out globally will move the MES technology closer to industrialization bring it on par with electrocatalytic CO_2 conversion.

4.3. CO_2 conversion in bioelectrochemical systems applying microalgae

Microalgal biomass is considered a propitious feedstock towards biofuels generation. Nevertheless, the technologies for the commercial/large scale applications of microalgae-derived biofuels are not economically viable yet [105,106]. Thus, to address this issue, the microalgal biorefinery approach could be a promising way to reduce the cost involved during bioenergy conversion. Among this, wastewater treatment and electricity generation from microalgae is recently paid more attention. Earlier reports showed that the microalgae had been identified as a potential resource for energy, remediation via wastewater treatment and also as a source of high value-added products and CO_2 sequestration.

Nevertheless, one of the newest applications in microalgal technology is microbial fuel cells (MFCs). This technology can be used for electricity generation during the microalgae degradation at anode and result in the release of electrons. Moreover, microalgae can be cultivated or grown in the cathode chamber aid in the carbon capture. In bacteria, the first electricity production was made in the year of 1911, however, until the beginning of the 1990s not much attention was paid towards MFCs [107,108]. Nowadays, many advanced approaches introduced towards new anode/cathode materials, efficient designs, low-cost catalysts or substrates. These improvements have resulted in the cost-effectiveness, enhanced efficiency that ultimately ended its application various places.

In comparison with other available technologies for bioenergy production, MFCs offer several unique advantages, and they were i) direct output either as energy/electricity, ii) high performances and turnovers at ambient temperature, iii) many times not necessary for the extra energy source, iv) reliable baseload power, v) cost-effective feedstock storage and vi) highly environmental friendly with almost no pollution impact [109]. Currently, one of the most promising advances in MFCs is the utilization of microalgae for power generation. Generally, in MFCs process microalgae can be used as substrate at the anode for the removal of nutrients or capture of CO_2 generated from the cathode [110,111]. In 2009, Powell et al. [112] developed an MFC which contained Saccharomyces cerevisiae in the anodic chamber and the microalgae *Chlorella vulgaris* at cathode chamber. The microalgal culture worked as a suitable electron acceptor, and this organism utilized the CO_2 generated from the cathode for its growth. This configuration managed to produce 2.7 mW m^{-2} using two cathodes. Besides, microalgae can play a vital role of electrons donor or acceptor simultaneously when they are in both the cathodic and anodic chambers. Microalgae-MFC can work in the presence and absence of light conditions, whereas photo microbial fuel cells can be functional while the photons are present [113,114]. **Table 4** revealed that different microalgal species involved MFCs synthesis and its configurations can be grouped into a single chamber, double chambers or photosynthetic sediment.

In microalgae based MFCs- as a substrate, the algal biomass can be used directly at the anode to remove nutrients or uptake of CO_2 generated from the cathode as compared with other systems [115]. Presently, in MFCs researchers showed more interest in using phototrophic microorganisms at cathode end due to its unique features such as oxygen production and ability to capture the generated CO_2 [116,117]. Notwithstanding, the power generation from abiotic control of MFCs might appear comparable with microalgal-based systems; this is restrained and not highly feasible option. Microalgal-based cathodes do not require any replenishment, and it provides continued operation. Thus, the positive response to light emission from photosynthetic cathodes showed the evidence of active oxygenators and therefore became vital biocatalysts. This reveals that the microalgae-based MFCs appears to be an excellent alternative biocatalyst for sustainable energy production, CO_2 fixation and appear thus to be the potentials material for solving various environment-related problems. For example, microalgae serve as a low-cost biomaterial which is suitable for producing many types of bioenergy such as biodiesel, bioethanol, biomethane, and biohydrogen. Nevertheless, microalgae have numerous benefits, still they hold a lot of limitations such as the cost involved in pre-treatment, oil extraction, etc. One of the notable limitations is towards the practical application of MFCs is oxygen delivery and carbon dioxide accumulation [116]. In MFCs technologies the drawback are based on irreversible reactions and processes in the cathode compartment which can grievously affect the performance of MFCs [118].

5. Future perspectives and concluding remarks

From papers in the literature it seems that biohydrogen fermentation was brought already to scaled-up level and successful attempts and models towards commercialization have been also communicated [119-121]. Additionally, adequate commercialization should consider the deployment of integrative biorefinery schemes for improved energy generation efficiency [122-124]. Overall, this would indicate that research on the production side has reached a promising level of maturity and further efforts should be put into the downstream side of the fermentative hydrogen technology in order to realize similar advancement.

Similar to the philosophy on upstream side, the downstreaming (recovery and purification) of biohydrogen should also rely on integrated process solutions, where a value-added step is attached subsequent to the actual separation methods e.g. membranes [6]. On the basis of the discussion and approaches presented thoroughly in this paper, several potential pathways for the valorization of CO_2 collected concurrently with H_2 purification are shown in **Fig. 4**. Actually, it is meant to be illustrated in **Fig. 4** that the membrane material and module (forming the membrane unit) have to be designed and modelled so as to take proper control on the CO_2/H_2 separation, resulting in the enhanced feed processing capacity, target gas recovery and purity. Afterwards, the secondary streams of the membrane purification system enriched with CO_2 can be supplied to various microbiologically-driven processes (**Fig. 4**), such as emerging bioelectrochemical systems to synthetize methane or other products via the reduction of CO_2 or the capability of algae could be exploited to generate useful chemicals.

These approaches should be investigated and feedback should be provided in order to reveal the best avenues to go for, both in technological and economical terms. For this reason, to take one step forward, the construction of innovative gas separation integrated membrane bioreactor – as shown in our previous paper [12] – is among the future plans to get more experimental feedback. In this aspect, again, membranes e.g. polymer, enzymatic, etc. and modules with superior CO_2 separation properties will be required in order to facilitate the consecutive conversion stages [152-155].

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References

[1] I.N. Mohamad, R. Rohani, M.T.M. Nor, P. Claassen, M.S. Muhammad, M.S. Mastar Masdar, et al., An overview of gas-upgrading technologies for biohydrogen produced from treatment of palm oil mill effluent, J. Eng. Sci. Technol. 12 (2017) 725–755.

[2] L.M. Robeson, Polymer membranes for gas separation, Curr. Opin. Solid State Mater. Sci. 4 (1999) 549–552. https://doi.org/10.1016/S1359-0286(00)00014-0

[3] B. Freeman, Y. Yampolskii, I. Pinnau, Materials Science of Membranes for Gas and Vapor Separation, John Wiley & Sons, Ltd, Chichester, UK, 2006.

[4] T.S. Chung, L.Y. Jiang, Y. Li, S. Kulprathipanja, Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation, Prog. Polym. Sci. 32 (2007) 483–507. https://doi.org/10.1016/j.progpolymsci.2007.01.008

[5] V. Giel, B. Galajdová, D. Popelková, J. Kredatusová, M. Trchová, E. Pavlova, et al., Gas transport properties of novel mixed matrix membranes made of titanate nanotubes and PBI or PPO, Desalin. Water Treat. 56 (2015) 3285-3293. https://doi.org/10.1080/19443994.2014.981931

[6] 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 (2013a) 9673-9687. https://doi.org/10.1016/j.ijhydene.2013.05.158

[7] 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 (2013b) 15092-15099. https://doi.org/10.1016/j.ijhydene.2013.09.133

[8] 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. https://doi.org/10.1016/j.ijhydene.2013.08.092

[9] N. Nemestóthy, P. Bakonyi, E. Szentgyörgyi, G. Kumar, D.D. Nguyen, S.W. Chang, et al., Evaluation of a membrane permeation system for biogas upgrading using model and real gaseous mixtures: The effect of operating conditions on separation behaviour, methane recovery and process stability, J. Clean. Prod. 285 (2018a) 44-51. https://doi.org/10.1016/j.jclepro.2018.03.047

[10] H. Lin, Z. He, Z. Sun, J. Vu, A. Ng, M. Mohammed, et al., CO_2-selective membranes for hydrogen production and CO_2 capture – Part I: Membrane development, J. Membr. Sci. 457 (2014) 149-161. https://doi.org/10.1016/j.memsci.2014.01.020

[11] L.M. Robeson, The upper bound revisited, J. Membr. Sci. 320 (2008) 390-400. https://doi.org/10.1016/j.memsci.2008.04.030

[12] P. Bakonyi, G. Kumar, K. Bélafi-Bakó, S.H. Kim, S. Koter, W. Kujawski, et al., A review of the innovative gas separation membrane bioreactor with mechanisms for integrated production and purification of biohydrogen, Bioresour.Technol. 270 (2018) 643–655. https://doi.org/10.1016/j.biortech.2018.09.020

[13] M. Mulder, Basic principles of membrane technology, Kluwer Academic, 1991.

[14] N.A. Ahmad, C.P. Leo, A.L. Ahmad, A.W. Mohammad, Separation of CO_2 from hydrogen using membrane gas absorption with PVDF/PBI membrane, Int. J. Hydrogen Energy. 41 (2016) 4855–4861. https://doi.org/10.1016/j.ijhydene.2015.11.054

[15] L.M. Robeson, Correlation of separation factor versus permeability for polymeric membranes, J. Membr. Sci. 62 (1991) 165–185. https://doi.org/10.1016/0376-7388(91)80060-J

[16] H. Rabiee, A. Ghadimi, T. Mohammadi, Gas transport properties of reverse-selective poly(ether-b-amide6)/[Emim][BF_4] gel membranes for CO_2/light gases separation, J. Membr. Sci. 476 (2015) 286–302. https://doi.org/10.1016/j.memsci.2014.11.037

[17] A. Car, C. Stropnik, W. Yave, K.V. Peinemann, PEG modified poly(amide-b-ethylene oxide) membranes for CO_2 separation, J. Membr. Sci. 307 (2008) 88–95. https://doi.org/10.1016/j.memsci.2007.09.023

[18] 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. https://doi.org/10.1016/j.memsci.2010.02.008

[19] G. Huang, A.P. Isfahani, A. Muchtar, K. Sakurai, B.B. Shrestha, D. Qin, et al., Pebax/ionic liquid modified graphene oxide mixed matrix membranes for enhanced CO_2 capture, J. Membr. Sci. 565 (2018) 370–379. https://doi.org/10.1016/j.memsci.2018.08.026

[20] P. Izák, K. Friess, V. Hynek, W. Ruth, Z. Fei, J.P. Dyson, et al., Separation properties of supported ionic liquid–polydimethylsiloxane membrane in pervaporation process, Desalination 241 (2009) 182–187. https://doi.org/10.1016/j.desal.2007.12.050

[21] A.S.L.S.L. Gouveia, L. Ventaja, L.C.C. Tomé, I.M.M. Marrucho, A.S.L.S.L. Gouveia, L. Ventaja, et al., Towards biohydrogen separation using poly(ionic liquid)/Ionic liquid composite membranes, Membranes 8 (2018) 124. https://doi.org/10.3390/membranes8040124

[22] Y. Li, S. Wang, G. He, H. Wu, F. Pan, Z. Jiang, Facilitated transport of small molecules and ions for energy-efficient membranes, Chem. Soc. Rev. 44 (2015a) 103–118. https://doi.org/10.1039/C4CS00215F

[23] J. Cheng, L. Hu, Y. Li, J. Liu, J. Zhou, K. Cen, Improving CO_2 permeation and separation performance of CO2-philic polymer membrane by blending CO_2 absorbents, Appl. Surf. Sci. 410 (2017) 206–214. https://doi.org/10.1016/j.apsusc.2017.03.084

[24] P. Li, Z. Wang, Z. Qiao, Y. Liu, X. Cao, W. Li, et al., Recent developments in membranes for efficient hydrogen purification, J. Membr. Sci. 495, (2015b) 130-168. https://doi.org/10.1016/j.memsci.2015.08.010

[25] L. Shao L, B.T. Low, T.S. Chung, A.R. Greenberg, Polymeric membranes for the hydrogen economy: contemporary approaches and prospects, J. Membr. Sci. 327 (2009) 18-31. https://doi.org/10.1016/j.memsci.2008.11.019

[26] P. Jajesniak, H.E.M. Omar Ali, T.S. Wong, Carbon dioxide capture and utilization using biological systems: opportunities and challenges, J. Bioproces. Biotechniq. 4 (2014) 155. https://doi.org/10.4172/2155-9821.1000155

[27] J. Hou, M.Y. Zulkifli, M. Mohammad, Y. Zhang, A. Razmjou, V. Chen, Biocatalytic gas-liquid membrane contactors for CO_2 hydration with immobilized carbonic anhydrase, J. Membr. Sci. 520 (2016) 303-313. https://doi.org/10.1016/j.memsci.2016.07.003

[28] J. Shi, Y. Jiang, Z. Jiang, X. Wang, X. Wang, S. Zhang, et al., Enzymatic conversion of carbon dioxide, Chem. Soc. Rev. 44 (2015) 5981-6000. https://doi.org/10.1039/C5CS00182J

[29] J.K.J. Yong, G.W. Stevens, F. Caruso, S.E. Kentish, The use of carbonic anhydrase to accelerate carbon dioxide capture processes, J. Chem. Technol. Biotechnol. 90 (2015) 3-10. https://doi.org/10.1002/jctb.4502

[30] L. Bao, M.C. Trachtenberg, Facilitated transport of CO_2 across liquid membrane: Comparing enzyme, amine, and alkaline, J. Membr. Sci. 280 (2006) 330-334. https://doi.org/10.1016/j.memsci.2006.01.036

[31] N. Nemestóthy, P. Bakonyi, Zs. Németh, K. Bélafi-Bakó, Evaluation of pectin-reinforced supported liquid membranes containing carbonic anhydrase: The role of ionic liquid on enzyme stability and CO_2 separation performance, J. CO_2 Util. 24 (2018b) 59-63. https://doi.org/10.1016/j.jcou.2017.12.001

[32] J.K.J. Yong, G.W. Stevens, F. Caruso, S.E. Kentish, In situ layer-by-layer assembled carbonic anhydrase-coated hollow fiber membrane contactor for rapid CO_2 absorption, J. Membr. Sci. 514 (2016) 556-565. https://doi.org/10.1016/j.memsci.2016.05.020

[33] M.Y.M. Abdelrahim, C.F. Martins, L.A. Neves, C. Capasso, C.T. Supuran, I.M. Coelhoso, et al., Supported ionic liquid membranes immobilized with carbonic anhydrases for CO_2 transport at high temperatures, J. Membr. Sci. 528 (2017) 225-230. https://doi.org/10.1016/j.memsci.2017.01.033

[34] Y.T. Zhang, L. Zhang, H.L. Chen, H.M. Zhang, Selective separation of low concentration CO_2 using hydrogel immobilized CA enyzme based hollow fiber membrane reactors, Chem. Eng. J. 65 (2010) 3199-3207. https://doi.org/10.1016/j.ces.2010.02.010

[35] A. Bednár, N. Nemestóthy, P. Bakonyi, L. Fülöp, G. Zhen, X. Lu, et al., Enzymatically-boosted ionic liquid gas separation membranes using

carbonic anhydrase of biomass origin, Chem. Eng. J. 303 (2016) 621-626. https://doi.org/10.1016/j.cej.2016.05.148

[36] L.A. Neves, C. Afonso, I.M. Coelhoso, J.G. Crespo, Integrated CO_2 capture and enzymatic bioconversion in supported ionic liquid membranes, Sep. Purif. Technol. 97 (2012) 34-41. https://doi.org/10.1016/j.seppur.2012.01.049

[37] C.F. Martins, L.A. Neves, M. Estevao, A. Rosatella, V.D. Alves, C.A.M. Afonso, et al., Effect of water activity on carbon dioxide transport in cholinium-based ionic liquids with carbonic anhydrase, Sep. Purif. Technol. 168 (2016) 74-82. https://doi.org/10.1016/j.seppur.2016.05.004

[38] F. Ojeda, P. Bakonyi, G. Buitrón, Improvement of methane content in a hydrogenotrophic anaerobic digester via the proper operation of membrane module integrated into an external-loop. Bioresour. Technol. 245 (2017) 1294-1298. https://doi.org/10.1016/j.biortech.2017.08.183

[39] G. Zhen, X. Lu, G. Kumar, P. Bakonyi, X. Kaiqin, Z. Youcai, Microbial electrolysis cell platform for simultaneous waste biorefinery and clean electrofuels generation: Current situation, challenges and future perspectives, Prog. Energy Combust. Sci. 63 (2017) 119-145. https://doi.org/10.1016/j.pecs.2017.07.003

[40] S. Srikanth, Y. Alvarez-Gallego, K. Vanbroekhoven, D. Pant, Enzymatic electrosynthesis of formic acid through carbon dioxide reduction in a bioelectrochemical system: effect of immobilization and carbonic

anhydrase addition, ChemPhysChem 18 (2017) 3174-3181. https://doi.org/10.1002/cphc.201700017

[41] D.T. Coker, B.D. Freeman, G.K. Fleming, Modeling multicomponent gas separation using hollow-fiber membrane contactors, AIChE J. 44 (1998) 1289-1302. https://doi.org/10.1002/aic.690440607

[42] T. Katoh, M. Tokumura, H. Yoshikawa, Y. Kawase, Dynamic simulation of multicomponent gas separation by hollow-fiber membrane module: Nonideal mixing flows in permeate and residue sides using the tanks-inseries model, Sep. Purif. Technol. 76 (2011) 362-372. https://doi.org/10.1016/j.seppur.2010.11.006

[43] Y. Shindo, T. Hakuta, H. Yoshitome, H. Inoue, Calculation methods for multicomponent gas separation by permeation, Sep. Sci. Technol. 20 (1985) 445-459. https://doi.org/10.1080/01496398508060692

[44] R.W. Baker, Membrane Technology and Applications, 2nd ed., Wiley, 2004.

[45] R. Krishna, Using the Maxwell-Stefan formulation for highlighting the influence of interspecies (1-2) friction on binary mixture permeation across microporous and polymeric membranes, J. Membr.Sci, 540 (2017) 261-276. https://doi.org/10.1016/j.memsci.2017.06.062

[46] K.S. Spiegler, Transport process in ionic membranes, Trans. Faraday Soc. 54 (1958) 1408-1428. https://doi.org/10.1039/TF9585401408

[47] A.A. Ghoreyshi, H. Asadi, K. Pirzadeh, A generic transport model for separation of gas mixtures by glassy polymer membranes based on

Maxwell-Stefan formulation, RSC Adv. 5 (2015) 48207-48216. https://doi.org/10.1039/C5RA05686A

[48] M. Grahn, J. Hedlund, Maxwell-Stefan modeling of high flux tubular silicalite-1 membranes for CO_2 removal from CO_2/H_2 gas mixtures, J Membr. Sci. 471 (2014) 328-337. https://doi.org/10.1016/j.memsci.2014.08.034

[49] G. Ji, G. Wang, K. Hooman, S. Bhatia, J.C. Diniz da Costa, Simulation of binary gas separation through multi-tube molecular sieving membranes at high temperatures, Chem. Eng. J. 218 (2013) 394-404. https://doi.org/10.1016/j.cej.2012.12.063

[50] J. Kangas, L. Sandstrom, I. Malinen, J. Hedlund, J. Tanskanen, Maxwell-Stefan modeling of the separation of H_2 and CO_2 at high pressure in an MFI membrane, J Membr. Sci 435 (2013) 186-206. https://doi.org/10.1016/j.memsci.2013.02.026

[51] L. Sandström, E. Sjöberg, J. Hedlund, Very high flux MFI membrane for CO_2 separation, J. Membr. Sci. 380 (2011) 232-240. https://doi.org/10.1016/j.memsci.2011.07.011

[52] G. He, X. Huang, R. Xu, B. Zhu, An improved resistance model for gas permeation in composite membranes, J. Membr. Sci. 118 (1996) 1-7. https://doi.org/10.1016/0376-7388(96)00023-3

[53] F.B. Peng, J.Q. Liu, J.T. Li, Analysis of the gas transport performance through PDMS/PS composite membranes using the resistances-in-series

model, J. Membr. Sci, 222 (2003) 225-234. https://doi.org/10.1016/S0376-7388(03)00293-X

[54] L.F. Xu, M.G. Sedigh, T.T. Tsotsis, M. Sahimi, Nonequilibrium molecular dynamics simulation of transport and separation of gases in carbon nanopores. II. Binary and ternary mixtures and comparison with the experimental data, J. Chem. Phys. 112 (2000) 910-922. https://doi.org/10.1063/1.480618

[55] X. Qin, Q. Meng, Y. Feng, Y. Gao, Graphene with line defect as a membrane for gas separation: Design via a first-principles modeling, Surf. Sci. 607 (2013) 153–158. https://doi.org/10.1016/j.susc.2012.08.024

[56] Y. Li, Z. Zhou, P. Shen, Z. Chen, Two-dimensional polyphenylene: experimentally available porous graphene as a hydrogen purification membrane, Chem. Commun. 46 (2010) 3672-3674. https://doi.org/10.1039/B926313F

[57] E. Atci, I. Erucar, S. Keskin, Adsorption and transport of CH_4, CO_2, H_2 mixtures in a Bio-MOF material from molecular simulations, J. Phys. Chem. C 115 (2011) 6833-6840. https://doi.org/10.1021/jp200429x

[58] J.I. Marriott, E. Sørensen, I.D.L. Bogle, A general approach to modelling membrane modules, Chem. Eng. Sci. 58 (2003) 4975-4990. https://doi.org/10.1016/j.ces.2003.07.005

[59] D. Bucsu, N. Nemestothy, Z. Pientka, L. Gubicza, K. Belafi-Bako, Modelling of biohydrogen production and recovery by membrane gas

separation, Desalination 240 (2009) 306-310. https://doi.org/10.1016/j.desal.2007.10.094

[60] W.P. Walawender, S.A. Stern, Analysis of membrane separation parameters. II. counter-current and cocurrent flow in a single permeation stage, Sep. Sci. 7 (1972) 553-584. https://doi.org/10.1080/00372367208056054

[61] A. Aghaeinejad-Meybodi, K. Ghasemzadeh, A.A. Babaluo, P. Morrone, A. Basile, Modeling study of silica membrane performance for hydrogen separation, Asia-Pac. J. Chem. Eng. 10 (2015) 781-790. https://doi.org/10.1002/apj.1915

[62] M.J. Thundyil, W.J. Koros, Mathematical modeling of gas separation permeators for radial crossflow, countercurrent, and cocurrent hollow fiber membrane modules, J. Membr. Sci. 125 (1997) 275–291. https://doi.org/10.1016/S0376-7388(96)00218-9

[63] M. Peer, S.M. Kamali, M. Mahdeyarfar, T. Mohammadi, Separation of hydrogen from carbon monoxide using a hollow fiber polyimide membrane: Experimental and simulation, Chem. Eng. Technol. 30 (2007) 1418-1425. https://doi.org/10.1002/ceat.200700173

[64] M. Peer, M. Mahdyarfar, T. Mohammadi, Evaluation of a mathematical model using experimental data and artificial neural network for prediction of gas separation, J. Nat. Gas Chem. 17 (2008) 135–141. https://doi.org/10.1016/S1003-9953(08)60040-7

[65] M. Rezakazemi, A. Dashti, M. Asghari, S. Shirazian, H_2-selective mixed matrix membranes modeling using ANFIS, PSO-ANFIS, GA-ANFIS, Int. J. Hydrogen Energy 42 (2017) 15211-15225. https://doi.org/10.1016/j.ijhydene.2017.04.044

[66] G. Dreyfus, Neural Networks: Methodology and Applications, Springer-Verlag Berlin Heidelberg 2005.

[67] A. Abbas, N. Al-Bastaki, Modeling of an RO water desalination unit using neural networks, Chem. Eng. J. 114 (2005) 139–143. https://doi.org/10.1016/j.cej.2005.07.016

[68] N. Aryal, T. Kvist, F. Ammam, D. Pant, L.D. Ottosen, An overview of microbial biogas enrichment, Bioresour. Technol. 264 (2018) 359-369. https://doi.org/10.1016/j.biortech.2018.06.013

[69] B. Lecker, L. Illi, A. Lemmer, H. Oechsner, Biological hydrogen methanation – A review, Bioresour. Technol. 245 (2017) 1220-1228. https://doi.org/10.1016/j.biortech.2017.08.176

[70] I. Bassani, P.G. Kougias, L. Treu, I. Angelidaki, Biogas upgrading via hydrogenotrophic methanogenesis in two-stage continuous stirred tank reactors at mesophilic and thermophilic conditions, Environ. Sci. Technol. 49 (2015) 12585-12593. https://doi.org/10.1021/acs.est.5b03451

[71] M. Burkhardt, G. Busch, Methanation of hydrogen and carbon dioxide, Appl. Energy 111 (2013) 74-79. https://doi.org/10.1016/j.apenergy.2013.04.080

[72] L. Rachbauer, G. Voitl, G. Bochmann, W. Fuchs, Biological biogas upgrading capacity of a hydrogenotrophic community in a trickle-bed reactor, Appl. Energy 180 (2016) 483-490. https://doi.org/10.1016/j.apenergy.2016.07.109

[73] D.L. Wise, C.L. Cooney, D.C. Augenstein, Biomethanation: Anaerobic fermentation of CO_2, H_2 and CO to methane, Biotechnol. Bioeng. 20 (1978) 1153-1172. https://doi.org/10.1002/bit.260200804

[74] S.K.M. Rittmann, A critical assessment of microbiological biogas to biomethane upgrading systems, Adv. Biochem. Eng. Biotechnol. 151 (2015a) 117-135. https://doi.org/10.1007/978-3-319-21993-6_5

[75] Y. Bajón Fernández, A. Soares, K. Koch, P. Vale, E. Cartmell, Bioconversion of carbon dioxide in anaerobic digesters for on-site carbon capture and biogas enhancement – A review, Crit. Rev. Environ. Sci. Technol. 47 (2017) 1555-1580. https://doi.org/10.1080/10643389.2017.1372001

[76] L. Rachbauer, R. Beyer, G. Bochmann, W. Fuchs, Characteristics of adapted hydrogenotrophic community during biomethanation, Sci. Total Environ. 595 (2017) 912-919. https://doi.org/10.1016/j.scitotenv.2017.03.074

[77] D.G. Mulat, F. Mosbæk, A.J Ward, D. Polag, M. Greule, F. Keppler, et al., Exogenous addition of H_2 for an in situ biogas upgrading through biological reduction of carbon dioxide into methane, Waste Manag. 68 (2017) 146-156. https://doi.org/10.1016/j.wasman.2017.05.054.

[78] B. Demirel, P. Scherer, The roles of acetotrophic and hydrogenotrophic methanogens during anaerobic conversion of biomass to methane: a review, Rev. Environ. Sci. Bio. 7 (2008) 173-190. https://doi.org/10.1007/s11157-008-9131-1

[79] S. Sarker, J.J Lamb, D.R Hjelme, K.M Lien, Overview of recent progress towards in-situ biogas upgradation techniques, Fuel 226 (2018) 686-697. https://doi.org/10.1016/j.fuel.2018.04.021

[80] G. Luo, S. Johansson, K. Boe, L. Xie, Q. Zhou, I. Angelidaki, Simultaneous hydrogen utilization and in situ biogas upgrading in an anaerobic reactor, Biotechnol. Bioeng. 109 (2012) 1088-1094. https://doi.org/10.1002/bit.24360

[81] I. Bassani, P.G Kougias, I. Angelidaki, In-situ biogas upgrading in thermophilic granular UASB reactor: key factors affecting the hydrogen mass transfer rate, Bioresour. Technol. 221 (2016) 485-491. https://doi.org/10.1016/j.biortech.2016.09.083

[82] S. Rittmann, A. Seifert, C. Herwig, Essential prerequisites for successful bioprocess development of biological CH_4 production from CO_2 and H_2, Crit. Rev. Biotechnol. 35 (2015b) 141-151. https://doi.org/10.3109/07388551.2013.820685

[83] M. Götz, J. Lefebvre, F. Mörs, A.M. Koch, F. Graf, S. Bajohr, et al., Renewable Power-to-Gas: A technological and economic review, Renew. Energ. 85 (2016) 1371-1390. https://doi.org/10.1016/j.renene.2015.07.066

[84] E.A. Cazier, E. Trably, J.P. Steyer, R. Escudié, Biomass hydrolysis inhibition at high hydrogen partial pressure in solid-state anaerobic digestion, Bioresour. Technol. 190 (2015) 106-113. https://doi.org/10.1016/j.biortech.2015.04.055

[85] S. Fukuzaki, N. Nishio, M. Shobayashi, S. Nagai, Inhibition of the fermentation of propionate to methane by hydrogen, acetate, and propionate, Appl. Environ. Microbiol. 56 (1990) 719-723

[86] G. Luo, I. Angelidaki, Co-digestion of manure and whey for in situ biogas upgrading by the addition of H_2: process performance and microbial insights, Appl. Microbiol. Biotechnol. 97 (2013) 1373-1381. https://doi.org/10.1007/s00253-012-4547-5

[87] P.G. Kougias, L. Treu, D.P. Benavente, K. Boe, S. Campanaro, I. Angelidaki, Ex-situ biogas upgrading and enhancement in different reactor systems, Bioresour. Technol. 225 (2017) 429-437. https://doi.org/10.1016/j.biortech.2016.11.124

[88] I. Bassani, P.G. Kougias, L. Treu, H. Porte, S. Campanaro, I. Angelidaki, Optimization of hydrogen dispersion in thermophilic up-flow reactors for ex situ biogas upgrading, Bioresour. Technol. 234 (2017) 310-319. https://doi.org/10.1016/j.biortech.2017.03.055

[89] I. Díaz, C. Pérez, N. Alfaro, F. Fdz-Polanco, A feasibility study on the bioconversion of CO_2 and H_2 to biomethane by gas sparging through polymeric membranes, Bioresour. Technol. 185 (2015) 246-253. https://doi.org/10.1016/j.biortech.2015.02.114

[90] A. ElMekawy, H.M. Hegab, G. Mohanakrishna, A.F. Elbaz, M. Bulut, D. Pant, Technological advances in CO_2 conversion electro-biorefinery: A step toward commercialization, Bioresour. Technol. 215 (2016) 357–370. https://doi.org/10.1016/J.BIORTECH.2016.03.023

[91] J. Sadhukhan, J.R. Lloyd, K. Scott, G.C. Premier, E.H. Yu, T. Curtis, I.M. Head, A critical review of integration analysis of microbial electrosynthesis (MES) systems with waste biorefineries for the production of biofuel and chemical from reuse of CO_2, Renew. Sust. Energ. Rev. 56 (2016) 116–132. https://doi.org/10.1016/j.rser.2015.11.015

[92] R. Mateos, A. Escapa, K. Vanbroekhoven, S.A. Patil, A. Moran, D. Pant, Microbial Electrochemical Technologies for CO_2 and Its Derived Products Valorization, Microb. Electrochem. Technol. (2019) 777–796. https://doi.org/10.1016/B978-0-444-64052-9.00032-7

[93] R. Takors, M. Kopf, J. Mampel, W. Bluemke, B. Blombach, B. Eikmanns, et al., Using gas mixtures of CO, CO_2 and H_2 as microbial substrates: the do’s and don’ts of successful technology transfer from laboratory to production scale, Microb. Biotechnol. 11 (2018) 606–625. https://doi.org/10.1111/1751-7915.13270

[94] G. Mohanakrishna, K. Vanbroekhoven, D. Pant, Imperative role of applied potential and inorganic carbon source on acetate production through microbial electrosynthesis, J CO_2 Util. 15 (2016) 57–64. https://doi.org/10.1016/j.jcou.2016.03.003

[95] T. Zhang, P.L. Tremblay, Possible Industrial Applications for Microbial

Electrosynthesis From Carbon Dioxide, Microb. Electrochem. Technol. (2019) 825–842. https://doi.org/10.1016/B978-0-444-64052-9.00034-0

[96] C.W. Marshall, D.E. Ross, K.M. Handley, P.B. Weisenhorn, J.N. Edirisinghe, C.S. Henry, et al., Metabolic Reconstruction and Modeling Microbial Electrosynthesis, Sci. Rep. 7 (2017) 8391. https://doi.org/10.1038/s41598-017-08877-z

[97] Y. Gong, A. Ebrahim, A.M. Feist, M. Embree, T. Zhang, D. Lovley, et al., Sulfide-Driven Microbial Electrosynthesis, Env. Sci. Technol. 47 (2013) 568–573. https://doi.org/10.1021/es303837j

[98] A.G. Olabi, Renewable energy and energy storage systems, Energy 136 (2017) 1–6. https://doi.org/10.1016/J.ENERGY.2017.07.054

[99] M. del P. Anzola Rojas, R. Mateos, A. Sotres, M. Zaiat, E.R. Gonzalez, A. Escapa, et al., Microbial electrosynthesis (MES) from CO_2 is resilient to fluctuations in renewable energy supply, Energy Convers. Manag. 177 (2018a) 272–279. https://doi.org/10.1016/J.ENCONMAN.2018.09.064

[100] M. del P. Anzola Rojas, M. Zaiat, E.R. Gonzalez, H. De Wever, D. Pant, Effect of the electric supply interruption on a microbial electrosynthesis system converting inorganic carbon into acetate, Bioresour. Technol. 266 (2018b) 203–210. https://doi.org/10.1016/J.BIORTECH.2018.06.074

[101] X. Christodoulou, T. Okoroafor, S. Parry, S.B. Velasquez-Orta, The use of carbon dioxide in microbial electrosynthesis: Advancements,

sustainability and economic feasibility, J. CO_2 Util. 18 (2017) 390–399. https://doi.org/10.1016/j.jcou.2017.01.027

[102] D.C. Aiken, T.P. Curtis, E.S. Heidrich, Avenues to the financial viability of microbial electrolysis cells [MEC] for domestic wastewater treatment and hydrogen production, Int. J Hydrogen. Energy 44 (2019) 2426–2434. https://doi.org/10.1016/J.IJHYDENE.2018.12.029

[103] S. Bajracharya, K. Vanbroekhoven, C.J.N. Buisman, D. Pant, D.P.B.T.B. Strik, Application of gas diffusion biocathode in microbial electrosynthesis from carbon dioxide, Environ. Sci. Pollut. R. 23 (2016) 22292–22308. https://doi.org10.1007/s11356-016-7196-x

[104] T. Bouchez, A. Bridier, E. Le Quéméner, Method and device for controlling the activity of a bioelectrochemical system comprising both a bioanode and a biocathode, (2017). U.S. Patent Application 15/515,393.

[105] T. Jafary, M. Rahimnejad, A.A. Ghoreyshi, G. Najafpour, F. Hghparast, W.R.W. Daud, Assessment of bioelectricity production in microbial fuel cells through series and parallel connection, Energ. Convers. Manag. 75 (2013) 256-262. https://doi.org/10.1016/j.enconman.2013.06.032

[106] M. Ghasemi, S. Shahgaldi, M. Ismail, B.H. Kim, Z. Yaakob, W.R.W. Daud, Activated carbon nanofibers as an alternative cathode catalyst to platinum in a two-chamber microbial fuel cell, Int. J. Hydrogen Energy 36 (2011) 13746-13752. https://doi.org/10.1016/j.ijhydene.2011.07.118

[107] R.M. Allen, H.P. Bennetto, Microbial fuel-cells, Appl. Biochem. Biotechnol. 39 (1993) 27-40. https://doi.org/10.1007/BF02918975

[108] V.M. Ortiz-Martínez, M.J. Salar-García, F.J. Hernández-Fernández, A.P. de los Ríos, Development and characterization of a new embedded ionic liquid based membrane-cathode assembly for its application in single chamber microbial fuel cells, Energy 93 (2015) 1748-1757. https://doi.org/10.1016/j.energy.2015.10.027

[109] F.J. Hernández-Fernández, A. Pérez de los Ríos, M.J. Salar-García, V.M. Ortiz-Martínez, L.J. Lozano-Blanco, C. Godínez, et al., Recent progress and perspectives in microbial fuel cells for bioenergy generation and wastewater treatment, Fuel Process. Technol. 138 (2015) 284-297. https://doi.org/10.1016/j.fuproc.2015.05.022

[110] I. Gajda, J. Greenman, C. Melhuish, I. Ieropoulos, Self-sustainable electricity production from algae grown in a microbial fuel cell system, Biomass Bioenerg. 82 (2015) 87-93. https://doi.org/10.1016/j.biombioe.2015.05.017

[111] M.J. Salar-García, I. Gajda, V.M. Ortiz-Martínez, J. Greenman, M.M. Hanczyc, A.P. de los Ríos, et al., Microalgae as substrate in low cost terracotta-based microbial fuel cells: Novel application of the catholyte produced, Bioresour. Technol. 209 (2016) 380-385. https://doi.org/10.1016/j.biortech.2016.02.083

[112] E.E. Powell, M.L. Mapiour, R.W. Evitts, G.A. Hill, Growth kinetics of Chlorella vulgaris and its use as a cathodic half cell, Bioresour. Technol. 100 (2009) 269-274. https://doi.org/10.1016/j.biortech.2008.05.032

[113] Y. Cui, N. Rashid, N. Hu, M.S.U. Rehman, J.I. Han, Electricity generation and microalgae cultivation in microbial fuel cell using microalgae-enriched anode and bio-cathode, Energy Convers. Manag. 79 (2014) 674-680. https://doi.org/10.1016/j.enconman.2013.12.032

[114] C. Xu, K. Poon, M.M.F. Choi, R. Wang, Using live algae at the anode of a microbial fuel cell to generate electricity, Environ. Sci. Pollut. Res. 22 (2015) 15621-15635. https://doi.org/10.1007/s11356-015-4744-8

[115] X.A. Walter, J. Greenman, B. Taylor, I.A. Ieropoulos, Microbial fuel cells continuously fuelled by untreated fresh algal biomass, Algal Res. 11 (2015) 103-107. https://doi.org/10.1016/j.algal.2015.06.003

[116] I. Gajda, J. Greenman, C. Melhuish, I. Ieropoulos, Photosynthetic cathodes for Microbial Fuel Cells, Int. J. Hydrogen Energy 38 (2013) 11559-11564. https://doi.org/10.1016/j.ijhydene.2013.02.111

[117] L. Xiao, Z. He, Applications and perspectives of phototrophic microorganisms for electricity generation from organic compounds in microbial fuel cells, Renew. Sust. Energ. Rev. 37 (2014) 550-559. https://doi.org/10.1016/j.rser.2014.05.066

[118] H. Rismani-Yazdi, S.M. Carver, A.D. Christy, O.H. Tuovinen, Cathodic limitations in microbial fuel cells: An overview, J Power Sources 180 (2008) 683-694

[119] C.W. Hsu, C.Y. Lin, Commercialization model of hydrogen production technology in Taiwan: Dark fermentation technology applications, Int. J.

Hydrogen Energy 41 (2016) 4489-4497. https://doi.org/10.1016/j.ijhydene.2015.07.080

[120] C.Y. Lin, S.Y. Wu, P.J. Lin, J.S. Chang, C.H. Hung, K.S. Lee, et al., A pilot-scale high-rate biohydrogen production system with mixed microflora, Int. J. Hydrogen Energy 36 (2011) 8758-8764. https://doi.org/10.1016/j.ijhydene.2010.07.115

[121] E. Tapia-Venegas, J.E. Ramirez-Morales, F. Silva-Illanes, J. Toledo-Alarcón, F. Paillet, R. Escudie, et al., Biohydrogen production by dark fermentation: scaling-up and technologies integration for a sustainable system, Rev. Environ. Sci. Biotechnol. 14 (2015) 761-785. https://doi.org/10.1007/s11157-015-9383-5

[122] D. Das, Commercialization of biohydrogen production process from distillery effluent, Int. J. Hydrogen Energy 2019. https://doi.org/10.1016/j.ijhydene.2019.05.056

[123] T. Rózsenberszki, L. Koók, P. Bakonyi, N. Nemestóthy, W. Logrono, M. Pérez, et al., Municipal waste liquor treatment via bioelectrochemical and fermentation (H_2 + CH_4) processes: Assessment of various technological sequences, Chemosphere 171 (2017) 692-701. https://doi.org/10.1016/j.chemosphere.2016.12.114

[124] P. Bakonyi, G. Kumar, L. Koók, G. Tóth, T. Rózsenberszki, T., Bélafi-Bakó, K., et al., Microbial electrohydrogenesis linked to dark fermentation as integrated application for enhanced biohydrogen production: A review on process characteristics, experiences and lessons, Bioresour. Technol. 251

(2018) 381-389. https://doi.org/10.1016/j.biortech.2017.12.064

[125] H. Lin, E. Wagner, J. Swinnea, B. Freeman, S. Pas, A.J. Hill, et al., Transport and structural characteristics of crosslinked poly(ethylene oxide) rubbers, J. Membr. Sci. 276 (2006) 145–161. https://doi.org/10.1016/j.memsci.2005.09.040

[126] C.H. Lau, S. Liu, D.R. Paul, J. Xia, Y.C. Jean, H. Chen, et al., Silica nanohybrid membranes with high CO_2 affinity for green hydrogen purification, Adv. Energy Mater. 1 (2011) 634–642. https://doi.org/10.1002/aenm.201100195

[127] L. M. Agneessens, L.D.M. Ottosen, N.V. Voigt, J.L. Nielsen, N. de Jonge, C.H. Fischer, et al., In-situ biogas upgrading with pulse H2 additions: The relevance of methanogen adaption and inorganic carbon level, Bioresour. Technol. 233 (2017) 256-263. https://doi.org/10.1016/j.biortech.2017.02.016

[128] A. Grimalt-Alemany, M. Łężyk, D.M. Kennes-Veiga, I.V. Skiadas, H.N. Gavala, Enrichment of Mesophilic and Thermophilic Mixed Microbial Consortia for Syngas Biomethanation: The Role of Kinetic and Thermodynamic Competition, Waste Biomass Valor. (2019) 1-17. https://doi.org/10.1007/s12649-019-00595-z

[129] M.B. Jensen, M.V.W. Kofoed, K. Fischer, N.V. Voigt, L.M. Agneessens, D.J. Batstone, et al., Venturi-type injection system as a potential H_2 mass transfer technology for full-scale in situ

biomethanation, Appl. Energy 222 (2018) 840-846. https://doi.org/10.1016/j.apenergy.2018.04.034

[130] L.M. Agneessens, L.D.M. Ottosen, M. Andersen, C.B. Olesen, A. Feilberg, M.V.W. Kofoed, Parameters affecting acetate concentrations during in-situ biological hydrogen methanation, Bioresour. Technol. 258 (2018) 33-40. https://doi.org/10.1016/j.biortech.2018.02.102

[131] M.A. Voelklein, D. Rusmanis, J.D. Murphy, Biological methanation: Strategies for in-situ and ex-situ upgrading in anaerobic digestion, Appl. Energy 235 (2019) 1061-1071. https://doi.org/10.1016/j.apenergy.2018.11.006

[132] M. Burkhardt, I. Jordan, S. Heinrich, J. Behrens, A. Ziesche, G. Busch, Long term and demand-oriented biocatalytic synthesis of highly concentrated methane in a trickle bed reactor, Appl. Energy 240 (2019) 818-826. https://doi.org/10.1016/j.apenergy.2019.02.076

[133] D. Strübing, A.B. Moeller, B. Mößnang, M. Lebuhn, J.E. Drewes, K. Koch, Anaerobic thermophilic trickle bed reactor as a promising technology for flexible and demand-oriented H_2/CO_2 biomethanation, Appl. Energy 232 (2018) 543-554. https://doi.org/10.1016/j.apenergy.2018.09.225

[134] H. Porté, P.G. Kougias, N. Alfaro, L. Treu, S. Campanaro, I. Angelidaki, Process performance and microbial community structure in thermophilic trickling biofilter reactors for biogas upgrading, Sci. Total Environ. 655 (2019) 529-538. https://doi.org/10.1016/j.scitotenv.2018.11.289

[135] H. Wang, D. Liu, L. Lu, Z. Zhao, Y. Xu, F. Cui, Degradation of algal organic matter using microbial fuel cells and its association with trihalomethane precursor removal, Bioresour. Technol. 116 (2012) 80-85. https://doi.org/10.1016/j.biortech.2012.04.021

[136] S.B. Velasquez-Orta, T.P.Curtis, B.E. Logan, Energy from algae using microbial fuel cells, Biotechnol. Bioeng. 103 (2009) 1068–1076. https://doi.org/10.1002/bit.22346

[137] K. Nishio, K. Hashimoto, K. Watanabe, Digestion of Algal Biomass for Electricity Generation in Microbial Fuel Cells, Biosci. Biotechnol. Biochem. 77 (2013) 670-672. https://doi.org/10.1271/bbb.120833

[138] J.C.W. Lan, K. Raman, C.M. Huang, C.M. Chang, The impact of monochromatic blue and red LED light upon performance of photo microbial fuel cells (PMFCs) using Chlamydomonas reinhardtii transformation F5 as biocatalyst, Biochem. Eng. J. 78 (2013) 39-43. https://doi.org/10.1016/j.bej.2013.02.007

[139] A.M. Lakaniemi, O.H. Tuovinen, J.A. Puhakka, Production of Electricity and Butanol from Microalgal Biomass in Microbial Fuel Cells, BioEnerg. Res. 5 (2012) 481-491. https://doi.org/10.1007/s12155-012-9186-2

[140] S. Kondaveeti, K.S. Choi, R. Kakarla, B. Min, Microalgae Scenedesmus obliquus as renewable biomass feedstock for electricity generation in microbial fuel cells (MFCs), Front. Env. Sci. Eng. 8 (2014) 784-791. https://doi.org/10.1007/s11783-013-0590-4

[141] R. Kakarla, B. Min, Evaluation of microbial fuel cell operation using algae as an oxygen supplier: carbon paper cathode vs. carbon brush cathode, Bioprocess Biosyst. Eng. 37 (2014a) 2453-2461. https://doi.org/10.1007/s00449-014-1223-4

[142] R. Kakarla, B. Min, Photoautotrophic microalgae Scenedesmus obliquus attached on a cathode as oxygen producers for microbial fuel cell (MFC) operation, Int. J. Hydrogen Energy 39 (2014b) 10275-10283. https://doi.org/10.1016/j.ijhydene.2014.04.158

[143] D.B. Wang, T.S. Song, T. Guo, Q. Zeng, J. Xie, Electricity generation from sediment microbial fuel cells with algae-assisted cathodes, Int. J. Hydrogen Energy 39 (2014) 13224-13230. https://doi.org/10.1016/j.ijhydene.2014.06.141

[144] A. González del Campo, P. Cañizares, M.A. Rodrigo, F.J. Fernández, J. Lobato, Microbial fuel cell with an algae-assisted cathode: A preliminary assessment, J. Power Sources 242 (2013) 638-645. https://doi.org/10.1016/j.jpowsour.2013.05.110

[145] E. Bazdar, R. Roshandel, S. Yaghmaei, M.M. Mardanpour, The effect of different light intensities and light/dark regimes on the performance of photosynthetic microalgae microbial fuel cell, Bioresour. Technol. 261 (2018) 350-360. https://doi.org/10.1016/j.biortech.2018.04.026

[146] C.T. Wang, Y.S. Huang, T. Sangeetha, Y.M. Chen, W.T. Chong, H.C. Ong, et al., Novel bufferless photosynthetic microbial fuel cell (PMFCs) for

enhanced electrochemical performance, Bioresour. Technol. 255 (2018) 83-87. https://doi.org/10.1016/j.biortech.2018.01.086

[147] M. Li, M. Zhou, J. Luo, C. Tan, X. Tian, P. Su, T. Gu, Carbon dioxide sequestration accompanied by bioenergy generation using a bubbling-type photosynthetic algae microbial fuel cell, Bioresour. Technol. 280 (2019) 95-103. https://doi.org/10.1016/j.biortech.2019.02.038

[148] X.Y. Wu, T.S. Song, X.J. Zhu, P. Wei, C.C. Zhou, Construction and Operation of Microbial Fuel Cell with Chlorella vulgaris Biocathode for Electricity Generation, Appl. Biochem. Biotechnol. 171 (2013) 2082-2092. https://doi.org/10.1007/s12010-013-0476-8

[149] Y. Zhang, Q. He, L. Xia, Y. Li, S. Song, Algae cathode microbial fuel cells for cadmium removal with simultaneous electricity production using nickel foam/graphene electrode, Biochem. Eng. J. 138 (2018) 179-187. https://doi.org/10.1016/j.bej.2018.07.021

[150] L. Gouveia, C. Neves, D. Sebastião, B.P. Nobre, C.T. Matos, Effect of light on the production of bioelectricity and added-value microalgae biomass in a Photosynthetic Alga Microbial Fuel Cell, Bioresour. Technol. 154 (2014) 171-177. https://doi.org/10.1016/j.biortech.2013.12.049

[151] D.J. Lee, J.S. Chang, J.Y. Lai, Microalgae–microbial fuel cell: A mini review, Bioresour. Technol. 198 (2015) 891-895. https://doi.org/10.1016/j.biortech.2015.09.061

[152] L.T. Angenent, J.G. Usack, J. Xu, D. Hafenbradl, R. Posmanik, J.W. Tester, Integrating electrochemical, biological, physical, and

thermochemical process units to expand the applicability of anaerobic digestion, Bioresour. Technol. 247 (2018) 1085-1094. https://doi.org/10.1016/j.biortech.2017.09.104

[153] S. Mazinani, R. Ramezani, S. Darvishmanesh, G.F. Molelekwa, R.D. Felice, B. Van der Bruggen, A ground breaking polymer blend for CO_2/N_2 separation, J. CO_2 Util. 27 (2018) 536-546. https://doi.org/10.1016/j.jcou.2018.08.024

[154] P.C. Sahoo, M. Kumar, S.K. Puri, S.S.V. Ramakumar, Enzyme inspired complexes for industrial CO_2 capture: Opportunities and challenges, J. CO_2 Util. 24 (2018) 419-429. https://doi.org/10.1016/j.jcou.2018.02.003

[155] P.R. Yaashikaa, P.S. Kumar, S.J. Varjani, A. Saravanan, A review on photochemical, biochemical and electrochemical transformation of CO2 into value-added products, J. CO_2 Util. 33 (2019) 131-147. https://doi.org/10.1016/j.jcou.2019.05.017

Figure legends

Fig. 1 – Comparison of CO_2/H_2 most promising membrane materials (with assumed 1 µm-thick selective layer). PEBAX®/PEG [17]; PEGDA/PEGMEA [125]; PEO/PDMS [18]; PEGMEA+particles [126] and Polaris™ membrane developed by MTR Inc. Reprinted from Journal of Membrane Science, 457, Lin et al., CO_2-selective membranes for hydrogen production and CO_2 capture – Part I: Membrane development, 149-161, Copyright (2014), with permission from Elsevier.

Fig. 2 – Working principle of gas separation membrane containing carbonic anhydrase (CA) enzyme

Fig. 3 – Flow patterns analysed in [43]: a) co-current flow, b) counter-current flow, c) cross flow, d) one-side mixing, e) perfect mixing.

Fig. 4 – Scheme of membrane-based biohydrogen purification and utilization of CO_2-rich gaseous fraction obtained in the separation process

Fig. 1

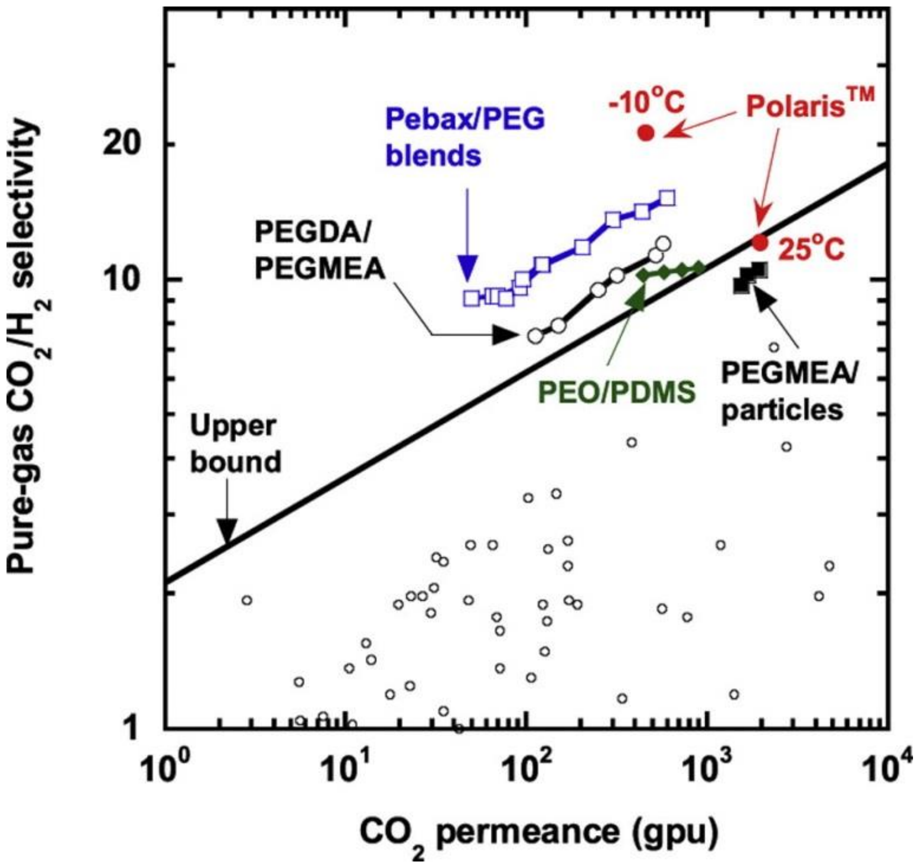
Pebax/PEG blends
-10°C
PolarisTM
PEGDA/ PEGMEA
25°C
PEO/PDMS
PEGMEA/ particles
Upper bound
Pure-gas CO2/H2 selectivity
20
10
1
10^0
10^1
10^2
10^3
10^4
CO2 permeance (gpu)

Fig. 2

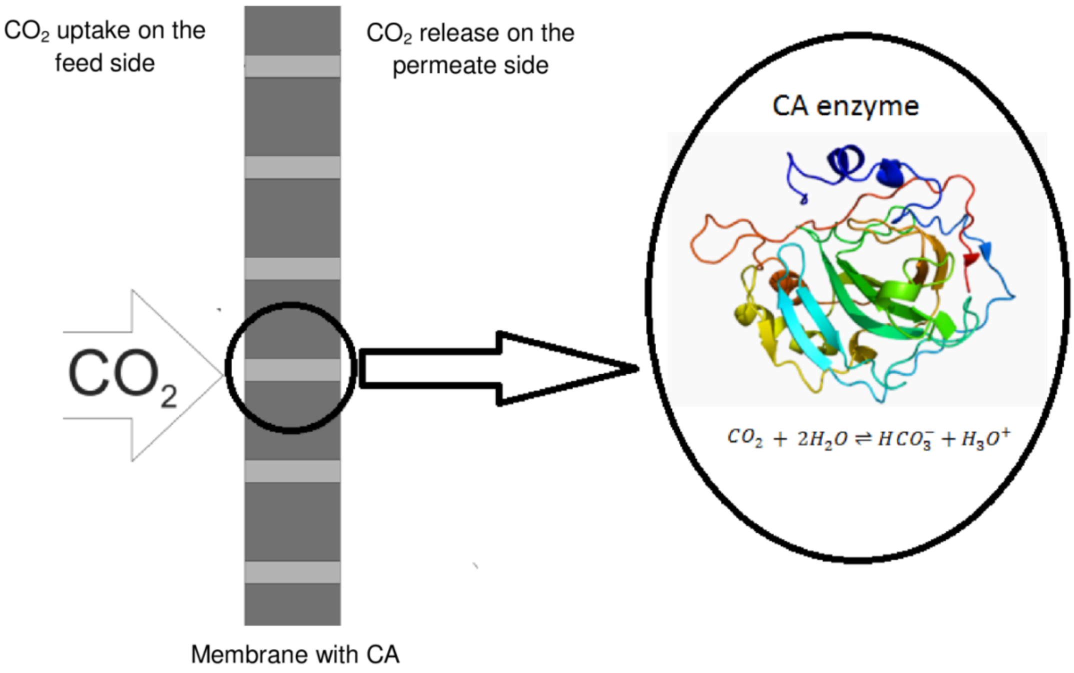
CO₂ uptake on the feed side
CO₂ release on the permeate side
CO₂
CA enzyme
$CO_2 + 2H_2O \rightleftharpoons HCO_3^- + H_3O^+$
Membrane with CA

Fig. 3

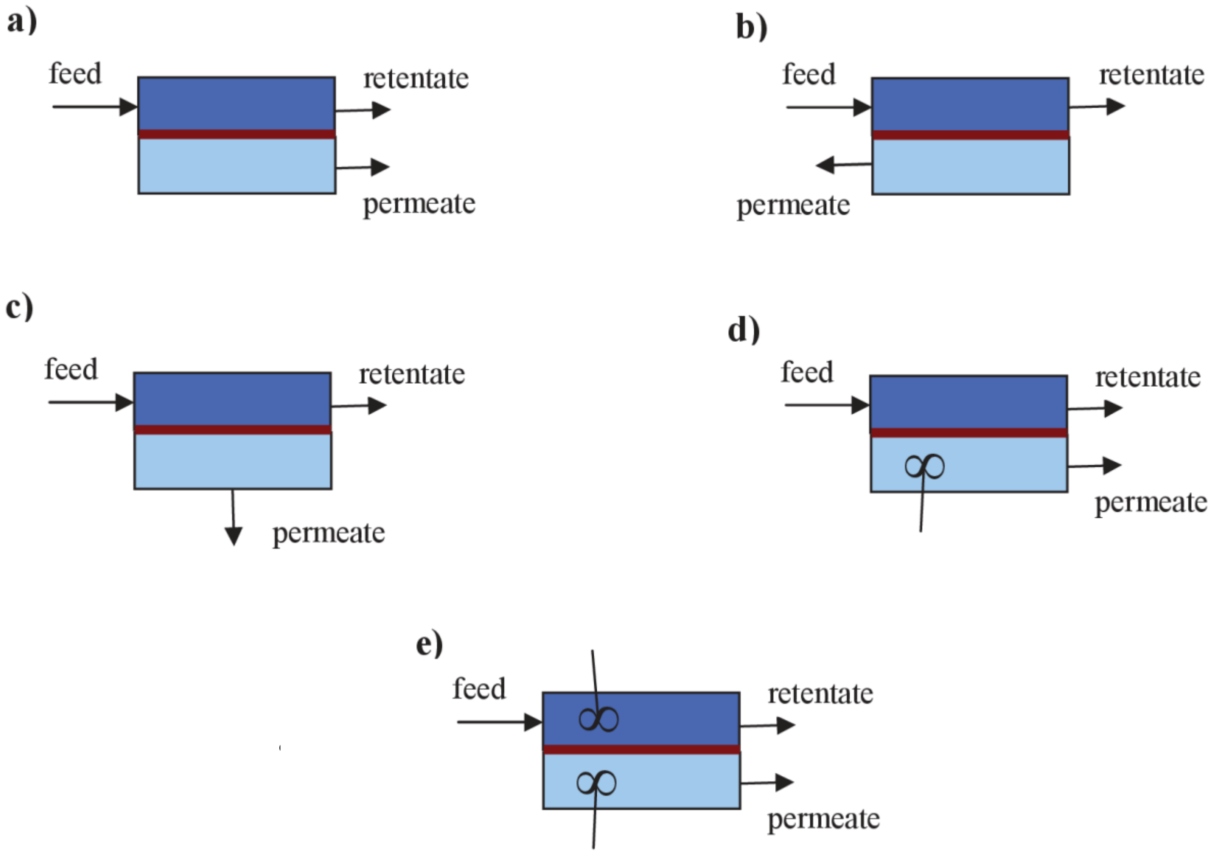
a)
feed
retentate
permeate
b)
feed
retentate
permeate
c)
feed
retentate
permeate
d)
feed
retentate
permeate
e)
feed
retentate
permeate

Fig. 4

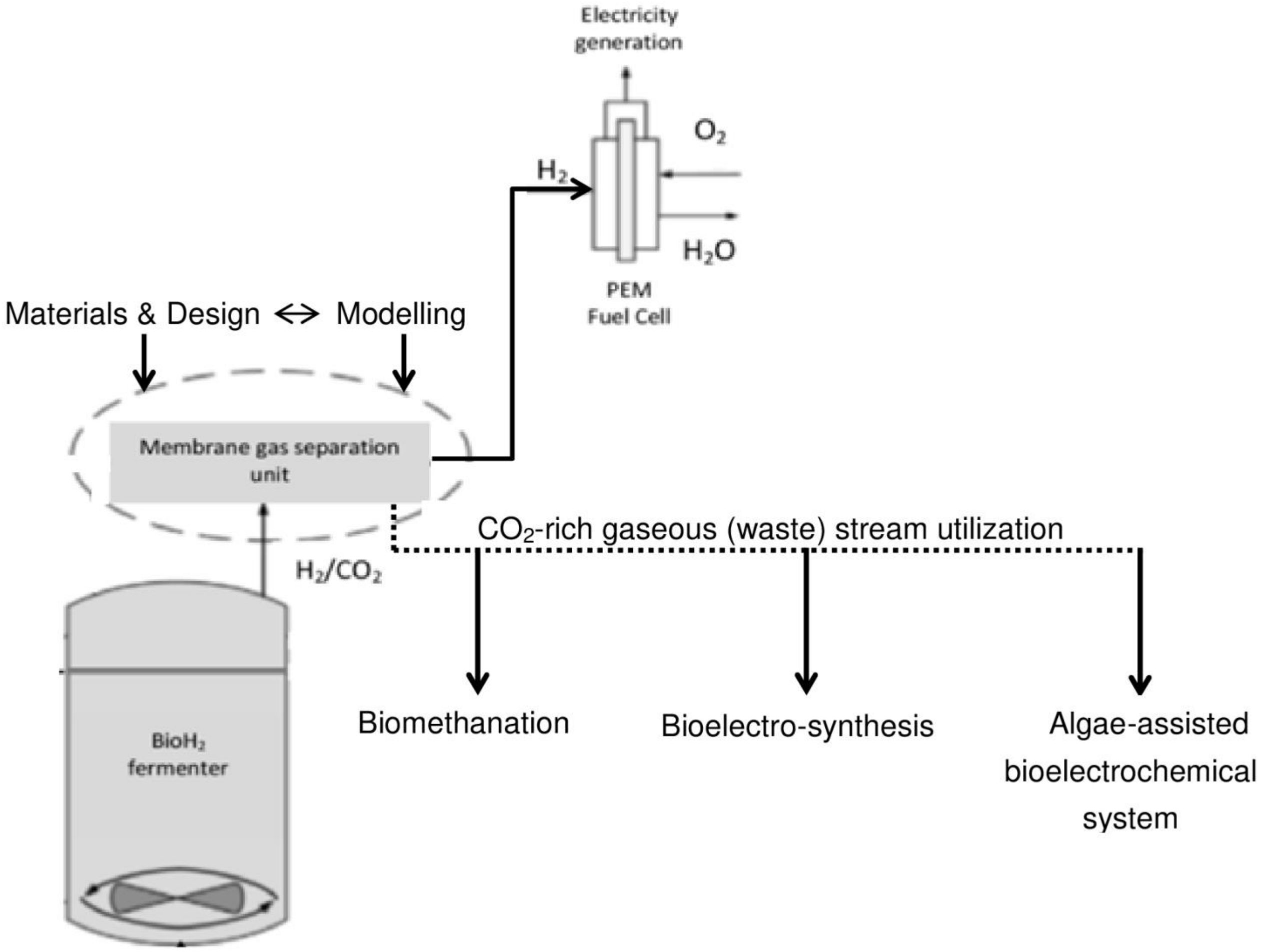
Electricity generation
O2
H2
H2O
PEM Fuel Cell
Materials & Design <-> Modelling
Membrane gas separation unit
CO2-rich gaseous (waste) stream utilization
H2/CO2
BioH2 fermenter
Biomethanation
Bioelectro-synthesis
Algae-assisted bioelectrochemical system

Table 1 – Examplary results regarding in-situ biogas upgrading technologies

Keywords of the application	CH_4 enrichment (%)	References
Continuous sterile tank reactor (CSTR) mesophilic condition (38 °C), mesophilic sludge from biogas plant, HRT: 23 days, pulse H_2, injections	76.8-100	[127]
Batch mode, 37 and 60 °C, syngas, mesophilic and thermophilic enriched microbial consortia, 0.1 L active volume	64.9 ± 8.3	[128]
Full-scale, venturi-type injector, thermophilic condition (52 °C), manure-based anaerobic digester, working volume ~1110 m^3, deep litter, grass silage, maize silage, HRT: 13 days	increasing 1.7-7	[129]
Continouos and bach lab reactors, mesophilic (38 °C), manure biogas plant, HRT: 20 days, working volume 0.3 L.	71-94	[130]
Upflow anaerobic sludge, thermophilic condition (55 °C), potato-strach wastewater, mesophilic granules, 1.4 L working volume, HRT: 7 days	82	[81]
Exogenous H_2 addition, batch mode, lab scale, labelled maize leaf, unlabelled maize leaf, thermophilic condition (52 °C), 24 days	89.4	[77]
Batch mode, total volume of 9.5 L, grass silage, thermophilic condition (55°C)	6.1 – 60.3	[131]

Table 2 – Examplary results on ex-situ biogas upgrading technologies

Keywords of the application	CH_4 enrichment (%)	References
Hydrogenotrophic methanogens, digestate from biogas plants, CSTR, bubble column reactor, upflow reactor, working volume: 1.2 – 1.4 L, 52 °C	98	[87]
Thermophilic condition (55°C), up-flow reactor, digestate from biogasplant, hydrogenotrophic inoculum, 0.85 L working volume	96	[88]
Batch and continuous operation, total volume of 9.5 L, thermophilic condition (55°C)	32-96	[131]
Trickle bed, digested sewage sludge, maize silage, 90 L volume, mesophilic condition, (38 °C), biogas/H2	> 94	[132]
Pilot-scale trickle bed reactor, thermostatic 55 °C, anaerobic sludge from a mesophilic waste water treatment plant digester	> 96	[133]
Trickling biofilter, enriched hydrogenotrophic culture, thermophilic temperature (54 °C), 1 L working volume, continuous operation, *Methanothermobacter* sp.	> 97	[134]

Table 3 – Instances of targeted products in MES from CO_2 sorted by group [92]

Group	Product	Chemical reaction	Standard potentials (vs. SHE)
Gas fuel	Methane (Biogas)	$CO_2 + 8e^- + 8H^+ \Rightarrow CH_4$	-0.24
Alcohols	Methanol	$CO_2 + 6e^- + 6H^+ \Rightarrow CH_4O + H_2O$	-0.38
	Ethanol	$2CO_2 + 12e^- + 12H^+ \Rightarrow C_2H_6O + 3H_2O$	-0.31
	Butanol	$4CO_2 + 24e^- + 24H^+ \Rightarrow C_4H_{10}O + 7H_2O$	-0.30
	Isopropanol	$3CO_2 + 18e^- + 18H^+ \Rightarrow C_3H_8O + 5H_2O$	-0.30
	Glycerol	$3CO_2 + 14e^- + 14H^+ \Rightarrow C_3H_8O_3 + 3H_2O$	-0.39
Volatile fatty acids	Formic acid	$CO_2 + 2e^- + 2H^+ \Rightarrow CH_2O_2$	-0.42
	Acetate	$CO_2 + 8e^- + 7H^+ \Rightarrow C_2H_3O_2{}^- + 2H_2O$	-0.28
	Butyrate	$4CO_2 + 20e^- + 19H^+ \Rightarrow C_4H_7O_2{}^- + 6H_2O$	-0.28

Table 4 – Some characteristics of algae-assisted bioelectrochemical systems

Microalgal species	**MFCs Chamber type**	**Anode**	**Cathode**	**Max. power density ($mW\cdot m^{-2}$)**	**References**
Anode based Microalgae in MFCs					
Chlorella pyrenoidosa	Double chamber	Graphite rod	Graphite rod	30.15	[114]
Chlorella vulgaris	Double chamber	Graphite brushes	Graphite brushes	*13*	[135]
	Single chamber	Graphite fiber brush	Carbon cloth-coated P	980	[136]
Chlamydomonas reinhardtii	Single chamber	Graphite felt	Carbon cloth-coated	78	[137]
Chlamydomonas reinhardtii	Double chamber	Graphite electrodes	Graphite electrodes	12.947	[138]
Dunaliella tertiolecta	Double chamber	Graphite plate	Graphite plate electrodes	5.3	[139]
Scenedesmus obliquus	Double chamber	Toray carbon paper	Toray carbon paper	102	[140]
Cathode based Microalgae in MFCs					
Chlorella vulgaris	Double chamber	Carbon fiber brush	Carbon cloth	23.9	[141]
Chlorella vulgaris	Single chamber sediment	Graphite felt	Multi-walled carbon nanotubes	38	[143]
Chlorella vulgaris	Double chamber	Toray carbon	Toray carbon	13.5	[144]

		cloth	cloth		
Chlorella vulgaris	Double chamber	carbon paper platinum coated	carbon fel	126	[145]
Marine *Chlorella* sp.	Single chamber	carbon cloth	carbon cloth	4.06	[146]
Chlorella vulgaris	Double chamber	carbon felt	carbon fiber cloth	1.82	[147]
Chlorella vulgaris	Modified MFC + tubular photobioreactor	Carbon felt	Carbon paper-coated Pt	27.5	[148]
Chlorella sp.	Double chamber	NF	NF/rGO	36.4	[149]
Chlorella vulgaris	Double chamber	Plain graphite	Plain graphite	62.7	[150]
Desmodesmus sp. A8	Double chamber	Plain graphite fel	Plain graphite felt	99.09	[151]
Scenedesmus obliquus	Double chamber	Plain carbon paper	Plain carbon paper	159	[142]