Journal of Engineering Physics and Thermophysics, Vol. 77, No. 5, 2004

THEORY OF MEMBRANE SEPARATION OF BINARY GAS MIXTURES

V. I. Baikov, I. Yu. Kostareva, and N. V. Primak

UDC 66.064

A general approach to the solution of the problem on convective mass transfer in the process of separation of binary gas mixtures in the channels of membrane units is proposed. An integral equation for the main separation parameter — the rate of flow of a binary-mixture component through a membrane — has been obtained.

Membrane separation of gases is finding increasing use in the processing of gases, enrichment of air with oxygen, concentration of hydrogen from the scavenging gases used in ammonia synthesis, etc. [1]. Among the advantages of membrane separation of gases are the high efficiency of the process, the absence of reagents, the simplicity of the equipment used, the long working life of membranes, and the possibility of automatization of the work of apparatus [1, 2]. The characteristics of this process can be further improved by optimization of the design of the flow-through membrane filter. To do this, it is necessary to know the main mechanisms of convective separation of gases.

The calculation of a membrane separation module involves the solution of the complex-conjugate problem on the mass transfer through the membrane and the heat exchange in the head and drainage channels under the conditions where the separation process is optimized due to a large number of interdependent variables. In this case, the external diffusion resistance in the head and drainage channels is usually ignored and the gas composition is assumed to be equal everywhere over their cross sections because of the high diffusivity of gases at comparatively low pressures and the low penetrability and selectivity of the membrane [1, 3, 4]. In the solution of the above problem, prominence is given to calculation of the mass transfer through the membrane since this stage is considered as limiting [1, 5]. However, the development of high-selectivity, asymmetric, polymeric membranes, which can be used at high pressures in the head channel, has changed the situation. In apparatus with such membranes, the external diffusion resistance is comparable with the resistance to the internal mass transfer in the membrane. Therefore, it makes sense to calculate separately and analyze the operation of apparatus in which the external diffusion resistance or the resistance inside the membrane prevails.

Apparatus with plane, hollow-fiber, and roll membrane modules are used for separation of gas mixtures. However, the effect of the external diffusion resistance on the separation of gases in plane and hollow-fiber membrane units is not clearly understood at present and there are practically no works devoted to detailed mathematical investigation of this problem.

We will consider a binary gas mixture flow that is completely developed at the input to a plane slot or a hollow fiber and is symmetric relative to the axis of the channel (see the diagram in Fig. 1). It is assumed that the flow is steady, the gas is noncompressible, the process is isothermal, and the viscosity and diffusion coefficients are constant. The volume viscosity and the pressure diffusion will be ignored. Then the continuity equation, the equation of motion (in projections), and the equation of convective diffusion can be written in dimensionless form as

$$\frac{\partial u}{\partial x} + r^{-\alpha} \frac{\partial (r^{\alpha} v)}{\partial r} = 0 , \tag{1}$$

A. V. Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus, 15 P. Brovka Str., Minsk, 220072, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 77, No. 5, pp. 113–117, September–October, 2004. Original article submitted December 29, 2003.

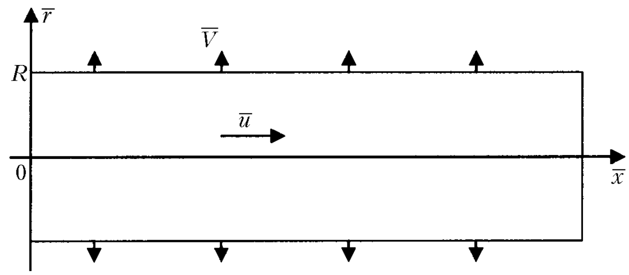

Fig. 1. Diagram of membrane separation of a gas mixture.

$$u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial r}=-\frac{\partial p}{\partial x}+\frac{1}{\mathrm{Re}\,\varepsilon}\left[\varepsilon^2\frac{\partial^2 u}{\partial x^2}+r^{-\alpha}\frac{\partial}{\partial r}\left(r^{\alpha}\frac{\partial u}{\partial r}\right)\right], \tag{2}$$

$$u\frac{\partial v}{\partial x}+v\frac{\partial v}{\partial r}=-\frac{1}{\varepsilon^2}\frac{\partial p}{\partial r}+\frac{1}{\mathrm{Re}\,\varepsilon}\left[\varepsilon^2\frac{\partial^2 v}{\partial x^2}+\frac{\partial}{\partial r}\left(r^{-\alpha}\frac{\partial (r^{\alpha}v)}{\partial r}\right)\right], \tag{3}$$

$$u\frac{\partial c}{\partial x}+v\frac{\partial c}{\partial r}=\frac{1}{\mathrm{Pe}_D\,\varepsilon}\left[\varepsilon^2\frac{\partial^2 c}{\partial x^2}+r^{-\alpha}\frac{\partial}{\partial r}\left(r^{\alpha}\frac{\partial c}{\partial r}\right)\right] \tag{4}$$

at the boundary conditions

$$c=c_0\,,\quad p=p_0\,,\quad u=\frac{\alpha+3}{2}(1-r^2) \tag{5}$$

at the input to the channel (at $x = 0$);

$$\frac{\partial u}{\partial r}=0\,,\quad v=0\,,\quad \frac{\partial c}{\partial r}=0 \tag{6}$$

at the axis (plane) of symmetry (at $r = 0$);

$$u=0\,,\quad \left.\left((1-c)\,v+\frac{1}{\mathrm{Pe}_D\,\varepsilon}\frac{\partial c}{\partial r}\right)\right|_{\bar r=1}=0\,, \tag{7}$$

$$v\,(x,1)=V\,(x)=\frac{\Lambda M u_0}{\varepsilon\delta_{\mathrm{m}}}\,p\,(x,1)\,c\,(x,1) \tag{8}$$

on the membrane (at $r = 1$). Here, $\alpha = 0$ corresponds to a plane-frame module and $\alpha = 1$ corresponds to a hollow-fiber module.

As follows from the formulation of the problem, the continuity equation, the equation of motion, and the equation of convective diffusion are interconnected since the unknown rate of mass transfer through the membrane $V(x)$ depends on the concentration and pressure of the gas at the wall. The problem will be solved on the assumption that $V(x)$ is known. In this case, the equation of motion and the equation of convective diffusion can be solved independently.

The equation of motion will be solved at the following parameters of the membrane channel: $L = 1$ m, $R = 10^{-3}$–10^{-4} m, $u_0 = 1$ m/sec, $\bar V = 10^{-5}$ m/sec, $\nu \sim 10^{-5}$ m^2/sec, and $D = 1.7\cdot10^{-5}$ m^2/sec.

Since the mean rate of flow u_0 through the cross section of the channel is much higher than the rate of mass transfer $\overline{V}$, the convective terms in the equations of motion (2) and (3) can be ignored. In this case, with an accuracy to terms of the order of ε^2, we obtain

$$\frac{\partial u}{\partial x} + r^{-\alpha} \frac{\partial (r^{\alpha} v)}{\partial r} = 0 , \tag{9}$$

$$\frac{\partial p}{\partial x} = \frac{1}{\mathrm{Re}\,\varepsilon} \left[r^{-\alpha} \frac{\partial}{\partial r} \left(r^{\alpha} \frac{\partial u}{\partial r} \right) \right], \quad \frac{\partial p}{\partial r} = 0 \tag{10}$$

at the boundary conditions

$$x = 0 : \quad p = p_0 , \quad u = \frac{\alpha + 3}{2} (1 - r^2) ; \tag{11}$$

$$r = 0 : \quad \frac{\partial u}{\partial r} = 0 , \quad v = 0 ; \tag{12}$$

$$r = 1 : \quad u = 0 , \quad v = V (x) . \tag{13}$$

It follows from the equations of motion (10) that the pressure p depends only on x; then the first relation (10) takes the form

$$p' (x) = \frac{1}{\mathrm{Re}\,\varepsilon} r^{-\alpha} \frac{\partial}{\partial r} \left(r^{\alpha} \frac{\partial u}{\partial r} \right).$$

Upon integration with respect to r at conditions (12) and (13), we obtain

$$u (x, r) = - \frac{\mathrm{Re}\,\varepsilon}{2 (\alpha + 1)} p' (x) (1 - r^2) . \tag{14}$$

Substitution of this formula into the continuity equation (9) gives

$$\frac{\partial (r^{\alpha} v)}{\partial r} = \frac{\mathrm{Re}\,\varepsilon r^{\alpha}}{2 (\alpha + 1)} p'' (x) (1 - r^2) .$$

A solution of this equation at the boundary conditions (12) and (13) has the form

$$v (x, r) = \frac{(\alpha + 1) (\alpha + 3)}{2} V (x) \left(\frac{r}{\alpha + 1} - \frac{r^3}{\alpha + 3} \right), \tag{15}$$

$$p'' (x) = \frac{(\alpha + 1)^2 (\alpha + 3) V (x)}{\mathrm{Re}\,\varepsilon} . \tag{16}$$

It follows from relation (16) that

$$p' (x) = p' (0) + \frac{(\alpha + 1)^2 (\alpha + 3)}{\mathrm{Re}\,\varepsilon} \int_0^x V (x) \, dx , \tag{17}$$

consequently, formula (14) takes the form

$$u\,(x, r) = -\frac{\mathrm{Re}\,\varepsilon}{2\,(\alpha+1)}\left(p'\,(0) + \frac{(\alpha+1)^2\,(\alpha+3)}{\mathrm{Re}\,\varepsilon}\int_0^x V\,(x)\,dx\right)(1-r^2)\,. \tag{18}$$

At the boundary condition (11), we obtain

$$p'\,(0) = -\frac{(\alpha+1)\,(\alpha+3)}{\mathrm{Re}\,\varepsilon}\,. \tag{19}$$

In the final analysis, from Eqs. (16)–(18) and formulas (11) and (19) we find the distribution of the longitudinal velocity and the pressure in the membrane channel:

$$u\,(x, r) = \frac{\alpha+3}{2}\left(1-(\alpha+1)\int_0^x V\,(x)\,dx\right)(1-r^2)\,, \tag{20}$$

$$p\,(x) = p_0 - \frac{(\alpha+1)\,(\alpha+3)}{\mathrm{Re}\,\varepsilon}\int_0^x\left(1-(\alpha+1)\int_0^x V\,(x)\,dx\right)dx\,. \tag{21}$$

Now, we will analyze the equation of convective diffusion (4). Since the first term on the right side of this equation is small, it can be written in the following form:

$$u\,\frac{\partial c}{\partial x} + v\,\frac{\partial c}{\partial r} = \frac{1}{\mathrm{Pe}_D\,\varepsilon}\,r^{-\alpha}\,\frac{\partial}{\partial r}\left(r^{\alpha}\,\frac{\partial c}{\partial r}\right).$$

Using the continuity equation (9), we write the equation of convective diffusion in the conservative form

$$\frac{\partial\,(r^{\alpha}u\,(1-c))}{\partial x} + \frac{\partial\,(r^{\alpha}v\,(1-c))}{\partial r} = -\frac{1}{\mathrm{Pe}_D\,\varepsilon}\,\frac{\partial}{\partial r}\left(r^{\alpha}\,\frac{\partial c}{\partial r}\right). \tag{22}$$

Since the diffusion Prandtl number is small (0.7–1) for gas mixtures, the diffusion boundary-layer zone occupies a small part of the membrane channel in a laminar regime and so can be ignored.

We propose to solve the equation of convective diffusion (22) at the boundary conditions (6) and (7) by a semiintegral method. The essence of this method is as follows. We write Eq. (22) in the form

$$\frac{\partial\,(r^{\alpha}u\,(1-c))}{\partial x} + \frac{\partial}{\partial r}\left[\frac{1}{\mathrm{Pe}_D}\,r^{\alpha}\,\frac{\partial c}{\partial r} + r^{\alpha}v\,(1-c)\right] = 0\,. \tag{23}$$

Let us drop the first term of the equation and integrate the remainder with respect to r at the boundary conditions (6) and (7). As a result, we obtain

$$\ln\,(1-c) = \ln\,(1-c_{\mathrm{w}}\,(x)) - \mathrm{Pe}_D\int_r^1 \varepsilon v dr \Rightarrow\ 1-c = (1-c_{\mathrm{w}})\,\exp\left(-\,\mathrm{Pe}_D\varepsilon\int_r^1 v dr\right),$$

where $c_{\mathrm{w}}(x)$ is the concentration on the surface of the membrane. Substitution of the expression for the velocity v from (15) into this concentration distribution gives

$$c\,(x, r) = 1 - (1 - c_{\mathrm{w}}\,(x))\,\exp\left(-\,\mathrm{Pe}_D\,\varepsilon V\,(x)\left(\frac{\alpha+5}{8} - \frac{\alpha+3}{4}\,r^2 + \frac{\alpha+1}{8}\,r^4\right)\right). \tag{24}$$

The concentration distribution (24) is true for the region near the membrane. To determine such a distribution everywhere over the cross section of the membrane channel, we will derive an integral equation of mass balance. For this purpose, let us integrate Eq. (23) with respect to r from 0 to 1 at the boundary conditions (6) and (7):

$$\frac{\partial}{\partial x}\int_0^1 r^\alpha u\,(1 - c)\,dr = 0\,.$$

This expression can be written, in view of (5), as

$$\int_0^1 r^\alpha u\,(1 - c)\,dr = \frac{1 - c_0}{\alpha + 1}\,. \tag{25}$$

To determine the dependence $c_{\mathrm{w}}(w)$, we substitute relation (24) into formula (25) and, using expression (20), obtain

$$\int_0^1 r^\alpha\,(1 - r^2)\,\exp\left(-\,\mathrm{Pe}_D\,\varepsilon V\,(x)\left(\frac{\alpha+5}{8} - \frac{\alpha+3}{4}\,r^2 + \frac{\alpha+1}{8}\,r^4\right)\right)dr =$$

$$= \frac{2\,(1 - c_0)}{(\alpha+1)\,(\alpha+3)\left(1 - (\alpha+1)\int_0^x V\,(x)\,dx\right)(1 - c_{\mathrm{w}}\,(x))}\,.$$

The membrane separation of gases is characterized by small values of $\mathrm{Pe}_D\varepsilon V(x)$. Therefore, we may expand the exponent into a series and consider only the two first terms of the expression. As a result, we find

$$c_{\mathrm{w}}\,(x) = 1 - \frac{1 - c_0}{\left(1 - (\alpha+1)\int_0^x V\,(x)\,dx\right)\left(1 - \frac{5\alpha+17}{(\alpha+5)\,(\alpha+7)}\,\mathrm{Pe}_D\varepsilon V\,(x)\right)}\,. \tag{26}$$

Substituting (21) and (26) into (8), we obtain an equation for $V(x)$:

$$V\,(x) = \frac{\Lambda M u_0}{\varepsilon\delta_{\mathrm{m}}}\left[p_0 - \frac{(\alpha+1)\,(\alpha+3)}{\mathrm{Re}\varepsilon}\int_0^x\left(1 - (\alpha+1)\int_0^x V\,(x)\,dx\right)dx\right]\times$$

$$\times\left[1 - \frac{1 - c_0}{\left(1 - (\alpha+1)\int_0^x V\,(x)\,dx\right)\left(1 - \frac{5\alpha+17}{(\alpha+5)\,(\alpha+7)}\,\mathrm{Pe}_D\varepsilon V\,(x)\right)}\right]. \tag{27}$$

The integral equation obtained allows one to calculate the most important characteristic of the membrane separation of binary gas mixtures — the rate of mass transfer through the membrane.

NOTATION

c, concentration of the penetrating component; D, diffusion coefficient, m^2/sec; L, length of the channel, m; M, molar mass of the penetrating component, kg/mole; p, pressure, Pa; $p = \bar{p}/(\bar{\rho} u_0^2)$, dimensionless pressure; $\mathrm{Pe}_D = u_0 R/D$, diffusion Peclet number; R, radius (halfwidth) of the channel, m; $\bar{r}$, radial coordinate, m; $r = \bar{r}/R$, dimensionless radial coordinate; $\mathrm{Re}_D = u_0 R/\nu$, Reynolds number; $\bar{u}$, longitudinal projection of the velocity, m/sec; $u = \bar{u}/u_0$, dimensionless longitudinal projection of the velocity; u_0, mean flow rate at the input of the channel, m/sec; $\bar{v}$, radial projection of the velocity, m/sec; $v = \bar{v}L/(u_0 R)$, dimensionless radial projection of the velocity; $\bar{V}$, rate of mass transfer through the membrane, m/sec; $V = \bar{V}L/(u_0 R)$, dimensionless rate of mass transfer through the membrane; $\bar{x}$, longitudinal coordinate, m; $x = \bar{x}/L$, dimensionless longitudinal coordinate; δ_m, effective thickness of the membrane, m; $\varepsilon = R/L$, ratio between two characteristic sizes of the channel; Λ, penetrability of the membrane, mole·m/(N·sec); ν, kinematic viscosity, m^2/sec; ρ, density, kg/m^3. Subscripts: 0, value at the input of the channel; m, membrane; w, value at the wall of the channel; $'$, $''$, derivative functions.

REFERENCES

1. Yu. I. Dytnerskii, V. P. Brykov, and G. G. Kagramanov, *Membrane Separation of Gases* [in Russian], Khimiya, Moscow (1991).
2. N. I. Nikolaev, I. S. Knyazev, N. I. Laguntsov, and G. A. Sulaberidze, Theory of optimal cascades for separation of mixtures on semipermeable membranes. Separation characteristics of a membrane-type unit, *Teor. Osnovy Khim. Tekhnol.*, **13**, No. 1, 10–16 (1979).
3. B. D. Borisevich, V. Yu. Kozhevnikov, N. I. Laguntsov, and G. A. Sulaberidze, Separation of multicomponent gas mixtures in membrane units, *Teor. Osnovy Khim. Tekhnol.*, **17**, No. 1, 60–65 (1983).
4. L. L. Murav'ev and L. A. Murav'ev, Model for calculation and optimization of hydrogen-permeable capillaries of membrane apparatus, *Teor. Osnovy Khim. Tekhnol.*, **36**, No. 2, 176–180 (2002).
5. L. L. Murav'ev, A. B. Vandyshev, and V. M. Makarov, Modeling of the process of membrane extraction of hydrogen from multicomponent gas mixtures, *Teor. Osnovy Khim. Tekhnol.*, **33**, No. 2, 190–192 (1999).