

# Overview of Biohydrogen Production Technologies and Application in Fuel Cell

Rahman S. N. A.<sup>1</sup>, Masdar M. S.<sup>2,\*</sup>, Rosli M. I.<sup>3</sup>, Majlan E. H.<sup>1</sup>, Husaini T.<sup>1</sup>

<sup>1</sup>Fuel Cell Institute, Universiti Kebangsaan Malaysia

<sup>2</sup>Research Centre for Sustainable Process Technology (CESPRO), Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia

<sup>3</sup>Department of Chemical and Process Engineering, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia

---

**Abstract** Hydrogen gas is clean and efficient energy carrier. Currently, hydrogen is produced by carbon-based non-renewable source such as natural gases, coal, heavy oil and naphtha as well as from electrolysis of water. However, the productions of hydrogen from fossil fuels generate greenhouse gases and require high energy. Thus, it is important to develop alternative hydrogen production routes that are renewable such as biohydrogen. In this paper, a review of biohydrogen production technologies including the mechanism and bioreactor system, and the hydrogen purification system is focused and discussed for the application of polymer electrolyte membrane fuel cell (PEMFC). Besides that, the bioreactor sizes that require generating hydrogen to power the PEMFC stack is calculated and compared in order to determine the potential application of hydrogen production through the biological pathway.

**Keywords** Biohydrogen, Purification, Membrane separation, PEMFC, Bioreactors

---

## 1. Introduction

Hydrogen has highest energy content per unit weight of any known fuel (142kJ/g) which is 2.75 times more energy density than other existing biofuels [1]. Besides that, the combustion of hydrogen gas to generate energy is environment friendly as combustion product only water vapours. Currently, hydrogen is produced from compound that containing hydrogen which natural gases, heavy oil and naphtha, coal, electrolysis of water and biomass. However, the carbon-based non-renewable source from fossil not able to sustain energy for the long term future as they currently depleted and also require high thermal energy, emit greenhouse gases to atmospheres which the disadvantage in environment view [2]. Therefore, generate hydrogen from renewable source such as biohydrogen production processes is important in order to make hydrogen as a possible clean energy carrier.

Biological hydrogen (biohydrogen) production processes is a hydrogen production technology that utilise renewable energy resources by using microorganisms. The process is operating at ambient temperature and atmospheric pressure, and use less energy. These biohydrogen production technologies are possible candidate for sustain the world power energy supply, potential to replace fossil fuels and do

not discharge greenhouse gases such as carbon dioxide. The biohydrogen is generating by three different mechanisms which can be categorised as light dependent (direct or indirect biophotolysis and photo fermentation) and independent (dark fermentation) [3, 4].

The best energy utilisation from hydrogen is in fuel cell application. The hydrogen gas generated from conventional process is commercially used as fuel in fuel cell system to generate electricity. However, the hydrogen produced from biohydrogen production technology for application in fuel cell is not yet commercial and the study about the application is also limited. This is because of some technical challenges of biohydrogen production technologies is need to be settled out with respect to using the hydrogen in fuel cell application. One of challenges is the hydrogen from biohydrogen production process must follow the particular fuel requirement of different fuel cell [5]. Therefore, it is important to study about the potential hydrogen separation and purification system from biohydrogen production process. Besides that, it is crucial to find a potential pathway to generate hydrogen from biohydrogen production which could bring a new step in the progress of fuel cell technologies.

Therefore, this review is focused on the comparison of hydrogen production rate, advantages and disadvantages from those three mechanisms of biohydrogen production process. Other than that, the hydrogen separation and purification from bioreactor is focused and will be discussed on the membrane gas technology.

---

\* Corresponding author:

shahbud@ukm.edu.my (Masdar M. S.)

Published online at <http://journal.sapub.org/chemistry>

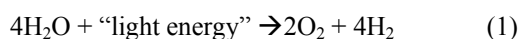
Copyright © 2015 Scientific & Academic Publishing. All Rights Reserved

In order to determine the potential application of hydrogen from biohydrogen production process in fuel cell system, polymer electrolyte membrane fuel cell (PEMFC) is chosen as it seems promising fuel cell for various applications such as stationary and portable fuel cell power generator. The comparison is done based on the calculated bioreactor size that required producing enough hydrogen from biohydrogen production process for power the PEMFC at 5W to 250kW which represent particular fuel cell application i.e. 5W-5kW represent portable power generator, 500W-100kW is stationary power generator, 5-250kW is demonstrated transportation application. The biohydrogen production process which potentially to commercial is determine based on the capability of the hydrogen produce to supply the PEMFC stack for 24 h in a continuous basis. Despite of various challenges and technical barrier to be handle and solve in order to generate hydrogen for large scale, however the purpose of this review is to give basis evaluation of fuel cell potential application from hydrogen generate from biohydrogen production process.

## 2. Biological Mechanism and Bioreactor for Hydrogen Production

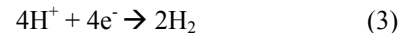
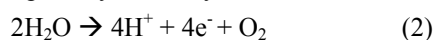
### 2.1. Biophotolysis

Photoautotrophic organism such as microalgae and cyanobacteria are capable to generate hydrogen and carbon dioxide in biophotolysis process. They utilize the light as energy source and carbon dioxide as carbon source to split water into hydrogen [6]. They produce biohydrogen by direct photolysis of water under the anaerobic conditions (1) [7]. There are two types of biophotolysis which are direct biophotolysis and indirect biophotolysis, as discussed next.



#### 2.1.1. Direct Biophotolysis

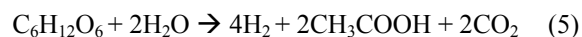
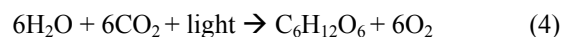
Hydrogen production by direct biophotolysis process is used solar energy and photosynthetic system of algae to convert water into chemical energy which subdivided into one-stage or two-stages. In direct biophotolysis, the light absorbed by photosystem I (PSI) and photosystem II (PSII) which use in hydrogen production and energy to transport electrons linearly to ferredoxin. The light absorbed by PSII is required for oxidation of water into electrons, protons ( $\text{H}^+$ ) and oxygen molecules (2). These electrons then transfer through the electron transport chain using the light energy absorbed in PSI to ferredoxin to the hydrogenase enzyme without involving intermediates  $\text{CO}_2$  fixation. These enzymes are then catalyst for recombination process of proton and electrons to evolve the hydrogen gas (3). This mechanism is also refers as one-stage direct biophotolysis where the biohydrogen is produced directly from water and solar energy via algae photosynthesis system.



There is a major limitation for this process which is the sensitivity of Fe-fe hydrogenases enzyme to oxygen that produced by photosynthesis which give greatly prohibit the activity of the enzyme for evolution of molecular hydrogen and resulting low yield of biohydrogen production (3). Meanwhile, two-stage direct biophotolysis is a continuous and upgrade process from one-stage direct biophotolysis which the oxygen is removed through the respiration using exogenous or endogenous substrates such as sulfur deprivation method.

#### 2.1.2. Indirect Biophotolysis

Indirect biophotolysis is the production of hydrogen from water via microalgae and cyanobacteria photosynthetic system to convert solar energy into chemical energy which is hydrogen by two steps in series. The first step is the biomass production through photosynthetic system (4) and follow by second step which utilise the biomass rich-carbohydrate for hydrogen-producing fermentation (5).

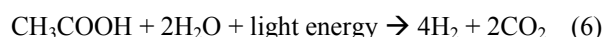


In this process, the evolutions of hydrogen and oxygen are temporally and/or spatially separation at different steps. In this way, the inhibition of hydrogenase enzyme activity to oxygen produced during photosynthesis process can be avoided. The examples of cyanobacteria organism that perform indirect biophotolysis such as *Gloebacter sp.*, *Synechocystis sp.*, and *Synechococcus sp.* [3].

The advantage of biophotolysis is the simplicity of the process to produce hydrogen without requirement of additional substrates as nutrient and can produce hydrogen directly from abundant source of water as electron donor; sunlight and carbon dioxide as basic needed for growth of microalgae and cyanobacteria. However, the process is requires high light intensity and the green algae and cyanobacteria have lower light conversion efficiency. The lower performance of the photobioreactors for light penetration in dense culture is contributed to lower hydrogen production.

### 2.2. Photo Fermentation

The hydrogen produce in photo fermentation is by photosynthetic organisms, in which using photosynthetic bacteria with additional of light. These photosynthetic bacteria are lack of Photosystem II (PSII) and perform the photosynthesis with Photosystem I (PSI) for hydrogen production. The process still requires light as source energy likely to biophotolysis, but the photosynthetic bacteria in this process not powerful enough to split water such in biophotolysis, so the process utilise organic acids, like acetic acid as electron donor to generate hydrogen (6).



Based in (6), there is no oxygen evolution during the process (anoxygenic photosynthesis) which gives no

inhibition effect to nitrogenase activity as they are sensitive to oxygen. The advantage of production hydrogen via photo fermentation with purple non-sulfur bacteria is the ability to liberate 100% of electrons from organic substrate to generate hydrogen and carbon dioxide which make fewer by-products in waste stream from this process [8]. Besides that, the photo fermentation bacteria are capable to use wide variety of organic substrate which can be obtained from available waste streams such as organic agricultural and industrial wastes. This will result in an advantage to economy of hydrogen production and waste management. For example, the usage of industrial wastewater as substrate has been successful in generating hydrogen in some studies [9, 10].

Even though there are many researches focused in this process, there are some technical barriers that prevent practical practice. These include low volumetric rates of production, low efficiency hydrogen production by nitrogenases, low photosynthetic conversion efficiency and low light conversion efficiency.

### 2.3. Dark Fermentation

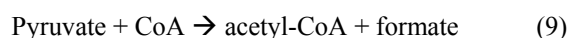
Dark fermentation is produced via heterotrophic mechanism in which uses carbohydrates like glucose as energy and carbon source and allocates the balance of energy in hydrogen and fermentation-related products and does not require light energy source which is the limitation in light-dependent processes, biophotolysis and photo fermentation. The same anaerobic method used in photo fermentation is also implemented in dark fermentation because this method eliminates the issue of sensitivity of hydrogenase to oxygen and gives high hydrogen production. Other than carbohydrates, the process can use various carbon sources including wastewater enriched with carbohydrates, organic compounds, polymers (i.e., starch, cellulose), and algae

biomass (i.e., macroalgae and microalgae) which give advantages on utilizing low value waste [11].

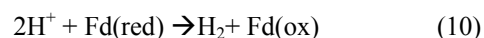
Hydrogen production in dark fermentation is a very complex process involving various bacteria by a series of biochemical reactions. In the early stage of dark fermentation, carbohydrate, mainly glucose which is the preferred carbon source for dark fermentation, is broken down into pyruvate and NADH which is called as glycolysis (7) [12].



The pyruvate is then converted to acetyl coenzyme A (acetyl-CoA) and depending upon the organism, which is catalyzed either through ferredoxin oxidoreductase (pyruvate: ferredoxin oxidoreductase, PFOR) which generates ferredoxin and carbon dioxide (8), or formate lyase (pyruvate: formate lyase, PFL) which generates formate (9) [13].



The production of hydrogen in the PFOR pathway is through the re-oxidation of ferredoxin which is catalyzed by a variety of Fe-Fe hydrogenase including ferredoxin-dependent hydrogenase (Fd-[FeFe]) (10). In some cases, the PFOR pathway also can derive some hydrogen from NADH which is the product of glycolysis reaction using one or more of several different Fe-Fe hydrogenases which are catalyzed either by reducing ferredoxin via NFOR (NADH:ferredoxine oxidoreductase), by directly reducing hydrogenase (NADH-[FeFe]), or as a co-substrate with reduced ferredoxin (Fd-NADH-[FeFe]) (11) [12].

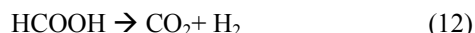


**Table 1.** Maximum hydrogen rate and yield based on biophotolysis, photo and dark fermentation processes

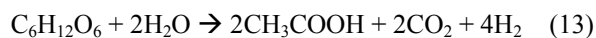
Types of biohydrogen production process	Bacterial strains	Maximum rate of hydrogen production (mL H <sub>2</sub> L <sup>-1</sup> h <sup>-1</sup> )	Maximum yield of hydrogen production	Refs
Direct biophotolysis	<i>Chlorella sorokiniana</i> strain Ce	1.35	na	[17]
	<i>Chlamydomonas reinhardtii</i> CC-124	1.1	na	[18]
Indirect biophotolysis	<i>Chlamydomonas MGA 161</i>	4.25	na	[19]
Photo fermentation	<i>Rhodobacter sphaeroides</i> ZX-5	102.23	1439 <sup>a</sup>	[20]
	<i>Rhodospseudomonas palustris</i> CQK 01	38.90	0.2 <sup>b</sup>	[21]
Dark fermentation	Municipal wastes	71.5	0.41 <sup>c</sup>	[22]
	Anaerobic digester sludge	500	2.3 <sup>b</sup>	[23]
	Municipal sewage	1800	4.26 <sup>d</sup>	[24]

na: not available, <sup>a</sup> ml H<sub>2</sub>/L<sub>cut</sub>, <sup>b</sup> mol H<sub>2</sub>/mol glucose, <sup>c</sup> mol H<sub>2</sub>/mol glycerol, <sup>d</sup> mol H<sub>2</sub>/mol sucrose

Meanwhile, the hydrogen produces from formate is catalysed either by formate hydrogen lyase (PFL pathway) which contain a Ni-fe hydrogenase or another pathway which contain a formate dependent Fe-fe hydrogenase (12). The hydrogen production of organisms via PFOR pathway is 2 to 4 mole of hydrogen per mole glucose greater than the organisms that produce hydrogen through PFL pathway which obtained 2 mole of hydrogen per mole glucose. This is because the additional NADH oxidation in PFOR pathway which not apply in PFL pathway. The remaining NADH is used to generate other reduced fermentation product such as ethanol, butanol and butyrate. Acetyl-CoA can also be used to generate ATP and giving a product which is acetate in the both cases.



Besides the hydrogen production pathway, the yield of hydrogen is also depending on the fermentation pathway end-product(s). If the acetic acid is the fermentation end-product, a theoretical 4 moles of hydrogen per mole glucose are generating (13) [14]. If the butyric acids are the fermentation end-product, only 2 moles of hydrogen per mole glucose are generating which is less than acetic acids end-product due to associated with propionate and reduced end-products such as alcohols and lactic acid (14) [15].



The anaerobic bacteria use in dark fermentation is classified into strict anaerobes or facultative anaerobes. The examples of strict anaerobes are from Clostridial species which produce hydrogen by PFOR pathway, thus produce 4 moles of hydrogen per mole glucose. Whereas facultative anaerobes such as *Escherichia coli* have PFL pathway, thus is limited to give 2 moles of hydrogen per mole glucose.

Three biohydrogen production technologies have been discussed above and dark fermentation process seems to be an attractive route for renewable production of hydrogen for a many reasons. Firstly is an anaerobic hydrogen fermenting bacterium are capable to use sugars and carbohydrates riches, readily available and wide variety waste and biomass as substrate. Besides that, hydrogen producing enzyme, Ni-fe hydrogenase and Fe-fe hydrogenase can actively generate hydrogen as no oxygen is consumed and evolution in this anaerobic process. The highest hydrogen rate can be obtained from dark fermentation process as shown in Table 1. Besides that, the operation of fermentation process is easy as well as fermentation reactor technology and bioprocess controls are well known since other fermentations process are already existing in the industrial scale. Since dark fermentation is light independence process, so light energy input is not required as well as the substrates.

All the superiority of dark fermentation makes it great potential to be developed for practical biohydrogen production application. Besides that, long-term research and development are required for biophotolysis and photofermentation to encounter intractable problems such as

oxygen sensitivity of hydrogenase and photobioreactor design if they are establish for practical application [16]. However, the dark fermentation processes produce a mixed biogas which containing mainly hydrogen and carbon dioxide, and possible also contain lesser amounts of carbon monoxide, methane, and/or hydrogen sulfide. Small amount  $\text{CO}_2$  present in fuel of the fuel cell is able to reduce it performances. In order to utilise hydrogen from biohydrogen production process as fuel in fuel cell, so the separation and purification system is very important. Thus, in the next section, the various separation and purification of biohydrogen process will be presented and discussed along with potential candidate to integrate with biohydrogen production technology.

### 3. Purification of Biohydrogen Gas

Hydrogen that produced during dark fermentation process is required to remove continuously for the potential continuous mode of the operation and eliminate the hydrogen accumulation that reduced hydrogen production rate. High hydrogen concentration in the bioreactor appears to inhibit the hydrogen production and more by-products such as ethanol, butanol, lactate, and acetone is generating [25]. Thus, separation and purification of biohydrogen is essential for the hydrogen utilization and also for sustained the biohydrogen production process.

Many technologies have been applied for hydrogen separation such as pressure swing adsorption, solvent adsorption, cryogenic recovery and membrane. The separation and selective purification of hydrogen via membrane technology appear to be promising to replace the conventional hydrogen separation system.

There are many types of membranes are existing to enrich hydrogen which can be categorised as organic or inorganic membrane and can be subdivided into porous or non-porous membrane. The catalytic (de)hydrogenation reaction has been applied for hydrogen separation by using catalytic inorganic membrane reactors which is operated at high temperature [25]. Thus, non-porous metallic (e.g palladium) membrane is used because of their high thermostable membranes and selectivity to hydrogen. However, this type of membrane very expensive (palladium cost), less commercially available and operate at elevated temperature is impractical for biohydrogen separation as the operational condition of biohydrogen production to nearly the ambient conditions.

Organic (polymer) has been tested for the separation of  $\text{H}_2/\text{CO}_2$  mixture shows the promising results [26]. Non-porous polymeric membrane (NPPM) is performing separation based on transport mechanism known as solution diffusion. Generally, these type of membranes is operated at nearly same the conditions (ambient temperature and pressure) of biohydrogen production process as well as low cost, make it have a potential technology for biohydrogen separation. This type of membrane is use for gas separation

in a device called as membrane contactor (MC). In another polymeric membrane, porous type is used as supporting material in which incorporates with ionic liquids (ILs) and produce supported liquid ionic membranes (SLIMs) that possible for biohydrogen separation.

### 3.1. Non Porous Polymeric Membranes

Mass transfer occurs in non-porous polymeric membrane is based on solution-diffusion model. The transport rate of  $H_2$  is diffusion-based and  $CO_2$  is condensable gas and possess solubility-based transport rate [27].

The membrane can be classified  $H_2$ -selective or  $CO_2$ -selective polymeric membranes. The  $H_2$ -selective polymeric membrane is where only  $H_2$  is able permeating the membrane and preferred made from glassy polymers. The selectivity of this type of membrane is high when diffusivity of  $H_2$  is high and solubility of  $CO_2$  is low [28]. Whereas,  $CO_2$ -selective polymeric membrane allow  $CO_2$  to go through it where the less soluble  $H_2$  flow as retentate and mostly of these membrane fabricate by rubbery polymers. The selectivity of this membrane is high by increase the solubility of  $CO_2$  and decrease the diffusivity of  $H_2$  (28).

The performance of separation  $H_2/CO_2$  also can be improved by blend polymeric membranes. The study from Car et al. has proven high selectivity  $CO_2/H_2$  (10.8) was achieved by using  $CO_2$ -selective, blend Pebax® MH 1657 with 50 wt.% of polyethylene glycol (PEG) dense membranes than pure Pebax® (9.1 selectivity) [29]. They have tested the performance of this membrane with  $CO_2/N_2$  and  $CO_2/CH_4$  gas mixture, but it only enhanced the separation  $CO_2/H_2$  gas mixture which feasible for hydrogen separation process. However, the selectivity of  $CO_2/H_2$  when  $H_2/CO_2$  mixed gas is used is smaller than ideal selectivity in both studies. This phenomenon also occurs in the separation  $H_2/CO_2$  by using  $H_2$ -selective membranes. According to study by David et al., the selectivity of  $H_2/CO_2$  is reduce by 4.2 (ideal selectivity) to 2.7 (measure when 10/90 vol.%  $H_2/CO_2$  mixed feed gas), by using planar polyimide Matrimid® 5218 membrane [29]. This is because the reduction of available sorption sites on  $H_2$ -selective membrane for  $H_2$  components as these sorption sites has been filled by presence  $CO_2$  component, so the transport rate also lowered than pure gas transport rate.

There another factor that should be considered in order to select if this membrane applicable to be integrate with biohydrogen production process is elimination of hydrogen sulphide from the gas mixture of fermentation production process. Even though the composition of this gas is very low compare to  $CO_2$ , but it can reduce the fuel cell performance by contaminant the catalyst of fuel cell in the form of sulfur dioxide [30]. However, there is unavailable research regarding the separation of  $H_2/H_2S$  especially for biohydrogen purification. Hydrogen sulphide separation in biogas processing is a possible way to give a view about the separation of this gas by non-porous polymeric membrane. The study from Harasimowicz et al. has been using

polyimide membranes for biogas purification and enrichment by separation of  $H_2S$  and  $CO_2$  [31]. Based on their findings, it is important for further investigate the separation of  $H_2S$  for biohydrogen separation since the hydrogen was included in the gas mixtures that have been studied.

Operating conditions such as feed temperature and pressure are possible impact to mass transfer of gas separation. Theoretically, the higher feed pressure and lower the permeate side pressure leads the higher pressure difference, the greater the flux and higher selectivity can be achieved. Thus, the possible way to do so is by increase the feed partial pressure or lower the pressure on the permeate side. A study by David et al., the high selectivity of  $H_2/CO_2$  (4.6) at 80/20 vol. %  $H_2/CO_2$  with  $H_2$  partial pressure of 8bar compared to the selectivity of  $H_2/CO_2$  (3.1) at 20/80 vol. %  $H_2/CO_2$  with  $H_2$  partial pressure of 2bar at the same 10 bar total pressure [32].

As mentioned earlier, transport rate of  $H_2$ -selective glassy polymer membranes and  $CO_2$ -selective rubbery polymer membranes, are dependent on diffusivity and solubility respectively. The diffusion of gas into membrane is improved by increasing the operating temperature or vice versa. Meanwhile, increasing temperature on reduced the solubility of gas into membranes or vice versa. Bakonyi et al. illustrate high permeability rates of pure  $H_2$  and  $CO_2$  on  $H_2$ -selective, polyimide membrane increased as the separation increases from 21-65°C [33]. However, it is essential to determine the effect of temperature on separation of  $H_2/CO_2$  gas mixture as both component exhibit different gas transport method. This can be demonstrated by study from Car et al., the selectivity of  $CO_2/H_2$  is decreased as the temperature increase when the 50/50 vol% of  $CO_2/H_2$  gas mixture is separate by  $CO_2$ -selective, Pebax®/PEG blend membrane [29]. The study also demonstrated high temperature resulting high  $CO_2$  flux, this can be correlated with Arrhenius equation between permeability/flux with temperature [29].

Non-porous polymeric membranes can be promising candidates to be coupled with hydrogen producing bioreactors and hence giving the chance for in situ biohydrogen concentration. As the study by Bakonyi et al., they demonstrated that the 18% increase in  $H_2$  concentration and 22% decrease in  $CO_2$  content can be obtained by using polyimide membrane, where the feed mixed gas of separation unit are generate generate from continuous fermentation process by *Escherichia coli* (XL1-BLUE) and formate as carbon source [33]. Besides that, non-porous polymeric membrane is also suitable for use in a membrane technology, membrane contractor (MC) since it prevent contaminant of gas with liquid phases.

Membrane contactors, MCs is also known as gas-liquid membrane contactor (GLMC), is a device in which the mass transfer between gas to be separated and liquid absorption is occurring through a membrane. Thus, GLMC is generally a combination of membrane absorber (absorption) and membrane desorption (desorption) and operate in a circular

mode.

The mechanism of gas separation of GLMC system is same with the present absorption-desorption separation system, but the difference is the presence of a membrane between gas and liquid phase which separate them from contact in each unit separation. In the case of H<sub>2</sub>/CO<sub>2</sub> gas mixture, the feed gas mixture will flow in the absorption unit at different direction with input liquid absorbent. During the flow, permeable component, CO<sub>2</sub> is going through the polymeric membrane and non-permeable component, pure H<sub>2</sub> is flow out the unit as retentate. CO<sub>2</sub> that permeable through the membrane is absorbed in absorption liquid. The high concentration CO<sub>2</sub> liquid absorbent is then flown in to the desorption unit. In the desorption unit, the CO<sub>2</sub> is going through the membrane from the liquid absorbent and the separated CO<sub>2</sub> is flow out the system. While, the free CO<sub>2</sub> liquid absorbent is pump back to absorption unit to provide a continuous operation.

The porous type membrane seem not practical for gas separation in GLMC due to the formation of bubbles in liquid and penetration of liquid into the membrane pore which contaminant the gas product [34]. While the non-porous, polymeric membrane appear more potential to use in membrane contactor since the membrane is possess higher mass transfer coefficient than porous type membrane, able resist high feed pressure and no contaminant take place. Modigell *et al.* has been demonstrated lab scale GLMC system with Polyvinyltrimethylsilane (PVTMS) membrane with potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) as liquid absorbent [35]. High CO<sub>2</sub> removal efficiency from H<sub>2</sub>/CO<sub>2</sub> gas mixture can be obtained on their finding. Different liquid absorbent such as monoethanolamine (MEA) provide high CO<sub>2</sub> separation efficiency (99.7%) than K<sub>2</sub>CO<sub>3</sub> solution (separation efficiency of 57%) that demonstrated in lab scale GLMC that consist of PVTMS membranes [36].

The GLMC system also been investigated to couple with biohydrogen production system. A study conducted by Beggel *et al.* show the about 99% of CO<sub>2</sub> separation efficiency from real biogas (H<sub>2</sub>/CO<sub>2</sub> mixture) and high purity hydrogen 90 v/v% can be achieved when integrate membrane contactor with from a photofermentation [37]. The batch separation process is done in their study since the biogas production rate of the photofermenter is too low to operate GLMC. Even though, GLMC have a potential for the separation of hydrogen mixture from biohydrogen production system, but their application get less consideration than supported ionic liquid membranes (SILMs).

### 3.2. Supported Ionic Liquid Membranes

Ionic liquids (ILs) are salt-like materials with composition of inorganic anion or organic cation which can be can be adjusted following to the separation task. It is use as replacement of convectional volatile organic solvent that use in liquid membrane technology. This is because ILs has unique properties such as non-volatile characteristic that prevent loss of solution and also fine-tunable properties.

Generally, liquid membrane is a non-porous which containing thin layer organic solvent that interposed between to aqueous phases of different compositions [38].

ILs is combined with porous polymeric membrane by filled the pores with ILs solvent, act as support/carrier matrixes and transforms porous membrane to non-porous polymeric membranes, known as supported ionic liquid membrane (SILM) [38]. The mechanism of separation in SILMs by the dissolving solute molecules into membrane at the feed/membrane interface and the dissolved species then diffuse through the membrane and desorb at the opposite membrane (38). ILs also known as room temperature ionic liquids (RTILs), in which the liquid at ambient temperature with no vapour pressure loss by evaporation. The advantage of using SILMs for gas separation is high solubility of different gas components in ionic liquids which make it has potential for separation of H<sub>2</sub> and CO<sub>2</sub>.

Cserjési *et al.* studied the permeability of pure CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub> and ideal selectivity from binary gas mixture of these components by using four novel VACEM type ionic liquids which integrate with hydrophobic porous PVDF membrane as supporting phases [39]. Based on their study, CO<sub>2</sub> has higher permeability than N<sub>2</sub> and H<sub>2</sub> through the all four VACEM-PVDF membrane and high ideal selectivity of CO<sub>2</sub>/H<sub>2</sub> gas mixtures was obtained. In another research by Cserjési *et al.*, they incorporated twelve unconventional different types of ILs with the similar membrane in order to determine H<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> gas separation efficiency [40]. They indicated that not all ILs are suitable for SILMs as they spoiled the PVDF membrane during membrane preparation and high permeability of CO<sub>2</sub> are achieved for the rest of applicable ILs compared to other gas.

The anion alteration and cation configuration are able change the behaviour of the membranes resulting change of gas separation efficiency. Neves *et al.* used imidazolium-cation based RTILs with hydrophobic PVDF membrane for separation of H<sub>2</sub> from H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub> has highest permeability [41]. Their finding showed that the increasing length alkyl chain of RTIL cation and resulting high permeability of pure gas, but it not give any effect to selectivity of gas separation. However, different viscosity anion integrates with imidazolium-based cation give high ideal selectivity. Kanehashi *et al.* demonstrated increasing permeability of pure gases was obtained by increasing the mass ratio of IL content (51-81 wt %) which incorporated glassy fluorine-containing polyimide (PI) [42]. They stated the formation of IL domain with increase IL mass ratio enhances the gas diffusivity, thus contribute to high permeability.

The study for hydrogen separation for mixed gas CO<sub>2</sub>/H<sub>2</sub> specifically from biohydrogen gas by SILMs is currently unavailable. In spite of that, the other mixed gas separation such as CO<sub>2</sub>/N<sub>2</sub> by SILMs can be investigating for future SILMs fabrication considerations. Neves *et al.* studied the gas separation by using integrated ILs with porous PVDF membrane and their finding show the selectivity CO<sub>2</sub>/N<sub>2</sub> (50 v/v %) gas mixture by is lower than ideal selectivity (112).

However, the finding from Gu et al. demonstrated that the selectivity of CO<sub>2</sub>/N<sub>2</sub> (50 v/v %) gas mixture was almost similar with ideal selectivity [43]. They used porous PVDF membrane that filled by supported ion gel as supporting phase which then integrate with IL. The liquid-like gels properties make the selectivity does not depend on diffusivity but from the solubility ratio of ionic liquids, but is not affected when gas mixture exposed at low operating pressure [43].

The configuration of SILMs nearly similar to non-porous polymeric membranes, thus the separation principle is based on the diffusivity and solubility of gas mixture which are affected by operating pressure and temperature. Higher gas permeability can be obtained by increasing transmembrane pressure gradient as the driving force for the gas transport is increasing. However, the elevated pressure may contribute to loss of ILs from the pores of supporting material, porous polymeric membrane as well as bring the SILMs to defect or leakages. Therefore, it is important to study the effect of transmembrane pressure to determine pressure limit that membrane able to resist, known as critical displacement pressure which depend on the structure and size of the pores in the support matrix, interface tension of ILs and the contact angle [44]. In order to overcome instability and improved the mechanical durability, many techniques have been applied during fabrication process such as nano-filtration as supporting material [45] and coating the ILs with dense polymer films [46].

The study by Gan et al. obtained that the increasing gas permeation rate through the SILMs based nano filtration with increasing feed pressure (3-7 bar), which the pressure way higher than normal SILM (<0.1bar) and the membrane also able maintain stability at high pressure and [45]. However, the gas permeability from Cserjési et al. showed the decrease as the transmembrane pressure increasing (>5 bar) and slightly instability also been observed at pressure greater than 10 bar [40]. The unclear explanation stated in this study that deformation of the size and shape of the supporting polymer membrane is occur at high pressure which reduce the pores volume of separation [40].

The operating temperature also affects the permeability and gas separation efficiency. Finotella et al. study H<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub> permeability in imidazolium-based room temperature ionic liquids at nearly ambient pressure [47]. Based on their study, high selectivity obtained as the high gas flux generate by high temperature. The explanation of temperature and selectivity effect of SILMs is based on the correlation between temperature and Arrhenius equation.

Based on discussion above, non-porous polymeric membrane, membrane contactors and supported liquid ionic membranes have potential to use in biohydrogen separation. However, the research that integrated those membranes with real hydrogen fermentation conditions is limited. Thus, long and extensive research is requiring determining which operation conditions (temperature, pressure) and separation system (single stage, multi-stage, combined different membrane) is feasible for gas separation, where biohydrogen

production and separation system can occur together. If high hydrogen purity can be obtained from the biohydrogen integrate system which is feasible to fuel cell technology application.

## 4. Integrated Biohydrogen and Fuel Cells System

Fuel cell is an electrochemical energy conversion devices that generating electricity from the conversion of chemical energy. There are various fuel cell technologies that have been develop such as and also their application also varies. The distinct types of fuel cell technologies are including polymer electrolyte membrane fuel cell (PEMFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), solid oxide fuel cells (SOFC) and direct methanol fuel cell (DMFC). The fuel cell requires fuel and oxygen to produce electricity, heat and water.

Hydrogen from biohydrogen separation system is able to utilise as fuel for fuel cell technology. Based on all the fuel cell technologies above, PEMFC has got many attentions due the operation at low temperature and also been demonstrated successfully as portable fuel cell. PEMFC is operate at very low temperatures, below 100°C, use hydrogen proton as mobile ion, and the fuel require is high purity hydrogen and cannot tolerate CO, H<sub>2</sub>S at concentration (>10ppm) which can poison at low temperature.

### 4.1. Bioreactor Sizing

This analysis is to determining if biohydrogen production technology is sufficient to provide enough hydrogen to power up various fuel cell powers for different applications continuous basis. Besides that, we assume that calculated fuel is containing high purity hydrogen gas from efficiency biohydrogen production integration with hydrogen purification system.

Some calculation has been done in order to find hydrogen flow rate require (Table 2) for generate certain power output. These hydrogen flow rate is used to calculate size of bioreactor that produce hydrogen as shown in Table 3.

The Table 2 and 3 illustrated required flow rate of hydrogen gas is increasing as the power output of fuel cell is increasing which resulting larger size of bioreactor. Based on table 3, the hydrogen produce from biohydrogen production technologies not enough to power PEMFC greater than 5kW as the size of bioreactor are too large and the systems is impractical for application of transportation and high power of stationary generator. The hydrogen production from direct and indirect biophotolysis is very low and required very large bioreactor size to power PEMFC greater than. However, it may be applicable to generate hydrogen for low power may be applicable generate hydrogen for low power portable PEMFC power generator which power output less than 100 W.

*Rhodobacter sphaeroides* ZX-5 with highest

hydrogen flow rate than other bacteria in photo fermentation system show seems reasonable required bioreactors size from 26.3 L to 526 L to power 5W to 100W of PEMFC. Meanwhile, the *Rhodospseudomonas palustris* CQK 01 and *Rhodospseudomonas faecalis* RLD-53 bacteria in photo fermentation need 69.2 L to 1400 L of bioreactor size in order to power 5W to 100W PEMFC, which is seems reasonable bioreactor size. Thus, the photo fermentation systems may be only suitable for low portable PEMFC power generator.

The size of bioreactor of some dark fermentation systems seems appears promising for certain power PEMFC. The bacteria from municipal wastes and mixed culture of *Clostridium* species in dark fermentation system generate hydrogen at reasonable size of bioreactor, 34.8 L to 753 L that enough to power up till 100W PEMFC which applicable for low power portable PEMFC power generator. The highest hydrogen flow rate that generate from bacteria from municipal sewage in dark fermentation system is able to power PEMFC till 5kW with bioreactor size of 1500 L. The

hydrogen produce from this dark fermentation is able suitable to apply in high portable PEMFC power generator and stationary power. The biomass feedstock, municipal waste that use in this dark fermentation system is available in high quantities at constant supply and inexpensive which may advantage for large scale dark fermentation process.

**Table 2.** Hydrogen usage (flow rate) required to power PEMFC

PEMFC power output (kW)	H <sub>2</sub> usage required to generate power (kg H <sub>2</sub> /s) ( $\times 10^{-3}$ )	H <sub>2</sub> usage required to generate power (mL H <sub>2</sub> /h)
0.005	0.0000672	0.75
0.5	0.00672	75
1	0.0134	149
5	0.0672	747
80	1.08	11958
100	1.34	14947
250	3.36	37368

**Table 3.** Sizes of bioreactor required to power the PEMFC

Biohydrogen production technology	Maximum rate of hydrogen production (mL H <sub>2</sub> L <sub>tank</sub> <sup>-1</sup> h <sup>-1</sup> )	Working volume of bioreactor (L) required to power :								Refs
		5 W	100 W	500 W	1kW	5kW	80kW	100kW	250kW	
		Portable power generator				Stationary power				
		Transportation (light duty vehicles, buses)								
Direct biophotolysis										
<i>Chlorella sorokiniana</i> strain Ce	1.35	1.99 $\times 10^3$	3.99 $\times 10^4$	1.99 $\times 10^5$	3.99 $\times 10^5$	1.99 $\times 10^6$	3.19 $\times 10^7$	3.99 $\times 10^7$	9.96 $\times 10^7$	[17]
<i>Anabaena variabilis</i> ATCC 29143 mutant PK84	20	1.35 $\times 10^2$	2.69 $\times 10^3$	1.35 $\times 10^4$	2.69 $\times 10^4$	1.35 $\times 10^5$	2.15 $\times 10^6$	2.69 $\times 10^6$	6.73 $\times 10^6$	[18]
Indirect biophotolysis										
<i>Chlamydomonas</i> MGA 161	4.25	6.33 $\times 10^2$	1.27 $\times 10^4$	6.33 $\times 10^4$	1.27 $\times 10^5$	6.33 $\times 10^5$	1.01 $\times 10^7$	1.27 $\times 10^7$	3.17 $\times 10^7$	[19]
Photo fermentation										
<i>Rhodobacter sphaeroides</i> ZX-5	102.23	2.63 $\times 10^1$	5.26 $\times 10^2$	2.63 $\times 10^3$	5.26 $\times 10^3$	2.63 $\times 10^4$	4.21 $\times 10^5$	5.26 $\times 10^5$	1.32 $\times 10^6$	[20]
<i>Rhodospseudomonas palustris</i> CQK 01	38.90	6.92 $\times 10^1$	1.38 $\times 10^3$	6.92 $\times 10^3$	1.38 $\times 10^4$	6.92 $\times 10^4$	1.11 $\times 10^6$	1.38 $\times 10^6$	3.46 $\times 10^6$	[21]
<i>Rhodospseudomonas faecalis</i> RLD-53	36.60	7.35 $\times 10^1$	1.47 $\times 10^3$	7.35 $\times 10^3$	1.47 $\times 10^4$	7.35 $\times 10^4$	1.18 $\times 10^6$	1.47 $\times 10^6$	3.68 $\times 10^6$	[48]
Dark fermentation										
Municipal wastes	71.5	3.76 $\times 10^1$	7.53 $\times 10^2$	3.76 $\times 10^3$	7.53 $\times 10^3$	3.76 $\times 10^4$	6.02 $\times 10^5$	7.53 $\times 10^5$	1.88 $\times 10^6$	[22]
<i>Clostridium butyricum</i> -NRRL 1024 and <i>Clostridium pasteurianum</i> -NRRL B-598 (mixed culture)	77.38	3.48 $\times 10^1$	6.95 $\times 10^2$	3.48 $\times 10^3$	6.95 $\times 10^3$	3.48 $\times 10^4$	5.56 $\times 10^5$	6.95 $\times 10^5$	1.74 $\times 10^6$	[49]
Anaerobic digester sludge	500	5.38	1.08 $\times 10^2$	5.38 $\times 10^2$	1.08 $\times 10^3$	5.38 $\times 10^3$	8.61 $\times 10^4$	1.08 $\times 10^5$	2.69 $\times 10^5$	[23]
<i>Clostridium butyricum</i> CGS2	520	5.17	1.03 $\times 10^2$	5.17 $\times 10^2$	1.03 $\times 10^3$	5.17 $\times 10^3$	8.28 $\times 10^4$	1.03 $\times 10^5$	2.59 $\times 10^5$	[50]
Municipal sewage	1800	1.49	2.99 $\times 10^1$	1.49 $\times 10^2$	2.99 $\times 10^2$	1.49 $\times 10^3$	2.39 $\times 10^4$	2.99 $\times 10^4$	7.47 $\times 10^4$	[24]

Even though dark fermentation technology may be applicable for some application, but there are some technical barriers which must be examined such as efficiency of bioreactor to be scaled up to high volume to provide high flow rate of required hydrogen. Besides that, other process production steps such as biomass feedstock pre-conditioning, waste processing and hydrogen separation and purification also must be considered before this system can be generating hydrogen to power the PEMFC. The further research also requires to determine if the rate of hydrogen production still remains as high as in lab scale if the system is brought to scale up.

The operating and manufacturing cost also must be considered to determine if the system is practical for generating hydrogen on a large scale.

## 5. Conclusions

In conclusion, dark fermentation would appear to be a potential candidate to generate hydrogen compared to other biohydrogen production technologies to power the fuel cells at sufficient size and would be applicable for portable fuel cell and stationary power generator. However, more research and development are required such as increasing the rates and yields of hydrogen production and optimizing the bioreactor sizing so that hydrogen from biohydrogen production process is able to replace non-renewable energy sources, fossil fuels and also able to sustain the world power energy supply. Besides that, it is essential to study and conduct extensive research on membrane gas technology in hydrogen separation together with hydrogen fermentation process to determine the possibility of integrated applications.

## ACKNOWLEDGEMENTS

This study was partially supported by UKM – YSD Research Project under code KK-2014-013.

## REFERENCES

- [1] Argun H., Kargi F., Kapdan I. K., Oztekin R., "Biohydrogen Production by Dark Fermentation of Wheat Powder Solution: Effects of C/N And C/P Ratio on Hydrogen Yield and Formation Rate", *International Journal of Hydrogen Energy*, vol. 33, pp. 1813-1819, 2008.
- [2] Manish S., Banerjee R., "Comparison of Biohydrogen Production Processes", *International Journal of Hydrogen Energy*, vol. 33, pp. 6046–6057, 2008.
- [3] Das D., Veziroglu T. N., "Advances in Biological Hydrogen Production Processes", *International Journal of Hydrogen*, vol. 33, pp. 6046–6057, 2008.
- [4] Levin D. B., Islam R., Cicek N., Sparling R., "Hydrogen Production by *Clostridium Thermocellum* 27405 from Cellulosic Biomass Substrates", *International Journal of Hydrogen Energy*, vol. 31, pp. 1496-1503, 2006.
- [5] Larminie J., Dicks A., *Fuel Cell Systems Explained*. Volume 2: John Wiley & Sons Ltd, England, 2003.
- [6] Ghirardi M. L., Zhang L., Lee J.W., Flynn T., Seibert M., Greenbaum E., "Microalgae: A Green Source of Renewable Hydrogen.", *Trends in Biotechnology*, vol. 18, pp. 506–511, 2000.
- [7] Debabrata Das, Namita Khanna, Chitralakha Nag Dasgupta., *Biohydrogen Production, Fundamentals and Technology Advances*, Taylor & Francis Group, London, New York, 2014
- [8] Harwood C. S., *Bioenergy*, ASM Press, Washington. 2008.
- [9] Yetis M., Gunduz U., Eroglu I., Yucel M., Turker L., "Photoproduction of Hydrogen from Sugar Refinery Wastewater by *Rhodobacter Sphaeroides O.U.001*", *International Journal of Hydrogen Production*, vol. 25, pp. 1035-1041, 2000.
- [10] Seifert K., Waligorska M., Laniecki M., "Brewery Wastewaters in Photobiological Hydrogen Generation in Presence Of *Rhodobacter Sphaeroides O.U. 001*", *International Journal of Hydrogen Energy*, vol. 35, pp. 4085-4091, 2010.
- [11] Hallenbeck P. C., Ghosh D., "Advances in Fermentative Biohydrogen: The Way Forward?", *Trends in Biotechnology*, vol. 27, pp. 287-297, 2009.
- [12] Das D., Veziroglu T. N., "Hydrogen Production by Biological Processes: A Survey of Literature", *International Journal of Hydrogen Energy*, vol. 26, pp. 13-28, 2001.
- [13] Hallenbeck P. C., Benemann J. R., "Biological Hydrogen Production: Fundamentals and Limiting Processes", *International Journal of Hydrogen Energy*, vol. 27, pp. 1185-1193, 2002.
- [14] Benemann J., "Hydrogen Biotechnology: Progress And Prospects", *Nature Biotechnology*, vol. 14, pp. 1101-1103, 1996.
- [15] Levin D. B., Pitt L., Love M., "Biohydrogen Production: Prospects and Limitations to Practical Application", *International Journal of Hydrogen Energy*, vol. 29, pp. 173-185, 2004.
- [16] Hallenbeck P. C., Abo-Hashesh M., Ghosh D., "Strategies for Improving Biological Hydrogen Production", *Bioresource Technology*, vol. 110, pp. 1-9, 2012.
- [17] Chader S., Haceneb H., Agathos S. N., "Study of Hydrogen Production by Three Strains of *Chlorella* Isolated from the Soil in The Algerian Sahara", *International Journal of Hydrogen Energy*, vol. 34, pp. 4941-4946, 2009.
- [18] Tamburic B., Zemichael F.W., Maitland G. C., Hellgardt K., "Parameters Affecting the Growth and Hydrogen Production of the Greenalga *Chlamydomonas Reinhardtii*", *International Journal of Hydrogen Energy*, vol. 35, pp. 1-5, 2010.
- [19] Ohta S., Miyamoto K., Miura Y., "Hydrogen Evolution as a Consumption Mode of Reducing Equivalents in Green Algal Fermentation", *Plant Physiology*, vol. 83, pp. 1022-1026, 1987.
- [20] Raksajit W., Satchasataporn K., Lehto K., Maenpaa P., Incharoensakdi A., "Enhancement of Hydrogen Production

- by the filamentous Non-Heterocystous *Cyanobacterium Arthrospira Sp. PCC 8005*", International Journal of Hydrogen Energy, vol. 37, pp. 18791-18797, 2012.
- [21] Tian X., Liao Q., Zhu X., Wang Y., Zhang P., Li J., "Characteristics of a Biofilm Photobioreactor as Applied to Photo-Hydrogen Production", Bioresource Technology, vol. 101, pp. 977-983, 2010.
- [22] Seifert K., Waligorska M., Wojtowski M., Laniecki M., "Hydrogen Generation from Glycerol in Batch Fermentation Process", International Journal of Hydrogen Energy, vol. 34, pp. 3671-3678, 2009.
- [23] Kim M. S., Lee D. Y., "Fermentative Hydrogen Production from Tofu-Processing Waste and Anaerobic Digester Sludge Using Microbial Consortium", Bioresource Technology, vol. 101, pp. S48-S52, 2010.
- [24] Lin C. N., Wu S. Y., Chang J. S., Chang J. S., "Biohydrogen Production in a Three-Phase Fluidized Bed Bioreactor using Sewage Sludge Immobilized by Ethylene-Vinyl Acetate Copolymer", Bioresource Technology, vol. 100, pp. 3298-3301, 2009.
- [25] Morreale B. D., Ciocco M. V., Enick R. M., Morsi B. I., Howard B. H., Cugini A. V., Rothenberger K. S., "The Permeability of Hydrogen in Bulk Palladium at Elevated Temperatures and Pressures", Journal of Membrane Science, vol. 212, pp. 87-97, 2003.
- [26] Barillas M. K., Enick R. M., O'Brien M., Perry R., Luebke D. R., Morreale B. D., "The CO<sub>2</sub> Permeability and Mixed Gas CO<sub>2</sub>/H<sub>2</sub> Selectivity of Membranes Composed", Journal of Membrane Science, vol. 372, pp. 29-39, 2011.
- [27] David O. C., Gorri D., Urriaga A., Ortiz I., "Mixed Gas Separation Study for the Hydrogen Recovery from H<sub>2</sub>/CO/N<sub>2</sub>/CO<sub>2</sub> Post Combustion Mixtures using a Matrimid Membrane", Journal of Membrane Science, vol. 378, pp. 359-368, 2011.
- [28] Shao L., Low B. T., Chung T. S., Greenberg A. R., "Polymeric Membranes for the Hydrogen Economy: Contemporary Approaches and Prospects for the Future", Journal of Membrane Science, vol. 327, pp. 18-31, 2009.
- [29] Car A., Stropnik C., Yave W., Peinemass K. V., "PEG Modified Poly(Amide-B-Ethylene Oxide) Membranes for CO<sub>2</sub> Separation", Journal of Membrane Science, vol. 307, pp. 85-95, 2008.
- [30] Lopes T., Paganin V. A., Gonzalez E. R., "The Effects of Hydrogen Sulfide on the Polymer Electrolyte Membrane Fuel Cell Anode Catalyst: H<sub>2</sub>S-Pt/C Interaction Products", Journal of Power Source, vol. 196, pp. 6256-6263, 2011.
- [31] Harasimowicz M., Orluk P., Zakrzewska-Trznade G., Chmielewski A.G., "Application of Polyimide Membranes for Biogas Purification and Enrichment", Journal of Hazardous Materials, vol. 144, pp. 698-702, 2007.
- [32] David O. C., Gorri D., Nijmeijer k., Ortiz I., Urriaga A., "Hydrogen Separation from Multicomponent Gas Mixtures Containing CO, N<sub>2</sub> and CO<sub>2</sub> using Matrimids Asymmetric Hollow Fiber Membranes", Journal of Membrane Science, vols. 419-420, pp. 49-56, 2012.
- [33] Bakonyi P., Nemestothy N., Ramirez J., Ruiz-Filippi R., Belafi-Bako K., "Escherichia Coli (XL1-BLUE) for Continuous Fermentation of Biohydrogen and Its Separation by Polyimide Membrane", International Journal of Hydrogen Energy, vol. 37, pp. 5623-5630, 2012.
- [34] Shalygin M. G., Abramov S. M., Netrusov A. I., Teplyakov V. V., "Membrane Recovery of Hydrogen from Gaseous Mixtures of Biogenic and Technogenic Origin", International Journal of Hydrogen Energy, vol. 40, pp. 3438-3451, 2015.
- [35] Modigell M., Schumacher M., Teplyakov V. V., Zenkevich V. B., "A Membrane Contactor for Efficient CO<sub>2</sub> Removal on Biohydrogen Production", Desalination, vol. 224, pp. 186-190, 2008.
- [36] Beggel F., Modigell M., Shalygin M., Teplyakov V., Zenkevitch V., "Novel Membrane Contactor for Gas Upgrading in Biohydrogen Production", Chemical Engineering Transactions, vol. 18, pp. 397-402, 2009.
- [37] Beggel F., Novik I. J., Modigell M., Shalygin M. G., Teplyakov V.V., Zenkevitch V. B., "A Novel Gas Purification System for Biologically Produced Gases", Journal of Cleaner Production, vol. 18, pp. S43-S50, 2010.
- [38] Malik M. A., Hashim M. A., Nabi F., "Ionic Liquids in Supported Liquid Membrane Technology", Chemical Engineering Journal, vol. 171, pp. 242-254, 2011.
- [39] Cserjési P., Nemestóthy N., Vass A., Csanádi Z., Bélafi-Bakó K., "Study on Gas Separation by Supported Liquid Membranes Applying Novel Ionic Liquids", Desalination, vol. 245, pp. 743-747, 2009.
- [40] Cserjési P., Nemestóthy N., Bélafi-Bakó K., "Gas Separation Properties of Supported Liquid Membranes Prepared with Unconventional Ionic Liquids", Journal of Membrane Science, vol. 349, pp. 6-11, pp.1-8, 2010.
- [41] Neves L.A., Nemestothy N., Alves V.D., Cserjesi P., Belafi-Bako K., Coelho I. M., "Separation of Biohydrogen by Supported Ionic Liquid Membranes", Desalination, vol. 240, pp. 311-315, 2009.
- [42] Kanehashi S., Kishida M., Kidesaki T., Shindo R., Sato S., Miyakoshi T., Nagai K., "CO<sub>2</sub> Separation Properties of a Glassy Aromatic Polyimide Composite Membranes Containing High-Content 1-Butyl-3-Methylimidazolium Bis (Trifluoromethylsulfonyl)Imide Ionic Liquid", Journal of Membrane Science, vol. 430, pp. 211-222, 2013.
- [43] Gu Y., Cussler E. L., Lodge T. P., "ABA-Triblock Copolymer Ion Gels for CO<sub>2</sub> Separation Applications", Journal of Membrane Science, Vols. 423-424, pp. 20-26, 2012.
- [44] Zha F.F., Fane A.G., Fell C.J.D., Schofield R.W., "Critical Displacement Pressure of a Supported Liquid Membrane", Journal of Science, vol. 75, pp. 69-80, 1992.
- [45] Gan Q., Rooney D., Xue M., Thompson G., Zou Y., "An Experimental Study of Gas Transport and Separation Properties of Ionic Liquids Supported on Nanofiltration Membranes", Journal of Membrane Science, vol. 280, pp. 948-956, 2006.
- [46] Xie G. J., Liu B. F., Wen H. Q., Li Q., Yang C. Y., Han W. L., "Bioflocculation of Photo-Fermentative Bacteria induced by Calcium Ion for Enhancing Hydrogen Production", International Journal of Hydrogen Energy, vol. 38, pp. 7780-7788, 2013.
- [47] Finotella A., Bara J. E., Camper D., Noble R. D., "Room Temperature Ionic Liquid: Temperature Dependence of Gas

Solubility Selectivity", *Industry & Engineering Chemistry Research*, Vol. 47, pp. 3453-3459, 2008.

- [48] Izak P., Ruth W., Fei Z., Dyson P. J., Kragl U., "Selective Removal of Acetone and Butan-1-ol From Water with Supported Ionic Liquid–Polydimethylsiloxane Membrane by Pervaporation", *Chemical Engineering Journal*, vol. 139, pp. 318-321, 2008.
- [49] Ozmihi S., Kargi F., "Dark Fermentative Bio-Hydrogen Production from Waste Wheat Starch using Co-Culture with Periodic Feeding: Effects of Substrate Loading Rate", *International Journal of Hydrogen Energy*, vol. 36, pp. 7089-7093, 2011.
- [50] Chen S. D., Lo Y.C., Lee K. S., Huang T. I., Chang J. S., "Sequencing Batch Reactor Enhances Bacterial Hydrolysis of Starch Promoting Continuous Bio-Hydrogen Production from Starch Feedstock", *International Journal of Hydrogen Energy*, vol. 34, pp. 8549-8557, 2009.