Integrated membrane systems for gas separation in biotechnology: potential and prospects

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Integrated non-porous membrane systems were applied for microbial combustible gas separation processes. Methane/CO_2, mixtures of various concentrations from methane fermentation processes (biogas) were separated using a membrane-separation complex of permabsorber type into individual components of technical grade (more than 95% purity). In experiments with three-component mixtures, using a selective membrane valve with various liquid carriers, all the gases of interest (H_2, CH_4 and CO_2) were obtained at greater than 90% purity in one separation step. The perspectives for the further application of non-porous membrane separating devices for various gaseous mixtures from different microbial processes are discussed.

Key words: Combustible gases, gas separation membranes, microorganisms.

The development of new, low energy-consuming and clean technologies is a main direction for the biotechnology and chemical industries. The central idea underlying such improvements is the intensification of all processes included, which is a new design philosophy providing essential up to date modification of chemical, biological and/or physical equipment. It can be achieved by the optimization of all dynamic fluid operations. The advantages include decreased capital outlay and operating costs and an increase in the process efficiency. Yield increases and improvement of industry internal safety are also very important.

All of the above mentioned can be achieved by interdisciplinary research with contributions from biology, chemistry and physics. It is known that one of the main directions for creation of effective and compact installations is the design 1 and development of commercial membrane reactors. The construction of a hybrid apparatus comprising traditional membrane reactors (chemical, biological) and integrated membrane systems with moving liquid carriers is especially promising.

A good example of an integrated membrane system is the membrane permabsorber (Hiroyuki et al. 1987, Johnson et al. 1987, Noble & Way 1987, Shelekhin et al. 1989, Teplyakov et al. 1993), that combines membrane and absorption separation techniques. In this case, the non-porous polymeric membrane with its own gas separation properties provides the sterile and permselective walls of the membrane reactor. Gas-selective membranes can be microporous or non-porous, and inorganic or organic. Here, we will review our work with non-porous, organic polymer membranes which are especially attractive for biotechnology. In the simplest case the permabsorber is a membrane module continuously flushed the liquid carrier. In gas separation systems the carrier dissolves, usually selectively, one of the gas mixture components. In converter-type systems intended not only for separation, but for simultaneous conversion of the gas mixture, the carrier can react with one of the components of the mixture and transform it into other substances. These converter systems are usually the membrane reactors themselves, but they can be built into traditional membrane reactors. The prospects for such "double integrated" systems which can be called hybrid (or combined) membrane reactors are considered in this paper.

Materials and Methods

Polymeric Membrane Selection

Non-porous organic polymer membranes have several advantages: they provide molecular diffusion fluxes and sterile compartments, have high selectivity in relation to the number of gases and allow operation at variable pressures and temperatures. All of these features make it attractive to industrial microbiology. These membranes are obtained from polymers which should have high permeability and high selectivity for certain gas mixtures, and be suitable for the production of very thin and durable films (e.g. membranes). Permeability coefficients, for example, to argon vary over eight orders of magnitude in different polymers. Among highly permeable polymers, the silicon-containing hydrocarbons are the most suitable for gas separating membranes (Table 1). Accumulated knowledge about the selective gas transfer through polymers (Teplyakov & Meares 1990) allows estimations of the separation properties in relation to permanent, rare, acid gases and lower hydrocarbons. It is shown in Figures 1, 2 and 3 that polymeric membranes can possess different permselectivity. For example, polyvinyltrimethylsilane (PVTMS, Figure 1), commercially available in Russia (costing about US$40/square meter, lifetime at least 5 years), can be used for the separation of "light' gases from other permeants, or for CO_2/CH_4, O_2/N_2, mixtures etc. Polydimethylsiloxan (PDMS. Figure 2), can perform lower hydrocarbon recovery from mixtures with permeant gases. Polytrimethylsilylpropine (PTMSP, Figure 3), which is a "champion" in gas permeability, can be used for separation of acid gases from others.

Table 1. Permeability and selectivity of different membrane polymers for separation of biogas components.

Polymer	P_{CO2}, B*	P_{CO2}/P_{CH4}
Polyacrilonitrile	$1.8*10^{-5}$	150
Polyvinylmethylketone	$3.7*10^{-2}$	15
Polyethyleneterephtalate	0.3	33
Polysulphone	5.6	22
Poly-4-methylpentene-1	94	5.3
Polyvinyltrimethylsilane(PVTMS)	170	8.2
Polydimethylsiloxane (PDMS)	4500	3.4
Polytrimethylsilylpropyne (PTMSP)	19000	4.4

- B (Barrer) = 10^{-10} cc*cm/cm^2*s*cmHg

Active Membrane Systems

The above mentioned passive membrane separation cannot provide very high selectivity; it is in the range 2 - 6 for O_2/N_2, or 10 - 40 for CO_2/CH_4, mixtures. Recently, membrane-based methods of separation with moving liquid carriers have been developed, which allow a much higher separation efficiency to be achieved. The membrane permabsorber (Figure 4) is the simplest integrated system, in which the membrane and absorption methods for gas separation are combined in one block. The permabsorber consists of absorption (absorber) and desorption (stripper) membrane modules which operate in a cyclic mode. In the absorption module the feed gas mixture is flushed over the composition membrane consisting of the polymer film and a thin layer of flowing liquid. The component of the gas mixture to which the polymer membrane is permeable and which is soluble in the liquid phase (CO_2 in this case), moves with it into the desorption module for the reverse degassing process through another polymer membrane. These membranes can be similar or different. The flowing liquid can be (*i*) non-specific in relation to the gas mixture components; (*ii*) the solubility of the gas components in a liquid can differ considerably; and (*iii*) the liquid can react with one or several gas components. This type of permabsorber is an integrated system in which the selectivity factors and the rate of the process might be changed depending on the aim of the experiment.

The example of a selective membrane valve (SMV) for separation of three-component gas mixture

is shown in Figure 5. The feed gas enters the permeator module first and in this module the gas mixture is divided into three individual components in one step. Component one of the gas mixture (retentate) is not permeable through membrane and leaves the module via an outlet, already separated from the mixture. Component three of the mixture (permeant) is a highly permeable gas and goes easily through both membranes and the liquid layer of the permeator module, separating from the mixture and flushing as an individual component from permeator's outlet.
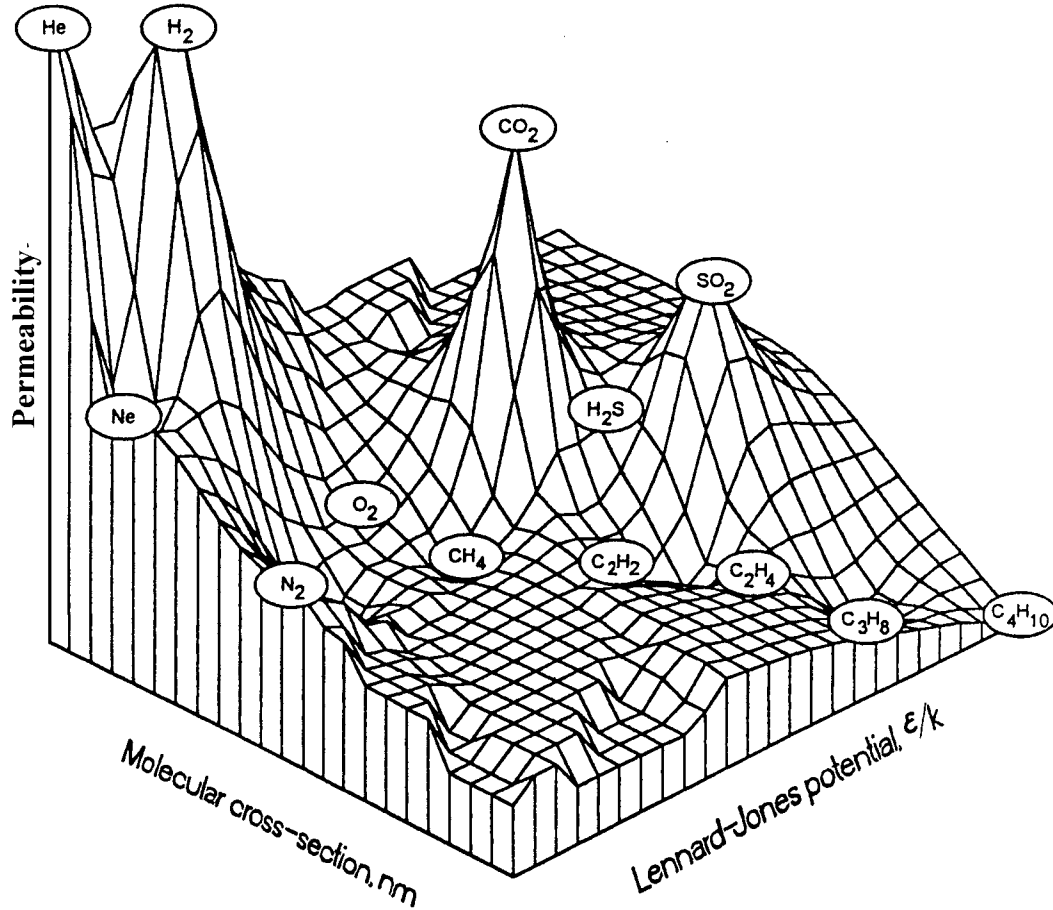

Figure 1. The permeation-selectivity profile of PVTMS membranes.

Component two of the mixture goes through first membrane of permeator, enters the liquid layer, reacts specifically with liquid and is transferred by pump into the stripper module of the SMV. Here, by the reverse process, it separates from the liquid and goes through another membrane into the stripper's outlet as an individual component. The liquid absorbent can operate in flowing (as shown in Figure 5) or circulating mode with steady state achievement during 0.5 to 3 h depending on the operating conditions. In the first case the gas content of the liquid phase leaving the module will depend on the degassing conditions in the stripper (the CO_2 recovery can be 90-95%, Beckman et al. 1993).

Theoretical Approach

The operation of a membrane absorption-desorption gas separation systems can be described by the following equations:

$$\Omega_a \frac{d\Theta_{La}}{d\xi} = 1 - \Theta_{La} \quad \left(0 \le \xi \le 1\right) \qquad (1a)$$

$$\Omega_d \frac{d\Theta_{Ld}}{d\xi} = \Theta_{Ld} \quad \left(0 \le \xi \le \eta\right) \qquad (1b)$$

where $\Theta = C/C_o$; $\Omega = SvL_lL_{ma}/(S_{ma}D_{ma}h_a) = S_Lv^*/Q_{ma}$; $\Omega_d = S_lv^*/Q_{ma}$; $\eta = (h_a + h_d)$; $\xi = y/h_a$; $C_0 = S_Lp_0$ and $A = hd$, and where p_0 is the partial pressure of the permeant (atm), $Q_m = ADS/L_m$ is the productivity $[cm^3(STP)/(s*Pa)]$, v^* is the volume flow rate of the liquids (cm^3/s), v is the linear rate of the liquids in a membrane absorber (cm/s), S is the solubility coefficient, D is the diffusivity coefficient, L is the membrane thickness, h is the membrane length, d is the membrane width, c is the gas concentration, y is the coordinate in the direction of moving liquids, and the subscripts are as follows: a, absorber; d, desorber; L, liquid absorbent; m, membrane.
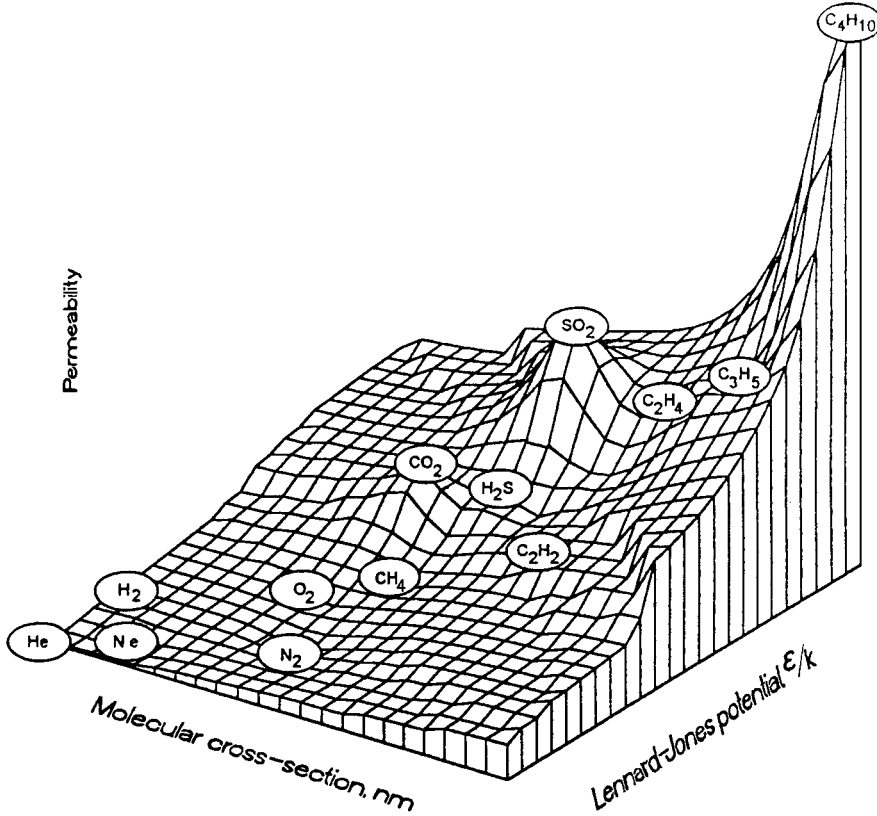

Figure 2. The permeation-selectivity profile of POMS membranes.

The solution of the ordinary differential equations la and lb has the following form:

$$C_{1a} = C_0\left[1 - K_a \exp\left(-\frac{\xi}{\Omega_a}\right)\right] \qquad (2a)$$

$$C_{1d} = C_0K_d \exp\left(-\frac{\xi}{G_d}\right) \qquad (2b)$$

where K_a and K_d are constants determined from the boundary conditions.

In a circulatory -membrane permabsorber the extractant, after leaving the desorber, is again fed to the absorber inlet. The main advantage of this modification is that the extractant is continuously circulating between the absorber and the desorber and is not consumed.

In this case the boundary conditions are as follows: $\Theta La = \Theta Ld$ and $\Theta Ld(0) = \Theta(\eta)$. Then

$$K_a = \frac{1 - \exp\left(\dfrac{\eta - 1}{\Omega_d}\right)}{\exp\left(-\dfrac{1}{\Omega_a}\right) - \exp\left(\dfrac{\eta - 1}{\Omega_d}\right)}$$
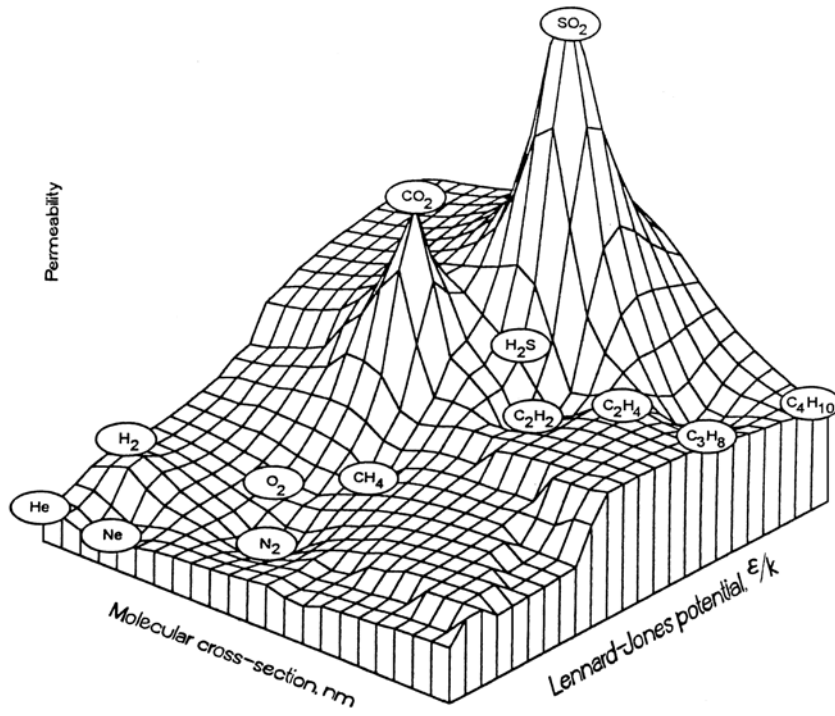
(3a)

Figure 3. The permeation-selectivity profile of PTMSP membranes.
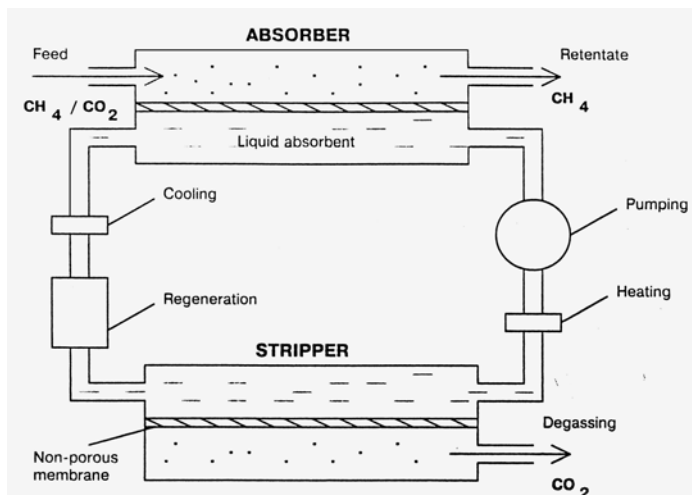

Figure 4. Membrane module for the selection of two-component gas mixtures (permabsorber type).

$$K_d = \frac{\left[\exp\left(-\frac{1}{\Omega_a}\right)-1\right]\exp\left(\frac{\eta}{\Omega_d}\right)}{\exp\left(-\frac{1}{\Omega_a}\right)-\exp\left(\frac{\eta-1}{\Omega_d}\right)} \tag{3b}$$

The total flux of the penetrant at the desorber outlet is:

$$J = \frac{AS_L L_L v p_0}{h_d} K_d \left[\exp\left(-\frac{1}{\Omega_d}\right)-\exp\left(-\frac{\eta}{\Omega_d}\right)\right] \tag{4}$$

FEED
$CO_2/CH_4/H_2$

non-porous membrane

PERMEATOR

RETENTATE
CH_4

LIQUID ABSORBENT

PERMEANT

H_2
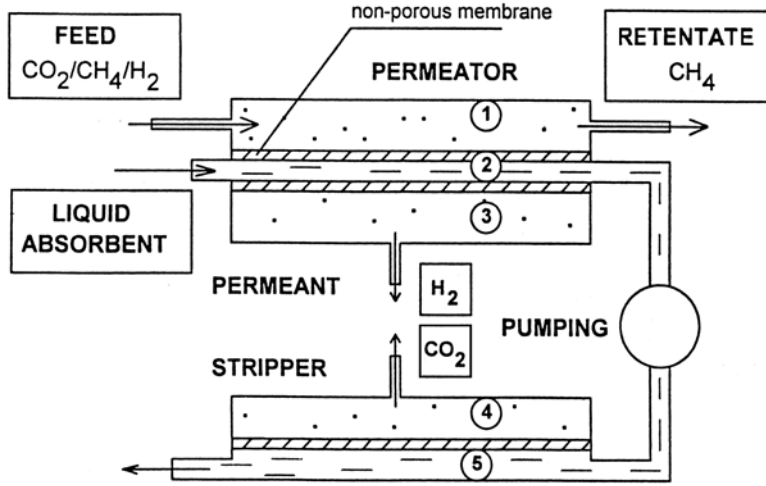
CO_2

PUMPING

STRIPPER

Figure 5. Membrane module for the selection of three-component gas mixtures (selective membrane valwe type).

with $\Omega_a = \Omega_d = \Omega$ and $h_a = h_d$, the flux is:

$$J = \Psi \frac{\left[1-\exp\left(-\frac{1}{\Omega}\right)\right]^2}{1-\exp\left(-\frac{2}{\Omega}\right)} \tag{5a}$$

$$\Psi = \frac{AS_L L_L v p_0}{h} = S_L p_0 v^*$$

If $v^* \to 0$ then $J \to 0$. At small values $J \sim v^*$. i.e., the flow linearly increases with increasing volumetric flow rate of the liquid. With large values of v^*, $J \to 0.5\ Q_m^* p_0$. The limits for the selectivity factor are

$$\lim_{v^* \to 0} \alpha^{G_1/G_2} = \frac{S_L^{G_1}}{S_L^{G_2}} \quad \text{and} \quad \lim_{v^* \to \infty} \alpha^{G_1/G_2} = \frac{Q_m^{G_1}}{Q_m^{G_2}}$$

The maximum productivity to be achieved in a circulatory membrane permabsorber is one half of the membrane productivity for the gas under investigation (Figure 4).

The separation factor in circulatory membrane permabsorber is determined by the following formula:

$$\alpha^{G_1/G_2}(v^*) = \frac{S_L^{G_1}\left[1-\exp\left(-\frac{1}{\Omega^{G_1}}\right)\right]^2}{S_L^{G_2}\left[1-\exp\left(-\frac{1}{\Omega^{G_2}}\right)\right]^2} * \frac{1-\exp\left(-\frac{2}{\Omega^{G_1}}\right)}{1-\exp\left(-\frac{2}{\Omega^{G_2}}\right)}$$

where the limits are:

$$\lim_{v^* \to 0} \alpha^{G_1/G_2} = \frac{S_L^{G_1}}{S_L^{G_2}} \quad \text{(selectivity of absorption liquid)}$$

$$\lim_{v^* \to \infty} \alpha^{G_1/G_2} = \frac{Q_m^{G_1}}{Q_m^{G_2}} \quad \text{(selectivity of membrane)}$$

By varying the flow rate of the liquid absorbent, one can change the separation factors for various gases.

Results and Discussion

The preliminary results show that there is the possibility to separate the gases from a methane bioreactor, where the agricultural waste (mostly cellulose fibers) is converted to a mixture of gases, predominantly CH_4 and CO_2, by the process of methane fermentation. The membrane system allows separation of the gas mixture into its pure components, such that further utilization of methane as fuel, and carbon dioxide as the carbon source for phototrophic bacteria or algae may take place.

Separation of CH₄/CO₂ Gas Mixture by Permabsorber

In our experiments on the two-component gas mixture separation we used the following parameters for the membrane permabsorber: the CO_2: CH_4 mixture had a composition of 46:54; liquid flux was varied from 1.66 to 8.24 *l/h*; gas flux was varied from 0.01 to 1.0 *l/h*. The temperature of the absorber was 18°C and that of the desorber was varied between 18 and 60°C For the flowing liquid absorbents aqueous solutions of monoethanolamine or carbonates of alkaline metals (Li_2CO_3, Na_2CO_3 and K_2CO_3) in various concentrations (1-3 M) were used (Table 2).

The best results were obtained with the 3 M solution of K_2CO_3 as the following liquid and the temperature of desorber's units at 60°C. In this case >99% pure carbon dioxide component might be separated from the mixture and > 94% pure methane could be obtained in one separation step.

Three-component Gas Mixture Separation by SMV

The separation of a three-component gas mixture CH_4: H_2: CO_2 (30:30:40) was carried out using SMV consisting of permeator and stripper blocks (Figure 5). By varying the experimental conditions (gas and liquid flow rates, temperature difference of absorber and desorber, composition of the liquid carriers) the best conditions for the separation of the three-component gas mixtures were determined: a 20% solution of monoethanolamine in water was used as the liquid carrier and the desorber's temperature was 50°C (Table 3, Beckman et al. 1993). In this experiment the separation of a three-gas component system might provide the technical grade of hydrogen, carbon dioxide and methane in one separation step. Further purification might be achieved using the same construction of module or a combination of SMV and permabsorber.

The above integrated systems are universal and can be further developed for obtaining molecular hydrogen with purple phototrophic bacteria and lactate (or dairy wastes) as the electron donor in anoxygenic photosynthesis. Preliminary results show that hydrogen gas might be obtained from a PVTMS membrane-attached photobioreactor containing phototrophic bacteria using lactate. Further research is needed on the reactor design and the process dynamics calculation and intensification.

Table 2. The separation of a bi-component gas mixture of CH_4:CO_2 (54:46 vol.%) by PVTMS membrane permabsorber (steady-state conditions).

Liquid carrier	Desorber temperature (˚C)	Gas flux (l/h)	Liquid flux (l/h)	Gas concentration % at outlets of:			
				absorber		desorber	
				CO_2	CH_4	CO_2	CH_4
H_2O	18	0.570	1.97	25	75	95	5
H_2O	18	0.078	1.97	16	84	73	27
H_2O	18	0.252	3.66	26	74	75	25
K_2CO_3	18	0.252	3.66	26	74	92	8
K_2CO_3	60	0.252	3.66	6	94	100	0

Table 3. The separation of three-component gas mixture by non-porous PVTMS membranes in SMV (steady-state conditions).

Gas feed (% vol.)	Temperature (°C) of:		% Vol. of gases at outlets for:		
	permeator	stripper	retentate	permeant	stripper
CH_4 (30)	18	50	CH_4 90	CH_4 1	CH_4 1
H_2 (30)	18	50	H_2 9	H_2 99	H_2 1
CO_2 (40)	18	50	CO_2 1	CO_2 0	CO_2 98

Table 4. Example of microbial gas transformation processes which can be connected with gas separation units of the permabsorber' type.

Physiological group of microbes	Mode of gas transformations
Hydrogen bacteria	$H_2 + CO_2 + O_2 \rightarrow H_2O + (CH_2O)_n$
	$H_2 + CO_2 + (CO) + O_2 + N_2 \rightarrow (CH_2O)_n$
Carboxydrobacteria:	
aerobic	$CO + O_2 + (H_2) + (N_2) \rightarrow CO_2 + (CH_2O)_n$
anaerobic	$CO + H_2O \rightarrow CO_2 + H_2 + (CH_2O)_n$
Acetogens	$H_2 + CO_2 + (CO) \rightarrow$ acetate $+ (CH_2O)_n$
Methanogens	$H_2 + CO_2 + (CO) \rightarrow CH_4 + H_2O + (CH_2O)_n$
Chemolithautotrophs	$H_2S, S^\bullet + O_2 + CO_2 \rightarrow SO_4^{2-} + (CH_2O)_n$
Methanotrophs	$CH_4 + O_2 \rightarrow CO_2 + (CH_2O)_n$

Conclusion and Perspectives

The development of gas separation using passive diffusion has reached a high technological level. Membrane technology for gas separation finds application in concentration, purification, and separation of different gases from mixtures. In particular, membrane devices exist which can increase the oxygen content in air up to 35-40% (Teplyakov & Meares 1990), select for CO_2 and CH_4 from biogas (Teplyakov et al. 1993), or for hydrogen from mixtures (Henis & Tripody 1980), and regulate the gas atmosphere in the agricultural products storage processes (Gladkov et al. 1993). The further development of membrane methods of gas selection is limited by the narrow gas-selection properties of polymer materials and membranes based on these materials. The separation selectivity of the gas mixture O_2/N_2 is in the range of 1-6 and CO_2/CH_4 is in the range of 10-40. There is thus a need for the development of membrane systems which have considerably higher selectivity levels. Recently membrane systems with stable or moving liquid carriers have attracted special attention. In the first case, the effects of facilitated diffusion of the

gases (mostly CO_2 and O_2) using the special liquid carriers is exploited (Ward 1970; Eishun et al. 1987; Hiroyuki et al. 1987; Johnson et al. 1987; Noble & Way 1987). In the second case, so-called active transport is realized when the outside energy is used for the transportation of the liquid carrier from the entrance to the efflux side of the membrane (Shelekhin et al. 1989; Teramoto et al. 1989). In this system, a high degree of selection can be achieved, tens to hundred times higher than that of passive membrane devices.

In this study, experiments with modules constructed of "permabsorber" and "selective membrane valve" types using a non-porous synthetic PVTMS membrane demonstrated high effective gas separation for the biogas mixture. Multi-membrane permabsorbers are very compact. Energy consumption for this system is low due to the absence of a pressure compressor for gas or liquid flows. The application of polymeric non-porous membranes provides the long- term stability of, and prevents the pollution of gas products by, the liquid phase. The presence of two modules (absorption and desorption) provides the regeneration of liquid carriers.

Table 5. Examples of microbial gas transformation processes which can be connected with gas separation units of the 'selective membrane valve' type.

Liquid carrier	Desorber temperature (°C)	Gas flux (l/h)	Liquid flux (l/h)	Gas concentration % at outlets of:			
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The next stage in the development of membrane technology seems to be the creation of membrane systems with 'microbiological carriers' which can provide not only the selective transfer of certain components of gas mixtures but also their transformation into valuable and ecologically friendly products. These systems may be new unusual energy sources (Chadwick & Irgens 1991). The principles of these types of systems are realized in certain living organisms. It is obvious that the development of the new membrane biotechnology is necessary for the solution of long-term ecological problems.

It is of interest to apply, as a moving converter, the aqueous suspensions of microorganisms capable of interacting with components of the gas mixture and to transform it into new (not necessarily gaseous) useful compounds. The prospects of bioconvertor application are connected with the potential for transformations which cannot be done using chemical techniques at ambient temperatures and pressures, or with the high selectivity of biotechnological approaches. Microbiological converters can accomplish important processes, namely, transformation of gases into other gases, transformation of gases into biomass and liquid wastes into desired gases for subsequent utilization. Several examples of microbial gas producing/utilization processes which can be connected with gas-separation modules are shown in Tables 4 and 5.

The creation of integrated systems with moving bioconverters would be useful for toxic compound recovery from industrial exhaust gases, for transformation of "green house" gases into useful energy carriers (for example, carbon dioxide into hydrogen), for treatment of gaseous pollutants, for utilization of different industrial and agricultural wastes, as well as for additional shifts in chemical equilibria in

traditional membrane reactors for improvement "of product yield and purity. The further development of integrated membrane systems could provide sterile membrane bioreactors with flexible control of the gas feed and products in the medium by using the microorganisms as active gas carriers.

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