

Fuel gases from organic wastes using membrane bioreactors

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Abstract

One way to produce fuel gases is using bioreactors producing CH₄/CO₂, H₂/CO₂ and CH₄/H₂/CO₂ gas mixtures. This method has many advantages; for example, low energy consumption, high ecological efficiency, utilization of organic wastes, accessibility and simplicity of hardware implementation. The results of organic waste bioconversion into methane and hydrogen by using an active membrane system integrated with aerobic and anaerobic bioreactors are presented. The suggested biomembrane system includes three types of fermenters: an aerobic phototrophic biomass producing reactor for CO₂ consumption and O₂ production from *Anabaena variabilis*, an anaerobic methane bioreactor for biomass transformation into biogas by using the methanogenic community, and *Rhodobacter capsulatus* immobilized in a polymeric matrix. The latter system was used for lactate or other low organics decomposition. The combination of the biosystem with membrane contactors and a selective membrane valve achieves a continuous process for energy production and total removal of CO₂ from microbial gas mixtures, which can be fed back into the first aerobic productive reactor. In total, the developed system obtains energy from sunlight in the form of combustible gases (CH₄ and H₂) with a net CO₂ consumption.

Keywords: Membrane contactors; Gas separation; Bioreactor; Carbon dioxide removal

1. Introduction

The development of new, low energy consuming and clean technologies has to include the

utilization of organic wastes with producing high-quality fuel gases (methane, hydrogen). The requirement of new renewable energy sources such as fuel gases increases every year. One way to produce fuel gases is with bioreactors, which

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as a rule produce gas mixtures such as CH_4/CO_2 , H_2/CO_2 , and $\text{CH}_4/\text{H}_2/\text{CO}_2$. These have many advantages such as low energy consumption, high ecological efficiency, utilization of organic wastes, accessibility and simplicity of hardware implementation. This work combines all aspects of modern membrane processes, advanced microbiology and biotechnology needed for the creation of new, solar energy-depending source of environmental friendly fuel production as hydrogen and methane with oxygen as a by-product.

It is known that hydrogen can be produced by biological processes, including direct biophotolysis, indirect biophotolysis, photo-fermentations and dark fermentation [1]. Fermentative hydrogen production can be realized without light by several strains, e.g., on glucose [2]. Photosynthetic bacteria are able to produce hydrogen from organic compounds, even organic wastes by an anaerobic light-dependent electron transfer process [3]. Many kinds of phototrophic purple bacteria were tested to produce hydrogen [4] from dairy wastes containing whey with lactate as the main carbon source [5]. It is known how the anaerobic microbial community digests the polymers to biogas [6], and many microbes have been isolated as hydrolytics, acetogens, syntrophs, fermenting, and methanogens [7].

Basically, the process of biomass digestion can be described as a consequence of reactions that lead to complete hydrolysis of cell polymers to monomers, fermentation of the sugars, organic acids, amino acids, purines and pyrimidines to volatile organic acids (mainly butyric, propionic, lactic and acetic) and conversion of C_5 - C_3 organic acids to C_2 acid–acetate. Methanogens convert acetate to CH_4 and CO_2 , and H_2 and CO_2 to CH_4 .

The problem of biogas separation on pure individual components (methane and carbon dioxide) has been, in principle, solved by using active membrane systems of the permabsorber type with flowing liquid carriers. This is a result of new silicon-containing high permeable polymer development [8]. Standard (passive) mem-

brane processes are restricted by definite selectivity of desired gases separation (not more than 1–2 orders of magnitude) and not suitable for integration with bioreactors since they need to use the compressor (or vacuum pump) for the gas feed before membrane modules.

Membrane separation techniques have already been applied for biological hydrogen production for CO_2 removal [5,8,9] or for hydrogen recovery and concentration [10]. Membrane contactors (MC) [5] and selective membrane valves (SMV) [8] as active membrane systems provide higher separation selectivity (3–4 orders of magnitude) and can be used for effective recovery of fuel gases from gas phase of bioreactors. Active membrane gas-selective systems can be also applied for monitoring optimal concentrations of CO_2 in solar bioreactors with cyanobacteria, removing simultaneously with oxygen from the gas phase of the reactor (by-product of oxygenic photosynthesis). Mass cultures of microalgae and cyanobacteria with various productivity — from $15 \text{ g m}^{-2} \text{ d}^{-1}$ for *Spirulina* sp. [11], up to $21 \text{ g m}^{-2} \text{ d}^{-1}$ for *Chlorella* sp. [12], $30 \text{ g m}^{-2} \text{ d}^{-1}$ for *Scenedesmus obliquus* [13] and to $60 \text{ g m}^{-2} \text{ d}^{-1}$ for *Dunaliella salina* [14] are known.

It is presumed that cyanobacterial growth can be optimized by monitoring CO_2/O_2 content in the gas phase of bioreactors by connected active permabsorber-type membrane systems. The data of the CO_2 fixation rate of $16 \mu\text{g C h}^{-1} \text{ mg}^{-1}$ of dry weight by cyanobacteria *Anabaena flos-aquae*, reported in the literature [15], are far from the maximum rates for the same bacteria 0.78 d^{-1} [16]. The main goal of this study was to connect the aerobic productive photobioreactor with cyanobacterial biomass to an anaerobic digestive bioreactor in a continuous mode where the biomass produced could be continuously decomposed, yielding a biogas (methane). The outflow liquid from the digestive bioreactor after filtration in the third, anaerobic, phototrophic reactor was cleaned from residual low-weight organic acids. All the pure CO_2 flows from three reactors after

separation by MC were combined. Then they were fed back to first productive bioreactor. The combination of three above-mentioned bioreactors and active membrane systems have never been used before.

2. Materials and methods

2.1. Solar-powered system of combined three-block bioreactors to produce hydrogen, methane and oxygen

A solar-powered system for microbial combustible gas production in an integrated membrane bioreactor (see Fig. 1) shows the separation effectiveness of CO_2/O_2 , CO_2/CH_4 and $\text{CO}_2/\text{H}_2/\text{CH}_4(\text{Ar})$ mixtures of microbial origin by the active membrane system based on a polymeric membrane with a liquid carrier, consisting of three blocks. The first one contains *Anabaena variabilis* (cyanobacteria) which consumes carbon dioxide with oxygen production induced by

sunlight. For the first bioreactor the selection of microorganisms among various phototrophs (*Spirulina platensis*, *Anabaena variabilis*, *Chlorella* sp.) was made. Based on the growth rates, *Anabaena variabilis* was selected for further experiments [5].

Biomass from the first block was transferred into the second one. An active membrane system connected with the aerobic bioreactor provides the effective recovery of oxygen from the gas phase. Biomass produced in a solar reactor is the feed for the methanogens community located in the second part of system. As a result of biochemical reactions, the biogas (CH_4 and CO_2) and low-molecular residual organics are produced. Continuous operation of the anaerobic digester was an advantage of the tri-reactor scheme, that allowed for the effective digestion of fresh cyanobacterial cells into CO_2 and CH_4 with a 50% conversion rate for a 2-week retention time. In continuous mode of operation, the methanogenic community was filtered through an anaerobic

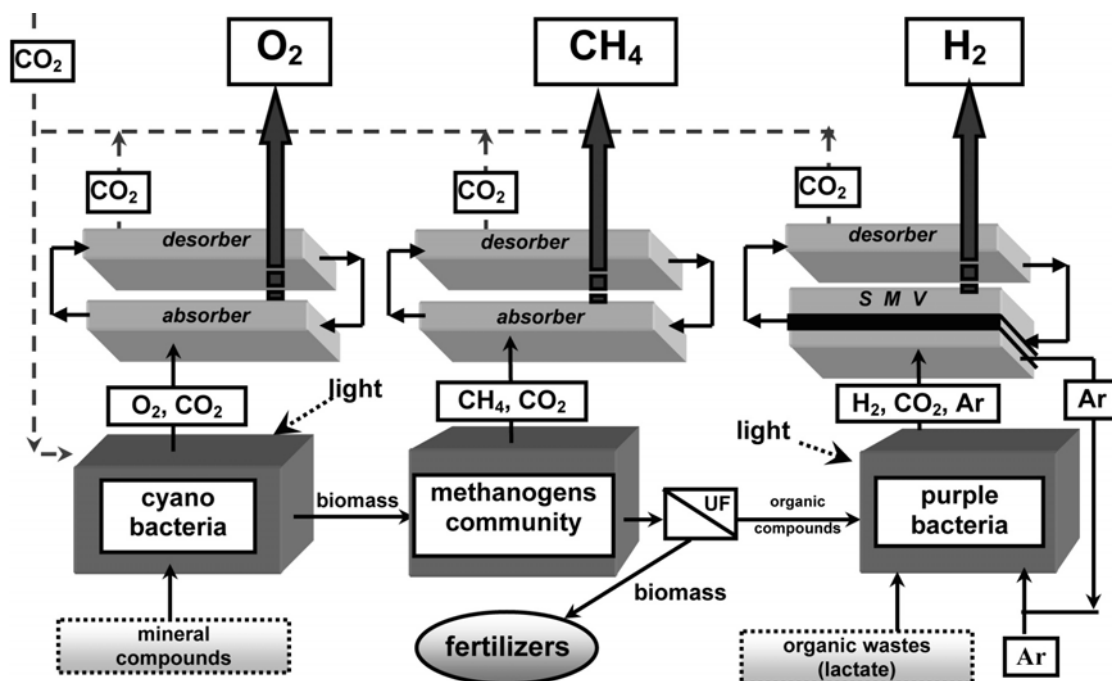


Fig. 1. Three-block system for fuel gas production.

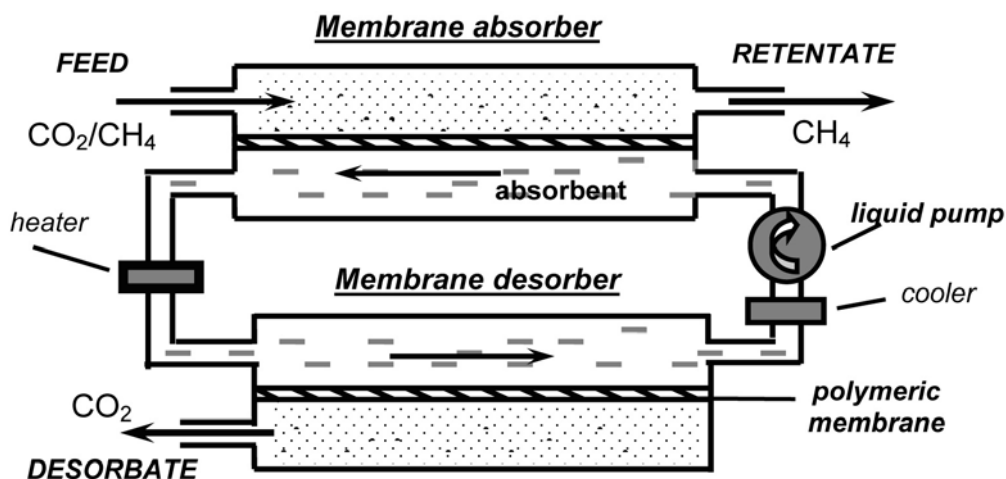


Fig. 2. Recirculating scheme of the membrane contactor.

membrane ultrafiltration unit, and liquid with low-weight organic acids was fed into the third, anaerobic photobioreactor with immobilized purple photobacteria. Methanogenic flocks could be used after as fertilizer and/or forage additives. Binary gas mixtures are effectively separated by the active membrane system with methane recovery for use of and CO_2 recycling into the first part.

Low-molecular organics are used as a substrate for purple bacteria treatment (free or immobilized *Rhodobacter capsulata*) with hydrogen and carbon dioxide production under sunlight. At this stage organic wastes (e.g., lactate) can be added as a feed. Hydrogen recovery from ternary gas mixtures is done by selective membrane valves with CO_2 recycling into the first part. The reason for the ternary gas mixture appearance in the third block is the use of argon as the stripping gas to enhance hydrogen production. In case of SMV, recirculating of Ar can take place.

2.2. Active membrane systems (membrane contactor and selective membrane valve)

An active membrane system is the MC which combines the membrane and absorption separa-

tion technique [17]. In the simplest case MC is a membrane module continuously flushed with a liquid carrier (external energy is needed to flush the liquid). Traditionally, in active membrane systems for CO_2 recovery, the liquid carriers can be carbonates of alkali metals, ethanolamines (MEA, MDEA), propylenecarbonate, etc. MC can be used effectively in recirculating mode of operating (Fig. 2).

Non-porous polymeric membranes were used in MC for separation of gas mixtures of microbial origin. This type of membrane has some advantages: it provides sterile conditions, prevents leakage of liquids, is highly selective and can be operated at different pressures, making it especially attractive for biotechnology. These membranes are obtained from polymers which must have high permeability, high selectivity for certain gas mixtures and be suitable for the production of very thin and stable films, i.e., membranes. Nevertheless, it should be noted that passive membrane methods of gas separation are limited by the narrow gas separation properties of polymeric membranes. The separation selectivity of H_2/CH_4 (ratio of single gas permeability or productivity) is in the range of 0.7–100; CO_2/CH_4 is in the range of 2–100, which is not enough to

provide separation of gases up to high purity. The silicon-containing polymers [polytrimethylsilylpropyne (PTMSP), polyvinyltrimethylsilane (PVTMS) and polydimethylsiloxane (PDMS)] demonstrate the highest permeability but only a moderate selectivity of separation. Asymmetric PVTMS membranes with a 0.2 micron dense layer providing high gas fluxes (CO_2 permeability, e.g., is $1600 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$) were selected for the experiments. High selectivity levels (1,000–10,000 units) can be achieved by using active membrane systems.

SMV is actually a MC where a “sandwich” membrane with a liquid carrier in between is used for ternary mixture separation. In this case methane was the retentate, hydrogen the permeant through the “sandwich”, and CO_2 the sorbate in a moving liquid layer [18,19].

3. Results

3.1. Optimization of *Anabaena variabilis* growth in connection with a permabsorber

The bioreactor with *S. platensis* was started and showed high biomass output. Feeding of the

anaerobic bioreactor with freshly grown *S. platensis* continued for almost half a year, and it was shown that biogas output constantly decreased with time mainly due to the incompatibility of the media between two bioreactors (phototrophic, aerobic and methanogenic, anaerobic). It was decided then that the phototrophic producer and growth medium must be changed. As an alternative microorganism for the phototrophic biomass producer, *Anabaena variabilis* (cyanobacterium) was used instead of *S. platensis*.

The cultivation of that microorganism was made on a Kratz–Mayers medium. The results of cultivation are 1.5 g of dry biomass×day for *Spirulina platensis* and 2.7 g of dry biomass×day for *Anabaena variabilis*. An evaluation of the volume of the bioreactor was made and CO_2 consumption was measured and calculated (see Fig. 3).

A connection between aerobic and anaerobic reactors was achieved where continuous flow of biomass from the first (productive, aerobic) bioreactor was fed to the second (digestive, anaerobic) reactor. Special “anaerobic loops” were designed to achieve self-respiring removal of oxygen from the biomass suspension, feed in the

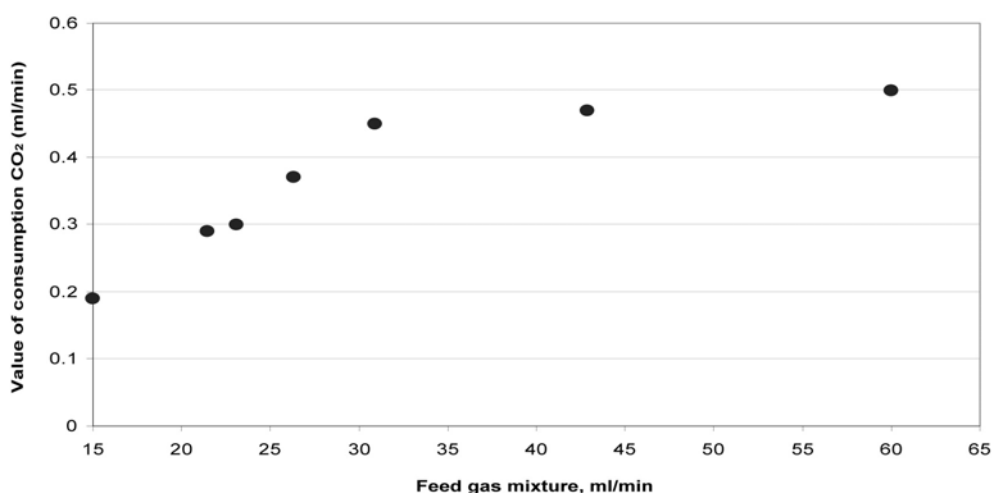


Fig. 3. CO_2 uptake by *Anabaena variabilis* depending on the rate of feed gas.

anaerobic digester. Respiration rates of continuously grown *A. variabilis* suspensions were determined, and the length of the dark respiration time was doubled from that calculated to be safe for removing the last traces of oxygen from the suspension. The need for continuously stable anaerobic digester work is foreseen for successful operation of the entire process.

Preliminary results show that the maximum feeding rate is 0.1 d^{-1} for the first productive bioreactor with *A. variabilis* as the biomass producer. This rate of feeding is allowed to keep the producer at a high speed of growth, close to the maximum rate, while simultaneously ensuring that culture is not washed out from the continuous fermentor.

CO_2 consumption by the first block was estimated as $22.1 \text{ L/g (dry biomass)} \times \text{day}$ by *A. variabilis* cells.

3.2. Anaerobic methane tank for cyanobacterial biomass digestion

Several anaerobic methane tanks were started with various inoculums as starter methanogenic microbial communities: anaerobic bogs, anaerobic digester of municipal wastewater, lake and river sediments, etc. Several anaerobic digesters showed a good rate for biogas output on fresh and dried biomass of *S. platensis* with an almost “classical” distribution of the gas content: $\approx 70\%$ of methane, $\approx 30\%$ of CO_2 with traces of other gases. Continuous feeding of an anaerobic bioreactor with freshly grown *S. platensis* failed in half a year due to the incompatibility of the media between two bioreactors (phototrophic, aerobic and methanogenic, anaerobic; see also above).

To provide growth in the media compatible with that in the anaerobic reactor, cultures of *A. variabilis* (cyanobacterium) and *Chlorella* sp. (alga) were chosen. The first experiments showed that the biomass of the two new phototrophic producers could be digested in methane tanks with good biogas output. In order to feed the

phototrophic biomass to the anaerobic digester continuously, the traces of oxygen had to be removed from the feeding suspension to be digested. For this reason the endogenous respiration of *S. platensis*, *A. variabilis* and *Chlorella* sp. suspensions were determined in the dark.

The biomass of *A. variabilis* and *Chlorella* sp. was fed continuously into an anaerobic digester. As a result (Table 1), it can be seen that the biomass of these phototrophic microorganisms is digested well under anaerobic conditions. The experiments showed that a continuous culture of *A. variabilis* consumes $780 \text{ mL of CO}_2 \text{ h}^{-1} \text{ L}^{-1}$ from the feed gas mixture of $\text{N}_2/\text{CO}_2/\text{O}_2$ in the proportions of 80/10/10%. This is important for the calculation of: (1) solar aerobic reactor's productivity rate; (2) maximum load rate into the anaerobic digester; (3) construction and working volume of the permabsorber, which will be used for the feed of the solar aerobic reactor with CO_2 from the anaerobic digester and hydrogen solar bioreactor.

It can be seen from the data in Table 1 that our the next biomass producer of choice (*A. variabilis*) is only slightly less productive compared to the *S. platensis* output of biogas (calculated as mL of biogas per g of biomass per day). But, as the medium for *A. variabilis* growth is compatible with two consecutive anaerobic bioreactors, this microorganism merits further study. Methane release was $0.3 \text{ L(gas)/g (dry biomass).day}$.

3.3. Optimization of H_2/CO_2 Rhodobacter Capsulatus B-10

Based on a literature search, seven promising cultures of purple phototrophic bacteria were selected from the Microbiology Department of Moscow University and were tested for their ability to growth in standard media. Based on the results obtained (Tables 2 and 3), three cultures with best growth performance and ability to produce hydrogen were selected for the future

Table 1

Comparison of the productivity for selected producers with biogas output after anaerobic digestion of phototrophic biomass

Biomass	Biomass productivity (g/L.d)	Biogas output (mL/L.day)	Biogas production per day (mL/g of biomass)
<i>Spirulina platensis</i>	0.25	125	500
<i>Anabaena variabilis</i>	0.66	300	450
<i>Chlorella</i> sp.	1	300	300

Table 2

Performances of selected strains of grown free cell suspension of purple phototrophic bacteria *Rb. capsulatus* B10, *Rb. sphaeroides* 2R and *R. rubrum* 2R in medium No. 2 towards hydrogen production

Strain	Maximum hydrogen productivity per reactor volume (mL H ₂ h ⁻¹ L ⁻¹)	Maximum hydrogen productivity per cells (mL H ₂ g ⁻¹ of protein)	Maximum hydrogen productivity per cells in hour (mL H ₂ h ⁻¹ g ⁻¹ of protein)
<i>Rb. capsulatus</i> B10	0.67	307.6	2.6
<i>Rb. sphaeroides</i> 2R	0.22	300	1.8
<i>R. rubrum</i> 2R	0.26	258.8	1.6

Table 3

H₂ productivity of free and immobilized cells of purple phototrophic bacteria *Rb. capsulatus* B10, *Rb. sphaeroides* 2R and *Rb. sphaeroides* GL-1

Microorganisms	H ₂ generation velocity, Carrier mL/h×g dry biomass		
	Free cells	Immobilized cells	
<i>Rb. sphaeroides</i>	20	1800	Porous glass
<i>Rb. sphaeroides</i> GL-1	82	3800	Porous glass
<i>Rb. capsulatus</i> B10	300	2900	PVA

studies: *Rb. capsulatus* B10, *Rb. sphaeroides* 2R and *R. rubrum* 2R.

All three strains were tested for the ability to produce hydrogen during their growth. The calculated performance of three selected strains tested showed that the strain of *Rb. capsulatus* B10 was superior among others tested for growth and

hydrogen production; based on these results, *Rb. capsulatus* B10 was chosen for further experiments as the best hydrogen producer.

3.4. Development of and testing the method for immobilization of the selected phototrophic bacteria

To develop a suitable method for the immobilization of cells of purple phototrophic bacteria *R. capsulatus*, several aspects were considered. The immobilization material and method should be easy to perform, harmless to live cells, transparent to visible light, cost-effective, resistant to wear in liquid over long periods of time, and resistant to microbial attack. After several attempts, (poly) vinyl alcohol was selected to create cryogels with immobilized cells of *Rb. capsulatus* in it. It was shown that cells were resistant to the immobilization method had a performed good residual hydrogen-producing capacity. The optimal concentrations of cells in gels and gels thickness (concentrations) were

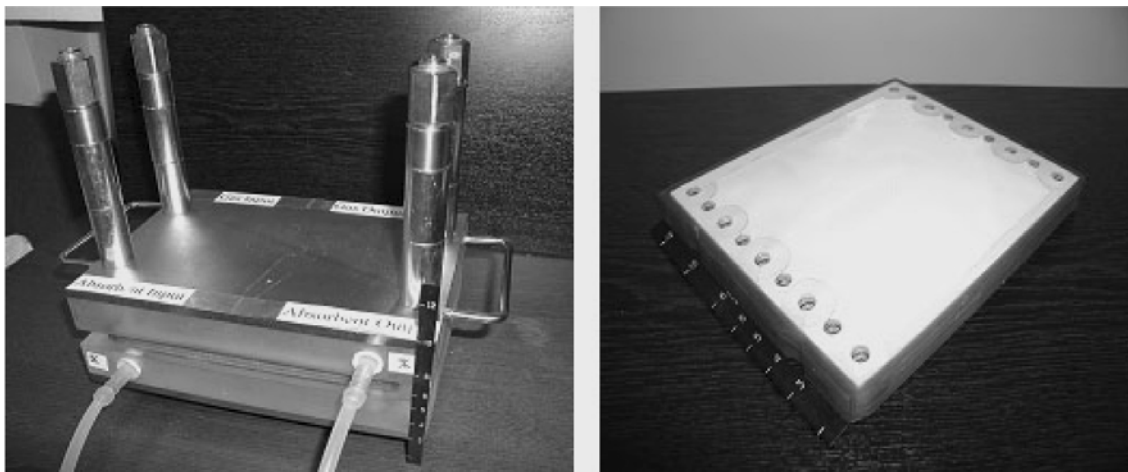


Fig. 4. General view of pilot flat sheet MC and membrane cassette.

Table 4

Minimum liquid adsorbent flow needed for total CO₂ removal from feed gas mixture by pilot flat sheet MC and propylene carbonate as liquid carrier

Gas mixture flow (9 % CO ₂), mL/s	Absorbent saturation by CO ₂ time (in the module), min	Minimum liquid adsorbent flow, mL/min
0.3	136	2.1
0.5	130	2.2
1	58	4.9
1.4	39	7.4
3.3	13	22

experimentally found. It was also found that the best hydrogen-producing capacity have cells grown in nitrogen-fixing conditions for maximum activation of nitrogenase, the hydrogen-producing enzyme system. The yield of the cells in that condition was small, but their hydrogen-producing activity was highest among all the growth conditions tested if calculated on cell protein. It is shown in Table 3 that immobilized cells are more stable in hydrogen production over time. It was also found that after immobilization the H₂ productivity of cells was increased by 40%. The productivity of anaerobic hydrogen fermenters immobilized in PVA *R. capsulate* under sunlight was 70 L H₂/(g of biomass.day).

3.5. Laboratory-scale design of recirculating active membrane system for CO₂/O₂ and CO₂/CH₄ gas mixtures separation

Based on previous experience, it was shown that the highest degree of gas purification is achieved using the MC scheme operated in parallel for the liquid phase but serially for the gas phase. It is possible to solve the task of purification of biotechnological gas mixtures up to 97% for a target component like hydrogen or methane with a given hydrodynamic circuit. The PVTMS-based pilot membrane cassettes were developed in this study for use in MC (Fig. 4) and SMV. The membrane area can vary in the range of 0.6–6 m². The developed pilot-scale MC and

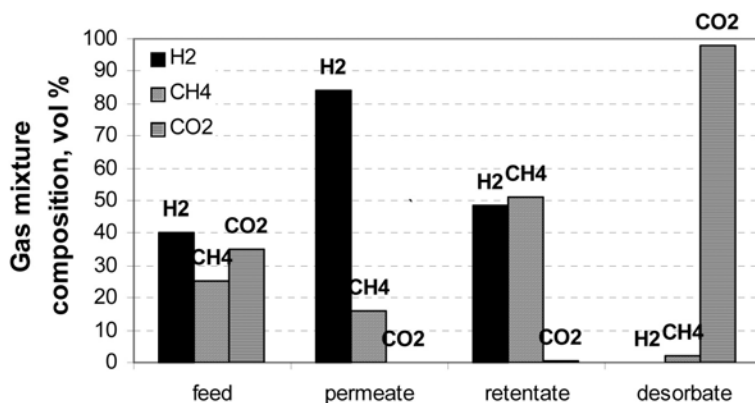


Fig. 5. Gas mixture compositions for SMV: feed, permeate, retentate, desorbate. Rate of liquid carrier (water solution of K_2CO_3) is 5 mL/min; feed gas flux and gas carrier flux are 30 mL/min each.

SMV were tested for the separation of gas mixtures of microbiological origin.

The results of the pilot-scale module MC testing for CO_2 total removal from binary gas mixture are presented in Table 4. As can be seen, the developed MC can be successfully used for separation of CO_2/CH_4 , CO_2/O_2 and CO_2/H_2 gas mixtures. The effluence of flow rates of liquid carriers (distilled H_2O and concentrated K_2CO_3) on gas separation ($H_2/CO_2/CH_4$) by a perm-absorber was studied. It was shown that even low rates of carrier gas flow (1–5 mL/min) with the fixed flow rate of liquid carrier (1 mL/min) could provide good separation (up to 95% of H_2 was removed). The need of a gas carrier for effective removal of hydrogen stimulated the development of MC for triple gas mixture separation (SMV). It was shown that SMV could efficiently remove CO_2 from a mixture of $CH_4/H_2/CO_2$ (Fig. 5) by a flowing liquid carrier. It was found that methane could be effectively used as the gas carrier for stripping H_2 from the SMV. It was demonstrated that active membranes from non-porous polyvinyltrimethylsilane provide effective recovery of methane (at >95% purity), carbon dioxide (>99.99% purity) by MC and hydrogen (>90% purity) by SMV.

The main intention of this study was to con-

nect the productive (model of organic waste) and digestive (model of biogas productive unit) fermenters into one consequent operating unit with the aim of continuous production of organics and its digestion with CH_4 production. In this process CO_2 is fixed and forms organic biomass under sunlight. This biomass decomposes in a digester-forming combustible gas (energy). CO_2 as component of biogas is successfully removed from the gas mixture with the membrane and then it can be re-directed into the first bioreactor again. The net surplus of the energy gain is CH_4 production on a continuous basis when light is the driving energy source.

The other part of biomass is the ecologically clean fertilizer. In a continuous process the out-flow water from the two reactors and UF unit passes through a third anaerobic reactor where low-molecular-weight organic acids decompose into a H_2/CO_2 mixture. However, in the experiments the organic load in the third reactor was quite low, so it was necessary to feed the third reactor with lactate or whey to maintain live cells. The mixture of the UF effluent and lactate source did not interfere with each other in the decomposing process — up to 90% addition (by volume) as whey — as the addition of lactate only increased the rate of decomposition of the

UF effluent. Third photobioreactor can be considered as an independent unit of the entire system, as part of the combined membrane system.

4. Conclusions

A solar-powered membrane bioreactor for fuel gas production is currently under development. It was shown that a combination of aerobic and anaerobic bioreactors with active membrane systems allows for the construction of a closed loop for the CO₂ and liquid phases.

Two types of active membrane systems are suggested for binary gas mixture separation. An active membrane system with a moving liquid carrier (without compressor) combined into one block: the membrane and absorption methods operating in the recirculating mode were integrated with laboratory-scale bioreactors. It was shown that MC based on non-porous polyvinyltrimethylsilane membranes provide effective recovery of methane (at >95% purity) and hydrogen (>90% purity). Non-porous polymeric membranes provide molecular diffusion fluxes and sterile compartments. These membranes remain stable and have good selectivity in relation to the number of gases, which make them attractive for industrial microbiology. The suggested type of membrane bioreactor can be a good example for ecologically clean renewable energy sources in the form of combustible gases for local supply.

One way to improve performance of the system is to select a more productive producer from algae or cyanobacteria, but it should be borne in mind that the growth medium for the first reactor should be 100% compatible with the one in the anaerobic digester. Otherwise, the two reactors will be unbalanced after a short time. Another advantage of the developed scheme is the possibility of using organic waste feed for the second anaerobic bioreactor for digestion and obtaining methane (biogas); the resulting CO₂ after CH₄

separation can be fed back into the photobioreactor as an additional source of carbon for the whole system. However, after UF separation, the resulting biomass can be used as fertilizer.

The anaerobic photobioreactor can be used independently from the entire system for decomposing local dairy plant wastes, containing lactate as the main low-weight organic acid. The suggested membrane bioreactor could be a good example for ecologically clean renewable energy sources in the form of combustible gases for local supply.

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