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INTEGRATED MEMBRANE SYSTEMS WITH MOVING LIQUID CARRIERS FOR BIOGAS SEPARATION IN BIOTECHNOLOGY

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ABSTRACT

The gas separation membrane systems with moving liquid carriers are considered in this paper. The combination of non-porous gas separation membranes with moving liquid carriers of different kinds allows to separate multi-component gas mixtures on the constituents.

The theoretical basis and practical approach of membrane gas-liquid modules in circulating mode with non-specific and active carriers for biogas separation are discussed. Computer simulation of the separation processes was carried out. The results of CO_2/CH_4 separation by pilot equipment connected with lab-scale bioreactor are shown. The gas mixture separation was carried out by using multi layer membrane module with polyvinyltrimethylsilane (PVTMS) membranes. Some prospects of membrane gas separating system applications for aerobic and anaerobic bioprocesses are considered.

INTRODUCTION

The biotechnology which uses effective aerobic or anaerobic processes needs the gas mixtures of optimal composition (Aragno a. Schlegel, 1992).

It is of interest for many years to find the convenient and reliable way to separate methane fermentation gas to increase the efficiency of the further methane gas burning (Bhatnagar et al., 1991). It is possible to pass the outlet methane tank through the scrubber for chemical bounding of CO_2 to get more pure methane. The problems of CO_2 utilization and waste effluent treatment are obvious (Whitman et al., 1992). Our method of gas separation has the advantage in getting more pure methane as a fuel for local energy plants and the side product of CO_2. It is of interest for the biotechnological use of the exhaust CO_2 as a carbon source for algae or cyanobacterial growth (Drews a Imhoff, 1991). Phototrophic eu- and prokariotes are ready to use CO_2 as the only carbon source for reductive pentose phosphate cycle of carbon dioxide fixation and conversion it to the carbohydrates (Kondratieva et al., 1992). The other way of CO_2 is obvious - to make "dry ice" for dairy industry.

Other aspect of use of gas separation membrane modules is not so obvious. The idea is based on the gas supply to the acetate-forming bacteria which used the H_2/CO_2 mixture to make acetate (Wood a. Ljungdahl, 1991). The strict anaerobic bacteria called homoacetogenes make acetate as the by-products of their metabolism and way of energy obtaining from the hydrogen oxidation concomitant with carbon dioxide reduction. The bacteria use unique acetyl-CoA pathway for CO_2 fixation and use only a little of formed acetate as a building blocks for their anabolism. Most of the formed acetate is excreted into the medium (Diekert, 1992). The potential problem might be in the different speed of the supply of two gases due to their various solubility and the rates of consumption. It is a little engineering problem to remove formed acetate as Ca-Mg-acetate after adding a lime to the side circle of the fermenter.

One more interesting feature for the methane/air mixture supply to the fermenter of methane-oxidizing process for single-cell protein obtaining was successfully solved in pilot plant production unit in Svetly Yar town on Volga river (near Volgograd). The plant has the output of 10,000 ton/year of SCP on natural gas and the product is available under the trade name of Gaprin. The problem of methane/air addition into the fermentation process under the pressure of 7 bars (99 psi) to increase the solubility of methane in the medium was solved by insertion of membrane gas exchange unit into the fermenter. The output of the process was increased 6 times without changing other parameters which is of great interest for the aerobic fermentation processes worldwide (Sheiekhin and Beckman, 1989, 1990).

It is also of interest to have the system available for the decomposition of waste water of dairy plants mostly have the lactose as the main carbon contaminant. There is one kind of phototrophic bacteria which fulfills the anoxygenic photosynthesis and have a several organic compounds as the electron donors for this process. This bacteria are autotrophic and have CO_2 as the only carbon source for cell growth.

Thus the development of integrated membrane systems which possess by the gas separation and simultaneously sterile barrier properties can de useful for improvement of bioprocess itself and for utilization of the gas products.

THE PHENOMENOLOGICAL DESCRIPTION OF GAS TRANSFER IN PERMABSORBER.

The membrane permabsorber (Fig.1) is the simplest integrated system combining in one equipment the membrane and absorption methods of separation. Recently the new types of the flowing liquid membranes in which a liquid solution flows along microporous (Sirkar, 1988) , (Teramoto, 1989) or non-porous membrane (Shelekhin and Beckman, 1989, 1990) have been proposed.

As a rule the permabsorber consists of the absorption and desorption membrane modules operating in circulating mode. The principle of permabsorber operating is very simple (Fig.1) In absorption module the feed gas mixture is blowing over the composition membrane (6a) consisting of thin polymer film and thin layer of flowing liquids. The gas components which are permeable through polymeric membrane and soluble in liquid layer are moving into the desorption module for degassing through other polymeric membrane (6b). These membranes can be similar or different. The flowing liquid can be non-specific in relation to the gas mixture components; secondly, the solubility of the gas components in a liquid can considerably differ; finally, a liquid can react with one or several gas components.

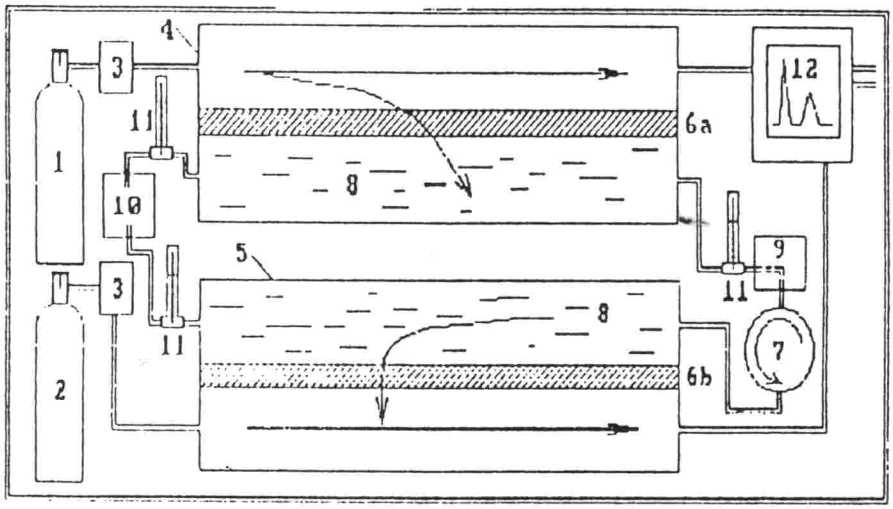

Fig.1. The block-scheme of the permabsorber for separation of gas mixtures. 1-source of feed gas mixture; 2-source of gas-bearer; 3-block of gas allocation; 4-absorbing cell; 5-desorbing cell; 6a-, 6b-polymeric membranes; 7-transfer pump; 8-liquid carrier; 9-heating thermostat; 10-refrigeratory thermostate; 11-thermometers; 12-gas chromatograph.

Here we consider that gas A reacts with carrier C dissolved in the liquid with creation of AC-complex:

$$A + C \underset{k_2}{\overset{k_1}{\rightleftarrows}} AC \qquad (1)$$

where:
k_1 - is the constant of a direct chemical reaction; k_2 - is the constant of a reverse chemical reaction; the gas B does not react with the carrier C. Let the concentration of C is enough high so that constant $k_1 = k_1 C_L^C$ and scheme (1) is a reversible process. The AC-complex does not diffuse through polymeric membranes.

The steady-state diffusion in permabsorber and co-current type module, in which well-mixed mode is maintained in gas phases over the membranes is considered; in a liquid layer the mixing occures in the transverse direction (x) while the mixing in the direction (y) does not take place.

The co-current or countercurrent fluxes of gas and liquid in permabsorber are described by the following equations:

$$W_L h \frac{dC^A_{La}}{dy} = \frac{D_m S \sigma_m}{\ell_m \sigma_L} (\sigma_L C^A_{ga} - C^A_{La}) - V_{La}(k_1^* C^A_{La} - k_2 C^{AC}_{La})$$

$$W_L h \frac{dC^{AC}_{La}}{dy} = \left(k_1^* C^A_{La} - k_2 C^{AC}_{La}\right) \cdot V_{La} \qquad (2)$$

$$W_{ga} h \frac{dC^A_{ga}}{dy} = - \frac{D_m S \sigma_m}{\ell_m \sigma_L} (\sigma_L C^A_{ga} - C^A_{La})$$

where W_L is the volume speed of liquid; V_{La} is the volume of liquid layer; W_{ga} is the flow rate of feed. h is a membrane length; S is surface of membrane. D_m , σ_m , ℓ_m ; σ_L are diffusion coefficients, solubility coefficients of gases and layer thickness for the membrane and the solubility coefficient in a liquid layer, respectively (here subscript $_m$ is membrane; $_L$ is liquid, $_g$ is a gas phase, $_a$ is absorber).

The calculations of the permeability and selectivity dependences of biogas separation on speed of liquid and gas fluxes (co-current and countercurrent modes), the carriers concentration and temperature were made by using of suggested approach. The good agreement between solution of equations (2) and experiment has been found. It was shown that selectivity of gas separation can be flexible varied from the solubility selectivity in liquid to the permeability selectivity in polymeric membranes. There are a big choice of the both.

SEPARATION OF GAS MIXTURE CO_2/CH_4 BY PERMABSORBER

The bimembrane permabsorber has one inlet for the feed gas and two outlets for the products (retentate and desorbate) (Fig.1). Additionally, one can be maintained the difference between temperatures of absorber and desorber. In our experiments we used absorption and desorption modules consisting of 24 cells with active surface 0.6 m^2. Scheme of module is shown on Fig.2. The general view of experimental module is shown on Fig.3 and Fig.4. The proposed technique was tested on the separation of gas mixture CO_2/CH_4 with composition 46:54. Liquid flux was varied from 1.66 to 8.24 l/h. The absorber's temperature was 18°C. The desorber's temperature was varied from 18 to 60°C. We used water and water solutions of monoethanolamine and carbonates of alkaline metals (Li_2CO_3, Na_2CO_3, K_2CO_3), as the absorbing liquid. The majority of experiments was carried out using K_2CO_3 solution with the concentration from 0 to 3 mol/l. The main results are shown in Table 1. As it is seen from Table 1 high purity of the both separated components can be achieved by using permabsorber.

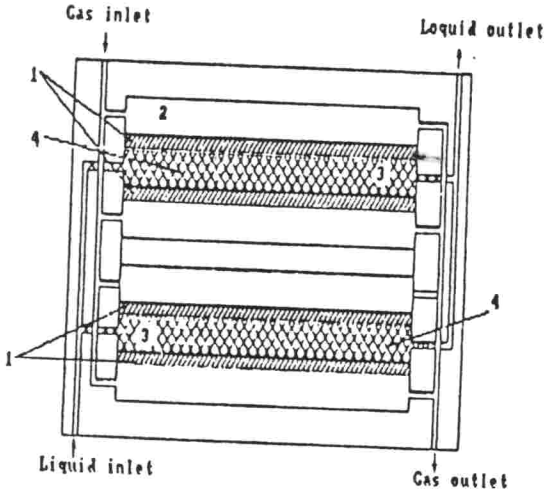

Fig.2. The scheme of multi membranes module: 1-polymeric membranes; 2 - gas layer; 3 - liquid layer, 4 - turbulizing washer.

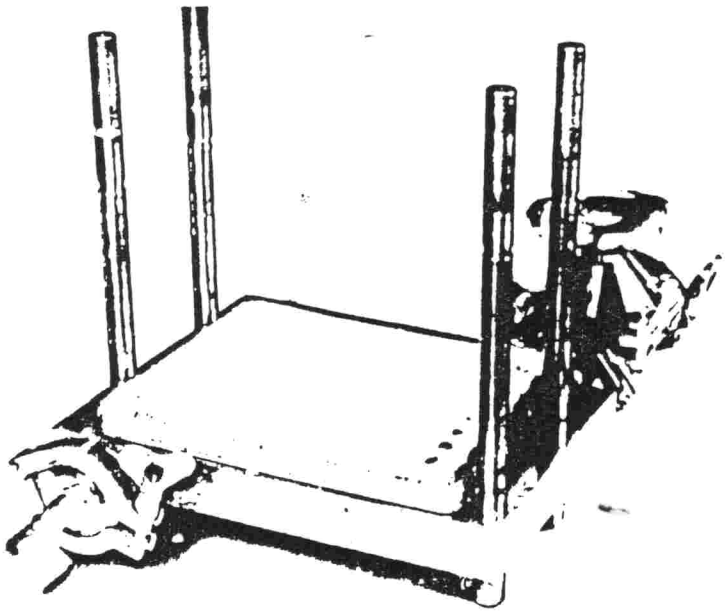

Fig.3. The gas-liquid multi layer module (open view).

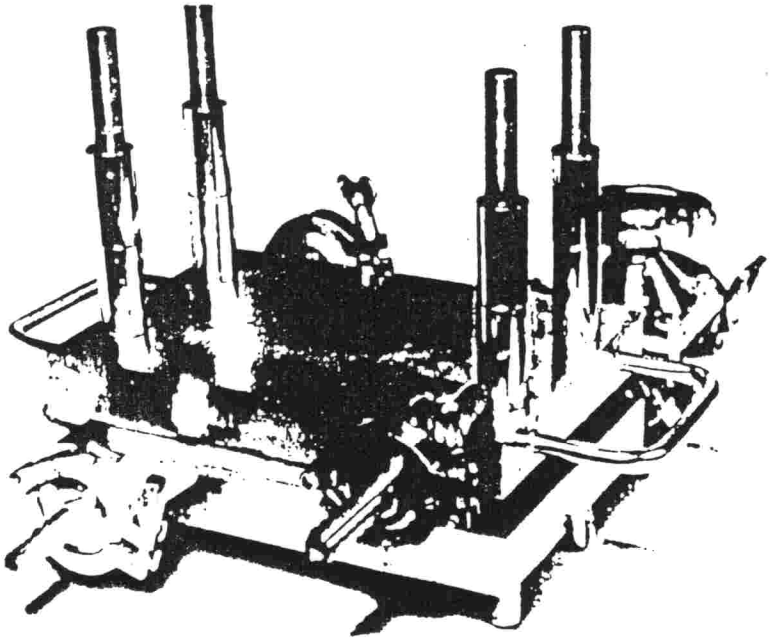

Fig.4. The gas-liquid multi layer module (completely collected).

Table 1.

The separation of bicomponent gas mixture CO_2/CH_4 by PVTMS membrane permabsorber.

Liquid carrier	Temper. of desorber T°C	Gas flux l/h	Liquid l/h	At the absorber's outlet,%		At the desorber's outlet,%	
				CO_2	CH_4	CO_2	CH_4
H_2O	~18	0.57	1.97	24.5	75.5	94.5	5.5
H_2O	18	0.078	1.97	15.9	84.1	73.1	26.9
H_2O	18	0.252	3.66	25.5	74.5	75.2	24.8
K_2CO_3(3M)	18	0.252	3.66	25.6	74.4	92.2	7.8
K_2CO_3(3M)	60	0.252	3.66	5.6	94.4	99.6	0.4

The pilot membrane unit connected with lab-scale bioreactor was tested in Institute of Microbiology (Riga, Latvia). The following results were obtained: capacity of pilot unit on biogas (composition CH_4/CO_2 was 62/38) was 5 m^3/day. The application of gas separation membrane system with moving liquid carrier allowed simultaneously to get components of biogas of technical grade: CH_4 (purity >96%) and CO_2 (purity >98%).

CONCLUSION

The experiments with integrated membrane systems consisting of non-porous asymmetric PVTMS membranes and flowing liquid have demonstrated high effective gas separation for biogas (for example, the selectivity CO_2/CH_4 ~ 1000 in comparison with CO_2/CH_4 = 10 for the PVTMS membranes). Multimembranes permabsorbers are very compact. The energy consumption for these systems is rather small due to the absent of the pressure compressor for gases and liquid. The application of polymeric non-porous membranes provides the stability of liquid phase for a long period of time and prevents the pollution of gas products by the liquid phase. The presence of two modules (desorption and absorption) provides the regeneration of liquid carriers. The mathematical simulation of above considered integrated systems allows to find the optimal gas separation conditions.

The further development of integrated membrane systems can provide the creation of the sterile membrane bioreactor with flexible controlling of feed gas medium as well as gas products by using microorganisms as active gas carriers.

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