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MEMBRANE UNIT FOR INTEGRATED GAS SEPARATION – MEMBRANE BIOREACTOR (GS-MBR) SYSTEM

ZBYNĚK PIENTKA *[1], JAKUB PETER[1], AND ROBERT VÁLEK[2]

[1]Institute of Macromolecular Chemistry CAS, Heyrovského nám. 2, 162 06 Prague 6, CZECH REPUBLIC
[2]MemBrain s.r.o., Pod Vinicí 87, 471 27 Stráž pod Ralskem, CZECH REPUBLIC

One of the research directions of renewable energy sources is the production of biohydrogen from the dark fermentation of organic matter. During this fermentation process, since hydrogen is produced along with a complex mixture of other gases and vapors, hydrogen gas requires further purification. One relatively easy solution to this problem might be the utilization of gas separation membrane modules given their low energy consumption, simple operation and ease of upscaling. In this work, hollow fiber (HF) membranes based on polyetherimide (PEI) were developed and tested. HF membranes were spun from a polymer solution of PEI using the wet phase inversion process into a water bath using a pilot-scale spinning device. Gas transport measurements showed that membranes exhibited permeances of between 9.3 and 19.2 GPU with CO_2/H_2 selectivities within the range of $3.3 - 5.6$. Morphology studies showed regular shapes resembling hollow fibers with outer diameters within the range of $250-320$ microns, depending on various parameters of the spinning process. The best performing membranes were selected and a morphological analysis carried out. Selected fibers were incorporated into two types of membrane modules. One type was a laboratory-scale membrane mini-module used for preliminary tests, while the other membrane module was designed for the treatment of larger amounts of biohydrogen. Two types of laboratory-scale membrane separation units were constructed. For laboratory use, the low-pressure unit proved more accurate regulation to match the fermenters performance with the separation unit in comparison with the high-pressure one.

Keywords: polymer membranes, gas separation, hollow fibers, membrane module

1. Introduction

The motivation of this research is the need to reduce the ecological footprint of society by developing green technologies enabling carbon sequestration, sustainable production of valuable chemicals and environmentally-friendly energy production. This task is to be completed by the development of a novel, circular-loop gas separation membrane bioreactor system.

Microalgae grown in a photobioreactor capture refused-CO_2 from the fermentative reactor, which simply ferments these microalgae. During the process, a mixture of hydrogen and CO_2 is produced. The hydrogen can be separated and utilized for energy production. In addition, some valuable chemicals are produced. The newly developed system is known as a Gas Separation Membrane Bioreactor (GS-MBR) [1].

A key component of the GS-MBR is a membrane unit, which forms technological solutions for the separation of H_2 and CO_2 from the fermentation product. The basic elements in the membrane unit are membrane modules that utilize hollow fiber (HF) membranes.

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*Correspondence: pientka@imc.cas.cz

2. Experimental

2.1 Materials

PEI (ULTEM™ 1000 Resin grade) was purchased from SABIC. The chemical structure of a repeated unit of ULTEM™ 1000 Resin and the details regarding its preparation have previously been presented [2].

2.2 Development of HF membranes

Hollow fiber membranes were prepared with the strategic cooperation of the company MemBrain s.r.o. located in the Czech Republic. The procedure was described in our previous paper [2]. The spinline used for fabrication of the membranes is shown in Fig. 1.

2.3 Development of HF membrane modules

The HC1 HF membrane mini-module was prepared by fixing $10 - 20$ fibers into the Swagelok tube fitting using

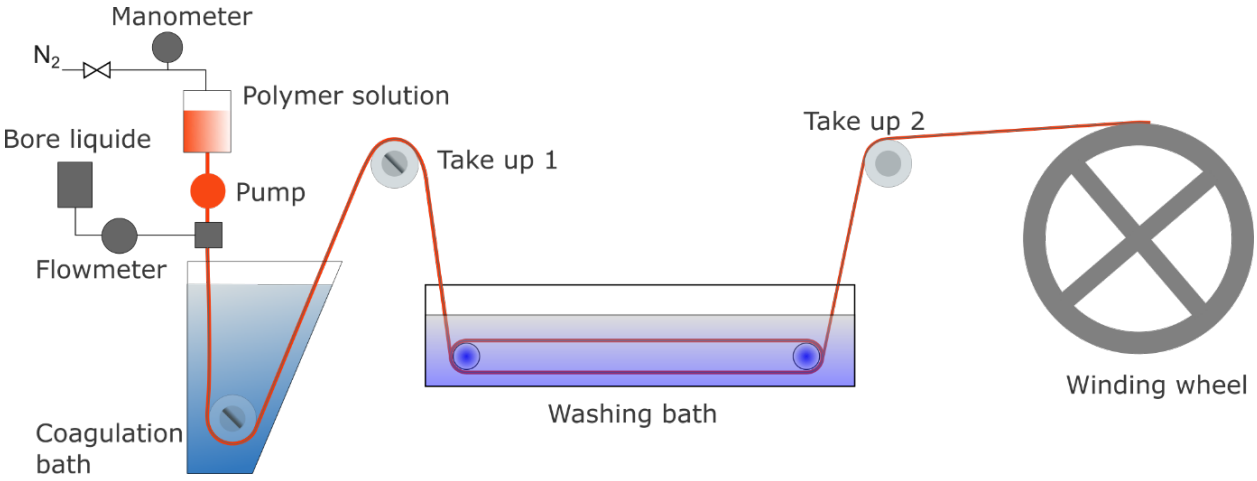


Figure 1: The spinline used for the fabrication of HF membranes

3M of the epoxy resin DP100. The same resin was used to create the dead end of the fibers. The whole assembly was inserted into the 12-mm-wide tube using the corresponding Swagelok tube fittings as presented in Fig. 2. The module was equipped with 6-mm-wide connectors.

P2-type HF membrane modules were constructed in a similar manner to those reported in [2], that is, from an arranged bundle of 250 A5-7 fibers (membrane area: 844 cm^2) inserted into a PVC pipe. A schematic diagram of the P2-type HF membrane module and a photograph of it are presented in Fig. 3.

Figure 2: HC1 HF membrane mini-module

2.4 Determining the gas transport properties of the HF membrane

Laboratory modules containing $10 - 20$ fibers of about 20 cm in length were prepared. One end of the fibers was sealed by an epoxy resin. The outer surface of the fibers was exposed to a mixture of gases which permeate into their hollow centers. Gas permeation experiments were carried out using a mixture of CO_2 and H_2 ($1 : 1$ volume ratio) at 2.0 and 4.2 bars (Δp was 1.0 and 3.2 bars, respectively) to determine the separation properties of the asymmetric PEI HF membrane. Its composition, pressures and flow rates were managed by the Poseidon

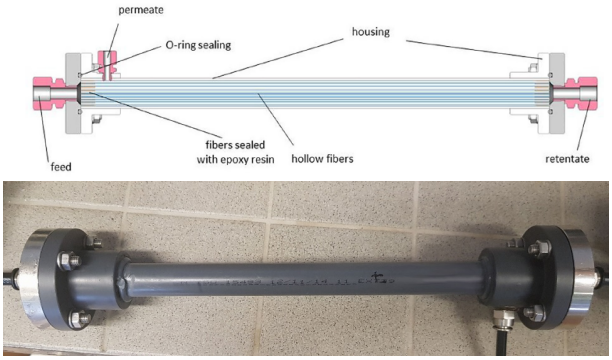


Figure 3: Schematic diagram of a cross-section of the P2-type HF membrane module

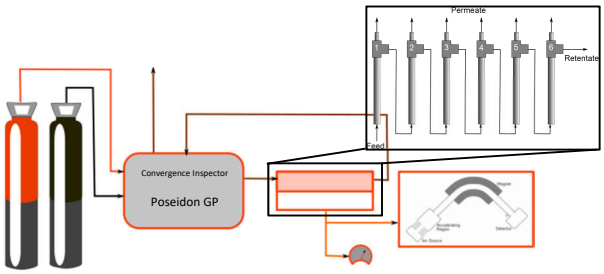


Figure 4: Testing of gas tranport properties of prepared HF membranes

Table 1: Process parameters with regard to the production of asymmetric PEI membranes

Sample	Polymer dope dose ml/min	Bore liquid dose ml/min	Towing speed m/min	Air gap cm	OD μm	ID μm
A5-1	4.2	2.1	12	2	417	248
A5-2	4.2	2.1	9.7	5	405	234
A5-3	4.2	2.6	12	5	410	265
A5-7	6	2.6	12	2	420	239
B3-1	0.75	0.625	12	2.5	289	186
B3-2	0.75	0.625	15	6	270	190
B3-3	0.75	0.45	12	6	290	185
B3-7	0.9	0.45	12	2.5	320	171

Convergence Inspector Gas Permeation (Convergence Industry B.V.). The permeate flow rate was measured by a bubble flowmeter and the composition of the permeate stream analyzed by a Prima BT Bench Top mass spectrometer (Thermo Fisher Scientific). Six laboratory modules were tested in series, where the retentate from the first module was used as a feed for the second module and so on (Fig. 4). Although this setting minimizes gas consumption and saves time, the correct mass balance on each module should be calculated. More information with regard to this can be found in [3].

The permeance P_i for CO_2 and H_2 as well as the CO_2/H_2 mixed gas selectivity $\alpha^*_{i/j}$ were evaluated from measured data. The permeance P_i is defined as the volumetric flow rate per unit driving force per unit area:

$$P_i = \frac{Q_P \cdot y_i}{(p_P \cdot x_i - p_P \cdot y_i) \cdot A} \tag{1}$$

where Q_P denotes the flow rate of the permeate, y_i stands for the mole fraction of gas i in the permeate, p represents the absolute pressure in the feed or permeate and A is the membrane area.

2.5 Development of the membrane separation unit

The membrane apparatus was built using fittings from SUPERLOK; tubing 6 mm in diameter and Parker 201LG solenoid valves manufactured by Parker, 250 kPa BD Sensors pressure sensors and a BP300-1-S back pressure regulator by Pressure Tech; a KK15 A 035/62 compressor by Dürr Technik: oil-free, max. performance = 25 l/min, 8 bar, max. pressure = 12 bar; a Rocker 410 oil-free vacuum pump; a control unit based on an Arduino Uno microcomputer and software developed by the authors.

3. Results and discussion

3.1 Preparation of HF membranes

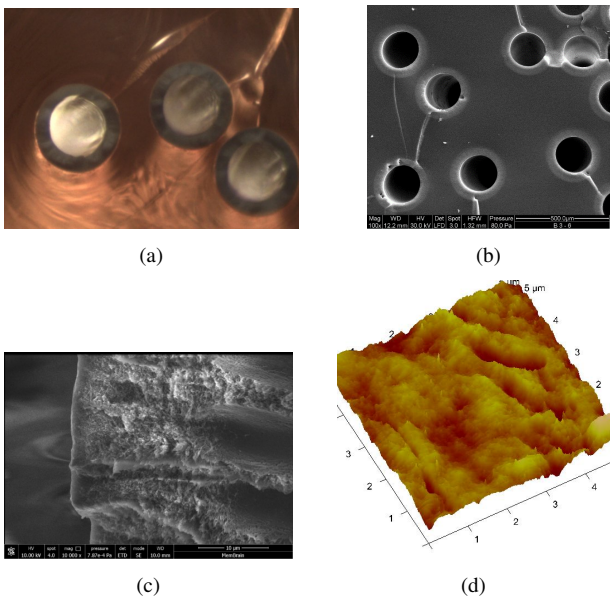
The preparation of HF membranes was carried out using 4 spinnerets simultaneously, resulting in a higher towing speed (15 m/min) which corresponds to the production of 3600 m of HF membrane per hour. There were two series (denoted as A5 and B3) of fibers prepared using various spinning process parameters. The significant difference between the A5 and B3 series are the dimensions of the nozzles. For the A5 series, the outer outlet diameter (OD) of the larger nozzle was used (0.512 mm), whereas for the B3 series, the outer OD of the nozzle was 0.330 mm. The process parameters with regard to the production of the asymmetric PEI membranes are listed in Table 1. As can be seen, all the membranes with a dosing of polymer dope of 0.75 ml/min apparently had a smaller outer outlet diameter (OD) than the fibers with a flow rate of polymer dope of 0.9 ml/min. It can also be observed that at higher towing speeds, the ODs of HF membranes were lower (with the exception of membranes B3-6).

3.2 Characterization of gas transport across HF membranes

Each sample of membrane was measured in three membrane modules by simultaneously connecting six modules to a Poseidon Group system (i.e. two samples of membrane were tested simultaneously). The average values were recorded and presented in Table 2. The results showed that all the membranes exhibited permeances within the range of $9.3-19.2$ GPU and H_2/CO_2 selectivities within the range of $3.3-5.6$. It is well known that gas separation in polymers can be described by a solution-diffusion model [4] which states that the permeability coefficient is the product of the diffusion and solubility co-

Table 2: Gas transport properties of the prepared HF membranes for the H_2/CO_2 mixture measured at a pressure of 8 bars.

Sample	CO_2 permeance (GPU)	H_2/CO_2 selectivity
A5-1	11.5	4.4
A5-2	10.3	4
A5-3	17.5	5.3
A5-7	19.2	5.6
B3-1	9.5	4.4
B3-2	9.3	4
B3-3	10.3	5.3
B3-7	20.3	4.5



(a) (b) (c) (d)

Figure 5: Optical microscopy image (a); SEM micrographs (b-c) and AFM micrograph (d) of the cross-section and surface of the prepared HF membranes.

efficients. In our case, H_2 permeates faster than CO_2 and since the diffusion coefficient of H_2 is significantly larger than that of CO_2 [5], it can be concluded that the separation is based on differences in diffusivities. This is typical for glassy polymers, including the PEI applied in this paper.

The best membrane from the A5 series was used to fabricate the P2 membrane module containing 250 fibers. From the whole B3 series, the two best membranes, namely B3-3 and B3-7, were selected to be incorporated into the membrane mini-modules.

3.3 Morphology of HF membranes

The resulting hollow fiber membranes (Fig. 5) had a regular round shape with a sponge-like structure containing typical relatively small finger-like pores (<30 μm). As determined using an optical microscope, the outer and inner diameters of the hollow fibers were 313 ± 9 μm and 290 ± 5 μm, respectively. The separation layer was on the outer surface for all the fibers. Atomic Force Microscopy (AFM) of the surfaces of the fibers revealed a relatively smooth surface consisting of a protective coating of PDMS with no defects.

3.4 Hollow fiber membrane modules

HC1 mini-modules

Once the best membranes from the B3 series had been chosen (B3-3 and B3-6), the requirements of the project coordinator with regard to modules for membrane bioreactors were established. According to the requirements, three HC1 modules were manufactured with assistance from MemBrain s.r.o. Their single gas transport properties were measured and are summarized in Table 3. The first two modules (HC1_1 and HC1_2) contained the same B3-7 HF membrane, the only difference between them was the number of fibers they consisted of and thus their membrane areas. HC1_1 consisted of 10 fibers with a corresponding membrane area of 19.7 cm^2, while HC1_2 consisted of 20 fibers with a corresponding membrane area of 39.3 cm^2. Hydrogen permeation flow rates were 28.2 (for HC1_1) and 53.0 ml/min (for HC1_2) at a feed pressure of 4.2 bars (abs) and achieving ideal H_2/CO_2 selectivities of 4.4 and 3.7, respectively. The permeate was released at atmospheric pressure. The slightly lower selectivity of the second module can be attributed to the variation in the membrane properties, minuscule leakage within the module or a combination of both.

The HC2 mini-module consisted of 23 fibers of B3-3 membrane, corresponding to a membrane area of 41.9 cm^2. As can be seen in Table 3, the permeate fluxes of the membrane modules were more than two times lower and only yielded negligibly higher selectivities. The modules were handed over to a Korean participant in the aforementioned project for further testing on real biogas.

The same modules were also tested for the H_2/CO_2 mixture to demonstrate their ability to concentrate the hydrogen. From Table 4, it can be seen that the modules were able to concentrate hydrogen from an initial percent concentration of 57 % to 88 % in the case of the HC1_1 module at a membrane stage cut of 96 % and from 57 % to 77 % in the case of the HC2 module at a membrane stage cut of 88 %. The membrane stage cut is defined as the ratio of the permeate flow rate to the feed flow rate. Generally, by increasing the membrane stage cut, the concentration of the more permeating penetrant is also higher. On the other hand, the hydrogen recovery is lower because most of the hydrogen from the feed is transferred into the low-concentration permeate.

P2-type module

Thicker HF membranes with an average OD of 420 μm were incorporated into a quarter-scale membrane module. From the number of fibers the module consisted of, that is, 250, and their active length, namely 25.6 cm, the total membrane area of the module was calculated to be 844 cm^2. The membrane module was tested against the gas transport properties of various single gases. The measured values are presented in Table 5. According to the measurements, the permeances more than doubled compared to the same membrane measured in a small-scale laboratory module. Furthermore, different values of H_2/CO_2 selectivities were calculated, the selectivity dropped from 5.6 to almost 3.0 to be exact. This perhaps indicates the presence of some microdefect on one of the fibers or a minuscule leakage between the feed and permeate. Nevertheless, the separation performance was sufficient to demonstrate the concept of biohydrogen purifi-

Table 3: Characterization of HC1 and HC2 mini-modules - gas transport properties were measured for single gases at pressure differentials of 1.0 and 3.2 bars as well as at a temperature of 25 °C

Gas	Number of fibers	Fiber diameter (cm)	Fiber length (cm)	Δp (bar)	Permeate flow rate (ml/min)	Membrane area (cm^2)	Permeance (GPU)	H_2/CO_2 selectivity
				Module HC1_1				
CO_2	10	0.0313	20	1	1.96	19.7	22.1	4.41
	10	0.0313	20	3.2	6.45	19.7	22.8	4.37
H_2	10	0.0313	20	1	8.65	19.7	97.7	
	10	0.0313	20	3.2	28.2	19.7	99.6	
				Module HC1_2				
CO_2	20	0.0313	20	1	3.92	39.3	22.1	4.46
	20	0.0313	20	3.2	14.3	39.3	25.2	3.71
H_2	20	0.0313	20	1	17.5	39.3	98.9	
	20	0.0313	20	3.2	53	39.3	93.6	
				Module HC2				
CO_2	23	0.029	20	1	1.65	41.9	8.7	4.5
	23	0.029	20	3.2	5.54	41.9	9.2	4.3
H_2	23	0.029	20	1	7.43	41.9	39.4	
	23	0.029	20	3.2	23.8	41.9	39.4	

Table 4: Gas transport properties of the HC1 and HC2 membrane mini-modules for the CO_2/H_2 mixture measured at a feed pressure of 3.6 bars (abs)

Module	Parameter		Composition [%]		
			Feed	Retentate	Permeate
HC1_1	H_2 Permeance (GPU)	–	57	54	88
	CO_2 Permeance (GPU)	–	43	46	12
	Membrane stage cut	0.96	–	–	–
	CO_2/H_2 Selectivity	4.2	–	–	–
HC1_2	H_2 Permeance (GPU)	–	41	40	63
	CO_2 Permeance (GPU)	–	59	60	37
	Membrane stage cut	0.94	–	–	–
	CO_2/H_2 Selectivity	4.3	–	–	–
HC2	H_2 Permeance (GPU)	–	57	38	77
	CO_2 Permeance (GPU)	–	43	62	23
	Membrane stage cut	0.88	–	–	–
	CO_2/H_2 Selectivity	5.7	–	–	–

cation.

3.5 Development of the membrane gas separation unit

Using the membrane modules, this project included the construction of a membrane gas separation unit, the optimization of the fermentation system and the integration of the gas separation unit into the GS-MBR.

Table 5: Gas separation properties of the P2 membrane module measured for single gases at 25 °C (number of fibers = 250, average OD = 420 microns, membrane area = 844 cm^2)

Gas	Δp (bar)	Permeate flow rate (ml/min)	Permeance (GPU)	H_2/CO_2 selectivity
CO_2	2	356	46.2	2.92
	5.6	949	44	2.99
H_2	1.2	625	135.3	–
	2	1012	131.5	–
O_2	0.65	28	11.2	–
	1.1	46	10.9	–

High-pressure membrane unit utilizing a laboratory air compressor

The model membrane unit consisted of a P2 HF membrane module, a laboratory air compressor, three pressure sensors, a pressure regulator valve, two solenoid valves, a back pressure regulator, fittings and an Arduino control unit. A schematic diagram and photograph of the unit are presented in Fig. 6. Both bioreactors were simulated by pressure vessels with inlets. The control unit senses the pressures in both pressure vessels (bioreactors) and at the feed of the membrane module. To achieve a high degree of efficiency, it is necessary to match the fermentation performance of both bioreactors to the performance of the membrane gas separation unit.

An attempt was made to control the compressor using pulses, namely the compressor was switched on when the fermented amount of biogas in the main bioreactor reached the specified limit. Since the power of the compressor considerably exceeded the performance of both fermenters and the membrane unit, it was necessary to control the flow of the compressed gas mixture into the membrane module by means of a back pressure regulator, which transferred the excess amount of compressed gas into the bypass. In order to maintain the pressure in the loop at close to atmospheric pressure, an expansion vessel was connected to it.

The compressor was controlled by pulses once again – an Arduino microcontroller opened the solenoid valves when the amount of biogas in the main bioreactor exceeded the set limit. The regulating valve in the retentate stream of the membrane module regulates its stage cut. When the pressure in the main bioreactor decreased under the set limit, the Arduino microcontroller closed the solenoid valves. This type of control guaranteed that the feed pressure in the membrane module was sufficiently high to maintain the required separation efficiency. The pressure was kept by back-pressure regulator. The flow rate of the gas mixture that was simultaneously fed into the membrane module varied from 0 to 3 l/min, which is given by the pulse width or duty cycle.

It should be noted that the mixture of hydrogen and carbon dioxide is reactive under certain conditions [6]. It probably cannot be ruled out that the pressures and temperatures in the compressor together with the presence of metal alloys will not trigger any undesired hydrogenation. The compressor must therefore be an internal ATEX version. The problem can be managed as shown in [7], where the same gas mixture was pressurized up to 380 bars.

Low-pressure membrane unit utilizing a vacuum pump

The second model membrane unit generates the driving force at the membrane by the suction force supplied by a vacuum pump. The unit again consists of the P2 HF membrane module, a laboratory vacuum pump, two pressure sensors, two solenoid valves, a peristaltic pump, fittings and an Arduino microcontroller. A schematic diagram and photograph of the unit is presented in Fig. 7. When the pressure of the biogas in the main bioreactor exceeded the set limit, the Arduino microcontroller opened both solenoid valves and started the peristaltic pump. The flow rate produced by this pump regulated the membrane stage cut. The permeate flux was considerably lower as the pressure differential was smaller than in the first unit. However, regulation in laboratory-scale experiments more accurately matched the performance of the fermenter with that of the gas separation unit. The amount of gas mixture fed into the membrane module can vary from 0 to 0.5 l/min, which is given by the pulse width or duty cycle as presented in the first set-up.

4. Conclusion

A series of 8 batches of HF membranes was prepared. Each batch had different spinning process parameters. The morphology and gas transport properties were characterized to select the 2 best HF membranes which were incorporated into 2 types of membrane modules. The first module was designed for laboratory tests and had a small membrane area and low permeate flow rate. The other module consisting of 250 hollow fibers was constructed for larger flow rates and scale. All membrane modules were tested for single- as well as mixed-gas transport properties and exhibited good levels of performance.

The design and development of a membrane separation unit is a very complex task. Firstly, membranes in the form of hollow fibers based on PEI were prepared. Then modules from each batch were built and characterized according to gas transport. The most efficient module achieved a separation factor for H_2/CO_2 in excess of 5. Three modules of this type were fabricated as well as tested using a model mixture and may hopefully be appropriate for real-life gas separation [8], which is going to be carried out by our partners.

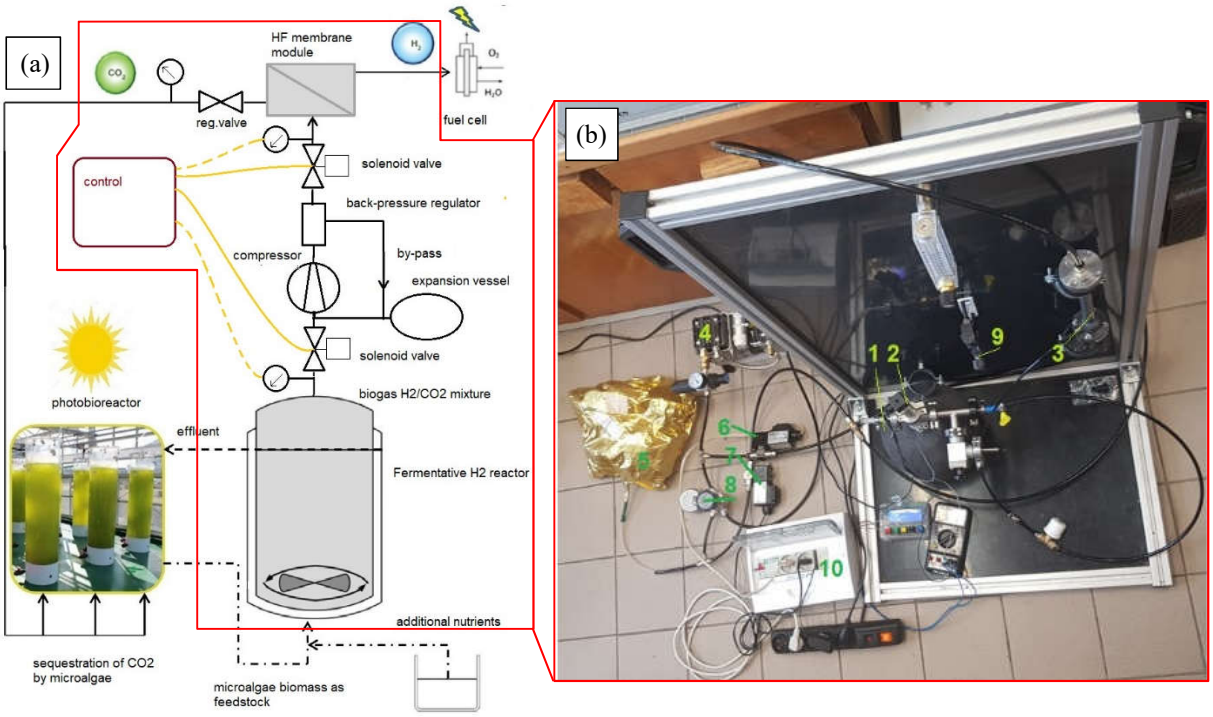


Figure 6: Schematic diagram (a) and photograph (b) of the high-pressure membrane unit for the integrated GS-MBR system: 1 - pressure vessel, 2 - pressure sensor, 3 - P2 membrane module, 4 - laboratory air compressor, 5 - expansion vessel, 6-7 - two solenoid valves, 8 - back pressure regulator, 9 - regulating valve with a flow meter, 10 - Arduino microcontroller.

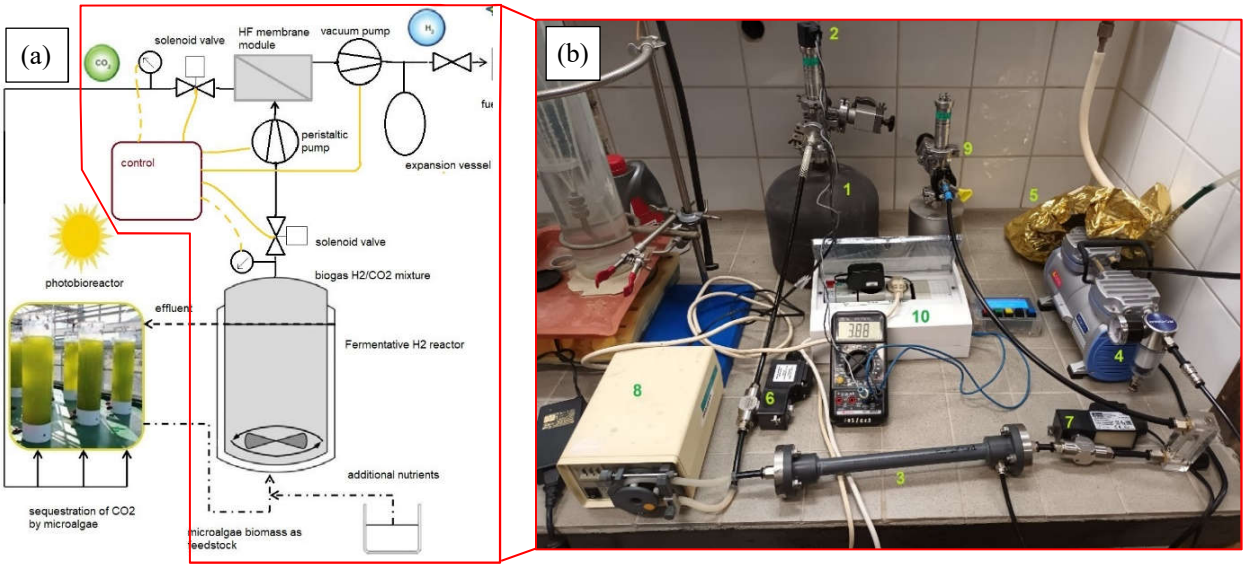


Figure 7: Schematic diagram (a) and photograph (b) of the low-pressure laboratory-scale membrane unit: 1 - pressure vessel, 2 - pressure sensor, 3 - P2 membrane module, 4 - laboratory vacuum pump, 5 - expansion vessel, 6-7 - two solenoid valves, 8 - peristaltic pump, 9 - pressure vessel – retentate recipient, 10 - Arduino control unit.

Two types of laboratory membrane separation units were constructed using the larger P2 HF membrane module. The high-pressure unit utilizes a compressor to pressurize the gas mixture into the feed of the module, while the low-pressure unit utilizes a vacuum pump to maintain a low pressure in the permeate of the membrane module. To ensure the separation efficiency remains high, pulse regulation was utilized. For laboratory use the low-pressure unit proved more accurate regulation to match the fermenters performance with the separation unit.

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REFERENCES

[1] Bakonyi, P.; Kumar, G.; Bélafi-Bakó, K.; Kim, S.-H.; Koter, S.; Kujawski, W.; Nemestóthy, N.; Peter, J.; Pientka, Z.: A review of the innovative gas separation membrane bioreactor with mechanisms for integrated production and purification of biohydrogen, *Bioresour. Technol.*, 2018, **270**, 643–655 DOI: 10.1016/j.biortech.2018.09.020

[2] Bakonyi, P.; Peter, J.; Nemestóthy, N.; Malý, D; Kumar, G; Koter, S; Kim, S.-H.; Kujawski, W.; Bélafi-Bakó, K.; Pientka, Z.: Feasibility study of polyetherimide membrane for enrichment of carbon dioxide from synthetic biohydrogen mixture and subsequent utilization scenario using microalgae, *Int. J. Energy Res.*, 2021, **45**, 8327–8334 DOI: 10.1002/er.5732

[3] Válek, R.; Malý, D.; Peter, J.; Gruart, M.: Effect of the preparation conditions on the properties of polyetherimide hollow fibre membranes for gas separation, *Desalin. Water Treat.*, 2017, **75**, 300–304 DOI: 10.5004/dwt.2017.20747

[4] Wijmans, J. G.; Baker, R. W.: The solution-diffusion model: a review, *J. Membr. Sci.*, 1995, **107**(1–2), 1–21 DOI: 10.1016/0376-7388(95)00102-I

[5] Freeman, B.; Yampolskii, Y.; Pinnau, I. (eds.): Materials science of membranes for gas and vapor separation (John Wiley & Sons, Ltd, Chichester, UK) 2006. DOI: 10.1002/047002903X

[6] Zeng, L.; Wang, Z.; Wang, Y.; Wang, J.; Guo, Y.; Hu, H.; He, X.; Wang, C.; Lin, W.: Photoactivation of Cu centers in Metal-Organic Frameworks for selective CO_2 conversion to ethanol, *J. Am. Chem. Soc.* 2020, **142**, 75–79 DOI: 10.1021/JACS.9B11443

[7] Härtel, G.; Püschel, T.: Permselectivity of a PA6 membrane for the separation of a compressed CO_2/H_2 gas mixture at elevated pressures, *J. Membr. Sci.* 1999, **162**, 1–8 DOI: 10.1016/S0376-7388(99)00066-6

[8] Rózsenberszki, T.; Koók, L.; Bakonyi, P.; Nemestóthy, N.; Bélafi-Bakó, K.: Comparative study on anaerobic degradation processes of pressed liquid fraction of organic solid waste, *Hung. J. Ind.Chem.*, 2021, **49**(1), 31–35 DOI: 10.33927/hjic-2021-05