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INTEGRATED MEMBRANE SYSTEMS WITH MOVING LIQUID CARRIERS
FOR MULTICOMPONENT GAS SEPARATION

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ABSTRACT

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

The phenomenological theory of gas separation by membrane gas-liquid modules in circulating and flowing modes with non-specific and active carriers is considered. Computer simulation of the separation processes was carried out. The proposed technique for separation of gases was tested by separation of CO₂/CH₄/H₂, CO₂/CH₄ and He/O₂ gas mixtures by using membrane module with polyvinyl-trimethylsilane (PVTMS) membranes.

INTRODUCTION

In many cases the development of membrane technology is connected with the improvement of productivity, selectivity and flexibility of the membrane gas separation systems. 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.

In this paper a new type of integrated membrane systems combining the membrane and absorption gas separation methods (selective membrane valve and permabsorber) are considered. One of the objects is a mathematical estimation for reasonable selection of the absorption liquid, its flow rate and approaches to module constructions. The 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. Here we consider that gas A reacts with carrier C dissolved in the liquid with creation of AC-complex:



where:

k_1 - is the constant of a direct chemical reaction ($\text{cm}^{-1}\text{s}^{-1}$); k_2 - is the constant of a reverse chemical reaction (s^{-1}); 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.

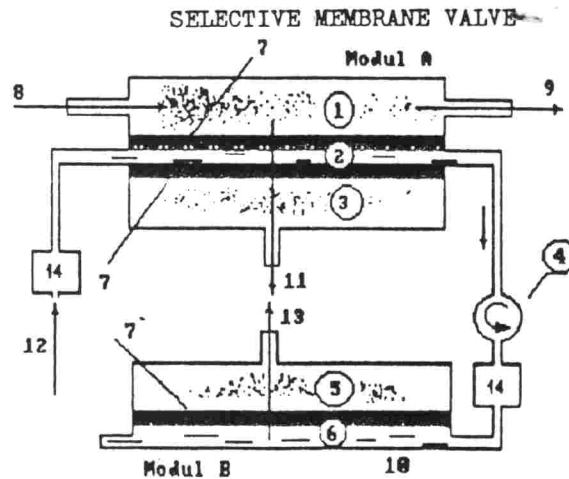


Fig.1. Schematic diagram of the selective membrane valve: flowing mode with desorber. 1,3- The gas chambers. 2- The thin liquid layer. 4- Pump. 5- The desorber gas chamber. 6- The liquid layer. 7- The polymeric non-porous membranes. 8- Feed gases ($\text{CO}_2/\text{CH}_4/\text{H}_2$). 9- Retentate (CH_4). 10- Dissolved gas (CO_2). 11- Permeate (H_2). 12- Liquid. 13- Degassing (CO_2). 14- Thermostates.

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The selective membrane valve (SMV) consists of a permeation module (A) and a desorption module (B) (Fig. 1). SMV is the version of the integrated membrane system with a liquid flowing between two non-porous membranes. Three component gas mixture can be separated by SMV: first component (retentate) is insoluble in a liquid carrier; second one (permeate) diffuses through the membrane sandwich; third component dissolved well in a liquid layer is pumped to desorption module for degassing. Thus, the SMV has one inlet (Modul A) for the feed gas and three outlets for the products (Modules A and B). Desorption module (B) contains the same polymeric membranes and intends for degassing of a liquid. There are two thermostates for liquid in this system: on the inlet of modul A (cooling) and on the inlet of desorber (heating). For simplicity one-membrane desorption module is considered. The possible modes of SMV operation are following: a flowing mode without or with a desorber; a circulation mode without or with a desorber.

MATHEMATICAL MODEL OF MASS-TRANSFER IN SMV.

The steady-state diffusion through SMV 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 occurs in the transverse direction (x) while the mixing in the direction (y) does not take place. The three-layered membrane sandwich in Module A has a rectangular shape were d is a width, h is a membrane length, v (cm/s) is a linear velocity of liquid. (Here subscript p - is permeator and d - is desorber). Let D_{1m} , σ_{1m} , ℓ_{1m} ; D_{2L} , σ_{2L} , ℓ_{2L} ; D_{3m} , σ_{3m} , ℓ_{3m} are diffusion coefficients, solubility coefficients of gases and layer thicknesses for the inlet membrane 1, the liquid layer and the outlet membrane 2, respectively (here subscript m is membrane; L is liquid)(Fig.1). The total sandwich thickness is $H = \ell_{1m} + \ell_{2L} + \ell_{3m}$. The partial pressure of the feed gas is p_{10} , and of the permeate is p_{H0} . The parameters of desorber are D_d , σ_d , ℓ_d respectively. Here $D_{2L} \gg D_{1m}$; $D_{2L} \gg D_{3m}$; $D_{2L} \gg D_d$.

In the case of chemical reaction (1) of carrier with component of gas mixture the gas diffusion through the sandwich being under steady-state conditions can be described by the equations:

$$\begin{aligned} \mathcal{W}_2 \frac{dC_{2L}^A}{dy} &= t_1^A - t_2^A + k_2 C_{2L}^{AC} l_{2L} - k_1^* C_{2L}^A l_{2L} \\ \mathcal{W}_2 \frac{dC_{2L}^{AC}}{dy} &= k_1^* l_{2L} C_{2L}^A - k_2 C_{2L}^{AC} l_{2L} \end{aligned} \quad (2)$$

where:

$$t_1^A = -D_1 \frac{dC_{1m}^A}{dx} \Big|_{x=\ell_1}, \quad t_2^A = -D_3 \frac{dC_{3m}^A}{dx} \Big|_{x=\ell_1+\ell_2} \quad (3)$$

t_1^A is the local flux of A component through the first polymeric membrane, t_2^A is the local flux of A component through the sandwich; C_{2L}^A , C_{2L}^C , C_{2L}^{AC} are the concentrations of gas A, carrier C and AC-complex in the liquid. The complete permeate flux (I_2^A) of component A through the sandwich is:

$$I_2^A = \int_0^h t_2^A(y) dy, \quad \text{and} \quad C_3^A(y) = \frac{\sigma_3}{\sigma_2} C_2^A \quad (4)$$

In the steady-state the gas concentration profile along coordinate x in the polymeric membrane is known to be linear. Therefore the derivatives in eq.3 can be replaced by concentration differences. Hence according Fick's law the system 2 is equivalent to the differential equation of the second order with the characteristic equation:

$$\alpha^2 + \alpha \frac{b + k_2 + k_1^*}{\nu} + \frac{bk_2}{\nu^2} = 0 \quad (5)$$

$$\text{where } b = \frac{\left[\frac{D_{1m} \sigma_{1m}}{\ell_{1m} \sigma_{2L}} + \frac{D_{3m} \sigma_{3m}}{\ell_{3m} \sigma_{2L}} \right]}{\ell_{2L}} \quad \text{and } \alpha_1, \alpha_2$$

are the negative roots of (5). Here we consider the case when: $\ell_{1m} = \ell_{3m} = \ell \neq \ell_{2L}$; $\sigma_{1m} = \sigma_{3m} = \sigma \neq \sigma_{2L}$; $D_{1m} = D_{3m} = D_{md} = D$; $h_p = h_d = h$.

The flowing mode with a desorber (fig.1).

In this case the fresh liquid is fed on the inlet of permeator (p) and then pumped on the inlet of desorber module (d). When gas A reversibly reacts with carrier C the boundary conditions are:

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$$C_{1m}^A \Big|_{x=0} = \sigma p_{10}; C_{3m}^A \Big|_{x=H} = 0; C_{2Lp}^A \Big|_{y=0} = 0; C_{2Lp}^{AC} \Big|_{y=0} = 0; C_{2Lp}^A \Big|_{y=h} = C_{2Ld}^A \Big|_{y=h};$$

$$C_{2Lp}^{AC} \Big|_{y=h} = C_{2Ld}^{AC} \Big|_{y=h}$$

In this case the complete permeate flux through the sandwich is :

$$I_2^A = \frac{P^A S}{\sigma_{2L} l} \left[\frac{a_{1F}}{h \alpha_1} (1 - \exp(-\alpha_1 h)) + \frac{a_{2F}}{h \alpha_2} (1 - \exp(-\alpha_2 h)) + \frac{p_0 \sigma_{2L}}{2} \right] \quad (6)$$

$$\text{where } a_{1F} = \frac{p_{10} (2D\sigma - \alpha_2 l l_{2L} \omega_{2L})}{2 l l_{2L} (\alpha_2 - \alpha_1) v}, a_{2F} = \frac{p_{10} (2D\sigma - \alpha_1 l l_{2L} \omega_{2L})}{2 l l_{2L} (\alpha_1 - \alpha_2) v} \quad (7)$$

are the constants from boundary conditions (subscript F - is the index of Flowing mode).

When two modules consist of the same membranes and flowing liquid, the gas flux from one-membrane desorber is

$$I_d^A = \frac{P^A S}{\sigma_{2L} l} \left[- \frac{a_{1F}}{h \alpha_1} (1 - \exp(-\alpha_1 h))^2 - \frac{a_{2F}}{h \alpha_2} (1 - \exp(-\alpha_2 h))^2 \right] \quad (8)$$

where the constants a_{1dF} and a_{2dF} are expressed by constants a_{1F} and a_{2F} .

Consequences.

1. For the flux of the permeate through the sandwich,

$$I_2^A \rightarrow S \frac{D\sigma}{2l} \cdot p_0 \text{ at } v \rightarrow 0; I_2^A \rightarrow 0 \text{ at } v \rightarrow \infty.$$

Thus in the flowing mode with a desorber the gas flux through the permeator can be completely closed. Hence, by variation of the liquid flux one can change the composition of the gas mixture after SMV. The gas flux after SMV can be closed also by increasing the value of k_1 .

2. For one-membrane desorber flux $I_d^A \rightarrow 0$ at $v \rightarrow 0$; $I_d^A \rightarrow 0$ at $v \rightarrow \infty$. Thus the gas flux via SMV can be varied from the value $I_2^A = \frac{S P p_0}{2l}$ to zero.

The circulation mode with a desorber.

In this case a liquid from the module (B) is returned to the module (A) by pump operating in a circle. The liquid passed through modul (B) is degassed in some extent. The desorber parameters are the same as above. In the case when gas B does not react with the carrier C and gas A reacts

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$$C_{1m}^A \Big|_{x=0} = \sigma_{p_{10}}; C_{3m}^A \Big|_{x=H} = 0; C_{2LP}^A \Big|_{y=h} = C_{2Ld}^A; C_{2LP}^{AC} \Big|_{y=h} = C_{2Ld}^{AC};$$

$$C_{2LP}^{AC} \Big|_{y=0} = C_{2Ld}^{AC}; C_{2LP}^A \Big|_{y=0} = C_{2Ld}^A$$

MATHEMATICAL SIMULATION OF GAS SEPARATION

Separation of the CO₂ containing gas mixture

In the case of three components mixture CO₂/CH₄/H₂ (40/30/30) for given polymer (polyvinyltrimethylsilane (PVTMS)) under 298K solubility coefficients σ and diffusion coefficients D are $\sigma(\text{CO}_2) = 0,038$; $\sigma(\text{CH}_4) = 0,01$; $\sigma(\text{H}_2) = 0,0011$; $D(\text{CO}_2) = 5 \cdot 10^{-7}$; $D(\text{CH}_4) = 1,8 \cdot 10^{-7}$; $D(\text{H}_2) = 180 \cdot 10^{-7}$

where $(\sigma) [\text{cm}^3 \text{ gas/cm}^3 \text{ PVTMS} \cdot \text{cm.Hg.}]$; $(D) [\text{cm}^2/\text{sec}]$ The pure water and water solutions of MEA (monoethanolamine) were used as a moving carriers of CO₂. The area of the membrane in one module was 75 cm². Thickness of the liquid layer was 0.2 cm. Thickness of the membrane 0,0001 cm.

Figure 2 shows the dependences of permeate fluxes (I_2) on speed of liquid pumping under different values of constant k_1 . In this case H₂ flux decreases smoothly with increasing of liquid speed (non-reactive gas); CO₂ passes away by liquid due to high solubility and reactivity; CH₄ is retentate. Figure 3 shows the dependences of desorption fluxes from desorber in flowing mode with consideration the chemical reaction between liquid carrier and gas component on speed of liquid.

PERMABSORBER.

In order to separate bicomponent gas mixture with very high selectivity it is possible to use the simplest integrated membrane system which is permabsorber. The principles and modes of its operating are the same as in SMV. In bimebrane permabsorber (Fig.1) the feed gas is fed in both gas chambers 1 and 3 (these chambers are connected each other). Thus, bimebrane permabsorber has one inlet for the feed gas and two outlets for the products (retentate and desorbate). In our experiments we used absorption and desorption modules consisting of 24 cells type of modules shown on Fig.1.

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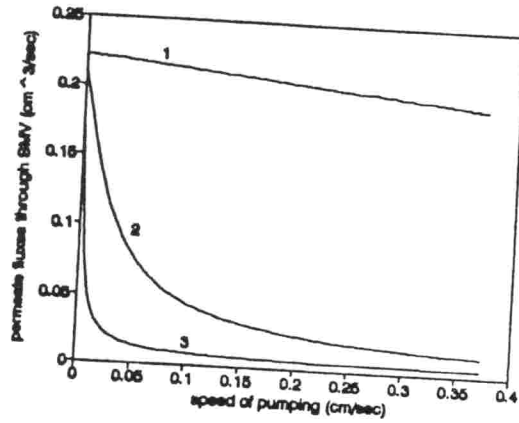


Fig.2. The dependences of permeate fluxes on speed of pumping in module A of SMV in flowing mode. Hydrogen is the most permeable component (1) (non-reactive gas), 2 - CO₂ (k₁^{*} = 0,05 k₂^{*} = 0,001), 3 - CO₂ (k₁^{*} = 0,1 k₂^{*} = 0,001).

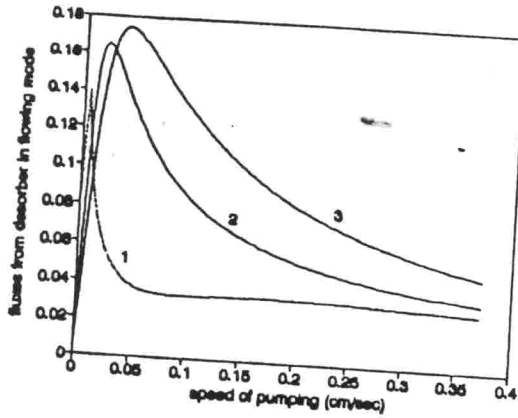


Fig.3. The dependences of desorption fluxes of CO₂ on speed of pumping in module B of SMV in flowing mode: 1- (k₁^{*} = 0,01 k₂^{*} = 0,001), (k₁^{*} = 0,01 k₂^{*} = 0,01), (k₁^{*} = 0,01 k₂^{*} = 0,1).

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

$$W_L h \frac{dC_{La}^A}{dy} = \frac{D_m S G_m}{\tau_m \sigma_L} (\sigma_L C_{ga}^A - C_{La}^A) - V_{La} (k_1^* C_{La}^A - k_2 C_{La}^{Ac})$$

$$W_L h \frac{dC_{La}^{Ac}}{dy} = (k_1^* C_{La}^A - k_2 C_{La}^{Ac}) \cdot V_{La} \quad (9)$$

$$W_{ga} h \frac{dC_{ga}^A}{dy} = - \frac{D_m S G_m}{\tau_m \sigma_L} (\sigma_L C_{ga}^A - C_{La}^A)$$

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. The boundary conditions in this case are the same as above. These equations can be solved by above mentioned procedure.

SEPARATION OF GAS MIXTURE CO_2/CH_4 BY PERMABSORBER

The separation of bicomponent gas mixture CO_2/CH_4 by PVTMS membrane permabsorber. Table 1.

Liquid carrier	Temper. of desorber $T^\circ C$	Gas flux ml/min	Liquid l/h	At the absorber's outlet, %		At the desorber's outlet, %	
				CO_2	CH_4	CO_2	CH_4
H_2O	18	9.5	1.97	24.5	75.5	94.5	5.5
H_2O	18	1.3	1.97	15.9	84.1	73.1	26.9
H_2O	18	4.2	3.66	25.5	74.5	75.2	24.8
K_2CO_3 (3M)	18	4.2	3.66	25.6	74.4	92.2	7.8
K_2CO_3 (3M)	60	4.2	3.66	5.6	94.4	99.6	0.4

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 l/h to 8.24 l/h. The absorber's temperature was $18^\circ C$. The desorber's temperature was varied from 18 to $60^\circ C$. 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

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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.

(9)

SEPARATION OF $CO_2/CH_4/H_2$ AND He/O_2 GAS MIXTURES USING SELECTIVE MEMBRANE VALVE.

The parameters of SMV construction are above mentioned. The speed of liquid pumping was varied in the range from 0.0013 cm^3/sec to 0.1 cm^3/sec . The pure water, water solutions of MEA and liquid $N(C_2F_5)_3$ were used as a carriers of CO_2 and O_2 respectively. The velocity of feed gas mixture was 0.66 cm^3/sec . The experiments were carried out with single Module A and SMV operating in the circulation mode with desorber (Module B). The main results are summarized in the Table 2.

The separation of $CO_2/CH_4/H_2$ and He/O_2 gas mixtures by PVTMS membrane SMV Table 2.

FEED %	LIQUID MEMBRANE	SPEED OF PUMPING cm^3/sec	RETENTATE %	PERMEATE %	DESORBER GAS %
CO_2 - 40 CH_4 - 30	water	0,04	CH_4 - 75 CO_2 - 20 H_2 - 5	CH_4 - 2 CO_2 - 7 H_2 - 91	CH_4 - 24 CO_2 - 75 H_2 - 1
H_2 - 30	25% water solution of MEA	0,04	CH_4 - 97 CO_2 - 1 H_2 - 2	CH_4 - 1 CO_2 - 0 H_2 - 99	
He - 70 O_2 - 30	$N(C_2F_5)_3$	0,01		He - 98 O_2 - 2	

CONCLUSION
The experiments with integrated membrane systems consisting of non-porous asymmetric PVTMS membranes and

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flowing liquid have demonstrated high effective gas separation for two and three components mixtures (for example, the selectivity $\text{CO}_2/\text{CH}_4 \sim 1000$ in comparison with $\text{CO}_2/\text{CH}_4 = 10$ for the PVTMS membranes). Multymembranes permabsorbers are very compact. The energy consumption for these systems is rather small due to the absence 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.

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