INTENSIFICATION OF SEPARATION EFFECTS OF NANOPOROUS POLYMERIC MEMBRANES IN THE GAS SEPARATION PROCESSES

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ABSTRACT

The purpose of the present work is the intensification of the separation effects of nanoporous polymeric membranes in the gas separation processes by the use of the membrane modules with feeding reservoir.

Key words: gas separation, membrane, purification

1. INTRODUCTION

The membrane gas separation is a comparatively new separation process having practical application. It is characterized by low energy and material consumption as well as by relative simplicity of mass transfer apparatus used. There is a possibility of separation process effectiveness change by the change of a type of membrane. On the other hand it is also possible by optimization of apparatus design and organization of gas mixture separation processes.
The purpose of present work is the development of physical-chemical basis of gases high purification with the help of membrane module with feeding reservoir characterized by a new type of separation process organization.

2. THEORY

Membrane module with feeding reservoir is absolutely new type of membrane apparatus. In the membrane module with feeding reservoir the purified gas mixture is placed in the feeding reservoir from where it is actually flown into the membrane module for separation. The impurity component is partially removed while the purified mixture is returned into the feeding reservoir. It allows to carry out the separation and purification of incoming gas mixture repeatedly to the purity level required. After the processes the purified gas stays in a reservoir. That is why the whole process is discontinuous opposing the continuous gas separation used nowadays.
In the lately mentioned method the feed continuously flows into the membrane module while permeate and retentate are continuously isolated from module. The case when the part of permeate and retentate is returned to the feed is called the membrane module with recirculation [1].

The method suggested is based on the statement that selectivity does not depend on the impurity concentration at low level (the same as rectification). In this case the selectivity of the process does not change with time.

Let us analyze the case of low permeable impurity purification processes. The first step is to determine the effective selectivity and the degree of separation of gas mixture component in membrane module. Let's take it for granted that the separation process is carried out in the regime of ideal displacement and counter flow. Impurity concentration here is much smaller than concentration of main component. Moreover the pressure of the cavities of membrane module is constant. The selectivity α does not depend on impurity concentration and more than unity. In case of the low permeable impurity separation it equals:

$$\alpha = \frac{Q_B}{Q_A}, \tag{1}$$

where $\mathbf{Q_B}$ and $\mathbf{Q_A}$ are permeabilities of main components and impurity, respectively.
Let's find the effective selectivity α^* from the mass transfer equation of impurity and main components having run through the elementary part of the membrane [2]. The value α^* is determined as relation of impurity concentration at the membrane surface at any point in the high pressure ($\mathbf{C_1}$, mole fraction) and low pressure($\mathbf{C_2}$, mole fraction) cavities. In case when $\mathbf{C_1}$ and $\mathbf{C_2}$ are much more less than unity it equals:

$$\alpha^* = \frac{C_1}{C_2} = \alpha - \frac{P_{12}}{P_1}(\alpha - 1), \tag{2}$$

where $\mathbf{P_1}$ and $\mathbf{P_2}$ are pressure of high and low pressure cavities, respectively.
The value of effective selectivity characterizes the separation for the regimes of ideal mixing and counter flow.
Equation (2) shows that effective selectivity does not depend on concentration and stays constant for the whole process of gases high purification in case of low impurity concentration.
The equation of effective selectivity for the high permeable impurity [2] substantially differs from equation (2) and is presented as

$$\alpha^* = \frac{\alpha}{1 + \frac{P_2}{P_1}(\alpha - 1)} \tag{3}$$

which depends on pressure ration of membrane module. In this case selectivity equals

$$\alpha = \frac{Q_A}{Q_B}, \tag{4}$$

The equation (4) is vice versa to equation (1) and more than unity.

From (2) and (3) equation comparison it is evident that for low permeable impurities the dependence of effective selectivity on pressure ration is substantially smaller than for high permeable impurities. It is described by the fact that low permeable impurities are concentrated in high pressure cavity and P_2 change produces less effect on their partial pressure in low pressure cavity and value of α^* than for high permeable impurities. That is why for the separation and purification from low permeable impurities it is possible to use gas compressors with a lower degree of compression.
From mass transfer balance of impurity component at elementary part of the membrane it can be determined the equation for separation factor as ration of impurity concentration in feed and retentate flows.

$$F^{-1} = \frac{C_{1out}}{C_{1in}} = \left(\frac{L_{1in}}{L_{1out}}\right)^{\frac{\alpha^*-1}{\alpha^*}} \tag{5}$$

where α^* is determined by equation (2) and C_{1in}, C_{1out} are impurity concentration values of feed and retentate flows, L_{1in} and L_{1out} are values of feed and retentate flows.
This equation is similar to Rayleigh equation for the case of separation from low boiling impurity where the effective selectivity (2) is used instead separation coefficient.
In case of separation and purification from high permeable component the equation for the separation factor shown as [3-4]

$$F = \frac{C_{1in}}{C_{1out}} = \left(\frac{L_{1in}}{L_{1out}}\right)^{\alpha^*-1} \tag{6}$$

From equation (5) and (6) it is evident that in membrane module it is possible to obtain high value of separation factor at comparatively high values of L_{1in}/L_{1out}.
It is necessary to note that in case of change α to $1/\alpha$ in equation (3) and α^* to $1/\alpha^*$ in equation (6) these equation are also similar to Rayleigh distillation equation as (2) and (5).

Let's consider the gases high purification from low permeable impurity with the help of membrane module with feeding reservoir (Fig. 1) [5]. In this case purified mixture follows from feeding reservoir 1 as feed flow into the membrane module 3 at constant pressure. Permeate (more permeable mixture component) returns into feeding reservoir 1 with the help of vacuum-compressor 4. Mixture coming out from apparatus is being enriched by low permeable impurity.
The purification degree of gas mixture in feeding reservoir will be characterized by purification ration **f** which is determined as the impurity concentration relation in the feeding reservoir before C_0 and after **C** purification, $f=C_0/C$. Let's agree that mixture in a reservoir is mixing intensively enough and impurity concentration is the same at all volume of the reservoir.

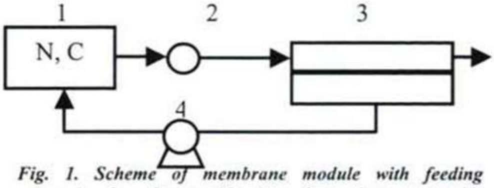

Fig. 1. Scheme of membrane module with feeding reservoir for the purification from low permeable impurities.
1 –feeding reservoir; 2 – pressure reducer; 3 – membrane module; 4 – vacuum compressor.

Also let's agree that the amount of mixture in the membrane module is too small comparing to the amount of mixture in the feeding reservoir. In this case the change of the impurity concentration in the feeding reservoir throughout the purification process will flow analogously to Rayleigh distillation where instead of separation coefficient separation factor F-1 which is found from equation (2) is used.

$$f = \frac{C_0}{C} = \left(\frac{N_0}{N}\right)^{F^{-1}-1} \qquad (7)$$

where N_0, N are the quantities of mole of mixture in the feeding reservoir at the beginning and the end of the purification process, respectively.
Let's consider gases high purification from high permeable impurities with the help of membrane module with feeding reservoir (fig. 2a). In this case purified mixture follows from feeding reservoir 1 through pressure reducer 2 and mixes with permeate flow of the membrane module 3. Than with the help of vacuum-compressor 4 the mixture is sent as feed flow into the membrane module 3 where high permeable impurity permeate through the membrane and purified mixture is coming back to the feeding reservoir 1.
Thus the flow $\mathbf{L_{out}}$ coming out from apparatus is enriched by high permeable impurity and mixture left in apparatus is purified from it. The equation for purification ration is obtained from mass transfer equations for impurity and main components in membrane module and whole apparatus

$$f = \frac{C_0}{C} = \left(\frac{N_0}{N}\right)^{\frac{F-1}{bF+1}} \qquad (8)$$

where coefficient **b** is equal to the relation of retentate and flow coming out from apparatus $\mathbf{b=L_{out}/L_{1out}}$. And **F** is defined by equation (6).
Accordingly it is possible to find the equation for gas mixture purification from high permeable impurities with the help of apparatus with feeding reservoir with additional membrane module (fig. 2b) where the same membrane is used as in the main module. It is acknowledged that the permeate flow

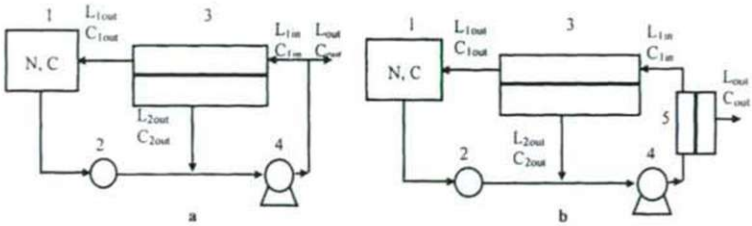

Fig. 2. Scheme of apparatus with feeding reservoir for the purification from high permeable impurities,
a – with one membrane module, b – with additional membrane module 1 –feeding reservoir;
2 – pressure reducer; 3 – membrane module; 4 – vacuum compressor;
5 – additional membrane module.

$\mathbf{L_{out}}$ of additional membrane module is much smaller than retentate flow $\mathbf{L_{1in}}$ of this module which is a feed flow for the main membrane module. That is why additional membrane module works in a regime of ideal mixing. For this additional module there is a condition $\mathbf{C_{out}/C_{1in}}$ equals to α^*.α^* is found from equation (3).

And the pressure of the cavities of additional module is the same as in the main module. In this case the equation for purification ration is found as

$$f = \frac{C_0}{C} = \left(\frac{N_0}{N}\right)^{\frac{\alpha^* F-1}{\alpha^* bF+1}} \qquad (9)$$

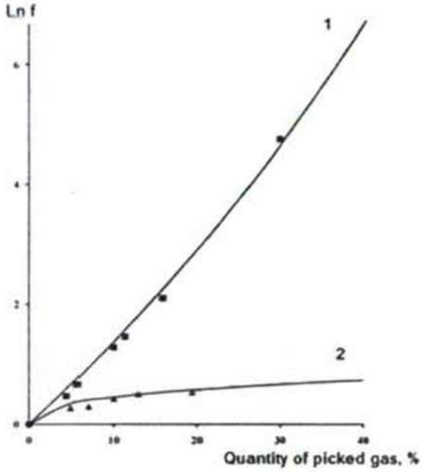

Fig 3. The dependence of purification ratio from quantity of picked substances
for mixture CCl_2F_2 – impurity of C_3F_8
1 – membrane module with a feeding reservoir (F-1 = 14);
2 – single membrane module
Δ, □ - experimental data

3. RESULT AND DISCUSSION

For the estimation of the separation power of this apparatus diclorodifluoromethane (CCl_2F_2) high purification from perfluoropropane C_3F_8 was considered. The ideal selectivity for this system CCl_2F_2 - C_3F_8 is equal to 2.94. As the membrane Silar® (the membrane on the base of polydimethylsiloxane) was used. It was shown (figure 3) that application of membrane module with feeding reservoir allows purifying main component from low permeable impurities at low product loss.
The comparison with single module is carried out also. It was shown that new apparatus with feeding reservoir more effective than single membrane module (figure 3). The degree of separation is increased with the help of multistage returning of gas mixture and constant selection of impurity from the feeding reservoir.

4. CONCLUSION

In conclusion we can say that such new apparatus might be of interest for gases and vapor purification from low penetrating impurities and also for high penetrating impurities.

Acknowledgements
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Symbols
α - selectivity
Q – permeability, (mole·m)/(m^2·s·Pa)
α^* - effective selectivity
C – concentration, mole fraction
P – pressure, Pa
F – separation factor,
L – flow, mole/s
f – purification degree
N – quantities of mixture in the feeding reservoir, mole
b – coefficient

Indexes
A - impurity
B – main component
1 – high pressure cavity
2 – low pressure cavity
in – input to the cavity of the membrane module
out – output from the cavity of the membrane module
0 – initial value, before the purification process

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